

Cp'M(NO)R₂: 16-Electron Piano-Stool Molecules of Molybdenum and Tungsten

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A fundamental principle of transition-metal organometallic chemistry is the 18-valence-electron rule, which states that stable organometallic complexes will contain a total of 18 valence electrons.¹ The valence-bond basis of this rule, which is analogous to the octet rule in organic chemistry, is that organometallic complexes generally owe their stability to the filling of the nine valence orbitals of the transition metal with 18 electrons provided by the metal and the ligands of the complex. In molecular-orbital terms, the rule may be rationalized in terms of the filling of all bonding and nonbonding valence molecular orbitals of the complex by the 18 electrons and the existence of a large HOMO–LUMO energy gap. Although the vast majority of known transition-metal organometallic complexes obey this rule, many compounds have now been isolated that violate it. Particularly interesting among the latter are the complexes that contain 16 valence electrons since such electronically and coordinatively unsaturated organometallic complexes are known to play an important role in catalytic systems.²

Like the 18-electron species, the isolable 16-electron complexes also owe their stability to a large HOMO–LUMO gap, but their LUMOs need not be filled with a pair of electrons in order to attain a stable electronic configuration. Until the systems described in this Account were discovered, the most common 16-electron complexes were the square-planar d⁸ group 10 compounds of the type L₂MR₂ (L = two-electron donor; M = Pt or Pd; R = hydrocarbyl)³ and the pseudotetrahedral d⁰ group 4 metallocene bis(hydrocarbyl) complexes Cp₂MR₂ (Cp = η⁵-C₅H₅; M = Ti, Zr, or Hf).⁴ To this list may now be added the pseudooctahedral Cp'M(NO)R₂ systems [Cp' = Cp or Cp* (η⁵-C₅Me₅); M = Mo or W; R = alkyl or aryl],⁵ whose chemistry we have been actively investigating for the past seven years. These latter complexes are typically 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 to the metal center and is a strong π-acid ligand, stronger indeed than the well-known CO group.^{6,7}

Peter Legzdins was born in Riga, Latvia, on September 24, 1942. He received his Honours B.Sc. from Carleton University (1964) and his Ph.D. from MIT (1968) with F. A. Cotton. After a postdoctoral year with G. Wilkinson at Imperial College in London, he joined the faculty at the University of British Columbia, where he is currently Professor of Chemistry and Head of the Department of Chemistry.

John Veltheer was born on October 6, 1965 in Winnipeg, Manitoba. After receiving his Honours B.Sc. degree from Queen's University at Kingston in 1988, he joined the Legzdins research group, where he is presently completing his doctoral studies. Research interests in the group are focused on establishing a fundamental understanding of the fascinating role that coordinated nitric oxide plays in transition-metal organometallic chemistry.

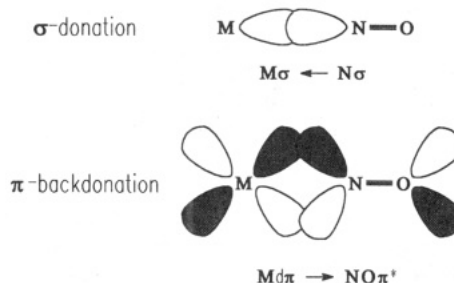


Figure 1. Synergic interactions between a transition metal and a linear nitrosyl ligand.

The M–NO orbital overlaps commonly invoked to account for this synergic bonding are diagrammed in Figure 1. The strong π-acidity of the nitrosyl ligand is a key contributor to the molecular-orbital energy levels of the model complex CpMo(NO)Me₂, which has the requisite large HOMO–LUMO gap, the LUMO being a nonbonding, metal-centered orbital.⁸ It may be noted at this point that the degree of M(dπ)–NO(π*) back-bonding is a direct function of the amount of electron density at the metal center. Transfer of electron density into the NO(π*) antibonding orbital decreases the N–O bond order and thus decreases the nitrosyl stretching frequency (ν_{NO}) as measured in the IR spectrum of the complex. As we shall see later, this sensitive indicator is one of the most useful spectroscopic probes in organometallic nitrosyl chemistry.

A long-term goal of our research program is the development of organometallic nitrosyl complexes as specific reactants or selective catalysts for organic or organometallic transformations of practical significance. To attain this goal specifically with our Cp'M(NO)R₂ systems we developed new methods for their synthesis, established their characteristic physical and chemical properties, and are currently endeavoring to exploit those properties which are unique to the complexes.

(1) Elschenbroich, C.; Salzer, A. *Organometallics—A Concise Introduction*, 2nd ed.; VCH Publishers: New York, 1992; pp 186, 412.

(2) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Part II.

(3) Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; W. B. Saunders: Toronto, 1977; p 804.

(4) Negishi, E.; Takahashi, T. *Aldrichimica Acta* 1985, 18, 31 and references therein.

(5) Unless explicitly stated otherwise, throughout this Account Cp' will always denote both η⁵-C₅H₅ (Cp) and η⁵-C₅Me₅ (Cp*), M will indicate both Mo and W, and R will indicate both alkyl and aryl.

(6) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley-Interscience: New York, 1988; Chapter 22.

(7) Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyls*; Oxford University Press: New York, 1992; Chapter 1.

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

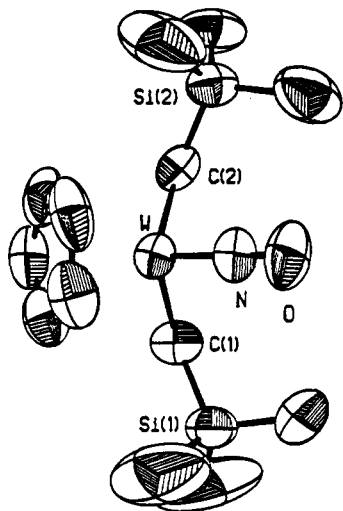
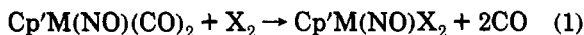


Figure 2. Molecular structure of $\text{CpW}(\text{NO})(\text{CH}_2\text{SiMe}_3)_2$.

During our investigations, we have discovered that the $\text{Cp}'\text{M}(\text{NO})\text{R}_2$ complexes 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 group of complexes. Indeed, we have found that the chemical properties of these systems are often dependent on the metal, the nature of the R groups, and the type of Cp' ligand. In this Account we summarize the synthesis, characterization, comparative reactivity, and distinctive chemical properties of the 16-electron $\text{Cp}'\text{M}(\text{NO})\text{R}_2$ complexes known to date.

Early Work

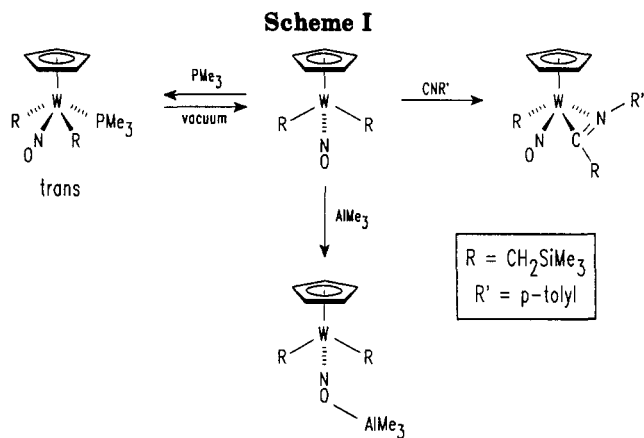
Our original idea was that the bis(hydrocarbyl) derivatives, $\text{Cp}'\text{M}(\text{NO})\text{R}_2$, should be preparable by metathesis reactions from their known dihalide precursors, $\text{Cp}'\text{M}(\text{NO})\text{X}_2$ ($\text{X} = \text{I}, \text{Br}, \text{or Cl}$).⁹ The preparations of these latter complexes described in the literature involve treatment of $\text{Cp}'\text{M}(\text{NO})(\text{CO})_2$ complexes with elemental halogen (eq 1).¹⁰ Since solid



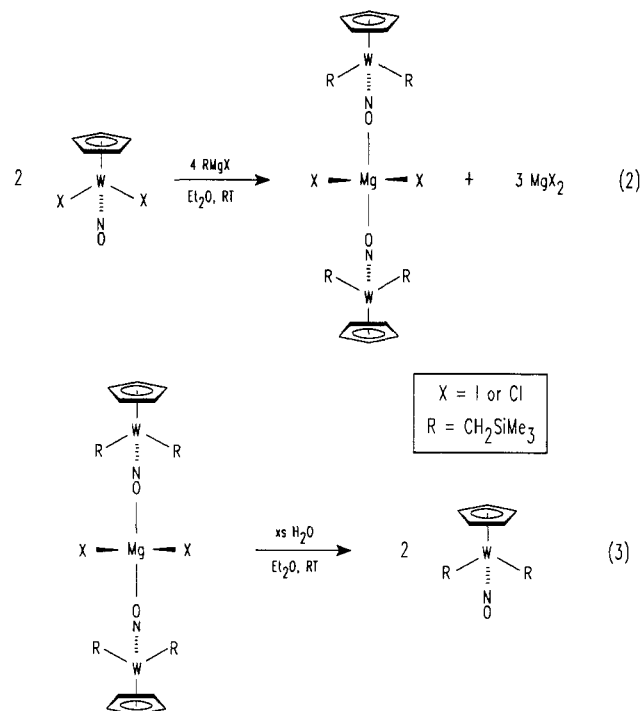
iodine is the easiest of the halogens to handle stoichiometrically, our work in this area began by our using the diiodide complexes as the synthetic precursors. In 1985, Luis Sánchez, a Spanish postdoctoral fellow in our group, discovered that treatment of $\text{CpW}(\text{NO})\text{I}_2$ with 2 equiv of the Grignard reagent $\text{Me}_3\text{SiCH}_2\text{MgCl}$ in Et_2O affords an unusual 4-coordinate L_2MgX_2 complex in which the NO oxygens are the binding sites of the organometallic ligands L (eq 2). Hydrolysis of this intermediate isonitrosyl complex (eq 3) affords a high yield of the prototypical complex $\text{CpW}(\text{NO})(\text{CH}_2\text{SiMe}_3)_2$ as relatively air-stable and thermally stable violet crystals.⁸ An X-ray crystallographic analysis

(9) These complexes possess either monomeric or halide-bridged dimeric molecular structures in the solid state, but evidently they all exist as solvated monomers in solutions. Hence, they are represented exclusively by their monomeric formulas throughout this Account.

(10) For $\text{Cp}' = \text{Cp}$, see: (a) Seddon, D.; Kita, W. G.; Bray, J.; McCleverty, J. A. *Inorg. Synth.* 1976, 16, 24. (b) Hunter, A. D.; Legzdins, P.; Martin, J. T.; Sánchez, L. *Organomet. Synth.* 1986, 3, 58. For $\text{Cp}' = \text{Cp}^*$, see: (c) Dryden, N. H.; Legzdins, P.; Einstein, F. W. B.; Jones, R. H. *Can. J. Chem.* 1988, 66, 2100. (d) Gomez-Sal, P.; de Jesús, E.; Michiels, W.; Royo, P.; de Miguel, A. V.; Martínez-Carrera, S. *J. Chem. Soc., Dalton Trans.* 1990, 2445.



established the monomeric nature of the complex in the solid state (Figure 2).



A survey of the reactivity of this 16-electron dialkyl compound soon showed its chemistry to be dominated by its ability to function as a Lewis acid. In other words, the LUMO of the parent complex is sufficiently low in energy that it can accept electrons from classic Lewis bases. After initial coordination to the metal center, these Lewis bases often undergo subsequent intramolecular insertion reactions involving the alkyl ligands.^{8b} In addition to functioning as a Lewis acid at tungsten, the prototypical dialkyl complex also possesses a good Lewis base site at the nitrosyl oxygen atom (cf. eq 2). Hence, the reaction of $\text{CpW}(\text{NO})(\text{CH}_2\text{SiMe}_3)_2$ with AlMe_3 provides a monomeric isonitrosyl AlMe_3 adduct (Scheme I).

Subsequent work showed that neopentyl (CH_2CMe_3) and neophyl ($\text{CH}_2\text{CMe}_2\text{Ph}$) analogues of $\text{CpW}(\text{NO})(\text{CH}_2\text{SiMe}_3)_2$ can be prepared in a similar manner, albeit in lower isolated yields.¹¹ On occasion, $\text{CpMo}(\text{NO})(\text{CH}_2\text{SiMe}_3)_2$ could also be prepared, but for reasons we shall discuss later, a more reliable synthetic route was desirable.

(11) Hunter, A. D.; Legzdins, P.; Martin, J. T.; Sánchez, L. *Organomet. Synth.* 1986, 3, 66.

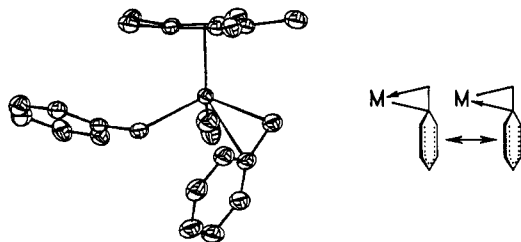
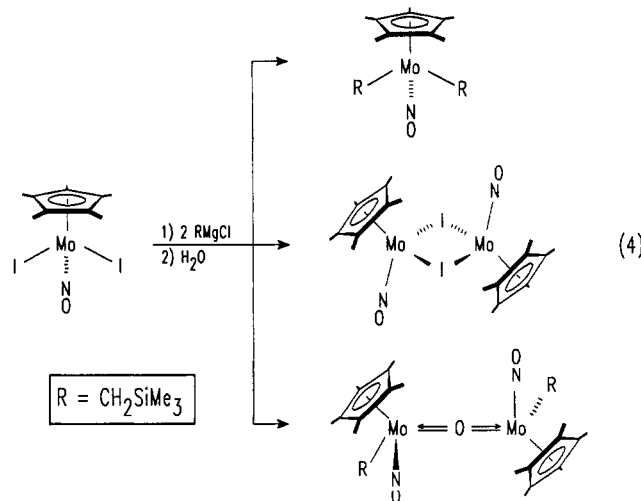


Figure 3. Molecular structure of $\text{Cp}^*\text{Mo}(\text{NO})(\text{CH}_2\text{Ph})_2$ with a valence-bond description of the bonding in the $\text{M}-\eta^2$ -benzyl linkage.

Unique members of the $\text{Cp}'\text{M}(\text{NO})\text{R}_2$ family of complexes preparable by the methodology summarized in eqs 2 and 3 are the fluxional dibenzyl species which have the limiting structures $\text{Cp}'\text{M}(\text{NO})(\eta^2\text{-CH}_2\text{Ph})(\eta^1\text{-CH}_2\text{Ph})$.¹² In these compounds the metal centers attain the favored 18-valence-electron configuration by virtue of bearing an unusual *dihapto* benzyl ligand which functions as a formal three-electron donor to the metal center. This feature indicates that the metal centers in the $\text{Cp}'\text{M}(\text{NO})\text{R}_2$ complexes will avail themselves of any available intramolecular electron density. To date we have crystallographically characterized nine benzyl nitrosyl complexes, all of which show the propensity to bear benzyl ligands in an η^2 fashion rather than the more conventional η^1 or η^3 manners. A particularly good illustration of this mode of attachment is provided by the solid-state molecular structure of $\text{Cp}^*\text{Mo}(\text{NO})(\text{CH}_2\text{Ph})_2$ (Figure 3).¹²

Advances: "One Step Sideways"

We next wished to extend our original synthetic procedures (eqs 2 and 3) to encompass a wider range of $\text{Cp}'\text{M}(\text{NO})\text{R}_2$ species. However, the hydrolytic instability of the desired molybdenum complexes almost immediately thwarted that goal. For instance, treatment of $\text{Cp}^*\text{Mo}(\text{NO})\text{I}_2$ with 2 equiv of an Et_2O solution of $\text{Me}_3\text{SiCH}_2\text{MgCl}$ followed by quenching with water leads to the formation of three isolable organometallic products, the *minor* one being the expected $\text{Cp}^*\text{Mo}(\text{NO})(\text{CH}_2\text{SiMe}_3)_2$ (eq 4). In other words, the desired



dialkyl complex is indeed among the isolable products, but certainly not in preparative yields. In fact, reduc-

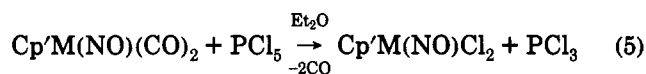
(12) Legzdins, P.; Jones, R. H.; Phillips, E. C.; Yee, V. C.; Trotter, J.; Einstein, F. W. B. *Organometallics* 1991, 10, 986.

tion of the organometallic reactant to form $[\text{Cp}^*\text{Mo}(\text{NO})\text{I}]_2$ and hydrolysis of $\text{Cp}^*\text{Mo}(\text{NO})(\text{CH}_2\text{SiMe}_3)_2$ to form $[\text{Cp}^*\text{Mo}(\text{NO})(\text{CH}_2\text{SiMe}_3)_2(\mu\text{-O})]$ account for 80–90% of the isolated materials.¹³ Indeed, we have now established that *all* such Mo dialkyl and diaryl compounds are readily hydrolyzed to form bimetallic $[\text{Cp}^*\text{Mo}(\text{NO})\text{R}]_2(\mu\text{-O})$ complexes.¹³ Clearly, this hydrolytic instability of the products required us to develop a synthetic strategy to $\text{Cp}'\text{M}(\text{NO})\text{R}_2$ (R = alkyl or aryl) complexes that did not require the use of water. Furthermore, as our investigations progressed, it became clear that our original choices of solvent, reaction temperature, and dihalo starting material for the preparation of the dialkyl complexes were inappropriate for the synthesis of the diaryl analogues.

A New General Synthetic Methodology: "Two Steps Forward"

Curiously enough, our development of a reliable and reproducible synthesis of $\text{Cp}'\text{M}(\text{NO})\text{R}_2$ complexes began with some electrochemical investigations of their dihalo precursors.¹⁴ These investigations established that one-electron reduction of $\text{Cp}'\text{M}(\text{NO})\text{X}_2$ affords radical anions of the type $[\text{Cp}'\text{M}(\text{NO})\text{X}_2]^-$ whose thermal stability diminishes as $\text{X} = \text{Cl} > \text{Br} > \text{I}$. Cyclic voltammetry and ESR spectroscopy then showed that the initial step in the metathesis reactions forming the dialkyl nitrosyl complexes (eq 2) is also a one-electron transfer from the Grignard reagent to the organometallic reactant to generate the same $[\text{Cp}'\text{M}(\text{NO})\text{X}_2]^-$ radical anions (Figure 4). On the basis of these observations, we thus developed the view that our general synthetic methodology leading to $\text{Cp}'\text{M}(\text{NO})\text{R}_2$ complexes should be designed to maximize the stability of these radical anion intermediates in order to promote the halide for the alkyl metathesis step. This requirement implies the concomitant use of (1) dichloro nitrosyl starting materials, since the $[\text{Cp}'\text{M}(\text{NO})\text{Cl}_2]^-$ species are the most thermally stable dihalo radical anions; (2) solvating solvents such as THF to stabilize ionic intermediates; and (3) low temperatures to avoid possible decomposition pathways of the newly formed organometallics.

Our next task was to find a new, reliable, high-yielding route to the $\text{Cp}'\text{M}(\text{NO})\text{Cl}_2$ starting materials. We subsequently discovered that employing PCl_5 as a source of two chloride ligands is both simple and efficient (eq 5).¹⁵ The conversions summarized in eq 5 may be



effected on at least a 100-mmol scale. They are reliable, present no unusual hazards or difficulties, and are far superior to the use of elemental chlorine (eq 1). The tungsten dichloro complexes are more temperature sensitive and photosensitive than are their molybdenum congeners, and hence they must be stored at low temperatures in the dark.

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

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

(15) Dryden, N. H.; Legzdins, P.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* 1991, 10, 2077.

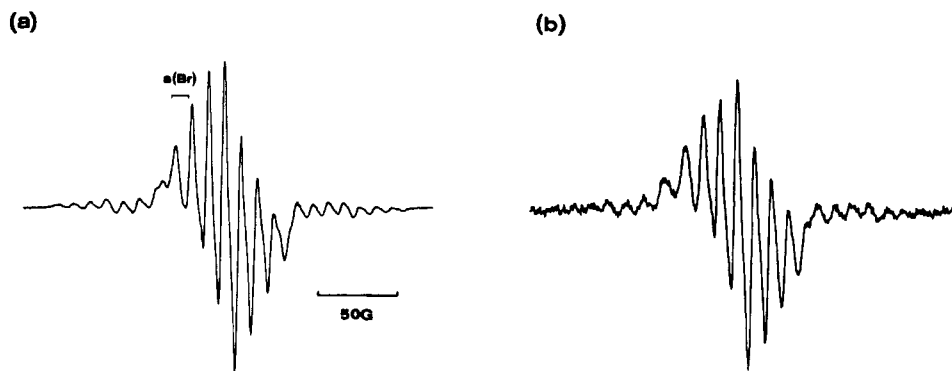
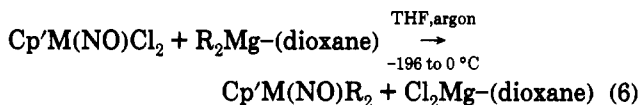


Figure 4. (a) X-band ESR spectrum of isolated $[\text{Cp}_2\text{Co}][\text{Cp}^*\text{Mo}(\text{NO})\text{Br}_2]$ in DMF. (b) X-band ESR spectrum of an equimolar mixture of $\text{Cp}^*\text{Mo}(\text{NO})\text{Br}_2$ and $\text{Me}_3\text{SiCH}_2\text{MgCl}$ in DMF.

Next, we needed to overcome the inherent need for water in reactions 3. We found that this could be accomplished by the use of R_2Mg -(dioxane) reagents instead of Grignard reagents in metathesis reactions 2. Such a replacement offers two advantages, namely, (1) the R_2Mg -(dioxane) reagents are solids having exact compositions and (2) dioxane ligates the MgCl_2 byproduct considerably more efficiently than does the oxygen atom of the nitrosyl ligand of the desired $\text{Cp}^*\text{M}(\text{NO})\text{R}_2$ products.¹⁶ Gratifyingly, application of these ideas does indeed lead to successful and more efficient syntheses of all $\text{Cp}^*\text{M}(\text{NO})\text{R}_2$ complexes, both those that we had previously isolated and many that we had not. This synthetic route, which is now routinely used to prepare these molecules in our laboratories, is summarized in eq 6.

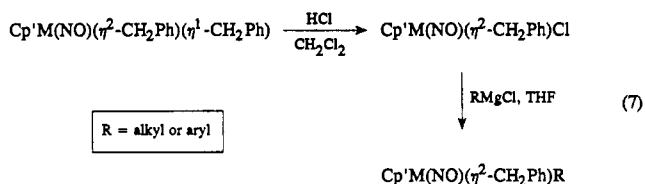


Two other points concerning eq 6 merit special mention. One is that the Cl_2Mg -(dioxane) byproduct is very insoluble in even moderately polar solvents, thereby allowing the sparingly soluble $\text{Cp}^*\text{M}(\text{NO})(\text{aryl})_2$ complexes to be extracted uncontaminated from the final reaction mixtures. The other point is that the isolation of these $\text{Cp}^*\text{M}(\text{NO})(\text{aryl})_2$ complexes is dependent on the nature of the cyclopentadienyl ligand. All Cp^* compounds are isolable, but the only Cp diaryl complex that we have yet been able to isolate from conversions 6 is $\text{CpW}(\text{NO})(o\text{-tolyl})_2$ ($\nu_{\text{NO}} = 1602 \text{ cm}^{-1}$).¹⁷ Interestingly, the others ($\nu_{\text{NO}} = 1628\text{--}1599 \text{ cm}^{-1}$) can be generated in situ by reactions 6 and derivatized.¹⁶

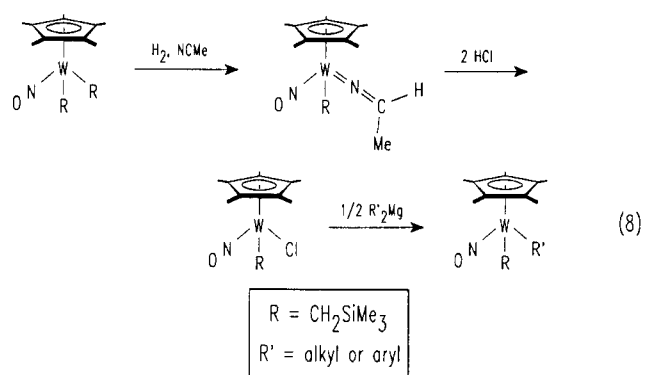
Introduction of Asymmetry: Preparation of $\text{Cp}^*\text{M}(\text{NO})(\text{R})\text{Cl}$ Complexes

Our first expectation was that $\text{Cp}^*\text{M}(\text{NO})(\text{R})\text{Cl}$ complexes should result from treatment of their $\text{Cp}^*\text{M}(\text{NO})\text{R}_2$ precursors with 1 equiv of HCl . However, this is only feasible for the 18-electron systems containing the stabilizing η^2 -benzyl group, as shown in the first part of eq 7. Nevertheless, having synthesized the 18-electron benzyl halide complexes, we were then able

to convert them to the mixed hydrocarbyl complexes $\text{Cp}^*\text{M}(\text{NO})(\eta^2\text{-CH}_2\text{Ph})\text{R}$ (eq 7).^{18,19}



Our first successful synthesis of a 16-electron alkyl chloro complex resulted from a two-step route beginning with $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{SiMe}_3)_2$ (eq 8).²⁰ Hydrogenolysis of the reactant in acetonitrile leads to an ethylidene-amido complex which upon treatment with excess HCl affords the deep blue $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{SiMe}_3)\text{Cl}$ complex, a 16-electron monomer both in solution and in the solid state. Reaction of the monochloro complex with appropriate alkylating reagents produces the mixed $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{SiMe}_3)\text{R}$ complexes in good yields.



Since this initial discovery, we have found that we can indeed synthesize alkyl and aryl chloro complexes directly from their dichloro precursors, although the syntheses are often difficult to control. Treatment of $\text{Cp}^*\text{M}(\text{NO})\text{Cl}_2$ with $1/2 \text{ R}'_2\text{Mg}$ -(dioxane) in THF at very low temperatures in dilute solution ($<0.1 \text{ M}$) affords the monoalkylated products, $\text{Cp}^*\text{M}(\text{NO})(\text{R})\text{Cl}$, in moderate yields.²¹ The preparative difficulties lie in the

(18) Dryden, N. H.; Legzdins, P.; Phillips, E. C.; Trotter, J.; Yee, V. C. *Organometallics* 1990, 9, 882.

(19) Dryden, N. H.; Legzdins, P.; Trotter, J.; Yee, V. C. *Organometallics* 1991, 10, 2857.

(20) Debad, J. D.; Legzdins, P.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* 1992, 11, 6.

(21) Debad, J. D.; Legzdins, P.; Ross, K. J.; Veltheer, J. E. Unpublished observations.

(16) Dryden, N. H.; Legzdins, P.; Rettig, S. J.; Veltheer, J. E. *Organometallics* 1992, 11, 2583.

(17) Legzdins, P.; Rettig, S. J.; Ross, K. J.; Veltheer, J. E. *J. Am. Chem. Soc.* 1991, 113, 4361.

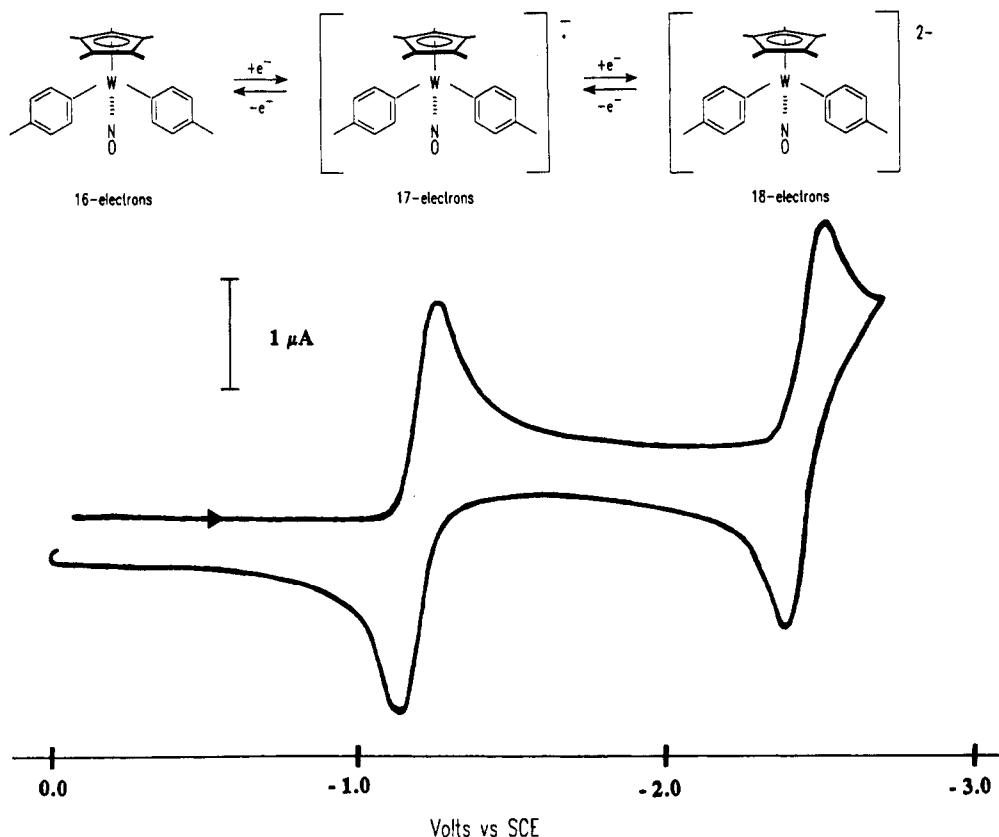


Figure 5. Ambient temperature cyclic voltammogram of $\text{Cp}^*\text{W}(\text{NO})(p\text{-tolyl})_2$ from 0 to -3 V in THF.

solubilities of the species involved. The dichlorides are insoluble in cold THF, whereas the monoalkyl chloro complexes are completely soluble. Thus, the temperature of the reaction mixture must be maintained at sufficiently low temperatures so that the $\text{Cp}^*\text{M}(\text{NO})(\text{R})\text{Cl}$ is formed, but does not react with the remaining RMgCl and R_2Mg reagents in the mixture.²²

The availability of the monoalkylated products allows us a direct route to the preparation of a wide variety of chiral (although as yet unresolved) nitrosyl compounds. For instance, conversion of these materials to their $\text{Cp}^*\text{M}(\text{NO})(\text{R})\text{R}'$ derivatives permits us to compare directly the reactivities of two different metal-carbon σ bonds at the same metal center. For instance, the reactions of CO with $\text{Cp}^*\text{W}(\text{NO})(\text{R})\text{R}'$ under ambient conditions to give $\text{Cp}^*\text{W}(\text{NO})(\eta^2\text{-C}\{\text{O}\}\text{R})\text{R}'$ indicate the migratory aptitudes of various alkyl and aryl groups, R and R'. We have thus established that the bulky alkyl groups are the most prone to migrate, followed in turn by the aryl groups, and then by methyl groups.²³ The utility of these chiral dialkyl complexes as reagents, catalysts, and mechanistic probes remains to be investigated.

Chemical and Physical Properties

(1) Redox Properties. The results of Fenske-Hall MO calculations on the model complexes $\text{CpM}(\text{NO})\text{Me}_2$ ($\text{M} = \text{Mo}^{8a}$ or W^{24}) indicate that their LUMOs are metal-centered and nonbonding in nature. Therefore, there

is no loss of metal-ligand binding or stability in these compounds despite their formal electron deficiency. The redox properties of all the $\text{Cp}^*\text{M}(\text{NO})\text{R}_2$ compounds are fully in accord with these theoretical calculations. The cyclic voltammogram of $\text{Cp}^*\text{W}(\text{NO})(p\text{-tolyl})_2$ in THF (Figure 5) is representative of this family of compounds. It exhibits reduction features indicating the occurrence of two reversible, one-electron reductions at $E^{\circ'}$ values of -1.21 and -2.46 V.¹⁶ If the LUMO of $\text{Cp}^*\text{W}(\text{NO})(p\text{-tolyl})_2$ is also metal-centered and nonbonding, it is not surprising that filling this orbital with two electrons should be a fully reversible process. Indeed, all the $\text{Cp}^*\text{M}(\text{NO})\text{R}_2$ complexes show similar electrochemical behavior; however, some $\text{Cp}^*\text{M}(\text{NO})\text{R}_2$ complexes evidently have $E^{\circ'}$ values at potentials beyond the limit of the THF solvent.^{16,25}

(2) Relative Lewis Acidities. The existence of the vacant, metal-centered orbital on the $\text{Cp}^*\text{M}(\text{NO})\text{R}_2$ compounds imparts Lewis acid characteristics to these entities. For instance, the electrochemical reduction potentials of various $\text{Cp}^*\text{M}(\text{NO})\text{R}_2$ complexes correlate well with the IR stretching frequencies of the nitrosyl ligands in these compounds, since these latter frequencies are directly proportional to the electron density at their metal centers (Figure 6). In all cases there is an inverse dependence of ν_{NO} and $E^{\circ'}$, the more electron-deficient species exhibiting higher ν_{NO} and less negative $E^{\circ'}$ values.

On the basis of data such as those presented in Figure 6, we can rank the $\text{Cp}^*\text{M}(\text{NO})\text{R}_2$ complexes in terms of their relative Lewis acidities (i.e., electron deficiencies) as $\text{Cp} > \text{Cp}^*$, aryl > alkyl, and $\text{Mo} > \text{W}$. We thus conclude that $\text{CpMo}(\text{NO})(\text{aryl})_2$ complexes, if isolable

(22) $\text{Cp}^*\text{Mo}(\text{NO})(\text{Me})\text{Br}$ has been prepared from $\text{Cp}^*\text{Mo}(\text{NO})\text{Br}_2$ and AlMe_3 ; see: de Jesús, E.; de Miguel, V.; Royo, P.; Lanfredi, A. M. M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* 1990, 2779.

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(25) Dryden, N. H. Ph.D. Dissertation, The University of British Columbia, 1990.

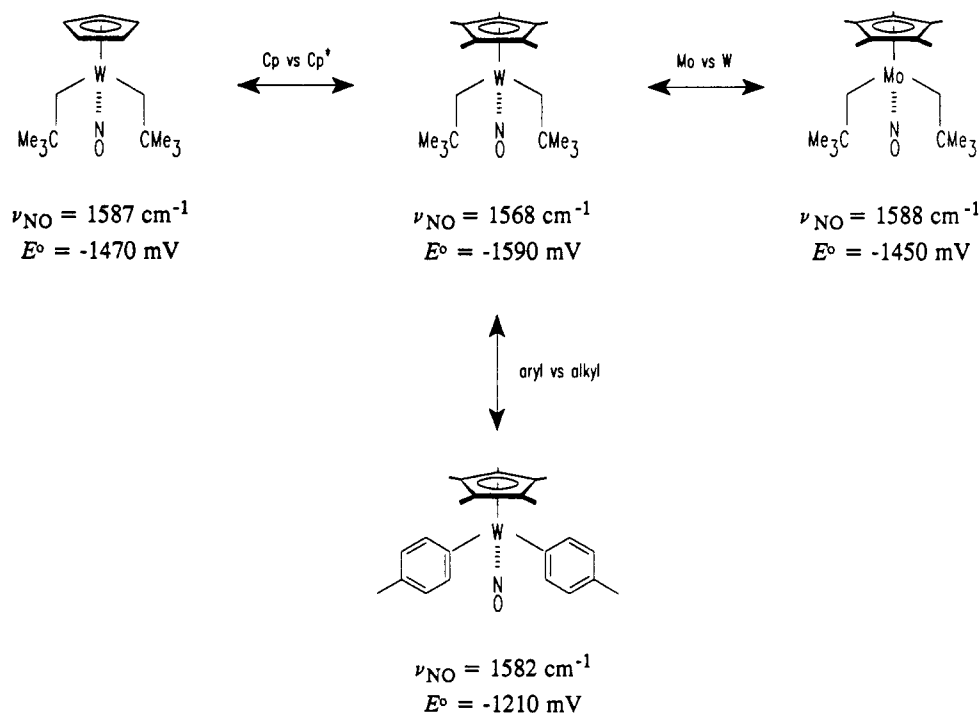


Figure 6. Representative $\text{Cp}^*\text{M}(\text{NO})\text{R}_2$ complexes and their corresponding nitrosyl stretching frequencies (THF) and electrochemical reduction potentials (THF) vs SCE.

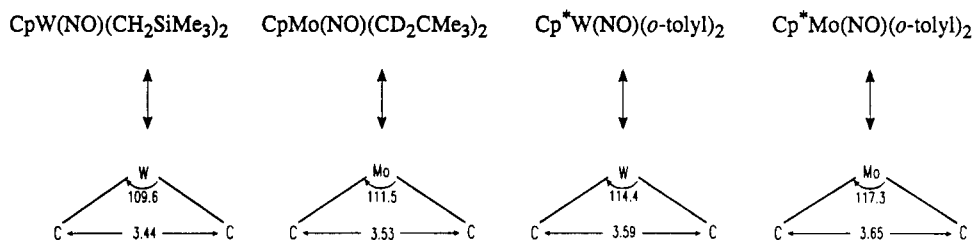
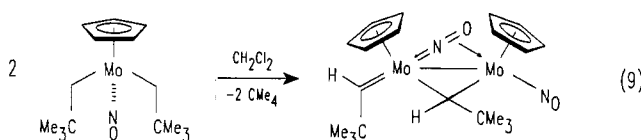


Figure 7. Pictorial representation of the open coordination site at each metal center in four $\text{Cp}^*\text{M}(\text{NO})\text{R}_2$ complexes, the C-M-C bond angle (deg), and the *nonbonded* separation (Å) between the first two carbons of the alkyl or aryl ligands being specified.

(vide supra), are the most electron-deficient of the $\text{Cp}^*\text{M}(\text{NO})\text{R}_2$ family of complexes. Conversely, the most easily handled complexes, namely, the $\text{Cp}^*\text{W}(\text{NO})(\text{alkyl})_2$ species, are also the weakest Lewis acids.^{16,25}

(3) Thermal Stability. The Lewis acidity rankings summarized in the preceding paragraph also mirror the relative thermal stabilities of $\text{Cp}^*\text{M}(\text{NO})\text{R}_2$ complexes. The most thermally unstable (and as yet unisolated) species belong to the $\text{CpMo}(\text{NO})(\text{aryl})_2$ family. After these compounds we would expect a $\text{CpMo}(\text{NO})(\text{alkyl})_2$ complex to be the next most thermally unstable. This is indeed the case. The most thermally sensitive complex that we have isolated to date is $\text{CpMo}(\text{NO})(\text{CH}_2\text{CMe}_3)_2$, which readily transforms to an unprecedented type of organometallic complex at room temperature in dichloromethane solution (eq 9).²⁶



The side-on, linear bridging nitrosyl ligand in $[\text{Cp}^*\text{Mo}(\text{NO})](\mu\text{-}\eta^1\text{:}\eta^2\text{-NO})(\mu\text{-CHCMe}_3)[\text{Cp}^*\text{Mo}(\text{NO})]$

(26) Legzdins, P.; Rettig, S. J.; Veltheer, J. E. *J. Am. Chem. Soc.* 1992, 114, 6922.

(=CHCMe₃) is the first example of this bonding mode for coordinated NO.²⁷ Kinetic studies suggest that the rate-determining step in the thermolysis reaction is an intramolecular expulsion of neopentane to form the transient 16-electron alkylidene nitrosyl complex, $\text{CpMo}(\text{NO})(=\text{CHCMe}_3)$, which may be trapped with phosphines to obtain the isolable adducts, $\text{CpMo}(\text{NO})(=\text{CHCMe}_3)(\text{PR}_3)_2$.²⁶

(4) Structural Comparisons. The solid-state molecular structures of four $\text{Cp}^*\text{M}(\text{NO})\text{R}_2$ complexes have been established to date (cf. Figure 1). Their metrical parameters shed some light on their reactivities with small molecules. Their most interesting feature is the relative size of the vacant coordination site at their metal centers as illustrated in Figure 7. From the determined nonbonded C-C separations it is apparent that aryl complexes have less sterically crowded metal centers than do alkyl complexes, i.e., 3.65 Å > 3.53 Å and 3.59 Å > 3.44 Å. In addition, molybdenum complexes have a greater accessibility to their metal centers than do analogous tungsten complexes, i.e., 3.53 Å > 3.44 Å and 3.65 Å > 3.59 Å.

In other words, the diaryl complexes are also more accessible Lewis acids, in addition to being more potent Lewis acids (vide supra). Both of these properties render the diaryl species considerably more reactive

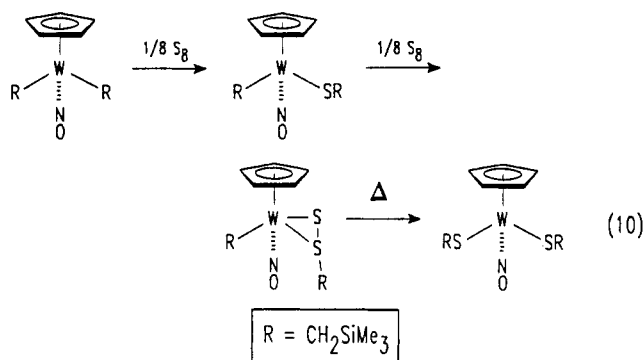
(27) Reference 7, Chapter 2.

than their dialkyl analogues. For instance, $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{SiMe}_3)_2$ does not coordinate PMe_3 , but $\text{CpW}(\text{NO})(\text{CH}_2\text{SiMe}_3)_2$ in the presence of PMe_3 is in equilibrium with the 18-electron adduct, $\text{CpW}(\text{NO})(\text{CH}_2\text{SiMe}_3)_2(\text{PMe}_3)$.^{8b} In contrast, $\text{Cp}^*\text{W}(\text{NO})(\text{aryl})_2$ complexes form adducts with PMe_3 irreversibly, even in the presence of the more sterically demanding Cp^* ligand.¹⁶

Chemical Reactivity

(1) Metal- and Ligand-Independent Reactions.

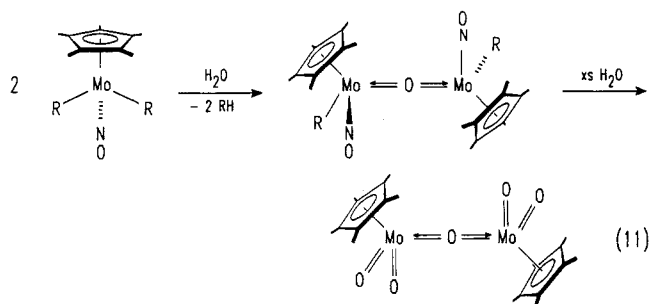
In general, the $\text{Cp}^*\text{M}(\text{NO})\text{R}_2$ complexes exhibit similar reactivity patterns for both the Mo and W complexes. For example, $\text{Cp}^*\text{M}(\text{NO})(\text{alkyl})_2$ complexes react with molecular oxygen to produce the dioxo complexes, $\text{Cp}^*\text{M}(\text{O})_2(\text{alkyl})_2$.²⁸ In terms of reaction rates, however, the Mo complexes react much faster than do the W complexes, and diaryl complexes react much faster than dialkyl complexes. This trend again emphasizes that reactivity is directly proportional to Lewis acidity in these systems. Thus, solid $\text{Cp}^*\text{Mo}(\text{NO})(\text{CH}_2\text{SiMe}_3)_2$ reacts with dioxygen in a matter of minutes, whereas solutions of $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{SiMe}_3)_2$ must be treated with oxygen for several hours in order to convert it to $\text{Cp}^*\text{W}(\text{O})_2(\text{CH}_2\text{SiMe}_3)_2$.²⁹ Similarly, $\text{CpW}(\text{NO})(\text{CH}_2\text{SiMe}_3)_2$ reacts with elemental sulfur in a stepwise manner (eq 10),³⁰ whereas $\text{CpW}(\text{NO})(p\text{-tolyl})_2$ reacts nearly instantaneously to give only $\text{CpW}(\text{NO})(S\text{-}p\text{-tolyl})_2$.^{16,21} The dialkyl species thus provide us the opportunity to isolate intermediate complexes otherwise inaccessible with the more reactive diaryl substrates.



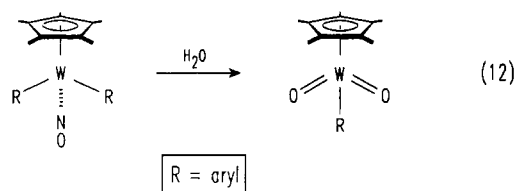
In some cases, however, the increased reactivity of the diaryl complexes is beneficial. Consider, for instance, the reactions with molecular hydrogen. $\text{CpW}(\text{NO})(\text{CH}_2\text{SiMe}_3)_2$ reacts with high pressures of H_2 to give low yields of $[\text{CpW}(\text{NO})(\text{H})_2]_2$ and other partially hydrogenated species.³¹ On the other hand, $\text{CpW}(\text{NO})(o\text{-tolyl})_2$ reacts with H_2 at 1 atm to produce high yields of $[\text{CpW}(\text{NO})(\text{H})_2]_2$ within minutes.²¹

(2) Metal-Dependent Reactions. In other cases, the differences created by changing the metal in related $\text{Cp}^*\text{M}(\text{NO})\text{R}_2$ complexes have a much more pronounced effect on the characteristic chemical properties of these species. For example, the reactions with water of

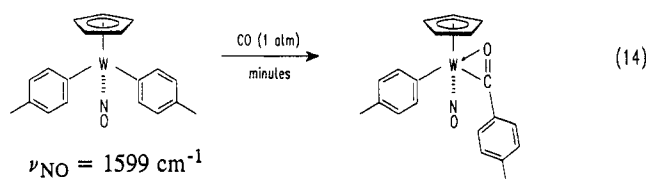
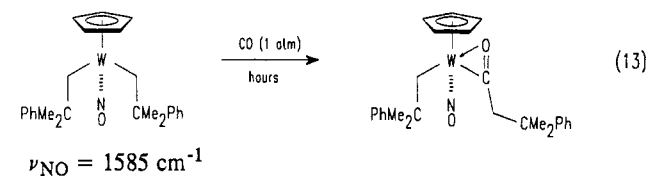
$\text{Cp}^*\text{Mo}(\text{NO})(\text{aryl})_2$ are markedly different from those of the congeneric tungsten species. The former reactions yield bimetallic complexes, first $[\text{Cp}^*\text{Mo}(\text{NO})(\text{aryl})]_2(\mu\text{-O})$ (vide supra) and then ultimately $[\text{Cp}^*\text{Mo}(\text{O})_2]_2(\mu\text{-O})$ (eq 11).¹³ The latter yield $\text{Cp}^*\text{W}(\text{O})_2(\text{aryl})$ complexes exclusively (eq 12).



$\text{R} = \text{alkyl or aryl}$



(3) Ligand-Dependent Reactions. The reactions of $\text{Cp}^*\text{W}(\text{NO})\text{R}_2$ complexes with carbon monoxide provide excellent examples of transformations which are ligand-dependent. Consider, for instance, the two conversions depicted in eqs 13 and 14. As indicated,



reaction 14 proceeds much faster than reaction 13 under ambient conditions, and we conclude again that it is the increased Lewis acidity of the diaryl complex ($\Delta\nu_{\text{NO}} = 14 \text{ cm}^{-1}$ in THF) that enhances the reaction rate. After CO insertion, neither 18-electron product complex is particularly Lewis acidic. Hence, the rate of a second insertion of CO to form bis(acyl) complexes depends on the relative bond strengths of a W-sp^2 versus a W-sp^3 carbon bond and not on the relative Lewis acidities of the monoacyl reactants. Consistent with this view is the fact that we have isolated and characterized several $\text{Cp}^*\text{W}(\text{NO})(\text{C}(\text{O})\text{alkyl})_2$ complexes but no $\text{Cp}^*\text{W}(\text{NO})(\text{C}(\text{O})\text{aryl})_2$ compounds to date.³²

Other ligand-dependent reactions are also interpretable in terms of relative Lewis acidities. Thus, noto-

(32) Dryden, N. H.; Legzdins, P.; Lundmark, P. J. *Organometallics*, submitted for publication.

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

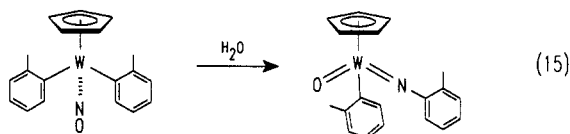
(29) Veltheer, J. E.; Legzdins, P. In *Handbook of Preparative Inorganic Chemistry*, 4th ed.; Herrmann, W. A., Ed., in press.

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

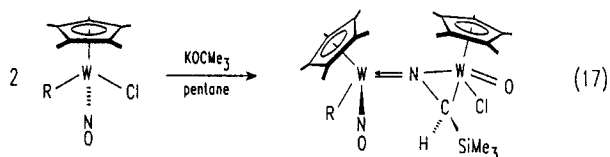
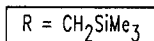
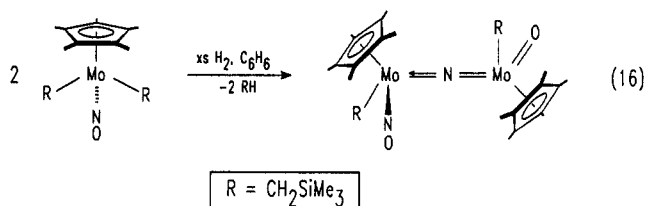
(31) (a) Legzdins, P.; Martin, J. T.; Einstein, F. W. B.; Jones, R. H. *Organometallics* 1987, 6, 1826. (b) Legzdins, P.; Martin, J. T.; Einstein, F. W. B.; Willis, A. C. *J. Am. Chem. Soc.* 1986, 108, 7971.

riously inert substrates such as CO_2 insert into W-aryl bonds but not into W-alkyl bonds.³³

(4) **New Avenues: NO Bond Cleavage.** A new type of chemical reactivity that we are observing more and more often with these systems is that of nitrosyl N-O bond cleavage. Our first example of such reactivity occurred when solid $\text{CpW}(\text{NO})(o\text{-tolyl})_2$ was exposed to water vapor at room temperature. An immediate reaction resulted in the conversion of the starting material to its arylimido oxo structural isomer, $\text{CpW}(\text{O})(\text{N}-o\text{-tolyl})(o\text{-tolyl})$ (eq 15). This rearrangement reaction is completely intramolecular and is the first documented example of such a transformation.¹⁷ We



have recently discovered two other examples of this type of reactivity. The first example involves exposure of $\text{Cp}^*\text{Mo}(\text{NO})(\text{CH}_2\text{SiMe}_3)_2$ to H_2 in benzene, an operation which leads to the formation of $[\text{Cp}^*\text{Mo}(\text{NO})(\text{CH}_2\text{SiMe}_3)](\mu\text{-N})[\text{Cp}^*\text{Mo}(\text{O})(\text{CH}_2\text{SiMe}_3)]$ in high yields (eq 16).³⁴ The second example is the reaction of



(33) Brouwer, E. B. M.Sc. Dissertation, The University of British Columbia, 1992.

(34) Legzdins, P.; Young, M. A.; Einstein, F. W. B.; Batchelor, R. J. Presented at the 75th Canadian Chemical Conference, Edmonton, Alberta, June 1992; Abstract 370.

(35) Legzdins, P.; Lundmark, P. J. Unpublished observations.

$\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{SiMe}_3)\text{Cl}$ with KOtBu in pentane, which produces $[\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{SiMe}_3)](\mu\text{-}\eta^1\text{:}\eta^2\text{-NC(H)(SiMe}_3))[\text{Cp}^*\text{W}(\text{O})(\text{Cl})]$ (eq 17).³⁵ The latter conversion probably proceeds via initial deprotonation of the starting material by the butoxide anion, but both reaction mechanisms are currently unknown.

Epilogue

During our work with these fascinating mononitrosyl complexes of Mo and W we have shown that a variety of hydrocarbyl derivatives are synthesizable and that the characteristic chemistry of these species is dominated by their ability to act as Lewis acids. Our investigations also indicate that Cp, Mo, and aryl derivatives are more Lewis acidic than Cp^* , W, and alkyl derivatives, respectively. In essence, the chemistry of the $\text{Cp}^*\text{M}(\text{NO})\text{R}_2$ complexes is dominated by their tendency to form 1:1 adducts with Lewis bases; these adducts either are isolable as such or undergo subsequent intramolecular transformations involving the hydrocarbyl ligands. As we synthesize a greater variety of compounds belonging to this family, we continue to observe new modes of intramolecular reactivity with ever increasing frequency. We are thus optimistic that this area of chemistry still holds a wealth of exciting chemical opportunities awaiting discovery.

Other ongoing research in our laboratories is aimed at determining the effect of $\text{Cp}^*\text{M}(\text{NO})$ fragments on ancillary ligands other than hydrocarbyl groups. To date α -heteroatom-containing ligands such as alkoxides and amides have provided us with complexes of the form $\text{Cp}^*\text{M}(\text{NO})(\text{ER})\text{X}$ [$\text{E} = \text{O}$ or NH , $\text{X} = \text{Cl}$ or ER], and the physical and chemical properties of these species are currently under investigation. Preliminary results indicate that these systems exhibit different chemistry by virtue of the fact that the π -donor ligands result in their possessing more electron-rich metal centers than do the $\text{Cp}^*\text{M}(\text{NO})\text{R}_2$ complexes.

We are grateful to the Natural Sciences and Engineering Research Council of Canada for generously supporting our research efforts over the years. Without the hard work and insight of the various graduate students and postdoctoral fellows cited in the references, this Account would certainly not have been possible. Finally, we gratefully acknowledge our fruitful collaborations with Drs. Jim Trotter (UBC), Steve Rettig (UBC), Fred Einstein (Simon Fraser), Bruce Bursten (Ohio State), and their co-workers.