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Reviews

Distinctive Properties of Cp′M(NO)(alkyl)$_2$ (M = Mo, W) Complexes

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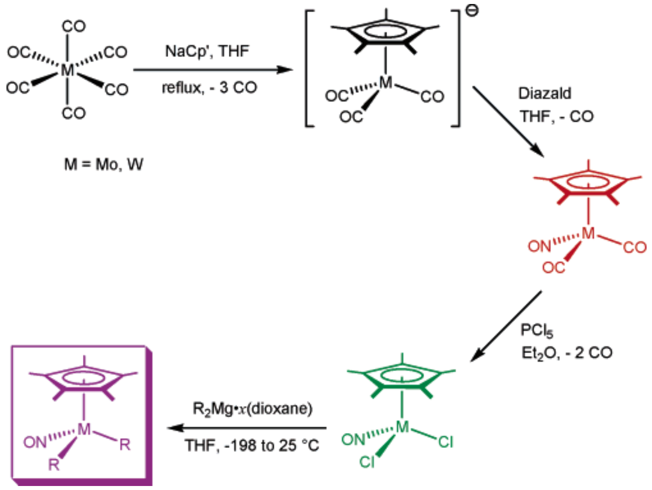
This account summarizes our work with the title complexes, which are rare examples of electronically and coordinatively unsaturated transition-metal alkyls that can be isolated under ambient conditions. It first outlines the synthetic methods employed for the preparation of these compounds and then presents their distinctive physical properties. It then classifies the characteristic chemical properties of these complexes in terms of the reactivity being either metal or ligand based, and specific examples of particular transformations are illustrated with reference to the most studied systems.

I. Introduction

The long-term goal of our research program over the years has been the development of organometallic nitrosyl complexes as specific reactants or selective catalysts for chemical transformations of practical significance. Typically, the attainment of this goal involves a three-step process. First, methods for synthesizing new complexes are developed. Then the newly prepared compounds are isolated and characterized fully by conventional spectroscopic means (including the electrochemistry and single-crystal X-ray crystallography of representative compounds). Finally, their characteristic chemical properties are established, and those that are unique to them are productively exploited. One particular family of compounds that has been investigated in this manner involves Cp′M(NO)(alkyl)$_2$ (M = Mo, W) complexes, which are rare examples of electronically and coordinatively unsaturated transition-metal alkyls that can be isolated under ambient conditions. The first three members of this remarkable family were first described some 20 years ago.[1] Today, Cp′M(NO)(alkyl)$_2$ complexes having Cp′ = Cp (η^5-C_5H_5), Cp* (η^5-C_5Me_5), Cp$^\phi$ (η^5-C_5Ph_4H) and alkyl = CH_2SiMe_3, CH_2CMe_3, CH_2CMe_2Ph, CH_2CPh_3, CH_2Ph, Me are known for molybdenum and/or tungsten.[2] During our investigations of the characteristic chemistry of these fascinating compounds, we have discovered that they react with a variety of small molecules, often in an unprecedented manner. We have also established several unique transformations that are not exhibited by all members of this family of complexes. Indeed, we have found that their chemical properties are often dependent on the metal, the nature of the alkyl group, and the type of Cp′ ligand. In this review we summarize what is currently known about these compounds.

Scheme 1. General Method for the Synthesis of Cp′M(NO)(alkyl)$_2$ Complexes



II. Syntheses and Physical Properties of Cp′M(NO)(alkyl)$_2$ Complexes

The complexes of interest may be synthesized on a large scale and in good yields from commercially available M(CO)$_6$ (M = Mo, W) by the four-step procedure summarized in Scheme 1. The orange Cp′M(NO)(CO)$_2$[3] and green Cp′M(NO)Cl$_2$[4,5] intermediate complexes are best isolated prior to being utilized as reactants in the subsequent step. The red-to-violet Cp′M(NO)(alkyl)$_2$ products[7] are isolable as analytically pure crystals from the final reaction mixtures by fractional crystallization.

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(1) Legzdins, P.; Rettig, S. J.; Sánchez, L.; Bursten, B. E.; Gatter, M. G. *J. Am. Chem. Soc.* **1985**, *107*, 1411.
(2) Legzdins, P.; Veltheer, J. E. *Acc. Chem. Res.* **1993**, *26*, 41.
(3) Chin, T. T.; Hoyano, J. K.; Legzdins, P.; Malito, J. T. *Inorg. Synth.* **1990**, *28*, 196.
(4) Dryden, N. H.; Legzdins, P.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1991**, *10*, 2077.

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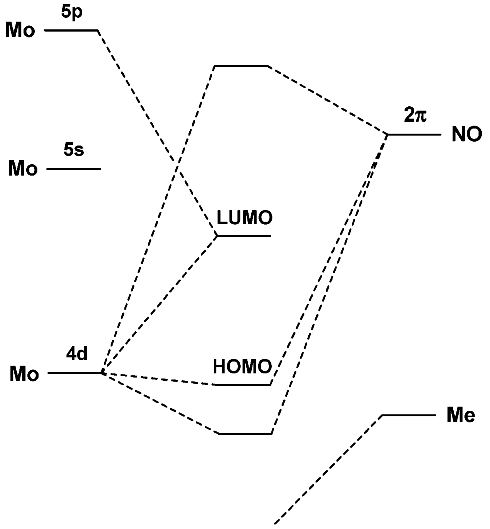

Figure 1. Molecular orbital diagram of the upper valence orbitals of $CpMo(NO)Me_2$.

In some instances mixed alkyl complexes can be obtained by sequential treatment of $Cp'M(NO)Cl_2$ in the last step with 0.5 equiv of two different magnesium alkylating agents.[8]

Under ambient conditions, the $Cp'M(NO)(alkyl)_2$ complexes are diamagnetic solids which are freely soluble in common organic solvents to give red-to-violet solutions. The compounds are monomeric and possess piano-stool molecular structures in which the M−NO linkages are essentially linear. In this configuration, the nitrosyl group functions as a formal three-electron donor and is a strong π-acid ligand. The existence of considerable M→NO back-bonding in these compounds is indicated by the short M−N and long N−O bond lengths in their solid-state molecular structures as well as the very low ν_{NO} values (1600−1625 cm^{-1}) evident in their IR spectra in hexanes.[2] Theoretical calculations on the model 16-electron complexes $CpM(NO)Me_2$ (M = Mo,[1] W[9]) produce molecular orbital diagrams of the type shown for $CpMo(NO)Me_2$ in Figure 1. These calculations reveal that the LUMOs of these compounds are localized on the metal centers, are situated between the two alkyl ligands, and are nonbonding. In other words, there is no loss of metal−ligand binding in the $Cp'M(NO)(alkyl)_2$ complexes, despite their formal electron deficiency, and the LUMOs confer Lewis acid properties on these compounds.

The Lewis acidity of the metal centers in the $Cp'M(NO)(alkyl)_2$ complexes is manifested by the fact that they avail themselves of any available intramolecular electron density. For instance, the dibenzyl compounds are stereochemically nonrigid species that have the limiting structures $Cp'M(NO)(\eta^2\text{-}CH_2Ph)(\eta^1\text{-}CH_2Ph)$ in which the η^2-benzyl ligand functions as a formal three-electron donor to the metal center.[10] In a similar vein, the solid-state molecular structure of $Cp^*W(NO)(CH_2CMe_3)_2$ (Figure 2) contains one neopentyl ligand with a "strongly agostic" methylene hydrogen atom (C1−H1A = 1.153(6) Å; W−C1−H1A = 80.6(3)°) and another with a "weakly agostic" interaction (C6−H6B = 1.094(6) Å; W−C6−H6B = 99.3(3)°), as shown by a neutron diffraction analysis at 120 K.[11] The molecular structure of the related $Cp^*W(NO)(CH_2SiMe_3)_2$ complex at −20 °C possesses a crystallographically imposed mirror plane, and so only the average existence of a relatively strong C−H···M interaction for each alkyl ligand in the solid state can be established. Furthermore, the ^1H and gated $^{13}C\{^1H\}$ NMR spectra of representative $Cp'M(NO)(alkyl)_2$ complexes exhibit spectral parameters for the α-H and α-C atoms that provide evidence for the presence of α-agostic interactions in the molecular structures of these complexes in solution. Indeed, these compounds are stereochemically nonrigid in these solutions and probably interconvert between two limiting structures having one strongly agostic and one weakly agostic alkyl ligand.[11]

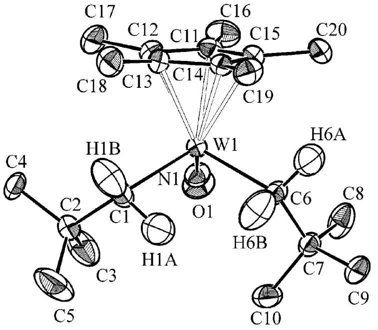

Figure 2. Solid-state molecular structure of $Cp^*W(NO)(CH_2CMe_3)_2$, as viewed down the metal-centered LUMO. Methyl group hydrogen atoms have been omitted for clarity.

Electrochemical reduction potentials of various $Cp'M(NO)(alkyl)_2$ complexes and their corresponding nitrosyl-stretching frequencies have established that the relative Lewis acidities of these species are Cp > Cp* and Mo > W.[2] One of the principal aspects of the chemistry of these compounds is, thus, their tendency to form 1:1 adducts with Lewis bases. These acid−base adducts are either isolable as such or undergo subsequent intramolecular transformations involving the alkyl ligands. This chemistry is presented in the next sections of this account, with the specific examples cited being chosen from the most studied systems.

III. Metal-Based Reactivity of $Cp'M(NO)(alkyl)_2$ Complexes

Reactions with Phosphines. Superimposed on the expectation that the $Cp'M(NO)(alkyl)_2$ complexes can function as Lewis acids is the fact that the accessibility

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(5) The $Cp'M(NO)Cl_2$ complexes possess either monomeric or chloro-bridged dimeric molecular structures in the solid state. However, the physical and chemical properties of these compounds in solution are most consistent with their existing as solvated monomers.[6] Consequently, in this review they are represented exclusively by their monomeric formulas.

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

(7) For representative procedures, see: (a) Hunter, A. D.; Legzdins, P.; Martin, J. T.; Sánchez, L. *Organomet. Synth.* **1986**, *3*, 66. (b) Veltheer, J. E.; Legzdins, P. In *Synthetic Methods of Organometallic and Inorganic Chemistry*; Herrmann, W. A., Ed.; Thieme Verlag: New York, 1997; Vol. 8, pp 79−85.

(8) (a) Debad, J. D.; Legzdins, P.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1993**, *12*, 2094. (b) Debad, J. D.; Legzdins, P.; Rettig, S. J.; Veltheer, J. E. *Organometallics* **1993**, *12*, 2714.

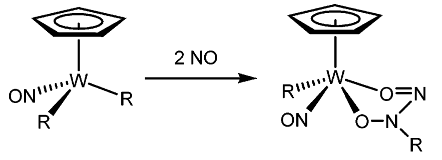
(9) Bursten, B. E.; Cayton, R. H. *Organometallics* **1987**, *6*, 2004.

(10) Legzdins, P.; Jones, R. H.; Phillips, E. C.; Yee, V. C.; Trotter, J.; Einstein, F. W. B. *Organometallics* **1991**, *10*, 986.

(11) Bau, R.; Mason, S. A.; Patrick, B. O.; Adams, C. S.; Sharp, W. B.; Legzdins, P. *Organometallics* **2001**, *20*, 4492.

of their LUMOs to incoming Lewis bases will also be restricted somewhat by the steric bulk of the alkyl and the cyclopentadienyl ligands. Thus, the greater air stability and lower reactivity of $Cp^{\phi}W(NO)(CH_2SiMe_3)_2$ may be attributed to the much more hindered approach of incoming reactants toward the tungsten atom than in the analogous Cp complex. $CpW(NO)(CH_2SiMe_3)_2$ itself is most prone to react with small, strongly basic molecules.[12] Hence, it readily forms a 1:1 adduct in hexanes with PMe_3, but it does not incorporate the more sterically demanding $PMePh_2$ or PPh_3. Furthermore, its solutions are unaffected by treatment with 2−3 atm of the relatively weak Lewis bases N_2, C_2H_4, and CO_2.[12] The monophosphine adduct $CpW(NO)(CH_2SiMe_3)_2(PMe_3)$ is an air-sensitive, lemon yellow solid that loses PMe_3 and reverts back to $CpW(NO)(CH_2SiMe_3)_2$ when exposed to 5×10^{-3} Torr at 20 °C for 48 h. However, there is no evidence during the reactions of $CpW(NO)(CH_2SiMe_3)_2$ with PMe_3 for the accompanying migratory insertion of the bound nitrosyl ligand into one of the $W-CH_2SiMe_3$ linkages, as has been observed to occur for some other alkyl nitrosyl complexes.[13] Indeed, as described in subsequent sections of this account, $Cp'M(NO)(alkyl)_2$ complexes only insert external nucleophiles into their M−C bonds.

Reactions with NO. Treatment of $CpW(NO)(CH_2SiMe_3)_2$ in hexanes with NO gas (eq 1) affords quantitatively the *N*-alkyl-*N*-nitrosohydroxylaminato compound $CpW(NO)(CH_2SiMe_3)(\eta^2\text{-}O_2N_2[CH_2SiMe_3])$, which exists in nonpolar solvents as a mixture of two isomers.[12] This reactivity with NO is as expected for a diamagnetic transition-metal alkyl complex.[14]



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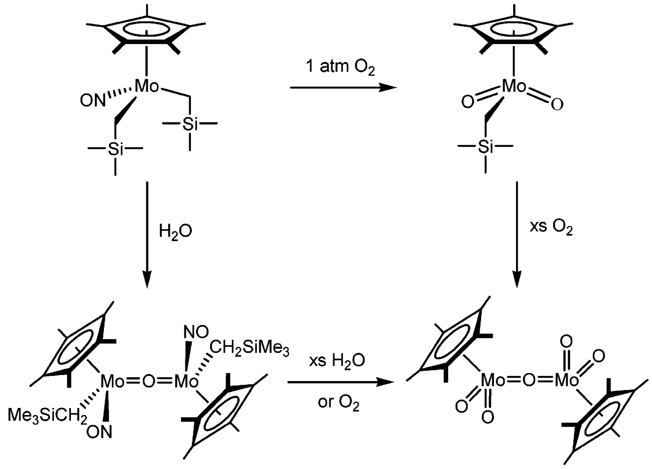
Reactions with Dioxygen and Water. $Cp'M(NO)(alkyl)_2$ complexes react with molecular oxygen to produce the dioxo complexes $Cp'M(O)_2(alkyl)$, with the more Lewis acidic molybdenum compounds reacting much more quickly than the tungsten congeners.[15] Thus, solid $Cp^*Mo(NO)(CH_2SiMe_3)_2$ reacts with O_2 in air in a matter of minutes, whereas solutions of $Cp^*W(NO)(CH_2SiMe_3)_2$ must be treated with O_2 for several hours in order to convert them to $Cp^*W(O)_2(CH_2SiMe_3)$. Labeling studies are consistent with the first step in these transformations being coordination of O_2 to the metal centers in the organometallic reactants.

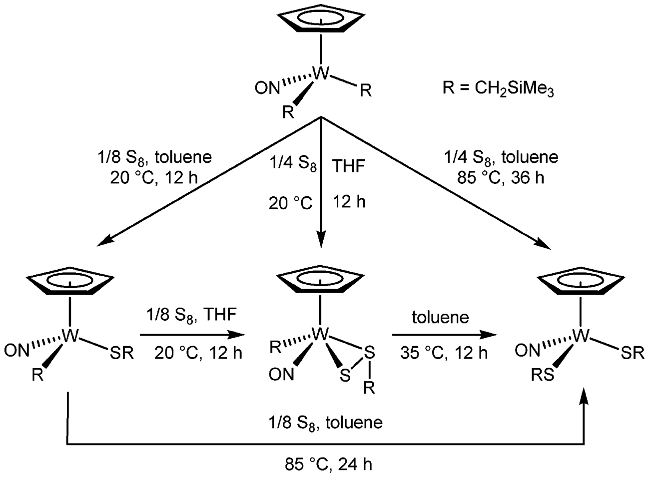
The reactivity of typical $Cp'M(NO)(alkyl)_2$ complexes toward H_2O exhibits a pronounced dependence on the metal. In general, the W−C bonds in the tungsten alkyl compounds are stable and are not easily hydrolyzed. In contrast, the analogous Mo−C linkages are readily hydrolyzed to form bimetallic complexes of the type $[Cp'Mo(NO)(alkyl)]_2(\mu\text{-}O)$ and free hydrocarbon.[16] Scheme 2 summarizes the reactions of $Cp^*Mo(NO)(CH_2SiMe_3)_2$ and its oxo derivatives with H_2O and O_2 and illustrates the variety of products that may be obtained. It is particularly noteworthy that even though $Cp^*Mo(O)_2(CH_2SiMe_3)$ and $[Cp^*Mo(NO)(CH_2SiMe_3)]_2(\mu\text{-}O)$ cannot be interconverted, both compounds do react with excess water or excess dioxygen to form the known complex $[Cp^*Mo(O)_2]_2(\mu\text{-}O)$ as the only isolable organometallic product.[16]

Scheme 2. Reactions of $Cp^*Mo(NO)(CH_2SiMe_3)_2$ and Its Oxo Derivatives with Dioxygen and Water



Reactions with Elemental Sulfur or Selenium. Reaction of $CpW(NO)(CH_2SiMe_3)_2$ with elemental sulfur results in the occurrence of the unprecedented sequential transformations summarized in Scheme 3.[12] All three product complexes are isolable as analytically pure solids, and their solid-state molecular structures have been established by X-ray crystallographic analyses.[17] However, when elemental selenium is the reactant, only $CpW(NO)(CH_2SiMe_3)(SeCH_2SiMe_3)$ and $CpW(NO)(SeCH_2SiMe_3)_2$ may be so obtained. The sulfur-contain-

Scheme 3. Experimental Conditions for the Insertion of Elemental Sulfur into the W−C Bonds of $CpW(NO)(CH_2SiMe_3)_2$



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(13) (a) Weiner, W. P.; White, M. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3612. (b) Weiner, W. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3922.

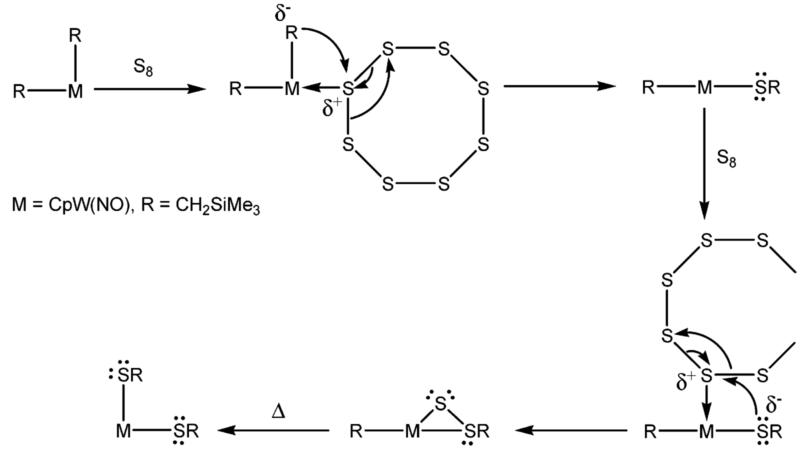
(14) Middleton, A. R.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1981**, 1898 and references therein.

(15) Legzdins, P.; Phillips, E. C.; Sánchez, L. *Organometallics* **1989**, *8*, 940.

(16) Legzdins, P.; Lundmark, P. J.; Phillips, E. C.; Rettig, S. J.; Veltheer, J. E. *Organometallics* **1992**, *11*, 2991.

(17) Evans, S. V.; Legzdins, P.; Rettig, S. J.; Sánchez, L.; Trotter, J. *Organometallics* **1987**, *6*, 7.

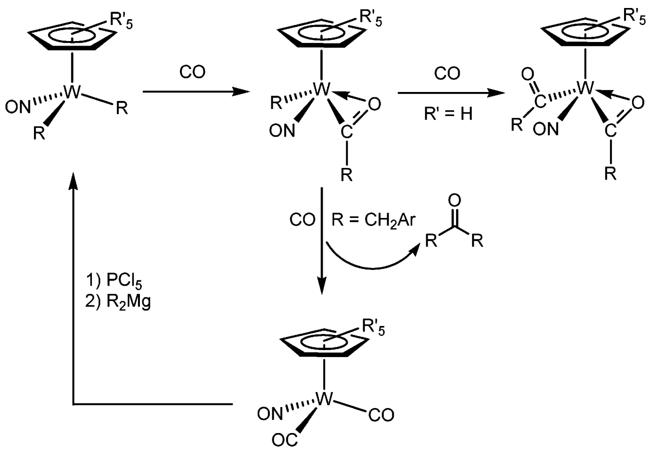
Scheme 4. Probable Mechanism for the Insertion of Elemental Sulfur into the W−C Bonds of $CpW(NO)(CH_2SiMe_3)_2$



ing products can be synthesized in high yields by employing the experimental conditions outlined in Scheme 3, and the sequential conversions may be viewed as occurring in the manner depicted in Scheme 4.

Reactions with CO. The reactions of the $Cp'M(NO)(alkyl)_2$ complexes with CO proceed in a stepwise fashion, and their outcomes are dependent on both the natures of Cp′ and the alkyl group and the experimental conditions employed.[18] As illustrated in Scheme 5 for the tungsten systems, treatment of solutions of $Cp'W(NO)(alkyl)_2$ with CO under ambient conditions affords the corresponding 18-electron monoacyl species $Cp'W(NO)(\eta^2\text{-}C\{O\}alkyl)(alkyl)$ via an initially formed carbonyl adduct that is detectable in some cases. Upon exposure to CO at higher pressures, only the CpW monoacyl compounds undergo insertion of a second equivalent of CO to form $CpW(NO)(C\{O\}alkyl)_2$, again probably via an initially formed carbonyl adduct. The spectroscopic properties of the $CpW(NO)(C\{O\}alkyl)_2$ complexes are consistent with their being stereochemically nonrigid and having the instantaneous 18-electron molecular structures $CpW(NO)(\eta^2\text{-}C\{O\}alkyl)(\eta^1\text{-}C\{O\}alkyl)$. The reactant complexes having alkyl = CH_2Ar (Ar = aryl) are unique in that exposure of the $Cp'M(NO)(CH_2Ar)_2$ complexes to CO does not produce isolable acyl alkyl complexes but rather leads to the reductive elimination of $(ArCH_2)_2CO$ and formation of the well-known $Cp'M(NO)(CO)_2$ compounds. The relative migratory aptitudes of the alkyl ligands have been established by treating mixed Cp*W(NO)(alkyl)(alkyl′) complexes with CO under ambient conditions to produce the corresponding η^2-acyl complex.[8a] As found in other systems, the trend is $CH_2CMe_3 > CH_2SiMe_3 > Me$ in order of decreasing migratory aptitude, the most sterically demanding ligands migrating to bound CO preferentially. Interestingly, all complexes containing a CH_2SiMe_3 ligand form enolate species, $Cp^*W(NO)(alkyl)(OC\{=CH_2\}SiMe_3)$, upon reaction with CO, probably via formation of an intermediate acyl complex and subsequent rearrangement via a 1,2-silyl shift (Scheme 6).

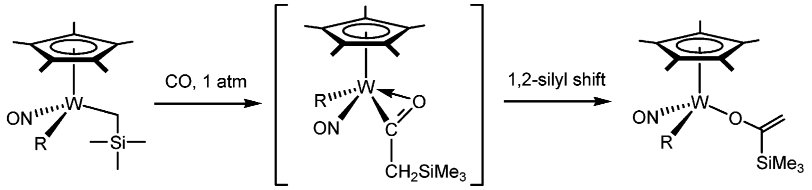
Scheme 5. Reactions of $Cp'W(NO)(alkyl)_2$ Complexes with Carbon Monoxide



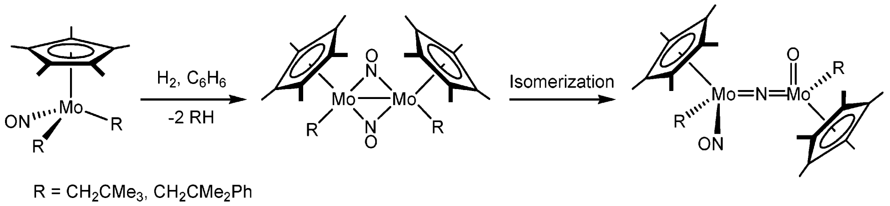
Reactions with Isonitriles. In light of the reactions with CO considered in the preceding section, it is not surprising that reaction of prototypal $CpW(NO)(CH_2SiMe_3)_2$ with t-BuNC affords the analogous insertion product $CpW(NO)(CH_2SiMe_3)(\eta^2\text{-}C(CH_2SiMe_3){=}N\text{-}t\text{-}Bu)$ in 94% isolated yield.[12] Hydrolysis of this iminoacyl complex cleanly produces the corresponding methyl derivative, $CpW(NO)(CH_2SiMe_3)(\eta^2\text{-}C(CH_3){=}N\text{-}t\text{-}Bu)$.

Reactions with H_2. The $Cp'M(NO)(alkyl)_2$ complexes exhibit several different reactivity patterns when exposed to dihydrogen. For instance, treatment of $Cp^*Mo(NO)R_2$ complexes (R = CH_2CMe_3, CH_2CMe_2Ph) in C_6H_6 at 5 °C with H_2 results in the formation of $[Cp^*MoR]_2(\mu\text{-}NO)_2$ products.[19] Both bimetallic complexes isomerize in solution at ambient temperatures to form $[Cp^*Mo(NO)R](\mu\text{-}N)[Cp^*Mo(O)R]$ (Scheme 7). In an analogous

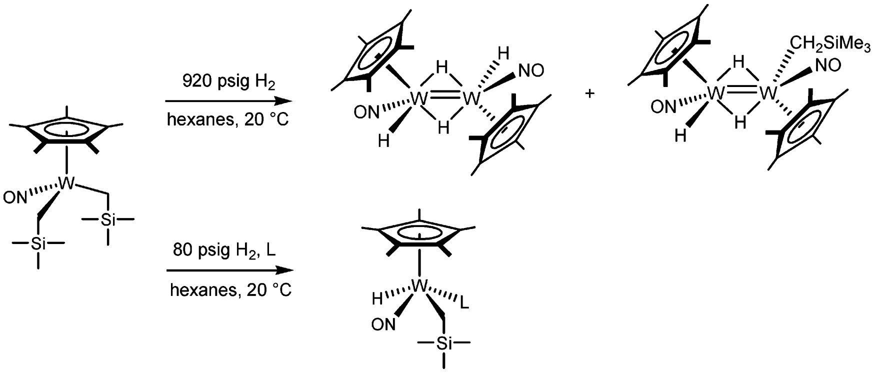
Scheme 6. Reactions of $Cp^*W(NO)(alkyl)(CH_2SiMe_3)$ Complexes with Carbon Monoxide



Scheme 7. Reactions of Cp*Mo(NO)(alkyl)$_2$ Complexes with Dihydrogen



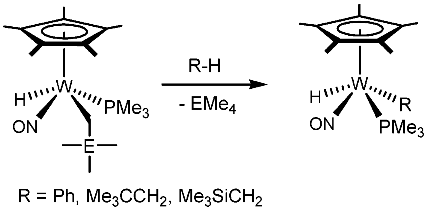
Scheme 8. Reactions of Cp′W(NO)(CH$_2$SiMe$_3$)$_2$ with H$_2$ under Different Conditions



manner, exposure of C_6H_6 solutions of Cp′Mo(NO)R$_2$ (Cp′ = Cp*, Cp$^\phi$; R = CH$_2$SiMe$_3$) to dihydrogen results in the formation of the dimolybdenum complexes [Cp′Mo(NO)R](μ-N)[Cp′Mo(O)R].[20] Similar treatment of an equimolar mixture of Cp*Mo(NO)R$_2$ and Cp*W(NO)R$_2$ (R = CH$_2$SiMe$_3$) with H$_2$ results in the formation of the heterobimetallic species [Cp*Mo(NO)R](μ-NO)$_2$[Cp*W(NO)R], which isomerizes to a 60:40 mixture of [Cp*W(NO)R](μ-N)[Cp*Mo(O)R] and [Cp*Mo(NO)R](μ-N)[Cp*W(O)R]. Kinetic and mechanistic studies indicate that these bimetallic isomerization processes occur in an intramolecular manner.[19]

Remarkably thermally stable alkyl hydride complexes of tungsten result from the treatment of Cp′W(NO)(CH$_2$SiMe$_3$)$_2$ (Cp′ = Cp, Cp*) with H$_2$ under differing experimental conditions (Scheme 8).[21,22] At low pressures of H$_2$ (e.g. 80 psig) in the presence of Lewis bases, L, the monometallic complexes *trans*-Cp′W(NO)(H)(CH$_2$SiMe$_3$)$_2$(L) are formed in moderate yields. At higher pressures of H$_2$ (e.g. 920 psig) in the absence of L's, Cp*W(NO)(CH$_2$SiMe$_3$)$_2$ is converted into a mixture of the bimetallic complexes [Cp*W(NO)H]$_2$(μ-H)$_2$[23] and [Cp*W(NO)H](μ-H)$_2$[Cp*W(NO)(CH$_2$SiMe$_3$)], which are separable by fractional crystallization.

As illustrated in eq 2, the monometallic complexes *trans*-Cp*W(NO)(CH$_2$EMe$_3$)(H)(PMe$_3$) (E = C, Si) effect the intermolecular activation of hydrocarbon C−H bonds under ambient conditions.[22]



(2)

In general, treatment of solutions of Cp*W(NO)(CH$_2$SiMe$_3$)$_2$ with H$_2$ generates in situ the reactive 16-electron species Cp*W(NO)(CH$_2$SiMe$_3$)(H), formed by hydrogenolysis of one of the W−C σ-bonds of the dialkyl reactant.[24] This Lewis acidic hydride complex has not yet been isolated, but its existence has been inferred on the basis of the varied chemical reactions that it undergoes when generated in the presence of reactive substrates (Scheme 9). Most notably, the characteristic chemistry of Cp*W(NO)(CH$_2$SiMe$_3$)(H) is dominated by the ability of its W−H bond to insert unsaturated linkages, the regioselectivity of the insertions portrayed in Scheme 9 indicating that the hydride ligand is hydridic in nature.

Most interestingly, treatment of solutions of Cp*M(NO)(CH$_2$SiMe$_3$)$_2$ with H$_2$ in the presence of acyclic, conjugated dienes constitutes a general method for the synthesis of Cp*M(NO)(η^4-*trans*-diene) complexes of both molybdenum and tungsten (Scheme 10). However, when 1,3-cyclooctadiene is employed as the trapping agent, it undergoes an unprecedented coupling in the metals' coordination spheres. The 2-cyclooct-2-en-1-yl-1,3-cyclooctadiene ligand thus formed is attached in a bis-η^2 fashion to the metal centers in the final products, and it can be released by treatment of these complexes with O$_2$ (Scheme 10).

Finally, treatment of Cp*W(NO)(CH$_2$CMe$_3$)$_2$ with H$_2$ in neat cyclohexene in a 1:30:100 molar ratio under ambient conditions for 3 h results in the formation of the three isolable organometallic complexes highlighted in Scheme 11.[25] These complexes result from three transformations of cyclohexene mediated by the Cp*W(NO) fragment. These transformations are initiated by

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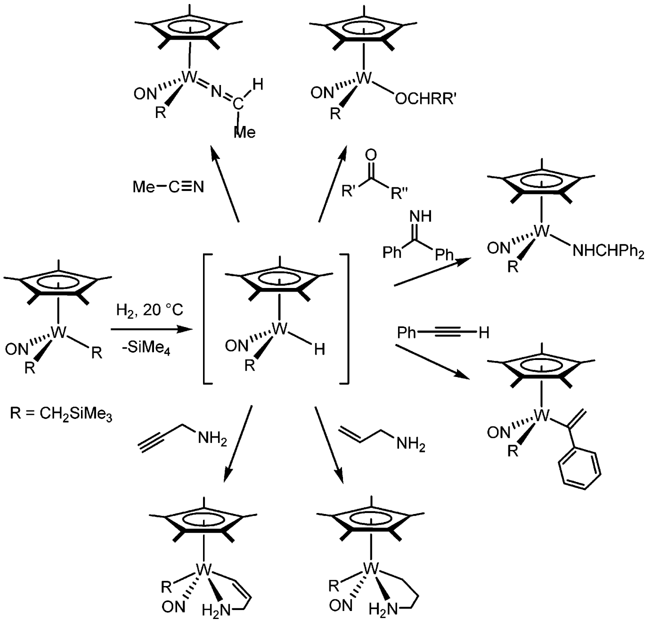
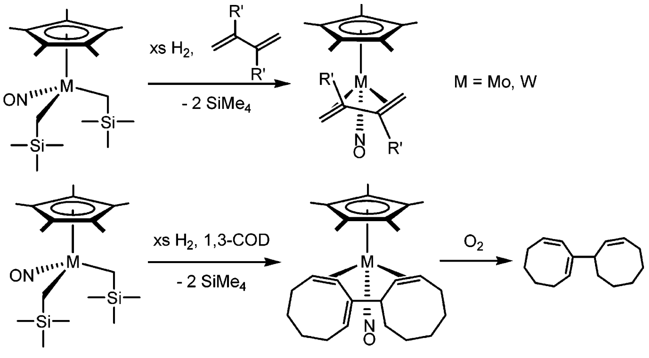
Scheme 9. Characteristic Reactions of Cp*W(NO)(CH$_2$SiMe$_3$)(H)



Scheme 10. Reactions of Cp*M(NO)(CH$_2$SiMe$_3$)$_2$ with H$_2$ in the Presence of Dienes



coordination of cyclohexene to the tungsten center and formally involve (a) intramolecular C−H activation of cyclohexene to form an η^3-cyclohexenyl hydrido complex, (b) combination of cyclohexene and H$_2$ to form an η^1-cyclohexyl hydrido complex, and (c) coupling of two molecules of cyclohexene with concomitant loss of two hydrogen atoms to form a novel η^1:η^3-(cyclohexyl)-cyclohexenyl ligand whose identity has been confirmed by an X-ray crystallographic analysis (Figure 3).

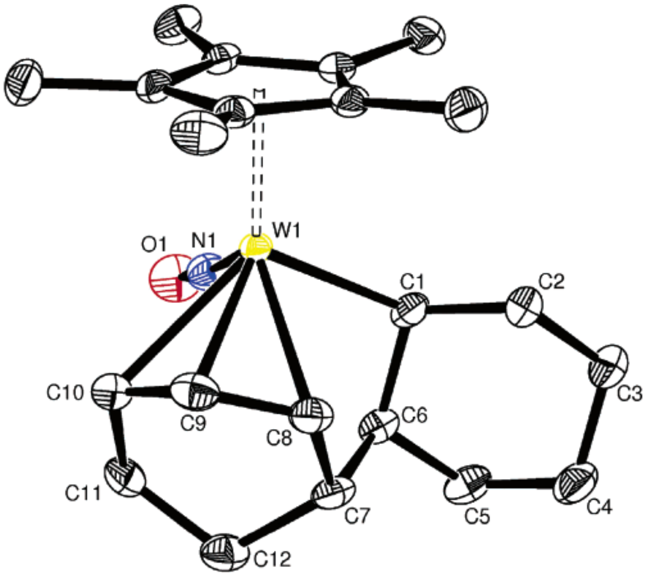


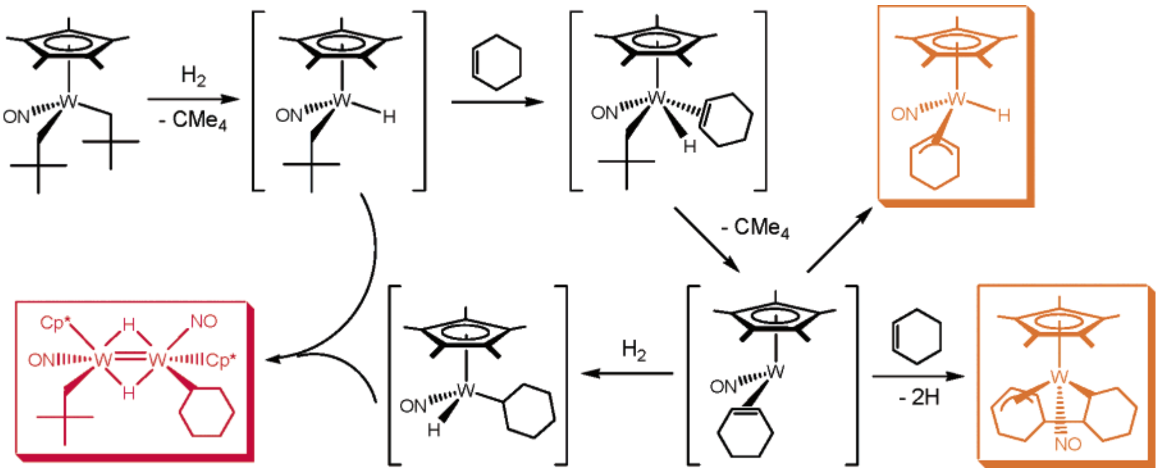
Figure 3. Solid-state molecular structure of the coupled cyclohexene complex.

Thermal Chemistry. Cp′M(NO)(alkyl)$_2$ complexes are generally thermally stable at room temperature when isolated in an analytically pure form. However, as the electron deficiency of these compounds increases, so too does their thermal instability.

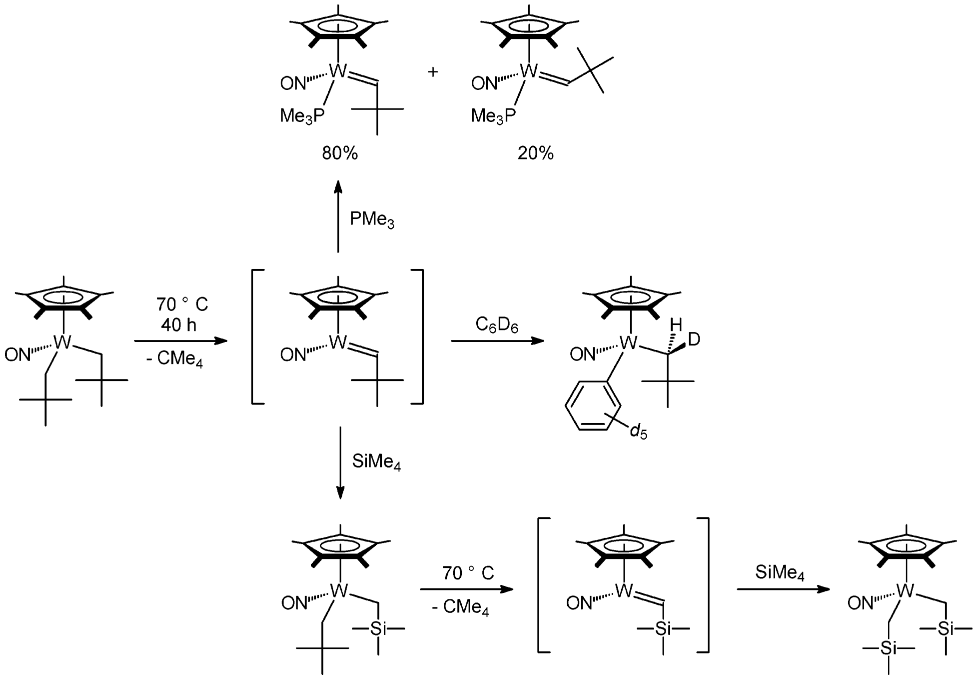
As noted above, Cp*W(NO)(CH$_2$CMe$_3$)$_2$ is appropriately configured to undergo cleavage of an α-H bond by a metal-assisted abstraction process. Thus, thermal activation of this complex at 70 °C in neat hydrocarbon solutions generates the highly reactive neopentylidene complex Cp*W(NO)(=CHCMe$_3$), which can be trapped by PMe$_3$ as the Cp*W(NO)(=CHCMe$_3$)(PMe$_3$) adduct in two isomeric forms (Scheme 12). The neopentylidene intermediate can effect the single activation of solvent C−H bonds (Scheme 12) as well as multiple C−H bond activations, even in the presence of excess PMe$_3$ (Scheme 13). This and related hydrocarbon C−H bond activation chemistry has recently been reviewed.[26]

Very recently it has been discovered that Cp*W(NO)(=CHCMe$_3$) can also be employed for the preferential activation of the more sterically hindered ortho C−H bonds of substituted arenes. Representative examples

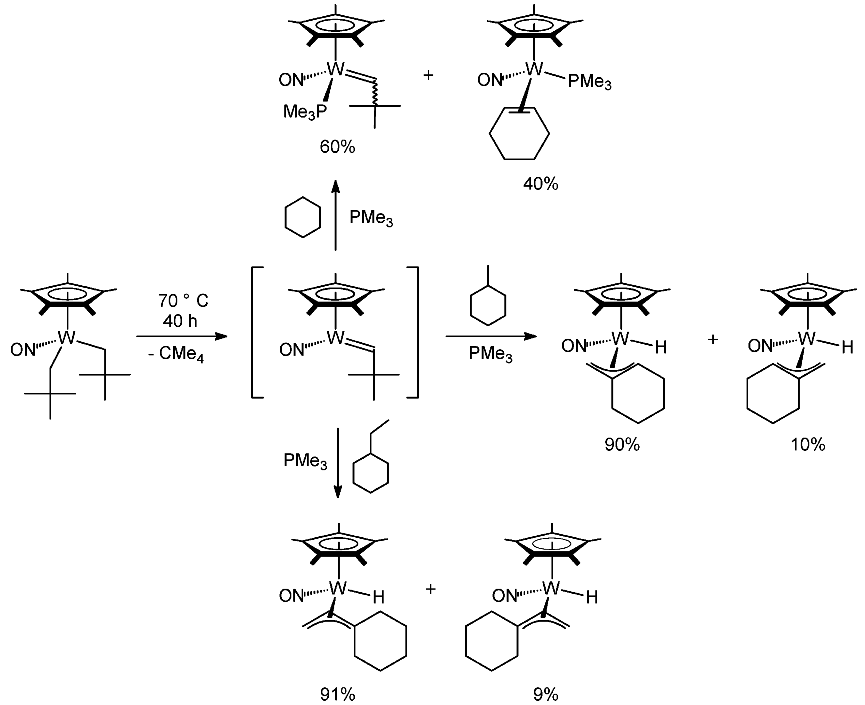
Scheme 11. Reactions of Cp*W(NO)(CH$_2$CMe$_3$)$_2$ with H$_2$ in the Presence of Cyclohexene



Scheme 12. Thermal Chemistry of Cp*W(NO)(CH$_2$CMe$_3$)$_2$



Scheme 13. Multiple C−H Bond Activations Effected by Cp*W(NO)(=CHCMe$_3$)



of these transformations are presented in Scheme 14. Interestingly, the arene substituents are not coordinated to the metals in the solid-state molecular structures of the product complexes, the electron-deficient tungsten centers engaging instead in agostic C−H interactions with the neopentyl ligands.[27]

In general, the thermal reactivity of Cp*Mo(NO)(CH$_2$CMe$_3$)$_2$ resembles that of its isostructural tungsten analogue, but it occurs under ambient conditions. These milder conditions permit the identification of transformations unknown for the tungsten system, such as the sequential activations of two molecules of benzene (Scheme 15), which involve the intermediacy of the benzyne complex Cp*Mo(NO)(η^2-C$_6$H$_4$) during the formation of Cp*Mo(NO)Ph$_2$.[28]

The more Lewis acidic CpMo(NO)(CH$_2$CMe$_3$)$_2$ converts in CH$_2$Cl$_2$ at room temperature into a bimetallic alkylidene nitrosyl complex that contains a unique μ-η^1:η^2-NO ligand (Scheme 16). When this thermolysis is effected in the presence of Lewis bases (L) such as phos-

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(25) Jin, X.; Legzdins, P.; Buschhaus, M. S. A. *J. Am. Chem. Soc.* **2005**, *127*, 6928.

(26) Pamplin, C. B.; Legzdins, P. *Acc. Chem. Res.* **2003**, *36*, 223.

(27) Tsang, J. Y. K.; Legzdins, P.; Buschhaus, M. S. A.; Patrick, B. O. Unpublished observations.

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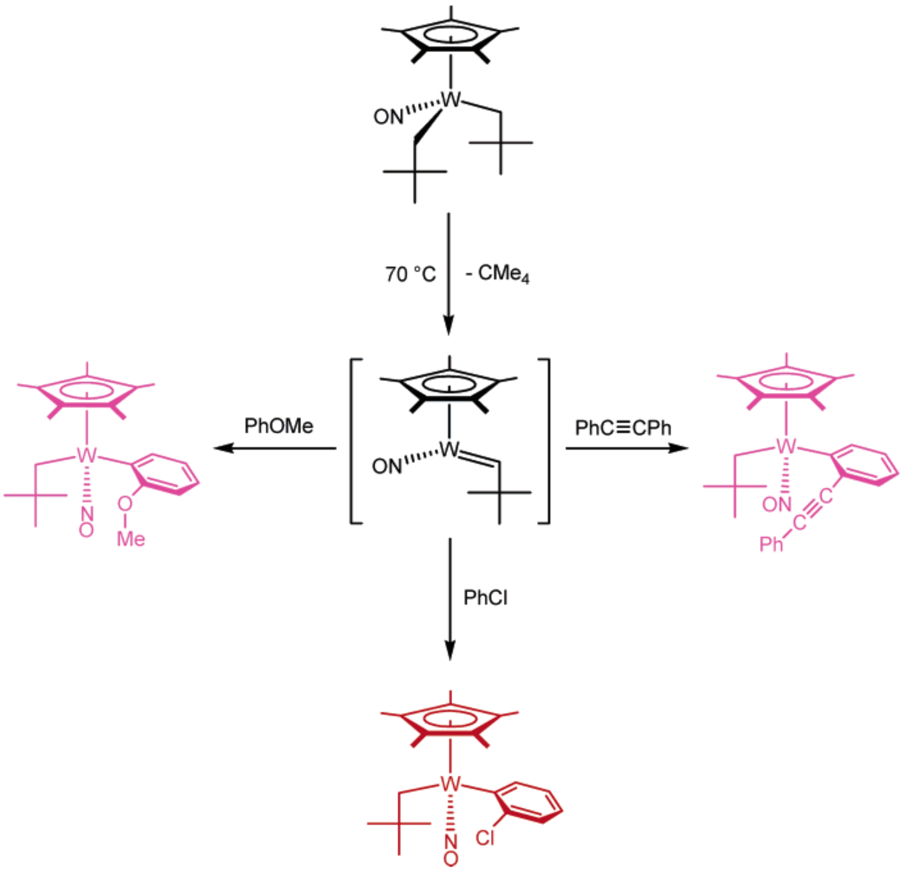
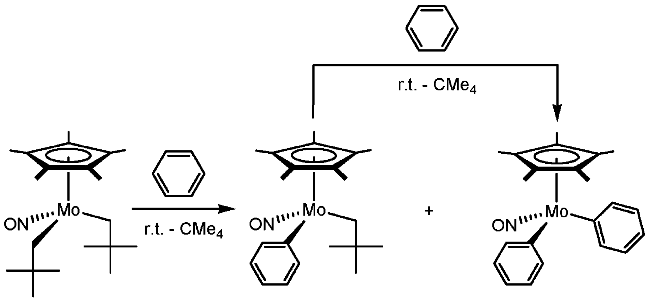
Scheme 14. Selective Intermolecular Ortho C−H Bond Activations of Substituted Arenes by Cp*W(NO)(=CHCMe$_3$)



Scheme 15. Sequential Activation of Two Molecules of Benzene by Cp*Mo(NO)(CH$_2$CMe$_3$)$_2$



phines and pyridine, the monomeric adducts CpMo(NO)(=CHCMe$_3$)$_2$(L) are the sole organometallic products.[29]

The intermediate neopentylidene complex shown in Scheme 16 also reacts with heteroatom−hydrogen bonds and can thus be derivatized to CpMo(NO)(CH$_2$CMe$_3$)(ER) complexes (ER = NHR, OR, SCMe$_3$, OC(O)Me) by treatment with amines, alcohols, thiols, and carboxylic acids, respectively (Scheme 17).[30] Analogous reactions with bifunctional reagents produce bimetallic complexes. The most plausible mechanism for these addition reactions involves initial formation of the EHR adducts CpMo(NO)(=CHCMe$_3$)(EHR), followed by subsequent syn E−H addition across the Mo=C linkage.

The unsymmetrical dialkyl complex CpW(NO)(CH$_2$SiMe$_3$)(CH$_2$CPh$_3$) is thermally unstable and converts to the metallacyclic compound $\mathrm{Cp\overline{W(NO)(CH_2C(C}_6H_4)Ph_2)}$(NCMe) in acetonitrile. Similarly, in the presence of PPh$_3$, the analogous neophyl complex thermally decomposes in CH$_2$Cl$_2$ to $\mathrm{Cp\overline{W(NO)(CH_2C(C}_6H_4)Me_2)}$(PPh$_3$) (Scheme 18).[31]

In closing this section, it may be noted that the structural and thermal properties of the Cp*M(NO)Me$_2$ members of this family of complexes are unique. Thus, metathesis of the chloro ligands of Cp*Mo(NO)Cl$_2$ by MeLi in toluene at low temperature produces Cp*Mo(NO)Me$_2$ in 75% isolated yield.[32] In solution, the dimethyl complex 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 spectroscopy. As expected, hydrolysis of Cp*Mo(NO)Me$_2$ affords *meso*- and *rac*-[Cp*Mo(NO)Me]$_2$(μ-O), and its reactions with a range of Lewis bases (L) to form the 18-electron adducts Cp*Mo(NO)(L)Me$_2$ (e.g. Cp*Mo(NO)(PMe$_3$)Me$_2$) have established it to be the most electrophilic complex in this family of compounds. Most notably, Cp*Mo(NO)Me$_2$ is thermally unstable in solution. However, unlike the other dialkyl complexes (vide supra), it does not undergo α-H elimination to form the methylidene complex Cp*Mo(NO)(=CH$_2$). Rather, it isomerizes via nitrosyl N−O bond cleavage to its oxo(imido) form, Cp*Mo(NMe)(O)Me, which is isolable from the final reaction mixture as the oxo-bridged adduct formed by the two isomers: i.e., Cp*Mo(NO)Me$_2$(μ-O)Cp*Mo(NMe)Me (Scheme 19). This rate of isomerization is significantly faster for the tungsten dimethyl complex; hence, Cp*W(NO)Me$_2$ is not isolable free of supporting donor

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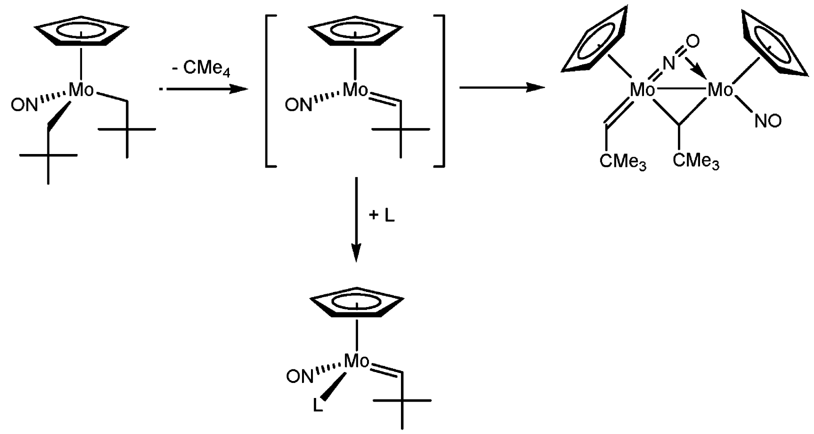
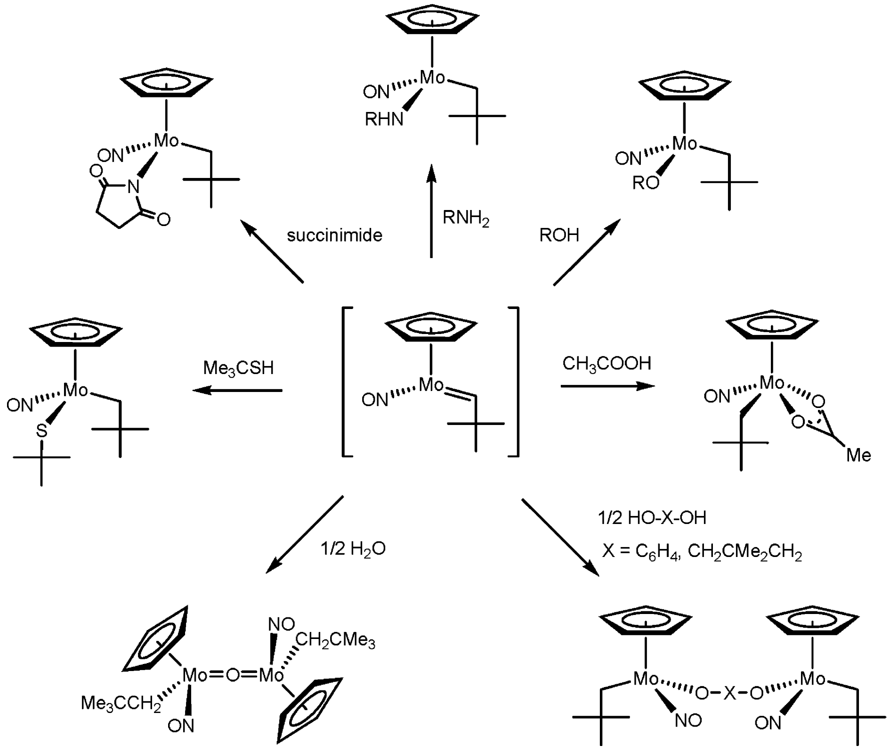
(29) Legzdins, P.; Rettig, S. J.; Veltheer, J. E.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1993**, *12*, 3575.

Scheme 16. Thermal Chemistry of $CpMo(NO)(CH_2CMe_3)_2$ at 20 °C

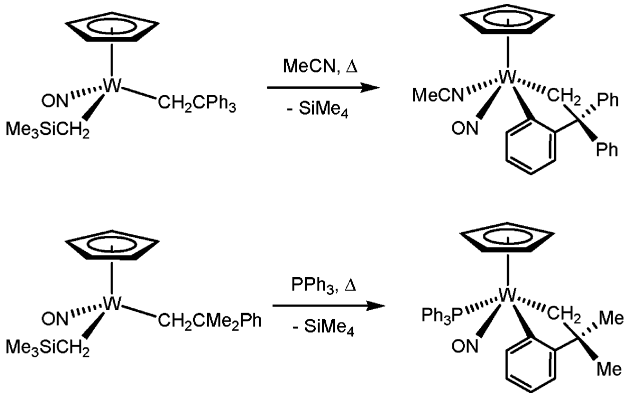


Scheme 17. Addition Reactions of $CpMo(NO)(=CHCMe_3)$



interactions and can only be isolated as $Cp^*W(NO)Me_2$-(μ-O)$Cp^*W(NMe)Me$ or $Cp^*W(NO)Me_2(PMe_3)$ adducts.

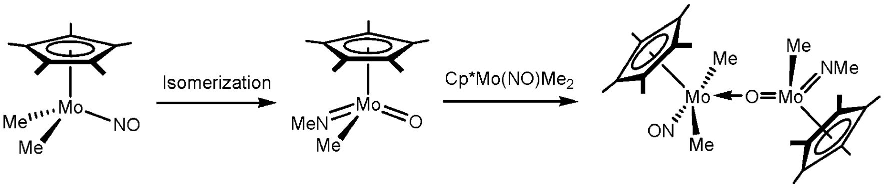
Scheme 18. Thermal Chemistry of $CpW(NO)(CH_2SiMe_3)$(alkyl) Complexes



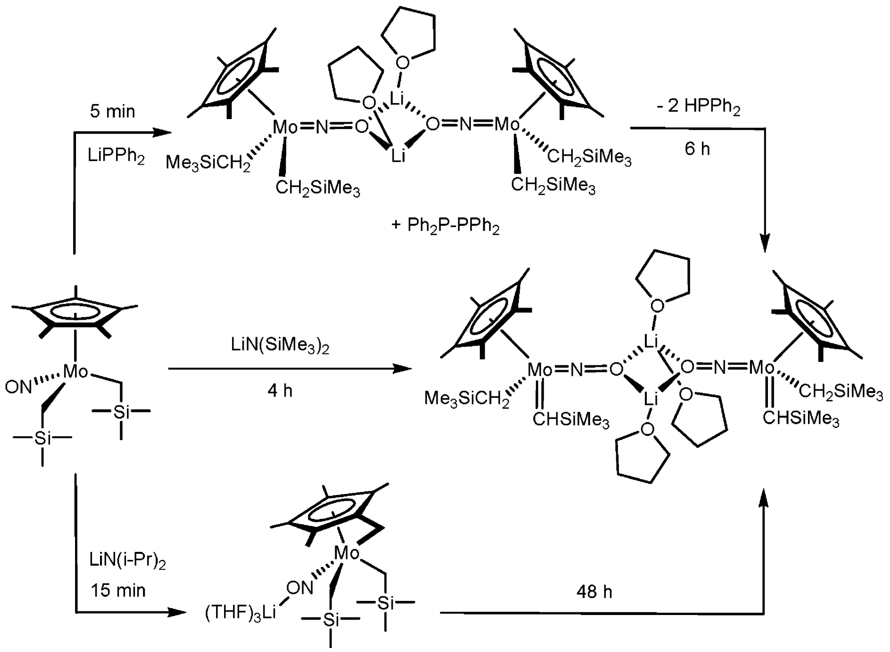
IV. Ligand-Based Reactivity of Cp′M(NO)(alkyl)$_2$ Complexes

Reactivity of the NO Ligands. In addition to functioning as Lewis acids at their metal centers, the dialkyl complexes also possess good Lewis base sites at the nitrosyl oxygen atoms. Thus, reaction of 1 equiv of the oxonium acids $[H(OEt_2)_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ and $[H(OEt_2)_2][B(C_6F_5)_4]$ with the dialkyl complexes $Cp^*WR_2(NO)$ (R = CH_2SiMe_3, CH_2Ph) results in quantitative formation of the corresponding cations $[Cp^*WR_2(NOH{\cdot}OEt_2)]^+$.[33] Crystallographic and spectral data indicate that the WNOH linkages in these complexes are best viewed as involving hydroxylimido ligands, i.e., W≡N−OH. The hydroxylimido protons are acidic and can be readily abstracted by bases such as pyridine to re-form the neutral nitrosyl species. Interestingly, a different mode of reactivity occurs during the reaction of $HBF_4{\cdot}OEt_2$ with the same dialkyl complexes. In this instance the nitrosyl−boron trifluoride adducts Cp^*WR_2-

Scheme 19. Thermal Behavior of Cp*Mo(NO)Me$_2$



Scheme 20. Reactions of Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$ with Lithium Reagents



(NO→BF$_3$) are immediately and quantitatively formed, the solid-state molecular structure of the R = CH$_2$SiMe$_3$ complex being shown in Figure 4.[33] These adducts are similar to the monomeric isonitrosyl complex CpW(CH$_2$SiMe$_3$)$_2$(NO→AlMe$_3$).[12]

Reactivity of the Alkyl Ligands. Only one such study has been reported to date, and it involves deprotonation of one of the alkyl ligands in one of these compounds.[34] Thus, conversion of the dialkyl nitrosyl complex Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$ to the lithium salt of the anionic alkylidene complex, Cp*Mo(NO)(CH$_2$SiMe$_3$)(=CHSiMe$_3$)]$_2$[Li$_2$(THF)$_3$], may be effected with each of the lithium reagents LiN(SiMe$_3$)$_2$, LDA, and LiPPh$_2$. However, as indicated in Scheme 20, each transformation follows a different mechanistic pathway.

V. Epilogue

As summarized in this account, the pseudooctahedral Cp′M(NO)(alkyl)$_2$ complexes possess a rich and varied chemistry. As we synthesize and investigate a greater variety of compounds belonging to this family, we continue to encounter new modes of intramolecular reactivity exhibited by them. We are thus confident that this area of chemistry still holds a wealth of fascinating chemical opportunities awaiting discovery. In addition to delineating these reactivity patterns, we are also focusing our current research efforts on effecting some of the stoichiometric chemical transformations outlined in this review in a catalytic manner.

The complexes most closely related to the Cp′M(NO)(alkyl)$_2$ systems described in this review are the pseudotetrahedral d^0 group 4 metallocene bis(hydrocarbyl)

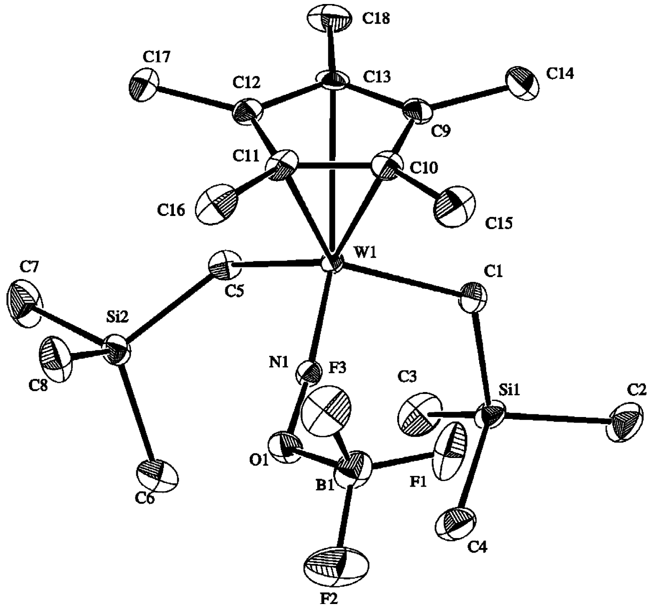


Figure 4. Solid-state molecular structure of Cp*W(CH$_2$SiMe$_3$)$_2$(NO→BF$_3$).

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[30] Legzdins, P.; Veltheer, J. E.; Young, M. A.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1995**, *14*, 407.

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[32] Sharp, W. B.; Daff, P. J.; McNeil, W. S.; Legzdins, P. *J. Am. Chem. Soc.* **2001**, *123*, 6272.

[33] Sharp, W. B.; Legzdins, P.; Patrick, B. O. *J. Am. Chem. Soc.* **2001**, *123*, 8143.

[34] Legzdins, P.; Sayers, S. F. *Organometallics* **1996**, *15*, 3907.

species Cp_2MR_2 (M = Zr, Hf), which have been extensively studied by many researchers over the years.[35] While there are some parallels in the chemistry exhibited by the two classes of compounds containing the 14-electron Cp_2M (M = Zr, Hf) and $Cp'M(NO)$ (M = Mo, W) fragments (e.g. the formation of *trans*-diene complexes,[36] sulfur-insertion reactions,[37] etc.), many of the chemical properties of the nitrosyl systems remain unique to them. We attribute this uniqueness to the presence of the strongly π-acidic nitrosyl ligands in the molybdenum and tungsten coordination spheres. This feature is clearly illustrated by the fact that isoelectronic rhenium carbonyl analogues of the various tungsten nitrosyl complexes described in this review simply do not exist. Thus, while 16-electron $Cp'W(NO)Cl_2$ is the synthetic precursor to the title $Cp'W(NO)(alkyl)_2$ compounds, the most closely related carbonyl complexes of rhenium are $Cp'Re(CO)_2X_2$ (X = Cl, Br, I), all stable 18-electron entities.[38]

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OM0504396

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(35) For a readable account of organozirconium chemistry, see: Rouhi, A. M. *Chem. Eng. News* **2004**, *82*, 36 and references therein.

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