The Elusive 16-Electron Cp*M(NO)Me_2 (M = Mo, W) Complexes and Their Spontaneous Conversions to Cp*M(NMe)(O)Me Isomers

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Abstract: Treatment of [Cp*Mo(NO)Cl(μ-Cl)]$_2$ with magnesium (Me_2Mg·dioxane, MeMgCl) or aluminum (Me_3Al) methylating reagents affords the known compound [Cp*Mo(NO)Me(μ-Cl)]$_2$ (**1**). Similar treatment of the dichloro precursor with MeLi in ethereal solvents generates an equimolar mixture of **1** and the trimethyl "ate" complex, Cp*$MoMe_3$(NO−Li$(OEt_2)_n$), (**2**-Et_2O). Reaction of **2**-Et_2O with a source of $[Me]^+$ forms Cp*$MoMe_3$(≡N−OMe) (**3**), a rare terminal alkoxylimido complex. Metathesis of the chloro ligands of [Cp*Mo(NO)Cl(μ-Cl)]$_2$ by MeLi in toluene at low temperatures produces the target dimethyl complex, Cp*Mo(NO)Me_2 (**4**), in 75% isolated yield. In solution, **4** is predominantly a monomeric species, whereas in the solid state it adopts a dimeric or oligomeric structure containing isonitrosyl bridges as indicated by IR and $^{15}N/^{13}C$ NMR spectroscopies. Hydrolysis of **4** affords *meso*- and *rac*-[Cp*Mo(NO)Me]$_2$(μ-O) (**5**), and the reactions of **4** with a range of Lewis bases, L, to form the 18e adducts Cp*Mo(NO)(L)Me_2 (e.g., Cp*Mo(NO)$(PMe_3)Me_2$ (**7**)), have established it to be the most electrophilic complex of its family. Acidolysis of the methyl groups of **4** is also facile. Most notably, **4** is thermally unstable in solution and undergoes isomerization via nitrosyl N−O bond cleavage to its oxo(imido) form, Cp*Mo(NMe)(O)Me (**11**), which is isolable from the final reaction mixture as the μ-oxo-bridged adduct formed by **4** and **11**, i.e., Cp*Mo(NO)Me_2(μ-O)Cp*Mo(NMe)Me (**4** ← **11**). The rate of this isomerization is significantly faster for the tungsten dimethyl complex; hence, Cp*W(NO)Me_2 (**12**) is not isolable free of a supporting donor interaction and can only be isolated as Cp*W(NO)Me_2(μ-O)Cp*W(NMe)Me (**12** ← **13**) or Cp*W(NO)$Me_2(PMe_3)$ (**14**) adducts.

Introduction

The importance of Lewis acidic alkyl complexes derives principally from their utility in mediating the coupling of alkyl ligands to unsaturated organic substrates, processes that are of pivotal importance in organometallic chemistry.[1] Indeed, alkyl migration is the key chain-growth step in several catalytic cycles of industrial importance, such as transition-metal-catalyzed olefin polymerization and hydroformylation reactions.[2] For instance, in the case of olefin polymerization, electron-deficient alkyls (M)R_n (where (M) = metal-containing fragment, R = alkyl) are well-defined precursors to the highly electrophilic, catalytically active cations $[(M)R_{n-1}]^+$.[3]

The vast majority of alkyl-containing catalyst precursors feature an early transition-metal atom in its highest oxidation state, specific examples being the d^0 metallocenes, Cp'_2MR_2 and $Cp'_2M'R$ (Cp′ = substituted cyclopentadienyl groups; M = Ti, Zr, Hf, Th; M′ = Sc, Y, lanthanides; R = alkyl).[4] However, Lewis acidic alkyls of the mid- and late-transition metals are also known, and these often contain metal atoms with non-zero d-electron counts. Notable examples of these complexes include the square planar d^8 group 10 compounds L_2MR_2 (L = electroneutral 2e ligands; M = Ni, Pd, Pt)[5] and the d^3 chromium complexes Cp*CrR_2 (Cp* = η^5-C_5Me_5) and related derivatives.[6]

We have an abiding interest in the series of 16e, d^4 metallonitrosyl complexes of general formula Cp′M(NO)R_2 (Cp′ = η^5-C_5H_5 (Cp), η^5-C_5Me_5 (Cp*); M = Mo, W; R = −alkyl, aryl), and we continue to explore their rich and diverse chemistry.[7] During our investigations, we have established that the Lewis-acid character of these compounds is due to the π-acidic nitrosyl ligand stabilizing two of the three metal d π orbitals. The remaining d π orbital is nonbonding, perpendicular to the M−NO axis, and of relatively low energy. It is thus

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(2) (a) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed.; Wiley: New York, 1992. (b) Moser, W. R., Slocum, D. W. Eds. *Homogeneous Transition Metal Catalyzed Reactions*; Advances in Chemistry Series 230; American Chemical Society: Washington, DC, 1992; Chapters 39−41. (c) Skupinska, J. *Chem. Rev.* **1991**, *91*, 613.

(3) Typically, treatment of alkyl complexes with powerful Lewis acids effects this transformation: (a) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920. (b) Yang, X.; Stren, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015. (c) Jia, L.; Yang, X.; Ishihara, A.; Marks, T. J. *Organometallics* **1995**, *14*, 3135. (d) Li, L.; Marks, T. J. *Organometallics* **1998**, *17*, 3996. (e) Chen, Y.; Metz, M. V.; Li, L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 6287. (f) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927. (g) Chen, E. Y.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391.

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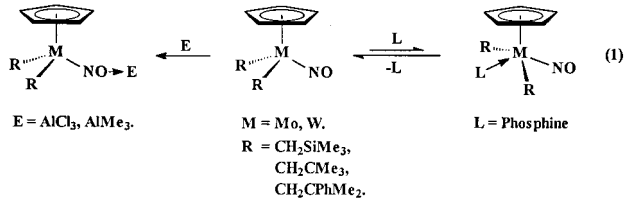
ideally suited for small-molecule coordination.[8] Furthermore, we have shown that while the relative Lewis acidities of these compounds are determined by the electronic structures of the different Cp′M(NO) fragments, the relative electrophilicities of these complexes are strongly dependent upon the steric properties of R. In general, the steric influences of the alkyl ligands in Cp′M(NO)R$_2$ complexes preclude reaction pathways that are initiated by close approach to the metal center of all but the smallest nucleophiles. Thus, bulky alkyl ligands such as $-CH_2CMe_3$ and $-CH_2SiMe_3$ are able to shield the metal center and impede the coordination of electron-rich molecules to M.[7a,8a] The behavior of these complexes toward electrophiles is similarly dictated by steric effects and usually involves the generation of adducts at the nitrosyl O atom (eq 1), as opposed to cleavage of a M−C bond.[8a] Hence, the most significant reactivity patterns for these compounds are initiated by the unimolecular extrusion of R−H, rather than via addition reactions.[9]

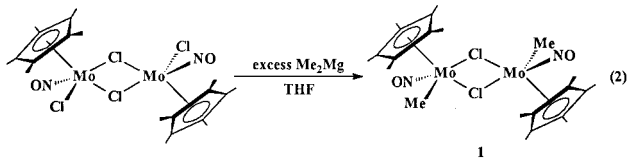


Methyl ligands in the Cp′M(NO)Me$_2$ (M = Mo, W) complexes would obviously afford the maximum steric accessibility for these systems and therefore lead to predominantly metal-centered reactivity pathways. However, the dimethyl complexes have been surprisingly elusive research objectives in our laboratories,[10] and we have been unable to repeat the apparently straightforward synthesis of Cp*Mo(NO)Me$_2$, reported briefly in 1990,[11] or to prepare it by our customary methods.[12,13]

This contribution focuses upon the array of organometallic products that result from attempted metathesis reactions of the dichlorides [Cp*M(NO)Cl(μ-Cl)]$_2$ (M = Mo, W) with synthetic equivalents of the [Me]$^-$ ion. The reaction solvent has a vital role in determining the course of these conversions, and this effect is first delineated and then utilized during the rational development of an efficient synthesis of Cp*Mo(NO)Me$_2$. The results of a preliminary survey of the reactivity of Cp*Mo(NO)Me$_2$ with both nucleophiles and strong electrophiles are next presented. Finally, an unprecedented thermal transformation of Cp*Mo(NO)Me$_2$ that involves both spontaneous nitrosyl N−O bond cleavage and Mo−Me migration to the N atom to afford the isomeric molybdenum(VI) compound, Cp*Mo(NMe)(O)Me, is described.

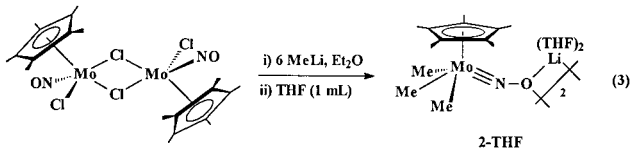
Results and Discussion

Metathesis Reactions of [Cp*Mo(NO)Cl(μ-Cl)]$_2$. (A) With Magnesium Reagents. Treatment of cold THF suspensions of [Cp*Mo(NO)Cl(μ-Cl)]$_2$ with 2 equiv of Me$_2$Mg·dioxane fails to generate Cp*Mo(NO)Me$_2$ in detectable quantities. Instead, the known monosubstituted dimeric complex, [Cp*Mo(NO)Me(μ-Cl)]$_2$ (**1**),[14] is isolated as a yellow/orange powder in high yields (eq 2).



It is noteworthy that Me$_2$Mg·dioxane is incapable of effecting metathesis of the chloro ligands of **1** even after a THF solution of **1** and Me$_2$Mg has been stirred at elevated temperatures for several days. Furthermore, neither Me$_3$Al nor MeMgCl is capable of effecting this metathesis. Other examples of the failure of standard alkylating reagents to effect such metathesis transformations of transition-metal nitrosyl halides have been reported in the past.[15,16]

(B) With Methyllithium in Ether Solvents. Addition of 2 equiv of MeLi in Et$_2$O to an ethereal suspension of [Cp*Mo(NO)Cl(μ-Cl)]$_2$ affords an equimolar mixture of **1** and the lithium-isonitrosyl "ate" complex, Cp*MoMe$_3$(NO−Li(OEt$_2$)$_n$) (**2**-Et$_2$O). The generation of **2** demonstrates that under these experimental conditions the transiently formed Cp*Mo(NO)Me$_2$ is significantly more reactive toward MeLi than is complex **1**. Solid samples of **2**-Et$_2$O are prone to desolvate rapidly in the absence of Et$_2$O vapor, but the more robust THF solvate, [Cp*MoMe$_3$(NO-μ-Li(THF)$_2$)]$_2$ (**2**-THF), may be synthesized as shown in eq 3 and crystallized from a mixture of Et$_2$O/hexanes/THF.



A single-crystal X-ray crystallographic analysis has established the solid-state molecular structure of **2**-THF (Figure 1). Dimeric **2**-THF resides on a crystallographic center of symmetry with the monomeric units being linked via lithium−isonitrosyl

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(8) (a) Legzdins, P.; Rettig, S. J.; Sánchez, L. *Organometallics* **1988**, *7*, 2394. (b) Legzdins, P.; Rettig, S. J.; Sánchez, L.; Bursten, B. E.; Gatter, M. G. *J. Am. Chem. Soc.* **1985**, *107*, 1411. (c) Bursten, B. E.; Cayton, R. H. *Organometallics* **1987**, *6*, 2004.

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(10) Several unsuccessful attempts have been made to prepare Cp′M(NO)Me$_2$ complexes in these laboratories: Phillips, E. C.; Veltheer, J. E. V.; Debad, J. D.; Sayers, S. F.; Legzdins, P., unpublished observations.

(11) de Jesús, E.; de Miguel, A. V.; Royo, P.; Lanfredi, A. M. M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1990**, 2779.

(12) While never isolated or detected spectroscopically Cp′M(NO)Me$_2$ (Cp′ = Cp, Cp*; M = Mo, W), complexes have been synthesized in situ at low temperature and reacted with H_2O_2 to form Cp′M(O)$_2$Me complexes. See: Legzdins, P.; Phillips, E. C. *Organometallics* **1989**, *8*, 940.

(13) (a) Herring, F. G.; Legzdins, P.; Richter-Addo, G. B. *Organometallics* **1989**, *8*, 1485. (b) Dryden, N. H.; Legzdins, P.; Rettig. S. J.; Veltheer, J. E. *Organometallics* **1992**, *11*, 2583. (c) Debad, J. D.; Legzdins, P.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1993**, *12*, 2094.

(14) Complex **1** has been previously prepared by Royo by the reaction of Al$_2$Me$_6$ with [Cp*Mo(NO)Cl(μ-Cl)]$_2$; see ref 11.

(15) Alegre, B.; de Jesús, E.; de Miguel, A. V.; Royo, P.; Lanfredi, A. M. M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1988**, 819.

(16) Brumaghim, J. L.; Priepot, J. G.; Girolami, G. S. *Organometallics* **1999**, *18*, 2139.

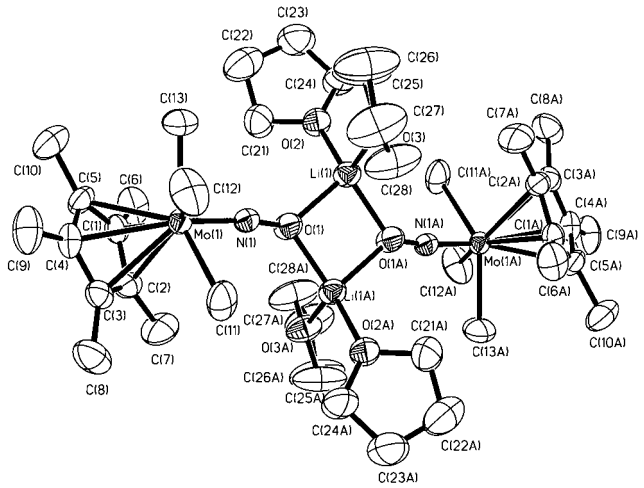
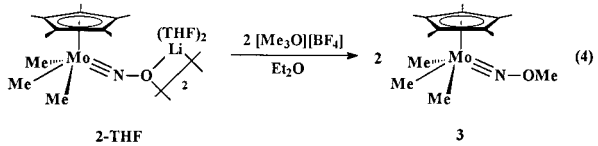


Figure 1. Solid-state molecular structure of **2**-THF with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (deg): Mo(1)−N(1) 1.742(2), N(1)−O(1) 1.279(3), Mo(1)−C(13) 2.218(3), Mo(1)−C(12) 2.268(3), Mo(1)−C(11) 2.237(3), O(1)−Li(1) 1.929(5), Mo(1)−N(1)−O(1) 169.6(2), N(1)−O(1)−Li(1) 130.5(2), O(1)−Li(1)−O(1A) 86.1(2), C(12)−Mo(1)−N(1) 114.59(12), C(11)−Mo(1)−C(13) 140.0(2), C(11)−Mo(1)−C(12) 72.7(2), C(12)−Mo(1)−C(13) 73.5(2).

bridges.[17] The coordination geometry at each metal center is best described as a distorted four-legged "piano stool", the distortions from an idealized square pyramidal $CpML_4$ structure being well precedented.[18]

The metrical parameters within the Mo−N−O−Li chain of atoms in **2**-THF clearly illustrate the oxo-imido nature of this fragment. Thus, the short Mo−N contact is within the range typical for Mo−N(imido) bond lengths,[19] while the N−O contact is longer than a typical nitrosyl N−O bond.[20] Consistently, the IR spectrum of **2**-THF exhibits a single NO-derived stretching vibration centered at 1399 cm^{-1}, which is significantly lower in energy than the N−O stretches of typical terminal nitrosyl-containing complexes.[21] **2**-THF is also quite thermally robust and, unlike the related $Cp^*MoMe(CH_2SiMe_3)_2(NO-Li-(THF)_3)$,[7b] fails to generate a methylidene derivative and CH_4 even after 24 h in boiling toluene.[22]

The *mono*methyl complex **1** and *tri*methyl derivative **2** coexist in solutions at room temperature for up to 2 h[23] and do not undergo transmetalation[24] to produce the desired $Cp^*Mo(NO)Me_2$ in a transformation driven by the elimination of LiCl. Also, a ^1H NMR analysis of the reaction of **1**-d_6 with a large excess (>6 equiv) of protio-MeLi establishes the exclusive product to be **2**-d_6, thereby demonstrating that significant methyl group exchange between the Mo−CH_3/CD_3 ligands of **2** and CH_3Li does not occur under the reaction conditions. Hence, **2** is probably best viewed as solvated $Cp^*MoMe_3(NO-Li)$ in solution. Consistently, the addition of $[Me_3O][BF_4]$ to **2** effects a quantitative conversion to $Cp^*MoMe_3(\equiv NOMe)$ (**3**) (eq 4).



Complex **3** is a yellow solid that is soluble in most organic solvents, although single crystals suitable for a crystallographic analysis have not yet been obtained. Nevertheless, the spectroscopic data of **3** fully support its formulation as a methoxylimido complex. For instance, its Nujol mull IR spectrum is devoid of bands in the 1500−1700 cm^{-1} region, but an intense absorption at 1260 cm^{-1}, that shifts to 1230 cm^{-1} in the spectrum of **3**-^{15}N, can be assigned to an N−O flexing vibration.[25] The NMR spectra of isotopically labeled samples of **3** establish the Mo≡N−OMe connectivity. The NO-methyl group of **3**-^{15}N is evidenced by a doublet in both its ^1H and ^{13}C spectra, with coupling constants of 2.7 and 1.6 Hz, respectively. The $^{15}N-^{13}C$ coupling constant is significantly lower than the range expected for $^1J_{^{13}C-^{15}N}$ values (between 4.5 and 8 Hz) but is well within the typical range of $^2J_{^{13}C-^{15}N}$ values (between 1 and 3 Hz).[26] To our knowledge, only one other class of complex containing an alkoxylimido ligand has been reported previously, namely $Cp'NbX_2(\equiv NOBu^t)$ ($Cp' = \eta^5$-C_5H_5, η^5-C_5H_4Me; X = Cl, CH_2SiMe_3), although these compounds are not derived from a nitrosyl precursor.[27]

(C) With Methyllithium in Toluene. As expected, the reaction of **1** with 2 equiv of MeLi in a nondonor solvent such as toluene permits ligand reorganization in the equimolar mixture of **1** and **2** and affords a yellow microcrystalline powder whose analytical and spectroscopic data confirm its identity as $Cp^*Mo(NO)Me_2$ (**4**). Its cryoscopic molecular weight in benzene solution is 260 (±50), its IR spectrum in CH_2Cl_2 exhibits a ν(NO) at 1577 cm^{-1}, and its room-temperature ^1H NMR spectrum in benzene-d_6 comprises two singlets (δ 1.46 (15H) and 1.05 (6H)). In conflict with these observations, the literature report

(17) Li_2O_2 bridging interactions such as this have been reported previously in similar anionic nitrosyl "ate" complexes, see ref 7b. For a recent example of Li bridges in titanocene oxo complexes, see: (a) Lukens, W. W., Jr.; Matsunaga, P. T.; Andersen, R. A. *Organometallics* **1998**, *17*, 5240. Related Li bridges in dimeric alkoxides have also been described: (b) Kodiok-Khön, G.; Pickardt, J.; Schumann, H. *Acta Crystallogr.* **1991**, *C47*, 2649. (c) Huffman, J. C.; Geerts, R. L.; Caulton, K. G. *J. Crystallogr. Spectrosc. Res.* **1984**, *14*, 541 (d) Hvoslef, J.; Hope, H.; Murray, B. D.; Power, P. P. *J. Chem. Soc., Chem. Commun.* **1983**, 1438.

(18) (a) Poli, R.; Smith, K. *Organometallics* **2000**, *19*, 2858. (b) Lin, Z.; Hall, M. B. *Organometallics* **1993**, *12*, 19. (c) Poli, R. *Organometallics* **1990**, *9*, 1892. (d) Kubácek, P.; Hoffman, R.; Havlas, Z. *Organometallics* **1982**, *1*, 180.

(19) (a) Nugent, W. A.; Mayer, J. M. *Metal Ligand Multiple Bonds*; Wiley: New York, 1988. (b) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239.

(20) Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyls*; Oxford University Press: New York, 1992.

(21) (a) Legzdins, P.; Lundmark, P. J.; Phillips, E. C.; Rettig, S. J.; Veltheer, J. E. *Organometallics* **1992**, *11*, 2991. (b) Legzdins, P.; Young, M. A.; Batchelor, R. J.; Einstein, F. W. B. *J. Am. Chem. Soc.* **1995**, *117*, 8798.

(22) Alkylidene formation via α-H elimination of hydrocarbons from sterically crowded metal centers is well documented; see: (a) Li, L.; Hung, M.; Xue, Z. *J. Am. Chem. Soc.* **1995**, *117*, 12746. (b) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1 and references therein.

(23) Equimolar mixtures of **1** and **2** were maintained at room temperature for up to 2 h. Solution infrared and ^1H NMR spectroscopies of the mixture revealed that no bimolecular ligand redistribution had occurred.

(24) (a) Jordan, R. F. *J. Organomet. Chem.* **1985**, *294*, 321. (b) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729. (c) Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521. Interestingly, cyclopentadienyl ligand exchange between the metal centers of Cp'_2ZrCl_2 and $ZrCl_4$ is facile in toluene and affords high yields of $Cp'ZrCl_3$, but the reverse process occurs in THF; see: (d) Hitchcock, P. B.; Lappert, M. F.; Liu, D.-S.; Ryan, E. J. *Polyhedron* **1995**, *14*, 2745.

(25) The coordination of a Lewis acid to a nitrosyl O atom typically results in a marked reduction in ν(NO). However, firm conclusions regarding the N−O bond order cannot be drawn from such data since this absorption does not arise from a pure N−O vibrational mode. See: Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed.; Part A, Theory and Applications in Inorganic Chemistry; Wiley: New York, 1997.

(26) Witanowski, M.; Stefaniak, L. In *Annual Reports on NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press Inc.: New York, 1981; Vol. 11B.

(27) Green, M. L. H.; James, J. T.; Saunders, J. F. *Chem. Commun.* **1996**, 1343.

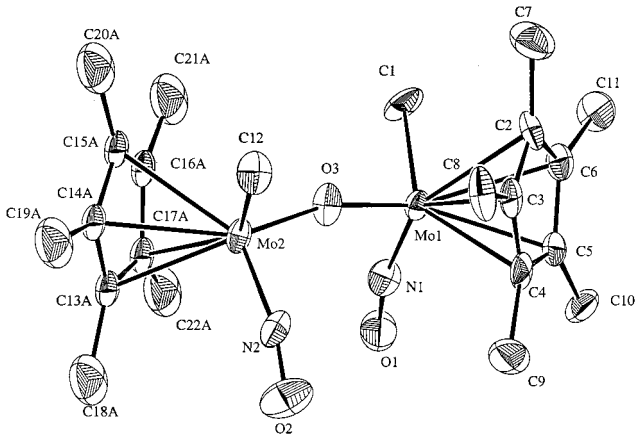


Figure 2. Solid-state molecular structure of **5** with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (deg): Mo(1)−N(1) 1.770(5), N(1)−O(1) 1.229(6), Mo(2)−N(2) 1.756(4), N(2)−O(2) 1.220(7), Mo(1)−O(3) 1.902(4), Mo(2)−O(3) 1.883(4), Mo(1)−C(1) 2.161(6), Mo(2)−C(12) 2.161(6), Mo(1)−N(1)−O(1) 167.3(5), Mo(2)−N(2)−O(2) 170.6(5), Mo(1)−O(3)−Mo(2) 164.0(2).

of Cp*Mo(NO)Me$_2$ describes it as being a thermally stable, red-violet material (both in the solid state and in solution) whose IR spectrum in CH_2Cl_2 exhibits a ν(NO) at 1582 cm^{-1}, and whose ^{1}H NMR spectrum in benzene-d_6 consists of singlets at δ 1.58 (15H) and δ 1.52 (6H).[11] In a bid to explain this discrepancy, we have reinvestigated the literature procedure for the preparation of **4**. In our hands, treatment of a toluene suspension of [Cp*Mo(NO)Br(μ-Br)]$_2$ with 4 equiv of MeLi in Et_2O affords an insoluble yellow precipitate that contains **4**. Addition of acetone to this solid produces a red-purple solution from which a red crystalline material is obtained after standard workup.[11] Single-crystal X-ray diffraction unambiguously identifies this material as [Cp*Mo(NO)Me]$_2$(μ-O) (**5**) (Figure 2) that probably arises from the hydrolysis of Cp*Mo(NO)Me$_2$.[12,21a] The structural parameters determined for **5** lie within the expected ranges of distances and angles for compounds of this general class.[21a] The crystallographically characterized molecule of **5** is the meso *S,S*-diastereomer, but ^{1}H NMR spectroscopy reveals that solutions of **5** contain a thermodynamic mixture of both meso and rac forms. In the context of the previous report of Cp*Mo(NO)Me$_2$ (vide supra), it is noteworthy that careful integration of the Cp* resonances of **5** at δ 1.60 and δ 1.58 establishes that the ratio of concentrations [*meso*-**5**]:[*rac*-**5**] is 5:2. Furthermore, the ν(NO) of the major isomer of **5** occurs at 1584 cm^{-1}.

Solid-State Structure of Cp*Mo(NO)Me$_2$. The physical properties of solid **4** are similar to those of monomethyl **1**, but contrast with the established trend generally associated with this class of bis(alkyl) complexes. For example, the monomeric complexes Cp*Mo(NO)R$_2$ (R = CH_2SiMe_3, CH_2CMe_3, CH_2CMe_2Ph) are red-purple crystalline solids which dissolve readily in all common organic solvents to form intensely purple solutions.[7,21] In contrast, solid **4** is a pale-yellow microcrystalline powder that is sparingly soluble in alkane solvents and Et_2O and dissolves readily only in CH_2Cl_2 and $CHCl_3$, producing intensely purple solutions. A dimeric formulation for solid **4** is indicated by an intense peak at m/z = 583 in its MALDI TOF spectrum, but EI and FAB experiments reveal only the presence of monomeric **4**. The IR spectrum of **4** in CH_2Cl_2 exhibits a ν(NO) (1577 cm^{-1}) in the range typical for monomeric Cp′M(NO)R$_2$ complexes,[7] but the Nujol mull spectrum of solid **4** exhibits no absorptions in the terminal nitrosyl range (1700−1500 cm^{-1}).[20] However, a strong signal at 1377 cm^{-1}, which

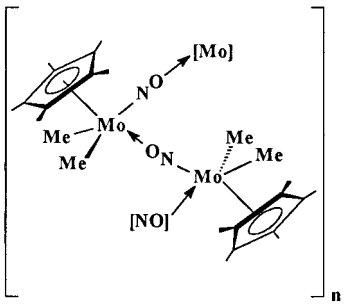


Figure 3. Proposed solid-state structure of **4**.

shifts to 1352 cm^{-1} in the spectrum of **4**-^{15}N, can be assigned to an N−O-derived stretching vibration. These data suggest the presence of either bridging, bent, or isonitrosyl groups in solid **4**. Both the solution- and solid-state MAS ^{15}N NMR spectra of **4**-^{15}N consist of single resonances at δ 36.1 and δ 43.1, respectively, and both signals are in the spectral region indicative of linear sp-hybridized nitrosyl moieties (δ −110 to δ 200).[20,28] The absence of any ^{15}N NMR resonances in the region δ 350−950 eliminates the possibility of any bent and bridging (μ^2-NO) bonding modes as structural possibilities for solid **4** while not eliminating the possibility of an isonitrosyl interaction.[29] Finally, whereas the Mo−CH_3 carbon nuclei of a $CDCl_3$ solution of **4** provide a single, broad resonance in the ^{13}C NMR spectrum at δ 48.3, the CP MAS spectrum of **4**-^{13}C exhibits two signals of approximately equal intensities at δ 28.8 and δ 31.4.

The main conclusions to emerge from the above study of solid **4** are (a) the material does not consist of monomeric Cp*Mo(NO)Me$_2$, (b) the NO ligand exhibits isonitrosyl bonding interactions, but these are relatively weak and are cleaved in solution, and (c) the two methyl groups are inequivalent, but they exhibit similar NMR chemical shifts. Consequently, we propose that solid **4** adopts a microstructure such as that shown in Figure 3, in which cisoidal Mo centers of **4** are linked by relatively weak isonitrosyl bridges.

Reactions of Cp*Mo(NO)Me$_2$ with Lewis Bases. The addition of donor solvents (in >10-fold excess) such as pyridine, acetonitrile, or THF to purple CH_2Cl_2 solutions of **4** results in the immediate formation of yellow products. The 18e solvento complexes thus produced are detectable in solution by ^{1}H NMR spectroscopy, even though the coordinated solvent ligands are quite labile. Nevertheless, the pyridine complex, Cp*Mo(NO)Me$_2$(NC_5H_5) (**6**), which exists in solutions predominantly as the trans isomer, can be isolated as a yellow crystalline solid. Furthermore, the addition of excess PMe_3 to solutions of **4** rapidly generates a thermodynamic mixture of *cis*- and *trans*-Cp*Mo(NO)Me$_2$(PMe_3) (*cis*-**7** and *trans*-**7**) in a ca. 98:2 ratio (eq 5). The thermodynamic preference for the trans isomer is consistent with that calculated for the model complexes *cis*- and *trans*-CpMo(NO)Me$_2$(NH_3).[18a] Unlike analogous materials having sterically demanding alkyl ligands,[8a] complexes **7** display no tendency to dissociate the coordinated phosphine. The solid-state molecular structure of *trans*-**7** (Figure 4) consists of a distorted square-pyramidal array resembling that established for

(28) Duffin, P. A.; Larkworthy, L. F.; Mason, J.; Stephens, A. N.; Thompson, R. M. *Inorg. Chem.* **1987**, *26*, 2034. (b) Bell, L. K.; Mason, J.; Mingos, D. M. P.; Tew, D. G. *Inorg. Chem.* **1983**, *22*, 3297. (c) Mason, J. *Chem. Rev.* **1981**, *81*, 205.

(29) Isonitrosyl complexes have been shown to exhibit ^{15}N NMR signals in the same range as their nitrosyl precursors: Sharp, W. B.; Legzdins, P.; Patrick, B. O., manuscript in preparation.

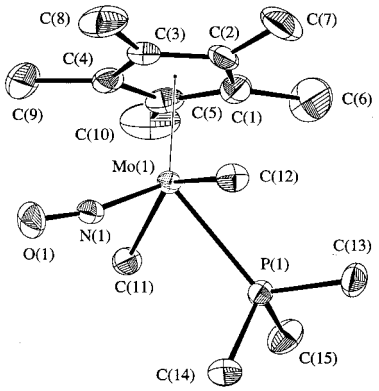
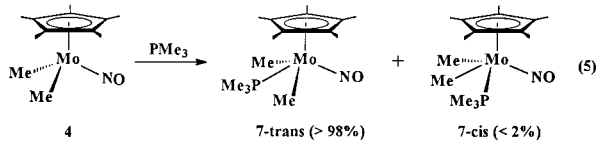
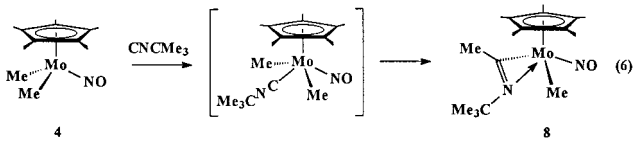


Figure 4. Solid-state molecular structure of **7** with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (deg): Mo(1)−N(1) 1.764(2), N(1)−O(1) 1.223(2), Mo(1)−P(1) 2.5454(6), Mo(1)−C(12) 2.244(2), Mo(1)−C(11) 2.249(2), Mo(1)−N(1)−O(1) 168.9(2), N(1)−Mo(1)−P(1) 105.70(7), C(11)−Mo(1)−C(12) 143.11(9).

2-THF (vide supra), and it exhibits no unusual metrical parameters.

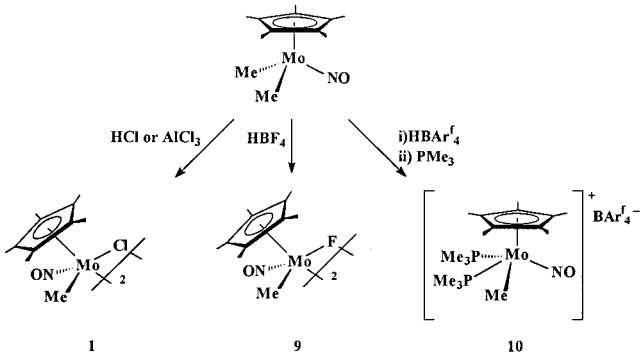


The addition of 1 equiv of *tert*-butylisocyanide to a CH_2Cl_2 solution of **4** results in conversion to Cp*Mo(NO)(η^2-MeC(=NBu^t))Me (**8**) (eq 6). This material probably results via formation of an unobserved isocyanide adduct of **4** followed by a rapid intramolecular migratory insertion of $CNBu^t$ into a Mo−Me bond. The η^2-bonding mode of the iminoacyl ligand is confirmed by comparison of its C−N stretching frequency (ν(CN) = 1702 cm^{-1}) with those of closely related compounds.[8a,9b]



Reactions of Cp*Mo(NO)Me$_2$ with Electrophiles. The dimethyl complex reacts with strong electrophiles at a metal−carbon bond, whereas the bulkier Cp*M(NO)R_2 analogues do not.[29] Thus, treatment of an Et_2O suspension of **4** with 1 equiv of HCl in Et_2O leads to the evolution of methane and the formation of **1** (Scheme 1). Similarly, while $AlCl_3$ typically leads to NO adduct formation with the bulky bis(alkyl) derivatives,[7a,8a]

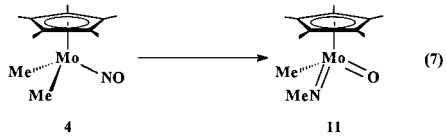
Scheme 1



the reaction of **4** with this reagent also generates **1** and (presumably) $AlCl_n(Me)_{3-n}$. Finally, treatment of **4** with HBF_4 in Et_2O results in the production of [Cp*Mo(NO)Me(μ-F)]$_2$ (**9**) in 66% isolated yield. This fluoride abstraction from BF_4^- is a striking example of the high electrophilicity of the [Cp*Mo(NO)Me]$^+$ cation and is analogous to the reactivity of [Cp_2ZrMe]$^+$ with PF_6^-.[30] The ^{1}H NMR spectrum of **9** in $CDCl_3$ exhibits a virtual triplet at δ 0.70 that is attributable to the terminal methyl ligands. This virtual coupling provides proof that **9** retains its dimeric nature in solution, even though the highly electronegative fluoride is the ligand that is expected to show the lowest propensity of the halides to form such bridging interactions.[31]

The highly electrophilic nature of the [Cp*Mo(NO)Me]$^+$ cation led us to attempt its preparation with the very weakly coordinating anion [BAr$^f_4$]$^-$ (BAr$^f_4$ = [(3,5-$(CF_3)_2C_6H_3)_4$B]). The reaction of **4** with H($OEt_2)_2$[BAr$^f_4$] effects protonolysis of a methyl group and forms [Cp*Mo(NO)Me][BAr$^f_4$]. While the cation in this salt is unstable above −30 °C in chlorinated solvents, it is moderately stable at room temperature in Et_2O and can be trapped by the addition of PMe_3 as [Cp*Mo(NO)Me($PMe_3)_2$][BAr$^f_4$] (**10**) (Scheme 1). The metal-bound methyl group of **10** exhibits a doublet of doublets in its ^{1}H NMR spectrum with proton−phosphorus coupling constants consistent with phosphine ligands being in both cis ($^2J_{C-H}$ = 4.2 Hz) and trans ($^2J_{C-H}$ = 13.5 Hz) conformations relative to the methyl group.

Spontaneous Thermal Isomerization of Cp*Mo(NO)Me$_2$. When maintained in an inert atmosphere, **4** is indefinitely stable as a solid at room temperature. However, solution samples undergo an unprecedented rearrangement to yield a thermodynamically preferred isomer of **4**, namely Cp*Mo(O)(NMe)Me (**11**) (eq 7). Formally, **11** derives from cleavage of the nitrosyl N−O bond of **4**, accompanied by Mo−methyl migration to the nitrosyl N atom. The transformation is conveniently monitored in CD_2Cl_2 by ^{1}H NMR spectroscopy, and integration of the appropriate Cp* resonances shows that after 24 h at room temperature the consumption of **4** is ca. 60% complete. While the cleavage of nitrosyl ligands in unsaturated Group 6 complexes can occur under a variety of conditions,[32,33] the spontaneous conversion of a well-defined nitrosyl(alkyl) complex to its oxo imido isomer, as occurs with Cp*Mo(NO)Me_2, is without precedent in metallonitrosyl chemistry.



The identity of **11** has been confirmed by an X-ray crystallographic analysis which reveals that the complex crystallizes as a Lewis base adduct of the parent **4**. The ORTEP diagram of adduct **4** ← **11** (Figure 5) shows that the material is comprised of two distinct Mo coordination environments linked by a

(30) Jordan, R. F.; Dasher, W. E.; Echols, S. F. *J. Am. Chem. Soc.* **1986**, *108*, 1718.

(31) Wulfsberg, G. *Inorganic Chemistry*; University Science Books: Sausalito, CA, 2000.

(32) Legzdins, P.; Young, M. A. *Comments Inorg. Chem.* **1995**, *17*, 239 and references therein.

(33) We recently noted that treatment of Cr(NO)(NPr$^i_2$)(O_2CPh)$_2$ with $Ar_2Mg\cdot x$(dioxane) affords Cr(NAr)(O)(NPr$^i_2$)Ar (Ar = 2-Me-C_6H_4), but there is no evidence that the final product results from isomerization of Cr(NO)(NPr$^i_2$)Ar_2; see: Jandciu, E. W.; Legzdins, P.; McNeil, W. S.; Patrick, B. O.; Smith, K. M. *Chem. Commun.* **2000**, 1809.

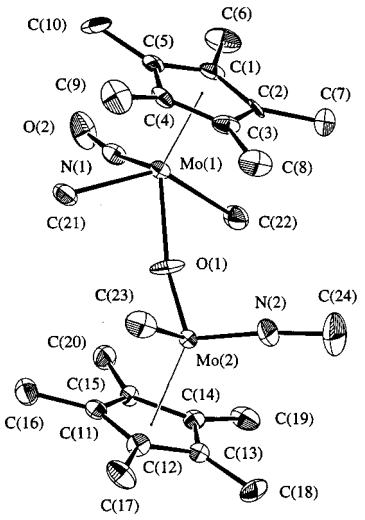
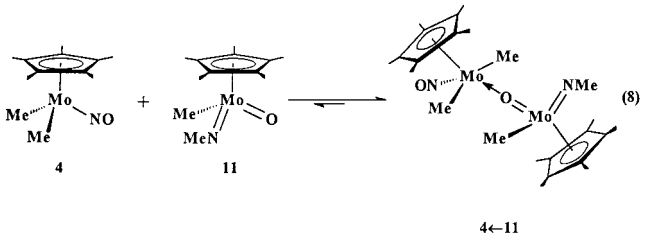


Figure 5. Solid-state molecular structure of **4** ← **11** with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (deg): Mo(1)−N(1) 1.773(5), N(1)−O(2) 1.236(6), Mo(1)−O(1) 2.149(4), Mo(2)−O(1) 1.760(4), Mo(2)−N(2) 1.738(5), N(2)−C(24) 1.359(9), Mo(2)−C(23) 2.151(6), Mo(1)−C(21) 2.240(5), Mo(1)−C(22) 2.233(5), Mo(1)−N(1)−O(2) 167.3(4), O(1)−Mo(1)−N(1) 119.0(2), Mo(1)−O(1)−Mo(2) 166.4(3), C(21)−Mo(1)−C(22) 138.7(2), Mo(2)−N(2)−C(24) 169.4(6).

bridging oxo ligand. The unequal Mo−O bond distances (Mo(1)−O(1) = 2.149(4) Å and Mo(2)−O(1) = 1.760(4) Å) establish that the Mo(2)−O(1) linkage has multiple-bond character and that the interaction between the oxo ligand and the Mo(1) metal center is dative in nature. The methyl ligands of **4** in **4** ← **11** exhibit identical bond lengths that compare well with Mo−Me distances in related complexes such as **2**, **7**, and Cp*Mo(NO)(Br)(Me)(PPh$_3$).[15] The molecular structure of **11** in **4** ← **11** has a Mo−methyl distance (Mo(2)−C(23) = 2.151(6) Å) that is shorter than the analogous interactions in **4**, thereby reflecting the higher formal oxidation state of the Mo atom in **11**.[34] Finally, **11** in **4** ← **11** reveals an essentially linear methylimido ligand with an Mo−N bond distance that lies within the range of typical Mo−N(imide) lengths.[19]

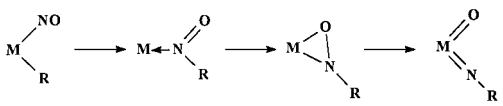
Despite the apparent lack of symmetry in bimetallic **4** ← **11**, the diastereotopic methyl ligands are evidenced in the room-temperature ^{1}H NMR spectrum of the pure adduct by a singlet at δ 0.01 (CD_2Cl_2 solution). The chemical exchange implied by this observation has been investigated further. Thus, in the −50 °C ^{1}H NMR spectrum of **4** ← **11** in the same solvent, the methyl groups of **4** exhibit two singlets at δ −0.12 and δ −0.27. Spectra at successively higher temperatures result in the incremental broadening of these resonances, which eventually coalesce at ca. −25 °C. Addition of pure **4** to a sample of **4** ← **11** establishes the origin of the exchange process because, somewhat surprisingly, the ^{1}H NMR spectra of such admixtures do not reveal separate signals for both free and complexed **4**. Indeed, the only qualitative difference from the spectra of pure **4** ← **11** is in the relative intensities of the signals. We therefore conclude that **4** ← **11** adduct formation is reversible in solution (eq 8) and that this process is rapid under the conditions of the room-temperature ^{1}H NMR experiment. Direct evidence for the existence of equilibrium 8 is provided by IR spectra of the mixtures which display distinct absorptions due to the nitrosyl ligands in **4** and **4** ← **11** at 1562 and 1530 cm^{-1}, respectively, in an approximate ratio of 1:3.



The importance of the above equilibrium is most telling in relation to the characterization of pure **4**. Since the transformation of **4** into **11** is spontaneous in solution, it is therefore inevitable that samples of **4** are contaminated by small quantities of **4** ← **11**. The latter is formed either during the synthetic procedure that generates **4** or during the preparation of samples of **4** for spectroscopic study. As a consequence, ^{1}H NMR spectra of **4** display variable chemical shifts and line-broadening at low temperature, the extent of which depends strongly upon the actual concentration of **4** ← **11** in the sample. Similarly, the anomalous broadening of the Mo−methyl resonance in room-temperature ^{13}C NMR spectra of **4** is also probably due to contamination of the sample by **4** ← **11** rather than to the adoption of non-C_s-symmetric structures by pure Cp*Mo(NO)Me$_2$ in solution. Equilibrium 8 can be disrupted by the addition of excess PMe$_3$, which results in the clean formation of **7** and **11**, thereby permitting the characterization of uncomplexed **11** in solution by ^{1}H NMR spectroscopy (^{1}H NMR (C_6D_6, 200 MHz, 25 °C) δ 0.82 (s, Me), 1.66 (s, C_5Me_5) 3.55 (s, NMe)).

The tungsten-containing analogue of **4**, namely Cp*W(NO)Me$_2$ (**12**), undergoes the same isomerization at a significantly faster rate, such that it is impossible to isolate **12** free of a stabilizing adduct interaction. Thus, addition of MeLi to a toluene suspension of [Cp*W(NO)Cl(μ-Cl)]$_2$ at −78 °C, followed by warming to room temperature, generates Cp*W(O)(NMe)Me (**13**) as the major tractable product. The bimetallic tungsten species **12** ← **13** can also be isolated in low yields from these mixtures. The transformation was monitored in this case by removal of an aliquot of the reaction mixture at appropriate time intervals and addition of PMe$_3$ (>5 equiv) to quench the reaction. Integration of the room-temperature ^{1}H NMR resonances of Cp*W(NO)Me$_2$(PMe$_3$) (**14**) and **13** in the mixture revealed the extent of the isomerization reaction immediately prior to the quench. Complex **14** exhibits unexceptional spectroscopic features. However, the thermodynamic preference of *trans*-**14** over *cis*-**14** is reduced as compared to that of its molybdenum analogue (**7**), the two tungsten complexes existing as a ca. 70:30 equilibrium mixture.[18a]

Mechanism of Isomerization of Dimethyl Complexes. Currently available experimental evidence concerning the probable mechanism of the dimethyl to oxo(imide) isomerization is consistent with this process being a rare example of nitrosyl migratory insertion, the principal steps of which are depicted below.[35]



Unfortunately, a complete mechanistic evaluation of this system is hindered by the fact that the transformation does not lend itself to a quantitative kinetic study. Once isolated, **4** exhibits little solubility in both benzene-d_6 and toluene-d_8. Indeed,

(34) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*, 4th ed.; Harper Collins: New York, 1993.

saturated solutions of **4** in these solvents are of such low concentrations that various decomposition pathways are favored over the isomerization reaction. Complex **4** is highly soluble in chlorinated solvents; however, CD_2Cl_2 or $CDCl_3$ solutions of **4** decompose to form numerous products over 24 h. ^{1}H NMR spectra of such mixtures reveal that only ca. 5% conversion to **11** has occurred. It thus appears that the conditions that favor the transformation to form **11** are accessible only when the dimethyl complex is generated as a monomer in aromatic solvents.

The transformations of **4** and its tungsten congener **12** to form their oxo imido isomers were therefore monitored by PMe_3 quenching (vide supra) that resulted in irreversible formation of the phosphine adducts **7** and **14**, respectively. In this manner it was established that the transformation of **12** to **13** diminishes significantly as the concentration of **13** increases. For instance, while the proportion of **13** in the mixture is ca. 40% after 5 min at −70 °C, its relative amount increases to only ca. 60% after an additional 1 h at −50 °C. Similar observations can be made during monitoring of the isomerization of molybdenum complex **4**. These findings are consistent with an autoinhibition process, in which the product **11** retards the rate of conversion by trapping **4** as the adduct **4** ← **11** (eq 8). Due to this stabilizing equilibrium, a reliable indicator of the order of the reaction can, in principle, be obtained only at very early reaction times. Unfortunately, the heterogeneous nature of the methylation reaction makes any concentration data obtained during the first 20 min of the conversion erratic and irreproducible.

Apparent literature precedent for these findings stems from the investigation of an unusual nitrosyl migratory insertion reaction reported by Bergman and co-workers.[35a−c] Their studies revealed that the rate of formation of the nitrosoalkane complex CpCo(RN═O)L (R = Me, Et, Pr^i, *p*-$CH_3C_6H_4$; L = phosphine) from the alkyl(nitrosyl) precursor, CpCo(NO)R, is retarded by increasing [L]. Furthermore, it was established that the rate-limiting step of this reaction is the intramolecular migration of R to the nitrosyl N atom. In light of these considerations, it is significant that the tungsten complex Cp*W(NO)Me_2 isomerizes much faster than its molybdenum congener **4** under essentially identical experimental conditions. Third-row metals such as tungsten usually exhibit higher metal−ligand bond strengths than their second-row congeners.[1b] For a mechanism that involves rate-limiting alkyl ligand migration, the higher bond dissociation energy of the W−C σ bond would therefore result in the opposite dependence of rate upon the choice of metal atom. Another factor that militates against a straightforward intramolecular insertion mechanism is the fact that such thermal bis(alkyl)-to-oxo(imide) transformations are unprecedented. The other Cp′M(NO)$(alkyl)_2$ complexes that have been isolated to date simply do not exhibit this reactivity mode,[7] despite the greater migratory aptitude established for $-CH_2SiMe_3$ and $-CH_2CMe_3$ groups as compared to that for $-CH_3$.[13c,36] These considerations thus suggest that a bimolecular reaction pathway, in which the steric differences between $-CH_3$ and $-CH_2EMe_3$ (E = C, Si) ligands would be strongly manifest, is probably

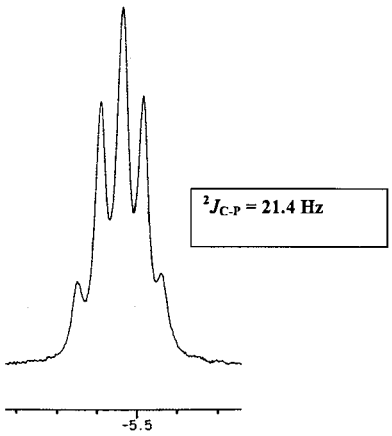


Figure 6. ^{31}P NMR resonance of the trans isomer of a statistical mixture of **7**, **7**-$^{13}C_1$, and **7**-$^{13}C_2$.

significant. A pre-equilibrium involving an unobserved, dinuclear reactive intermediate, for example, might also account for the higher reactivity of the W complex.

To test this possibility, a crossover experiment was conducted in which an equimolar mixture of **4** and Cp*Mo(^{15}NO)$(CD_3)_2$ (**4**-^{15}N-d_6) in CD_2Cl_2 was permitted to isomerize to **4** ← **11** at room temperature. NMR spectra of the crude product mixtures revealed a statistical distribution of the isotopic labels over *all possible sites*. For instance, in the ^{1}H NMR spectrum, label crossover was confirmed by the detection of both a singlet and a ^{15}N-split doublet at δ 3.7 ppm (^2J = 3.3 Hz) assigned to the imido methyl group. Deuterium label was not apparent in the Cp* methyl groups, however. While this experiment clearly establishes that complex **4** participates in bimolecular reaction pathways, it does not distinguish between (a) label-scrambling as a direct consequence of the **4**-to-**11** isomerization process and (b) rapid ligand redistribution *prior* to the alkyl migration event. A second crossover experiment, however, unequivocally demonstrated that the methyl ligands of **4** undergo facile intermolecular exchange under the conditions of the **4**-to-**11** conversion. Thus, a CH_2Cl_2 solution containing an equimolar mixture of **4** and Cp*Mo(NO)($^{13}CH_3)_2$ (**4**-$^{13}C_2$) was stirred at room temperature for 10 min prior to the addition of PMe_3 (>5-fold excess). A ^{31}P NMR spectrum of a C_6D_6 solution of the product revealed an apparent 1:3:5:3:1 "quintet" at δ −5.46 ppm (Figure 6). This pattern does not represent a single resonance, but rather is composed of three superimposed signals due to the PMe_3-containing trans adducts **7** (singlet), (*R*)- and (*S*)-**7**-$^{13}C_1$ (doublet), and **7**-$^{13}C_2$ (triplet) that are present in equal concentrations. The intermolecular exchange of the methyl ligands that is responsible for this observation probably occurs via an unobserved methyl-bridged intermediate.[6a,c,37] The significantly faster rate of exchange, as compared to the rate of **4**-to-**11** conversion, establishes the mechanistic independence of these processes.

These findings underscore the difficulty in experimentally identifying the mechanistic sequence that leads from the

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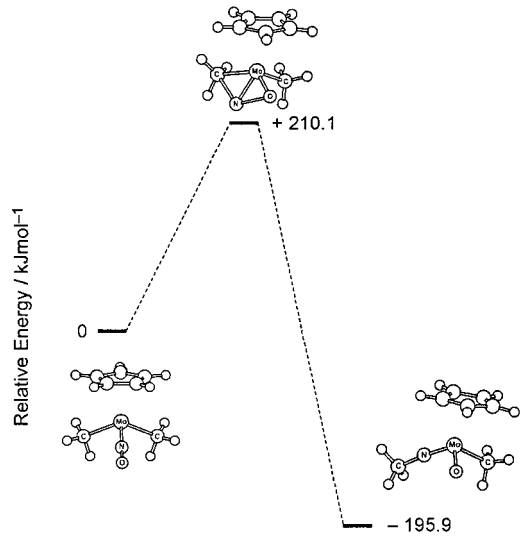

Figure 7. Calculated structures and a reaction coordinate for the unimolecular path, CpMo(NO)Me$_2$ → CpMo(NMe)(O)Me.

dimethyl structure to the oxo(imide) isomeric form. Nevertheless, an MNO → M isonitrosyl interaction (which was detected in solid **4**) may well play an important role in this conversion, perhaps via the electrophilic promotion of insertion.[38]

Theoretical Considerations. The NO cleavage reaction has also been investigated using density functional theory (DFT). The calculated structures and relative energies, including zero-point energy corrections, of the model complexes CpMo(NO)Me$_2$ (**A**) and CpMo(O)(NMe)Me (**B**) are shown in Figure 7. The calculated energy and geometry of **A** is indistinguishable from that previously determined by the same method.[18a] The isomerization reaction is calculated to be nearly 200 kJ mol^{-1} downhill, a thermodynamic driving force consistent with the formation of multiple bonds in an electronically saturated product. A transition state along a *uni*molecular pathway between **A** and **B** is optimized at an energy of +210.1 kJ mol^{-1} above the reactant ground state. This extremely high barrier is inconsistent with the experimentally observed reaction rate and suggests that such a proposed unimolecular path is not a possible mechanism for the reaction.

Summary

An investigation of the unexpected influence of ethereal solvents upon the course of the reaction of [Cp*Mo(NO)Cl(μ-Cl)]$_2$ with methyllithium has led to the development of an efficient preparation of 16e Cp*Mo(NO)Me$_2$. Lewis acidic Cp*Mo(NO)Me$_2$ is monomeric in solution but has been shown by both physical and spectroscopic methods to exist as higher oligomers in the solid state. The high electrophilicity of the material is evidenced by its reactions with Lewis bases such as CNBu^t, PMe$_3$, pyridine, acetonitrile, and THF. Most interestingly, Cp*Mo(NO)Me$_2$ is unstable at room temperature in solution, and it transforms spontaneously into the isomeric oxo imido complex, Cp*Mo(NMe)(O)Me, during an unprecedented conversion that involves both migratory insertion and N−O bond cleavage.

Experimental Section

General Methods. All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions either under high vacuum or an atmosphere of dinitrogen or argon. General procedures routinely employed in these laboratories have been described in detail previously.[39] Toluene, hexane, pentane, diethyl ether, 1,4-dioxane, PMe$_3$, benzene-d_6, and hexamethyldisiloxane (Aldrich) were dried and distilled from sodium or sodium/benzophenone ketyl. Tetrahydrofuran was distilled from molten potassium, and dichloromethane was distilled from calcium hydride. Pyridine was dried by distillation from KOH pellets, followed by storage over activated 4 Å molecular sieves. CDCl$_3$ was dried by storage over activated 4 Å molecular sieves for 2 days and degassed prior to use. MeLi (Acros) was titrated against diphenylacetic acid before use, and CD$_3$MgI (Aldrich) was used as received. The complexes [Cp*Mo(NO)Cl(μ-Cl)]$_2$,[40] [Cp*Mo(NO)Br(μ-Br)]$_2$,[41] Me$_2$Mg·*x*(dioxane),[42] and H(OEt$_2$)$_2$[BAr$^f_4$][43] were prepared by published procedures. Isotopically labeled complexes were prepared by making appropriate modifications to the standard preparative methodologies. ^{15}N-labeled *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald) was prepared by the treatment of a cold acetic acid solution of *N*-methyl-*p*-toluenesulfonamide (Aldrich) with aqueous Na[^{15}NO$_2$], collected by filtration, and rinsed with water.[44] All other reagents were obtained from commercial suppliers and were used as received.

Solution-phase NMR spectra were recorded on Bruker AC 200, Varian XL 300, or Bruker AMX 500 instruments. ^{1}H and ^{13}C spectra are referenced to external SiMe$_4$ using the residual protio solvent peaks as internal standards (^{1}H NMR experiments) or the characteristic resonances of the solvent nuclei (^{13}C NMR experiments). ^{31}P and ^{15}N spectra were referenced to external 85% H$_3$PO$_4$ and MeNO$_2$, respectively. Where appropriate, NMR spectral assignments were supported by conventional homonuclear decoupling, HMQC, HMBC, and gate-decoupled ^{13}C NMR experiments. CP MAS ^{13}C and MAS ^{15}N spectra were obtained on a Bruker MSL 400 MHz spectrometer with a Bruker double-tuned probe and Doty 7 mm standard stator. Samples were contained in a 7 mm ceramic rotor with ceramic end caps and rubber O-rings. ^{1}H 90° pulse lengths of 7.2 μs (^{13}C CP MAS) and 5 μs (^{15}N MAS) were utilized with a ^{1}H decoupling field strength of 35 kHz. ^{15}N MAS experiments used a 60 s delay between pulses to allow full relaxation of the nitrosyl nitrogen. Spinning speeds were 2.5 kHz, and recycle times were 4 s. MALDI TOF spectra were recorded on a Bruker Biflex spectrometer utilizing a nitrogen laser at 337 nm.

Preparation of [Cp*Mo(NO)Me(μ-Cl)]$_2$ (1). THF (~10 mL) was vacuum transferred onto an intimate mixture of [Cp*Mo(NO)Cl(μ-Cl)]$_2$ (2 g, 3.01 mmol) and Me$_2$Mg·*x*(dioxane) (541 mg, 6.00 mmol of Me$^-$) at −196 °C. The reaction vessel was permitted to warm slowly to room temperature, and its contents were vigorously stirred for 30 min. The resulting turbid orange mixture was evaporated to dryness in vacuo, and the remaining yellow/orange powder was treated with CH$_2$Cl$_2$ (20 mL) and 1,4-dioxane (1 mL). The orange mixture was then filtered through a column of Celite (3 × 3 cm) supported on a medium-porosity glass frit, and the assembly was washed with CH$_2$Cl$_2$ until all orange color had been removed from the Celite. The filtrate was concentrated to ca. 10 mL under reduced pressure, and hexanes (30 mL) were added in a layer above the solution prior to storage at −30 °C overnight. Complex **1** was isolated as an analytically pure yellow/orange powder (1.67 g, 89% yield) via filter cannulation from the cooled mixture. The characterization data for this complex match those previously reported.[11] Anal. Calcd for C$_{22}$H$_{36}$Cl$_2$Mo$_2$N$_2$O$_2$: C, 42.38; H, 5.82; N, 4.49. Found: C, 42.08; H, 5.85; N, 4.43. IR (Nujol mull): ν(NO) 1606 (s) cm^{-1}. NMR data: ^{1}H (CDCl$_3$, 200 MHz, 25 °C) δ 0.62 (s, Me), 1.76 (s, C$_5$*Me*$_5$). MS (EI, 150 °C): *m*/*z* 560 [P$^+$ − 2NO].

Preparation of [Cp*MoMe$_3$(NO-μ-Li(THF)$_2$]$_2$ (2-THF). To a stirred suspension of [Cp*Mo(NO)Cl(μ-Cl)]$_2$ (150 mg, 0.26 mmol) in

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Et_2O (10 mL) was added dropwise a solution of MeLi (1.4 mL, 1.6 M in Et_2O, 2.25 mmol) at room temperature until the red solid had been consumed. When the mixture was completely yellow, addition of the MeLi was ceased, and a small quantity of THF (ca. 1 mL) was added. The solution was then filtered through a column of Celite (1 × 3 cm) supported on a medium-porosity glass frit, and the residue was rinsed with Et_2O until the washings were colorless. The combined filtrates were evaporated to dryness in vacuo to obtain a tan solid that was triturated with pentane. The supernatant solution was decanted from the resulting yellow powder via cannulation, and the powder was recrystallized from Et_2O/hexanes, affording **2**-THF (160 mg, 65% yield) as yellow prisms. Anal. Calcd for $C_{42}H_{80}Li_2Mo_2N_2O_6$: C, 55.20; H, 8.75; N, 3.06. Found: C, 54.97; H, 8.65; N, 3.14. IR (Nujol mull): ν(NO) 1399 (s) cm^{-1}. NMR data: ^{1}H (C_6D_6, 300 MHz, 25 °C) δ 0.16 (s, Me), 0.45 (s, 2 Me), 1.51 (br, THF), 1.75 (s, C_5Me_5), 3.69 (br, THF); ^{13}C{^{1}H} ($CDCl_3$, 75 MHz, 25 °C) δ 10.0 (C_5Me_5), 19.3 (2 Me), 22.8 (Me), 25.7 (THF), 68.2 (THF), 107.9 (C_5Me_5).

Preparation of Cp*MoMe$_3$(NOMe) (3). Onto a mixture of **2**-THF (300 mg, 0.66 mmol) and [Me_3O][BF_4] (97 mg, 0.66 mmol) at −196 °C was vacuum transferred dichloromethane (7 mL), and the mixture was allowed to warm slowly to room temperature. The clear pink solution was evaporated to dryness in vacuo, and the resulting yellow solid was extracted with pentane. The suspension was filtered through a column of Celite (1 × 3 cm) supported on a medium-porosity glass frit. The filtrate was then concentrated under reduced pressure to incipient crystallization, and the mixture was cooled to −30 °C overnight to obtain a yellow powder (95 mg, 45% yield) that was found to be analytically pure **3**. Anal. Calcd for $C_{14}H_{27}MoNO$: C, 52.33; H, 8.47; N, 4.36. Found: C, 52.44; H, 8.39; N, 4.26. IR (KBr pellet): ν(NO) 1260 (s) cm^{-1}. NMR data: ^{1}H (C_6D_6, 300 MHz, 25 °C) δ 0.44 (s, Me), 0.94 (s, 2 Me), 1.53 (s, C_5Me_5), 3.33 (s, NOMe); ^{13}C{^{1}H} ($CDCl_3$, 75 MHz, 25 °C) δ 10.3 (C_5Me_5), 22.8 (2 Me), 28.2 (Me), 64.2 (NOMe), 109.8 (C_5Me_5)). MS (EI, 200 °C): *m*/*z* 308 [P$^+$ − Me].

Preparation of Cp*Mo(NO)Me$_2$ (4). To a vigorously stirred suspension of [Cp*Mo(NO)Cl(μ-Cl)]$_2$ (2.00 g, 3.01 mmol) in toluene (30 mL) at −70 °C was added dropwise methyllithium (7.53 mL, 1.6 M solution in Et_2O, 12.04 mmmol) via a fine-bore cannula. The mixture was stirred for 2 h as it warmed slowly to 0 °C. The toluene was completely evaporated in vacuo at this temperature, and the remaining yellow solid was extracted with dichloromethane (40 mL). The resulting purple solution was filtered through a column of Celite (3 × 3 cm) supported on a medium-porosity glass frit into a Schlenk tube maintained at −70 °C, and the assembly was washed with copious amounts of CH_2Cl_2 (10 ×10 mL). The product precipitated from the cold solution as a yellow powder and was isolated by filter cannulation to obtain 1.33 g (75% yield) of analytically pure **4**. Anal. Calcd for $C_{12}H_{21}MoNO$: C, 49.49; H, 7.27; N, 4.81. Found: C, 49.43; H, 7.30; N, 4.73. IR: ν(NO) 1577 (s, CD_2Cl_2), 1377 (s, Nujol mull) cm^{-1}. NMR data: ^{1}H ($CDCl_3$, 500 MHz, 25 °C) δ 0.97 (s, Me), 1.80 (s, C_5Me_5); ^{13}C{^{1}H} ($CDCl_3$, 125 MHz, 25 °C) δ 10.0 (C_5Me_5), 48.3 (br, Me), 110.44 (C_5Me_5); ^{13}C (CP MAS, 100.5 MHz, 25 °C) δ 10.3 (C_5Me_5), 31.4 (Me-^{13}C), 28.8 (Me-^{13}C) 112.4 (C_5Me_5); ^{15}N ($CDCl_3$, 30 MHz, 25 °C) δ 36.1; ^{15}N (CP MAS, 40.5 MHz, 25 °C) δ 43.1. MS (EI, 120 °C): *m*/*z* 293 [P$^+$], MALDI TOF (no matrix) 581.4.

Preparation of Cp*Mo(NO)Me$_2$(μ-O)Cp*Mo(NMe)Me (4 ← 11). A solution of methyllithium (7.53 mL, 1.6 M solution in Et_2O, 12.05 mmol) was added dropwise via a cannula to a stirred suspension of [Cp*Mo(NO)Cl(μ-Cl)]$_2$ (2 g, 3.01 mmol) in toluene (30 mL) at room temperature. Upon completion of the addition, the mixture was stirred for an additional 30 min. The final deep-red solution was filtered through a column of Celite (3 × 3 cm) supported on a medium-porosity glass frit, and the residue was washed with toluene (2 × 15 mL). The combined filtrates were evaporated to dryness in vacuo, and the resulting red solid was dissolved in THF (ca. 30 mL). This solution was concentrated and cooled to −30 °C overnight to induce the deposition of a deep red microcrystalline powder (0.983 mg, 56% yield) which was analytically pure **4** ← **11**. Anal. Calcd for $C_{24}H_{42}Mo_2N_2O_2$: C, 49.49; H, 7.27; N, 4.81. Found: C, 49.60; H,7.28; N, 4.70. IR (KBr pellet): ν(NO) 1542 (s); ν(Mo═O) 840 cm^{-1}. NMR data: ^{1}H ($CDCl_3$, 300 MHz, 25 °C) δ 0.11 (s, 2 Me), 0.67 (s, Me), 1.69 (s, C_5Me_5 of **4**), 1.86 (s, C_5Me_5 of **11**), 3.73 (s, NMe); ^{13}C{^{1}H} ($CDCl_3$, 75 MHz, 25 °C) δ 9.3 (C_5Me_5 of **11**), 10.6 (C_5Me_5 of **4**), 20.1 (Me), 24.3 (br, 2 Me), 50.2 (NMe), 107.4 (C_5Me_5 of **4**), 116.5 (C_5Me_5 of **11**); ^{1}H (CD_2Cl_2, 500 MHz, −50 °C) δ −0.30 (s, Me of **4**), −0.14 (s, Me of **4**), 0.60 (s, Me of **11**), 1.59 (s, C_5Me_5 of **4**), 1.80 (s, C_5Me_5 of **11**), 3.65 (s, NMe); ^{13}C{^{1}H} (CD_2Cl_2, 125 MHz, −50 °C) δ 8.9 (C_5Me_5 of **11**), 10.2 (C_5Me_5 of **4**), 14.9 (Me of **11**), 19.4 (Me of **4**), 23.6 (Me of **4**), 53.8 (NMe), 106.8 (C_5Me_5 of **4**), 116.2 (C_5Me_5 of **11**). MS (EI, 150 °C): *m*/*z* 293 [P$^+$/2].

Preparation of [Cp*Mo(NO)Me]$_2$(μ-O) (5). Methyllithium (0.60 mL, 1.6 M solution in Et_2O, 0.96 mmol) was added dropwise to a suspension of [Cp*Mo(NO)Cl(μ-Cl)]$_2$ (200 mg, 0.24 mmol) in toluene (10 mL) at −78 °C. The mixture was stirred and allowed to warm slowly to room temperature over 2 h, whereupon the solution became pale red and a tan-colored suspension formed. Filter cannulation permitted isolation of the solid, to which was added acetone (10 mL) with stirring. Over the course of 3 min, the solid dissolved, forming a deep red solution that was subsequently filtered. The solvent was allowed to evaporate slowly from the filtrate in an inert atmosphere to induce the deposition of **5** (22 mg, 16% yield) as a red crystalline material. Anal. Calcd for $C_{22}H_{36}Mo_2N_2O_3$: C, 46.49; H, 6.38; N, 4.93. Found: C, 46.22; H, 6.42; N, 4.78. IR (KBr): ν(NO) 1584, 1562 (s); ν(Mo−O−Mo) 790 cm^{-1}. NMR data: ^{1}H (C_6D_6, 200 MHz, 25 °C), Isomer A, δ 1.08 (s, Me), 1.58 (s, C_5Me_5), isomer B, δ 1.16 (s, Me),1.60 (s, C_5Me_5); ^{13}C{^{1}H} (C_6D_6, 50 MHz, 25 °C), isomer A, δ 9.3 (C_5Me_5), 29.3 (Me) 111.8 (C_5Me_5), isomer B, δ 10.3 (C_5Me_5), 29.0 (Me) 111.7 (C_5Me_5). MS (EI, 120 °C): *m*/*z* 568 [P$^+$].

Preparation of Cp*Mo(NO)Me$_2$(NC$_5$H$_5$) (6). To a purple solution of **4** (300 mg, 0.103 mmol) in toluene (7 mL) was added pyridine (5 mL) dropwise at room temperature until the solution became yellow. The solution was then reduced in volume to ca. 5 mL, and an equal volume of hexanes was layered above the toluene/pyridine mixture. After being maintained at −30 °C for 48 h, this solution had deposited yellow plates of analytically pure **6** (282 mg, 74% yield). Anal. Calcd for $C_{17}H_{26}MoN_2O$: C, 55.13; H, 7.08; N, 7.56. Found: C, 55.32; H, 7.25; N, 7.51. IR (Nujol mull): ν(NO) 1540 (s) cm^{-1}. NMR data: ^{1}H (C_6D_6, 300 MHz, 25 °C) δ 0.43 (s, Me), 1.63 (s, C_5Me_5), 6.26 (m, 2 H, py), 6.65 (m, py), 7.91 (m, py); ^{13}C{^{1}H} (C_6D_6, 75 MHz, 25 °C) 9.5 (C_5Me_5), 23.1 (Me), 107.2 (C_5Me_5), 124.3, 134.8, 150.3 (py). MS (EI, 150 °C): *m*/*z* 293 [P$^+$ − C_5H_5N].

Preparation of Cp*Mo(NO)Me$_2$(PMe$_3$) (7). A solution of **4** (300 mg, 0.103 mmol) in toluene (7 mL) was frozen at −196 °C, and an excess of PMe_3 (0.2 mL, 1.9 mmol) was vacuum transferred onto the frozen matrix. The mixture was allowed to warm slowly to room temperature while being stirred, whereupon its color changed from purple to bright yellow. The solution was stirred for an additional 15 min before it was evaporated to dryness in vacuo. The resulting yellow solid was extracted with THF (5 mL), and the extracts were filtered through a column of Celite (1 × 3 cm) that was supported on a medium-porosity glass frit. Hexanes (5 mL) were added to the filtrate, and the solution was then concentrated under reduced pressure to the point of incipient crystallization. After 3 h at −30 °C, this mixture had deposited orange/yellow plates of analytically pure **7** (325 mg, 86% yield). Anal. Calcd for $C_{15}H_{30}MoNOP$: C, 49.05; H, 8.23; N, 3.81. Found: C, 49.40; H, 8.27; N, 3.84. IR (Nujol mull): ν(NO) 1570 (s) cm^{-1}. NMR data: ^{1}H (C_6D_6, 400 MHz, 25 °C), *trans*-**7**, δ 0.21 (d, $^3J_{PH}$ = 14.6 Hz, Me), 0.77 (d, $^2J_{PH}$ = 7.5 Hz, PMe_3), 1.53 (s, C_5Me_5), *cis*-**7**, δ 1.01 (d, $^3J_{PH}$ = 8.7 Hz, Me), 1.14 (d, $^3J_{PH}$ = 1.7 Hz, Me), 1.14 (d, $^2J_{PH}$ = 9.6 Hz, PMe_3), 1.51 (s, C_5Me_5); ^{13}C{^{1}H} (C_6D_6, 50 MHz, 25 °C), *trans*-**7**, δ 6.3 (d, $^2J_{PC}$ = 21 Hz, Me), 9.5 (C_5Me_5), 13.4 (d, $^1J_{PC}$ = 22 Hz, PMe_3), 106.1 (C_5Me_5), *cis*-**7** undetected; ^{31}P{^{1}H} (C_6D_6, 202 MHz, 25 °C) δ −3.4 , −7.8. MS (EI, 150 °C): *m*/*z* 293 [P$^+$ − PMe_3].

Preparation of Cp*Mo(NO)(η^2-MeC(═NBu^t))Me (8). A purple solution of **4** (100 mg, 0.034 mmol) in dichloromethane (10 mL) was cooled to −60 °C, and excess *tert*-butylisocyanide (80 μL, 0.707 mmol) was added slowly via syringe. Upon completion of the addition, the mixture was allowed to warm to room temperature, whereupon its color became yellow. The clear solution was evaporated to dryness in vacuo, and the resulting solid was dissolved in Et_2O (5 mL). This solution was then filtered through a column of Celite (3 × 1 cm) supported on a medium-porosity glass frit, and hexanes were added to the filtrate. The solution was then cooled to −30 °C overnight to obtain **8** as pale

yellow crystals (90 mg, 70% yield). Anal. Calcd for $C_{17}H_{30}MoN_2O$: C, 54.52; H, 8.07; N, 7.48. Found: C, 54.15; H, 8.19; N, 7.27. IR (KBr): ν(C═N) 1702 (s); ν(NO) 1539 (s) cm^{-1}. NMR data: ^{1}H (C_6D_6, 200 MHz, 25 °C) δ 0.92 (s, Mo-Me), 1.03 (s, Me), 1.65 (s, C_5Me_5), 2.36 (s, C-Me); ^{13}C{^{1}H} (C_6D_6, 50 MHz, 25 °C) 5.57 (Me), 9.8 ($C_5\mathit{Me}_5$), 19.2 (Me), 29.7 (CMe_3), 61.1 (CMe$_3$), 108.1 (C_5Me$_5$). MS (EI, 120 °C)*:* *m*/*z* 376 [P$^+$].

Preparation of [Cp*Mo(NO)Me(μ-F)]$_2$ (9). A suspension of **4** (300 mg, 0.103 mmol) in Et$_2$O (7 mL) was cooled to −70 °C, and HBF$_4$ (55 wt % solution in Et$_2$O, 0.14 mL, 0.103 mmol) was added quickly via syringe. The tan suspension instantly lightened to yellow, and the solid became more flocculent. The mixture was allowed to warm to room temperature before the solution was removed via filter cannulation, and the remaining yellow solid was dried under reduced pressure. The resulting yellow solid was extracted with THF (5 mL), and the extracts were filtered through a column of Celite (1 × 3 cm) that was supported on a medium-porosity glass frit. Hexanes (5 mL) were added to the filtrate, and the solution was then concentrated under reduced pressure to the point of incipient crystallization. After 24 h at −30 °C, this mixture had deposited **9** as an analytically pure yellow powder (200 mg, 66% yield). Anal. Calcd for $C_{22}H_{36}Cl_2Mo_2N_2O_2$: C, 44.76; H, 6.15; N, 4.74. Found: C, 44.95; H, 6.27; N, 4.75. IR (Nujol mull): ν(NO) 1594 (s) cm^{-1}. NMR data: ^{1}H ($CDCl_3$, 200 MHz, 25 °C) δ 0.70 (vt, J = 17.1 Hz, Me), 1.76 (s, C_5Me_5); ^{13}C{^{1}H} ($CDCl_3$, 125 MHz, 25 °C) δ 9.2 (d, $^3J_{CF}$ = 22.5 Hz, $C_5\mathit{Me}_5$), 34.2 (m, Me), 113.4 (d, $^2J_{CF}$ = 17.5 Hz, C_5Me$_5$). MS (EI, 120 °C): *m*/*z* 539 [P$^+$ − 2NO], 297 [P$^+$/2].

Preparation of [Cp*Mo(NO)Me(PMe$_3$)$_2$][BAr$^f_4$] (10). To a suspension of **4** (100 mg, 0.343 mmol) in Et$_2$O (10 mL) was added via cannula a solution of H(OEt$_2$)$_2$[(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$B] (347 mg, 0.343 mmol) in Et$_2$O (5 mL). The tan suspension quickly dissolved to form a red solution. The solution was stirred for 1 min before PMe$_3$ (0.3 mL, 2.9 mmol) was added via syringe. The resulting yellow solution was evaporated to dryness in vacuo to obtain a tacky yellow solid that was triturated with pentane (2 × 5 mL). This solid was dissolved in 70/30 Et$_2$O/hexanes, and the resulting solution was concentrated under reduced pressure to the point of incipient crystallization. After 24 h at −30 °C, this mixture had deposited analytically pure **10** as a yellow microcrystalline powder (149 mg, 36% yield). Anal. Calcd for $C_{49}H_{48}BF_{24}MoNOP_2$: C, 45.57; H, 3.75; N, 1.08. Found: C, 45.66; H, 3.84; N, 1.15. IR (Nujol mull): ν(NO) 1640 (s) cm^{-1}. NMR data: ^{1}H ($CDCl_3$, 200 MHz, 25 °C) δ 0.35 (dd, J = 13.5, 4.2 Hz, Me), 1.32 (d, J = 8.5 Hz, PMe$_3$), 1.47 (d, J = 8.8 Hz, PMe$_3$), 1.76 (s, C_5Me_5), 7.51 (s, BAr$^f_4$), 7.66 (s, BAr$^f_4$); ^{13}C{^{1}H} ($CDCl_3$, 50 MHz, 25 °C) δ 10.0 (s, C_5Me_5) 11.0 (d, J_{CP} = 22.2 Hz, Me), 16.7 (d, J_{CP} = 23.7 Hz, 2PMe$_3$), 113.4 (s, C_5Me_5), 117.5 (m, p-C), 124.5 (q, J_{CF} = 270.8 Hz, CF$_3$), 128.9 (q, J_{CF} = 28.4 Hz, m-C), 134.8 (m, o-C), 161.7 (q, J_{CB} = 9.6 Hz); ^{31}P{^{1}H} (C_6D_6, 81 MHz, 25 °C) δ −9.46 (d, J = 58.5 Hz), −0.37 (d, J = 58.5 Hz).

Isolation of Cp*Mo(NMe)(O)Me (11). PMe$_3$ (ca. 2 mmol) was added by vacuum transfer to a frozen red CH_2Cl_2 solution of **4** ← **11** (500 mg, 0.85 mmol). The mixture was allowed to warm slowly to room temperature while being stirred, whereupon its color changed from purple to bright yellow. The solution was stirred for an additional 15 min before it was evaporated to dryness in vacuo. The resulting yellow solid was extracted with Et$_2$O (5 mL), and the extracts were filtered through a column of Celite (1 × 3 cm) that was supported on a medium-porosity glass frit. Hexanes (5 mL) were added to the filtrate, and the solution was then concentrated under reduced pressure to the point of incipient crystallization. After several fractional crystallizations yielding complex **7**, complex **11** could be obtained as a slightly impure yellow powder (104 mg, 42%) via removal of the remaining solvent in vacuo. IR (Nujol mull): ν(M═O) 873 (s) cm^{-1}. NMR data: ^{1}H (C_6D_6, 200 MHz, 25 °C) δ 0.82 (s, Me), 1.66 (s, C_5Me_5) 3.55 (s, NMe); ^{13}C{^{1}H} (C_6D_6, 50 MHz, 25 °C) δ 9.2 (s, $C_5\mathit{Me}_5$), 14.4 (s, Me), 53.2 (s, NMe), 116.0 (s, C_5Me$_5$). MS (EI, 150 °C): *m*/*z* 293.

Preparation of Cp*W(NO)Me$_2$(μ-O)Cp*W(NMe)Me (12 ← 13). A solution of methyllithium (4.46 mL, 1.6 M solution in Et$_2$O, 7.14 mmol) was added dropwise via a cannula to a stirred green suspension of [Cp*W(NO)Cl(μ-Cl)]$_2$ (1.5 g, 1.79 mmol) in toluene (30 mL) at −70 °C. Upon completion of the addition, the mixture was allowed to warm to room temperature over 20 min, during which time the color changed from red to a turbid tan. The mixture was then evaporated to dryness in vacuo, and the resulting tan/brown powder was extracted with CH_2Cl_2 (30 mL). This pale orange solution was filtered through a column of Celite (3 × 3 cm) supported on a medium-porosity glass frit, and the residue was washed with CH_2Cl_2 (2 × 30 mL). The combined filtrates were taken to dryness in vacuo to obtain slightly impure **13** (1.00 g, 74% yield). IR (Nujol mull): ν(M═O) 864 (s) cm^{-1}. NMR data: ^{1}H (C_6D_6, 200 MHz, 25 °C) δ 1.04 (s, Me), 1.90 (s, C_5Me_5) 3.90 (s, NMe); ^{13}C{^{1}H} (C_6D_6, 50 MHz, 25 °C) δ 10.9 (s, $C_5\mathit{Me}_5$), 14.2 (s, Me), 48.8 (s, NMe), 115.9 (s, C_5Me$_5$). MS (EI, 100 °C): *m*/*z* 379.

Dissolution of this solid in a minimum amount of THF, followed by cooling to −30 °C for 24 h, led to the precipitation of **12** ← **13** as an analytically pure orange powder (70 mg, 5.2% yield). Anal. Calcd for $C_{24}H_{42}W_2N_2O_2$: C, 38.01; H, 5.58; N, 3.69. Found: C, 38.18; H, 5.43; N, 3.53. IR (Nujol mull): ν(NO) 1519 (s); ν(W═O) 873 cm^{-1}. NMR data: ^{1}H (CD_2Cl_2, 500 MHz, 25 °C) δ −0.22 (s, 2 Me), 0.74 (s, Me), 1.73 (s, C_5Me_5 of **12**), 2.00 (s, C_5Me_5 of **13**), 3.81 (s, NMe); ^{1}H (CD_2Cl_2, 500 MHz, −50 °C) δ −0.44 (s, Me of **12**), −0.26 (s, Me of **12**), 0.68 (s, Me of **13**), 1.67 (s, C_5Me_5 of **12**), 1.93 (s, C_5Me_5 of **13**), 3.75 (s, NMe); ^{13}C{^{1}H} (CD_2Cl_2, 125 MHz, −50 °C) δ 9.0 ($C_5\mathit{Me}_5$ of **12**), 10.1 ($C_5\mathit{Me}_5$ of **13**), 13.8 (Me of **13**), 20.3 (Me of **12**), 25.7 (Me of **12**), 48.0 (NMe), 106.5 (C_5Me$_5$ of **12**), 115.7 (C_5Me$_5$ of **13**).

Preparation of Cp*W(NO)Me$_2$(PMe$_3$) (14). A solution of methyllithium (1.80 mL, 1.6 M solution in Et$_2$O, 2.86 mmol) was added dropwise via a cannula to a stirred suspension of [Cp*W(NO)Cl(μ-Cl)]$_2$ (0.6 g, 0.72 mmol) in toluene (20 mL) at −70 °C. Upon completion of the addition, the mixture was stirred for 5 min, and an excess of PMe$_3$ (0.3 mL, 2.9 mmol) was added quickly via syringe. The final yellow solution was warmed to room temperature and filtered through a column of Celite (3 × 3 cm) supported on a medium-porosity glass frit, and the residue was washed with toluene (2 × 15 mL). The combined filtrates were evaporated to dryness in vacuo, and the resulting orange oil was triturated in pentane before extraction with Et$_2$O (ca. 4 mL). Repeated fractional crystallization of this solution at −30 °C led to the isolation of orange microcrystalline **14** (85 mg, 13% yield) free of **13**. Anal. Calcd for $C_{15}H_{30}WNOP$: C, 39.58; H, 6.64; N, 3.08. Found: C, 39.42; H, 6.54; N, 3.14. IR (Nujol mull): ν(NO) 1547 (s) cm^{-1}. NMR data: ^{1}H (C_6D_6, 400 MHz, 25 °C), *trans*-**14** δ 0.24 (d, $^3J_{PH}$ = 15.0 Hz, Me), 0.80 (d, $^2J_{PH}$ = 7.8 Hz, PMe$_3$), 1.57 (s, C_5Me_5), *cis*-**14** δ −0.17 (d, $^3J_{PH}$ = 16.4 Hz, trans-Me), 0.56 (d, $^3J_{PH}$ = 2.8 Hz, cis-Me), 1.03 (d, $^2J_{PH}$ = 8.8 Hz, PMe$_3$), 1.57 (s, C_5Me_5); ^{13}C{^{1}H} (C_6D_6, 100 MHz, 25 °C), *trans*-**14**, δ 0.8 (d, $^2J_{PC}$ =13.9 Hz, Me), 9.4 ($C_5\mathit{Me}_5$), 13.0 (d, $^2J_{PC}$ =25.5 Hz PMe$_3$), 105.0 (C_5Me$_5$), *cis*-**14**, δ 9.9 ($C_5\mathit{Me}_5$), 10.6 (s, Me), 12.5 (d, $^2J_{PC}$ = 28.5 Hz, PMe$_3$), 13.3 (d, $^2J_{PC}$ = 12.5 Hz, Me), 105.6 (C_5Me$_5$); ^{31}P{^{1}H} (C_6D_6, 202 MHz, 25 °C) δ −25.4 (trans isomer), 4.95 (cis isomer).

Theoretical Calculations. All DFT calculations were performed using Gaussian 98.[45] The LANL2DZ basis set was employed to perform geometry optimizations with a DFT approach. The three-parameter form of the Becke, Lee, Tang, and Parr functional (B3LYP)[46] was used in all cases, and no spatial symmetry constraints were imposed. The LANL2DZ basis set includes both Dunning and Hay's D95 sets for H, C, N, and O,[47] and the relativistic electron core potential (ECP) sets of

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Table 1. X-ray Crystallographic Data for Complexes **2**-THF, **5**, **7**, and **4** ← **11**

crystal data	**2**-THF	**5**	**7**	**4** ← **11**
empirical formula	$C_{42}H_{80}Li_2N_2O_6Mo_2$	$C_{22}H_{36}N_2O_3Mo_2$	$C_{15}H_{30}NOPMo$	$C_{24}H_{42}N_2O_2Mo_2$
crystal habit, color	arrowhead, amber	chip, red	plate, pale yellow	prism, red
crystal size (mm)	0.50 × 0.45 × 0.30	0.20 × 0.15 × 0.10	0.20 × 0.40 × 0.45	0.25 × 0.20 × 0.10
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1$	$P2_1/a$	$P2_1$
volume (Å^3)	2428.89(5)	1210.4(1)	1772.1(2)	1284.9(3)
a (Å)[a]	11.0904(1)	7.9714(5)	14.533(2)	8.4317(14)
b (Å)	15.8879(2)	14.4705(8)	8.9356(7)	15.063(3)
c (Å)	13.7861(2)	11.1315(7)	15.1592(4)	10.4887(4)
α (deg)	90	90	90	90
β (deg)	90.840(1)	109.489(5)	115.8204(7)	105.3085(8)
γ (deg)	90	90	90	90
Z	2	2	4	2
formula weight (g/mol)	914.84	568.42	367.32	582.49
density (calculated) (Mg/m^3)	1.251	1.560	1.377	1.505
absorption coefficient (cm^{-1})	5.58	10.58	8.23	9.95
F_{000}	968	580	768	600
radiation	Mo Kα, 0.71073 Å	Mo Kα, 0.71069 Å	Mo Kα, 0.71069 Å	Mo Kα, 0.71069 Å
		Data Refinement		
final R indices[b]	$R_F = 0.030$, w$R_F = 0.075$	$R_1 = 0.046$, w$R_2 = 0.065$	$R_1 = 0.029$, w$R_2 = 0.027$	$R_1 = 0.035$, w$R_2 = 0.031$
goodness-of-fit on F^2 c	1.045	1.85	1.63	1.22
largest diff. peak and hole[d] (e$^-$ Å^{-3})	0.72 and −0.28	1.17 and −1.07	1.39 and −0.92	1.68 and −1.37

[a] Cell dimensions based on the following: **2**-THF, 8192 reflections, 4.0° ≤ 2θ ≤ 50°; **5**, 7717 reflections, 4.0° ≤ 2θ ≤ 55.8°; **7**, 12331 reflections, 4.0° < 2θ < 60.3°; **4** ← **11**, 9976 reflections, 4.0° ≤ 2θ ≤ 60.1°. [b] Number of observed reflections: **2**-THF, 3713 ($I_o > 2\sigma I_o$); **5**, 4288 ($I_o > 3\sigma I_o$); **7**, 3264 ($I_o > 3\sigma I_o$); **4** ← **11**, 3833 ($I_o > 3\sigma I_o$). R_F: **2**-THF, **5**, **7**, **4** ← **11**, $R_F = \Sigma \mid (|F_o| - |F_c|) \mid / \Sigma |F_o|$. w$R_F$: **2**-THF, **5**, **7** and **4** ← **11**, w$R_F = [\Sigma (w(|F_o|^2 - |F_c|^2)^2)/\Sigma w F_o^4]^{1/2}$. w: **2**-THF, $w = [\sigma^2 F_o^2 + (AP)^2 + (BP)]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$, $A = 0.0318$, and $B = 2.2934$; **5**, **7**, and **4** ← **11**, $w = [\sigma^2 F_o 2]^{-1}$. [c] GOF = $[\Sigma(w(|F_o| - |F_c|)^2/\text{degrees of freedom}]^{1/2}$. [d] **2**-THF, 1.1 Å from C24; **5** and **7**, near Mo; **4** ← **11**, 0.44 Å from Mo(2).

Hay and Wadt for Mo.[48] Reported energies for all species include zero-point energy corrections. Transition states were optimized by a quasi-Newton method and were shown by frequency calculations to possess one and only one imaginary frequency.

X-ray Crystallographic Analyses. Data collection and structure solution for complex **5** were conducted at the University of British Columbia by Dr. Brian O. Patrick. All measurements were recorded on a Rigaku/ADSC CCD area detector with graphite-monochromated Mo Kα radiation. The data were collected at −100(1) °C to a maximum 2θ value of 55.8°. Data were collected in 0.50° oscillations with 35.0 s exposures. A sweep of data was done using ϕ oscillations from 0.0 to 190.0° at $\chi = 0°$, and a second sweep was performed using ω oscillations between −19.0 and 23.0° at $\chi = 90°$. The crystal-to-detector distance was 40.55 mm. The detector swing angle was −5.46°. The solid-state structure was solved by heavy-atom Patterson methods and was expanded using Fourier techniques. One Cp* is disordered and was modeled with rigid groups in two orientations. Subsequent refinement led to relative populations of 0.64 and 0.36 for the two fragments. All non-hydrogen atoms not included in the rigid groups were refined anisotropically, while the rest were refined isotropically. All calculations were performed using the *teXsan*[49] crystallographic software package from Molecular Structure Corp.

Data collection and structure solution for complexes **7** and **4** ← **11** were conducted at the University of British Columbia by Dr. Steven J. Rettig (deceased October 27, 1998). All measurements were recorded on a Rigaku/ADSC CCD area detector with graphite-monochromated Mo Kα radiation. The data were collected at −93(1) °C to a maximum 2θ value of 60.3°. Data were collected in 0.50° oscillations with 28.0 s exposures for **4** ← **11** and 45.0 s exposures for **7**. A sweep of data was done using ϕ oscillations from 0.0 to 190.0° at $\chi = -90°$, and a second sweep was performed using ω oscillations between −23.0 and 18.0° at $\chi = -90°$. The crystal-to-detector distance was 39.21(1) mm. The detector swing angle was −10.0°. The solid-state structures were solved by heavy-atom Patterson methods and were expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were fixed in calculated positions with d(C−H) = 0.98 Å. For **7**, the hydrogen atoms of the C(8) and C(9) methyl groups were modeled as 1:1 two-fold disordered on the basis of difference map peaks. All calculations were performed using the *teXsan*[49] crystallographic software package.

Data collection and structure solution for complex **2**-THF were conducted at the X-ray Crystallographic Laboratory in the Chemistry Department of the University of Minnesota by Dr. Victor G. Young, Jr. Data were recorded at 100(2) °C with a Siemens SMART system using graphite-monochromatized Mo Kα radiation. A successful direct methods solution was calculated which provided most non-hydrogen atoms from the E-map. Several full-matrix least-squares/difference Fourier cycles were performed which located the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters unless stated otherwise. All hydrogen atoms were placed in ideal positions and refined as riding atoms with individual (or group if appropriate) isotropic displacement parameters. All calculations were performed using SGI INDY R4400-SC or Pentium computers using the SHELXTL V5.0 suite of programs.

X-ray crystallographic data for the four complexes are collected in Table 1, and their selected bond distances and angles are presented in the captions to the figures in which their solid-state molecular structures are portrayed.

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Supporting Information Available: Tables listing crystallographic information, atomic coordinates and B_{eq}, anisotropic thermal parameters, and intramolecular bond distances, angles, and torsion angles (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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