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Different Modes of Reaction of Lithium Phosphides with Cp*M(NO)(X)Cl Complexes of Molybdenum and Tungsten

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Treatment of Cp*M(NO)(X)Cl complexes (M = Mo, W; X, = CH_2SiMe_3, CH_2CMe_3, $NHCMe_3$, $OCMe_3$, Cl) with lithium phosphides can result in one of three different types of reactions. Some reactions involve the starting material undergoing metathesis of a chloro ligand, and others effect reduction of the organometallic reactant, while a third class results in a scrambling of the ligands of the starting complex. Reactions of Cp*M(NO)(X)Cl with $LiPPh_2$ lead to formation of the respective phosphido-containing complexes Cp*M(NO)(X)(PPh_2) [M = W, X = CH_2SiMe_3 (**1**), CH_2CMe_3 (**2**), $NHCMe_3$ (**3**), $OCMe_3$ (**4**); M = Mo, X = $NHCMe_3$ (**5**)]. In contrast, treatment of the molybdenum complexes Cp*Mo(NO)(X)Cl (X = CH_2SiMe_3, CH_2CMe_3, $OCMe_3$) with $LiPPh_2$ under identical conditions affords no isolable products. When metathesis of the chloro ligands in the Cp*M(NO)Cl_2 complexes of Mo and W is attempted with either $LiPPh_2$ or LiPPhH, the only isolable products formed are those resulting from the reduction of the organometallic reactant. Thus, treatment of Cp*W(NO)Cl_2 with 1 equiv of $LiPPh_2$ leads to isolation of the NO bond-cleaved product, [Cp*W(NO)(Cl)](μ-N)[Cp*W-(O)Cl] (**6**), in low (15%) yield, while reactions of Cp*M(NO)Cl_2 (M = Mo, W) with 2 equiv of either $LiPPh_2$ or LiPPhH afford modest yields of the bimetallic products [Cp*W(NO)(μ-PPh_2)]$_2$ (**7**), [Cp*Mo(NO)(μ-PPh_2)]$_2$ (**8**), and [Cp*Mo(NO)(μ-PHPh)]$_2$ (**9**). Finally, the reaction of Cp*W-(NO)($NHCMe_3$)Cl with LiPPhH induces a ligand-scrambling process in which an amide ligand from one molecule of the starting material is transferred to the tungsten center of another to produce Cp*W(NO)($NHCMe_3$)$_2$ (**10**). A similar example of ligand scrambling occurs during the reaction of Cp*Mo(NO)(CH_2SiMe_3)Cl with LiPPhH. In this case the unexpected product {[Cp*Mo(NO)(CH_2SiMe_3)$_2$][Li(THF)]}$_2$ (**11**, isolated in 3% yield) has also undergone a further one-electron reduction at the metal center. The solid-state molecular structures of compounds **9**−**11** have been established by X-ray crystallographic analyses.

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Introduction

The chemistry of organometallic complexes containing metal−heteroatom bonds (sometimes termed inorganometallic chemistry) is garnering ever increasing interest. In particular, recent investigations of multiply bonded metal−heteroatom derivatives have been motivated by the potential use of these compounds as, for example, specific reagents in organic synthesis.[1] A particularly notable development in this regard is the identification and characterization of M═PR (phosphinidene) fragments both transiently and in isolable complexes.[2] For example, Stephan and Breen have recently isolated the terminal phosphinidene complex Cp_2Zr-(PC_6H_2-2,4,6-*t*-Bu_3)(PMe_3) and shown it to undergo phosphinidene group-transfer reactions when treated with substrates such as aldehydes, ketones, organic dihalides, or epoxides.[3]

In recent years we have been particularly interested in the properties of Cp′M(NO)-containing complexes [Cp′ = Cp (η^5-C_5H_5) or Cp* (η^5-C_5Me_5); M = Cr, Mo, or W], and to date we have investigated the characteristic reactivity of M−C,[4] M−N,[5] and M−O[6] bonds in these compounds. A logical extension of this earlier work is to encompass the related complexes containing M−P linkages. In this paper we describe our attempts to synthesize such complexes by metatheses reactions involving the treatment of Cp*M(NO)(X)Cl species (X = CH_2SiMe_3, CH_2CMe_3, $NHCMe_3$, $OCMe_3$) with various lithium phosphides. While the desired products were obtained in some cases, in others reduction of the organometallic reactants occurred. The insights provided by this study bear directly on our earlier work and aid our understanding of the processes operative during metathesis reactions of these nitrosyl complexes.

Experimental Section

General procedures routinely employed in these laboratories have been described in detail previously.[7] The complexes Cp*M(NO)Cl_2,[8] Cp*M(NO)(X)Cl (M = W, Mo; X = CH_2SiMe_3,[9]

⊗ Abstract published in *Advance ACS Abstracts,* December 15, 1996.

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CH_2CMe_3,[10] $NHCMe_3$,[5] $OCMe_3$[6]] were prepared according to published procedures. $PHPh_2$, PH_2Ph, and *n*-BuLi (Aldrich) were used as received. H_2NCMe_3 was vacuum transferred from CaH_2 prior to use. Both lithium phosphide reagents were prepared by deprotonation of the parent phosphine with *n*-BuLi in hexanes and were recrystallized from Et_2O before use. It should be noted that both the parent phosphines and the derived lithium phosphide reagents have a strong stench associated with them and should be handled in a well-ventilated fumehood.

Preparation of Cp*M(NO)(X)(PPh_2) [M = W, X = CH_2SiMe_3 (1), CH_2CMe_3 (2), $NHCMe_3$ (3), $OCMe_3$ (4); M = Mo, X = $NHCMe_3$ (5)]. These complexes were all prepared in a similar manner, with all procedures being performed in an inert-atmosphere drybox. The synthesis of Cp*W(NO)(CH_2CMe_3)(PPh_2) is described as a representative example.

Cp*W(NO)(CH_2CMe_3)Cl (450 mg, 1.0 mmol) and $LiPPh_2$ (180 mg, 1.0 mmol) were mixed as dry powders and were cooled to approximately −100 °C. THF (5 mL) was added dropwise to the mixture, and the orange slurry was allowed to warm to room temperature while being stirred (ca. 15 min). The final red solution was taken to dryness in vacuo, and the residue was dissolved in hexanes. The solution was filtered through a plug of Celite (1 × 1 cm) supported on a medium-porosity glass frit. The volume of the filtrate was decreased under reduced pressure until the onset of crystallization. It was then maintained at −30 °C for 2 d to complete the deposition of dark orange blocks of **2** (110 mg, 35% yield) which were isolated by decanting off the supernatant solution.

Reaction of Cp*W(NO)Cl_2 with $LiPPh_2$. Cp*W(NO)Cl_2 (250 mg, 0.6 mmol) and $LiPPh_2$ (115 mg, 0.6 mmol) were mixed as dry powders and were cooled to approximately −100 °C. THF (5 mL) was added dropwise, and the stirred brown slurry was allowed to warm to room temperature (15 min). The final red solution was taken to dryness in vacuo, and the resulting residue was washed with a small amount (1 mL) of C_6H_6. The remaining solids were dissolved in toluene (5 mL), and the solution was filtered through a plug of Celite (1 × 1 cm) supported on a medium-porosity glass frit. Pentane (1 mL) was added to the filtrate, and the solution was placed in a freezer at −30 °C overnight to induce the deposition of [Cp*W(NO)Cl](*μ*-N)[Cp*W(O)Cl] (**6**) as a black microcrystalline solid (35 mg, 15% yield).

Preparation of [Cp*W(NO)(*μ*-PPh_2)]$_2$ (7), [Cp*Mo(NO)(*μ*-PPh_2)]$_2$ (8), and [Cp*Mo(NO)(*μ*-PHPh)]$_2$ (9). These complexes were all prepared in a manner similar to that described above for the synthesis of Cp*W(NO)(CH_2CMe_3)(PPh_2) by starting from the parent dichloro complexes and 2 equiv of the LiPPhR reagents. However, after being warmed to room temperature, the final red solutions were taken to dryness in vacuo, and the residues were redissolved in toluene. The toluene solutions were filtered through plugs of Celite (1 × 1 cm), and the volumes of the filtrates were diminished under reduced pressure. After addition to the filtrates of a small amount of either pentane or Et_2O (typically 1−2 mL), the solutions were maintained at −30 °C for a few days. Dark orange microcrystalline powders of the products (17−38% yield) were isolated by removal of the supernatant solutions with a cannula.

Reaction of Cp*W(NO)($NHCMe_3$)Cl with LiPPhH. Cp*W(NO)($NHCMe_3$)Cl (450 mg, 1.0 mmol) and LiPPhH (120 mg, 1.0 mmol) were mixed as dry powders and were cooled to approximately −100 °C. THF (5 mL) was added dropwise, and the stirred orange slurry was allowed to warm to room temperature (15 min). The orange solution was taken to dryness in vacuo, and the remaining residue was taken up in Et_2O. The solution was filtered through a plug of Celite (1 × 1 cm) supported on a medium-porosity glass frit. The volume of the filtrate was decreased under reduced pressure until the onset of crystallization. It was then maintained at −30 °C for 2 d to complete the deposition of dark orange needles of Cp*W(NO)($NHCMe_3$)$_2$ (**10**) (170 mg, 70% yield based on amide) which were isolated by decanting off the supernatant solution.

Reaction of Cp*Mo(NO)(CH_2SiMe_3)Cl with LiPPhH. This reaction was performed and worked up in a manner analogous to that described for the reaction of Cp*W(NO)($NHCMe_3$)Cl with LiPPhH in the preceding paragraph. The final solution afforded small red crystals of dimeric {[Cp*Mo(NO)(CH_2SiMe_3)$_2$][Li(THF)]}$_2$ (**11**) (3% yield) which were isolated by decanting off the supernatant solution.

X-ray Crystallographic Analyses of [Cp*Mo(NO)(*μ*-PHPh)]$_2$(solvate) (9), Cp*W(NO)($NHCMe_3$)$_2$ (10), and {[Cp*Mo(NO)(CH_2SiMe_3)$_2$][Li(THF)]}$_2$ (11). Crystallographic data for **9**−**11** appear in Table 4. The final unit-cell parameters were obtained by least-squares on the setting angles for 25 reflections with $2\theta = 23.1{-}26.4°$ for **10**, 15.5−23.6° for **11**, and 8.7−17.0° for **9**. The intensities of three standard reflections, measured every 200 reflections throughout the data collections, decayed linearly for **10** (3.5%), **11** (10.3%), and **9** (54.6%). Due to excessive crystal decay, the data for **9** were only collected to $2\theta = 45°$. The data were processed[11] and corrected for Lorentz and polarization effects, decay, and absorption (empirical, based on azimuthal scans).

The structures were solved by Patterson methods. The structure analysis of **11** was initiated in the noncentrosymmetric space group *C*2 and that of **9** in the centrosymmetric space group *C*2/*c* (both on the basis of the *E*-statistics), these choices being confirmed by subsequent calculations. Molecules of **11** and **9** both have exact (crystallographic) C_2 symmetry. The THF carbon atoms in **11** are disordered; various disorder models were tested, but none was satisfactory since the five-membered ring apparently adopts a combination of various puckered and envelope conformations. The simple anisotropic ordered model employed for the THF carbon atoms satisfactorily accounts for the electron density in the region but results in anomalous geometric parameters. The solvent in **9** (assumed to be pentane, although it may be diethyl ether) is disordered about a center of symmetry. The terminal solvent atom C(19) was assigned 50% occupancy. All non-hydrogen atoms were refined with anisotropic thermal parameters. The N−H hydrogen atoms in **10** were refined with isotropic thermal parameters. The P−H hydrogen atom in **9** was included in a difference map position but was not refined. All carbon-bound hydrogen atoms in **9**−**11** were fixed in calculated positions with C−H = 0.98 Å and $B_H = 1.2B_{\text{bonded atom}}$. A secondary extinction correction was applied for **10** (Zachariasen type 1 isotropic), the final value of the extinction coefficient being $7.1(4) \times 10^{-8}$. No extinction corrections were necessary for the other two compounds. Neutral atom scattering factors and anomalous dispersion corrections were taken from the ref 12. A parallel refinement of the mirror-image structure of **11** gave slightly higher residuals, the *R* and R_w factor ratios being 1.008 and 1.012, respectively.

Selected bond lengths and bond angles for the three complexes appear in Tables 5−7. Tables of final atomic coordinates and equivalent isotropic thermal parameters, anisotropic thermal parameters, bond lengths and angles, torsion angles, intermolecular contacts, and least-squares planes are included as Supporting Information. Views of the solid-state molecular structures of complexes **9**−**11** are displayed in Figures 1−3, respectively.

Results and Discussion

Treatment of Cp*M(NO)(X)Cl complexes (M = Mo, W; X, = CH_2SiMe_3, CH_2CMe_3, $NHCMe_3$, $OCMe_3$, Cl) with

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Table 1. Numbering Scheme, Color, Yield, and Elemental Analysis Data for Complexes 1−11

complex	compd no.	color (yield, %)	anal.: found (calcd) C	H	N
$Cp^*W(NO)(CH_2SiMe_3)(PPh_2)$	**1**	red (53)	50.43 (50.25)	5.84 (5.84)	2.32 (2.25)
$Cp^*W(NO)(CH_2CMe_3)(PPh_2)$	**2**	red (53)	53.57 (53.57)	6.08 (5.95)	2.45 (2.31)
$Cp^*W(NO)(NHCMe_3)(PPh_2)$	**3**	orange (25)	51.57 (51.50)	5.92 (5.82)	4.70 (4.62)
$Cp^*W(NO)(OCMe_3)(PPh_2)$	**4**	red (52)	51.51 (51.41)	5.72 (5.64)	2.25 (2.31)
$Cp^*Mo(NO)(NHCMe_3)(PPh_2)$	**5**	red (56)	60.00 (60.26)	6.79 (6.75)	5.38 (5.40)
$[Cp^*W(NO)(Cl)](\mu\text{-}N)[Cp^*W(O)Cl]$	**6**	black (15)	37.63 (37.67)[a]	4.11 (4.41)	3.49 (3.25)
$[Cp^*W(NO)(\mu\text{-}PPh_2)]_2$	**7**	orange (15)	49.03 (49.40)	4.76 (4.68)	1.96 (2.62)
$[Cp^*Mo(NO)(\mu\text{-}PPh_2)]_2$	8	orange (17)	b		
$[Cp^*Mo(NO)(\mu\text{-}PHPh)]_2$	**9**	orange (38)	54.40 (54.09)	5.90 (5.98)	3.15 (3.35)
$Cp^*W(NO)(NHCMe_3)_2$	**10**	orange (30)	43.50 (43.82)	7.22 (7.15)	8.36 (8.52)
$\{[Cp^*Mo(NO)(CH_2SiMe_3)_2][Li(THF)]\}_2$	**11**	red (3)	b		

[a] Calculated with one C_7H_8 included. [b] A satisfactory elemental analysis could not be obtained.

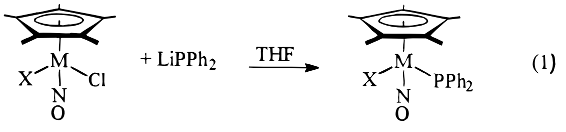
Table 2. MS and IR Data for Complexes 1−11

compd no.	MS: m/z (ion)	probe temp, °C	IR (Nujol) ν_{NO}, cm^{-1}	other, cm^{-1}
1	621 [P^+]	120	1574	
2	605 [P^+]	150	1588	
3	605 [$P^+ - H$]	120	1538	
4	607 [P^+]	120	1590	
5	520 [P^+]	150	1576	
6	768 [P^+]	100	1582	958, 882[a]
7	1068 [P^+]	250	1604	1557
8	892 [P^+]	150	1618	1575
9	740 [P^+]	150	1600	1567
10	493 [P^+]	100	1536	
11	b		1352	

[a] Assigned to ν_{WNW} stretches (see text). [b] Due to the extreme air-sensitivity of **11** only fragments due to the neutral Cp*Mo(NO)(CH_2SiMe_3)$_2$ complex were detected.

lithium phosphides can result in one of three different types of reactions. Some reactions involve the starting material undergoing metathesis of a chloro ligand, and others effect reduction of the organometallic reactant, while a third class results in a scrambling of the ligands of the starting complex. Each type of reactivity is discussed in turn below.

Metathesis Reactions. The expected reaction of a lithium phosphide reagent with the alkyl, alkoxy, or amido chloro starting materials summarized in the preceding paragraph is a metathesis of the chloro ligand for a phosphido group. This reaction pathway mirrors that of other lithium reagents that we have previously employed to synthesize related complexes with heteroatom-containing ligands.[13] Consequently, it is not surprising that treatment of Cp*M(NO)(X)Cl (M = W, X = CH_2SiMe_3, CH_2CMe_3, $NHCMe_3$, $OCMe_3$; M = Mo, X = $NHCMe_3$) with $LiPPh_2$ leads to formation of the respective phosphido-containing complexes Cp*M(NO)(X)(PPh_2) [M = W, X = CH_2SiMe_3 (**1**), CH_2CMe_3 (**2**), $NHCMe_3$ (**3**), $OCMe_3$ (**4**); M = Mo, X = $NHCMe_3$ (**5**)], i.e. eq 1. These complexes are all air-sensitive, red crystalline solids which display spectral properties (collected in Tables 1−3) consistent with their formulations. For instance, compounds **1**−**4** exhibit signals in their C_6D_6 ^{31}P NMR spectra that are attributable to the phosphido groups and that display satellites due to coupling between the phosphorus and tungsten nuclei. The Nujol-mull IR spectra of **1**−**5** display nitrosyl-stretching frequencies between 1538 and 1590 cm^{-1} consistent with the existence of nitrosyl ligands bound in a linear manner.[14] Complexes **1**−**5** are thermally stable and undergo no change discernible by ^1H NMR spectroscopy when heated in $CDCl_3$ solution at 55 °C for 3 days in the absence of air.



(1)

M = W, X = CH_2SiMe_3, CH_2CMe_3, $NHCMe_3$, $OCMe_3$
M = Mo, X = $NHCMe_3$

In contrast, treatment of the molybdenum complexes Cp*Mo(NO)(X)Cl (X = CH_2SiMe_3, CH_2CMe_3, $OCMe_3$) with $LiPPh_2$ under identical conditions affords no isolable products. Analysis of the final product mixtures of each of these reactions by ^1H NMR spectroscopy indicates a large number of products, as judged by the numerous signals evident in the Cp* region of the spectrum (i.e., from 1 to 2 ppm). A possible explanation for why the molybdenum systems produce no isolable products when the congeneric tungsten complexes are readily formed by the metathetical processes of eq 1 may be that the final products are inherently unstable under the reaction conditions employed. Our earlier work has shown that molybdenum complexes of this type are generally more labile than are their tungsten analogues.[4]

Attempts to effect metatheses similar to those summarized in eq 1 by employing LiPPhH as the phosphide reagent meet with little success.[15] Treatment of Cp*M(NO)(X)Cl (M = W; X = CH_2SiMe_3, CH_2CMe_3, $OCMe_3$; M = Mo; X = CH_2CMe_3, $NHCMe_3$, $OCMe_3$) with LiPPhH leads in all cases to no isolable products. One possible cause for the lack of success of these reactions is that the products of these reactions, like those described in the preceding paragraph, are also inherently unstable. In the two cases which did afford isolable products (i.e. M = W, X = $NHCMe_3$, and M = Mo, X = CH_2SiMe_3), neither of the products is the result of a straightforward metathesis reaction (vide infra).

Reduction Reactions. When metathesis of the chloro ligands in the Cp*M(NO)Cl_2 complexes of Mo and W is attempted with either $LiPPh_2$ or LiPPhH, the only isolable products formed are those resulting from the

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(13) (a) Legzdins, P.; Lundmark, P. J.; Rettig, S. J. *Organometallics* **1996**, *15*, 2988. (b) Reference 6 and references cited therein.

(14) Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyls*; Oxford University Press: Oxford, U.K., **1992**.

(15) These reactions were all performed in a manner similar to that outlined for the preparation of Cp*W(NO)(X)(PPh_2) with the difference that, rather than being dissolved in hexanes, the final products of these reactions were dissolved in C_6D_6, and their ^1H NMR spectra were recorded. In all cases the spectra indicated the presence of a plethora of products as judged by the numerous signals in the Cp* region. The reactions were also effected in MeCN as the reaction solvent with similar results.

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Table 3. NMR Data for Complexes 1−10

compd no. (solvent)	^{1}H NMR, δ	^{13}C{^{1}H} NMR, δ	^{31}P NMR, δ ($J_{\mathrm{W-P}}$, Hz)
1 $(\mathrm{C_6D_6})$	7.82 (t, 2 H, $\mathrm{P}\mathit{Ph}_2$), 7.34 (t, 4 H, $\mathrm{P}\mathit{Ph}_2$), 7.04 (m, 4 H, $\mathrm{P}\mathit{Ph}_2$), 1.62 (s, 15 H, $\mathrm{C}_5\mathit{Me}_5$), 0.40 (s, 9 H, $\mathrm{Si}\mathit{Me}_3$), 0.25 (dd, 1 H, $\mathrm{C}\mathit{H}_2$), −0.06 (dd, 1 H, $\mathrm{C}\mathit{H}_2$)	132−129 (*Ph*), 107 ($\mathit{C}_5\mathrm{Me}_5$), 9.8 ($\mathrm{C}_5\mathit{Me}_5$), 23.6 ($\mathit{C}\mathrm{H_2SiMe_3}$), 2.25 ($\mathrm{CH_2Si}\mathit{Me}_3$)	−183 (569)
2 $(\mathrm{C_6D_6})$	7.85 (br s, 2 H, $\mathrm{P}\mathit{Ph}_2$), 7.35 (br s, 4 H, $\mathrm{P}\mathit{Ph}_2$), 7.00 (br s, 4 H, $\mathrm{P}\mathit{Ph}_2$), 1.62 (s, 15 H, $\mathrm{C}_5\mathit{Me}_5$), 1.44 (s, 9 H, $\mathrm{Si}\mathit{Me}_3$), 1.05 (dd, 1 H, $\mathrm{C}\mathit{H}_2$)	133−128 (*Ph*), 108 ($\mathit{C}_5\mathrm{Me}_5$), 59.0 ($\mathit{C}\mathrm{H_2CMe_3}$), 36.5 ($\mathrm{CH_2}\mathit{C}\mathrm{Me_3}$), 32.0 ($\mathrm{CH_2C}\mathit{Me}_3$), 10.1 ($\mathrm{C}_5\mathit{Me}_5$)	−179 (581)
3 $(\mathrm{C_6D_6})$	7.70 (t, 4 H, $\mathrm{P}\mathit{Ph}_2$), 7.50 (br s, 1 H, $\mathrm{N}\mathit{H}$), 7.19 (br s, 4 H, $\mathrm{P}\mathit{Ph}_2$), 7.00 (br s, 2 H, $\mathrm{P}\mathit{Ph}_2$), 1.61 (s, 15 H, $\mathrm{C}_5\mathit{Me}_5$), 1.04 (s, 9 H, $\mathrm{C}\mathit{Me}_3$)	134−127 (*Ph*), 111 ($\mathit{C}_5\mathrm{Me}_5$), 32.6 ($\mathrm{NHC}\mathit{Me}_3$), 9.9 ($\mathrm{C}_5\mathit{Me}_5$)	+46.4 (226)
4 $(\mathrm{C_6D_6})$	7.55 (t, 4 H, $\mathrm{P}\mathit{Ph}_2$), 7.13 (m, 4 H, $\mathrm{P}\mathit{Ph}_2$), 6.96 (t, 2 H, $\mathrm{P}\mathit{Ph}_2$), 1.69 (s, 15 H, $\mathrm{C}_5\mathit{Me}_5$), 1.37 (s, 9 H, $\mathrm{C}\mathit{Me}_3$)	134−127 (*Ph*), 111 ($\mathit{C}_5\mathrm{Me}_5$), 82.0 ($\mathrm{O}\mathit{C}\mathrm{Me_3}$), 32.5 ($\mathrm{CH_2C}\mathit{Me}_3$), 10.0 ($\mathrm{C}_5\mathit{Me}_5$)	+88.9 (351)
5 $(\mathrm{CDCl_3})$	7.40 (t, 4 H, $\mathrm{P}\mathit{Ph}_2$), 7.20 (t, 4 H, $\mathrm{P}\mathit{Ph}_2$), 7.10 (d, 2 H, $\mathrm{P}\mathit{Ph}_2$), 7.08 (s, br, $\mathrm{N}\mathit{H}$), 1.76 (s, 15 H, $\mathrm{C}_5\mathit{Me}_5$), 1.04 (s, 9 H, $\mathrm{C}\mathit{Me}_3$)	134−126 (*Ph*), 112 ($\mathit{C}_5\mathrm{Me}_5$), 60.0 ($\mathrm{NH}\mathit{C}\mathrm{Me_3}$), 32.2 ($\mathrm{NHC}\mathit{Me}_3$), 10.6 ($\mathrm{C}_5\mathit{Me}_5$)	+71.1
6 $(\mathrm{C_6D_6})$	1.92 (s, $\mathrm{C}_5\mathit{Me}_5$), 1.89 (s, $\mathrm{C}_5\mathit{Me}_5$)	116 ($\mathit{C}_5\mathrm{Me}_5$), 115 ($\mathit{C}_5\mathrm{Me}_5$), 10.9 ($\mathrm{C}_5\mathit{Me}_5$), 10.0 ($\mathrm{C}_5\mathit{Me}_5$)	no signal
7 $(\mathrm{CDCl_3})$	7.95 (m, 2 H, $\mathrm{P}\mathit{Ph}_2$), 7.40 (m, 4 H, $\mathrm{P}\mathit{Ph}_2$), 7.10 (m, 4 H, $\mathrm{P}\mathit{Ph}_2$), 1.73 (s, 15 H, $\mathrm{C}_5\mathit{Me}_5$)	136−128 (*Ph*), 109 ($\mathit{C}_5\mathrm{Me}_5$), 10.3 ($\mathrm{C}_5\mathit{Me}_5$)	+134 (363)
8 $(\mathrm{CDCl_3})$	7.65 (t, 4 H, $\mathrm{P}\mathit{Ph}_2$), 7.25 (m, 6 H, $\mathrm{P}\mathit{Ph}_2$), 1.66 (s, 15 H, $\mathrm{C}_5\mathit{Me}_5$)	141−127 (*Ph*), 108 ($\mathit{C}_5\mathrm{Me}_5$), 10.3 ($\mathrm{C}_5\mathit{Me}_5$)	+180
9 $(\mathrm{CDCl_3})$	7.65 (m, 2 H, $\mathrm{PH}\mathit{Ph}$), 7.30 (m, 3 H, $\mathrm{PH}\mathit{Ph}$), 5.23 (d, 1 H, $\mathrm{P}\mathit{H}\mathrm{Ph}$, $^1\mathrm{J}_{\mathrm{PH}} = 340$ Hz), 1.90 (s, 15 H, $\mathrm{C}_5\mathit{Me}_5$)	132−128 (*Ph*), 104 ($\mathit{C}_5\mathrm{Me}_5$), 11.3 ($\mathrm{C}_5\mathit{Me}_5$)	+130 $^1J_{\mathrm{PH}} = 340$ Hz
10 $(\mathrm{C_6D_6})$	4.4 (s, br, $\mathrm{N}\mathit{H}$), 1.65 (s, 15 H, $\mathrm{C}_5\mathit{Me}_5$), 1.43 (s, 9 H, $\mathrm{C}\mathit{Me}_3$)	110 ($\mathit{C}_5\mathrm{Me}_5$), 59.8 ($\mathrm{NH}\mathit{C}\mathrm{Me_3}$), 34.9 ($\mathrm{NHC}\mathit{Me}_3$), 9.9 ($\mathrm{C}_5\mathit{Me}_5$)	no signal

Table 4. Crystallographic Data[a]

	compound		
	[Cp*Mo(NO)-(μ-PHPh)]$_2$·$\mathrm{C_5H_{12}}$, **9**	Cp*W(NO)-$(\mathrm{NHCMe_3})_2$, **10**	[Cp*Mo(NO)-$(\mathrm{CH_2SiMe_3})_2$]-Li(THF)]}$_2$, **11**
formula	$\mathrm{C_{37}H_{54}Mo_2N_2O_2P_2}$	$\mathrm{C_{18}H_{35}N_{3O}W}$	$\mathrm{C_{44}H_{90}Li_2Mo_2N_2O_4Si_4}$
fw	812.67	493.34	1029.31
color, habit	yellow, plate	red-orange, needle	red, prism
cryst size, mm	0.10 × 0.20 × 0.25	0.20 × 0.20 × 0.45	0.20 × 0.30 × 0.35
cryst system	monoclinic	monoclinic	monoclinic
space group	$C2/c$	$P2_1/n$	$C2$
a, Å	22.501(4)	10.576(2)	29.194(3)
b, Å	9.371(4)	14.190(2)	9.877(3)
c, Å	18.756(3)	14.468(2)	10.569(2)
β, deg	101.86(1)	92.47(1)	108.13(2)
V, Å^3	3870(1)	2169.2(5)	2896(1)
Z	4	4	2
ρ_{calc}, g/cm^3	1.395	1.511	1.180
F(000)	1680	984	1092
μ(Mo Kα), cm^{-1}	7.62	53.39	5.50
transm factors	0.94−1.00	0.93−1.00	0.92−1.00
scan type	$\omega-2\theta$	$\omega-2\theta$	ω
scan range, deg in ω	0.89 + 0.35 tan θ	1.21 + 0.35 tan θ	1.05 + 0.35 tan θ
scan speed, deg/min	16 (up to 8 rescans)	16 (up to 8 rescans)	16 (up to 8 rescans)
data collcd	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$
$2\theta_{\mathrm{max}}$, deg	45	55	55
cryst decay, %	54.6	3.5	10.3
total reflcns	2806	5466	3585
unique reflcns	2722	5194	3513
R_{merge}	0.062	0.027	0.019
reflns with $I \geq 3\sigma(I)$	1118	2877	1939
no. of variables	208	217	261
R	0.041	0.025	0.036
R_{w}	0.035	0.022	0.031
gof	1.35	1.33	1.65
max Δ/σ (last cycle)	0.001	0.001	0.01
resid density, e/Å^3	−0.42, +0.58	−0.56, +0.44	−0.42, +0.25

[a] Temperature 294 K, Rigaku AFC6S diffractometer, Mo $K\alpha$ radiation ($\lambda = 0.710\,69$ Å), graphite monochromator, takeoff angle 6.0°, aperture 6.0 × 6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2:1), $\sigma^2(F^2) = [S^2(C + 4B)]/(Lp)^2$ (S = scan rate, C = scan count, B = normalized background count), function minimized $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, and gof $= [\sum w(|F_o| - |F_c|)^2/(m-n)]^{1/2}$. Values given for R, R_w, and gof are based on those reflections with $I \geq 3\sigma(I)$.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for [Cp*Mo(NO)(μ-PHPh)]$_2$, 9[a]

Mo(1)−Mo(1)*	3.099(2)	Mo(1)−C(3)	2.41(1)
Mo(1)−P(1)	2.401(2)	Mo(1)−C(4)	2.41(1)
Mo(1)−P(1)*	2.396(4)	Mo(1)−C(5)	2.345(9)
Mo(1)−N(1)	1.78(1)	Mo(1)−CP	2.04
Mo(1)−C(1)	2.319(9)	P(1)−C(11)	1.82(1)
Mo(1)−C(2)	2.33(1)	O(1)−N(1)	1.213(9)

P(1)−Mo(1)−P(1)*	99.48(9)	N(1)−Mo(1)−CP	122.9
P(1)−Mo(1)−N(1)	94.3(3)	Mo(1)−P(1)−Mo(1)*	80.50(9)
P(1)−Mo(1)−CP	121	Mo(1)−P(1)−C(11)	125.3(4)
P(1)*−Mo(1)−N(1)	93.6(4)	Mo(1)*−P(1)−C(11)	120.6(4)
P(1)*−Mo(1)−CP	119.2	Mo(1)−N(1)−O(1)	173.4(7)

[a] CP refers to the unweighted centroid of the C(1−5) ring; * denotes the symmetry operation $-x$, y, $^1/_2 - z$.

reduction of the organometallic reactant. This result is probably a manifestation of the fact that the dichloro complexes are more easily reduced (M = Mo, E° = −350 mV vs SCE; M = W, $E°$ = −750 mV vs SCE) than are the corresponding alkyl chlorides Cp*M(NO)$(\mathrm{CH_2CMe_3})$Cl (M = Mo, $E°$ = −960 mV vs SCE; M = W, E° = −1210 mV vs SCE).[10]

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Treatment of $Cp^*W(NO)Cl_2$ with 1 equiv of $LiPPh_2$ leads to isolation of the NO bond-cleaved product, $[Cp^*W(NO)(Cl)](\mu\text{-}N)[Cp^*W(O)Cl]$ (**6**), in low (15%) yield. The ^1H and ^{13}C NMR spectra of this complex display the expected two signals for the inequivalent Cp* ligands and show no evidence for the presence of any isomers. The Nujol-mull IR spectrum of this complex is very informative since in addition to the strong absorption for the stretching mode of the nitrosyl ligand ($\nu_{NO} = 1582$ cm^{-1}), there are also strong absorptions at 958 and 882 cm^{-1}. These latter bands are assigned to the W═O stretch and the asymmetric W═N−W bond vibration. Bands of this type have been previously noted in the IR spectra of other complexes containing the same molecular fragments, for example the W═N−W bridge in $[NH_4]_3(Br_5W)_2(\mu\text{-}N)$ ($\nu_{WNW} = 968$ cm^{-1})[16] and in $[Cp^*WMe_3]_2(\mu\text{-}N)$ ($\nu_{WNW} = 800$ cm^{-1})[17] and the W═O bonds in $Cp^*W(O)(Cl)_2(CH_2SiMe_3)$ ($\nu_{WO} = 939$ cm^{-1}) and $Cp^*W(O)({=}CHSiMe_3)(CH_2SiMe_3)$ ($\nu_{WO} = 949$ cm^{-1}).[18] Bimetallic complex **6** is similar to the $[Cp^*W(NO)R](\mu\text{-}N)[Cp^*W(O)Cl]$ products formed when the related $Cp^*W(NO)(R)Cl$ complexes are treated with Zn[19] and the $[Cp^*W(NO)R](\mu\text{-}N)[Cp^*W(O)R]$ compounds which are the ultimate products of the reactions of $Cp^*Mo(NO)R_2$ (R = CH_2CMe_3, CH_2CMe_2Ph) with H_2.[20] Reactions of $Cp^*M(NO)Cl_2$ with only 1 equiv of lithium phosphide lead in all other cases (i.e. M = W with LiPPhH and M = Mo with LiPPhH or $LiPPh_2$) to many products as judged by the large number of signals in the ^1H NMR spectra of the final reaction mixtures.

When the $Cp^*M(NO)Cl_2$ complexes are treated with 2 equiv of a phosphide reagent, completely different products are formed. In these cases the products are indicative of the dichloro reactants having undergone both a reduction and a metathesis of one chloro ligand. Thus, treatment of $Cp^*M(NO)Cl_2$ (M = Mo, W) with 2 equiv of either $LiPPh_2$ or LiPPhH leads to $[Cp^*W(NO)(\mu\text{-}PPh_2)]_2$ (**7**), $[Cp^*Mo(NO)(\mu\text{-}PPh_2)]_2$ (**8**), and $[Cp^*Mo(NO)(\mu\text{-}PHPh)]_2$ (**9**).[21] The solid-state molecular structure of **9** has been established by an X-ray crystallographic analysis, and an ORTEP plot of this structure is shown in Figure 1. The molecular structure of **9** consists of two three-legged piano-stool molecules sharing a common side of their bases. The molecule has a C_2 axis passing between the two molybdenum atoms, and the Mo−P distances are statistically equal (Mo(1)−P(1) = 2.401(2) Å, Mo(1)−P(1)′ = 2.396(4) Å). The Mo−NO linkage is effectively linear (Mo(1)−N(1)−O(1) = 173.4°), and the Mo−N and N−O distances are within the ranges normally found for such complexes (Mo(1)−N(1) = 1.78(1) Å, N(1)−O(1) = 1.213(9) Å).[22] At first glance, the large Mo−Mo′ separation of 3.099(2) Å suggests that probably no Mo−Mo interaction exists in the molecule. However, if this were the case, each metal center would have a formal valence-electron count of 17, and the complex would be expected to be paramagnetic. Since the complex exhibits sharp signals in both its ^1H and ^{13}C NMR spectra, it appears to be diamagnetic in nature. In order to account for this diamagnetism either a single Mo−Mo bond or the existence of some form of coupling through the phosphorus-atom bridges must be invoked. Precedence for long M−M interactions exists in the chemical literature, and ab initio calculations have demonstrated M−M interactions over distances as great as 4.25 Å in some zirconium systems.[23]

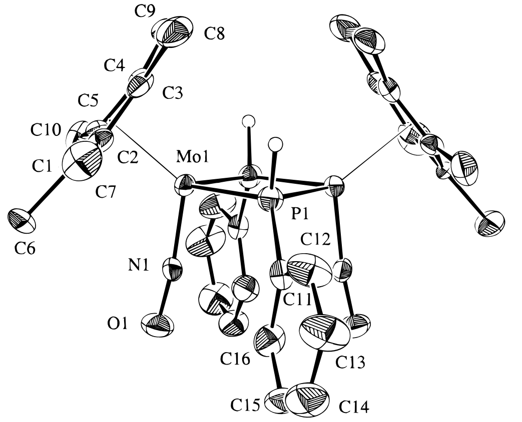

Figure 1. ORTEP diagram of $[Cp^*Mo(NO)(\mu\text{-}PHPh)]_2$ (**9**). Thermal ellipsoids of 50% probability are shown for the non-hydrogen atoms.

Interestingly, treatment of bimetallic complex **6** with a further 1 equiv of a phosphide reagent does not lead to production of a phosphido-bridged compound such as **7**, **8**, or **9**, thereby indicating that the two types of bimetallic products are obtained by different routes. The mechanism that we invoke to rationalize these observations for the tungsten complexes is shown in Scheme 1 in which $LiPPh_2$ is employed as a typical phosphide reagent.

Regardless of whether 1 or 2 equiv of phosphide is employed, the first step in either case is the rapid and complete reduction of the dichloro starting material to form a bimetallic complex, **A**. Consistent with this view is the fact that the analogous reduction of $Cp^*Mo(NO)(CH_2SiMe_3)_2$ by $LiPPh_2$ produces the symmetric lithium-bridged dimer $\{[Cp^*Mo(NO)(CH_2SiMe_3)_2][Li(THF)]\}_2$ (**11**),[24] which we have also isolated during the current study and have subjected to a single-crystal X-ray crystallographic analysis (vide infra). When only 1 equiv of phosphide reagent is added, completion of the first step results in a solution containing only **A** and PPh_2 (either as a free radical or as the $Ph_2P{-}PPh_2$ dimer). The next step involves the loss of 2 equiv of lithium chloride and formation of a bimetallic species in which the nitrosyl ligands bridge the two W atoms. In Scheme 1 this bimetallic complex is portrayed as having a symmetric $W(\mu\text{-}NO)_2W$ linkage since spontaneous isomerizations of such linkages to the (ON)-W═N═W═O grouping found in the final product, **6**, have been conclusively demonstrated to occur for related complexes.[20] When 2 equiv of the phosphide reagent is employed, the same initial reaction to form **A** ensues. In this case, however, the loss of LiCl and subsequent rearrangements are evidently superseded by the more rapid metathesis reaction of **A** with a second 1 equiv of phosphide (shown on the lower left side of Scheme 1).

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[20] Legzdins, P.; Young, M. A.; Batchelor, R. J.; Einstein, F. W. B. *J. Am. Chem. Soc.* **1995**, *117*, 8798.

[21] $[Cp^*W(NO)(\mu\text{-}PPhH)]_2$ is also formed upon treatment of $Cp^*W(NO)Cl_2$ with LiPPhH but is isolable only in an impure form and in very low yield.

[22] Legzdins, P.; Rettig, S. J.; Veltheer, J. E.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1993**, *12*, 3575 and references cited therein.

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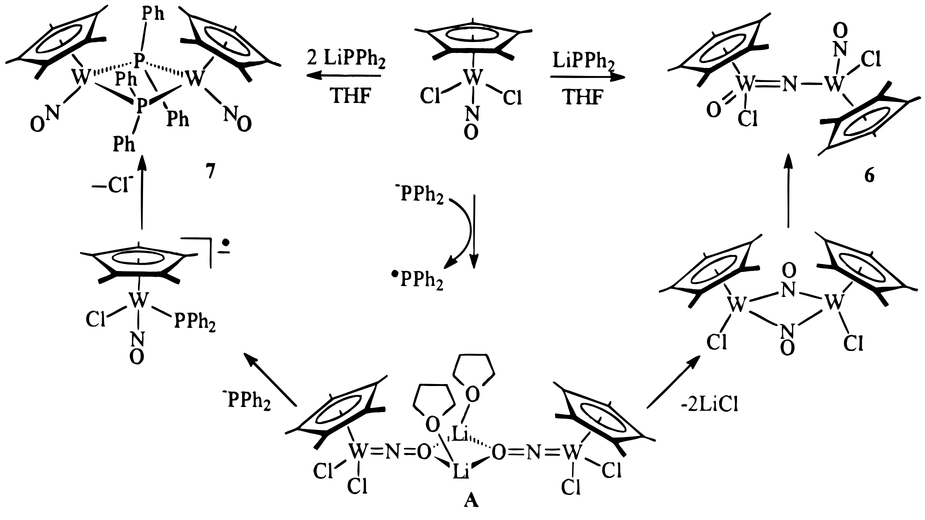
Scheme 1



The resulting phosphido chloro radical anion then transforms to the final product, **7**, by loss of a chloride ion and dimerization.

Some insight into the limitations of chloride metathesis from Cp*M(NO)Cl_2 as a route to compounds of the type Cp*M(NO)R_2 can be gained from the mechanism presented in Scheme 1 by considering the relative stability of the radicals produced by oxidation of the R-containing reactant. Reactive or unstable radicals (e.g. alkyl radicals) rapidly combine with the reduced species of type **A** to afford the desired metathesis products.[25] If, however, the radicals formed have a degree of inherent stability (e.g. phosphide radicals), then, in the absence of other anionic reagents, the reduced species follow other pathways to form nitrosyl NO bond-cleaved products. This inference is consistent with our previous observations concerning treatment of the dichloro starting materials with lithium amide reagents. Treatment of Cp*Mo(NO)Cl_2 with LiNH(*p*-MeC_6H_4) leads, in addition to the expected metathesis product, to the isolation of "[Cp*Mo(NO)Cl_2]Li" in 5% yield.[5] It would be expected that the amide radical formed after effecting initial reduction would be intermediate in stability between the alkyl and phosphide radicals. However, the amide radical is evidently sufficiently reactive that the metathesis product is formed preferentially over those resulting from reduction and nitrosyl cleavage, but it is not so reactive that small quantities of the intermediate reduction product cannot be isolated. One final point concerning Scheme 1 merits mention. The fact that the nitrosyl NO bond-cleaved product, **6**, is obtained only in low yield is probably indicative of the existence of other reaction pathways for **A**. One such possible pathway which we have documented during earlier work leads to formation of monochloro dimers of the type [Cp′M(NO)(μ-Cl)]$_2$.[26]

Ligand-Scrambling Reactions. The reaction of Cp*W(NO)($NHCMe_3$)Cl with LiPPhH induces a ligand-scrambling reaction in which an amido ligand from one molecule of the starting material is transferred to the tungsten center of another to afford Cp*W(NO)($NHCMe_3$)$_2$ (**10**), the molecular structure of which was established by an X-ray crystallographic analysis. The ORTEP plot of **10** is shown in Figure 2, and it illustrates that **10** is a regular three-legged piano-stool molecule whose intramolecular metrical parameters are within normal ranges (Table 6). An interesting point worthy of note about the structure is the orientation of the two amide ligands. In order that donation of π-electron density from the amide N to the W center can be achieved, it is imperative that the p-type orbital of the nitrogen atom be aligned with a π orbital of the metal that is not interacting significantly with the nitrosyl ligand. This feature has been previously delineated for other complexes.[27] If complex **10** is viewed as being pseudo-octahedral with the Cp* ligand occupying one

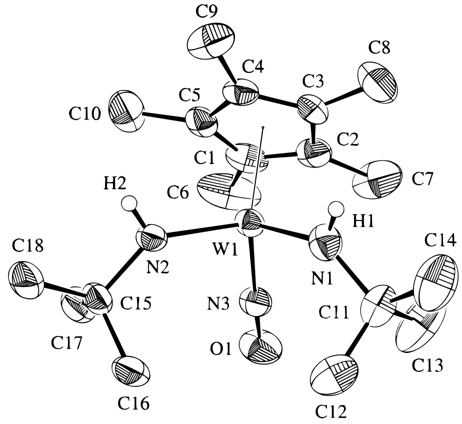


Figure 2. ORTEP diagram of Cp*W(NO)($NHCMe_3$)$_2$ (**10**). Thermal ellipsoids of 50% probability are shown for the non-hydrogen atoms.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for Cp*W(NO)($NHCMe_3$)$_2$, 10[a]

W(1)−N(1)	1.961(5)	W(1)−C(4)	2.444(5)
W(1)−N(2)	1.954(4)	W(1)−C(5)	2.414(5)
W(1)−N(3)	1.755(4)	W(1)−CP	2.08
W(1)−C(1)	2.341(5)	O(1)−N(3)	1.231(5)
W(1)−C(2)	2.346(5)	N(1)−C(11)	1.486(7)
W(1)−C(3)	2.445(5)	N(2)−C(15)	1.490(6)
N(1)−W(1)−N(2)	109.9(2)	N(3)−W(1)−CP	121.3
N(1)−W(1)−N(3)	98.9(2)	W(1)−N(1)−C(11)	137.1(4)
N(1)−W(1)−CP	113.2	W(1)−N(2)−C(15)	134.3(3)
N(2)−W(1)−N(3)	97.6(2)	W(1)−N(3)−O(1)	169.3(4)
N(2)−W(1)−CP	114.1		

[a] CP refers to the unweighted centroid of the C(1−5) ring.

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Table 7. Selected Bond Lengths (Å) and Angles (deg) for $[Cp^*Mo(NO)(CH_2SiMe_3)_2][Li(THF)]\}_2$, 11[a]

Mo(1)−N(1)	1.713(5)	Si(1)−C(13)	1.87(1)
Mo(1)−C(1)	2.430(8)	Si(1)−C(14)	1.843(9)
Mo(1)−C(2)	2.448(7)	Si(2)−C(15)	1.852(8)
Mo(1)−C(3)	2.397(9)	Si(2)−C(16)	1.882(9)
Mo(1)−C(4)	2.364(8)	Si(2)−C(17)	1.881(9)
Mo(1)−C(5)	2.380(8)	Si(2)−C(18)	1.88(1)
Mo(1)−C(11)	2.207(9)	O(1)−N(1)	1.323(6)
Mo(1)−C(15)	2.212(8)	O(1)−Li(1)	1.86(1)
Mo(1)−CP	2.09	O(1)−Li(1)*	1.87(1)
Si(1)−C(11)	1.852(9)	O(2)−Li(1)	1.92(1)
Si(1)−C(12)	1.86(1)	Li(1)−Li(1)*	2.67(2)
N(1)−Mo(1)−C(11)	102.0(4)	Li(1)−O(1)−Li(1)*	91.0(5)
N(1)−Mo(1)−C(15)	101.8(3)	Mo(1)−N(1)−O(1)	169.6(8)
N(1)−Mo(1)−CP	126.7	Mo(1)−C(11)−Si(1)	124.5(4)
C(11)−Mo(1)−C(15)	86.7(3)	Mo(1)−C(15)−Si(2)	114.6(4)
C(11)−Mo(1)−CP	118.3	O(1)−Li(1)−O(1)*	88.9(5)
C(15)−Mo(1)−CP	113.2	O(1)−Li(1)−O(2)	123.3(8)
N(1)−O(1)−Li(1)	135.5(5)	O(1)*−Li(1)−O(2)	116.1(7)
N(1)−O(1)−Li(1)*	130.7(5)		

[a] CP refers to the unweighted centroid of the C(1−5) ring; * denotes the symmetry operation 1 − x, y, $-z$.

triangular face and with the NO group being situated along the z axis, then the non-NO-interacting orbital on the metal can be considered to be a d_{xy}-type orbital. Interaction of the amido N p-orbitals with the metal M d_{xy}-type orbital should result in the N substituents lying in a plane also containing the nitrosyl group. The solid-state molecular structure of **10** exhibits just such an alignment, the torsion angles N(3)−W(1)−N(2)−C(15) and N(3)−W(1)−N(1)−C(11) being 2.7(5) and −0.7(6)°, respectively.

Ligand scrambling of this type has been previously observed for this system. For instance, treatment of $Cp^*W(NO)(NHCMe_3)Cl$ with sodium amalgam leads to formation of $Cp^*W(NO)(NHCMe_3)_2$ in 70% yield.[28] The most probable route for the formation of this product in both cases is via initial reduction of the amido chloro starting material to produce the $[Cp^*W(NO)(NHCMe_3)Cl]^-$ radical anion. This anion could then undergo displacement of a chloride ligand by a $NHCMe_3$ radical to afford the final product. We have now found that similar ligand scrambling evidently occurs during the reaction of $Cp^*Mo(NO)(CH_2SiMe_3)Cl$ with LiPPhH. In this case the unexpected product, $\{[Cp^*Mo(NO)(CH_2SiMe_3)_2][Li(THF)]\}_2$ (**11**, isolated in 3% yield), reflects that the initially formed $Cp^*Mo(NO)(CH_2SiMe_3)_2$ has also undergone a further one-electron reduction. The exact nature of **11** has been confirmed by an X-ray crystallographic analysis,[29] the results of which are pictorially represented in Figure 3. The dimeric structure of **11** possesses a C_2 axis passing through the center of the essentially planar (dihedral angle Li_2O planes = 3.15°) Li_2O_2 square (internal angles of the square = 90.0(5) ± 1°). Each lithium atom is three coordinate and is sterically shielded by the alkyl ligands of the complex,[30] with some of the Li−H(alkyl) distances being as short as 2.22 Å. As expected, the Mo−NO linkages in the molecule are essentially linear (169.6(8)°), and the bond lengths within the MoNO fragment (i.e. Mo−N = 1.713(5) Å and N−O = 1.323(6) Å) indicate a considerable degree of Mo→NO back-bonding. As noted earlier, the preferred synthetic route to complex **11** involves reaction of the parent dialkyl complex, $Cp^*Mo(NO)(CH_2SiMe_3)_2$, with 1 equiv of a lithium phosphide.[24]

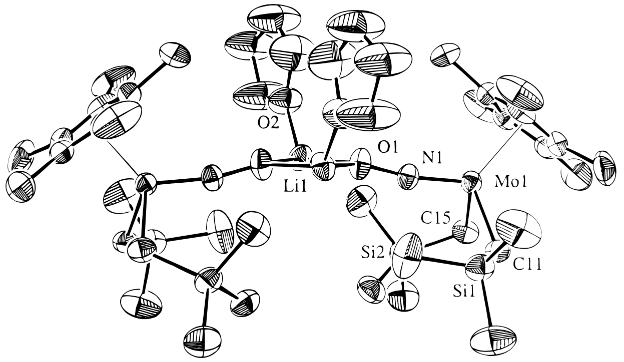

Figure 3. ORTEP diagram of $\{[Cp^*Mo(NO)(CH_2SiMe_3)_2][Li(THF)]\}_2$ (**11**). Thermal ellipsoids of 50% probability are shown for the non-hydrogen atoms.

Epilogue

Though metathesis of chloride ligands with anionic nucleophiles has proved to be a useful and reliable synthetic method in many systems, this work has shown that it is not always infallible. If the first step of the metathesis transformation involves initial reduction of the organometallic reactant, the eventual outcome of the reaction is apparently determined by the stability of this reduced species under the reaction conditions employed. The net result is that overall reduction reactions are not only possible but in some cases such reactions become the preferred pathway for the reacting organometallic species.

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Supporting Information Available: Tables of final atomic coordinates and equivalent isotropic thermal parameters, bond lengths, bond angles, hydrogen parameters, anisotropic thermal parameters, torsion angles, least-squares planes, and intermolecular contacts for complexes **9**−**11** and an ORTEP diagram (45 pages). Ordering information is given on any current masthead page.

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(28) Ross, K. J. Ph.D. Dissertation, University of British Columbia, 1994; p 103.

(29) Preliminary details of this structure have been communicated previously; see ref 24.

(30) For examples of similar three-coordinate lithium centers see: (a) Hvoslef, J.; Hope, H.; Murray, B. D.; Power, P. P. *J. Chem. Soc., Chem. Commun.* **1983**, 1438. (b) Huffman, J. C.; Geerts, R. L.; Caulton, K. G. *J. Cryst. Spectrosc.* **1984**, *14*, 541. (c) Becker, G.; Hartmann, H.-M.; Munch, A.; Riffel, H. *Z. Anorg. Allg. Chem.* **1985**, *29*, 530. (d) Engelhardt, L. M.; Harrowfield, J. M.; Lappert, M. F.; MacKinnon, I. A.; Newton, B. H.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1986**, 846. (e) Weese, K. H.; Bartlett, R. A.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1987**, *26*, 2409. (f) Askham, F. R.; Carroll, K. M.; Alexander, S. J.; Rheingold, A. L.; Haggerty, B. S. *Organometallics* **1993**, *12*, 4810. [Obtained from the Cambridge Structural Data Base: Allen, F. H.; Kennard, O. *Chem. Design Automation News* **1993**, *8*, 31.]

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