SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF
GROUP 6 ALKOXO NITROSYL COMPLEXES

by

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Abstract

Three new classes of alkoxo nitrosyl complexes of the type Cp*M(NO)(OR)X (Cp* = \( \eta^5\)-C\(_5\)Me\(_5\); M = Mo, W; R = alkyl, aryl; X = Cl, OR, alkyl), all of which have been fully characterized, are prepared by metathesis reactions. The molecular structures of Cp*W(NO)(OCMe\(_3\))\(_2\) and Cp*W(NO)(OCH\(_2\)Ph)\(_2\) have been established by X-ray crystallographic analyses. While in general the above metathesis reactions are straightforward, two interesting bimetallic complexes, [Cp*W(NO)(CH\(_2\)SiMe\(_3\))]\([\text{Cp*W(\text{Cl})(O)}]-\(\mu_2-\eta^1-\eta^2\)-NC(H)SiMe\(_3\))\] and [Cp*W(NO)(CH\(_2\)SiMe\(_3\))Cl]\([\text{Cp*W(\text{Cl}(\eta^2-N\{O\})\{H\})CH\(_2\)SiMe\(_3\)}]-\(\mu-N\)], are produced in attempts to prepare alkoxo alkyl complexes using potassium salts. X-ray crystallographic analyses of both products are presented.

The reaction chemistry of the three classes of alkoxo complexes, Cp*M(NO)(OR)X, with a variety of reagents such as oxygen, water, phosphines, carbon monoxide, dihydrogen, HCl, isonitriles and isocyanates has been investigated. In general, the 18-electron bis(alkoxo) complexes are chemically inert to most of these reagents; the only exceptions being the reactions of Cp*M(NO)(OR)\(_2\) with H\(_2\) and HCl. The inertness of the bis(alkoxo) complexes is attributed to donation of electron density from filled p-type orbitals on the oxygen atoms into empty metal orbitals on the metal center. The reactivity studies of the chloro compounds are limited because of their extreme air- and moisture-sensitivity. In contrast, the alkoxo alkyl complexes decompose cleanly to isolable organometallic species when treated with O\(_2\) or H\(_2\)O. In Lewis acid-base type reactions with PMe\(_3\), CNCMe\(_3\), PhNCO and \(p\)-tolylNCO, the Cp*M(NO)(R)(OR') species have sufficiently electron-deficient metal centers to form 1:1 adducts and/or insertion products. The diamagnetic bimetallic complex, [Cp*Mo(NO)(CH\(_2\)Ph)(\(\mu-O\))]\(_2\), is produced when Cp*Mo(NO)(CH\(_2\)Ph)(OCMe\(_3\)) is treated with H\(_2\) in THF.

Earlier work into the reactions of dialkyl complexes, Cp'W(NO)R\(_2\) (Cp' = \( \eta^5\)-C\(_5\)H\(_5\), \( \eta^5\)-C\(_5\)Me\(_3\)), with carbon monoxide has been extended to permit some general conclusions regarding CO-insertion reactions in these systems. These studies show that the products obtained from the
carbonylation of various Cp′W(NO)R2 complexes are very dependent upon the nature of the ancillary ligands. The nature of the cyclopentadienyl ligand determines the extent of the reactivity, with only the Cp complexes inserting a second equivalent of CO. The nature of the hydrocarbyl group influences the rate of the reaction such that the greater Lewis acidity of the diaryl complexes results in their forming monoacyl products faster than do the related dialkyl complexes. However, only the monoacyl alkyl complexes possess a sufficiently weak M-C σ bond to undergo a second insertion of CO to form bis(acyl) species, Cp′W(NO)(C{O}R)2. The nature of the hydrocarbyl ligand also plays an influential role in the case when R = CH2Ar in that putative reductive elimination of ketone occurs from the undetectable monoacyl intermediate complexes.
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the reaction between Cp$^*$Mo(NO)(CH$_2$C$_6$H$_4$-4-Me)$_2$ and CO

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List of Abbreviations

The following list of abbreviations, most of which are commonly used in the chemical literature, have been employed in this thesis.

Å  angstrom, $10^{-10}$ m
$a$, $b$, $c$, $\alpha$, $\beta$, $\gamma$  unit cell dimensions (in X-ray Crystallography)
anal.  analysis
APT  attached proton test (in NMR Spectroscopy)
Ar  aryl
atm  atmosphere(s)
benzyl  $\text{CH}_2\text{Ar}$
br  broad (spectral)
$\chi_g$  magnetic susceptibility per gram
$\chi_M$  molar magnetic susceptibility
°C  degree centigrade
$^{13}C$  carbon-13
$^{13}C\{^1H\}$  proton-decoupled carbon-13 (observe carbon while decoupling proton)
$C_{arom}$  aromatic carbon
calcd  calculated
$C_6D_6$  benzene-$d_6$
CDCl$_3$  chloroform-$d_1$
c.g.s.  centimeters grams seconds
$\text{cm}^{-1}$  wavenumbers
COSY  correlation spectroscopy
Cp  $\eta^5$-$C_5H_5$, perhydrocyclopentadienyl
Cp*  $\eta^5$-$C_5\text{Me}_5$, pentamethylcyclopentadienyl
Cp'  both Cp and Cp*
CV  cyclic voltammogram
Cy  cyclohexyl
δ   chemical shift in ppm
d   doublet (in an NMR spectrum); or day(s)
Δ   heat (in thermolysis), or difference
ΔGº  change in Gibbs free energy at standard conditions
dppe 1,2 bis(diphenylphosphino)ethane
dppm  bis(diphenylphosphino)methane
Eº'  formal reduction potential
EI   electron-impact (in mass spectrometry)
emu  electromagnetic units
Et   CH₂CH₃, ethyl
Et₂O (CH₃CH₂)₂O, ether, diethyl ether
eq  equation
equiv  equivalent
g   gram(s)
GC   gas chromatography
GCMS gas chromatographic mass spectroscopy
h   hour(s)
¹H  proton
HOMO  highest occupied molecular orbital
Hz   Hertz (s⁻¹)
J   intensity (in X-ray Crystallography)
i-Pr (CH₃)₂CH, isopropyl
IR   infrared
J   coupling constant (in NMR spectroscopy)
³JAB  n-bond coupling constant between atoms A and B
K   equilibrium constant
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA</td>
<td>LiN(i-Pr)₂, lithium diisopropylamide</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>m</td>
<td>multiplet (in NMR spectroscopy)</td>
</tr>
<tr>
<td>M</td>
<td>Mo and W; or molar</td>
</tr>
<tr>
<td>m/z</td>
<td>mass-to-charge ratio (in mass spectrometry)</td>
</tr>
<tr>
<td>Me</td>
<td>CH₃, methyl</td>
</tr>
<tr>
<td>mg</td>
<td>milligram(s)</td>
</tr>
<tr>
<td>min</td>
<td>minute(s)</td>
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<td>mL</td>
<td>milliliter(s)</td>
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<td>mmol</td>
<td>millimole(s)</td>
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<tr>
<td>MO</td>
<td>molecular orbital</td>
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<td>mol</td>
<td>mole</td>
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<tr>
<td>MS</td>
<td>mass spectrum</td>
</tr>
<tr>
<td>MW</td>
<td>molecular weight</td>
</tr>
<tr>
<td>v</td>
<td>stretching frequency (in IR spectroscopy)</td>
</tr>
<tr>
<td>neopentyl</td>
<td>CH₂CMe₃</td>
</tr>
<tr>
<td>neophyl</td>
<td>CH₂CMe₂Ph</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>ORTEP</td>
<td>Oak Ridge Thermal Ellipsoid Plot</td>
</tr>
<tr>
<td>³¹P</td>
<td>phosphorus-31</td>
</tr>
<tr>
<td>[P⁺]</td>
<td>parent molecular ion (in mass spectrometry)</td>
</tr>
<tr>
<td>Ph</td>
<td>C₆H₅, phenyl</td>
</tr>
<tr>
<td>pKₐ</td>
<td>antilog of acid dissociation constant, -log[Kₐ]</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million (in NMR spectroscopy)</td>
</tr>
<tr>
<td>psig</td>
<td>pounds per square inch at gauge</td>
</tr>
<tr>
<td>pz</td>
<td>C₃H₄N₂, pyrazole</td>
</tr>
<tr>
<td>q</td>
<td>quartet (in an NMR spectrum)</td>
</tr>
<tr>
<td>R, R'</td>
<td>alkyl and/or aryl</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$R$</td>
<td>residual index (in X-ray Crystallography)</td>
</tr>
<tr>
<td>$R_w$</td>
<td>weighted residual index (in X-ray Crystallography)</td>
</tr>
<tr>
<td>RT</td>
<td>room temperature</td>
</tr>
<tr>
<td>s</td>
<td>singlet (in an NMR spectrum)</td>
</tr>
<tr>
<td>SCE</td>
<td>standard calomel electrode</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
</tr>
<tr>
<td>t</td>
<td>triplet (in an NMR spectrum)</td>
</tr>
<tr>
<td>o-tolyl</td>
<td>C$_6$H$_4$-2-Me, ortho-tolyl</td>
</tr>
<tr>
<td>p-tolyl</td>
<td>C$_6$H$_4$-4-Me, para-tolyl</td>
</tr>
<tr>
<td>THF</td>
<td>C$_4$H$_8$O, tetrahydrofuran</td>
</tr>
<tr>
<td>V</td>
<td>volt</td>
</tr>
<tr>
<td>V/s</td>
<td>scan rate</td>
</tr>
<tr>
<td>$V$</td>
<td>volume of the unit cell (in X-ray Crystallography)</td>
</tr>
<tr>
<td>X</td>
<td>halide</td>
</tr>
<tr>
<td>$X$</td>
<td>number of molecules of solvate</td>
</tr>
<tr>
<td>Z</td>
<td>number of molecules in the unit cell (in X-ray Crystallography)</td>
</tr>
</tbody>
</table>
There are many people I wish to thank for seeing me through the last 5 years.

First, I thank the Coffee Club. At 9:30 a.m. and 3:00 p.m., we faithfully gathered to talk, to laugh and to share chemistry and our lives. Thank you Peter for your vision and supervision. Thank you Willy for listening to me and telling me about the Simpsons every Friday morning. Neil, I thank you for late night advice. Principally, my thanks go to JEV. Although you are not my Saviour, you have often been my Hero. You truly understood and provided practical help and wisdom in times of need. As opposite as we are, you have been a real friend to me.

Thank you for roots and wings, Mom and Dad. You have never doubted my abilities.

My friends, Roseanne, Sean, Letty, Sarah, Kirsten, Natania, Liz and Deb; you have all held me together emotionally and deeply enriched my life. For years you have loved me, listened to me, encouraged me, and prayed for me.

My husband, Mr. Love, I thank you for sharing the work (Task number 2).

Finally, my thanks go to God, in whom I have found my strength, my value and my hope.
CHAPTER 1

General Introduction

1.1 Background

1.1.1 Bonding in Organometallic Complexes

Organotransition-metal chemistry is concerned with compounds which have an organic group (ligand) attached to a transition metal through a direct M - C bond. Such compounds may contain purely σ-bonded ligands (alkyl, aryl, vinyl, alkynyl and acyl ligands) or ligands that can function as σ-donors/π-acceptors (carbene, Cp, arene, olefin, alkyne, allyl and carbonyl ligands).

![Metal-alkyl bond](image1)

Metal-alkyl bond

![Metal-carbene bond](image2)

Metal-carbene bond

![Metal-olefin bond](image3)

Metal-olefin bond
1.1.2 Bonding in Nitric Oxide

An understanding of the principles involved in the bonding of free nitric oxide is essential to understanding the bonding of nitric oxide to transition metals. Nitric oxide exists as a paramagnetic molecule which is thermodynamically unstable with respect to $N_2$ and $O_2$. The molecular-orbital diagram of nitric oxide is shown in Figure 1.1.

Figure 1.1 The molecular-orbital diagram of nitric oxide.

The odd electron of NO is based in a $\pi^*$ molecular orbital. The bonding in nitric oxide may also be understood in terms of a valence-bond description of the major resonance structures of NO, i.e.,

$$\dot{N}=\ddot{O} \quad \leftrightarrow \quad -\dot{N}=\ddot{O}^+$$

The NO molecule binds to electropositive transition metals through the nitrogen atom. This can be rationalized by the second resonance form of NO in which the negative charge is localized on
the nitrogen atom. Using a molecular-orbital argument, it is also correct to say that the $\sigma_2$ orbital, which donates electron density to the metal, is predominantly N in character.

1.1.3 Bonding in Transition-Metal-Nitrosyl Complexes

Although there are nine known modes of nitrosyl bonding to transition metals,\textsuperscript{1,3} in this work only linear, terminal nitrosyl ligands are observed. In valence-bond terms, the linear bonding mode of NO to a transition metal can be represented by several resonance forms, i.e.,

\[
\text{M} \equiv \text{N=O} : \quad \text{M} \equiv \text{N=0} \quad \text{M}=\text{N=0} \quad \text{M} \equiv \text{N=0} : \\
\text{M(\sigma)} \leftarrow \text{N(\sigma)}
\]

Molecular orbital theory describes the bonding of NO to a metal as a synergic interaction. Thus, the synergic bonding involved in a linear M-NO fragment is understood as (i) formal transfer of one electron from NO to the metal (thereby forming an NO\textsuperscript{+} ligand), (ii) donation of 2 electrons from a $\sigma$-type orbital on NO to the metal, and (iii) backdonation of electron density from the occupied metal d-orbitals to the $\pi^*$ antibonding orbitals of the NO ligand. The M-NO orbital overlaps commonly invoked to account for this synergic bonding are diagrammed below.

\[
\text{\sigma-donation} \quad \text{M} \equiv \text{N=O} \quad \text{M(\sigma)} \leftarrow \text{N(\sigma)}
\]

\[
\text{\pi-backdonation} \quad \text{M} \equiv \text{N=O} \quad \text{M(d\pi)} \rightarrow \text{NO(\pi^*)}
\]

Overall, a linear terminal nitrosyl ligand functions as a 3-electron donor to the central transition metal.
1.1.4 Oxidation States and Valence-Electron Count

In organometallic chemistry the assignment of oxidation state is a formality and often bears little resemblance to the actual charge on the metal. A more useful concept in describing organometallic species is the number of electrons in the valence shell of the central metal. The 18-electron rule arises from the observation that complexes in which the sum of the metal's valence electrons and the electrons donated from the ligands equals 18 are generally stable. In molecular-orbital terms, the rule may be rationalized by means of the formation of 9 bonding molecular orbitals from the interaction of metal atomic orbitals (i.e., s + 3p + 5d) and ligand orbitals, and the filling of these molecular orbitals by 18 electrons. The existence of a large HOMO-LUMO energy gap also contributes to the stability of such complexes.

The electron counting formalism used in this thesis considers all metals and ligands to be neutral, except where there is an overall charge on the complex. For example, $\text{CpW(NO)(η}^2\text{-C(O)-p-tolyl)(p-tolyl)}$ is an 18-electron complex: $5e^-\text{(Cp)} + 6e^-\text{(W)} + 3e^-\text{(NO)} + 3e^-\text{(C(O)-p-tolyl)} + 1e^-\text{(p-tolyl)} = 18e^-$.

1.2 Nitrosyl Complexes

An extensive review of transition-metal organometallic nitrosyl chemistry appeared in the literature in 1988. This review describes in detail the preparation and reactivity of transition-metal nitrosyl complexes. Recently, Legzdins and Richter-Addo published a book which provides a more in-depth discussion of metal nitrosyls. In this section, I will not reiterate the extensive amount of knowledge covered in these two publications; however, there are a few basic concepts regarding nitrosyl chemistry which should be noted:
(a) Terminal nitrosyl ligands are strong $\pi$-acids.
(b) They can adopt two bonding modes, linear or bent, though all of the complexes prepared in this thesis contain linear, terminal nitrosyl ligands.
(c) The infrared absorption of a nitrosyl ligand is one of the most distinctive physical properties of
nitrosyl complexes, and for this very reason, many of the reactions in this thesis are monitored by IR spectroscopy. The value of $v_{\text{NO}}$ reflects the degree of $\pi$-backbonding from filled transition-metal d orbitals to the $\pi^*$ acceptor orbitals on the linear nitrosyl ligand. Thus, complexes that have increased electron density at the metal center exhibit lower $v_{\text{NO}}$ values than complexes which are relatively electron deficient.

(d) In general, nitrosyl ligands are not involved directly in the chemistry of their complexes; however nitrosyl ligands greatly influence the electronic environment of the metal.

1.3 Alkoxo Complexes

1.3.1 Bonding in Transition-Metal-Alkoxo Complexes

This thesis describes the preparation of organometallic alkoxo nitrosyl complexes. Alkoxo ligands are considered to be hard $\pi$-donor ligands. They have a formal charge of -1. One important feature of alkoxo ligands is the presence of lone pairs on oxygen. Alkoxo ligands can provide additional electron density through a $\pi$ interaction between these p-type orbitals on oxygen and empty d-orbitals on the metal center. The following diagram depicts the two possible bonding interactions of an alkoxo ligand with a transition-metal.

\[
\begin{align*}
\text{\sigma donation} & \quad \text{M} & \scriptsize\text{\large O} & \quad \text{R} \\
& \quad \text{M(\sigma)} & \leftarrow & \text{OR(\sigma)}
\end{align*}
\]

\[
\begin{align*}
\text{\pi donation} & \quad \text{M} & \scriptsize\text{\large O} & \quad \text{R} \\
& \quad \text{M(\pi)} & \leftarrow & \text{OR(\pi)}
\end{align*}
\]
When only the first interaction occurs, the alkoxo ligand is bent and formally donates 1 electron to the metal. When both bonding interactions occur, the alkoxo ligand is linear and functions as a 3-electron donor. The angle M-O-R has been used to indicate the degree of multiple bonding between metals and alkoxo ligands.\textsuperscript{6}

In late-transition-metal complexes, which tend to possess 18 valence electrons and have filled d orbitals, the lone pairs on oxygen weaken the M-O bond by repelling the filled metal orbitals.\textsuperscript{7} Therefore, in late-transition-metal complexes, the alkoxide ligand donates only one electron to the metal in a \( \sigma \) interaction. There are very few examples of isolated late-transition-metal alkoxo complexes because of the unfavorable interactions between hard alkoxo ligands and soft late transition metals.

Alkoxo coordination and organometallic complexes of the early transition metals are well known.\textsuperscript{8} These species generally contain robust M-O bonds as a result of a favorable donor-acceptor interaction between the filled oxygen p-type orbitals and empty metal d-type orbitals. In the case of early transition metal complexes, the metal is often d\textsuperscript{0} and has less than 18 valence electrons. Empty d\textsubscript{\pi} orbitals available on the metal can accept electron density from the oxygen lone pairs. Overall, the alkoxo ligands donate three electrons to early transition metals; one in the \( \sigma \) interaction and two in the \( \pi \) interaction. In this way the M-O bond is strengthened rather than weakened as in the case of a late-transition-metal complex. Early metals are said to be oxophilic because of this strengthening effect.

1.3.2 Reactions of Alkoxo Complexes

1.3.2.1 Ligand-Based Reactivity of Alkoxo Complexes

Since alkoxo ligands are very strong \( \pi \)-donor ligands, the ligand-based reactivity of alkoxo complexes is very limited.\textsuperscript{9} Alkoxo ligands, considered to be pseudohalide ligands, can be involved in metathesis reactions since the driving force for reactions such as that shown in eq 1.1 is the formation of strong Li-O bonds.\textsuperscript{10}
Ce(OAr)$_3$ + LiR $\rightarrow$ RCe(OAr)$_2$ + LiOAr  \hspace{1cm} (1.1)

Alkoxo ligands are often introduced into metal systems to stabilize an electronically unsaturated metal center. Very bulky alkoxo ligands (e.g. $t$-butoxide or tri-$t$-butyl methoxide) are extremely useful since they also provide steric protection to a coordinatively unsaturated species. Complexes containing these sterically demanding alkoxo ligands are not prone to dimerize through alkoxo bridges in order to alleviate electron deficiency. Metal-alkoxo complexes which have $\beta$-hydrogens on the alkoxo ligand have been used to prepare metal-hydride complexes, e.g.,$^{11}$

\[ \text{M-OCHRR'} \rightarrow \text{M-H} + \text{RR'CO} \]  \hspace{1cm} (1.2)

Actinide alkoxo complexes have been used as models for the species which are responsible for transporting actinide elements in ground waters, and volatile uranium alkoxo complexes have been prepared for use in the separation and enrichment of isotopes.$^{12}$

### 1.3.2.2 Catalytic Reactivity of Alkoxo Complexes

One of the most important applications of organometallic complexes is in catalysis, and alkoxo complexes are involved in many of these catalytic processes.$^{13}$ Low-valent Group 6 transition-metal alkoxo complexes have been shown to catalyze aldehyde/ketone reductions$^{14}$ and methanol carboxylation.$^{15}$ The anionic complexes $[\text{M(CO)}_5(\text{OR})]^{-}$, prepared by Darensbourg and coworkers, have been extensively studied, and their systems catalyze the hydrogenation of ketones to alcohols.$^{16}$ Schrock's $\text{W(CCMe}_3\text{)(OCMe}_3\text{)}_3$ will catalytically metathesize dialkylacetylenes (eq 1.3), whereas the carbon analogue, $\text{W(CCMe}_3\text{)(CH}_2\text{CMe}_3\text{)}_3$, reacts with acetylenes, but does not metathesize them in a catalytic fashion.$^{13}$

\[ 2 \text{R}^1\text{C}=\text{CR}^2 \xrightarrow{\text{W(CCMe}_3\text{)(OCMe}_3\text{)}_3} \text{R}^1\text{C}=\text{CR}^1 + \text{R}^2\text{C}=\text{CR}^2 \]  \hspace{1cm} (1.3)
Although the π-donor ability of the alkoxide ligands does not seem to be important, the bulky alkoxide ligands on W(CCMMe₃)(OCMe₃)₃ encourage acetylene dissociation thereby enhancing methathesis activity.

Late-transition-metal alkoxo complexes are believed to be key intermediates in various metal-catalyzed synthetic organic transformations. These reactions include oxidation of alcohols, hydrogenation of ketones, condensation of aldehydes, decarbonylation of allylic esters and carbonates, and carbonylation of alcohols. The catalysts involved in these processes are usually Ni, Cu, Rh, Pt or Pd systems.

1.4 Scope and Format of This Thesis

The metal-carbon bond has, by definition, been the focus of traditional organometallic chemistry. In our group, a significant amount of effort has been directed into determining a rational, reproducible and general synthesis of organometallic complexes of the type Cp*ₐ₉(NO)R₂ (M = Mo, W; R = alkyl, aryl). The synthesis of this large class of complexes has allowed extensive studies of their reaction chemistry. Similarly, fundamental information on the preparation of transition-metal alkoxo complexes is required before it is possible to investigate whether these complexes, which contain strongly π-donating alkoxo ligands, exhibit reactivity that is different from those observed for alkyl (σ-donating) complexes.

This thesis addresses the synthesis, characterization and reactivity of three new classes of alkoxo nitrosyl complexes of the type Cp*ₐ₉(NO)(OR)X, where X is either a chloride, alkoxo or alkyl ligand. These species have been prepared by metathesis reactions and fully characterized by elemental analysis, mass spectrometry, infrared spectroscopy, ¹H and ¹³C{¹H} NMR spectroscopy (Chapters 2 and 3). Where appropriate, molecular structures of representative products have been confirmed by X-ray crystallographic analyses. This thesis also reports the preparation and characterization of two complex bimetallic compounds, [Cp*ₐ₉W(NO)(CH₂SiMe₃)][Cp*ₐ₉W(Cl)(O)]-(µ₂-ν¹:ν²-NC(H)SiMe₃) and
[Cp*W(NO)(CH2SiMe3)Cl][Cp*W(Cl)(η2-N{O}{H}CH2SiMe3)}-(μ-N), which were produced in the attempts to prepare alkyl alkoxo complexes (Chapter 3).

The subsequent reaction chemistry of representative examples of each class of alkoxo complexes, Cp*M(NO)(OR)X, with a variety of reagents such as O2, H2O, PMe3, CO, H2, HCl, CNMe3 and Me3CNCO constitutes a large part of this work (Chapters 2 and 4). Alkoxo alkyl species react with most of these reagents to form isolable organometallic complexes, whereas the bis(alkoxo) complexes are generally chemically inert towards these reagents. Since the alkoxo chloro complexes were found to be extremely sensitive to air and moisture, their reaction chemistry has not been explored to any great extent.

Chapter 5 discusses the reactions of dialkyl complexes, Cp*M(NO)(R)2, with carbon monoxide. Although the preliminary research in this area was performed by Dr. Neil Dryden of these laboratories, this chapter presents the completed research along with the general conclusions regarding CO-insertion reactions in these systems.

This thesis is organized using standard legal outlining procedures. For any given chapter X, the major sections are X.1 Introduction, X.2 Experimental, X.3 Characterization Data, X.4 Results and Discussion, and X.5 References and Notes. Subsections are numbered X.1.1, X.1.2, X.1.3, etc. Tables, Figures and Schemes for each chapter are numbered in a similar fashion. General methodologies and experimental procedures used throughout this thesis are located in Sections 2.2.1 and 2.2.2.

1.5 References and Notes


(2) Nitric oxide has a ΔHf° value of 90.2 kJ mol⁻¹. See reference 1, p 1.


(9) See reference 4, p 693.


CHAPTER 2

Synthesis, Characterization and Reactivity of Bis(Alkoxo) and Alkoxo Chloro Complexes

2.1 Introduction

Previous work in these laboratories has established that the monomeric, 16-valence-electron Cp'M(NO)R₂ complexes \([M = \text{Mo, W}; R = \text{alkyl, aryl}]\) have varied and interesting chemistries.² A logical extension of this work is the investigation of related compounds containing metal-heteroatom linkages such as metal-alkoxides in place of the metal-alkyl or -aryl groups. These complexes should possess greater metal-ligand bond polarity than their dialkyl or diaryl congeners and thus should exhibit increased reactivity with polar substrates. Furthermore, they should be weaker Lewis acids at the metal centers than the Cp'M(NO)R₂ systems since the electronic requirements of the metal centers may be satisfied to some extent by the existence of a degree of M-O multiple bonding.

There are two primary methods for making transition-metal alkoxo complexes.³ These involve the reaction of metal halide complexes with either an alkali-metal alkoxide salt,⁴
M-X + M'OR → M-OR + M'X

\[ \text{M}' = \text{Li, Na, K.} \]  

(2.1)

or with an alcohol in the presence of a base.\(^5\)

M-X + HOR \xrightarrow{\text{base, } B} M-OR + BH^+X^-  

(2.2)

Some other less-common routes to the desired complexes which have been described in the literature are as follows:

1) Bimolecular elimination of \( \text{H}_2 \), e.g.,\(^6\)

\[
(\text{Me}_3\text{CC}_3\text{H}_4)_3\text{Ce} \xrightarrow{\text{+HOR}} (\text{Me}_3\text{CC}_3\text{H}_4)_4\text{Ce}_2(\mu-\text{OR})
\]  

(2.3)

2) Insertion of a ketone into a metal-hydride bond, e.g.,\(^7\)

\[
\text{Re}_3(\text{O-}i\text{-Pr})_5(\mu-\text{O-}i\text{-Pr})_3 + \text{Me}_2\text{C} = \text{O} \xrightarrow{} \text{Re}_3(\text{O-}i\text{-Pr})_6(\mu-\text{O-}i\text{-Pr})_3
\]  

(2.4)

3) Alcohol exchange, e.g.,\(^8\)

\[
\text{Cp}^*\text{Ir}(\text{PPh}_3)(\text{H})(\text{OR}) + \text{HOR'} \xrightarrow{} \text{Cp}^*\text{Ir}(\text{PPh}_3)(\text{H})(\text{OR'}) + \text{HOR}
\]  

(2.5)

4) Oxidative addition of an alcohol, e.g.,\(^9\)

\[
\text{Pt(PC}_3\text{)}_2 + \text{PhOH} \xrightarrow{} \text{Pt(PC}_3\text{)}_2(\text{H})(\text{OPh})
\]  

(2.6)

In our group, previous workers attempted to prepare alkoxo nitrosyl complexes of the type \(\text{Cp}'\text{M(NO)(OR)}_2\) by treatment of \(\text{Cp}^*\text{M(NO)}_2\) with alcohols (cf. equation 2.2). In the case of methanol, a insoluble tan solid, formulated as \([\text{Cp}^*\text{M(NO)(OMe)}]_2\), was isolated.\(^10\) Other alcohols did not result in any isolable organometallic species. The preparation of alkoxo complexes via the halide metathesis reaction of the diiodide complexes, \(\text{Cp}'\text{M(NO)}_2\), with
KOCMe$_3$ was also attempted (cf. equation 2.1). Unfortunately, this operation resulted in only the decomposition of the starting materials. Thus, the desired bis(alkoxo) complexes were not obtained by either of these routes.

This chapter summarizes the successful synthesis, characterization, and some characteristic chemistry of representative alkoxo chloro and bis(alkoxo) complexes having the compositions Cp$^*$M(NO)(OR)Cl and Cp$^*$M(NO)(OR)$_2$ ($M = Mo, W$; $R = alkyl, aryl$).

2.2 Experimental Procedures

2.2.1 Methods

The synthetic methodologies employed throughout this thesis are described in detail in this section. All reactions and subsequent manipulations involving organometallic reagents were performed under anhydrous conditions in an atmosphere of purified dinitrogen. Purification of N$_2$ was achieved by passing it through a double-walled glass column (10 x 60 cm) containing MnO and activated 4Å molecular sieves. Conventional glovebox and greaseless vacuum line Schlenk techniques were utilized throughout. The specific gloveboxes used in this work were Vacuum Atmospheres HE-553-2 and HE-43-2 models. All IR samples were either as THF, Et$_2$O, hexanes, pentane or CH$_2$Cl$_2$ solutions in NaCl cells or as Nujol mulls sandwiched between NaCl or CsI plates. IR spectra were recorded on a Nicolet 5DX FT-IR instrument, internally calibrated with a He/Ne laser. All NMR spectra were obtained on a Varian Associates XL-300 or a Bruker AC-200 spectrometer and are reported in parts per million. $^1$H NMR spectra are referenced to the residual proton signal of C$_6$D$_6$ ($\delta$ 7.15) or CDCl$_3$ ($\delta$ 7.24). $^{31}$P{$^1$H} NMR spectra (121.42 MHz) are referenced to external P(OMe)$_3$ set at $\delta$ 141.00 ppm relative to 85% H$_3$PO$_4$. $^{13}$C{$^1$H} NMR spectra (75.43 MHz) are referenced to the natural abundance carbon signals of the solvent employed: C$_6$D$_6$ ($\delta$ 128.00). Mrs. M. T. Austria, Ms. L. K. Darge, and Dr. S. O. Chan assisted in obtaining the NMR data. Mass spectra were recorded by Dr. G. K. Eigendorf and the staff of the mass spectrometry laboratory. Low-resolution mass spectra (EI, 70 eV) were recorded on a
Kratos MS50 spectrometer using the direct-insertion method. All elemental analyses were performed by Mr. P. Borda of this Department.

2.2.2 Reagents

The organometallic reagents, Cp'M(NO)Cl$_2$ (M = Mo, W), were prepared by established procedures.\textsuperscript{12} Cp'Mo(NO)Cl$_2$ complexes were further purified by Soxhlet extraction with CH$_2$Cl$_2$, and the Cp'W(NO)Cl$_2$ complexes were stored at -30 °C.

PMe$_3$ was prepared from P(OMe)$_3$ and MeMgI and was dried over, and transferred from, sodium/benzophenone.\textsuperscript{13} Me$_3$COH (Aldrich) was freshly distilled from CaH$_2$. PhCH$_2$OH (Matheson) and MeOH (Fisher) were dried over activated 4Å molecular sieves (Fisher). PhOH (Mallinckrodt), S$_8$ (Fisher), NHPh$_2$ (Fisher), acetone (reagent grade, Fisher), CO (Matheson) and O$_2$ (Medigas, 99.5 %) were used without any further purification. All other reagents were purchased from Aldrich Chemical Co. and used as received, unless otherwise specified.

Solvents were freshly distilled from appropriate drying agents under a dinitrogen atmosphere and were either purged for 10 min with argon prior to use or were directly vacuum transferred from the appropriate drying agent. Dioxane, tetrahydrofuran and diethyl ether were distilled from sodium/benzophenone; hexanes, benzene and pentane were distilled from sodium/benzophenone/tetraglyme; dichloromethane was doubly distilled from P$_2$O$_5$.\textsuperscript{14} C$_6$D$_6$ was dried over activated 4Å molecular sieves and degassed using 3 freeze-pump-thaw cycles. Other deuterated solvents were used as received. Filtrations were performed through either Celite 545 diatomaceous earth (Fisher), silica gel 60 (230 - 400 mesh, BDH) or Florisil (60 - 100 mesh, Fisher) that had been oven-dried and cooled in vacuo.
2.2.3 Preparation of LiOCMe$_3$\textsuperscript{15}

A fine white precipitate formed as an Et$_2$O solution (20 mL) of $n$-BuLi (66 mL, 1.6 M in hexanes) was slowly added via an addition funnel to an excess of Me$_3$COH (10 mL) in Et$_2$O (20 mL). After the addition was complete, the resulting mixture was stirred for 0.5 h and then taken to dryness in vacuo. The white solid remaining was washed with pentane (2 x 25 mL) and then redissolved in Et$_2$O (120 mL). The Et$_2$O extracts were filter cannulated into another Schlenk tube, and the filtrate was concentrated and cooled to induce the crystallization of [LiOCMe$_3$]$_x$ as large white blocks.\textsuperscript{16}

2.2.4 Preparation of NaOPh, NaOCH$_2$Ph and NaOMe

All the NaOR [R = Ph, CH$_2$Ph, Me] reagents were prepared in a similar fashion. Na metal was cut into small flakes in a glovebox and then transferred into a three-necked flask. THF (20 mL) was added to the flask via syringe. A THF (10 mL) solution of alcohol (excess) was cannulated into the flask containing the Na. This mixture was stirred for 0.5 h and then taken to dryness in vacuo. The remaining white solid was washed with pentane, dried in vacuo, and used without further purification.\textsuperscript{16}

2.2.5 Preparation of Bis(Alkoxo) Complexes, Cp*$_x$M(NO)(OR)$_2$ [M = Mo, R = CMe$_3$ (2.1); M = W, R = CMe$_3$ (2.2), Ph (2.3), CH$_2$Ph (2.4)]

All these complexes were synthesized in a similar manner. The preparation of Cp*W(NO)(OCMe$_3$)$_2$ (2.2) is described as a representative example.

A THF solution (20 mL) of LiOCMe$_3$ (0.58 g, 7.2 mmol) was added slowly via an addition funnel to a stirred THF solution (20 mL) of Cp*W(NO)Cl$_2$ (1.5 g, 3.6 mmol). The progress of the reaction was monitored by IR spectroscopy. The reaction proceeded in a straightforward manner with the initial diminution of the starting nitrosyl absorption band at 1630 cm$^{-1}$ occurring concomitantly with the appearance and growth of a new band at 1593 cm$^{-1}$. As the addition of
LiOCMe$_3$ continued, a second nitrosyl absorption band at 1557 cm$^{-1}$ appeared at the expense of the band at 1593 cm$^{-1}$. During this time the color of the reaction mixture changed from green to purple to deep orange-red. The solvent was removed from the final reaction mixture in vacuo, and the residue was extracted with hexanes ($2 \times 50$ mL). The combined extracts were filtered through Celite ($3 \times 6$ cm) supported on a sintered glass frit. The filtrate was concentrated in vacuo until incipient crystallization, and the mixture was then cooled at -30 °C overnight. The orange crystals of Cp$^*$W(NO)(OCMe$_3$)$_2$ (0.57 g, 32% yield) thus formed were isolated by removal of the supernatant solution by cannulation and drying of the crystals in vacuo.

The numbering scheme, color, yield, and elemental analysis data for complexes 2.1 - 2.4 are collected in Table 2.1. The mass spectral and IR data for these compounds are compiled in Table 2.2, and their $^1$H and $^{13}$C($^1$H) NMR data are presented in Table 2.3.

2.2.6 Preparation of Alkoxo Chloro Complexes, Cp$^*$M(NO)(OR)Cl [$M = Mo, R = CMe_3$ (2.5); $M = W, R = CMe_3$ (2.6), Ph (2.7)]

Since the synthetic approach to each of these complexes is similar, their syntheses are described in the next paragraph in a generalized manner.

In a glovebox, Cp$^*$M(NO)Cl$_2$ (1.00 mmol) and the appropriate alkoxide salt (1.00 mmol) were intimately mixed in a Schlenk tube. The tube was removed from the box, and THF (25 mL) was vacuum transferred onto the solids at -196 °C. The stirred reaction mixture was then allowed to warm slowly to 0 °C, whereupon the color changed from red ($M = Mo$) or green ($M = W$) to purple and $\nu_{NO}$ diminished by approximately 35 cm$^{-1}$ in the IR spectrum of the mixture. The solvent was removed in vacuo, the purple residues were extracted with pentane ($2 \times 20$ mL), and the extracts were filtered through Celite ($2 \times 5$ cm) supported on a sintered glass frit. The filtrate was concentrated in vacuo until the first signs of crystallization were evident. Additional crystallization occurred upon storing these concentrated solutions at -30 °C overnight. Finally, the desired alkoxo chloro complexes were isolated by removal of the supernatant solution by cannulation and drying of the remaining black to purple needle-like crystals in vacuo.
The numbering scheme, color, yield, and elemental analysis data for complexes 2.5 - 2.7 are collected in Table 2.1. The mass spectral and IR data for these compounds are compiled in Table 2.2, and their $^1$H and $^{13}$C{$_^1$H} NMR data are presented in Table 2.3.

2.2.7 Reactions of Cp$^*$W(NO)(OCMe$_3$)$_2$ (2.2) and Cp$^*$W(NO)(OCMe$_3$)Cl (2.6) with HCl

Complexes 2.2 (0.05 mmol) and 2.6 (0.05 mmol) were treated in Et$_2$O (20 mL) with 1 equiv of HCl (1.4 M solution in Et$_2$O). Work up of the final reaction mixtures involved removing the solvent in vacuo, extracting the residues with pentane or CH$_2$Cl$_2$, and cooling the combined extracts at -30 °C to obtain crystalline precipitates (80 - 90% yields) of the product complexes. Comparisons with authentic spectral data confirmed that the organometallic products of these reactions were Cp$^*$W(NO)(OCMe$_3$)Cl (2.6) and Cp$^*$W(NO)Cl$_2$, respectively.

2.2.8 Reactions of Cp$^*$W(NO)(OCMe$_3$)$_2$ (2.2) with H$_2$O, O$_2$, PMe$_3$, Me$_2$CHCN, PhCCH, acetone, CO, NHPh$_2$ or S$_8$

The experimental conditions for these experiments are presented here for completeness. In all cases, no reaction occurred as indicated by IR spectroscopy. In many cases, the reactants were isolated from the reaction mixture and were characterized by IR, MS, and $^1$H NMR spectroscopies. The scale of these reactions was 0.50 mmol in the organometallic reagent.

Cp$^*$W(NO)(OCMe$_3$)$_2$ was reacted with excess H$_2$O in THF and with O$_2$ (1 atm) in Et$_2$O. Hexanes solutions of complex 2.2 were reacted at ambient temperatures with an excess of PMe$_3$, Me$_2$CHCN, PhCCH, or acetone. CO (600 psig) was reacted with 2.2 overnight in C$_6$H$_6$. Reactions of 2.2 with NHPh$_2$ and S$_8$ were performed in Et$_2$O and toluene, respectively, at elevated temperatures.
2.2.9 Reaction of Cp*W(NO)(OCMe)_2 (2.2) with H₂

A THF solution (20 mL) of Cp*W(NO)(OCMe)_2 (0.30 g, 0.61 mmol) was placed in a Fischer and Porter pressure vessel, and the vessel was pressurized with H₂ (80 psig). After being stirred overnight, the reaction solution was taken to dryness under reduced pressure. The remaining orange residue was washed with hexanes (20 mL). The solid was then dissolved in a minimal amount of C₆H₆, and an equal volume of hexanes was added. This solution was cooled to -30 °C for 1 week to induce the crystallization of orange crystals.

Partial characterization data for the orange crystals: Anal. Found: C, 36.03; H, 4.51; N, 1.90. IR (Nujol mull): ν(NO) 1541 cm⁻¹. ¹H NMR (C₆D₆): δ 2.22 (s, 15H, C₅(CH₃)₅), 2.20 (s, 2H), 2.07 (s, 15H, C₅(CH₃)₅), 1.98 (s, 1H), 1.87 (s, 2H). ¹³C{¹H} NMR (C₆D₆): δ 119.9 (C₅(CH₃)₅), 119.6 (C₅(CH₃)₅), 10.9 (C₅(CH₃)₅), 10.8 (C₅(CH₃)₅), 10.2, 9.7, 9.5. Low-resolution mass spectrum (probe temperature 100 °C): m/z 718.17

2.2.10 Reactions of Cp*Mo(NO)(OCMe)_2 (2.1) and Cp*W(NO)(OCH₂Ph)_2 (2.3) with H₂

These reactions were performed in a manner similar to that described in the preceding section. Solution IR spectra of the resulting reaction mixtures showed only bands due to the organometallic reactants.

2.2.11 Reaction of Cp*Mo(NO)(OCMe)Cl (2.5) with H₂O

Complex 2.5 (0.33 g, 1.0 mmol) in Et₂O (20 mL) was treated with an excess of deaerated H₂O (50 μL). The stirred reaction mixture turned red-black immediately and was stirred for a further 2.5 h at room temperature. After this time, the reaction mixture was taken to dryness in vacuo, and the residue was redissolved in Et₂O (20 mL). The black Et₂O solution was filtered through Celite (2 x 5 cm) supported on a medium-porosity frit. Concentration of this filtrate and cooling at -30 °C afforded black crystals (0.11 g, 35% yield) formulated as [Cp*Mo(NO)(OH)(Cl)]₂ (2.8).
2.2.12 Reaction of Cp*W(NO)(OCMe3)Cl (2.6) with H2O

A stirred Et2O solution (15 mL) of complex 2.6 (0.23 g, 0.50 mmol) was treated with an excess of deaerated H2O (50 µL). The reaction mixture turned brown immediately. The brown mixture was taken to dryness in vacuo, and Et2O (20 mL) was added to the brown residues. The mixture was filtered through Celite (2 x 5 cm). The filtrate was concentrated under reduced pressure to incipient crystallization and was cooled to -30 °C overnight to obtain brown crystals (0.070 g, 35% yield) of a solid formulated as [Cp*W(NO)(OH)(Cl)]2 (2.9).

2.2.13 Reaction of Cp*W(NO)(OCMe3)Cl (2.6) with PMe3

A Schlenk tube containing a pentane solution (5 mL) of complex 2.6 (0.23 g, 0.50 mmol) was cooled to -196 °C until its contents had solidified. Excess PMe3 was then vacuum transferred into the tube. The reaction mixture was allowed to warm to -30 °C over 0.5 h as yellow precipitate formed. At -30 °C, the reaction mixture was taken to dryness in vacuo. The remaining solid remained yellow at low temperatures, but turned brown and decomposed upon warming to room temperature.

2.2.14 Synthesis of [Cp*W(NO)(OCMe3)]2 (2.10)

In a glovebox, Cp*W(NO)Cl2 (1.00 g, 2.38 mmol) was placed in the bottom of a Fischer and Porter pressure vessel. A vial containing KOCMe3 (0.54 g, 4.8 mmol) was also placed in the vessel. The vessel was removed from the glovebox, and THF (30 mL) was carefully syringed into the vessel without allowing the KOCMe3 in the vial to mix with the THF solution of Cp*W(NO)Cl2. The vessel was charged with H2 (40 psig). The vessel was then shaken to allow the KOCMe3 to enter into the reaction mixture. The reaction mixture turned from green to red in 5 min. After stirring the reaction mixture for a further 30 min, it was taken to dryness in vacuo. The remaining residue was extracted with hexanes (2 x 10 mL), and the extracts were filtered through Celite (3 x 5 cm) supported on a sintered glass frit. The amber-red filtrate was
concentrated to 10 mL and chromatographed on Florisil (2 x 5 cm). The column was eluted first with hexanes to develop a yellow band which was discarded. A second red-purple band was then eluted with Et₂O. Concentration and cooling of the Et₂O fraction afforded purple crystals (0.25 g, 25% yield) of complex 2.10.

2.3 Characterization Data

Table 2.1. Numbering Scheme, Color, Yield and Elemental Analysis Data for Complexes 2.1 - 2.10

<table>
<thead>
<tr>
<th>complex</th>
<th>compd no.</th>
<th>color (yield, %)</th>
<th>anal. found (calcd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp*Mo(NO)(OCMe₃)₂</td>
<td>2.1</td>
<td>orange (67)</td>
<td>C: 53.31 (53.07) H: 8.17 (8.16) N: 3.35 (3.44)</td>
</tr>
<tr>
<td>Cp*W(NO)(OCMe₃)₂</td>
<td>2.2</td>
<td>orange (32)</td>
<td>C: 43.59 (43.65) H: 6.66 (6.72) N: 2.84 (2.83)</td>
</tr>
<tr>
<td>Cp*W(NO)(OPh)₂</td>
<td>2.3</td>
<td>red (20)</td>
<td>C: 49.23 (49.36) H: 4.80 (4.71) N: 2.50 (2.62)</td>
</tr>
<tr>
<td>Cp*W(NO)(OCH₂Ph)₂</td>
<td>2.4</td>
<td>red (22)</td>
<td>C: 51.06 (51.17) H: 5.24 (5.19) N: 2.45 (2.49)</td>
</tr>
<tr>
<td>Cp*Mo(NO)(OCMe₃)Cl</td>
<td>2.5</td>
<td>purple (25)</td>
<td>C: 45.09 (45.48) H: 6.45 (6.54) N: 3.78 (3.78)</td>
</tr>
<tr>
<td>Cp*W(NO)(OCMe₃)Cl</td>
<td>2.6</td>
<td>purple-black (37)</td>
<td>C: 36.81 (36.74) H: 5.40 (5.29) N: 3.00 (3.06)</td>
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<tr>
<td>Cp*W(NO)(OPh)Cl</td>
<td>2.7</td>
<td>red-black (44)</td>
<td>C: 40.21 (40.23) H: 4.40 (4.22) N: 2.70 (2.93)</td>
</tr>
<tr>
<td>[Cp*Mo(NO)(OH)(Cl)]₂</td>
<td>2.8</td>
<td>black (35)</td>
<td>C: 38.57 (38.30) H: 5.13 (5.14) N: 4.50 (4.47)</td>
</tr>
<tr>
<td>[Cp*W(NO)(OH)(Cl)]₂</td>
<td>2.9</td>
<td>brown (35)</td>
<td>C: 29.72 (29.91) H: 4.20 (4.02) N: 3.30 (3.49)</td>
</tr>
<tr>
<td>[Cp*W(NO)(OCMe₃)]₂</td>
<td>2.10</td>
<td>purple (25)</td>
<td>C: 39.63 (39.83) H: 5.71 (5.73) N: 3.50 (3.32)</td>
</tr>
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</table>
Table 2.2. Mass Spectral and Infrared Data for Complexes 2.1 - 2.10

<table>
<thead>
<tr>
<th>compd no.</th>
<th>MS, m/z&lt;sup&gt;a&lt;/sup&gt;</th>
<th>temp&lt;sup&gt;b&lt;/sup&gt;, °C</th>
<th>IR, cm&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>ν&lt;sub&gt;NO&lt;/sub&gt; (THF)</th>
<th>ν&lt;sub&gt;NO&lt;/sub&gt; (Nujol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>409 [P&lt;sup&gt;+&lt;/sup&gt;]</td>
<td>80</td>
<td>1589</td>
<td>1601</td>
<td></td>
</tr>
<tr>
<td>2.2</td>
<td>495 [P&lt;sup&gt;+&lt;/sup&gt;]</td>
<td>80</td>
<td>1557</td>
<td>1550</td>
<td></td>
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<tr>
<td></td>
<td>439 [P&lt;sup&gt;+&lt;/sup&gt;- CMe&lt;sub&gt;3&lt;/sub&gt;]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.3</td>
<td>535 [P&lt;sup&gt;+&lt;/sup&gt;]</td>
<td>100</td>
<td>1593</td>
<td>1566</td>
<td></td>
</tr>
<tr>
<td></td>
<td>505 [P&lt;sup&gt;+&lt;/sup&gt;- NO]</td>
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<tr>
<td>2.4</td>
<td>563 [P&lt;sup&gt;+&lt;/sup&gt;]</td>
<td>80</td>
<td>1556</td>
<td>1557</td>
<td></td>
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<tr>
<td></td>
<td>533 [P&lt;sup&gt;+&lt;/sup&gt;- NO]</td>
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<tr>
<td></td>
<td>457 [P&lt;sup&gt;+&lt;/sup&gt;- OCH&lt;sub&gt;2&lt;/sub&gt;Ph]</td>
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<td>2.5</td>
<td>371 [P&lt;sup&gt;+&lt;/sup&gt;]</td>
<td>100</td>
<td>1622</td>
<td>1613</td>
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<tr>
<td>2.6</td>
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<td>100</td>
<td>1593</td>
<td>1578</td>
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<tr>
<td>2.7</td>
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<td>80</td>
<td>1595</td>
<td>1589</td>
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<tr>
<td></td>
<td>447 [P&lt;sup&gt;+&lt;/sup&gt;- NO]</td>
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<td></td>
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<tr>
<td>2.8</td>
<td>608 [P&lt;sup&gt;+&lt;/sup&gt;- H&lt;sub&gt;2&lt;/sub&gt;O]</td>
<td>80</td>
<td>1613 br&lt;sup&gt;d&lt;/sup&gt;</td>
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</tr>
<tr>
<td>2.9</td>
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<td>120</td>
<td>1588 br&lt;sup&gt;e&lt;/sup&gt;</td>
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<tr>
<td>2.10</td>
<td>844 [P&lt;sup&gt;+&lt;/sup&gt;]</td>
<td>80</td>
<td>1555</td>
<td>1543 br&lt;sup&gt;e&lt;/sup&gt;</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> m/z values are for the highest intensity peak of the calculated isotopic cluster, i.e. 98Mo and 184W.<br><sup>b</sup> Probe temperatures.<br><sup>c</sup> Not recorded.<br><sup>d</sup> ν<sub>OH</sub> = 3642, 3631<br><sup>e</sup> ν<sub>OH</sub> = 3641, 3626

Table 2.3. ¹H and ¹³C(¹H) NMR Data for Complexes 2.1 - 2.10 in C₆D₆

<table>
<thead>
<tr>
<th>compd no.</th>
<th>¹H NMR (δ, ppm)</th>
<th>¹³C(¹H) NMR (δ, ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>1.73 (s, 15H, C₅(CH₃)₅) 1.40 (s, 18H, OC(CH₃)₅)</td>
<td>116.3 (C₅(CH₃)₅) 81.3 (OC(CH₃)₅) 33.5 (OC(CH₃)₅) 10.0 (C₅(CH₃)₅)</td>
</tr>
<tr>
<td>2.2</td>
<td>1.80 (s, 15H, C₅(CH₃)₅) 1.40 (s, 18H, OC(CH₃)₅)</td>
<td>114.6 (C₅(CH₃)₅) 81.3 (OC(CH₃)₅) 33.4 (OC(CH₃)₅) 10.0 (C₅(CH₃)₅)</td>
</tr>
</tbody>
</table>
| 2.3 | 7.30 - 6.85 (m, 10H, O\textsubscript{6}H\textsubscript{5})  
1.60 (s, 15H, C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5}) | a |
| 2.4 | 7.60 - 7.00 (m, 10H, OCH\textsubscript{2}C\textsubscript{6}H\textsubscript{5})  
5.95 (s, 4H, OCH\textsubscript{2}C\textsubscript{6}H\textsubscript{5})  
1.60 (s, 15H, C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5}) | 142.7, 129.1, 128.6, 127.5 (OCH\textsubscript{2}C\textsubscript{6}H\textsubscript{5})  
114.7 (C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5})  
84.2 (OCH\textsubscript{2}C\textsubscript{6}H\textsubscript{5})  
9.4 (C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5}) |
| 2.5 | 1.67 (s, 15H, C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5})  
1.47 (s, 9H, OC(CH\textsubscript{3})\textsubscript{3}) | 118.4 (C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5})  
32.8 (OC(CH\textsubscript{3})\textsubscript{3})  
10.1 (C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5}) |
| 2.6 | 1.71 (s, 15H, C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5})  
1.42 (s, 9H, OC(CH\textsubscript{3})\textsubscript{3}) | 116.0 (C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5})  
86.0 (OC(CH\textsubscript{3})\textsubscript{3})  
32.7 (OC(CH\textsubscript{3})\textsubscript{3})  
9.9 (C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5}) |
| 2.7 | 7.22 - 6.85 (m, 5H, O\textsubscript{6}H\textsubscript{5})  
1.65 (s, 15H, C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5}) | 129.6, 123.7, 122.5, 118.9 (O\textsubscript{6}H\textsubscript{5})  
116.7 (C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5})  
9.7 (C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5}) |
| 2.8 | 1.75 (s, 15H, C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5})  
1.63 (s, 1H, OH) | 119.0 (C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5})  
10.2 (C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5}) |
| 2.9 | 1.94 (s, 15H, C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5})  
1.75 (s, 15H, C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5})  
1.44 (s, 2H, OH) | a |
| 2.10 | 2.04 (s, 15H, C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5})  
2.00 (s, 15H, C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5})  
1.44 (s, 9H, OC(CH\textsubscript{3})\textsubscript{3})  
1.26 (s, 9H, OC(CH\textsubscript{3})\textsubscript{3}) | a |

\(a\) Not recorded.  
\(b\) A resonance attributable to OC(CH\textsubscript{3})\textsubscript{3} was not observed.
2.4 Results and Discussion

2.4.1 Synthesis and Characterization of Bis(alkoxo) Complexes, Cp\(^\ast\)M(NO)(OR)\(_2\)

Bis(alkoxo) nitrosyl complexes of the type Cp\(^\ast\)M(NO)(OR)\(_2\) [R = alkyl, aryl] are preparable by treating Cp\(^\ast\)M(NO)Cl\(_2\) with 2 equiv of alkoxide salts such as LiOCMe\(_3\) or NaOR [R = Ph, CH\(_2\)Ph], i.e.

\[
\begin{align*}
\text{Cp}^\ast M(NO)Cl_2 + 2 \text{M'OR} & \rightarrow \text{THF} \rightarrow \text{RT} \\
\text{Cp}^\ast M(NO)(OR)_2 + 2 \text{M'Cl}
\end{align*}
\]

(2.7)

The four Cp\(^\ast\)M(NO)(OR)\(_2\) complexes synthesized during this work (2.1 - 2.4) are isolable as red to orange crystalline solids in 20 - 67% yields. They are very soluble in common organic solvents. As solids, the bis(alkoxo) complexes are indefinitely stable in air. The bis(alkoxo) complexes are also thermally stable in solution, as evidenced by the fact that 2.2 persists unchanged in C\(_6\)D\(_6\) after 16 h at 120 °C. The spectroscopic properties of 2.1 - 2.4, collected in Tables 2.2 and 2.3, are consistent with their possessing monomeric, three-legged piano-stool molecular structures.

The progress of reactions 2.7 can be monitored by observing the changes in the nitrosyl-stretching frequencies evident in the IR spectra of the reaction mixtures (Figure 2.1). For instance, the reaction of Cp\(^\ast\)W(NO)Cl\(_2\) (\(v_{NO} = 1630 \text{ cm}^{-1}\)) with 2 equiv of LiOCMe\(_3\) in THF exhibits first an intermediate nitrosyl-stretching band at 1593 cm\(^{-1}\) (vide infra) which appears at the expense of the band due to the starting material. As the transformation continues, this absorption feature decreases as the 1557 cm\(^{-1}\) band characteristic of the product complex appears and intensifies. In other words, the \(v_{NO}\) is shifted to lower energy as the chloro ligands are replaced by the more electron-donating alkoxo groups. In general, the nitrosyl-stretching frequency\(^{18}\) has proven to be an extremely powerful tool in estimating the Lewis acidity of a metal nitrosyl complex.\(^2\) The nitrosyl-stretching frequencies of the Cp\(^\ast\)M(NO)(OR)\(_2\) class of
Figure 2.1 Monitoring of the reaction between Cp*W(NO)Cl₂ and 2 equiv of LiOCMe₃ in THF by IR spectroscopy [spectral region 1850 - 1480 cm⁻¹].
complexes (Table 2.2) indicate that the metal is receiving significant donation of \( \pi \)-electron density from the alkoxide ligands. For comparison, it may be noted that a THF solution of \( \text{Cp}^*\text{W(NO)}(\text{CH}_2\text{CMe}_3)_2 \) exhibits a \( \nu_{\text{NO}} \) at 1568 cm\(^{-1} \), whereas \( \text{Cp}^*\text{W(NO)}(\text{OCMe}_3)_2 \) has the same feature at 1557 cm\(^{-1} \).

**2.4.2 Some Chemical Properties of Bis(Alkoxo) Complexes**

Consistent with \( \text{Cp}^*\text{M(NO)(OR)}_2 \) complexes having electron-rich metal centers, they are relatively inert chemically towards nucleophiles. As noted above, these bis(alkoxo) complexes are extremely air-stable. Furthermore, \( \text{Cp}^*\text{W(NO)}(\text{OCMe}_3)_2 \) (2.2) does not react with \( \text{O}_2 \) (1 atm) in \( \text{Et}_2\text{O} \) or with an excess of \( \text{H}_2\text{O} \) in THF. The stability of 2.2 towards \( \text{O}_2 \) suggests that complexes of this type are not easily oxidized. Consistent with this, a cyclic voltammogram of \( \text{Cp}^*\text{W(NO)}(\text{OCMe}_3)_2 \) in THF shows no oxidation features to the solvent limit of 0.85 V.\(^{19} \) The hydrolytic stability is somewhat surprising since the polar W-O bonds in complex 2.2 would be expected to be susceptible to nucleophilic attack.\(^{20} \)

Complex 2.2 also does not react with typical Lewis bases such as CO and PMe\(_3\). Consequently, I believe that the chemical inertness of the \( \text{Cp}^*\text{M(NO)(OR)}_2 \) complexes reflects their inability to form Lewis acid-base adducts at their relatively electron-rich metal centers. This behavior is in marked contrast to the 16-electron dialkyl and diaryl species, \( \text{Cp'M(NO)R}_2 \), which readily form 1:1 metal-centered adducts with a variety of Lewis bases.\(^2 \) \( \text{Cp}^*\text{W(NO)}(\text{OCMe}_3)_2 \) (2.2) is also inert to NCCH(Me)\(_2\), PhCCH, (Me)\(_2\)CO, NHPh\(_2\) and \( \text{S}_8 \) under the conditions described in Section 2.2.8. The reaction with \( \text{S}_8 \) with 2.2 was performed since it is known that sulfur adds across the metal-sulfur bond of \( \text{CpW(NO)}(\text{SCH}_2\text{SiMe}_3)(\text{CH}_2\text{SiMe}_3) \) to form the perthiolate species, \( \text{CpW(NO)}(\eta^2-\{\text{S}\})\text{CH}_2\text{SiMe}_3)(\text{CH}_2\text{SiMe}_3) \).\(^{21} \)
Bis(alkoxo) complexes react rapidly with HCl to form first the alkoxo chloro complex and then the corresponding dichloro species, i.e.,

\[
\begin{align*}
&\text{Me}_3\text{CO} \quad \text{N} \\
&W \quad \text{OCMe}_3 \\
&\text{Me}_3\text{CO} \quad \text{N} \\
&\text{O} \\
&\text{HCl} \\
&W \quad \text{Cl} \\
&\text{Me}_3\text{CO} \quad \text{N} \\
&\text{O} \\
&\text{HCl} \\
&W \quad \text{Cl} \\
&\text{Cl} \quad \text{N} \\
&\text{O}
\end{align*}
\]

(2.8)

The alkoxide ligands are replaced by chloride ligands with the production of alcohol. This type of reactivity has been observed previously by McCleverty's group.\(^\text{22}\)

Interestingly, \(\text{Cp}^*\text{W(NO)(OCMe}_3)_2\) (2.2) does react with \(\text{H}_2\) (80 psig) in THF to produce orange crystals. The exact nature of this product is uncertain. Partial characterization data for can be found in Section 2.2.9. The elemental analysis data support a \(\text{C}_{22}\text{H}_{33}\text{N}\) ratio. The mass spectrum shows the fragmentation pattern for a common decomposition product, \([\text{Cp}^*\text{W(O)}_2\text{]}\text{L}_2\text{-(4-O)}\).\(^\text{23}\) IR data indicate the presence of a nitrosyl ligand in the product \((\nu_{\text{NO}} = 1541 \text{ cm}^{-1})\), at lower energy than the starting bis(alkoxo) complex \((\nu_{\text{NO}} = 1557 \text{ cm}^{-1})\). The \(^1\text{H}\) NMR data suggest that this complex is a bimetallic species with two inequivalent \(\text{Cp}^*\) ligands whose protons resonate at \(\delta 2.22\) and 2.07 ppm. The \(^{13}\text{C}\{^1\text{H}\}\) NMR data support this conclusion in that there are two signals due to \(\text{C}_5(\text{CH}_3)_5\) (\(\delta 119.9, 119.6 \text{ ppm}\)) and two signals due to \(\text{C}_5(\text{CH}_3)_5\) (\(\delta 10.9, 10.8 \text{ ppm}\)) in the \(^{13}\text{C}\{^1\text{H}\}\)NMR spectrum of the orange crystals in the \(\text{C}_6\text{D}_6\). Additional signals in the \(^1\text{H}\) NMR spectra could not be assigned. A solid-state crystallographic analysis of the orange crystals was attempted by Dr. S. J. Rettig.
Due to severe disorder problems, the only information obtained was the identification of a W$_2$O$_2$ core unit, i.e.,

![Diagram of W$_2$O$_2$ core unit]

A similar core unit is observed in the structure of [Cp*Mo(NO)(CH$_2$Ph)(μ-O)]$_2$ (see Section 4.4.5). Surprisingly, Cp*Mo(NO)(OCMe$_3$)$_2$ (2.1) and Cp*W(NO)(OCH$_2$Ph)$_2$ (2.4) do not react with H$_2$ under similar experimental conditions.

### 2.4.3 X-ray Crystallographic Analyses of Complexes 2.2 and 2.4

X-ray crystallographic analyses of 2.2 (Figure 2.2)$^{24}$ and 2.4 (Figure 2.3)$^{25}$ demonstrate that these representative examples of Cp*W(NO)(OR)$_2$ complexes are best viewed as 18-valence-electron species, the ability of the alkoxo ligands to donate π-electron density effectively satisfying the electronic requirements of the metal centers. Both Cp*W(NO)(OCMe$_3$)$_2$ (2.2) and Cp*W(NO)(OCH$_2$Ph)$_2$ (2.4) are monomeric, and some selected bond angles and bond lengths are collected in Tables 2.4 - 2.5. Their chemically most interesting features are the dimensions about the alkoxide ligands. Since the OCMe$_3$ and OCH$_2$Ph ligands have very different steric requirements, we believe that the large W-O-C angles (averaging 135.9° for 2.2 and 128.3° for 2.4) and short W-O bond lengths (averaging 1.90 Å for 2.2 and 1.91 Å for 2.4) are a result of electronic rather than steric effects. The increased W-O bond order likely results from the donation of electron density from filled $p$ orbitals on oxygen to the empty $d_{xy}$ orbital on the metal center.$^{26}$ The W-O-C angle of alkoxide ligands can approach linearity as π donation from the alkoxide ligand to the metal increases.$^{27}$ The tungsten centers in 2.2 and 2.4 are thus relatively more electron rich (a fact also indicated by their IR and chemical properties, vide supra) than those in their dialkyl or diaryl analogues.$^2$ Consistent with this, no evidence for the existence of agostic interactions between the metal and the β-hydrogens of the alkoxo ligands is revealed by the crystallographic analysis of 2.4.
Figure 2.2 ORTEP diagram of Cp*W(NO)(OCMe$_3$)$_2$ (2.2). 50% probability thermal ellipsoids are shown for the non-hydrogen atoms.

Table 2.4. Selected Bond Lengths and Bond Angles for Cp*W(NO)(OCMe$_3$)$_2$ (2.2)

<table>
<thead>
<tr>
<th>bond lengths (Å)</th>
<th>bond angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W - O1</td>
<td>1.890 (5)</td>
</tr>
<tr>
<td>W - O2</td>
<td>1.903 (5)</td>
</tr>
<tr>
<td>O1 - C11</td>
<td>1.46 (1)</td>
</tr>
<tr>
<td>W - N</td>
<td>1.758 (7)</td>
</tr>
<tr>
<td>N - O3</td>
<td>1.232 (8)</td>
</tr>
<tr>
<td>W - O1 - C11</td>
<td>136.2 (5)</td>
</tr>
<tr>
<td>W - O2 - C15</td>
<td>135.6 (5)</td>
</tr>
<tr>
<td>O1 - W - O2</td>
<td>109.7 (2)</td>
</tr>
<tr>
<td>W - N - O3</td>
<td>168.1 (7)</td>
</tr>
</tbody>
</table>
Figure 2.3 ORTEP diagram of Cp*W(NO)(OCH₂Ph)₂ (2.4). 50% probability thermal ellipsoids are shown for the non-hydrogen atoms.

Table 2.5. Selected Bond Lengths and Bond Angles for Cp*W(NO)(OCH₂Ph)₂ (2.4)

<table>
<thead>
<tr>
<th>bond lengths (Å)</th>
<th>bond angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W - O₂</td>
<td>1.910 (4)</td>
</tr>
<tr>
<td>O₂ - C₈</td>
<td>1.444 (7)</td>
</tr>
<tr>
<td>W - N</td>
<td>1.759 (7)</td>
</tr>
<tr>
<td>N - O₁</td>
<td>1.218 (9)</td>
</tr>
<tr>
<td>W - O₂ - C₈</td>
<td>128.3 (4)</td>
</tr>
<tr>
<td>O₂ - W - O₂'</td>
<td>107.6 (3)</td>
</tr>
<tr>
<td>W - N - O₃</td>
<td>169.8 (7)</td>
</tr>
</tbody>
</table>
The structure of Cp*W(NO)(OCMe$_3$)$_2$ can be compared to the structure of Cp*W(NO)(OCMe$_3$)(NHCM$_3$), which has been recently completed. The metrical parameters of the two compounds are very similar, and the most interesting comparison involves their W-O bond lengths. Whereas the alkoxo amido complex has a W-O bond length of 1.916 (4) Å, the average W-O bond length in the bis(alkoxo) complex is 1.90 Å. These findings suggest that the very slight lengthening of the W-O bond in Cp*W(NO)(OCMe$_3$)(NHCM$_3$) may be a result of the amide ligand (W-N bond length of 1.939 (4) Å) have a greater π-donating ability than alkoxide ligand.

2.4.4 Systems Related to the Bis(alkoxo) Complexes

A bis(alkoxo) chromium complex related to the compounds synthesized during this work has recently been described by Hubbard and McVicar. They prepared Cp*Cr(NO)(O-i-Pr)$_2$ by treatment of Cp*Cr(NO)$_2$(CH$_2$C$_1$) with excess Na(O-i-Pr) in isopropanol, a process which results in the formal replacement of NO and CH$_2$Cl ligands by isopropoxide groups. Such chromium complexes cannot be synthesized via a route analogous to that portrayed in eq 2.7 because the Cp*Cr(NO)Cl$_2$ precursor remains unknown. In other work, McCleverty and coworkers have prepared an extensive series of isoelectronic pyrazolylborate alkoxide compounds, \{HB(Me$_2$pz)$_3$\}M(NO)(OR)$_2$ [M = Mo, W] which result from alcoholysis of \{HB(Me$_2$pz)$_3$\}M(NO)X$_2$ [X = Cl, I]. Interestingly, we find that similar treatment of Cp*M(NO)Cl$_2$ [M = Mo, W] with alcohols does not produce the bis(alkoxo) complexes synthesized during this work, but rather affords intractable materials. Both McCleverty and Hubbard have attributed the stability of their Group 6 bis(alkoxo) complexes to the electron-donating ability of the alkoxo ligands.

Sulfur analogues of the bis(alkoxo) complexes 2.1 - 2.4 have been prepared by the treatment of [CpMo(NO)I$_2$]$_2$ with thiolates or via direct sulfur insertion into the metal-alkyl bonds of CpW(NO)(CH$_2$SiMe$_3$)$_2$ to form CpW(NO)(SCH$_2$SiMe$_3$)$_2$. Ashby and Enemark have performed Fenske-Hall molecular-orbital calculations on CpMo(NO)(SPh)$_2$ to show that the
stability of the thiolate ligands may be attributed to the p\(\pi\)-d\(\pi\) interaction between the p-type orbitals on the thiolate ligands and the empty molybdenum d\(xy\) orbitals.\(^{32}\) Consistent with the molecular orbital calculations, CpMo(NO)(SPh)\(_2\) does not react with CO, PPh\(_3\), or I\(_2\).\(^{32}\)

Nitrogen analogues of the bis(alkoxo) complexes have been prepared in our group from Cp\(^*\)W(NO)Cl\(_2\) and an excess of t-butyl amine.\(^{28}\) In the same way that alkoxide ligands provide extra electron density to stabilize the bis(alkoxo) compounds, Cp\(^*\)W(NO)(NHCMe\(_3\))\(_2\) is also stable due to the electron donating ability of the amide groups.

### 2.4.5 Synthesis and Characteristic Properties of the Alkoxo Chloro Complexes, Cp\(^*\)M(NO)(OR)Cl

In order to explore the reactivity of more electron-deficient Group 6 alkoxo complexes, we decided to isolate the alkoxo chloro complexes, Cp\(^*\)M(NO)(OR)Cl, which are the intermediate organometallic species formed during conversions 2.7. The Cp\(^*\)M(NO)(OR)Cl compounds are best obtained via metathesis reactions utilizing 1 equiv of an alkoxide salt at low temperatures, i.e.

\[
\begin{array}{c}
\text{Cp}^* \text{M(NO)} \text{Cl} \quad + \quad \text{M'} \text{OR} \\
\text{Cl} \quad \text{Cl} \quad \text{N} \quad \text{O}
\end{array}
\xrightarrow{\text{THF}}
\begin{array}{c}
\text{Cp}^* \text{M(NO)} \text{Cl} \quad + \quad \text{M'Cl}
\end{array}
\]

The three such product complexes prepared during this work (2.5 - 2.7) are isolable as black to purple analytically pure needles in moderate yields (25 - 44\%). The alkoxo chloro complexes, like the bis(alkoxo) compounds, are very soluble in all common organic solvents. In contrast to complexes 2.1 - 2.4, however, the monoalkoxo species are very thermally, oxidatively and hydrolytically sensitive both as solids and in solutions.
The spectroscopic properties (Tables 2.2 - 2.3) of complexes 2.5 - 2.7 are consistent with their possessing monomeric, three-legged piano-stool molecular structures. The $v_{\text{NO}}$ bands evident in their IR spectra are higher in energy than those exhibited by the corresponding bis(alkoxo) complexes, but lower in energy than those characteristic of the dichloro starting materials. For example, the nitrosyl-stretching frequencies decrease in the order $\text{Cp}^*\text{W(NO)Cl}_2 (1630 \text{ cm}^{-1}) > \text{Cp}^*\text{W(NO)(OCMe}_3\text{)}\text{Cl} (1593 \text{ cm}^{-1}) > \text{Cp}^*\text{W(NO)(OCMe}_3\text{)}_2 (1557 \text{ cm}^{-1})$ for THF solutions of the various compounds. Such spectroscopic data indicate that the metal centers in the $\text{Cp}^*\text{M(NO)(OR)}\text{Cl}$ complexes are relatively more electron-deficient than in the analogous $\text{Cp}^*\text{M(NO)(OR)}_2$ compounds. A similar trend is observed between $\text{Cp}'\text{M(NO)R}_2$ and $\text{Cp}'\text{M(NO)(R)Cl}$ complexes. Thus, alkyl chloro complexes are markedly more Lewis acidic than their dialkyl counterparts.

Previous work in our laboratories by Dr. E. C. Phillips has shown that treatment of $\text{Cp}^*\text{M(NO)}\text{I}_2$ with MeOH results in insoluble tan powders which are thought to be $[\text{Cp}^*\text{M(NO)(OMe)}\text{I}]_2$ complexes. The mass spectral and $^1\text{H}$ NMR data of these species indicate that they are dimeric. This dimeric nature may account for the difference in their color and their solubility from the other alkoxo chloro complex isolated in this work. Dr. Phillips was not able to establish unequivocally the dimeric nature of the methoxide complexes because of their low solubility in common organic solvents. McCleverty's group were not able to determine the exact natures of $[\text{CpMo(NO)(OMe)}\text{X}]_2 (X = \text{I, Br})$ because of their low solubility. Molecular-weight determinations by the Signer method of $\text{Cp}^*\text{W(NO)(OCMe}_3\text{)}\text{Cl}$ and $\text{Cp}^*\text{W(NO)(OPh)}\text{Cl}$ in THF are unsuccessful because solutions of the alkoxo chloro complexes decompose slowly to black, cloudy mixtures.
2.4.6 Some Chemical Properties of Cp*\textit{M}(\textit{NO})(\textit{OR})\textit{Cl} Complexes

Consistent with the greater electron-deficiency at the metal centers of complexes 2.5 - 2.7, the Cp*\textit{M}(\textit{NO})(\textit{OR})\textit{Cl} complexes decompose rapidly both in solution and in the solid state when exposed to the atmosphere. Indeed, attempts to perform reactivity studies on this class of alkoxo chloro complexes has been hampered by their extreme sensitivity to air and moisture.

Upon treatment with dry O\textsubscript{2} (1 atm), compounds 2.5 - 2.7 decompose to intractable tan solids. Nevertheless, exposure to water results in compounds 2.5 and 2.7 being converted to the isolable [Cp*\textit{M}(\textit{NO})(\textit{OH})(\textit{Cl})]\textsubscript{2} species. The molybdenum and tungsten compounds may be crystallized from diethyl ether as black and brown crystals, respectively. The hydroxo complexes are formulated as dimers for several reasons. The mass spectra of complexes 2.8 and 2.9 show the parent peak of the dimer, and the $\nu_{\text{NO}}$'s are broad in the Nujol mull IR spectra of the complexes. In addition, both 2.8 and 2.9 exhibit two peaks in their Nujol-mull IR spectra between 3645 and 3625 cm\textsuperscript{-1} which are attributable to OH stretches. Finally the $^1\text{H}$ NMR spectrum of 2.9 exhibits signals attributable to two inequivalent Cp* ligands ($\delta$ 1.94 and 1.75 ppm). The molybdenum complex (2.8) is either a monomer, or a centrosymmetric dimer in solution since a single Cp* resonance is observed at $\delta$ 1.75 ppm in the $^1\text{H}$ NMR spectrum of the complex. McCleverty's group has prepared the analogous [Cp\textit{Mo}(\textit{NO})(\textit{OH})\textit{I}]\textsubscript{2} complex by hydrolysis of Cp\textit{Mo}(\textit{NO})(O\textsubscript{2}CMe)\textit{I}.$^{34}$

The monoalkoxo complexes do react with PMe\textsubscript{3} presumably to form adducts of the type Cp*\textit{M}(\textit{NO})(\textit{OR})(\textit{Cl})(\textit{PMe}_3), but these yellow adducts are only stable at low temperatures. Upon attempted work-up these adducts decompose to intractable brown solids and free PMe\textsubscript{3}. 
2.4.7 Systems Related to the Alkoxo Chloro Species

Nitrogen-containing analogues the alkoxo chloro complexes have also been prepared by K. Ross from \( \text{Cp}^*\text{M(NO)}\text{Cl}_2 \) in a two-step procedure (eq 2.10 - 2.11).

\[
\text{Cp}^*\text{Mo(No)}\text{Cl}_2 + \text{NH}_2\text{Ar} \rightarrow \text{Cp}^*\text{Mo(NO)(Cl)}_2(\text{NH}_2\text{Ar}) \quad (2.10)
\]

\[
\text{Cp}^*\text{Mo(NO)(Cl)}_2(\text{NH}_2\text{Ar}) \xrightarrow{\text{LiN(i-pr)}_2} \text{Cp}^*\text{Mo(NO)(NHAr)}\text{Cl} \quad (2.11)
\]

Alternatively these amido complexes can be made via a metathesis reaction as in eq 2.13.

\[
\text{Cp}^*\text{M(NO)}\text{Cl}_2 + \text{LiNHAr} \rightarrow \text{Cp}^*\text{M(NO)(NHAr)}\text{Cl} + \text{LiCl} \quad (2.12)
\]

The reactions of alkyl amines with \( \text{Cp}^*\text{M(NO)}\text{Cl}_2 \) proceed directly to the amido chloro complexes, \( \text{Cp}^*\text{M(NO)(NHR)}\text{Cl} \).

2.4.8 A Related Reaction with KOCMe₃

The reaction of \( \text{Cp}^*\text{W(NO)}\text{Cl}_2 \) with KOCMe₃ in the presence of \( \text{H}_2 \) (40 psig) affords the dimeric alkoxo complex 2.10. This air-sensitive complex is crystallized from Et₂O as purple needles in 25% yield.

\[
\text{Cp}^*\text{W(NO)}\text{Cl}_2 + \text{H}_2 + \text{KOCMe}_3 \rightarrow [\text{Cp}^*\text{W(NO)(OCMe}_3)_2] \quad (2.13)
\]

The IR spectrum of 2.10 as a Nujol mull exhibits a broad \( \nu_{\text{NO}} \) at 1543 cm⁻¹. The formulation of 2.10 as a dimer is based on the observation of the parent mass peak \((m/z = 844)\) in the mass spectrum of the complex and on the presence of two \( \text{Cp}^* \) resonances (δ 2.04 and 2.00 ppm) and two \( \text{C(CH}_3)_3 \) resonances (δ 1.44 and 1.26 ppm) in the \(^1\text{H NMR}\) spectrum of 2.10 in \( \text{C}_6\text{D}_6 \). The two sets of peaks in the \(^1\text{H NMR}\) result from the two isomers in which the \( \text{Cp}^* \) ligands are cis or trans to each other, i.e.,
A metal-metal bond is invoked in $[\text{Cp}^*\text{W(NO)(O} \text{CMe}_3)\text{]}_2$ to account for its apparent diamagnetism.

This type of dimer has precedent since $[\text{CpCr(NO)(OR)}\text{]}_2$ ($\text{R} = \text{Me, Et}$) dimers have been isolated previously by others in our group. In these paramagnetic chromium complexes, the heteroatom ligands bridge the two metals and there is no Cr-Cr bond. However, other complexes of the type $[\text{Cp}'\text{M(NO)X}\text{]}_2$ ($\text{M} = \text{Mo, W}$; $\text{X} = \text{OR, SR, SeR, TeR}$) and $[\text{CpCr(NO)(NHCMe}_3\text{)}\text{]}_2$ are formulated as diamagnetic, electronically saturated species with M-M bonds.

Under the conditions of the experiment outlined in Section 2.2.14, $\text{Cp}^*\text{W(NO)Cl}_2$ does not react with $\text{H}_2$ in THF until the potassium salt has been added. Consistently, it has also been shown that $\text{Cp}^*\text{W(NO)Cl}_2$ has a very low reduction potential of -750 mV (vs SCE in THF). Since $\text{Cp}^*\text{W(NO)(O} \text{CMe}_3\text{)}_2$ reacts with molecular hydrogen to form the bimetallic species described in Section 2.4.2., $\text{H}_2$ most likely reacts with the monoalkoxo species, $\text{Cp}^*\text{W(NO)(O} \text{CMe}_3\text{)}\text{Cl}$. Thus, the first step in the mechanism of reaction 2.13 is the formation of $\text{Cp}^*\text{W(NO)(O} \text{CMe}_3\text{)}\text{Cl}$ (eq 2.14).

$$\text{Cp}^*\text{W(NO)Cl}_2 + \text{KOCMe}_3 \rightarrow \text{Cp}^*\text{W(NO)(O} \text{CMe}_3\text{)}\text{Cl} + \text{KCl} \quad (2.14)$$

The subsequent reaction of $\text{Cp}^*\text{W(NO)(O} \text{CMe}_3\text{)}\text{Cl}$ with molecular hydrogen can then be envisioned to proceed in two ways. Either $\text{Cp}^*\text{W(NO)(O} \text{CMe}_3\text{)}\text{Cl}$ is reduced by $\text{H}_2$ to a radical which then couples to form $2.10$ (eq 2.15 - 2.16),
or 2.10 is produced by a bimolecular reductive elimination of \( \text{H}_2 \) from an intermediate hydride species according to equations 2.17 - 2.18.

\[
\text{Cp}^*\text{W(NO)}(\text{OCMe}_3)\text{Cl} + \text{H}_2 \rightarrow \text{Cp}^*\text{W(NO)}(\text{OCMe}_3)\text{H} + \text{HCl} \quad (2.17)
\]

\[
2 \ [\text{Cp}^*\text{W(NO)}(\text{OCMe}_3)]^* \rightarrow \ [\text{Cp}^*\text{W(NO)}(\text{OCMe}_3)]_2 \quad (2.16)
\]

I would suggest utilizing electron spin resonance (ESR) spectroscopy to determine if a radical mechanism is operative. In addition, the reaction of isolated \( \text{Cp}^*\text{W(NO)(OCMe}_3)\text{Cl} \) with \( \text{H}_2 \) would establish if the chloride is indeed the active species.

2.6 Epilogue and Future Work

The work presented in this chapter outlines the synthesis, characterization and some chemical reactivity of two classes of Group 6 alkoxo nitrosyl complexes. The 18-electron bis(alkoxo) complexes are chemically inert to a wide variety of reagents, whereas the monoalkoxo chloro species, \( \text{Cp}^*\text{M(NO)(OR)Cl} \), are highly reactive. The reactivity studies of the chloro compounds have been limited because of their air- and moisture- sensitivity. For future studies, I would recommend an examination of the reactivity of the second class of alkoxo complexes, \( \text{Cp}^*\text{M(NO)(OR)Cl} \). For example, \( \text{Cp}^*\text{M(NO)(OR)Cl} \ [R = \text{CMe}_3, \text{Ph}] \) complexes react with primary amines to afford alkoxo amido complexes, \( \text{Cp}^*\text{M(NO)(OR)(NHR)} \).

Clearly, the properties and chemical reactivity patterns of both the mono and bis(alkoxo) complexes are very different from those of the electronically unsaturated dialkyl complexes and therefore the reactivity of the alkoxo complexes with different types of reagents should be explored. Specifically, I would suggest polar species as reactants to exploit the polarity of the W-O bond. The possible reactivity patterns of these complexes will probably not proceed via
initial adduct formation since these species are electronically saturated. Investigations into the insertion reactions of CO$_2$, CS$_2$ and RNCO with the related Cp'M(NO)(OR)$_R$, CP'M(NO)(NHR)$_R$ and CP'M(NO)(NHR)(OR) systems have proven to be quite fruitful.

2.7 References and Notes

(1) Legzdins, P.; Lundmark, P. J.; Rettig, S. J. *Organometallics*, accepted for publication.


(16) The compositions of the solids with respect to their active alkoxide equivalents were established by hydrolysis of weighed solid samples and titration of the resulting solutions with 0.100 N HCl using phenolphthalein as the indicator.

(17) The mass spectum can be attributed to [Cp$^*$W(O)$_2$]$_2$-(μ-O), a common decomposition product of tungsten nitrosyl-containing complexes in our laboratories.


(19) General electrochemical experimental details are summarized in section 5.2.1. The cyclic voltammogram of 2.2 was recorded using a Pt-bead electrode in THF and 0.1 M [Bu$_4$N]PF$_6$ as the support electrolyte and SCE as the reference electrode. Scan rates ranged from 0.2 to 1.0 V s$^{-1}$.


(21) CpW(NO)(CH$_2$SiMe$_3$)$_2$ reacts with elemental sulfur in a stepwise fashion to form firstly the alkylthiolate complex CpW(NO)(SCH$_2$SiMe$_3$)(CH$_2$SiMe$_3$)$_2$, then the perthiolate species,
CpW(NO)(η²-S{S}CH₂SiMe₃)(CH₂SiMe₃). Thermolysis of the perthiolate complex results in the formation of CpW(NO)(SCH₂SiMe₃)₂. See Legzdins, P.; Rettig, S. J.; Sánchez, L. *Organometallics* 1988, 7, 2394.


(24) Crystals of 2.2 are orthorhombic of space group *Pbca* (#61); a = 23.627 (3) Å, b = 15.862 (2) Å, c = 11.009 (3) Å, V = 4126 (1) Å³, Z = 8. Dr. S. J. Rettig solved the structure using the Patterson method and full-matrix least-squares refinement procedures to R = 0.032, R_w = 0.035 for 2473 reflections with I ≥ 3σ(I).

(25) Crystals of 2.4 are orthorhombic of space group *Pnma* (#62); a = 8.758 (2) Å, b = 15.762 (1) Å, c = 16.352 (2) Å, V = 2257.3 (8) Å³, Z = 4. Dr. S. J. Rettig solved the structure using the Patterson method and full-matrix least-squares refinement procedures to R = 0.031, R_w = 0.034 for 1807 reflections with I ≥ 3σ(I).


(28) Legzdins, P; Rettig, S. J.; Ross, K. *Organometallics*, 1993, 12, 2103.


(33) Debad, J. D.; Legzdins, P.; Rettig, S. J; Veltheer, J. E. *Organometallics*, in press.


(36) The decomposition of the sample is due to a small amount of hydrolysis. See Section 2.4.6.


(40) Legzdins, P.; McNeil, W. S. unpublished observations.


(42) See section 4.4.4.4.

(43) Legzdins, P.; Ross, K. J. unpublished observations.
3.1 Introduction

During the last few years, research in the Legzdins' group has centered mainly on the synthesis and reactivity of the 16-electron dialkyl complexes Cp'M(NO)R₂.¹ The chemistry of these coordinatively and electronically unsaturated complexes is dominated by their ability to form 1:1 metal-centered adducts with Lewis bases.¹,²,³ When the Lewis base has an unsaturated link, e.g. CO, CNCMe₃, NO, these adducts often undergo intramolecular insertion of the coordinated Lewis base into the M-C σ bond.

The research direction of our group has recently moved towards other metal-heteroatom linkages. The impetus for this shift has been to compare the relative reactivity of alkyl ligands vs. amido⁴ or alkoxo ligands⁵ at the same metal center. For example, complexes such as Cp*M(NO)(R)(OR') (R, R' = alkyl or aryl) should allow for the direct comparison of R and OR ligand reactivities. This chapter describes the successful preparation and characterization of such
alkoxo alkyl complexes. Chapter 4 reports on the reaction chemistry of this class of alkoxo complexes.

The synthetic methodologies used to prepare the alkoxo alkyl compounds are described in detail since any variation of reaction conditions results in significantly different products being formed. These latter products, \([\text{Cp}^\# \text{W(NO)}(\text{CH}_2\text{SiMe}_3)][\text{Cp}^\# \text{W(O)}(\text{Cl})]\)\(_2\)(\(\mu_2-\eta^1:\eta^2-\text{NC}{\text{H}\text{SiMe}_3}\)) and \([\text{Cp}^\# \text{W(NO)}(\text{CH}_2\text{SiMe}_3)\text{Cl}][\text{Cp}^\# \text{W(O)}(\text{Cl})](\eta^2-\text{N}\{\text{H}\text{CH}_2\text{SiMe}_3}\)\(_2\)(\(\mu-N\)) are interesting organometallic bimetallic compounds in their own right. These bimetallic complexes have been isolated and characterized by conventional spectroscopic techniques as well as by X-ray crystallographic analysis. This chapter also reports some selected experiments, including a deuterium isotopic labeling study and phosphine reactions, conducted in an attempt to explain the mechanism of the reactions which led to these bimetallic complexes.

3.2 Experimental Procedures

3.2.1 Methods

The synthetic methodologies employed in this chapter are described in detail in Section 2.2.1.

3.2.2 Reagents

The organometallic dichloro complexes, \(\text{Cp}^\# \text{M(NO)}\text{Cl}_2\), were prepared and handled as described in Section 2.2.2. The preparation of \(\text{Cp}^\# \text{M(NO)}(\text{CH}_2\text{Ph})_2\) complexes \([\text{M = Mo, W}]\) and their subsequent conversion to \(\text{Cp}^\# \text{M(NO)}(\text{CH}_2\text{Ph})\text{Cl}\) have been previously reported.\(^6\,^7\)

Alkoxide salts \((\text{LiOCMe}_3, \text{NaOCMe}_3, \text{NaOPh and NaOMe})\) were prepared as described in Sections 2.3.3 - 2.3.4. \((\text{Me}_3\text{SiCH}_2)_2\text{Mg-X(dioxane)}^3\) and \((\text{PhCH}_2)_2\text{Mg-X(dioxane)}^8\) were prepared according to the published procedures. CD\(_3\)OD (MSD Isotopes) and KOEt (Aldrich) were used as received. PPh\(_3\) (Aldrich) was recrystallized from Et\(_2\)O. A 50% xylene dispersion of KH (Alfa) was washed with hexanes to remove the xylene and afford KH as a white powder. \(n\)-BuLi (1.6 M solution in hexanes, Aldrich) was diluted to 0.70 M with hexanes before use.
3.2.3 Reaction of Cp*Mo(NO)(OCMe3)Cl and (PhCH2)2Mg•X(dioxane)

A purple Et2O solution (20 mL) of Cp*Mo(NO)(OCMe3)Cl (2.5) (0.16 g, 0.50 mmol) was cannulated into a Schlenk tube containing (PhCH2)2Mg•X(dioxane) (0.50 mmol PhCH2-). The stirred reaction mixture turned red and deposited a white precipitate over the course of 1 h. After this time, the reaction mixture was filtered through Celite (2 x 5 cm) supported on a sintered glass frit. The filtrate was concentrated in vacuo, and cooled (-30 °C) to induce the crystallization of 0.12 g (62% yield) of orange crystals of Cp*Mo(NO)(CH2Ph)Cl. The spectral data of the product were identical to those of an authentic sample.

3.2.4 Reaction of Cp*Mo(NO)(OCMe3)2 and (PhCH2)2Mg•X(dioxane)

Cp*Mo(NO)(OCMe3)2 (2.1) (0.063 g, 0.15 mmol) and (PhCH2)2Mg•X(dioxane) (0.15 mmol PhCH2-) were mixed as solids in a Rotoflo pressure vessel in a glovebox. The vessel was removed from the glovebox, and THF (5 mL) was added via syringe. The orange reaction mixture was stirred overnight at 65 °C. No color change was observed, and a solution IR spectrum of the reaction mixture exhibited a single νNO (1589 cm⁻¹) corresponding to that of the starting material.

3.2.5 Preparation of Cp*M(NO)(CH2Ph)(OR) [M = Mo, R = CMe3 (3.1), Ph (3.2); M = W, R = CMe3 (3.3)]

All of these complexes were prepared in a similar manner. The synthesis of Cp*W(NO)(CH2Ph)(OCMe3) (3.3) is described in detail as a representative example.

Cp*W(NO)(CH2Ph)Cl (0.31 g, 0.65 mmol) and LiOCMe3 (0.050 g, 0.65 mmol) were intimately mixed in a Schlenk tube. Et2O (20 mL) was transferred to the tube via syringe, and the orange-red reaction mixture was stirred overnight with no apparent color change occurring. The solvent was then removed in vacuo, the remaining red residue was extracted with hexanes (2 x 20 mL), and the extracts were filtered through Celite (2 x 5 cm) supported on a medium-
porosity glass frit. The filtered solution was concentrated and cooled at -30 °C overnight to induce the precipitation of Cp*W(NO)(CH2Ph)(OCMe3) (0.33 g, 45% yield) as red needles which were collected by filtration.

Physical properties and spectroscopic data of complexes 3.1 - 3.3 are contained in Tables 3.1 - 3.3.

3.2.6 Preparation of Cp*W(NO)(CH2SiMe3)(OR) [R = CMe3 (3.4), Ph (3.5), Me (3.6), Et (3.7)]

A THF solution (30 mL) of Cp*W(NO)(CH2SiMe3)Cl9 was generated from Cp*W(NO)Cl2 (1.7 g, 4.0 mmol) and (Me3SiCH2)2Mg·X(dioxane) (4.0 mmol CH2SiMe3) in a Schlenk tube. The THF was removed from the blue reaction mixture in vacuo, and the blue residue was extracted with pentane (2 x 30 mL). The extracts were filtered through Celite (2 x 5 cm) supported on a sintered glass frit. The filtrate was divided equally into four Schlenk tubes.

To each of the blue pentane solutions11 (vNO = 1616 cm\(^{-1}\)) was added the appropriate alkoxide salt (LiOCMe3, NaOPh, NaOMe or KOEt; 1.0 mmol each, slight excess). The mixtures were stirred for 2 h and became red for R = CMe3 (vNO = 1572 cm\(^{-1}\)), Me (vNO = 1584 cm\(^{-1}\)), and Et (vNO = 1582 cm\(^{-1}\)), but purple for R = Ph (vNO = 1597, 1586 cm\(^{-1}\)). The final mixtures were filtered through Celite (2 x 5 cm) supported on sintered glass frits. The filtered solutions were then concentrated and cooled at -30 °C overnight to induce the deposition of the desired organometallic products. Cp*W(NO)(CH2SiMe3)(OCMe3) (3.4) and Cp*W(NO)(CH2SiMe3)(OEt) (3.7) were isolated as a red oils, whereas Cp*W(NO)(CH2SiMe3)(OPh) (3.5) and Cp*W(NO)(CH2SiMe3)(OMe) (3.6) were isolated as purple and red crystals, respectively.

Physical properties and spectroscopic data of complexes 3.4 - 3.7 are contained in Tables 3.1 - 3.3.
Attempts to prepare analogous cyclopentadienyl alkoxide complexes, CpM(NO)(R)(OR'), via methodology similar to that outlined in Sections 3.2.5 - 3.2.6 have been unsuccessful.

3.2.7 Preparation of \([\text{Cp}^*\text{W(NO)(CH}_2\text{SiMe}_3)]\text{[Cp}^*\text{W(Cl)(O)}(\mu_2-\eta^1:2\text{-NC}\{\text{H}\text{SiMe}_3}\text{]}\text{]} \quad (3.8)\)

A pentane solution of \(\text{Cp}^*\text{W(NO)(CH}_2\text{SiMe}_3)\text{Cl} \) (20 mL) (generated from \(\text{Cp}^*\text{W(NO)Cl}_2 \) (0.42 g, 1.0 mmol) and \((\text{Me}_3\text{SiCH}_2)_2\text{Mg} \times \text{dioxane} \) (1.0 mmol CH\(_2\text{SiMe}_3^-\)) as in Section 3.2.6) was cooled to -20 °C. This solution \((v_{\text{NO}} = 1616 \text{ cm}^{-1})\) was then cannulated into a Rotoflo pressure vessel containing \(\text{KOCH}_3 \) (0.11 g, 1.0 mmol). The heterogeneous reaction mixture was allowed to warm to room temperature and was stirred overnight. After this time, the reaction mixture consisted of a red-purple solution \((v_{\text{NO}} = 1624, 1570 \text{ cm}^{-1})\) and an off-white precipitate. Filtration of the mixture through Celite \((2 \times 3 \text{ cm})\) afforded a red-purple filtrate. The filtrate was concentrated in vacuo and maintained at -30 °C for several days. Purple needles of \([\text{Cp}^*\text{W(NO)(CH}_2\text{SiMe}_3)]\text{[Cp}^*\text{W(Cl)(O)}(\mu_2-\eta^1:2\text{-NC}\{\text{H}\text{SiMe}_3}\text{]}\text{]} \quad (3.8) \) (0.042 g, 9.3% yield) formed and were separated from the mother liquor by cannulation. The physical properties and spectroscopic data for complex 3.8 are collected in Tables 3.1 - 3.3.

3.2.8 Preparation of \([\text{Cp}^*\text{W(NO)(CH}_2\text{SiMe}_3)\text{Cl]}\text{[Cp}^*\text{W(Cl)(O)}(\eta^2-N\{\text{H}\text{CH}_2\text{SiMe}_3}\text{]})(\mu-N) \quad (3.9)\)

A cooled \((-20 °C)\) pentane solution of \(\text{Cp}^*\text{W(NO)(CH}_2\text{SiMe}_3)\text{Cl} \) (20 mL) (generated from \(\text{Cp}^*\text{W(NO)Cl}_2 \) (0.42 g, 1.0 mmol) and \((\text{Me}_3\text{SiCH}_2)_2\text{Mg} \times \text{dioxane} \) (1.0 mmol CH\(_2\text{SiMe}_3^-\)) as in Section 3.2.6) was cannulated into a Rotoflo pressure vessel containing \(\text{KOCH}_3 \) (0.070 g, 1.0 mmol). The heterogeneous reaction mixture was stirred and allowed to warm slowly to room temperature. Over the course of 5 h, the reaction mixture turned from blue to orange, and an orange precipitate formed. The reaction mixture was then taken to dryness in vacuo. The residue was extracted with pentane \((2 \times 20 \text{ mL})\). The combined extracts were filtered through Celite \((2 \times 3 \text{ cm})\) supported on a sintered glass frit, and the yellow filtrate was collected and
concentrated. Cooling the concentrated pentane solution at -30 °C overnight resulted in the crystallization of \( \text{Cp}^*\text{W(0)}_2(\text{CH}_2\text{SiMe}_3) \) (0.11 g, 0.25 mmol, 31% yield based on \( \text{Cp}^*\text{W(NO)Cl}_2 \)).

The remaining residue was also extracted with Et\(_2\)O (2 x 20 mL). The Et\(_2\)O extract was filtered through Celite (2 x 3 cm) supported on a sintered glass frit, and the filtrate was collected and concentrated. Maintaining the saturated orange solution at -30 °C overnight resulted in the deposition of \([\text{Cp}^*\text{W(NO)(CH}_2\text{SiMe}_3)]\text{Cl}[\text{Cp}^*\text{W(Cl)}(\eta^2-\text{N(O)}(\text{H})\text{CH}_2\text{SiMe}_3)]-(\mu-\text{N})\) (3.9) (0.097 g, 0.10 mmol, 13% yield based on \( \text{Cp}^*\text{W(NO)Cl}_2 \)) as orange needles. Physical properties and spectroscopic data of complex 3.9 are contained in Tables 3.1 - 3.3.

This reaction was also performed on an NMR scale to determine the exact ratio of product complexes. For example, \( \text{Cp}^*\text{W(NO)(CH}_2\text{SiMe}_3)(\text{OCMe}_3) \) (0.02 g, 0.04 mmol) and KOCMe (0.003 g, 0.04 mmol) were mixed as solids in a Rotoflo pressure vessel. Pentane (5 mL) was added via syringe, and the atmosphere of the vessel was removed. Overnight, the stirred reaction mixture turned from blue to yellow. The reaction mixture was then taken to dryness in vacuo. In a glovebox, the yellow residue was dissolved in \( \text{C}_6\text{D}_6 \), and the resulting amber-yellow solution was filtered through Celite (6 x 20 mm). The filtrate was collected in an NMR tube, and its \(^1\text{H} \text{NMR} \) spectrum exhibited resonances attributable to only \( \text{Cp}^*\text{W(O)(CH}_2\text{CMe}_3) \) and complex 3.9 in a 1:0.6 ratio.

### 3.2.9 Reaction of \( \text{Cp}^*\text{W(NO)(CH}_2\text{SiMe}_3)(\text{OCMe}_3) \) (3.4) with KOCMe

A red pentane solution of \( \text{Cp}^*\text{W(NO)(CH}_2\text{SiMe}_3)(\text{OCMe}_3) \) (20 mL) (1.0 mmol prepared as in Section 3.2.6) was cannulated into a Rotoflo vessel containing KOCMe (0.11 g, 1.0 mmol). The reaction mixture was stirred overnight, and the mixture was filtered through Celite (2 x 5 cm) supported on a sintered glass frit. The red filtrate was reduced in vacuo to obtain a red oil. The IR spectrum of this oil exhibited one nitrosyl-stretching frequency attributable to \( \text{Cp}^*\text{W(NO)(CH}_2\text{SiMe}_3)(\text{OCMe}_3) \) (3.4). In addition, the \(^1\text{H} \text{NMR} \) spectrum of the oil in \( \text{C}_6\text{D}_6 \) revealed 3.4 to be the only proton-containing species present.
3.2.10 Reaction of Cp*W(NO)(CH₂SiMe₃)Cl with KOClMe in the presence of PPh₃

A pentane solution of Cp*W(NO)(CH₂SiMe₃)Cl (20 mL) (1.0 mmol generated as in Section 3.2.6) was cannulated into a flask containing KOClMe (0.11 g, 1.0 mmol) and PPh₃ (0.36 g, 1.5 mmol). The reaction mixture turned red-purple within 5 min. After being stirred for 2 h, the reaction mixture was filtered through a Celite plug (2 x 5 cm) supported on a sintered glass frit. The red-brown pentane filtrate was concentrated and cooled to induce the crystallization of PPh₃ (0.19 g). The mother liquor was further concentrated to induce the precipitation of 0.040 g of [Cp*W(NO)(CH₂SiMe₃)][Cp*W(Cl)(O)]-(μ₂-η¹:η²-NH₂·NH₂·H₂O)SiMe₃ (3.8). The Celite plug was also washed with Et₂O (2 x 10 mL), and the purple Et₂O filtrate was collected and concentrated. A further 0.11 g of PPh₃ (83% total recovered yield) and 0.060 g of 3.8 (22% total yield) was isolated from this solution.

3.2.11 Preparation of Cp*W(NO)(CH₂SiMe₃)(Cl)(PMe₃) (3.10)

A pentane solution of Cp*W(NO)(CH₂SiMe₃)Cl (20 mL) (2.0 mmol generated as in Section 3.2.6) was frozen in liquid N₂, and excess PMe₃ was vacuum transferred onto the reaction mixture. As the reaction mixture warmed to room temperature, it turned yellow and deposited a yellow precipitate. The mixture was taken to dryness in vacuo, and the remaining yellow residue was washed with pentane (2 x 5 mL) and then dissolved in Et₂O (20 mL). This Et₂O solution was filtered through Celite (2 x 3 cm), and hexanes (5 mL) were added to the filtrate. The solution was then concentrated until the first signs of crystallization were evident. The concentrated solution was maintained at -30 °C to induce the crystallization of Cp*W(NO)(CH₂SiMe₃)(Cl)(PMe₃) (3.10) (0.63 g, 58% yield) as golden flakes. Physical properties and spectroscopic data of complex 3.10 are contained in Tables 3.1 - 3.3.
3.2.12 Reaction of Cp*W(NO)(CH₂SiMe₃)(Cl)(PMᵉ₃) (3.10) with KOCMe₃

Cp*W(NO)(CH₂SiMe₃)(Cl)(PMᵉ₃) (3.10) (0.27 g, 0.49 mmol) and KOCMe₃ (0.055 g, 0.49 mmol) were mixed as solids in a Rotoflo vessel, and pentane (20 mL) was added via syringe. The pale yellow stirred reaction mixture became red over the course of 2 days. The reaction solution was taken to dryness in vacuo, and the remaining red-brown oil was redissolved in pentane (15 mL). The pentane solution was filtered through Celite (2 x 5 cm) supported on a sintered glass frit. The filtrate was taken to dryness in vacuo to yield a red oil which was identified as Cp*W(NO)(CH₂SiMe₃)(OCMe₃) (3.4) from comparison of its spectral data to those of an authentic sample.

3.2.13 Reaction of Cp*W(NO)(CH₂SiMe₃)(Cl)(PMᵉ₃) (3.10) with KOMe

Cp*W(NO)(CH₂SiMe₃)(Cl)(PMᵉ₃) (0.22 g, 0.40 mmol) and KOMe (0.028 g, 0.40 mmol) were mixed as solids in a Rotoflo vessel, and pentane (20 mL) was added via syringe. The reaction mixture was stirred for 2 days, and over this time there was no color change. The reaction mixture was taken to dryness in vacuo, and the remaining residue was extracted with pentane (20 mL). The extract was filtered through Celite (2 x 5 cm). The yellow filtrate was concentrated and cooled to induce the crystallization of 0.18 g of the starting material, Cp*W(NO)(CH₂SiMe₃)(Cl)(PMᵉ₃) (3.10) (82% recovered yield).

3.2.14 Reaction of Cp*W(NO)(CH₂SiMe₃)Cl with KOCD₃

An excess of CD₃OD (0.5 mL) in Et₂O (10 mL) was slowly cannulated into a Schlenk tube containing KH (0.040 g, 1.0 mmol). As the addition proceeded, the KH dissolved and a gas evolved. The solvent was then removed in vacuo to afford a white solid which was washed with pentane (2 x 10 mL). Cp*W(NO)(CH₂SiMe₃)Cl (1.0 mmol, generated as in Section 3.2.6) in pentane (20 mL) was cannulated onto the white solid, which was assumed to be KOCD₃ (1.0 mmol). The heterogeneous reaction mixture was stirred overnight, and the color of the
mixture turned red. The mixture was then filtered through Celite (2 x 5 cm) supported on a sintered glass frit. The red pentane filtrate was concentrated and cooled to induce the crystallization of 0.040 g (9.1% yield based on Cp*W(NO)Cl2) of Cp*W(O)2(CH2SiMe3) as colorless crystals. The mother liquor was then taken to dryness to obtain Cp*W(NO)(CH2SiMe3)(OCD3) (3.6-d3) a red oil (~0.2 g, ~40% yield).

Data for Cp*W(NO)(CH2SiMe3)(OCD3). IR (Nujol mull): vC-D 2056, vNO 1574, vSi-C 1244, 1258 cm⁻¹. ¹H NMR (C6D6): δ 1.58 (s, 15 H, C5(CH3)5), 0.91 (d, 1 H, CHA Hß, JHH = 11.7 Hz), 0.84 (d, 1 H, CHAHß, JHH = 11.7 Hz), 0.34 (s, 9 H, Si(CH3)3).

This reaction was also performed on an NMR scale to determine the exact ratio of product complexes. For example, Cp*W(NO)(CH2SiMe3)Cl (0.17 g, 0.36 mmol) and KOCD3 (0.014 g, 0.36 mmol) were mixed as solids in a Rotoflo pressure vessel. Pentane (5 mL) was added via syringe, and the vessel was evacuated. Overnight, the stirred reaction mixture turned from blue to orange-red. The reaction mixture was then taken to dryness in vacuo. In a glovebox, the red residue was dissolved in C6D6, and the resulting red solution was filtered through Celite (6 x 20 mm). The filtrate was collected in an NMR tube, and its ¹H NMR spectrum exhibited resonances attributable to only Cp*W(O)2(CH2SiMe3) and Cp*W(NO)(CH2SiMe3)(OCD3) (3.6-d3) in a 1:5 ratio.

### 3.3 Characterization Data

#### Table 3.1. Numbering Scheme, Color, Yield and Elemental Analysis Data for Complexes 3.1 - 3.10

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<th>complex</th>
<th>compd no.</th>
<th>color</th>
<th>anal. found (calcd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp*Mo(NO)(CH2Ph)(OCMe3)</td>
<td>3.1</td>
<td>red (56)</td>
<td>C: 59.49 (59.29)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H: 7.52 (7.34)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>N: 3.31 (3.29)</td>
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<tr>
<td>Cp*Mo(NO)(CH2Ph)(OPh)</td>
<td>3.2</td>
<td>red (39)</td>
<td>C: 62.22 (62.02)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>H: 6.03 (6.11)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>N: 3.29 (3.14)</td>
</tr>
<tr>
<td>Cp*W(NO)(CH2Ph)(OCMe3)</td>
<td>3.3</td>
<td>red (45)</td>
<td>C: 49.05 (49.14)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H: 6.05 (6.09)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>N: 2.70 (2.73)</td>
</tr>
<tr>
<td>Cp*W(NO)(CH2SiMe3)(OCMe3)</td>
<td>3.4</td>
<td>red oil (~30)</td>
<td>C: 41.41 (42.44)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H: 6.73 (6.92)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>N: 2.87 (2.75)</td>
</tr>
<tr>
<td>Compd no.</td>
<td>MS, m/z&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Temp, °C</td>
<td>IR, cm&lt;sup&gt;−1&lt;/sup&gt; (Nujol)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>VN O</td>
</tr>
<tr>
<td>3.1</td>
<td>427 [P&lt;sup&gt;+&lt;/sup&gt;]</td>
<td>120</td>
<td>1596, 1586&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>3.2</td>
<td>447 [P&lt;sup&gt;+&lt;/sup&gt;]</td>
<td>120</td>
<td>1595, 1578&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>3.3</td>
<td>513 [P&lt;sup&gt;+&lt;/sup&gt;]</td>
<td>100</td>
<td>1593, 1557&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>3.4</td>
<td>509 [P&lt;sup&gt;+&lt;/sup&gt;]</td>
<td>120</td>
<td>1563</td>
</tr>
<tr>
<td>3.5</td>
<td>529 [P&lt;sup&gt;+&lt;/sup&gt;]</td>
<td>100</td>
<td>1584, 1545&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>3.6</td>
<td>467 [P&lt;sup&gt;+&lt;/sup&gt;]</td>
<td>80</td>
<td>1578</td>
</tr>
<tr>
<td>3.7</td>
<td>481 [P&lt;sup&gt;+&lt;/sup&gt;]</td>
<td>120</td>
<td>1566</td>
</tr>
<tr>
<td>3.8</td>
<td>879&lt;sup&gt;d&lt;/sup&gt;</td>
<td>120</td>
<td>1545</td>
</tr>
<tr>
<td>3.9</td>
<td>820&lt;sup&gt;d&lt;/sup&gt;</td>
<td>100</td>
<td>1571</td>
</tr>
<tr>
<td>3.10</td>
<td>525&lt;sup&gt;d&lt;/sup&gt;</td>
<td>100</td>
<td>1570, 1549</td>
</tr>
</tbody>
</table>

<sup>a</sup> m/z values are for the highest intensity peak of the calculated isotopic cluster, i.e. <sup>98</sup>Mo and <sup>184</sup>W.

<sup>b</sup> Probe temperatures.

<sup>c</sup> ν<sub>C=C</sub> are also observed in this region.

<sup>d</sup> The highest m/z peak reported is not assignable.

<sup>e</sup> ν<sub>W=O</sub>
Table 3.3. $^1$H and $^{13}$C($^1$H) NMR Data for Complexes 3.1 - 3.10 in C$_6$D$_6$

<table>
<thead>
<tr>
<th>compd no.</th>
<th>$^1$H NMR (δ, ppm)</th>
<th>$^{13}$C($^1$H) NMR (δ, ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.42 (d, 2H, o-ArH, $^2$J$_{HH}$ = 8.4 Hz)</td>
<td>147.3 (ipso C)</td>
<td></td>
</tr>
<tr>
<td>7.15 (t, 2H, m-ArH, $^2$J$_{HH}$ = 12.0 Hz)</td>
<td>129.8, 128.4, 124.2 (CH$_2$C$_6$H$_5$)</td>
<td></td>
</tr>
<tr>
<td>6.98 (t, 1H, p-ArH, $^2$J$_{HH}$ = 10.2 Hz)</td>
<td>112.8 (C$_5$(CH$_3$)$_5$)</td>
<td></td>
</tr>
<tr>
<td>2.86 (d, 1H, CH$_A$CH$<em>B$, $^2$J$</em>{HH}$ = 8.4 Hz)</td>
<td>83.0 (OC(CH$_3$)$_3$)</td>
<td></td>
</tr>
<tr>
<td>2.77 (d, 1H, CH$_A$CH$<em>B$, $^2$J$</em>{HH}$ = 8.4 Hz)</td>
<td>50.0 (CH$_2$C$_6$H$_5$)</td>
<td></td>
</tr>
<tr>
<td>1.59 (s, 15H, C$_5$(CH$_3$)$_5$)</td>
<td>32.0 (OC(CH$_3$)$_3$)</td>
<td></td>
</tr>
<tr>
<td>1.10 (s, 9H, OC(CH$_3$)$_3$)</td>
<td>9.7 (C$_5$(CH$_3$)$_5$)</td>
<td></td>
</tr>
<tr>
<td>3.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.3 - 6.8 (m, 10H, Ar-H)</td>
<td>167.6, 134.1, 130.2, 128.9, 128.8, 119.9, 118.6 (aryl C)</td>
<td></td>
</tr>
<tr>
<td>3.42 (d, 1H, CH$_A$CH$<em>B$, $^2$J$</em>{HH}$ = 6.0 Hz)</td>
<td>112.3 (C$_5$(CH$_3$)$_5$)</td>
<td></td>
</tr>
<tr>
<td>2.59 (d, 1H, CH$_A$CH$<em>B$, $^2$J$</em>{HH}$ = 6.0 Hz)</td>
<td>53.9 (CH$_2$C$_6$H$_5$)</td>
<td></td>
</tr>
<tr>
<td>1.58 (s, 15H, C$_5$(CH$_3$)$_5$)</td>
<td>9.8 (C$_5$(CH$_3$)$_5$)</td>
<td></td>
</tr>
<tr>
<td>3.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.47 (d, 2H, o-ArH, $^2$J$_{HH}$ = 8.7 Hz)</td>
<td>147.4 (ipso C)</td>
<td></td>
</tr>
<tr>
<td>7.20 (t, 2H, m-ArH, $^2$J$_{HH}$ = 7.5 Hz)</td>
<td>129.6, 128.0, 124.0 (CH$_2$C$_6$H$_5$)</td>
<td></td>
</tr>
<tr>
<td>6.98 (t, 1H, p-ArH, $^2$J$_{HH}$ = 7.2 Hz)</td>
<td>111.8 (C$_5$(CH$_3$)$_5$)</td>
<td></td>
</tr>
<tr>
<td>2.76 (d, 1H, CH$_A$CH$<em>B$, $^2$J$</em>{HH}$ = 11.2 Hz)</td>
<td>83.7 (OC(CH$_3$)$_3$)</td>
<td></td>
</tr>
<tr>
<td>2.64 (d, 1H, CH$_A$CH$<em>B$, $^2$J$</em>{HH}$ = 11.2 Hz)</td>
<td>46.0 (CH$_2$C$_6$H$_5$)</td>
<td></td>
</tr>
<tr>
<td>1.62 (s, 15H, C$_5$(CH$_3$)$_5$)</td>
<td>31.8 (OC(CH$_3$)$_3$)</td>
<td></td>
</tr>
<tr>
<td>1.08 (s, 9H, OC(CH$_3$)$_3$)</td>
<td>9.6 (C$_5$(CH$_3$)$_5$)</td>
<td></td>
</tr>
<tr>
<td>3.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.65 (s, 15H, C$_5$(CH$_3$)$_5$)</td>
<td>112.5 (C$_5$(CH$_3$)$_5$)</td>
<td></td>
</tr>
<tr>
<td>1.40 (s, 9H, OC(CH$_3$)$_3$)</td>
<td>83.2 (OC(CH$_3$)$_3$)</td>
<td></td>
</tr>
<tr>
<td>0.81 (d, 1H, CH$_A$CH$<em>B$, $^2$J$</em>{HH}$ = 12.9 Hz)</td>
<td>33.0 (OC(CH$_3$)$_3$)</td>
<td></td>
</tr>
<tr>
<td>0.49 (s, 9H, Si(CH$_3$)$_3$)</td>
<td>27.4 (CH$_2$)</td>
<td></td>
</tr>
<tr>
<td>-0.24 (d, 1H, CH$_A$CH$<em>B$, $^2$J$</em>{HH}$ = 12.9 Hz)</td>
<td>9.9 (C$_5$(CH$_3$)$_5$)</td>
<td></td>
</tr>
<tr>
<td>0.35 (s, 9H, Si(CH$_3$)$_3$)</td>
<td>3.1 (Si(CH$_3$)$_3$)</td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.28 (d, 2H, o-ArH, $^2$J$_{HH}$ = 7.5 Hz)</td>
<td>129.5, 123.0, 118.2, 100.3 (CH$_2$C$_6$H$_5$)</td>
<td></td>
</tr>
<tr>
<td>7.18 (t, 2H, m-ArH, $^2$J$_{HH}$ = 8.4 Hz)</td>
<td>111.9 (C$_5$(CH$_3$)$_5$)</td>
<td></td>
</tr>
<tr>
<td>6.84 (t, 1H, p-ArH, $^2$J$_{HH}$ = 6.9 Hz)</td>
<td>44.4 (CH$_2$)</td>
<td></td>
</tr>
<tr>
<td>1.60 (s, 15H, C$_5$(CH$_3$)$_5$)</td>
<td>9.9 (C$_5$(CH$_3$)$_5$)</td>
<td></td>
</tr>
<tr>
<td>0.25 (s, 9H, Si(CH$_3$)$_3$)</td>
<td>2.0 (Si(CH$_3$)$_3$)</td>
<td></td>
</tr>
<tr>
<td>3.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.70 (s, 3H, OCH$_3$)</td>
<td>111.7 (C$_5$(CH$_3$)$_5$)</td>
<td></td>
</tr>
<tr>
<td>1.59 (s, 15H, C$_5$(CH$_3$)$_5$)</td>
<td>70.4 (OC(CH$_3$)$_3$)</td>
<td></td>
</tr>
<tr>
<td>0.92 (d, 1H, CH$_A$CH$<em>B$, $^2$J$</em>{HH}$ = 12.0 Hz)</td>
<td>35.5 (CH$_2$)</td>
<td></td>
</tr>
<tr>
<td>0.84 (d, 1H, CH$_A$CH$<em>B$, $^2$J$</em>{HH}$ = 12.0 Hz)</td>
<td>9.5 (C$_5$(CH$_3$)$_5$)</td>
<td></td>
</tr>
<tr>
<td>0.35 (s, 9H, Si(CH$_3$)$_3$)</td>
<td>2.2 (Si(CH$_3$)$_3$)</td>
<td></td>
</tr>
</tbody>
</table>
### 3.4 Results and Discussion

Dr. E. C. Phillips of our laboratories previously attempted to prepare alkoxo alkyl complexes by treating dialkyl complexes with alcohols (eq 3.1).

$$\text{Cp'M(NO)R}_2 + \text{R'OH} \rightarrow \text{Cp'M(NO)(R)(OR')} + \text{RH} \quad (3.1)$$

| 3.7 | 4.93 (q, 2H, OCH$_2$CH$_3$, $^3J_{HH} = 6.9$ Hz) | 111.8 (C$_5$(CH$_3$)$_3$) |
|     | 1.53 (s, 15H, C$_5$(CH$_3$)$_3$) | 77.9 (OCH$_2$CH$_3$) |
|     | 1.17 (t, 3H, OCH$_2$CH$_3$, $^3J_{HH} = 6.9$ Hz) | 34.0 (WCH$_2$, $^4J_{WC} = 55.0$ Hz) |
|     | 0.76 (d, 2H, CH$_2$SiMe$_3$, $^2J_{HH} = 2.4$ Hz) | 20.7 (OCH$_2$CH$_3$) |
|     | 0.50 (s, 9H, Si(CH$_3$)$_3$) | 9.7 (C$_5$(CH$_3$)$_3$) |
|     | 1.98 (s, 15H, C$_5$(CH$_3$)$_3$) | 2.2 (Si(CH$_3$)$_3$) |
| 3.8 | 2.64 (s, 1H, CH) | 117.0 (C$_5$(CH$_3$)$_3$) |
|     | 1.70 (s, 15H, C$_5$(CH$_3$)$_3$) | 111.2 (C$_5$(CH$_3$)$_3$) |
|     | 1.68 (d, CH$_A$H$_B$) | 75.2 (CH) |
|     | 1.65 (s, 15H, C$_5$(CH$_3$)$_3$) | 44.1 (CH$_2$) |
|     | 0.68 (s, 9H, CHSi(CH$_3$)$_3$) | 11.1 (C$_5$(CH$_3$)$_3$) |
|     | 0.40 (d, CH$_A$H$_B$) | 10.4 (C$_5$(CH$_3$)$_3$) |
|     | 0.40 (s, 9H, Si(CH$_3$)$_3$) | 4.6 (Si(CH$_3$)$_3$) |
|     | 1.86 (s, 15H, C$_5$(CH$_3$)$_3$) | 1.6 (Si(CH$_3$)$_3$) |

| 3.9 | 9.50 (dd, 1H, NH, $^3J_{HH} = 5.4$ Hz, $^3J_{HH} = 6.6$ Hz) | 115.1 (C$_5$(CH$_3$)$_3$) |
|     | 2.40 (dd, 1H, N-CH$_A$H$_B$Si(CH$_3$)$_3$, $^3J_{HH} = 5.4$ Hz, $^2J_{HH} = 14.6$ Hz) | 105.5 (C$_5$(CH$_3$)$_3$) |
|     | 1.90 (s, 15H, C$_5$(CH$_3$)$_3$) | 40.1 (CH$_2$) |
|     | 1.76 (s, 15H, C$_5$(CH$_3$)$_3$) | 28.2 (CH$_2$) |
|     | 1.19 (d, 1H, W-CH$_A$H$_B$Si(CH$_3$)$_3$, $^2J_{HH} = 9.8$ Hz, $^2J_{WH} = 3.9$ Hz) | 6.1 (C$_5$(CH$_3$)$_3$) |
|     | 0.69 (s, 9H, Si(CH$_3$)$_3$) | 5.6 (C$_5$(CH$_3$)$_3$) |
|     | 0.10 (s, 9H, Si(CH$_3$)$_3$) | 0.3 (Si(CH$_3$)$_3$) |
|     | 0.45 (d, 1H, W-CH$_A$H$_B$Si(CH$_3$)$_3$, $^2J_{HH} = 9.8$ Hz) | -6.7 (Si(CH$_3$)$_3$) |

| 3.10$^d$ | 1.53 (s, 15H, C$_5$(CH$_3$)$_3$) | 108.6 (C$_5$(CH$_3$)$_3$) |
|         | 1.13 (d, 9H, P(CH$_3$)$_3$, $^2J_{HP} = 9.6$ Hz) | 26.5 (d, CH$_2$, $^2J_{CP} = 8.3$ Hz) |
|         | 0.58 (s, 9H, Si(CH$_3$)$_3$) | 12.1 (d, P(CH$_3$)$_3$, $^1J_{CP} = 29.7$ Hz) |
|         | 0.34 (d, 1H, CH$_A$H$_B$, $^2J_{HH} = 10.8$ Hz) | 9.9 (C$_5$(CH$_3$)$_3$) |
|         | -0.33 (dd, 1H, CH$_A$H$_B$, $^2J_{HH} = 10.8$ Hz, $^3J_{HP} = 2.4$ Hz) | 4.4 (Si(CH$_3$)$_3$) |

$^a$ The signals attributable to CH$_2$Si(CH$_3$)$_3$ were not observed.

$^b$ Signal was assigned using a COSY spectrum of the sample.

$^c$ The signal attributable to N-CH$_A$H$_B$Si(CH$_3$)$_3$ was not observed.

$^d$ The $^{31}$P($^1$H) NMR ($81.015$ MHz) spectrum of 3.10 in C$_6$D$_6$ exhibited a signal at $6.88$ ppm ($^1J_{PW} = 191$ Hz) due to coordinated PMe$_3$. 

---

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Signal was assigned using a COSY spectrum of the sample.

The signal attributable to N-CH$_A$H$_B$Si(CH$_3$)$_3$ was not observed.

The $^{31}$P($^1$H) NMR ($81.015$ MHz) spectrum of 3.10 in C$_6$D$_6$ exhibited a signal at $6.88$ ppm ($^1J_{PW} = 191$ Hz) due to coordinated PMe$_3$. 

---

3.4 Results and Discussion

Dr. E. C. Phillips of our laboratories previously attempted to prepare alkoxo alkyl complexes by treating dialkyl complexes with alcohols (eq 3.1).
$^1$H NMR spectra of these NMR-scale reaction mixtures exhibited signals which were consistent with the alkoxo alkyl complexes $\text{Cp}^*\text{W(NO)}(\text{CH}_2\text{Ph})(\text{OMe})$, $\text{Cp}'\text{W(NO)}(\text{CH}_2\text{SiMe}_3)(\text{OMe})$, $\text{CpW(NO)}(\text{CH}_2\text{SiMe}_3)(\text{OCMe}_3)$ and $\text{CpW(NO)}(\text{CH}_2\text{SiMe}_3)(\text{OC}_6\text{H}_4-p\text{-Me})$. However, attempts to isolate these alkoxo alkyl complexes were unsuccessful. From these experiments it was concluded that alkoxo alkyl complexes were synthetizable, but not isolable, under the experimental conditions depicted in equation 3.1. I therefore set out to prepare these complexes by a different synthetic route.

3.4.1 Synthesis of Alkoxo Alkyl Complexes

Three different routes to preparing alkoxo alkyl complexes can be envisioned as summarized in Scheme 3.1.

Scheme 3.1
The first route to the preparation of alkoxo alkyl complexes involves the metathesis of a chloride ligand for an alkyl group. This type of reactivity has precedent in the literature, as the \([\text{HB}(3,5-\text{Me}_2\text{C}_3\text{HN}_2)_2]\text{Ti(OR)}\text{Cl}_2\) species will react with Grignard reagents to form alkoxo dialkyl complexes. However, treatment of \(\text{Cp}^*\text{Mo(NO)(OCMe}_3\text{)}\text{Cl}\) with \((\text{PhCH}_2)_2\text{Mg.X(dioxane)}\) results in the production of the 18-electron \(\text{Cp}^*\text{Mo(NO)(CH}_2\text{Ph)}\text{Cl}\) complex and not the desired \(\text{Cp}^*\text{Mo(NO)(OCMe}_3\text{)}(\text{CH}_2\text{Ph})\) species (eq 3.2).

\[
\text{Cp}^*\text{Mo(NO)(OCMe}_3\text{)}\text{Cl} \xrightarrow{(\text{PhCH}_2)_2\text{Mg}} \text{Cp}^*\text{Mo(NO)(CH}_2\text{Ph)}\text{Cl}
\]  

(3.2)

The \(\text{Et}_2\text{O}\) reaction mixture turns from the distinctive purple color of the precursor monoalkoxo complex to orange, characteristic of \(\text{Cp}^*\text{Mo(NO)(CH}_2\text{Ph)}\text{Cl}\), over the course of 1 h. Reaction 3.2 is the result of metathesis of an alkoxide ligand rather than a halide ligand, the driving force likely being the formation of a very strong magnesium-oxygen bond. This type of reactivity has precedent in the literature and, in fact, metathesis of alkoxide ligands is often used to prepare alkyl complexes in systems where the metal halide complex is prone to reduction by Grignard reagents.

Since reaction 3.2 demonstrates that alkoxo groups can be replaced by alkyl groups via a metathesis reaction, I attempted to utilize this type of reactivity to prepare alkyl alkoxo complexes (cf. route 2 of Scheme 3.1). Unfortunately, no reaction occurs between \(\text{Cp}^*\text{Mo(NO)(OCMe}_3\text{)}_2\) and \((\text{PhCH}_2)_2\text{Mg.X(dioxane)}\) in THF overnight, even at elevated temperatures.

\[
\text{Cp}^*\text{Mo(NO)(OCMe}_3\text{)}_2 \xrightarrow{(\text{PhCH}_2)_2\text{Mg}} \text{No Reaction}
\]  

(3.3)

No color changes are observed, and the solution IR spectra of aliquots of the reaction mixture exhibit bands attributable to only the starting material. It has been demonstrated (Chapter 2) that the electronically saturated bis(alkoxo) complexes are extremely stable towards a number of reagents due to \(\pi\)-electron donation from the alkoxo groups, and so this lack of reactivity is not overly surprising. The alkoxo chloro species do react with Grignard reagents (eq 3.2),
presumably because the chloro complexes are less sterically crowded and/or less electron rich than the bis(alkoxo) complexes.

The third route envisioned to alkyl alkoxo complexes is an alkoxide for chloride metathesis reaction. Alkoxo alkyl complexes, Cp\(^*\)M(NO)(R)(OR') (3.1 - 3.7), are successfully prepared by treating the appropriate alkyl chloro precursor with an alkali metal alkoxide salt.

\[
\begin{align*}
\text{M} & \quad \text{R} \\
\text{N} & \quad \text{O} \\
\text{Cl} & \quad - \text{M'}\text{Cl}
\end{align*}
\]

Reaction 3.4 is conducted in pentane or Et\(_2\)O. Normally, metathesis reactions are performed in polar solvents such as THF in order to stabilize ionic intermediates. However, if reaction 3.4 is conducted in THF, the only products are intractable amber oils, and no alkoxo alkyl species are formed. The limiting factor in preparing this family of alkoxo compounds by metathesis reactions (eq 3.4) is the availability of the requisite alkyl chloro precursors. Until very recently\(^{16}\), only the benzyl chloro\(^7\) and trimethylsilylmethyl chloro\(^9,10\) complexes, Cp\(^*\)M(NO)(R)Cl [M = Mo, R = CH\(_2\)Ph; M = W, R = CH\(_2\)Ph, CH\(_2\)SiMe\(_3\)] were available. Therefore, the seven alkoxo alkyl complexes prepared during this work have been made from these starting materials. LiOCMe\(_3\), NaOCMe\(_3\), NaOPh, NaOMe and KOEt can be used as alkoxylation reagents. The potassium alkoxide salts, KOCMe\(_3\) and KOMe cannot be used since they do not afford the desired alkoxo alkyl complexes (Section 3.4.4).

The desired organometallic products are isolable from reactions 3.4 in yields that range from 20 - 67% (Table 3.1). The low isolated yields of complexes 3.4, 3.6 and 3.7 may be attributed to their high solubility in pentane. Of the complexes 3.1 - 3.7, Cp\(^*\)W(NO)(CH\(_2\)SiMe\(_3\))(OCMe\(_3\)) (3.4) and Cp\(^*\)W(NO)(CH\(_2\)SiMe\(_3\))(OEt) (3.7) are isolated as red oils. Complex 3.6 is thermally sensitive as a solid, its crystals undergoing decomposition to a brown oil if left at room temperature overnight.
3.4.2 Characterization of Alkoxo Alkyl Complexes

The spectroscopic properties of complexes 3.1 - 3.7 are collected in Tables 3.2 and 3.3. In these systems, the nitrosyl-stretching frequency in the IR spectrum of a given complex is diagnostic of the electronic environment at the metal. For example, as more electron density is donated from the ancillary ligands to the metal, the metal has more electron density to donate into the \( \pi^* \) orbital of the nitrosyl ligand. As the \( \pi^* \) orbital is filled, the N-O bond lengthens and weakens, and the \( \nu_{NO} \) decreases in frequency. Since alkoxide ligands can donate more electron density to the metal (Section 2.4.1) than alkyl ligands, alkoxo complexes generally have lower \( \nu_{NO} \)'s than analogous alkyl complexes. As expected, the nitrosyl-stretching frequencies of the alkoxo alkyl complexes lie midway between those for the symmetric bis(alkyl) and the bis(alkoxo) complexes. For instance, the \( \nu_{NO} \) exhibited in the IR spectrum of \( \text{Cp}^*\text{W(NO)}(\text{CH}_2\text{SiMe}_3)(\text{OCMe}_3) \) as a Nujol mull is 1563 cm\(^{-1}\), whereas \( \text{Cp}^*\text{W(NO)}(\text{CH}_2\text{SiMe}_3)_2 \) and \( \text{Cp}^*\text{W(NO)}(\text{OCMe}_3)_2 \) exhibit nitrosyl-stretching frequencies of 1572 and 1550 cm\(^{-1}\), respectively, in their Nujol mull IR spectra.

The formulation of compounds 3.1 - 3.7 as monomeric entities is supported by their low-resolution mass spectral data, since for all of these alkoxo alkyl complexes parent ions are observed. The \( \text{C}_6\text{D}_6 \) \( ^1\text{H} \) NMR spectra of 3.1 - 3.7 are straightforward (Table 3.3). The only exception to this generalization is the \( ^1\text{H} \) NMR spectrum of 3.5. Although the signals attributable to the methylene protons are not observed in the \( ^1\text{H} \) NMR spectrum, the resonance attributable to \( \text{CH}_2 \) is clearly observed in the \( ^{13}\text{C}\{^1\text{H}\} \) NMR spectrum of 3.5 at \( \delta \) 44.4 ppm.

It is reasonable to assume that the trimethlysilyl complexes 3.4 - 3.7 receive additional electron density from their alkoxide ligands in a manner similar to bis(alkoxo) and alkoxo chloro complexes (see Chapter 2). However, it has been shown that benzyl complexes can attain electron sufficiency at their metal centers by coordinating the benzyl ligand in an \( \eta^2 \) fashion. As demonstrated by X-ray crystallography, bis(benzyl) complexes, \( \text{Cp'}\text{M(NO)}(\text{CH}_2\text{Ph})_2 \), and benzyl chloro complexes, \( \text{Cp'}\text{M(NO)}(\text{CH}_2\text{Ph})\text{Cl} \), are 18-electron species by virtue of one benzyl ligand functioning as a three-electron donor. Therefore, to attain electron sufficiency at their
metal centers, the benzyl alkoxo species, \( \text{Cp}^*\text{M(NO)(CH}_2\text{Ph)(OR)} \), can, in principle, adopt one of two bonding modes shown below:

![Diagram of bonding modes](image)

The \(^1\text{H}\) and \(^{13}\text{C}(^1\text{H})\) NMR spectral data of these compounds clearly distinguish between these two structural possibilities. For instance, the ipso carbon chemical shift at \( \delta \) 147 ppm (Table 3.3) in the \(^{13}\text{C}(^1\text{H})\) NMR spectrum of \( \text{Cp}^*\text{Mo(NO)(CH}_2\text{Ph)(OCMe}_3\text{)} \) (3.1) in \( \text{C}_6\text{D}_6 \) is diagnostic for an \( \eta^1 \)-benzyl ligand. An APT experiment confirms the assignment of this resonance as the signal attributable to the ipso carbon. Furthermore, the \(^1\text{H}\) NMR spectrum of 3.1 in \( \text{C}_6\text{D}_6 \) (Figure 3.1) exhibits an AB pattern due to the diastereotopic methylene protons, for which the low-field chemical shifts (\( \delta \) 2.86 and 2.77 ppm) and the large \( ^2J_{\text{HH}} \) coupling constant (8.4 Hz) are typical of those displayed by \( \eta^1 \)-benzyl ligands. It thus appears that the benzyl ligand is functioning as a one-electron donor in complexes 3.1 - 3.3, and \( \pi \) donation from the alkoxide ligand provides additional electron density to stabilize the metal centers.

### 3.4.3 Related Systems

There are several related alkoxo alkyl systems reported in the literature. Group 4 alkoxo alkyl complexes, \( \text{Cp}_2\text{Ti(OR)(CH}_3\text{)} \) \([R = \text{alkyl and acyl}]\), valence isoelectronic analogues of complexes 3.1 - 3.7, are prepared by alcoholysis of \( \text{Cp}_2\text{Ti(CH}_3\text{)}_2 \). Bergman's group has obtained two late-transition-metal alkoxo alkyl systems. \( \text{Cp}^*\text{Ir(PPh}_3\text{(Me)(OR)} \) \([R = \text{acetyl, phenyl}]\) complexes were prepared in order to investigate the properties of \( \text{Ir-O} \) linkages as
Figure 3.1 $^1$H NMR spectrum of Cp$^*$Mo(NO)(CH$_2$Ph)(OCMe$_3$) in C$_6$D$_6$. 
compared to Ir-N bonds, and the ruthenium system, \((\text{PMe}_3)_4\text{Ru(Me)}(\text{OC}\{\text{CH}_2\}\text{Me})\), is known to exist as an equilibrium mixture of the oxygen- and carbon-bound transition metal enolates.

Recently our group has published a paper on the synthesis of the alkyl amido complexes \(\text{Cp}^*\text{M(NO)}(\text{R})(\text{NHCM}_3)\) \([\text{M} = \text{Mo, W}; \text{R} = \text{CH}_2\text{CMe}_3, \text{Me}]\). These complexes are prepared by treating the appropriate alkyl chloro precursor, \(\text{Cp}^*\text{M(NO)}(\text{R})\text{Cl}\), with an excess of amine. Like the alkoxo alkyl complexes, the 18-electron amido analogues are stabilized by donation of electron density from the heteroatom to the metal. A sulfur analogue, \(\text{CpW(NO)}(\text{SCH}_2\text{SiMe}_3)(\text{CH}_2\text{SiMe}_3)\), is also preparable from \(\text{CpW(NO)}(\text{CH}_2\text{SiMe}_3)_2\) by direct insertion of elemental sulfur into one of the metal-alkyl bonds.

3.4.4 Unique Reactions

The preparation of alkoxo alkyl complexes requires a sagacious choice of alkoxylating reagent. As noted above, \(\text{Cp}^*\text{W(NO)}(\text{CH}_2\text{SiMe}_3)(\text{OEt})\) \((3.7)\) is prepared from reaction of \(\text{Cp}^*\text{W(NO)}(\text{CH}_2\text{SiMe}_3)\text{Cl}\) and the potassium salt, KOEt. However, in the synthesis of either \(\text{Cp}^*\text{W(NO)}(\text{CH}_2\text{SiMe}_3)(\text{OCMe}_3)\) or \(\text{Cp}^*\text{W(NO)}(\text{CH}_2\text{SiMe}_3)(\text{OMe})\), the use of the potassium reagents, KOCMe or KOMe, results in the preparation of the bimetallic complexes [\(\text{Cp}^*\text{W(NO)}(\text{CH}_2\text{SiMe}_3)\)]\([\text{Cp}^*\text{W(Cl)}(\text{O})]\)\(=\mu_2-\eta^1:\eta^2-\text{NC}\{\text{H}\}\text{SiMe}_3\) \((3.8)\) and [\(\text{Cp}^*\text{W(NO)}(\text{CH}_2\text{SiMe}_3)\text{Cl}\)]\([\text{Cp}^*\text{W(Cl)}(\eta^2-\text{N}\{\text{O}\}\{\text{H}\}\text{CH}_2\text{SiMe}_3}\)]\(=\mu-\text{N}\) \((3.9)\), respectively.
3.4.4.1 Synthesis of [Cp\textsuperscript{*}W(NO)(CH\textsubscript{2}SiMe\textsubscript{3})][Cp\textsuperscript{*}W(Cl)(O)]-(μ\textsubscript{2}-η\textsuperscript{1}:η\textsuperscript{2}-NC{H}SiMe\textsubscript{3})

[Cp\textsuperscript{*}W(NO)(CH\textsubscript{2}SiMe\textsubscript{3})][Cp\textsuperscript{*}W(Cl)(O)]-(μ\textsubscript{2}-η\textsuperscript{1}:η\textsuperscript{2}-NC{H}SiMe\textsubscript{3}) (3.8) is produced by the heterogeneous reaction between Cp\textsuperscript{*}W(NO)(CH\textsubscript{2}SiMe\textsubscript{3})Cl and KOCMe\textsubscript{3}, i.e.,

\[ \text{Cp}^*\text{W(NO)(CH}_2\text{SiMe}_3)^{\text{Cl}^-} + 2\text{KOCMe}_3 \rightarrow \text{Cp}^*\text{W(NO)(CH}_2\text{SiMe}_3)^{\text{+}} + \text{Cl}^- + 2\text{Me}_3\text{SiC}H_2 = \text{Cl}^- \]

Reaction 3.5 can be monitored by IR spectroscopy, since the blue reaction mixture \((\nu_\text{NO} = 1616 \text{ cm}^{-1})\) slowly turns red-purple \((\nu_\text{NO} = 1624, 1570 \text{ cm}^{-1})\) as it is warmed to room temperature. The product 3.8 is isolated as purple needles in low yields from pentane. The low yield can be attributed to the extreme solubility of the complex. Complex 3.8 is both air- and temperature-sensitive. Thus, \(^1\text{H NMR spectroscopy shows that C}_6\text{D}_6\text{ solutions of 3.8 decompose thermally (120 °C) and that 3.8 reacts rapidly with O}_2\text{, as a solid or in solutions, to form the known Cp}^*\text{W(O)}_2(\text{CH}_2\text{SiMe}_3)\text{ complex.}^{22}\)

For the successful synthesis of 3.8, the choice of both the solvent and the cation of the alkoxide salt is crucial. For example, if reaction 3.5 is performed in THF or \(\text{Et}_2\text{O}\), \(\text{Cp}^*\text{W(NO)(CH}_2\text{SiMe}_3)(\text{OCMe}_3)_\text{2} \) (3.4) (~30% yield) is produced rather than the bimetallic complex 3.8. Similarly, if the alkoxylating reagent is changed to either the sodium or the lithium tertiary butoxide salt, 3.4 is also produced.

3.4.4.2 Characterization of Complex 3.8

The infrared spectrum of 3.8 as a Nujol mull (Figure 3.2) exhibits a low-energy \(\nu_\text{NO}\) at 1545 cm\(^{-1}\) and a \(\nu_\text{SiC}\) at 1240 cm\(^{-1}\). Typically, terminal W=O stretches appear between 1058 and 922 cm\(^{-1}\) in the infrared spectrum of terminal oxo-containing complexes;\(^{23}\) therefore, the band at
Figure 3.2 Nujol (marked by X) mull infrared spectrum (1658 - 490 cm\(^{-1}\)) of complex 3.8.
937 cm\(^{-1}\) in the IR spectrum of complex 3.8 is assigned to the \(\nu_{W=O}\). The values of \(\nu_{W=O}\) and \(\nu_{SiC}\) may be compared with those of \(\text{CpW(O)(CH}_2\text{SiMe}_3\))\(_3\) which as a Nujol mull exhibits a \(\nu_{W=O}\) at 941 cm\(^{-1}\) and \(\nu_{Si-C}\)'s at 1259 and 1240 cm\(^{-1}\).\(^{24}\) The band at 1154 cm\(^{-1}\) of the IR spectrum of 3.8 is most probably a N-C stretch,\(^{25}\) but confirmation of this assignment requires isotopic labeling of the bridging nitrogen.

The \(^1\)H NMR spectrum of \([\text{Cp}^*\text{W(NO)(CH}_2\text{SiMe}_3\)]\([\text{Cp}^*\text{W(Cl)(O)}]\)-(\(\mu_2-\eta^1:\eta^2\)-\(NC(H)\text{SiMe}_3\)) (Figure 3.3) exhibits two resonances attributable to the \(\text{Cp}^*\) ligands (\(\delta\) 1.70 and 1.65 ppm) and two signals attributable to the \(\text{SiMe}_3\) groups (\(\delta\) 0.68 and 0.40 ppm). The singlet at \(\delta\) 2.67 ppm is assigned to the hydrogen of the bridging ligand. Although the inequivalent methylene proton resonances are obscured in the standard \(^1\)H NMR spectrum, they can be observed in the COSY spectrum of 3.8. Thus, the resonances attributable to the methylene protons appear as doublets at \(\delta\) 1.68 and 0.40 ppm in the off-diagonal peaks of the \(C_6D_6\) COSY spectrum of 3.8. In addition to the signals due to the two inequivalent \(\text{Cp}^*\) ligands and the two inequivalent \(\text{SiMe}_3\) groups, the \(^{13}\)C\(\{^1\)H\} NMR spectrum of 3.8 clearly shows the signals attributable to the CH of the bridging ligand and the methylene carbon at \(\delta\) 75.2 and 44.1 ppm, respectively.

The structure of complex 3.8 has been determined by X-ray crystallography by Dr. S. J. Rettig.\(^{27}\) The ORTEP diagram of 3.8 is shown in Figure 3.4 and some selected bond lengths and angles are located in Table 3.4. The bimetallic complex 3.8 possesses a 14e\(^-\) \([\text{Cp}^*\text{W(Cl)(O)}]\) fragment and a normal 15e\(^-\) \(\text{Cp}^*\text{W(NO)(CH}_2\text{SiMe}_3\) fragment. The two metals are bridged by a \(NC(H)\text{SiMe}_3\) ligand.
Figure 3.3 $^1$H NMR spectrum of $[\text{Cp}^*\text{W(NO)}(\text{CH}_2\text{SiMe}_3)]\text{[Cp}^*\text{W(Cl)}(\text{O})]-(\mu_2-\eta^1:\eta^2-\text{NC(H)}\text{SiMe}_3)$ in $\text{C}_6\text{D}_6$. 
Figure 3.4 ORTEP diagram of [Cp*W(NO)(CH₂SiMe₃)][Cp*W(Cl)(O)]-μ₂-η¹:η²-
NC(H)SiMe₃). 33% probability thermal ellipsoids are shown for the non-hydrogen atoms.

Table 3.4. Selected Bond Lengths and Bond Angles for 3.8

<table>
<thead>
<tr>
<th>bond lengths (Å)</th>
<th>bond angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W1 - N1</td>
<td>2.004 (7)</td>
</tr>
<tr>
<td>W2 - N1</td>
<td>1.969 (7)</td>
</tr>
<tr>
<td>N1 - C21</td>
<td>1.44 (1)</td>
</tr>
<tr>
<td>W1 - C21</td>
<td>2.14 (1)</td>
</tr>
<tr>
<td>W1 - O1</td>
<td>1.697 (8)</td>
</tr>
<tr>
<td>W1 - N1 - W2</td>
<td>143.8 (4)</td>
</tr>
<tr>
<td>W1 - N1 - C21</td>
<td>74.9 (5)</td>
</tr>
<tr>
<td>W2 - N1 - C21</td>
<td>137.8 (6)</td>
</tr>
<tr>
<td>W2 - N2 - O2</td>
<td>166.4 (8)</td>
</tr>
</tbody>
</table>
The [Cp*W(Cl)(O)] fragment has four-legged piano-stool type geometry about W1, whereas, the Cp*W(NO)(CH₂SiMe₃) fragment has normal intramolecular parameters for a three-legged piano stool complex. These geometries are most clearly seen below in the Newman projections of the W1 fragment and the W2 fragment of complex 3.8, each looking down the W - Cp* centroid axis.

The W1-O1 bond length for complex 3.8 is 1.697 (8) Å, well within the typical range for terminal oxo ligands (1.58 - 1.78 Å).²⁸ For comparison, CpW(O)(CH₂SiMe₃) has a W-O bond length of 1.664 (8) Å.²⁴ The typical linear (166.4 (8)°) nitrosyl ligand of W2 has W2 - N2 and N2 - O2 bond distances of 1.767 (8) and 1.22 (1) Å, respectively. The bridging ligand, NC{H)SiMe₃, is η² to W1 and η¹ to W2, thereby acting as a two-electron donor to W1 and a one-electron donor to W2. In this way, each metal center attains a 16-valence-electron configuration. The geometry about C21 is approximately tetrahedral, i.e., W1 - C21 - Si1 = 120.0 (5)° and N1 - C21 - Si1 = 123 (2)°.

Overall, the structure indicates there is a formal loss of HCl and no incorporation of KOCMe₃ in reaction 3.5. For a discussion on the possible mechanism of this reaction, see Section 3.4.8.
3.4.4.3 Synthesis of [Cp*W(NO)(CH₂SiMe₃)Cl][Cp*W(Cl)(η²-N{O}{H}CH₂SiMe₃)]-(μ-N)

To determine if reaction 3.5 is independent of the type of potassium alkoxide salt used, Cp*W(NO)(CH₂SiMe₃)Cl was treated with potassium methoxide in pentane, i.e.,

The heterogeneous reaction mixture turns from blue to orange over the course of 5 h, and the bimetallic complex 3.9 is isolated as orange crystals from Et₂O in 13% yield (based on Cp*W(NO)Cl₂). Complex 3.9 is thermally sensitive and decomposes readily to the known oxo complex, Cp*W(O)₂(CH₂SiMe₃),²² in the presence of oxygen.

Reaction 3.6 does not occur in solvents other than pentane, nor with other methoxide salts. For instance, treatment of Cp*W(NO)(CH₂SiMe₃)Cl with KOMe in THF or with NaOMe in pentane, results in the formation of Cp*W(NO)(CH₂SiMe₃)(OMe) (3.6) (vide supra).

An important feature of reaction 3.6 is that Cp*W(O)₂(CH₂SiMe₃) is also produced (31% isolated yield based on Cp*W(NO)Cl₂). An NMR-scale reaction showed that the final reaction mixture contained a ratio of Cp*W(O)₂(CH₂SiMe₃) to 3.9 of 1:0.6. The Cp*W(O)₂(CH₂SiMe₃) produced in reaction 3.6 is not a result of the decomposition of the air-sensitive product complex.

Cp*W(O)₂(CH₂SiMe₃) was originally prepared from the dialkyl complex according to equation 3.7.²²

\[
\text{Cp*W(NO)(CH₂SiMe₃)₂ + O₂ } \rightarrow \text{Cp*W(O)₂(CH₂SiMe₃)} \quad (3.7)
\]

To date, the mechanism of reaction 3.7 is uncertain; however, one of the by-products of this reaction is thought to be the powerful oxidizing agent, Me₃SiCH₂NO. It has been established
独立地发现，PhNO在Et2O中将二烷基络合物转化为二氧物种的产率低（20 - 25%）。12,22

\[
\text{Cp}^*\text{W(NO)}(\text{CH}_2\text{SiMe}_3)_2 + \text{PhNO} \rightarrow \text{Cp}^*\text{W(O)}_2(\text{CH}_2\text{SiMe}_3)
\] (3.8)

在反应3.6中，由Cp*W(O)2(CH2SiMe3)的生产所得副产物可能与Cp*W(NO)(CH2SiMe3)Cl反应生成化合物3.9。这种类型的推理可能解释了产物中的额外氮原子。

### 3.4.4.4 Characterization of Complex 3.9

The Nujol mull IR spectrum of complex 3.9 (Figure 3.5) exhibits a broad νNO band at 1571 cm⁻¹ and two absorptions due to Si-C stretches at 1252 and 1233 cm⁻¹. The nitrosyl-stretching frequency is lowered by 28 cm⁻¹ from that of the starting material, a feature consistent with the tungsten center (W1) in 3.9 being more electron-rich than in the precursor complex. In unsymmetrically bridging transition-metal nitrides of the type M=N-M, the absorption due to the M-N bond is found in the range 948 - 1125 cm⁻¹.23 In this region, and in the terminal oxo region (960 - 885 cm⁻¹), there are a number of bands in the IR spectrum of 3.9, so neither of these stretching frequencies could be assigned unambiguously.

The $^1$H NMR spectrum of [Cp*W(NO)(CH2SiMe3)Cl][Cp*W(Cl)(η²-N{O}{H}CH2SiMe3)]-(μ-N) in C6D6 (Figure 3.6) exhibits two inequivalent Cp* resonances and two inequivalent SiMe3 resonances. The diastereotopic methylene protons of the simple alkyl group resonate at δ 1.19 ($^2$JHH = 9.8 Hz, $^2$WH = 3.9 Hz) and -0.45 ppm ($^2$HH = 9.8 Hz). The signal at low field (δ 9.50 ppm) is attributable to the hydrogen of the N(O){H}CH2SiMe3 ligand (Figure 3.6 inset). The coupling pattern of this signal ($^3$JHH = 5.4, $^3$JHH = 6.6 Hz) is a result of coupling to the diastereotopic methylene protons of the N-bound alkyl group. The signals due to the diastereotopic methylene protons of the N-bound alkyl group should appear as two doublets of doublets. Only one of these doublet of doublets is observed at δ 2.40 ppm ($^2$JHH = 14.7 Hz, $^3$JHH = 5.4 Hz). The other methylene-proton signal, probably obscured in the Cp*
Figure 3.5 Nujol (marked by X) mull infrared spectrum (1684 - 527 cm\(^{-1}\)) of complex 3.9.
Figure 3.6 $^1$H NMR spectrum of [Cp*W(NO)(CH$_2$SiMe$_3$)(Cl)][Cp*W(Cl)(η$^2$-N{O}{H}CH$_2$SiMe$_3$)]-(μ-N) in C$_6$D$_6$. Insets show the spectral regions δ 9.64 - 9.36 ppm and δ 2.48 - 2.12 ppm.
resonances, should show couplings of $^2J_{HaHm} = 14.7$ Hz and $^3J_{HxHa} = 6.6$ Hz. A representation of the coupling in this three-spin system is depicted below.

![Diagram](image)

An X-ray crystallographic analysis was performed by Dr. S. J. Rettig on a single crystal of 3.9. Selected bond lengths and angles for this complex are located in Table 3.5. A view of 3.9 (Figure 3.7) shows the four-legged piano-stool molecular geometry about each electronically saturated tungsten center.

The W1 moiety is essentially a 1:1 adduct of Cp*W(NO)(CH$_2$SiMe$_3$)Cl with the nitrido ligand of the W2 fragment acting as a Lewis base. Surprisingly, the bridging nitrido ligand is situated cis to the nitrosyl ligand and trans to the alkyl ligand. This is not expected since molecular orbital calculations and X-ray crystallographic analyses have indicated that the vacant coordination site in 16-electron complexes of the type Cp'M(NO)(Y)(Z) [Y, Z = 1-electron ligand] is located trans to the NO ligand. The solid-state molecular structure of Cp*W(NO)(CH$_2$SiMe$_3$)Cl has been previously reported and the angle between the alkyl group and the chloride ligand (C - W - Cl) is 109.9°, thereby indicating this is the most accessible site at the W atom (Table 3.6). Chemically, it has also been demonstrated that Cp*W(NO)(CH$_2$SiMe$_3$)Cl (Section 3.4.6) and Cp*M(NO)(CH$_2$CMe$_3$)Cl form 18-electron metal-centered phosphine adducts in which the phosphine coordinates trans to the nitrosyl group.
Figure 3.7 ORTEP diagram of \([\text{Cp}^*\text{W(NO)}(\text{CH}_2\text{SiMe}_3)(\text{Cl})][\text{Cp}^*\text{W}(\text{Cl})(\eta^2-N\{O\}H\text{CH}_2\text{SiMe}_3)]\)\-(\mu-N) with 20% probability thermal ellipsoids.

Table 3.5. Selected Bond Lengths and Bond Angles for 3.9

<table>
<thead>
<tr>
<th>bond lengths (Å)</th>
<th>bond angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>W1 - N3</td>
<td>2.10 (1)</td>
</tr>
<tr>
<td>W2 - N3</td>
<td>1.72 (1)</td>
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<tr>
<td>W2 - O2</td>
<td>1.93 (1)</td>
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<tr>
<td>W2 - N2</td>
<td>2.10 (1)</td>
</tr>
<tr>
<td>N1 - O1</td>
<td>1.22 (1)</td>
</tr>
<tr>
<td>N2 - O2</td>
<td>1.44 (1)</td>
</tr>
<tr>
<td>Cl1 - H1</td>
<td>2.29</td>
</tr>
</tbody>
</table>
The novel $N\{O\}{H}CH_2SiMe_3$ ligand is bound in an $\eta^2$ fashion to $W_2$. The geometry about $N_2$ is approximately trigonal planar, with $H_1/C25/O2$ defining the plane. Thus, $H1 - N2 - O2 = 119.9^\circ$, $C25 - N2 - O2 = 117 (1)^\circ$ and $C25 - N2 - H1 = 107.7^\circ$. The bond distances $W2 - N2$ (2.10 Å) and $N2 - O2$ (1.93 Å) suggest single bonds between these atoms; whereas, the distance between $W2$ and $O2$ (1.93 Å) indicates there is some degree of multiple bond character in this link.\textsuperscript{31} Several resonance structures could be drawn for this ligand. Overall, the $\eta^2-N\{O\}{H}CH_2SiMe_3$ ligand must donate a total of three electrons to $W_2$ to satisfy the 18-electron rule. The bonding of this ligand could be viewed as first involving formal transfer of one electron to the metal (thereby forming a $[N\{O\}{H}CH_2SiMe_3]^+$ ligand), then donation of 2 electrons from a $\pi$-type molecular orbital on $[N\{O\}{H}CH_2SiMe_3]^+$ to empty d orbitals on tungsten. In this way, the bonding of $[N\{O\}{H}CH_2SiMe_3]^+$ would be similar to the bonding of an $\eta^2$-ketone to a transition metal. Molecular orbital calculations on this type of ligand are required to fully explain how $N\{O\}{H}CH_2SiMe_3$ binds to this metal center.
The intramolecular dimensions of the N\{O\}\{H\}CH\textsubscript{2}SiMe\textsubscript{3} ligand in 3.9 can be compared to those of the nitrosobenzene ligand in Cp*W(\eta\textsuperscript{2}-N\{O\}Ph)(NPh)(Ph),\textsuperscript{32} i.e.,

\[
\begin{array}{c}
\text{Cp*W(\eta\textsuperscript{2}-N\{O\}Ph)(NPh)(Ph)} \\
\begin{array}{ccc}
W & 1.98 \text{ Å} & 2.06 \text{ Å} \\
O & 72.4^\circ & 66.1^\circ & 1.43 \text{ Å} \\
\end{array} \\
\end{array}
\begin{array}{c}
\text{Complex 3.9} \\
\begin{array}{ccc}
W & 1.93 \text{ Å} & 2.10 \text{ Å} \\
O & 75.7^\circ & 62.7^\circ & 1.44 \text{ Å} \\
CH_2SiMe_3 & & \\
\end{array} \\
\end{array}
\]

The bond lengths of the nitrosobenzene ligand in Cp*W(\eta\textsuperscript{2}-N\{O\}Ph)(NPh)(Ph) are similar to that found in the N\{O\}\{H\}CH\textsubscript{2}SiMe\textsubscript{3} ligand in 3.9. While \eta\textsuperscript{2}-N\{O\}Ph is a two-electron donor to tungsten, N\{O\}\{H\}CH\textsubscript{2}SiMe\textsubscript{3} provides three electrons to the tungsten in 3.9.

The bridging nitrido ligand is essentially linear with a W1 - N3 - W2 angle of 168.0°. The distance between W1 - N3 (2.10 (1) Å) indicates a single bond, whereas the distance between W2 - N3 (1.72 (1) Å) suggests N3 is triply bonded to W2.\textsuperscript{33} These distances can be compared to those between W2 - N2 (2.10 (1) Å) and W1 - N1 (1.77 (1) Å). The bridging nitrogen functions as a three-electron donor to W2 and a two-electron donor to W1, thereby satisfying each metal's electronic requirements. In other words, the nitrido ligand acts as a simple Lewis base to the 16-electron Cp*W(NO)(CH\textsubscript{2}SiMe\textsubscript{3})Cl fragment (vide supra). There are very few examples of this kind of nitrido bridging group, and most of them are found in polymeric species.\textsuperscript{23} Thus, comparisons can be made between \{W(\mu-N)(OCMe\textsubscript{3})\}_\infty and 3.9.\textsuperscript{34} For instance, \{W(\mu-N)(OCMe\textsubscript{3})\}_\infty contains the same type of bridging unit as complex 3.9 (i.e., W≡N→W). In this polymer, the W≡N bond length is 1.740 (15) Å, and the dative N→W bond distance is 2.661 (15) Å, barely short enough to call a bond.\textsuperscript{35}

An interesting feature of complex 3.9 is that it contains an intramolecular hydrogen bond between H1 located on the N\{O\}\{H\}CH\textsubscript{2}SiMe\textsubscript{3} ligand of W2 and the chloride ligand on W1. The hydrogen-chlorine bond distance (2.29 Å) is in the range expected for hydrogen bonding.\textsuperscript{36}
The N-H--Cl angle is 144.9°. Hydrogen bonding is common in organic and inorganic chemistry. Some of the most common types of inorganic complexes that contain hydrogen bonds are amine complexes of Co(III), Rh(III), Ru(III), and Cr(III). In these species the hydrogen bond is between the N-H moiety and the halide counteranion.

[Ir₂(CO)₂(μ-OH--Cl)(dppm)₂] contains a hydrogen bond between the bridging hydroxide ligand and the chloride counterion. (Ph₄C₄CO)(CO)₂Ru(NH₂Et₂) has a hydrogen bond between the carbonyl oxygen and the amide hydrogen, and a seven-coordinate tungsten(II) metallacycle complex contains both inter- and intramolecular bonds between chloride ligands and amide hydrogens. Intermolecular hydrogen bonding has been invoked to explain the rate acceleration of carbonylation reactions involving manganese α-hydroxyacyl complexes. Fryzuk and coworkers have attributed the stereoselective formation of octahedral Ir(III) and Rh(III) complexes to an intermediate involving a H-bond.

### 3.4.5 Trapping Attempts with Phosphines

To gain some insight into the above-mentioned complicated reactions, selected experiments were performed in an attempt to trap any possible intermediates of reactions 3.5 and 3.6.

Since PPh₃ does not coordinate to the precursor complex, Cp*W(NO)(CH₂SiMe₃)Cl, the reaction of Cp*W(NO)(CH₂SiMe₃)Cl with KOCMe₃ was performed in the presence of PPh₃.

\[
\text{Cp*W(NO)(CH₂SiMe₃)Cl + KOCMe₃ + PPh₃} \rightarrow 3.8
\]

Since the reaction proceeds to form the bimetallic complex 3.8 despite the presence of PPh₃, it is possible that PPh₃ is also too large to coordinate to any intermediate species.

The smaller phosphine, PMe₃, reacts readily with 16-electron alkyl chloro complexes to form metal-centered adducts, Cp*M(NO)(R)(Cl)(PMe₃). In this work, Cp*W(NO)(CH₂SiMe₃)(Cl)(PMe₃) (3.10) was prepared in a similar fashion from Cp*W(NO)(CH₂SiMe₃)Cl and an excess of PMe₃.
Like the other yellow 1:1 metal-centered adducts previously prepared, 
Cp*W(NO)(CH₂SiMe₃)(Cl)(PMe₃) (3.10) is an air- and temperature-stable complex which shows 
no tendency to undergo isomerization or phosphine dissociation. Complex 3.10 exhibits two 
νNO's (1570, 1549 cm⁻¹) in its Nujol mull IR spectrum. Each of these stretches are significantly 
lower than the νNO of the starting alkyl chloro complex (1599 cm⁻¹), thus indicating that the 
metal center in 3.10 becomes more electron rich with the addition of the Lewis base. The ¹H 
NMR spectrum for 3.10 (Figure 3.8) exhibits signals that are diagnostic for a 4-legged piano-stool 
molecular structure having the phosphine trans to the nitrosyl ligand.²,¹⁶ The stereochemistry at 
the metal is clearly seen in the Newman projection of Cp*W(NO)(CH₂SiMe₃)(Cl)(PMe₃) (3.10) 
down the W - Cp* centroid axis, i.e.,

The methylene protons of the alkyl group are positioned such that H_A is transoidal to the PMe₃ 
ligand (³J_HP = 2.4 Hz) and H_B is cisoidal (³J_HP = 0 Hz). The ³¹P{¹H} NMR spectrum of 3.10 
exhibits a signal at δ 6.88 ppm (J_PW = 95.3 Hz) due to coordinated PMe₃. The coupling to 
tungsten is clear evidence for a metal-centered adduct.

Complex 3.10 was made to be used as a reagent in subsequent reactions that attempted to 
trap intermediate complexes on the way to complexes 3.8 and 3.9.
Figure 3.8 $^1$H NMR spectrum of Cp$^*$W(NO)(CH$_2$SiMe$_3$)(Cl)(PMe$_3$) in C$_6$D$_6$. Inset shows the spectral region $\delta$ -0.29 to -0.39 ppm.
It was hoped that complex 3.10 would react with the potassium alkoxide salts to produce an intermediate species of reactions 3.5 and 3.6. However, Cp^*W(NO)(CH_2SiMe_3)(Cl)(PMe_3) (3.10) reacts with KOCMe_3 to produce Cp^*W(NO)(CH_2SiMe_3)(OCMe_3) (3.4), and the 18-electron phosphine adduct does not react at all with KOMe in pentane (Scheme 3.2).

### 3.4.6 Deuterium-Labeling Experiments

In an attempt to determine the source of the hydrogen involved in H-bonding in compound 3.9, Cp^*W(NO)(CH_2SiMe_3)Cl was treated with KOCD_3. Under the same experimental conditions as reaction 3.6, KOCD_3 effects the metathesis of the chloride ligand to form Cp^*W(NO)(CH_2SiMe_3)(OCD_3) (3.6-d_3).

\[
\text{Cp}^*\text{W(NO)(CH}_2\text{SiMe}_3)\text{Cl} \quad \rightarrow \quad \text{Cp}^*\text{W(NO)(CH}_2\text{SiMe}_3)\text{OCD}_3 + \text{Cp}^*\text{W(O)}_2(\text{CH}_2\text{SiMe}_3)
\]  

(3.11)

In this reaction, Cp^*W(O)_2(CH_2SiMe_3) is also isolated in low yields (9.1%), and there is no evidence for the formation of a bimetallic complex such as 3.9. ¹H NMR spectroscopy (Figure 3.9) shows a ratio of 1:5 of the dioxo alkyl species and complex 3.6-d_3 with no bimetallic species present. In comparison, a similar NMR tube experiment of reaction 3.6 demonstrated the
Figure 3.9 ¹H NMR spectra in C₆D₆ (•) of the reaction mixtures of (a) Cp⁴W(NO)(CH₂SiMe₃)(Cl) and KOCD₃ (b) Cp⁴W(NO)(CH₂SiMe₃)(Cl) and KOCH₃. The resonances attributable to Cp⁴W(O)₂(CH₂SiMe₃) are marked with x's.
ratio of the dioxo alkyl species to 3.9 of 1:0.6. In this case no signals due to the alkoxo alkyl complex were observed. For clarity, these product ratios are tabulated below.

Table 3.7. Product Ratios for the Reactions of Cp*W(NO)(CH₂SiMe₃)Cl with KOCH₃ and KOCD₃

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Cp*W(O)₂(CH₂SiMe₃)</th>
<th>3.6 (or 3.6-d₃)</th>
<th>3.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp*W(NO)(CH₂SiMe₃)Cl + KOCH₃</td>
<td></td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Cp*W(NO)(CH₂SiMe₃)Cl + KOCD₃</td>
<td></td>
<td>1</td>
<td>5</td>
</tr>
</tbody>
</table>

Clearly, there is a very large isotope effect which results in different mechanistic pathways being favored, and therefore different products are formed. Since C-D bonds are stronger than C-H bonds, this result suggests that β-H elimination may be operative in reaction 3.6. With the substitution of deuteriums for the hydrogens β to the metal, the β-elimination is slowed to the point where no bimetallic product is formed. To establish if two independent pathways are in operation, I would suggest reacting 1 equiv Cp*W(NO)(CH₂SiMe₃)Cl with a mixture of 0.5 equiv of KOCH₃ and 0.5 equiv of KOCD₃. Given independent pathways, I would expect a mixture of Cp*W(O)₂(CH₂SiMe₃), 3.6-d₃, and 3.9 to be formed in this reaction.

3.4.7 Reactions Resulting in Nitrosyl-Ligand Transformations

Until very recently, nitrosyl ligands were considered to be innocent spectator ligands by our group, affecting only the electronic environment of their complexes. Over the last two years, in addition to reactions 3.5 and 3.6, our group has discovered several other reactions in which the nitrosyl ligand is modified. For example, treatment of the diaryl complex, CpW(NO)(o-tolyl)₂ with water induces a formal isomerization to the oxo imido complex, i.e.,⁴¹
and a similar chromium complex is obtained according to equation 3.13.\(^{42}\)

Cp*W(NO)(Ph)\(_2\) undergoes a unique thermal reaction to afford Cp*W(\(\eta^2\)-N(O)Ph)(NPh)(Ph) and Cp*W(O)\(_2\)Ph (eq. 3.15).\(^{32}\)

Reactions of C\(_6\)H\(_6\) solutions of Cp*Mo(NO)(CH\(_2\)SiMe\(_3\))\(_2\) with hydrogen afford the bimetallic species shown in equation 3.15.\(^{43}\)
Similar tungsten complexes, \([\text{Cp}^*\text{W(NO)}(\text{R})][\text{Cp}^*\text{W(O)}\text{R}](\mu-\text{N})\) (R = CH\(_2\)CMe\(_3\), Ph) result when \(\text{Cp}^*\text{W(NO)}(\text{R})\text{Cl}\) is reacted with Zn.\(^{44}\)

\[
\text{Cp}^*\text{W(NO)}(\text{R})\text{Cl} + \text{Zn} \rightarrow [\text{Cp}^*\text{W(NO)}(\text{R})][\text{Cp}^*\text{W(O)}\text{R}](\mu-\text{N}) \quad (3.16)
\]

In addition, 1:1 mixtures \(\text{Cp}^*\text{W(NO)}\text{Cl}_2\) and \(\text{Cp}^*\text{W(NO)}(\text{R})\text{Cl}\) are reduced with to produce \([\text{Cp}^*\text{W(NO)}(\text{R})][\text{Cp}^*\text{W(O)}\text{Cl}](\mu-\text{N})\). This indicates that initial reduction must occur at \(\text{Cp}^*\text{W(NO)}\text{Cl}_2\) (which is more easily reduced than \(\text{Cp}^*\text{W(NO)}(\text{R})\text{Cl}\) complexes)\(^{45}\) and this reduction must somehow induce the cleavage of the nitrosyl ligand.

### 3.4.8 Mechanistic Considerations

The role of KOCMe\(_3\) and KOMe in reactions 3.5 and 3.6 is not clear, and to date, there are no reagents which effect similar chemical transformations. The potassium cation must play an important function in these reactions since simple metatheses occur if K\(^+\) is replaced by Li\(^+\) or Na\(^+\).

**Scheme 3.3**

It is also evident that the alkoxide anion (OCMe\(_3\)\(^-\) or OMe\(^-\)) also influences the pathway of these reactions. The three obvious functions of alkoxide salts are as reducing, metathesis and deprotonating reagents.
3.4.8.1 Reduction Mechanisms

Anions of potassium salts are often potent reducing agents. As stated in Section 3.4.7, reducing reagents such as zinc metal affect nitrosyl cleavage of Cp*W(NO)(R)Cl complexes; however, reduction leads to bridging nitrido complexes of the type [Cp*W(NO)(R)][Cp*W(O)R]- (μ-N) (eq 3.16) and not bimetallics such as 3.8 and 3.9. It is therefore improbable that reactions 3.5 and 3.6 occur via initial reduction, since there is nothing to indicate that Cp*W(NO)(CH2SiMe3)Cl would react differently than its neopentyl analogue under reducing conditions.

3.4.8.2 Metathesis Mechanisms

It is unlikely that the KOCMe3 is reacting further with the Cp*W(NO)(CH2SiMe3)(OCMe3) complexes, since it has been shown that Cp*W(NO)(CH2SiMe3)(OCMe3) is stable to excess KOCMe3 (Section 3.2.9). However, the deuterium labeling studies of reaction 3.6 indicate that there is a very large isotope effect which results in different products (Section 3.4.7). From those experiments, it follows that the initial step in the reaction to form 3.9 is probably metathesis to form Cp*W(NO)(CH2SiMe3)(OCH3). This alkoxo alkyl complex is isolable, but under these experimental conditions this species must undergo further reaction. It is possible that at some point in the mechanism of reaction 3.6, β-H elimination occurs. This would be consistent with the observations that (1) no alkoxo ligand is found in the product, (2) there is an extra hydrogen incorporated in 3.9, and (3) Cp*W(NO)(CH2SiMe3)(OCD3), having strong C-D bonds, is not likely to undergo β-D elimination. It is very difficult to account for the mass balance of this low-yielding reaction. However, it is important to remember that in reaction 3.6 Cp*W(O)2(CH2SiMe3) is produced, and the by-products of this reaction may be participating in the reaction to form complex 3.9.
3.4.8.3 Deprotonation Mechanisms

Literature indicates potassium salts may also react as deprotonating agents.\textsuperscript{46} For example, Ir(CH\(_3\))(PH\(_2\)Ph)[N(SiMe\(_2\)CH\(_2\)PPh\(_2\))\(_2\)] undergoes loss of KI and HO\textsubscript{C}Me\(_3\) to afford Ir(CH\(_3\))(PHPh)[N(SiMe\(_2\)CH\(_2\)PPh\(_2\))\(_2\)] when treated with KOCMe\(_3\).\textsuperscript{47} I propose that the reaction to form complex 3.8 occurs by initial deprotonation of the alkyl chloride complex by KOCMe\(_3\). Thus, the most plausible mechanism for reaction 3.5 is outlined in Scheme 3.4. Deprotonation of Cp\(^*\)W(NO)(CH\(_2\)SiMe\(_3\))Cl with KOCMe\(_3\) results in loss of alcohol and formation of an 18-electron anion (A). This species has a localized negative charge at the α-C, and nucleophilic attack of this carbon upon the nitrosyl leads to intermediate B. Intermediate B then attacks a second equivalent of Cp\(^*\)W(NO)(CH\(_2\)SiMe\(_3\))Cl to displace a chloride ligand. Finally, the neutral intermediate C undergoes an intramolecular rearrangement to form the final product. Overall this mechanism indicates loss of HO\textsubscript{C}Me\(_3\) and KCl and is consistent with the experimental data at hand.

Reaction 3.5 is very low yielding (9.3%), and therefore it is not unreasonable to envision a second pathway where intermediate A loses KCl to form the 16-electron alkylidene [Cp\(^*\)W(NO)(CHSiMe\(_3\))] species.

\[
\begin{array}{c}
\text{[O=N=W]}
\end{array}
\begin{array}{c}
\text{K}
\end{array}
\xrightarrow{-\text{KCl}}
\begin{array}{c}
\text{[W=O=CH\textsubscript{Me}\textsubscript{3}]}\end{array}
\xrightarrow{\Delta}
\text{decomposition}
\]

(3.17)

I would expect this intermediate to be thermally unstable under the reaction conditions and decompose in a manner similar to the analogous [CpMo(NO)(CHCMe\(_3\))] species, which can be trapped by Lewis bases (L) to form CpMo(NO)(CHCMe\(_3\))L or, in the absence of a trapping ligand, forms the asymmetric dimer [CpMo(NO)](μ-η\(^1\):η\(^2\)-NO)(μ-CHCMe\(_3\))[CpMo(CHCMe\(_3\))]\textsuperscript{48}. 
Scheme 3.4

\[
\begin{align*}
\text{Me}_3\text{SiCH}_2\text{N} & \quad \text{Cl} \quad \xrightarrow{\text{KOCMe}_3} \quad \text{Me}_3\text{SiCH}_2\text{N} \\
\text{W} & \quad \text{Cl} \quad \xrightarrow{\text{HOCMe}_3} \\
A & \quad \text{K}
\end{align*}
\]

\[+ \text{Cp}^*\text{W(NO)}(\text{CH}_2\text{SiMe}_3)\text{Cl}\]

\[
\begin{align*}
\text{Me}_3\text{SiCH}_2\text{N} & \quad \text{Cl} \quad \xrightarrow{\text{K}} \\
\text{W} & \quad \text{Cl} \quad \text{Me}_3\text{SiCH}_2\text{N} \\
B & \quad \text{K}
\end{align*}
\]

\[-\text{KCl}\]

\[
\begin{align*}
\text{Me}_3\text{SiCH}_2\text{N} & \quad \text{Cl} \quad \text{Me}_3\text{SiCH}_2\text{N} \\
\text{C} & \quad \text{H} \quad \text{Cl} \\
\text{SiMe}_3 & \\
C
\end{align*}
\]
Reaction 3.5 is solvent dependent. Thus, when reaction 3.5 is performed in pentane complex 3.8 is formed; however, in THF, the alkoxo alkyl complex is produced. Ionic species may be stabilized in THF making the metathesis reaction a more favorable pathway. In addition, THF is also a very good donor ligand, and in the presence of donors such as THF or PMe$_3$ only Cp$^*$W(NO)(CH$_2$SiMe$_3$)(OCMe$_3$) is produced. Apparently, the electronics of Cp$^*$W(NO)(CH$_2$SiMe$_3$)Cl may be sufficiently altered by coordination of a base, such that the mechanism outlined in Scheme 3.4 is not followed. The reaction of Cp$^*$W(NO)(CH$_2$SiMe$_3$)Cl with KOCMe$_3$ was also performed in the presence of PPh$_3$. Since complex 3.8 was formed despite the presence of the phosphine, this indicates that either the concentrations of the intermediate species are very low at any given time or PPh$_3$ is simply too large (cone angle 145°) to coordinate to any intermediates present.

Although the most likely mechanism for the formation of 3.8 is by initial deprotonation, other deprotonating reagents do not effect a similar transformation. As with the related Cp$^*$M(NO)(CH$_2$CMe$_3$)Cl$_6$ complexes, I have shown that Cp$^*$W(NO)(CH$_2$SiMe$_3$)Cl decomposes to a plethora of products when treated with classic deprotonators such as n-BuLi or LDA. It is likely that for steric and electronic reasons KOCMe$_3$ is the most effective deprotonating reagent for this transformation.

I would suggest three additional experiments that may give more mechanistic insight into this reaction. (1) Determine the correct stoichiometry for the reaction, since Scheme 3.4 indicates only 0.5 equiv of KOCMe$_3$ is required. (2) Use intermediate-sized phosphines such as PMe$_2$Ph (cone angle 122°), PE$_3$ (cone angle 132°) or PMePh$_2$ (cone angle 136°), since PMe$_3$ (cone angle 118°) coordinates to the alkyl chloride starting reagent and PPh$_3$ (cone angle 145°) is too large to trap any intermediate present. (3) Eliminate the possibility that this reaction proceeds via a radical mechanism by performing the reaction in the presence of a radical trapping reagent such as TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy).
3.5 Epilogue and Future Work

This chapter has presented the synthesis and characterization of alkoxo-containing complexes of the type \( \text{Cp}^* \text{W(NO)(R)(OR')} \). The characteristic chemistry of these complexes and future research suggestions can be found in Chapter 4.

The nitrosyl-altering reactions constitute the newest research interests of these laboratories. To date, the mechanisms of all of these "nitrosyl-cleavage" reactions are unknown; however, the current working hypothesis is that each of these processes at some point may proceed via an intermediate containing a \( \eta^2\text{-NO} \) group. As shown, nitrosyl-containing complexes are beginning to show interesting ligand-based chemistry, and these reactive NO ligands are proving to be more than just good \( \pi \)-acceptor ligands. For future studies of the nitrosyl altering reactions involving the potassium alkoxide salts, I have recommend several key experiments in Section 3.4.8. In order to elucidate the mechanisms of these reactions, an understanding of the role of the KOR salts and the apparent dependency of these reactions on the alkoxo group are essential.

3.6 References and Notes

5. Legzdins, P.; Lundmark, P. J.; Rettig, S. J. Organometallics, in press.
(8) \((\text{PhCH}_2)_2\text{Mg-X(dioxane)}\) was prepared in a manner similar to that outlined for \((\text{Me}_3\text{SiCH}_2)_2\text{Mg-X(dioxane)}\) in reference 3.


(11) This pentane solution can be concentrated in vacuo and cooled to induce the crystallization of pure \(\text{Cp}^*\text{W(NO)(CH}_2\text{SiMe}_3)\text{Cl}\) in \(~80\%\) yield.


(16) A series of \(\text{Cp'M(NO)(R)(Cl)}\) complexes has been prepared in our laboratories. For \(\text{M} = \text{W}\), see reference 10. For \(\text{M} = \text{Mo}\), see: Debad, J. D.; Legzdins, P.; Rettig, S. J.; Veltheer, J. E. *Organometallics* 1993, 12, 2714.


(25) The N-C vibration of an imide ligand is expected in the range of 1300 - 1100 cm\(^{-1}\), whereas W-N stretches can be found at lower energies (1125 - 948 cm\(^{-1}\)).


(27) Crystals of 3.8 are triclinic of space group $P\overline{1}$ (#2); $a = 12.140$ (2) Å, $b = 13.334$ (2) Å, $c = 11.627$ (1) Å, $\alpha = 90.54$ (1)°, $\beta = 103.30$ (2)°, $\gamma = 76.06$ (1)°, $V = 1742.8$ (4) Å\(^3\), $Z = 2$. Dr. S. J. Rettig solved the structure using the Patterson method and full-matrix least-squares refinement procedures to $R = 0.042$, $R_w = 0.041$ for 4300 reflections with $I \geq 3\sigma(I)$.


(29) Crystals of 3.9 are monoclinic of space group $P2_1/n$ (#14); $a = 9.948$ (2) Å, $b = 20.118$ (5) Å, $c = 19.002$ (5) Å, $\beta = 103.30$ (2)°, $V = 3701$ (3) Å\(^3\), $Z = 4$. Dr. S. J. Rettig solved the structure using the Patterson method and full-matrix least-squares refinement procedures to $R = 0.038$, $R_w = 0.034$ for 2595 reflections with $I \geq 3\sigma(I)$.


(31) (a) For N-O bond distances see reference 14. (b) For W-O, W-N single bond lengths see: Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G. *J. Chem. Soc.*, *Dalton Trans.* **1989**, S1. (c) The covalent radii of W, C, N, and O are 1.30, 0.77, 0.75, and 0.73 Å, respectively.

(32) Cp\(^\ast\)W(NO)(Ph)_2 undergoes a thermal reaction to afford the 16-electron Cp\(^\ast\)W(η\(^2\)-N{O}Ph)(NPh)(Ph) complex. The dihapto linkage in this complex is described

(33) W-N bond distances average 1.952 Å (see reference 31b), W=N bond distances range from 1.78 - 1.61 Å, and W≡N bond distances range from 1.74 - 1.55 Å (see reference 23).


(40) More energy (1.2 kcal/mol) is required to break a C-D bond than a C-H bond, see Fessenden, R. J.; Fessenden, J. S. *Organic Chemistry*, 3rd ed.; Brooks/Cole Publishing Co.: Monterey, CA, 1986; p 200.


(43) Legzdins, P.; Young, M. A., unpublished observations.

(44) Debad, J. D; Legzdins, P., unpublished observations.


4.1 Introduction

With any new class of organometallic complexes, it is important to determine characteristic physical and chemical properties of the compounds; therefore, this chapter describes investigations into the chemical reactivity patterns of alkoxo alkyl complexes, $\text{Cp}^*\text{M(NO)}(\text{OR})$. These complexes provide a system in which it is possible to compare directly the reactivity of a metal-carbon bond versus a metal-oxygen bond at the same metal center.

Alkoxo complexes which undergo ligand-based reactions are fairly rare. However, alkoxo complexes are known to undergo insertion of polar substrates into the M-O bond, and they have been postulated as intermediates in some important catalytic processes. The alkoxo complexes $\text{Cp}^*\text{M(NO)}(\text{OR})_2$ prepared in Chapter 2 are extremely inert evidently because electron density is donated from the alkoxo ligands to the formally unsaturated metal center. In comparison, the related and truly 16-electron dialkyl complexes, $\text{Cp}^*\text{M(NO)}_2$, have a rich reaction chemistry with
Lewis bases.\textsuperscript{2,3} For instance, the reactions of \( \text{Cp'}M(\text{NO})R_2 \) complexes with Lewis bases proceed by initial adduct formation followed by subsequent intramolecular insertion into the metal-carbon bonds, as depicted in Scheme 4.1.

Scheme 4.1

Since alkoxo ligands are generally unreactive towards Lewis bases, the reactivity of \( \text{Cp}^*M(\text{NO})(R)(OR') \) complexes was expected to involve primarily the metal-carbon bonds. It was hoped that some interesting intermediate complexes could be isolated by virtue of the stabilizing effect of the alkoxo ligand.
4.2 Experimental Procedures

4.2.1 Methods

The synthetic methodologies employed throughout this thesis are described in detail in Sections 2.2.1.

4.2.2 Reagents

The organometallic alkoxo alkyl complexes Cp*M(NO)(R)(OR') were prepared as described in Sections 3.2.5 - 3.2.6. LiOCMe3 was synthesized as in Section 2.2.3. (PhMe2CCH2)2Mg·X(dioxane)4 and CpMo(NO)(CH2Ph)Cl5 were prepared according to published procedures. CS2 (99+%, Aldrich) was distilled from P2O5. O2 (Medigas, 99.5 %), CO (Linde), CO2 (99.999%, Matheson), H2 (Linde), CNCMe3 (Aldrich), PhNCO (Aldrich), p-tolylnCO (Aldrich), LDA (LiN(i-propyl)2, Aldrich) and PhOH (Mallinckrodt) were used as received.

The numbering scheme, color, yield and elemental analysis data for all new complexes (4.1 - 4.6) are collected in Table 4.1, while their mass spectral and infrared data are compiled in Table 4.2. The 1H and 13C{1H} NMR data for 4.1 - 4.6 can be found in Table 4.3.

4.2.3 Reaction of Cp*M(0)(CH2Ph)(OCMe3) (3.1) and Cp*M(0)(CH2Ph)(OPh) (3.2) with O2

Treatment of complexes 3.1 and 3.2 (0.50 mmol each) in Et2O (10 mL) with O2 (1 atm) resulted in a color change from red to yellow over the course of several hours at room temperature. The solvents were removed in vacuo, the residues were extracted with Et2O (4 x 20 mL), and the extracts were filtered through Celite (2 x 5 cm). The filtrates were concentrated in vacuo and cooled at -30 °C overnight to induce the precipitation of small amounts of [Cp*M(0)2]2-(μ-O) (~20% yield).6
4.2.4 Reactions of Cp*W(NO)(CH2Ph)(OCMe3) (3.3) and Cp*W(NO)(CH2SiMe3)(OPh) (3.5) with O2 and H2O

Stirred Et2O solutions (10 mL) of complexes 3.3 and 3.5 (1.0 mmol each) were exposed to O2 (1 atm) or deaerated H2O (50 μL). The colors of the reaction mixtures immediately turned from red (3.3) or purple (3.5) to yellow. The final reaction mixtures were taken to dryness in vacuo, and the residues were extracted with Et2O (2 x 10 mL) and filtered through Celite (2 x 5 cm). The filtrates were concentrated in vacuo and cooled at -30 °C to induce the deposition of colorless crystals of the dioxo alkyl complexes, Cp*W(O)2(CH2Ph) and Cp*W(O)2(CH2SiMe3),7 respectively, in virtually quantitative yields.

4.2.5 Preparation of [CpMo(NO)(CH2Ph)]2-(μ-O) (4.1)

CpMo(NO)(CH2Ph)Cl (0.64 g, 2.0 mmol) and LiOCMe3 (0.16 g, 2.0 mmol) were mixed as solids in a Schlenk tube in a glovebox. The tube was removed from the glovebox, and Et2O (30 mL) was added to the solids via syringe. The reaction mixture was stirred for 1.5 h, during which time it turned red. The solvent was removed in vacuo from the reaction mixture to obtain a red oil. The oil was dissolved in pentane/Et2O (1:1, 20 mL). Over the course of the work-up this solution continued to darken.8 The solution was filtered through Celite (2 x 5 cm). Upon concentrating and cooling the solution, crystals formed. [CpMo(NO)(CH2Ph)]2-(μ-O) (4.1) (0.30 g, 42% yield) was isolated by cannulation as black needles.

4.2.6 Preparation of [Cp*Mo(NO)(CH2CMe2Ph)]2-(μ-O) (4.2)

Cp*Mo(NO)Cl2 (0.66 g, 2.0 mmol) and (PhMe2CCH2)2MgX(dioxane) (2.0 mmol Me3CCH2) were combined as solids in a Schlenk tube contained in a glovebox. The tube was removed from the glovebox and cooled to -80 °C. THF (20 mL) was added slowly to the solids via syringe. As the solution warmed to -40 °C, it turned purple (νNO = 1618 cm⁻¹).9 The solvent was then removed in vacuo without allowing the reaction mixture to warm above -30 °C. The
remaining purple residue was extracted with Et₂O (2 x 20 mL), and the extracts were filtered through Celite (2 x 5 cm). The purple filtrate was taken to dryness in vacuo and redissolved in THF (20 mL). The THF solution was cannulated into a Schlenk tube containing LiOMe (0.16 g, 2.0 mmol). The reaction mixture turned red within 0.5 h. After this time the solvent was removed in vacuo, and the remaining residue was extracted with hexanes (2 x 20 mL). Over the course of the work-up this solution continued to darken. The extracts were filtered through Celite (2 x 5 cm). The filtrate was concentrated and cooled to induce the crystallization of 0.80 g (50% yield) of \([\text{Cp}^\ast\text{Mo(NO)}(\text{CH}_2\text{CMe}_2\text{Ph})]_2-(\mu-\text{O})\) (4.2) as red-black needles.

### 4.2.7 Reactions of \(\text{Cp}^\ast\text{Mo(NO)}(\text{CH}_2\text{Ph})(\text{OCMe}_3)\) (3.1) and \(\text{Cp}^\ast\text{W(NO)}(\text{CH}_2\text{SiMe}_3)(\text{OPh})\) (3.5) with HCl

Complexes 3.1 and 3.5 were treated in Et₂O with 1 equiv of HCl (as a 1.4 M solution in Et₂O). The workup of the final reaction mixtures involved removing the solvent in vacuo, extracting the residues with Et₂O (for 3.1) or pentane (for 3.5), and cooling the combined extracts at -30 °C to obtain crystalline precipitates (80 - 90% yields) of the product complexes. Comparisons with authentic spectral data confirmed that the organometallic products of these reactions were \(\text{Cp}^\ast\text{Mo(NO)}(\text{CH}_2\text{Ph})\text{Cl}\), and \(\text{Cp}^\ast\text{W(NO)}(\text{CH}_2\text{SiMe}_3)\text{Cl}\), respectively.

### 4.2.8 Reaction of \(\text{Cp}^\ast\text{W(NO)}(\text{CH}_2\text{SiMe}_3)(\text{OMe})\) (3.6) with PhOH

Excess PhOH was vacuum transferred onto a red pentane solution of \(\text{Cp}^\ast\text{W(NO)}(\text{CH}_2\text{SiMe}_3)(\text{OMe})\) (3.6) (0.086 g, 0.18 mmol) \((\nu_{\text{NO}} = 1584 \text{ cm}^{-1})\). The mixture was stirred for 2 d after which time the IR spectrum of an aliquot of the red-purple reaction solution exhibited a new band at 1597 cm⁻¹. The reaction mixture was taken to dryness in vacuo and the remaining residue was extracted with pentane (2 x 10 mL). The extracts were filtered through Celite (2 x 5 cm), and the filtrate was concentrated and cooled to induce the crystallization of 0.060 g (60% yield) of \(\text{Cp}^\ast\text{W(NO)}(\text{CH}_2\text{SiMe}_3)(\text{OPh})\) (3.5).
Pentane solutions of \( \text{Cp}^*\text{W(NO)}(\text{CH}_2\text{SiMe}_3)(\text{OPh}) \) did not react with excess MeOH at room temperature overnight.

### 4.2.9 Reaction of \( \text{Cp}^*\text{W(NO)}(\text{CH}_2\text{SiMe}_3)(\text{OPh}) \) (3.5) with PMe\(_3\)

An excess of PMe\(_3\) was vacuum transferred from sodium/benzophenone into an NMR tube containing a CDCl\(_3\) solution of 3.5. Variable-temperature \(^1\)H NMR spectra from 24 °C to -60 °C of the reaction mixture were recorded.

On a larger scale, \( \text{Cp}^*\text{W(NO)}(\text{CH}_2\text{SiMe}_3)(\text{OPh}) \) (0.24 g, 0.46 mmol) was reacted neat with PMe\(_3\) to form a yellow precipitate. The excess PMe\(_3\) was removed under reduced pressure to obtain a yellow solid. Under dynamic vacuum, this solid reverted to the distinctive purple color of the starting organometallic species over the course of 0.5 h.

### 4.2.10 Reaction of \( \text{Cp}^*\text{W(NO)}(\text{CH}_2\text{SiMe}_3)(\text{OPh}) \) (3.5) with CNCMe\(_3\)

Complex 3.5 (0.10 g, 0.19 mmol) was dissolved in CNCMe\(_3\) (0.20 mL, excess). The purple solid turned yellow as it dissolved. After the reaction mixture had been stirred for 5 min, the excess CNCMe\(_3\) was removed in vacuo to obtain a yellow oil. This oil was dissolved in pentane (20 mL), and the resulting yellow solution was filtered through Celite (2 x 5 cm). The yellow filtrate was collected and concentrated in vacuo. Maintaining the concentrated solution at -30 °C resulted in the deposition of 0.092 g (80% yield) of \( \text{Cp}^*\text{W(NO)}(\text{OPh})(\eta^2-\text{C}\{\text{NCMe}_3\}\text{CH}_2\text{SiMe}_3) \) (4.3) as yellow nuggets.

### 4.2.11 Hydrolysis of \( \text{Cp}^*\text{W(NO)}(\text{OPh})(\eta^2-\text{C}\{\text{NCMe}_3\}\text{CH}_2\text{SiMe}_3) \) (4.3) to \( \text{Cp}^*\text{W(NO)}(\text{OPh})(\eta^2-\text{C}\{\text{NCMe}_3\}\text{Me}) \) (4.3')

\(^1\)H NMR spectroscopy established that \( \text{Cp}^*\text{W(NO)}(\text{OPh})(\eta^2-\text{C}\{\text{NCMe}_3\}\text{CH}_2\text{SiMe}_3) \) (4.3) was easily hydrolyzed by trace H\(_2\)O in C\(_6\)D\(_6\) to form \( \text{Cp}^*\text{W(NO)}(\text{OPh})(\eta^2-\text{C}\{\text{NCMe}_3\}\text{Me}) \) (4.3'). \(^1\)H NMR data for 4.3' can be found in Table 4.3.
4.2.12 Reaction of Cp*Mo(NO)(CH2Ph)(OCMe3) (3.1) with CO

The high-pressure treatment of Cp*Mo(NO)(CH2Ph)(OCMe3) (0.17 g, 0.40 mmol) in C6H6 with CO was carried out in a Parr reactor (see section 5.2.4). The resulting amber solution was reduced to a red-amber oil in vacuo. This oil was redissolved in pentane, and then transferred to the top of a silica gel column (2 x 8 cm) made up in pentane. The column was eluted with pentane, resulting in the elution of a single orange band which was collected and concentrated in vacuo. Cooling of this concentrated solution in a freezer (-10 °C) overnight resulted in the deposition of orange crystals of Cp*Mo(NO)(CO)2 (0.034 g, 27% yield).12 Subsequent elution of the column with Et2O developed an amber band which was also collected and reduced in vacuo to afford a small amount (<5% yield) of an amber oil. The spectroscopic properties of this oil were identical to those exhibited by an authentic sample of 1,3-diphenylacetone.13

Complex 3.1 was reacted with CO (1 atm) in C6D6. After several hours, the 1H NMR spectrum of this reaction mixture exhibited a large number of peaks in the region of Cp* resonances, thereby indicating a plethora of products.

4.2.13 Reaction of Cp*W(NO)(CH2SiMe3)(OPh) (3.5) with CO

Complex 3.5 was reacted with CO either at 1 atm in C6D6 or at higher pressures (600 psig) in C6H6. A large number of unidentified products were formed as evidenced by the 1H NMR spectra (C6D6) of the reaction mixtures which exhibited many peaks in the region of Cp* resonances.

4.2.14 Reactions of Cp*W(NO)(CH2SiMe3)(OPh) (3.5) with CO2 or CS2

A pentane solution (10 mL) of Cp*W(NO)(CH2SiMe3)(OPh) (0.23 g, 0.43 mmol) was exposed to CO2 (1 atm). The solution was stirred overnight with no color change being observed. An IR spectrum of the reaction mixture exhibited one vNO which was attributable to Cp*W(NO)(CH2SiMe3)(OPh).
100

An excess of CS₂ (~2 mL) was vacuum transferred to a pentane solution (10 mL) of Cp*W(NO)(CH₂SiMe₃)(OPh) (0.26 g, 0.50 mmol). The reaction mixture was stirred overnight with no color change being observed. The mixture was taken to dryness in vacuo, and the purple residue was extracted with pentane. Cp*W(NO)(CH₂SiMe₃)(OPh) (0.22 g, 85% recovered yield) was crystallized from the pentane extracts.

4.2.15 Reaction of Cp*W(NO)(CH₂SiMe₃)(OPh) (3.5) with RNCO [R = Ph, p-tolyl]

Crystals of Cp*W(NO)(CH₂SiMe₃)(OPh) (0.16 g, 0.30 mmol) were treated with an excess of PhNCO or p-tolylNCO (~0.5 mL). The purple crystals immediately turned orange upon the addition of the isocyanate reagent. Pentane (10 mL) was added to the mixtures to induce the precipitation of orange solids. The supernatant pentane solutions were discarded, and the remaining solids were washed with pentane (10 mL). The orange solids were dried in vacuo for 2 h, and recrystallized from Et₂O. Orange crystals of Cp*W(NO)(CH₂SiMe₃)(OPh)(PhNCO) (4.4) (0.065 g, 33% yield) and Cp*W(NO)(CH₂SiMe₃)(OPh)(p-tolylNCO) (4.5) (0.064 g, 26% yield) were isolated by cannulation.

4.2.16 Reaction of Cp*Mo(NO)(CH₂Ph)(OCMe₃) (3.1) with H₂

An infrared spectrum of a THF solution (40 mL) of complex 3.1 (0.57 g, 1.3 mmol) exhibited several absorption bands in the nitrosyl region (1611, 1580, 1578 cm⁻¹). This solution was pressurized to 40 psig with H₂ in a Fischer-Porter high-pressure vessel. The reaction mixture was left to stir for 4 d. After this time an IR spectrum of the reaction solution exhibited a single band at 1618 cm⁻¹. The solution was taken to dryness in vacuo, and the residue remaining was extracted with Et₂O (2 x 10 mL). The extracts were filtered over Celite, combined and concentrated. Amber crystals of [Cp*Mo(NO)(CH₂Ph)(μ-O)]₂ (4.6) (0.092 g, 19% yield) formed when the saturated solution was cooled to -30 °C for 2 days. Complex 4.7 can be recrystallized from CH₂Cl₂/hexanes solutions.
The alkoxy alkyl complexes Cp*W(NO)(CH₂Ph)(OCMe₃) (3.3), Cp*W(NO)(CH₂SiMe₃)(OCMe₃) (3.4) and Cp*W(NO)(CH₂SiMe₃)(OPh) (3.5) were treated with H₂ in fashion similar to that described above. In all cases, only the organometallic starting material was isolated.

4.2.17 Magnetic Susceptibility Measurements of [Cp*Mo(NO)(CH₂Ph)(μ-O)]₂ (4.7)

Crystals of [Cp*Mo(NO)(CH₂Ph)(μ-O)]₂ (4.7) (0.0748 g) were ground into a powder with a mortar and pestle in a glovebox. This powder was packed firmly into a capillary tube. A magnetic susceptibility measurement of this sample was recorded on a Johnson-Matthey magnetic susceptibility balance at room temperature.¹⁴ The susceptibility per gram of sample, χ₉, was measured directly by the Johnson-Matthey magnetic susceptibility balance according to the following formula: χ₉ = C₉/R₀/R - lR₀, where C₉ was the balance calibration constant (1.006), l was the length of the sample (1.5 cm), R was the reading of the tube plus the sample (-55), R₀ was the reading of the empty tube (+15) and m was the mass of the sample (0.0748 g). From this formula χ₉ was calculated to be -1.4 x 10⁻⁶ c.g.s emu for complex 4.6. The molar susceptibility for the monomer is -520 x 10⁻⁶ cm³mol⁻¹, since χ₉ = χ₉ x MW of monomer. The value of χ₉ obtained by summing Pascal's constants was estimated at -260 x 10⁻⁶ cm³mol⁻¹.¹⁵
4.3 Characterization Data

Table 4.1. Numbering Scheme, Color, Yield and Elemental Analysis Data for Complexes 4.1 - 4.6

<table>
<thead>
<tr>
<th>complex</th>
<th>compd no.</th>
<th>color (yield, %)</th>
<th>anal. found (calcd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CpMo(NO)(CH₂Ph)₂-(μ-O)]</td>
<td>4.1</td>
<td>black (42)</td>
<td>49.95(49.67) 4.28(4.17) 5.00(4.82)</td>
</tr>
<tr>
<td>[Cp⁺Mo(NO)(CH₂CMe₂Ph)]₂-(μ-O)</td>
<td>4.2</td>
<td>red-black (50)</td>
<td>59.33(59.69) 7.15(7.01) 3.23(3.48)</td>
</tr>
<tr>
<td>Cp⁺W(NO)(OPh)(η²-C{NCMe₃}CH₂SiMe₃)</td>
<td>4.3</td>
<td>yellow (80)</td>
<td>49.19(49.02) 6.59(6.58) 4.49(4.57)</td>
</tr>
<tr>
<td>Cp⁺W(NO)(C₂H₅)₂(OH)(PhNCO)</td>
<td>4.4</td>
<td>orange (33)</td>
<td>50.01(50.00) 5.59(5.66) 4.32(4.40)</td>
</tr>
<tr>
<td>Cp⁺W(NO)(C₂H₅)₂(OH)(p-tolylnCO)</td>
<td>4.5</td>
<td>orange (26)</td>
<td>50.76(50.63) 5.78(5.67) 4.32(4.01)</td>
</tr>
<tr>
<td>[Cp⁺Mo(NO)(CH₂Ph)(μ-O)]₂</td>
<td>4.7</td>
<td>amber (19)</td>
<td>55.41(55.51) 6.22(6.02) 3.79(3.80)</td>
</tr>
</tbody>
</table>

Table 4.2. Mass Spectral and Infrared Data for Complexes 4.1 - 4.6

<table>
<thead>
<tr>
<th>compd no.</th>
<th>MS, m/z</th>
<th>temp, °C</th>
<th>IR, cm⁻¹ (Nujol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>284 [CpMo(NO)(CH₂Ph)⁺]</td>
<td>100</td>
<td>1597, 1574 698c</td>
</tr>
<tr>
<td>4.2</td>
<td>805 [P⁺]</td>
<td>100</td>
<td>1578, 1564 764c</td>
</tr>
<tr>
<td>4.3</td>
<td>612 [P⁺]</td>
<td>200</td>
<td>1585 1670d</td>
</tr>
<tr>
<td>4.4</td>
<td>529 [P⁺- PhNCO]</td>
<td>120</td>
<td>1597, 1543 br 1263, 1241e</td>
</tr>
<tr>
<td>4.5</td>
<td>529 [P⁺-p-tolylnCO]</td>
<td>120</td>
<td>1554, 1539 1259, 1245e</td>
</tr>
<tr>
<td>4.7</td>
<td>526f</td>
<td>120</td>
<td>1599, 1588, 1568 756sh, 748, 700c</td>
</tr>
</tbody>
</table>

a m/z values are for the highest intensity peak of the calculated isotopic cluster, i.e. ⁹⁸Mo and ¹⁸⁴W.
b Probe temperatures.
c vMo-O
d vCN
e vSi-Me
f The mass of the parent ion can be attributed to [Cp⁺Mo(O)]₂-(μ-O), a common decomposition product of molybdenum nitrosyl-containing complexes.
Table 4.3. $^1$H and $^{13}$C{$^1$H} NMR Data for Complexes 4.1 - 4.6 in C$_6$D$_6$

<table>
<thead>
<tr>
<th>compd no.</th>
<th>$^1$H NMR (δ, ppm)</th>
<th>$^{13}$C{$^1$H} NMR (δ, ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.15 - 6.90 (m, 10 H, ArH)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.10 (s, 10 H, C$_5$H$_3$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.38 (d, 2 H, CH$<em>2$, $^2$J$</em>{HH}$ = 12.0 Hz)</td>
<td>130.5 (C$_{ipso}$)</td>
</tr>
<tr>
<td></td>
<td>3.28 (d, 2 H, CH$<em>2$, $^2$J$</em>{HH}$ = 12.0 Hz)</td>
<td>128.2 (aryl C)</td>
</tr>
<tr>
<td>4.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.71 (d, 4 H, o-ArH, $^2$J$_{HH}$ = 7.4 Hz)</td>
<td>135.42 (C$_{ipso}$)</td>
</tr>
<tr>
<td></td>
<td>7.32 (t, 4 H, m-ArH, $^2$J$_{HH}$ = 8.2 Hz)</td>
<td>128.40 (aryl C)</td>
</tr>
<tr>
<td></td>
<td>7.10 (t, 2 H, p-ArH, $^2$J$_{HH}$ = 7.3 Hz)</td>
<td>125.34 (aryl C)</td>
</tr>
<tr>
<td></td>
<td>2.18 (d, 2 H, CH$_A$CH$<em>B$, $^2$J$</em>{HH}$ = 12.4 Hz)</td>
<td>112.83 (C$_3$(CH$_3$)$_3$)</td>
</tr>
<tr>
<td></td>
<td>2.04 (d, 2 H, CH$_A$CH$<em>B$, $^2$J$</em>{HH}$ = 12.4 Hz)</td>
<td>69.91 (CH$_2$(CH$_3$)$_3$Ph)</td>
</tr>
<tr>
<td></td>
<td>1.84 (s, 6 H, CH$_2$C(CH$_3$)$_3$(CH$_3$)$_3$Ph)</td>
<td>43.78 (CH$_2$(CH$_3$)$_3$Ph)</td>
</tr>
<tr>
<td></td>
<td>1.78 (s, 6 H, CH$_2$C(CH$_3$)$_3$(CH$_3$)$_3$Ph)</td>
<td>32.02 ((CH$_3$)$_A$)</td>
</tr>
<tr>
<td></td>
<td>1.56 (s, 30 H, C$_3$(CH$_3$)$_3$)</td>
<td>30.77 ((CH$_3$)$_B$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.76 (C$_5$(CH$_3$)$_3$)</td>
</tr>
<tr>
<td>4.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.43 - 7.32 (m, 4 H, ArH)</td>
<td>216.9 (CNCMe$_3$)</td>
</tr>
<tr>
<td></td>
<td>6.87 - 6.74 (m, 1 H, ArH)</td>
<td>168.3, 129.5, 120.7, 117.1 (aryl C's)</td>
</tr>
<tr>
<td></td>
<td>2.94 (d, 2 H, J$_{HH}$ = 11.1 Hz, CH$_A$H$_B$)</td>
<td>110.9 (C$_3$(CH$_3$)$_3$)</td>
</tr>
<tr>
<td></td>
<td>2.45 (d, 2 H, J$_{HH}$ = 11.1 Hz, CH$_A$H$_B$)</td>
<td>29.8 (C(CH$_3$)$_3$)</td>
</tr>
<tr>
<td></td>
<td>1.73 (s, 15 H, C$_3$(CH$_3$)$_3$)</td>
<td>27.4 (CH$_2$)</td>
</tr>
<tr>
<td></td>
<td>1.18 (s, 9 H, NC(CH$_3$)$_3$)</td>
<td>9.8 (C$_3$(CH$_3$)$_3$)</td>
</tr>
<tr>
<td></td>
<td>0.21 (s, 9 H, SiC(CH$_3$)$_3$)</td>
<td>0.5 (Si(CH$_3$)$_3$)</td>
</tr>
<tr>
<td>4.3$^a$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.42 - 7.32 (m, 4 H, ArH)</td>
<td>216.8 (CNCMe$_3$)</td>
</tr>
<tr>
<td></td>
<td>6.87 - 6.80 (m, 1 H, ArH)</td>
<td>168.2, 129.5, 120.6, 117.1 (aryl C's)</td>
</tr>
<tr>
<td></td>
<td>2.08 (s, 3 H, CH$_3$)</td>
<td>110.8 (C$_3$(CH$_3$)$_3$)</td>
</tr>
<tr>
<td></td>
<td>1.71 (s, 15 H, C$_3$(CH$_3$)$_3$)</td>
<td>59.5 (CNC(CH$_3$)$_3$)</td>
</tr>
<tr>
<td></td>
<td>1.05 (s, 9 H, NC(CH$_3$)$_3$)</td>
<td>29.1 (C(CH$_3$)$_3$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>19.1 (CH$_3$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.6 (C$_5$(CH$_3$)$_3$)</td>
</tr>
<tr>
<td>4.4$^b$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.84 - 6.54 (m, ArH)</td>
<td>216.8 (CNCMe$_3$)</td>
</tr>
<tr>
<td></td>
<td>1.54 (s, 15 H, C$_3$(CH$_3$)$_3$)</td>
<td>168.2, 129.5, 120.6, 117.1 (aryl C's)</td>
</tr>
<tr>
<td></td>
<td>0.49 (d, 1 H, J$_{HH}$ = 11.1 Hz, CH$_A$H$_B$)</td>
<td>110.8 (C$_3$(CH$_3$)$_3$)</td>
</tr>
<tr>
<td></td>
<td>0.41 (s, 9 H, SiC(CH$_3$)$_3$)</td>
<td>59.5 (CNC(CH$_3$)$_3$)</td>
</tr>
<tr>
<td></td>
<td>-0.27 (d, 1 H, J$_{HH}$ = 11.1 Hz, CH$_A$H$_B$)</td>
<td>29.1 (C(CH$_3$)$_3$)</td>
</tr>
<tr>
<td>Complex</td>
<td>Chemical Shifts and Coupling Constants</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>--------------------------------------</td>
<td></td>
</tr>
</tbody>
</table>
| 4.5<sup>d</sup> | 7.75 - 6.75 (m, ArH)  
2.10 (s, 3 H, PhCH<sub>3</sub>)  
1.57 (s, 15 H, C<sub>5</sub>(CH<sub>3</sub>)<sub>3</sub>)  
0.46 (d, 1 H, J<sub>HH</sub> = 12.0 Hz, CH<sub>2</sub>AH<sub>B</sub>)  
0.39 (s, 9 H, SiC(CH<sub>3</sub>)<sub>3</sub>)  
-0.29 (d, 1 H, J<sub>HH</sub> = 12.0 Hz, CH<sub>2</sub>AH<sub>B</sub>) |
| 4.7<sup>e</sup> | 7.82 - 6.99 (m, 50 H)  
3.36-3.28 (m, 2 H)  
3.25 (d, 2 H, J = 11.1 Hz)  
3.05 (d, 2 H, J = 9.6 Hz)  
2.86 (d, 2 H, J = 11.1 Hz)  
2.71 (d, 2 H, J = 9.6 Hz)  
2.14 (d, 4 H, J = 8.1 Hz)  
2.02 (d, 4 H, J = 8.7 Hz)  
1.90 (d, 4 H, J = 8.7 Hz)  
1.82 (d, 4 H, J = 8.1 Hz)  
1.61 (s, 8 H)  
1.49 (s, 8 H)  
1.48 (s, 22 H)  
1.42 (s, 45 H)  
0.42 (d, 2 H, J = 1.2 Hz)  
-0.17 (s, 1 H)  
-1.74 (d, 2 H, J = 1.2 Hz) |

<sup>a</sup> Cp<sup>3</sup>W(NO)(OPh)((η<sup>2</sup>−C{NCMe<sub>3</sub>})Me) (4.3') is derived in situ by hydrolysis of 4.3. See Section 4.4.4.2

<sup>b</sup> Crystals of 4.4 partially dissociate in C<sub>6</sub>D<sub>6</sub> to Cp<sup>3</sup>W(NO)(CH<sub>2</sub>SiMe<sub>3</sub>)(OPh) (3.5) and PhNCO such that 4.4 and 3.5 exist in a 1:2.7 ratio. 4.4 exists in a 3.5:1 ratio with 3.5 in the presence of excess PhNCO.

<sup>c</sup> Not recorded.

<sup>d</sup> Crystals of 4.5 partially dissociate in C<sub>6</sub>D<sub>6</sub> to Cp<sup>3</sup>W(NO)(CH<sub>2</sub>SiMe<sub>3</sub>)(OPh) (3.5) and p-tolylNCO such that 4.5 and 3.5 exist in a 1:6 ratio. 4.5 exists in a 2.3:1 ratio with 3.5 in the presence of excess p-tolylNCO [δ 6.68 (d, 2 H, J<sub>HH</sub> = 8.4 Hz, ArH), 6.56 (d, 2 H, J<sub>HH</sub> = 8.4 Hz, ArH), 1.95 (s, 3 H, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>) ppm].

<sup>e</sup> The <sup>1</sup>H NMR data for complex 4.7 was not assigned. See Section 4.4.5 for a discussion of this data.
4.4 Results and Discussion

The investigation into the chemical reactivity patterns of alkoxo alkyl complexes involved the treatment of representative Cp*M(NO)(R)(OR') species with a variety of reagents such as oxygen, water, HCl, phenol, trimethylphosphine, carbon monoxide, tert-butyl isocyanide, CO₂, CS₂, isocyanates, and dihydrogen. The reactions of the alkoxo alkyl species are not easily generalized. The outcomes of these reactions are sensitive to changes in the metal, the alkoxo ligand, the alkyl ligand, and the reaction conditions employed. Diverse reactivity patterns including an insertion reaction, a dimerization, and the formation of several Lewis acid-base adducts are observed for the family of alkoxo alkyl complexes, Cp*M(NO)(R)(OR').

4.4.1 Reactions of Alkoxo Alkyl Complexes with Oxygen and Water

Most organometallic complexes are sensitive to the atmosphere, with oxygen and water being the key reactive components of the atmosphere. Organometallic complexes are prone to oxidation by oxygen, and undergo hydrolysis reactions with water because of their polar M-C bonds. Not surprisingly, therefore, the alkoxo alkyl complexes Cp*M(NO)(R)(OR') decompose when exposed to the atmosphere. However, when Cp*M(NO)(R)(OR') complexes are treated with pure O₂ or H₂O under controlled conditions, they afford isolable organometallic compounds which in several cases retain their metal-carbon bonds.

4.4.1.1 Reactions of Tungsten Alkoxo Alkyl Complexes with Oxygen

Both in solutions and in the solid state, Cp*M(NO)(R)(OR') complexes react rapidly when exposed to oxygen. Interestingly, the products of these oxygen reactions are dependent on the metal of the starting alkoxo alkyl species. Thus, in the case of M = W, O₂ effects the transformations depicted in eq 4.1.7.
Reactions 4.1 afford the organometallic dioxo products in high yields. These products can be identified by the presence of two strong $\nu_{W-O}$ bands in their Nujol mull IR spectra. However, a GCMS trace of the remaining reaction mixture shows at least 9 organic byproducts. The parent ion masses of these products range from $m/z = 59-223$. The large number of organic species indicates that reaction 4.1 probably proceeds via a complex mechanism. As with the related dialkyl and diaryl complexes of tungsten, which undergo a similar type of reaction with oxygen (eq 4.2), a considerable amount of effort has been expended in attempting to identify the organic complexes produced in these transformations.

$$\text{Cp}^*\text{W(NO)}(\text{R})(\text{OR}') + \text{O}_2 \rightarrow \text{Cp}^*\text{W(O)}_2\text{R} \quad (4.1)$$

$\text{R} = \text{CH}_2\text{Ph}; \text{R}' = \text{CMe}_3$

$\text{R} = \text{CH}_2\text{SiMe}_3; \text{R}' = \text{Ph}$

The most important aspect of reactions 4.1, is that reactivity occurs at the M-O bond, while the M-C bond remains intact. This is most certainly not a thermodynamic affect, since group 6 metal-oxygen bonds are stronger than M-C bonds.

4.4.1.2 Reactions of Molybdenum Alkoxo Alkyl Complexes with Oxygen

Molybdenum alkoxo alkyl species react with $\text{O}_2$ to form the known complex $[\text{Cp}^*\text{Mo(O)}_2]_2-(\mu-\text{O})$, i.e.,

$$\text{Cp}^*\text{Mo(NO)}(\text{R})(\text{OR}') + \text{O}_2 \rightarrow [\text{Cp}^*\text{Mo(O)}_2]_2-(\mu-\text{O}) \quad (4.3)$$

$\text{R} = \text{CH}_2\text{Ph}; \text{R}' = \text{CMe}_3$

$\text{R} = \text{CH}_2\text{Ph}; \text{R}' = \text{Ph}$

Reactions 4.3 demonstrate that the molybdenum species are more reactive than their tungsten congeners (eq 4.1). It has been shown in our laboratories previously that the thermodynamically
stable $[\text{Cp}^*\text{Mo(O)}_2]_2-(\mu-O)$ species is a ubiquitous decomposition product of molybdenum nitrosyl complexes.\(^6\) $[\text{Cp}^*\text{Mo(O)}_2]_2-(\mu-O)$ is easily identified by its Nujol IR spectrum which exhibits two strong terminal oxo stretches at 910 and 878 cm\(^{-1}\) as well as a broad absorption due to the bridging oxo ligand at 762 cm\(^{-1}\).\(^6\) Additionally, the \(^1\)H NMR spectrum of $[\text{Cp}^*\text{Mo(O)}_2]_2-(\mu-O)$ in C\(_6\)D\(_6\) displays a single signal at \(\delta\) 1.78 ppm due to the protons of the permethylcyclopentadienyl ligands.

4.4.1.3 Reactions of Isolated Tungsten Alkoxo Alkyl Complexes with Water

It has been previously shown that $\text{Cp}^*\text{W(NO)}R_2$ species are inert with respect to hydrolysis when $R = \text{alkyl}$, but react with $\text{H}_2\text{O}$ to form $\text{Cp}^*\text{W(O)}_2(\text{aryl})$ when $R = \text{aryl}$.\(^6\)\(^b\)

\[
\begin{align*}
\text{Cp}^*\text{W(NO)}(\text{alkyl})_2 & \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{No Reaction} \\
\text{Cp}^*\text{W(NO)}(\text{aryl})_2 & \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{Cp}^*\text{W(O)}_2(\text{aryl})
\end{align*}
\]

The tungsten alkoxo alkyl compounds 3.3 and 3.5 resemble the diaryl systems in that they both react with $\text{H}_2\text{O}$ to produce the known $\text{Cp}^*\text{W(O)}_2(\text{CH}_2\text{Ph})$ and $\text{Cp}^*\text{W(O)}_2(\text{CH}_2\text{SiMe}_3)$ complexes, respectively (eq 4.6).

\[
\begin{align*}
\text{R} & = \text{CH}_2\text{SiMe}_3, \; \text{R'} = \text{Ph} \\
\text{R} & = \text{CH}_2\text{Ph}, \; \text{R'} = \text{CMe}_3
\end{align*}
\]
In reactions 4.6 the yield of the dioxo alkyl complexes is high. As for any of these dioxo producing reactions, a GCMS trace of the reaction mixture indicates a large number of organic byproducts (Section 4.4.1.1).

4.4.1.4 Preparation of \( [\text{Cp}'\text{M}(\text{NO})(\text{R})]_2-(\mu-\text{O}) \) Complexes: Reactions of In Situ Generated Molybdenum Alkoxo Alkyl Complexes with Trace Water

The molybdenum alkoxo alkyl complexes \( \text{CpMo(NO)}(\text{CH}_2\text{Ph})(\text{OCMe}_3) \) and \( \text{Cp}^*\text{Mo(NO)}(\text{CH}_2\text{CMe}_2\text{Ph})(\text{OCMe}_3) \) have not been isolated to date. However, in attempts to prepare these species, \( [\text{CpMo(NO)}(\text{CH}_2\text{Ph})]_2-(\mu-\text{O}) \) (4.1) and \( [\text{Cp}^*\text{Mo(NO)}(\text{CH}_2\text{CMe}_2\text{Ph})]_2-(\mu-\text{O}) \) (4.2) have been isolated.

\[
\begin{align*}
\text{Cp'} = \text{Cp}, & \quad \text{R} = \text{CH}_2\text{Ph}; \\
\text{Cp'} = \text{Cp}^*, & \quad \text{R} = \text{CH}_2\text{CMe}_2\text{Ph}
\end{align*}
\]

In these experiments, \( \text{Cp'Mo(NO)}(\text{R})\text{Cl} \) is generated in situ from an equimolar solution of \( \text{Cp'Mo(NO)}\text{Cl}_2 \) and the appropriate magnesium dialkyl reagent.\(^9\) The reaction mixtures are filtered to remove \( \text{MgCl}_2\cdot\text{X(dioxane)} \) and cannulated to a flask containing the lithium alkoxide salt. The reaction mixtures turn the characteristic red color of the alkoxo alkyl species; however, as these solutions are worked up they darken to a deep red-black color. Presumably, the molybdenum alkoxo species are extremely water sensitive and are easily hydrolyzed by trace water present in the solvents used to work-up these complexes. From these solutions, pure crystalline samples of complexes 4.1 and 4.2 are isolated in moderate yields. These \( [\text{Cp'Mo(NO)}(\text{R})]_2-(\mu-\text{O}) \) complexes are moderately air-stable as solids, but in solution they are air-sensitive and decompose to \( [\text{Cp'Mo(O)}_2]_2-(\mu-\text{O}) \).\(^6\) The infrared spectra of 4.1 and 4.2 each
exhibit two nitrosyl stretches between 1600 and 1560 cm\(^{-1}\). Diagnostic Mo-O-Mo vibrations are observed at 698 cm\(^{-1}\) for complex 4.1 and 764 cm\(^{-1}\) for complex 4.2.\(^6\) The \(^1\)H NMR spectra of these bimetallic species indicate only one isomer is present in solution (Table 4.3).\(^16,17\)

Previous work has shown that analogous bimetallic complexes can be produced by treating molybdenum dialkyl or diaryl complexes with water, i.e.,\(^6\)

\[
2 \text{Cp'}\text{Mo(NO)}(\text{R})_2 \xrightarrow{\text{H}_2\text{O}} [\text{Cp'}\text{Mo(NO)}(\text{R})]_2- (\mu-\text{O}) \quad (4.7)
\]

\[\text{R} = \text{alkyl, aryl}\]

[\text{Cp'}\text{Mo(NO)}(\text{CH}_2\text{CMe}_2\text{Ph})]_2- (\mu-\text{O}) is more easily crystallized from the reaction mixture of water and the alkoxo alkyl complex than from the reaction mixture of water and the bis(neophyl) complex. This is because the byproduct of the latter reaction is Me\(_3\)CPh which is not easily separated from the product due to its low volatility. The byproduct of the alkoxo alkyl reaction is believed to be Me\(_3\)COH which can be easily removed in vacuo.

We believe that the most plausible mechanism for the formation of \(\mu\)-oxo bimetallic complexes from the alkoxo alkyl complexes is similar to the mechanism proposed for the hydrolysis of molybdenum dialkyl complexes.\(^6\) Thus, the putative alkoxo alkyl complex is hydrolyzed to form a hydroxide complex and \(t\)-butanol. In turn, the hydroxide intermediate reacts with a second equivalent of the alkoxo alkyl to eliminate alcohol and produce the bimetallic species (Scheme 4.2). The products obtained from the hydrolysis of the alkoxo alkyl complexes indicate reaction occurs preferentially at the alkoxo ligand rather than the alkyl ligand.

**4.4.2 Reactions of Alkoxo Alkyl Complexes with HCl**

It has been established previously that the bis(benzyl) complexes, \(\text{Cp'}\text{M(NO)}(\text{CH}_2\text{Ph})_2\), react with HCl to produce \(\text{Cp'}\text{M(NO)}(\text{CH}_2\text{Ph})\text{Cl}\).\(^5\) We have found that similar treatment of
Scheme 4.2

\[
\begin{align*}
\text{Mo}^\text{III} & \rightarrow \text{Mo}^\text{IV} \\
\text{ROR'} & \rightarrow \text{ROH}
\end{align*}
\]
Cp*W(NO)(OCMe₃)₂ with HCl provides first the monoalkoxo complex, Cp*W(NO)(OCMe₃)Cl, and then the dichloro compound, Cp*W(NO)Cl₂ (Section 2.4.2).

The reactions of Cp*M(NO)(R)(OR') with HCl provide some insight into the relative reactivities of M-C versus M-O bonds in these systems. As expected, the alkoxo alkyl complexes Cp*W(NO)(CH₂Ph)(OCMe₃) (3.3) and Cp*W(NO)(CH₂SiMe₃)(OPh) (3.5) react with HCl to produce exclusively the corresponding alkyl chloro species (eq 4.8).

\[
\text{Cp*M(NO)(R)(OR')} + \text{HCl} \rightarrow \text{Cp*M(NO)(R)(Cl)} + \text{HOR'}
\] (4.8)

Thus, the preferred site of reactivity of the Cp*M(NO)(R)(OR') complexes with the polar reagent HCl is the more polar M-O bond rather than the M-C linkage.

**4.4.3 Reaction of Cp*W(NO)(CH₂SiMe₃)(OMe) with PhOH**

Cp*W(NO)(CH₂SiMe₃)(OMe) reacts cleanly with PhOH to produce Cp*W(NO)(CH₂SiMe₃)(OPh) in moderate isolated yield (60%).

The reaction mixture turns from red to red-purple over the course of 2 d, and the progress of the reaction can be easily monitored by IR spectroscopy. For instance, the IR spectrum of the pentane solution of Cp*W(NO)(CH₂SiMe₃)(OMe) exhibits a ν₅O of 1584 cm⁻¹, and as it reacts with PhOH, the band at 1584 cm⁻¹ is slowly replaced by two bands at 1597 and 1586 cm⁻¹. This alcohol exchange reaction is favored (ΔG° < 0) since the pKₐ of PhOH is 10 and the pKₐ of MeOH is 15.2.¹⁸ This reaction is driven by the formation of a strong H-OMe bond.
Reaction 4.9 is not reversible; thus, Cp*W(NO)(CH₂SiMe₃)(OPh) does not react with MeOH to reform the methoxy species. It is also interesting to note that the metal-alkyl link is stable to excess phenol. It is not cleaved to form the bis(phenoxide) complex, Cp*W(NO)(OPh)₂, which can be prepared via a metathesis reaction (Section 2.2.5).

\[
\text{Cp}^*\text{W(NO)(CH}_2\text{SiMe}_3\text{)(OPh)} + \text{excess PhOH} \rightleftharpoons \text{Cp}^*\text{W(NO)(OPh)}_2 \quad (4.10)
\]

Several mechanisms for alcohol exchange reactions have been postulated.¹ In alkoxide transfer between coordinatively unsaturated metal centers exchange is thought to occur in a concerted, associative manner. Caulton and coworkers have suggested that the coordinatively saturated species Ir(H)₂(OR)(PCy₃)_2 undergoes alcohol exchange first via formation of a hydrogen bond to the uncoordinated alcohol, then through a four-centered transition state, i.e.,¹⁹

\[
\text{Ir} - \text{O} - \text{R} \rightarrow \left[ \text{Ir} - \text{O} - \text{R'} \right]^{\ddagger} \rightarrow \text{Ir} - \text{O} - \text{HOR} \quad (4.11)
\]

Alternatively, the coordinated alkoxo ligand could reversibly dissociate from the metal to give an alkoxide anion and a metal cation, and exchange could occur between free ions in solution.¹²⁰

Exchange reactions are important since they indicate the potential for replacing alkoxo ligands with other heteroatom groups.²¹ Reagents with acidic protons such as chelating alcohols, carboxylic acids, alkyl and arylthiols may be prone to exchange reactions with these alkoxo alkyl species given their low pKₐ values.¹⁸ Consistently, the alkoxo alkyl complexes are converted to alkyl chloride species upon treatment with HCl (Section 4.4.2).
4.4.4 Reactions of Lewis Bases with Alkoxo Alkyl Complexes: Adduct Formation or Insertion

The dialkyl and diaryl complexes, \( \text{Cp}^*\text{M(NO)R}_2 \), are known to react with Lewis bases to form either 1:1 adducts (e.g. PMe_3)_2 or insertion products in which the base has inserted into the metal-carbon bond (e.g. CO). Currently, there is no clear way to predict whether a certain Lewis base will form an adduct complex or insert into the metal-carbon bond.

4.4.4.1 Reaction of \( \text{Cp}^*\text{W(NO)}(\text{CH}_2\text{SiMe}_3)(\text{OPh}) \) (3.5) with PMe_3

\( \text{Cp}^*\text{W(NO)}(\text{CH}_2\text{SiMe}_3)(\text{OPh}) \) (3.5) is a sufficiently potent Lewis acid to form an adduct with PMe_3 at low temperatures as evidenced by variable-temperature \(^1\text{H} \) NMR spectroscopy from 24 °C to -60 °C. At 24 °C, a purple CDCl_3 solution of 3.5 and excess PMe_3 exhibits signals due to the starting reagents (Figure 4.1). At -60 °C this solution is yellow, and all signals in the \(^1\text{H} \) NMR spectrum are broad (Figure 4.2). Nevertheless, new resonances consistent with the adduct complex are evident at this temperature, most notably a doublet at \( \delta 1.42 \) (\(^2\text{J}_{\text{PH}} = 6 \) Hz) attributable to coordinated PMe_3. When the sample is warmed to room temperature, its color reverts to purple, and its \(^1\text{H} \) NMR spectrum is identical to the original spectrum, thereby indicating that this adduct formation is a reversible process (eq 4.12).

![Diagram](image)

On a larger scale, a yellow solid formulated as \( \text{Cp}^*\text{W(NO)}(\text{CH}_2\text{SiMe}_3)(\text{OPh})(\text{PMe}_3) \) is formed by the treatment of \( \text{Cp}^*\text{W(NO)}(\text{CH}_2\text{SiMe}_3)(\text{OPh}) \) with neat PMe_3. In the presence of excess PMe_3 this solid is stable at low temperatures. However, it is not possible to isolate and further
Figure 4.1 $^1$H NMR spectrum of Cp*W(NO)(CH$_2$SiMe$_3$)(OPh) (3.5) and PMe$_3$ at 24 °C in CDCl$_3$. 
Figure 4.2 $^1\text{H}$ NMR spectrum of Cp*W(NO)(CH$_2$SiMe$_3$)(OPh) (3.5) and PMe$_3$ at -60 °C in CDCl$_3$. 
characterize this complex since at room temperature, under vacuum or in solution, the yellow adduct loses PMe$_3$.

### 4.4.4.2 Insertion Reaction of Cp*W(NO)(CH$_2$SiMe$_3$)(OPh) and CNCMe$_3$

Tert-butyl isocyanide forms stable inserted products with dialkyl complexes$^2$ and alkyl chloride complexes.$^9$ In a similar fashion, Cp*W(NO)(CH$_2$SiMe$_3$)(OPh) (3.5) reacts cleanly with CNCMe$_3$ to provide the yellow iminoacyl complex, Cp*W(NO)(η$^2$-C{NCMe$_3$}CH$_2$SiMe$_3$)(OPh) (4.3), in high yield (eq 4.13).

$$
\begin{align*}
\text{Cp*W(NO)(CH}_2\text{SiMe}_3\text{)(OPh)} & \quad \text{CNCMe}_3 \\
\text{PhO} & \quad \text{N} \\
\text{NO} & \quad \text{R} \\
& \quad \text{W} \\
\text{R} = \text{CH}_2\text{SiMe}_3
\end{align*}
$$

Purple crystals of complex 3.5 readily react with an excess of CNCMe$_3$ to form a yellow oily mixture. Excess CNCMe$_3$ can be removed in vacuo to afford complex 4.3 as yellow oil, which can be easily crystallized from pentane to afford yellow nuggets of analytically pure Cp*W(NO)(η$^2$-C{NCMe$_3$}CH$_2$SiMe$_3$)(OPh). Reaction 4.13 demonstrates the Lewis acidic nature of 3.5 and lends more credence to the proposed PMe$_3$ adduct proposed in the previous section.

Consistent with other iminoacyl complexes that we have previously isolated,$^2,9$ Cp*W(NO)(OPh)(η$^2$-C{NCMe$_3$}CH$_2$SiMe$_3$) (4.3) contains a dihapto iminoacyl ligand.$^{23}$ Thus, the Nujol mull IR spectrum (Figure 4.3) of complex 4.3 exhibits two strong bands attributable to ν$_{CN}$ and ν$_{NO}$ at 1670 and 1585 cm$^{-1}$, respectively. The $^1$H NMR spectrum of 4.3 is straightforward. The signals attributable to the diastereotopic methylene protons appear as two doublets at δ 2.94 and 2.45 ppm.
Figure 4.3 Nujol mull infrared spectrum (1739 - 953 cm$^{-1}$) of 
Cp*W(NO)(η²-C(=CNMe$_3$)CH$_2$SiMe$_3$)(OPh) (4.3).
Like the related iminoacyl complex CpW(NO)(η²-C\{NCMe₃\}CH₂SiMe₃)(CH₂SiMe₃),² Cp*W(NO)(η²-C\{NCMe₃\}CH₂SiMe₃)(OPh) is unstable to water. Thus, the phenoxo complex undergoes hydrolysis to form Cp*W(NO)(η²-C\{NCMe₃\}CH₃)(OPh) as evidenced by ¹H NMR spectroscopy (Figure 4.4).

4.3

\[
\text{PhO} \quad \text{N} \quad \text{C} \quad \text{NCMe}_3 \quad \text{CH}_2\text{SiMe}_3
\]

4.3'

\[
\text{PhO} \quad \text{N} \quad \text{C} \quad \text{NCMe}_3 \quad \text{CH}_3
\]

The most notable difference in the ¹H NMR spectra of 4.3 and 4.3' is the appearance of a singlet at δ 2.08 ppm at the expense of two doublets (δ 2.94 and 2.45 ppm) attributed to the methylene protons of the CH₂SiMe₃ group in 4.3.

4.4.4.3 Reactions of Alkoxo Alkyl Complexes with CO

Coordinatively unsaturated Cp'M(NO)R₂ complexes form adducts with carbon monoxide which undergo intramolecular insertion of the coordinated carbon monoxide into the metal-carbon bond to form acyl species.²² In contrast, the reactions of the 18-valence-electron dibenzyl complexes Cp'M(NO)(CH₂Ph)₂ with CO, described in detail in Section 5.4.1.3, result in the production of Cp'M(NO)(CO)₂ and (PhCH₂)₂CO. In a similar fashion, the benzyl alkoxo complex Cp*Mo(NO)(CH₂Ph)(OCMe₃) (3.1) reacts with an excess of carbon monoxide (600 psig) in benzene to form Cp*Mo(NO)(CO)₂ (27% yield) and small amounts of 1,3-diphenylacetone, i.e.,
Figure 4.4 Partial $^1\text{H}$ NMR spectrum (δ 3.1 - 0.1 ppm) of Cp*W(NO)(η$^2$-C{NCMe$_3$})CH$_2$SiMe$_3$)(OPh) (4.3) and its hydrolysis product Cp*W(NO)(η$^2$-C{NCMe$_3$})CH$_3$)(OPh) (4.3') marked with (●) in C$_6$D$_6$. 
The reaction mixture contains at least six other organic products as evidenced by a GC trace of the reaction mixture after it has been filtered through alumina (I). In attempts to isolate these organic products, the reaction mixture was chromatographed on silica gel. The fractions that can be separated by chromatography are inherently unstable and continue to decompose over time.

Cp\textsuperscript{*}Mo(NO)(CO)\textsubscript{2} and (PhCH\textsubscript{2})\textsubscript{2}CO are both air- and moisture-stable complexes, so it was not unreasonable to assume that workup of the reaction mixture from equation 4.15 could be done in the atmosphere in a traditional organic sense. It was soon discovered that mixtures of pentane or Et\textsubscript{2}O solutions of Cp\textsuperscript{*}Mo(NO)(CO)\textsubscript{2} and (PhCH\textsubscript{2})\textsubscript{2}CO decompose over the course of hours when they are exposed to the atmosphere. Therefore, isolation of the product complexes must be performed under anaerobic and anhydrous conditions.

The treatment of 3.1 with lower pressures of CO results in a mixture of organometallic products as evidenced by numerous resonances in the Cp\textsuperscript{*} region of a \textsuperscript{1}H NMR spectrum of the reaction mixture. Cp\textsuperscript{*}W(NO)(CH\textsubscript{2}SiMe\textsubscript{3})(OPh) (3.5) also reacts with CO in C\textsubscript{6}H\textsubscript{6} to afford a mixture of unisolable products.

Reaction 4.15 is thought to proceed first by initial adduct formation, then subsequent insertion of coordinated CO into the molybdenum-carbon bond. However, it is not possible to rule out the insertion of CO into the molybdenum-oxygen link.\textsuperscript{24} For a more complete discussion of reactions of this type, see Section 5.4.1.3. In the case of the alkoxo alkyl complex 3.1, if an intermediate acyl complex is formed [i.e. Cp\textsuperscript{*}Mo(NO)(\textit{\eta}^{2}-C\{O\}CH\textsubscript{2}Ph)(OCMe\textsubscript{3})], reductive elimination of the acyl and the alkoxo ligand from this intermediate would produce Cp\textsuperscript{*}Mo(NO)(CO)\textsubscript{2} and the ester (PhCH\textsubscript{2})C(0)OCMe\textsubscript{3}. There is no obvious reason why this
product would be unstable, but for some reason it is not isolated from the reaction mixture. It is possible that \((\text{PhCH}_2)_2\text{CO}\) is formed by either a radical coupling process or via a bimolecular reductive elimination reaction of \(\text{Cp}^*\text{Mo(NO)(\eta^2-C(O)CH}_2\text{Ph})(\text{OCH}_3)\) and \(\text{Cp}^*\text{Mo(NO)(OCH}_3)(\text{CH}_2\text{Ph})\). In order to distinguish between these two mechanisms, I would suggest the addition of a radical trap such as TEMPO to the reaction mixture or a crossover experiment (e.g. treatment of a 1:1 mixture of \(\text{Cp}^*\text{Mo(NO)(OCH}_3)(\text{CH}_2\text{Ph})\) and \(\text{Cp}^*\text{Mo(NO)(OCH}_3)(\text{CH}_2\text{C}_6\text{H}_4-4-\text{Me})\) with CO). In such an experiment, the asymmetric ketone, 4-Me-C\(_6\)H\(_4\)CH\(_2\)C(O)CH\(_2\)Ph, would be formed if bimolecular processes are in operation.

Carbon monoxide induces a complicated sequence of reactions with the alkoxo alkyl compounds 3.1 and 3.5 providing a number of organometallic and organic products. In contrast, CNCMe\(_3\), valence isoelectronic with CO, cleanly forms a stable insertion product with complex 3.5. There is no obvious explanation why the alkoxo complexes react differently with CO than with CNCMe\(_3\), since presumably both of these reagents form initial Lewis acid-base adducts with the alkoxo alkyl species.

4.4.4.4 Reactions of the Heterocumulenes \(\text{CO}_2\), \(\text{CS}_2\) and RNCO [R = \(\text{Ph}, p\)-tolyl] with \(\text{Cp}^*\text{W(NO)(CH}_2\text{SiMe}_3)(\text{OPh})\)

Alkoxo complexes are known to undergo insertion of \(\text{CO}_2\) and \(\text{CS}_2\).\(^{25}\) However, \(\text{Cp}^*\text{W(NO)(CH}_2\text{SiMe}_3)(\text{OPh})\) does not react with \(\text{CO}_2\) (1 atm) or with excess \(\text{CS}_2\) in pentane. In contrast, the related isocyanates PhNCO and \(p\)-tolylNCO react instantly with solid \(\text{Cp}^*\text{W(NO)(CH}_2\text{SiMe}_3)(\text{OPh})\) to form the orange complexes 4.4 and 4.5, respectively.

\[
\text{Cp}^*\text{W(NO)(CH}_2\text{SiMe}_3)(\text{OPh}) \rightleftharpoons \text{Cp}^*\text{W(NO)(CH}_2\text{SiMe}_3)(\text{OPh})(\text{RNCO})
\]

The product complexes are markedly less soluble in organic solvents than their precursor, therefore excess RNCO can be washed away with pentane to leave analytically pure samples of complexes 4.4 and 4.5. These complexes are relatively air-stable as solids and decompose slowly as solutions when exposed to the atmosphere.
In contrast to the diaryl compounds which form inserted products, \( \text{Cp}^*\text{M(NO)(aryl)}(\eta^2-\text{N}(p\text{-tolyl})\text{C}(\text{O}) \text{aryl}),^{26} \) complexes 4.4 and 4.5 have been formulated as adduct complexes for two reasons. The \( \text{Cp}^*\text{M(NO)(aryl)}(\eta^2-\text{N}(p\text{-tolyl})\text{C}(\text{O}) \text{aryl}) \) species are stable in solution, showing no tendency to liberate PhNCO; whereas, adducts of the type \( \text{Cp}'\text{M(NO)(alkyl)}_2\text{(PMe}_3\text{)} \) undergo loss of PMe\(_3\) in solution.\(^3\) The \(^1\)H NMR data for 4.4 and 4.5 indicate that the isocyanate ligands are labile in solution. Thus, the \(^1\)H NMR spectrum of an isolated sample of crystalline 4.4 (Figure 4.5) partially dissociates in \( \text{C}_6\text{D}_6 \) to \( \text{Cp}^*\text{W(NO)(CH}_2\text{SiMe}_3\text{)(OPh)} \) (3.5) and PhNCO such that complexes 4.4 and 3.5 exist in a 1:2.7 ratio. Addition of excess PhNCO changes this ratio to 3.5:1. In a similar manner, 4.5 dissociates into a 1:6 equilibrium mixture, and this equilibrium can be changed to 2.3:1 with the addition of excess \( p\text{-tolylNCO} \) (Figure 4.6). Further evidence for the lability of the RNCO ligands in these adducts is found in the mass spectral data. Thus, the highest \( m/z \) peak observed for 4.4 and 4.5 is \([\text{Pt-RNCO}]\) whereas \([\text{Pt}^+]\) and \([\text{Pt}^+-\text{NO}]\) are observed for the inserted species \( \text{Cp}^*\text{M(NO)(aryl)}(\eta^2-\text{N}(p\text{-tolyl})\text{C}(\text{O}) \text{aryl}).^{26} \)

The infrared spectra of the adducts as Nujol mulls exhibit two strong bands (1597, 1543 cm\(^{-1}\)) for complex 4.4 and 1554 and 1539 cm\(^{-1}\) for 4.5) in the nitrosyl region. The assignment of these bands is very difficult since nitrosyl, carbonyl, C-N and aryl stretches are commonly observed in this region. For comparison, the known \( \text{Cp}^*\text{W(NO)(Ph)}(\eta^2-\text{N}(p\text{-tolyl})\text{C}(\text{O}) \text{Ph}) \) complex exhibits three bands (\( \nu_{\text{CN}} = 1601, \nu_{\text{NO}} = 1576 \) and \( \nu_{\text{CO}} = 1397 \) cm\(^{-1}\)) in this region.\(^{26} \)
Figure 4.5 $^1$H NMR spectrum of 4.4 in C$_6$D$_6$; an equilibrium mixture of 4.4, Cp*W(NO)(CH$_2$SiMe$_3$)(OPh) (3.5) and PhNCO.
Figure 4.6 $^1$H NMR spectrum of a C$_6$D$_6$ mixture of Cp*W(NO)(CH$_2$SiMe$_3$)(OPh) (3.5) and excess p-tolylnCO (•).
4.4.5 Reactions of Alkoxo Alkyl Complexes with Dihydrogen

When Cp*Mo(NO)(CH$_2$Ph)(OCMe$_3$) (3.1) reacts with H$_2$ (40 psig), it is the metal-alkoxide linkage that is the preferred site of reactivity as the unusual bimetallic complex [Cp*Mo(NO)(CH$_2$Ph)(μ-O)]$_2$ (4.6) is isolable from the final reaction mixture in 19% yield (eq 4.17). This reaction, as written, implies the cleavage of O-C bonds of alkoxo ligands.

![Diagram](image)

(4.17)

In a typical experiment, a THF solution of complex 3.1 is pressurized to 40 psig with H$_2$ in a high-pressure vessel. An initial IR spectrum of this red-orange solution exhibits two bands in the nitrosyl region (1595, 1585 cm$^{-1}$). Over the course of several days, the IR spectrum changes and finally exhibits a broad band in the nitrosyl region at 1618 cm$^{-1}$. No color changes accompany this transformation. The amber product complex 4.7 is initially formed from diethyl ether in low yields (19%), and it is easily recrystallized from CH$_2$Cl$_2$/hexanes solutions. Compound 4.6 is an air-sensitive complex, and it decomposes thermally (>60 °C) in C$_6$D$_6$ solution.

The identity of complex 4.7 was determined by X-ray crystallography. An ORTEP diagram of [Cp*Mo(NO)(CH$_2$Ph)(μ-O)]$_2$ is shown in Figure 4.7, and selected bond lengths and bond angles are presented in Table 4.4. Complex 4.7 is a dimeric species with each molybdenum center in a four-legged piano-stool-type geometry. The nitrosyl ligands are essentially linear with Mo-N-O bond angles of 168.9 (4)$^\circ$ and 168.1 (4)$^\circ$. The crystallographic analysis reveals only one isomer in the solid state. The Cp* ligands are trans to each other, and it is possible to approximate the configuration as R,R if the oxo bridges are designated together as a O$_2$ ligand.
Figure 4.7 ORTEP diagram of [Cp*Mo(NO)(CH₂Ph)(µ-O)]₂ (4.6). 33% probability thermal ellipsoids are shown for the non-hydrogen atoms.
The metals are bridged by two oxo ligands. The slightly asymmetric $\text{Mo}_2\text{O}_2$ core unit of 4.7 is clearly seen in the stereoview (Figure 4.8), and its dimensions are depicted pictorially below.  

<table>
<thead>
<tr>
<th>Bond Lengths (Å)</th>
<th>Bond Angles (°)</th>
<th>Intramolecular Distances (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1 2.15 Mo1</td>
<td>O1 67 Mo1</td>
<td>O1 3.54 Mo2</td>
</tr>
<tr>
<td>O2 2.14 Mo2</td>
<td>O2 68 Mo2</td>
<td>O2 2.38 Mo2</td>
</tr>
</tbody>
</table>

The Mo-O bond distances are typical for single Mo-O bonds. A metal-metal bond is not invoked for this complex, since the Mo1-Mo2 separation is very long at 3.5407 (9) Å. O1 and O2 are also not close enough (2.380 (5) Å) to indicate a bond between these two atoms.

Considering that there is no metal-metal bond in complex 4.7, and that the benzyl ligands and the bridging oxo ligands are involved in simple sigma bonds, the electron count at each metal center in $\text{[Cp}^*\text{Mo(NO)(CH}_2\text{Ph)(μ-O)]}_2$ is $17e^-$ as determined below:

<table>
<thead>
<tr>
<th>C$^*$</th>
<th>Mo</th>
<th>NO</th>
<th>CH$_2$Ph</th>
<th>2 x μ-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-electron donor</td>
<td>6 electrons in its valence shell</td>
<td>3-electron donor</td>
<td>1-electron donor</td>
<td>2 electrons (one from each bridging oxo ligand)</td>
</tr>
</tbody>
</table>

$\text{Cp}^*\text{Mo(NO)(CH}_2\text{Ph)(μ-O)]}_2$ 17 electrons

From this simple electron count, one might expect complex 4.7 to be paramagnetic. Therefore, a magnetic susceptibility measurement of $\text{[Cp}^*\text{Mo(NO)(CH}_2\text{Ph)(μ-O)]}_2$ was recorded ($\chi_M = -520 \times 10^{-6} \text{ cm}^3\text{mol}^{-1}$) on a Johnson-Matthey magnetic susceptibility balance at room temperature (Section 4.2.17). Hence overall, complex 4.7 is diamagnetic. This is consistent with the fact that the $^1\text{H}$ NMR spectrum of 4.7 exhibits no unusual chemical shifts or line width broadening as is normally expected for paramagnetic species. To account for $\text{[Cp}^*\text{Mo(NO)(CH}_2\text{Ph)(μ-O)]}_2$ being diamagnetic, it is possible that there is through-space Mo-Mo coupling. However, it is more likely that coupling of the unpaired electrons through
Figure 4.8 A stereoview of [Cp*Mo(NO)(CH2Ph)(μ-O)]2 (4.6). 33% probability thermal ellipsoids are shown for the non-hydrogen atoms.

Table 4.4. Selected Bond Lengths and Bond Angles for [Cp*Mo(NO)(CH2Ph)(μ-O)]2 (4.6)

<table>
<thead>
<tr>
<th>bond lengths (Å)</th>
<th>bond angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo1 - O1</td>
<td>2.154 (3)</td>
</tr>
<tr>
<td>Mo1 - O2</td>
<td>2.122 (3)</td>
</tr>
<tr>
<td>Mo2 - O1</td>
<td>2.140 (3)</td>
</tr>
<tr>
<td>Mo2 - O2</td>
<td>2.118 (3)</td>
</tr>
<tr>
<td>Mo1 - Mo2a</td>
<td>3.5407 (9)</td>
</tr>
<tr>
<td>O1 - O2a</td>
<td>2.380 (5)</td>
</tr>
</tbody>
</table>

* Intermolecular distance.
Figure 4.10 Partial $^1$H NMR spectrum ($\delta$ 3.56 - 1.74 ppm) of $[\text{Cp}^*\text{Mo(VO)}(\text{CH}_2\text{Ph})(\mu-O)]_2$ (4.6) in $\text{C}_6\text{D}_6$. 
Figure 4.11 Partial $^1$H NMR spectrum ($\delta$ 1.64 - 1.36 ppm) of [Cp*Mo(NO)(CH$_2$Ph)(μ-O)$_2$ (4.6) in C$_6$D$_6$. 
Figure 4.12 Partial $^1$H NMR spectrum ($\delta$ 0.6 to -1.9 ppm) of [Cp$^*$Mo(NO)(CH$_2$Ph)(\textmu-O)]$_2$ (4.6) in C$_6$D$_6$. 
the oxygen bridges is occurring. This phenomenon is commonly called superexchange, and in this case the unpaired electrons are very strongly antiferromagnetically coupled.

The spectral data are not very informative in elucidating the identity of \([\text{Cp}^*\text{Mo(NO)}(\text{CH}_2\text{Ph})(\mu-O)]_2\). The mass spectrum of \([\text{Cp}^*\text{Mo(NO)}(\text{CH}_2\text{Ph})(\mu-O)]_2\) is attributed to \([\text{Cp}^*\text{Mo(O)}_2](\mu-O)\), a common decomposition product of molybdenum nitrosyl-containing complexes, and the IR spectrum of 4.7 exhibits a number of bands (1599, 1588, 1568 cm\(^{-1}\)) in the nitrosyl region as well as several absorptions (756, 748, 700 cm\(^{-1}\)) in the region expected for Mo-O-Mo stretches. The \(^1\)H NMR spectrum of \([\text{Cp}^*\text{Mo(NO)}(\text{CH}_2\text{Ph})(\mu-O)]_2\) in \(\text{C}_6\text{D}_6\) (Figures 4.9 - 4.12) is extremely complex and has not been assigned to date. Most notably in the \(^1\)H NMR spectrum of 4.6 there are at least four different resonances (\(\delta 1.61, 1.49, 1.48, 1.42\) ppm) in the \(\text{Cp}^*\) region. Signals that may be attributable to methylene protons occur at \(\delta 0.42\) and \(-1.74\) ppm (\(J = 1.2\) Hz). In addition, the \(^1\)H NMR spectrum of 4.6 exhibits two other complex patterns between \(\delta 3.25 - 2.71\) ppm and \(\delta 2.14 - 1.82\) ppm. It is clear from this data that \([\text{Cp}^*\text{Mo(NO)}(\text{CH}_2\text{Ph})(\mu-O)]_2\) does not retain the observed solid-state bimetallic structure in solution. Complex 4.6 most likely exists as a mixture of isomers in solution. The crystal structure indicates the \(\text{Cp}^*\) ligands are trans to each other; however, there are no steric reasons why this complex could not also exist in the cis configuration. It is also possible to envision diastereomers for each of these geometric isomers.

An alternative formulation of complex 4.6 is as \([\text{Cp}^*\text{Mo(NO)}(\text{CH}_2\text{Ph})(\mu-OH)]_2\). This 18-valence-electron species is analogous to complexes of the type \([\text{Cp}^*\text{M(NO)}(\text{Cl})(\mu-OH)]_2\) which were prepared in Chapter 2. \([\text{Cp}^*\text{Mo(NO)}(\text{CH}_2\text{Ph})(\mu-OH)]_2\) has a C/H/N ratio consistent with the data from elemental analysis, and the hydroxide complex would be expected to be diamagnetic. However, no hydroxide stretches (\(v_{\text{OH}} = 3650 - 3584\) cm\(^{-1}\))\(^{36}\) or bends (\(\delta_{\text{OH}} = 1420 - 1330\) cm\(^{-1}\))\(^{36}\) are observed in the infrared spectrum of 4.6.
The final difference map showed peaks of 0.30 - 0.35 e/Å³ that could correspond to hydrogen atoms associated with the bridging oxygen atoms. Attempts to refine these peaks as H atoms gave ambiguous results: one refined to a reasonable position and the other did not. Inclusion of the "μ-OH" protons in the model did not lead to any improvement of the residuals. ¹H NMR spectroscopy, mass spectrometry and elemental analysis cannot distinguish between the two possible formulations. If the ¹H NMR spectrum was not so complex, it would be possible to carry out labeling studies (e.g. ¹⁸O and ²H) and 2-D NMR experiments to determine if there are hydroxide ligands present in complex 4.6. Attempts were made to prepare [Cp*Mo(NO)(CH₂Ph)(μ-OH)]ₙ by reacting Cp*Mo(NO)(CH₂Ph)Cl with 1 equiv of NaOH in pentane, but these reaction mixtures decomposed to insoluble tan solids. Another possible independent route to [Cp*Mo(NO)(CH₂Ph)(μ-OH)]ₙ could be by the treatment of [Cp*Mo(NO)(Cl)(μ-OH)]₂ with Mg(CH₂Ph)₂.

Attempts to extend this chemistry to related alkoxo complexes have to date been unsuccessful. Thus, no reaction occurs between Cp*Mo(NO)(OCMe₃)₂ (2.1), Cp*Mo(NO)(CH₂Ph)₂, Cp*W(NO)(CH₂Ph)₂, Cp*W(NO)(CH₂Ph)(OCMe₃) (3.3), Cp*W(NO)(CH₂SiMe₃)(OCMe₃) (3.4), and Cp*W(NO)(CH₂SiMe₃)(OPh) (3.5) with H₂ (40 psig) in THF under similar experimental conditions. Since none of these analogues react with dihydrogen, the reaction between 3.1 and H₂ is quite possibly unique.

4.5 Epilogue and Future Work

Selected alkoxo alkyl complexes were reacted with a variety of reagents such as O₂ and H₂O, HCl, alcohols and H₂. In Lewis acid-base type reactions with PMe₃, CNCMe₃, PhNCO and p-tolylNCO, the alkoxo alkyl species were shown to be sufficiently electron deficient to form 1:1 adducts or insertion products. In the case of CO, subsequent reaction of the adduct occurs to produce a multitude of products. Many of the reactions described in this chapter cannot be generalized to other alkoxo alkyl complexes. This work has established that the reaction
chemistry of alkoxo alkyl complexes of the type Cp*M(NO)(R)(OR') is diverse; however it is unpredictable and not well-behaved.

The prototypal alcohol exchange reaction (eq 4.9) indicates that Cp*M(NO)(R)(OR') complexes may be utilized as synthetic reagents for preparing compounds with heteroatom groups. Chelating alcohols, carboxylic acids, alkyl and arylthiols may react with these alkoxo species to afford new alkoxo alkyl, alkyl amido and alkyl thiolate complexes.

An interesting diamagnetic bimetallic complex, [Cp*Mo(NO)(CH2Ph)(μ-O)]2, was produced when Cp*Mo(NO)(CH2Ph)(OCMe3) (3.1) was treated with H2 in THF. Elucidating the complex nature of the product in solution is essential before an investigation of its potentially rich reaction chemistry can be undertaken. Future work in this area may also include establishing the role of H2 in this oxygen-carbon bond cleavage reaction.

In general, reactivity studies of these three classes of alkoxo complexes, Cp*M(NO)(OR)R have shown that the alkoxo ligands either stabilize their complexes as in the case of the bis(alkoxo) complexes or the alkoxo ligands themselves are the site of reactivity.
4.6 References and Notes


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


(8) Presumably the complex is undergoing decomposition to the bridging oxo bimetallic as a result of residual water in the solvents.

(9) At this point the flask contains \(\text{Cp}^*\text{Mo(NO)(CH}_2\text{CMe}_2\text{Ph)}\text{Cl} \quad (\nu_{\text{NO}} = 1618 \text{ cm}^{-1})\), see Veltheer, J. E. Ph.D. Dissertation, The University of British Columbia, 1993.

(10) \([\text{Cp}^*\text{Mo(NO)(CH}_2\text{CMe}_2\text{Ph)}]_2-(\mu-\text{O})\) (4.2) can also be prepared by the treatment of \(\text{Cp}^*\text{Mo(NO)(CH}_2\text{CMe}_2\text{Ph)}_2 \) with \(\text{H}_2\text{O}\). The route described in section 4.2.6 leads to a less oily product, presumably because the byproduct is \(\text{HOCMe}_3\) rather than \(\text{Me}_3\text{CPh}\), and thus is more easily removed in vacuo.


(12) See Section 5.2.4 for the characterization data of \(\text{Cp}^*\text{Mo(NO)(CO)}_2\).

(13) See Tables 5.1 - 5.3 for the characterization data of 1,3-diphenylacetone.


(16) Some \([\text{Cp'}\text{Mo(NO)}(\text{R})]_2-(\mu-\text{O})\) complexes exist as a mixture of diastereomers, see reference 6b.

(17) The structure of \([\text{Cp}\text{Mo(NO)}(\text{CH}_2\text{SiMe}_3)]_2-(\mu-\text{O})\) has been published, see reference 6b.


(22) Dryden, N. H.; Legzdins, P.; Lundmark, P. J.; Riesen, A.; Einstein, F. W. B. *Organometallics* 1993, 12, 2085.


(27) Crystals of 4.7 are monoclinic of space group \(P2_1/c\) (\#14); \(a = 15.822 (4) \text{ Å}, b = 12.660 (4) \text{ Å}, c = 16.657 (2) \text{ Å}, \beta = 91.70 (2)\text{°}, V = 3335 (1) \text{ Å}^3, Z = 4.\) Dr. S. J. Rettig solved the structure using the Patterson method and full-matrix least-squares refinement procedures to \(R = 0.039, R_w = 0.042\) for 4156 reflections with \(I \geq 3\sigma(I)\).

(28) A similar \(\text{W}_2\text{O}_2\) core unit was observed in the partial X-ray structure determination for the product from the reaction of \(\text{Cp}^*\text{W(NO)(OCMe}_3\text{)}_2\) and \(\text{H}_2\) (Section 2.4.2).


(30) A bond is usually invoked if the distance between two atoms is less than 1.25 times the sum of the covalent radii. The covalent radii of Mo is 1.30 Å, therefore a Mo-Mo bond would be invoked if the Mo-Mo distance was less than 3.25 Å.

(31) For comparison \([\text{O}_2]^{2-}\) has an O-O bond distance of 1.49 Å, see *The CRC Handbook of Chemistry and Physics*, 62nd Edition; Weast, R. C., Astle, M. J., Eds.; CRC Press, Inc.: Boca Raton, Florida, 1982. The covalent radii of O is 0.73 Å.


(34) See, for example, Hatfield, W. E.; Paschal J. S. *J. Am. Chem. Soc.* 1964, 86, 3888.


5.1 Introduction

The migratory insertion of carbon monoxide into metal-carbon σ bonds is one of the most extensively studied reactions in organotransition-metal chemistry. The principal reason for this considerable expenditure of effort is the practical importance of both stoichiometric and catalytic carbonylation reactions in which migratory insertion is the means by which the CO becomes activated by the transition-metal center.¹

The prototypical example of migratory insertion of carbon monoxide is the conversion of an alkyl carbonyl complex into an acyl complex with concomitant incorporation of an external ligand, L, i.e.

$$R\text{-}M\text{-}CO + L \rightarrow L\text{-}M\text{-}C\{O\}R$$  (5.1)

A number of mechanistic pathways are available for reaction (5.1), the dominant path often being controlled by the nature of the solvent.² Much less common examples of carbon monoxide
insertions are systems in which an external CO molecule is the source of the inserted CO and no incorporation of a trapping ligand is necessary for the insertion to occur, i.e.\(^2\)

\[
\text{M-R} + \text{CO} \rightarrow \text{M-C(O)R} \quad (5.2)
\]

The interest in the organometallic chemistry of CO is largely centered on attempts to find new catalytic processes for the conversion of CO into useful organic chemicals or to clarify the steps of CO reduction in the Fischer-Tropsch process (eq. 5.3).\(^3\)

\[
\text{CO} + \text{H}_2 \xrightarrow{\text{catalyst; heat, pressure}} \text{CH}_3(\text{CH}_2)_n\text{CH}_2\text{OH} + \text{CH}_3(\text{CH}_2)_n\text{CH=CH}_2 + \text{CH}_3(\text{CH}_2)_n\text{CH}_3 \quad (5.3)
\]

Bidentate (\(\eta^2\)) acyls are believed to be kinetically important species in the C-O bond cleavage step of Fischer-Tropsch catalysis.\(^4\) However, most acyl ligands reported in the literature adopt an \(\eta^1\)-coordination.

It has been shown that the reactivity of 16-electron Cp'M(NO)R\(_2\) complexes is dominated by their ability to form 1:1 adducts with small Lewis bases; these adducts are either isolable as such or undergo subsequent intramolecular transformations involving the hydrocarbyl ligands.\(^5\) Neil Dryden initially investigated some reactions of selected Cp'W(NO)R\(_2\) [R = alkyl, aryl] complexes with carbon monoxide.\(^6\) He expected that the Cp'W(NO)R\(_2\) compounds would react with CO to produce stable insertion products such as the acyl alkyl complexes, Cp'M(NO)(C{O}R)R. Indeed this was the case, and in some instances treatment with additional CO resulted in stable bis(acyl) complexes, CpW(NO)(C{O}R)\(_2\). The following charts summarizes the research completed prior to this work. The ✓'s indicate the successful synthesis of the complex, whereas the ✗'s indicate that an attempt was made but the complex was not synthesizable. The blanks in the charts indicate that the synthesis was not attempted.
This chapter reports the extension of these CO reactions to include the four possible variants of \( \text{Cp'}W(\text{NO})R_2 \), namely where \( \text{Cp'} = \text{Cp} \) or \( \text{Cp}^* \), \( R = \text{alkyl} \) or \( \text{aryl} \). The charts presented below summarizes the research now completed.

From this completed set of reactions, it is now possible to draw some general conclusions about CO insertion reactions in \( \text{Cp'M(NO)R}_2 \) systems. It has been found that the outcome of these insertion reactions is profoundly dependent on the natures of \( \text{Cp'} \) and \( R \). The formation of the monoacyl species occurs for all four variants. Only when \( \text{Cp'} = \text{Cp} \) and \( R = \text{alkyl} \) does a second insertion occur to form the bis(acyl) products.

This chapter also reports on the reactions of \( \text{Cp'M(NO)(CH}_2\text{Ar)}_2 \) complexes with CO to form both ketones and the corresponding \( \text{Cp'M(NO)(CO)}_2 \) species. The 18-electron\(^7\) dialkyl complexes \( \text{Cp'M(NO)(CH}_2\text{Ar)}_2 \) presumably undergo insertion of carbon monoxide into a metal-benzyl bond to form, transiently, the monoinserted products. These products are not thermally stable and reductively eliminate the ketones, \( (\text{ArCH}_2)_2\text{CO} \). The remaining organometallic fragment is trapped by excess CO.
Finally, the reaction of \( \text{CpW(NO)}(\text{C} \{\text{O}\})\text{CH}_2\text{CMe}_2\text{Ph})(\text{CH}_2\text{CMe}_2\text{Ph}) \) with \( \text{PMc}_3 \) is described. This reaction results not in the expected metal-centered adduct but rather an ylide complex where \( \text{PMc}_3 \) is attached to the acyl carbon.

### 5.2 Experimental Procedures

#### 5.2.1 Methods

The synthetic methodologies employed in this chapter are described in detail in Section 2.2.1. The customary methodology employed during cyclic voltammetry (CV) studies has been described in detail previously.\(^8\) The potentials were supplied by a BAS CV27 voltammograph, and the resulting cyclic voltammograms were recorded on a Hewlett-Packard Model 7090A X-Y recorder in the buffered recording mode. The three-electrode cell consisted of a Pt-bead working electrode (\(-1\) mm diameter), a coiled Pt-wire auxiliary electrode, and a Ag-wire reference electrode. THF solutions were prepared in a glovebox to 0.10 M in the \([n-\text{Bu}_4\text{N}]\text{PF}_6\) support electrolyte and \(-6 \times 10^{-4} \text{M}\) in the organometallic complex to be studied. Ferrocene was used as an internal reference, with the redox couple \(\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+\) occurring at \(E^{\text{ox}} = 0.53\) V versus Ag wire in THF over the scan range used (0.10 - 0.80 V/s).

#### 5.2.2 Reagents

\[\text{Cp'M(NO)}(\text{CH}_2\text{Ph})_2 \ [M = \text{Mo, W}],^7,^9 \quad \text{CpW(NO)R}_2 \ [R = \text{CH}_2\text{CMe}_3, \text{CH}_2\text{CMe}_2\text{Ph}],^5\]
\[\text{Cp}^*\text{W(NO)}\text{R}_2 \ [R = p-\text{tolyl}, \text{CH}_2\text{CMe}_2\text{Ph}],^10 \quad \text{Cp}^*\text{Mo(NO)}(\text{CH}_2\text{C}_6\text{H}_4-4-\text{Me})_2\]
and Mg\((p-\text{tolyl})_2\cdot\text{X}(\text{dioxane})\)\(^10\) were synthesized by the published procedures. The derivative monoacyl compounds \(\text{CpW(NO)}(\eta^2-\text{C}\{\text{O}\}\text{R})(\text{R}) \ [R = \text{CH}_2\text{CMe}_2\text{Ph}, \text{CH}_2\text{CMe}_3],\)
\(\text{Cp}^*\text{W(NO)}(\eta^2-\text{C}\{\text{O}\}\text{R})(\text{R}) \ [R = p-\text{tolyl}, \text{CH}_2\text{CMe}_2\text{Ph}],\) and the bis(acyl) complexes \(\text{CpW(NO)}(\eta^2-\text{C}\{\text{O}\}\text{R})_2 \ [R = \text{CH}_2\text{CMe}_2\text{Ph}, \text{CH}_2\text{CMe}_3]\) were prepared as previously reported.\(^6,^12\) CO (Matheson CP grade) was used as received.
5.2.3 Reaction of CpW(NO)(p-tolyl)_2 with CO (1 atm)

A blue solution of CpW(NO)(p-tolyl)_2 was generated from CpW(NO)Cl_2 (0.70 g, 2.0 mmol) and Mg(p-tolyl)_2·X(dioxane)\textsuperscript{10} (2.0 mmol) in THF (25 mL) at -60 °C. The reaction solution was warmed to -10 °C and exposed to CO (1 atm) whereupon the solution quickly turned orange. The solvent was removed in vacuo, and the orange residue was extracted with CH\textsubscript{2}Cl\textsubscript{2} (4 x 50 mL). The combined CH\textsubscript{2}Cl\textsubscript{2} extracts were filtered through Florisil (2 x 8 cm) supported on a sintered-glass frit. The filtrate was taken to dryness and the remaining residue was extracted with Et\textsubscript{2}O (2 x 20 mL). These Et\textsubscript{2}O extracts were subsequently filtered through Celite (2 x 8 cm) supported on a sintered-glass frit. The Et\textsubscript{2}O filtrate was concentrated in vacuo and cooled to -10 °C to induce the crystallization of 0.038 g (4% yield based on CpW(NO)Cl\textsubscript{2}) of CpW(NO)(η\textsuperscript{2}-C{O}-p-toly1)(p-toly1) (5.1) as orange microcrystals. Spectroscopic data for complex 5.1 are contained in Tables 5.1 - 5.3.

5.2.4 General Synthetic Methodology Employed for High-Pressure Carbon Monoxide Reactions

All high-pressure CO reactions were performed under similar reaction conditions. Specifically, in an inert atmosphere glovebox, a solution of the organometallic reactant in C\textsubscript{6}H\textsubscript{6} (20 mL) was prepared in a Pyrex liner for a 300-mL Parr pressure reactor. The reactor was then assembled, removed from the glovebox, pressurized to 30 atm of CO, and left with its contents unstirred for 24 h. Excess CO pressure was then vented to a fumehood, and the reactor was taken back into the glovebox and disassembled. The final reaction solution was transferred into a flask and removed from the glovebox. The specific details of the workup of the individual reaction solutions are presented in the following sections.
5.2.5 Reaction of Cp*W(NO)(η²-C{O}CH₂CMe₂Ph)(CH₂CMe₂Ph) with CO (30 atm)

The reaction of Cp*W(NO)(η²-C{O}CH₂CMe₂Ph)(CH₂CMe₂Ph) with CO was performed as described in Section 5.2.4. The solvent was removed from the final orange reaction solution under reduced pressure. The IR spectrum of the remaining red-orange solid as a Nujol mull exhibited bands at 2000 (s), 1733 (m), and 1606 (br) cm⁻¹ in the region between 2200 and 1500 cm⁻¹. All attempts to crystallize this new material afforded only the initial reactant. For comparison, the IR spectrum of the Cp*W(NO)(η²-C{O}CH₂CMe₂Ph)(CH₂CMe₂Ph) reactant as a Nujol mull exhibited ν(NO) = 1561 cm⁻¹ and ν(CO) = 1537 cm⁻¹.

5.2.6 Treatment of CpW(NO)(η²-C{O}-p-tolyl)(p-tolyl) (5.1) with CO (30 atm)

The treatment of 5.1 with CO was effected in the manner described in Section 5.2.4. Removal of solvent from the final reaction solution in vacuo afforded an orange solid. A Nujol mull IR spectrum of this solid in the region 2200 - 1500 cm⁻¹ exhibited features diagnostic only of the organometallic reactant, i.e. 1603, 1580, 1568, and 1524 cm⁻¹.

5.2.7 Reactions of Cp'M(NO)(CH₂Ph)₂ [Cp = Cp, Cp*; M = Mo, W] with CO (30 atm)

These reactions were all effected under similar experimental conditions. The reaction of Cp*Mo(NO)(CH₂Ph)₂ with CO is described below as a representative example.

The high-pressure treatment of Cp*Mo(NO)(CH₂Ph)₂ (1.32 g, 3.00 mmol) with CO was carried out in a Parr reactor (see Section 5.2.4). The resulting amber solution was reduced to a yellow-brown, oily solid in vacuo. This solid was redissolved in pentane, and then transferred to the top of a silica gel column (2 x 8 cm) made up in pentane. The column was eluted with pentane, resulting in the elution of a single orange band which was collected and concentrated in vacuo. Cooling of this concentrated solution in a freezer (-10 °C) overnight resulted in the deposition of orange crystals (0.30 g, 32% yield) of Cp*Mo(NO)(CO)₂.
Anal. Calcd for C$_{12}$H$_{15}$NO$_3$Mo: C, 45.44; H, 4.77; N, 4.42. Found: C, 45.45; H, 4.80; N, 4.50. IR (Nujol mull): $\nu$$_{CO}$ 2000 (s), 1927 (s) cm$^{-1}$, $\nu$$_{NO}$ 1661 (s) cm$^{-1}$. $^1$H NMR (C$_6$D$_6$): $\delta$ 1.62 (s, C$_5$(CH$_3$)$_5$). $^{13}$C{$^1$H} NMR (C$_6$D$_6$): $\delta$ 220.0 (CO), 106.1 (C$_5$(CH$_3$)$_5$), 10.4 (C$_5$(CH$_3$)$_5$). Low-resolution mass spectrum (probe temperature 80 °C): $m/z$ 319 [P$^+$].

Subsequent elution of the silica column with Et$_2$O developed an amber band which was also collected and reduced to an amber oil 5.2 in vacuo. The spectroscopic properties of this oil (~0.15 g, ~24% yield) were identical to those exhibited by an authentic sample of 1,3-diphenylacetone (Tables 5.1 - 5.3).

The other Cp'M(NO)(CH$_2$Ph)$_2$ complexes also converted to 1,3-diphenylacetone and the appropriate Cp'M(NO)(CO)$_2$ complex when exposed to CO under the experimental conditions described above.

5.2.8 Reaction of Cp$^*$Mo(NO)(CH$_2$C$_6$H$_4$-4-Me)$_2$ with CO (30 atm)

The high-pressure treatment of Cp$^*$Mo(NO)(CH$_2$C$_6$H$_4$-4-Me)$_2$ (0.60 g, 1.3 mmol) with CO was effected in the manner described in Section 5.2.4. The final amber solution was reduced to an amber-red oil in vacuo. An IR spectrum of the oil as a Nujol mull exhibited bands at 2000 (s), 1930 (m), 1726 (m), 1713 (m), 1663 (s), and 1515 (m) cm$^{-1}$ in the region 2200-1500 cm$^{-1}$. The oil was dissolved in pentane and transferred to the top of a silica gel column (2 x 20 cm) made up in pentane. Elution of the column with pentane developed an orange band which was collected and concentrated in vacuo. Orange crystals (0.10 g, 25% yield) of Cp$^*$Mo(NO)(CO)$_2$ (vide supra) were deposited from this solution upon cooling to -10 °C overnight.

Further elution of the column with Et$_2$O/pentane (1:1) afforded a pale yellow band which was collected and taken to dryness in vacuo. The resulting pale yellow residue was recrystallized from pentane to obtain analytically pure (4-Me-C$_6$H$_4$CH$_2$)$_2$CO (5.3) (0.06 g, 20% yield) as a white, crystalline solid. Spectroscopic data for complex 5.3 are contained in Tables 5.1 - 5.3.
5.2.9 Preparation of CpW(NO)(C{O}{PMe3}CH2CMe2Ph)(CH2CMe2Ph) (5.4)

Excess PMe3 was vacuum transferred into an orange CH2Cl2 (10 mL) solution of CpW(NO)(η2-C{O}CH2CMe2Ph)(CH2CMe2Ph) (0.10 g, 0.17 mmol). The reaction mixture was stirred for 0.5 h by which time the solution was pale yellow. The final solution was taken to dryness in vacuo. The resulting solid was redissolved in 1:1 CH2Cl2/hexanes (20 mL) and filtered through Celite (2 x 4 cm) supported on a medium-porosity glass frit. The filtrate was concentrated under reduced pressure and was placed in the freezer at -30 °C overnight to induce the precipitation of CpW(NO)(C{O}{PMe3}CH2CMe2Ph)(CH2CMe2Ph) (5.4) as pale yellow flakes (0.07 g, 63% yield). Spectroscopic data for complex 5.4 are contained in Tables 5.1 - 5.3.

5.3 Characterization Data

Table 5.1. Numbering Scheme, Color, Yield and Elemental Analysis Data for Complexes 5.1 - 5.4

<table>
<thead>
<tr>
<th>complex</th>
<th>compd no.</th>
<th>anal. found (calcd)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
<td></td>
</tr>
<tr>
<td>CpW(NO)(C{O}·p-toly1)(p-toly1)</td>
<td>5.1</td>
<td>48.82 (48.10)</td>
<td>3.91 (3.91)</td>
<td>2.79 (2.86)</td>
<td></td>
</tr>
<tr>
<td>(PhCH2)2CO        a</td>
<td>5.2</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>(4-MeC6H4CH2)2CO</td>
<td>5.3</td>
<td>85.68 (85.67)</td>
<td>7.66 (7.61)</td>
<td>0.00 (0.00)</td>
<td></td>
</tr>
<tr>
<td>CpW(NO)(C{O}{PMe3}CH2CMe2Ph) (CH2CMe2Ph)</td>
<td>5.4</td>
<td>53.53 (53.63)</td>
<td>6.10 (6.20)</td>
<td>2.10 (2.16)</td>
<td></td>
</tr>
</tbody>
</table>

aElemental analysis of this compound was not obtained due to its oily nature.
Table 5.2. Mass Spectral and Infrared Data for Complexes 5.1 - 5.4

<table>
<thead>
<tr>
<th>compd no.</th>
<th>MS, m/z&lt;sup&gt;a&lt;/sup&gt;</th>
<th>temp&lt;sup&gt;b&lt;/sup&gt; °C</th>
<th>IR, cm&lt;sup&gt;-1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>ν&lt;sub&gt;NO&lt;/sub&gt; (CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;)</td>
</tr>
<tr>
<td>5.1</td>
<td>461 [P&lt;sup&gt;+&lt;/sup&gt;]</td>
<td>120</td>
<td>1592</td>
</tr>
<tr>
<td>5.2</td>
<td>210 [P&lt;sup&gt;+&lt;/sup&gt;]</td>
<td>150</td>
<td>-----</td>
</tr>
<tr>
<td>5.3</td>
<td>238 [P&lt;sup&gt;+&lt;/sup&gt;]</td>
<td>180</td>
<td>-----</td>
</tr>
<tr>
<td>5.4</td>
<td>649 [P&lt;sup&gt;+&lt;/sup&gt;]</td>
<td>100</td>
<td>1493</td>
</tr>
<tr>
<td></td>
<td>621 [P&lt;sup&gt;+&lt;/sup&gt; - CO]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>545 [P&lt;sup&gt;+&lt;/sup&gt; - CO - PMe&lt;sub&gt;3&lt;/sub&gt;]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> m/z values are for the highest intensity peak of the calculated isotopic cluster, i.e. 98Mo and 184W.

<sup>b</sup> Probe temperatures.

<sup>c</sup> IR spectrum is recorded neat.

<sup>d</sup> IR spectrum is recorded as a Nujol mull.

Table 5.3. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR Data for Complexes 5.1 - 5.4 in C<sub>6</sub>D<sub>6</sub>

<table>
<thead>
<tr>
<th>compd no.</th>
<th>&lt;sup&gt;1&lt;/sup&gt;H NMR (δ, ppm)</th>
<th>&lt;sup&gt;13&lt;/sup&gt;C{&lt;sup&gt;1&lt;/sup&gt;H} NMR (δ, ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>8.23 (d, 2H, o-ArH, 3&lt;sub&gt;J&lt;/sub&gt;_HH = 9 Hz)</td>
<td>204.8 (CO)</td>
</tr>
<tr>
<td></td>
<td>7.77 (d, 2H, o-ArH, 3&lt;sub&gt;J&lt;/sub&gt;_HH = 9 Hz)</td>
<td>135.7 (C&lt;sub&gt;ipso&lt;/sub&gt;)</td>
</tr>
<tr>
<td></td>
<td>7.35 (d, 2H, m-ArH, 3&lt;sub&gt;J&lt;/sub&gt;_HH = 9 Hz)</td>
<td>129.9 (C&lt;sub&gt;para&lt;/sub&gt;)</td>
</tr>
<tr>
<td></td>
<td>6.85 (d, 2H, m-ArH, 3&lt;sub&gt;J&lt;/sub&gt;_HH = 9 Hz)</td>
<td>128.9 (C&lt;sub&gt;meta&lt;/sub&gt;)</td>
</tr>
<tr>
<td></td>
<td>5.22 (s, 5H, C&lt;sub&gt;5&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)</td>
<td>127.0 (C&lt;sub&gt;ortho&lt;/sub&gt;)</td>
</tr>
<tr>
<td></td>
<td>2.34 (s, 3H, C(O)ArCH&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>49.0 (CH&lt;sub&gt;2&lt;/sub&gt;)</td>
</tr>
<tr>
<td></td>
<td>1.93 (s, 3H, WArCH&lt;sub&gt;3&lt;/sub&gt;)</td>
<td></td>
</tr>
<tr>
<td>5.2</td>
<td>7.20 - 6.90 (m, C&lt;sub&gt;6&lt;/sub&gt;CH&lt;sub&gt;5&lt;/sub&gt;)</td>
<td>204.0 (CO)</td>
</tr>
<tr>
<td></td>
<td>3.34 (s, CH&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>136.4, 131.8 (C&lt;sub&gt;ipso&lt;/sub&gt; and C&lt;sub&gt;para&lt;/sub&gt;)</td>
</tr>
<tr>
<td>5.3</td>
<td>6.92 (s, 8H, C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;)</td>
<td>129.7, 129.5 (C&lt;sub&gt;meta&lt;/sub&gt; and C&lt;sub&gt;ortho&lt;/sub&gt;)</td>
</tr>
<tr>
<td></td>
<td>3.39 (s, 4H, CH&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>48.6 (CH&lt;sub&gt;2&lt;/sub&gt;)</td>
</tr>
<tr>
<td></td>
<td>2.10 (s, 6H, CH&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>21.0 (CH&lt;sub&gt;3&lt;/sub&gt;)</td>
</tr>
<tr>
<td>5.4a</td>
<td>7.90 (d, 2H, o-ArH, $^3J_{HH} = 7.5$ Hz)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.81 (d, 2H, o-ArH, $^3J_{HH} = 7.5$ Hz)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.42-7.01 (m, 6H, ArH)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.19 (s, 5H, C$_5$H$_5$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.68 (d, 1H, WCH$<em>2$, $^2J</em>{HH} = 12.9$ Hz)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.37 (d, 1H, WCH$<em>2$, $^2J</em>{HH} = 12.9$ Hz)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.20 (dd, 1H, C(O)CH$<em>2$, $^2J</em>{HH} = 15.6$ Hz, $^3J_{HP} = 30.9$ Hz)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.09 (dd, 1H, C(O)CH$<em>2$, $^2J</em>{HH} = 15.6$ Hz, $^3J_{HP} = 10.8$ Hz)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.00, 1.98, 1.57, 1.31 (s, 4 x 3H, C(CH$_3$))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.640 (d, 9H, PMe$<em>3$, $^2J</em>{PH} = 9.6$ Hz)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>155.41 (C$_{ipso}$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>149.67 (C$_{ipso}$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>128.33 (C$_{arom}$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>128.06 (C$_{arom}$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>127.90 (C$_{arom}$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>127.02 (C$_{arom}$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>126.26 (C$_{arom}$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>124.73 (C$_{arom}$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>58.14 (d, $^1J_{CP} = 45.1$ Hz, C(O)(PMe$_3$))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>49.89 (d, $^2J_{CP} = 26.8$ Hz, C(O)(PMe$_3$)CH$_2$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>44.61 (C$_{quat}$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>44.41 (C$_{quat}$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40.21 (WCH$_2$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>36.53, 32.79, 31.21, 29.69 (4 x CH$_3$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>16.40 (P(CH$<em>3$), $^1J</em>{CP} = 13.2$ Hz)</td>
<td></td>
</tr>
</tbody>
</table>

$a$ The $^{31}$P$^{1}$H NMR spectrum exhibits a singlet at 6.88 ppm ($^1J_{PW} = 95.3$Hz) attributable to coordinated PMe$_3$. 

---

**Note:** The table and text describe the NMR spectral data for a compound, detailing the chemical shifts and coupling constants for various protons and carbon nuclei. The $^3J_{HH}$ and $^3J_{HP}$ couplings are specified for different proton-proton and proton-heteronuclear interactions, respectively. The chemical shifts for protons and carbons are listed in the respective columns, providing a comprehensive view of the compound's nuclear magnetic resonance properties.
5.4 Results and Discussion

The reactions of the various Cp\'W(NO)R₂ complexes with carbon monoxide proceed in the step-wise fashion summarized in Scheme 5.1. The first step involves the conversion of the 16-electron bis(alkyl) or bis(aryl) complex to the corresponding 18-electron monoacyl species, probably via an initially formed carbonyl adduct.\(^5\) The \(\eta^2\)-acyl-containing complex may be isolable as such or may undergo spontaneous reductive elimination of the symmetrical ketone if \(R = CH_2Ar\). The second step involves the uptake of a second equivalent of CO and the formation of the 18-electron bis(acyl) complex, again via an initially formed carbonyl adduct. Exactly which path is followed in a particular instance is dependent upon both the natures of Cp\' and R and the experimental conditions employed. These features are emphasized in the discussion that follows.

Scheme 5.1
5.4.1 Step 1: Formation of the Monoacyl Complexes

Neil Dryden observed that the treatment of Cp*W(NO)(p-toly1)$_2$ with 1 atm of CO in Et$_2$O at -38 °C resulted in the formation of a yellow-green precipitate which was formulated as the 18-electron, terminal carbonyl adduct of the starting complex (eq 5.4).$^6$

\[
\begin{align*}
\text{Cp*W(NO)} & \xrightarrow{\text{CO (1 atm)}} \text{Cp*W(NO)(CO)(p-toly1)$_2$} \\
R & = p\text{-tolyl}
\end{align*}
\]

This formulation of the product is based on the presence of a distinctive IR absorption at 2014 cm$^{-1}$ in the Nujol mull IR spectrum of the green solid attributable to a terminal CO ligand. Conversion 5.4 is also consistent with the documented ability of Cp'M(NO)R$_2$ complexes (M = Mo, W) to form 1:1 adducts with small Lewis bases.$^5,13$ As the terminal carbonyl adduct, Cp*W(NO)(CO)(p-toly1)$_2$, warms to room temperature the coordinated CO inserts into one of the tungsten-aryl bonds to form the corresponding red-orange acyl aryl complex (eq 5.5).

\[
\begin{align*}
\text{Cp*W(NO)(CO)} & \xrightarrow{\text{R = p-tolyl}} \text{Cp*W(NO)(C}_2\text{C}^1\text{R)}(R) \\
\end{align*}
\]

While there are no CO adducts observed during the carbonylations of the other Cp'W(NO)R$_2$ complexes, it is likely that all the Cp'W(NO)(\eta^2-C(O)R)(R) complexes synthesized during this
work result from initially formed terminal CO adducts. Carbonylation of the bis(hydrocarbyl) complexes, Cp'W(NO)R₂, occurs irreversibly under very mild conditions in a variety of solvents to afford the monoacyl complexes (eq 5.6).

\[
\text{Cp'W(NO)(R)}_2 + \text{CO (1 atm)} \rightarrow \text{Cp'W(NO)(}\eta^2-\text{C}\{O\}\text{R}R
\]

(5.6)

These Cp'W(NO)(η²-C{O}R)R product complexes [Cp' = Cp*, R = CH₂CMe₂Ph, p-tolyl; Cp' = Cp, R = CH₂CMe₂Ph, CH₂CMe₃, p-tolyl] constitute a new family of thermally stable monoacyl organometallic compounds. The reactions of the thermally-sensitive diaryl complexes with CO are best performed at lower temperatures since they are much more reactive than their congenic dialkyl complexes. This higher reactivity has been attributed to the greater Lewis acidity of the diaryl species relative to the dialkyl complexes.⁶ ¹³ The yellow acyl alkyl complexes and the red-orange acyl aryl complexes show reduced solubility in aliphatic hydrocarbon solvents when compared to their 16-electron precursors, but they are very soluble in aromatic and polar organic solvents.

### 5.4.1.1 Spectroscopic Properties of the Monoacyl Nitrosyl Complex

The IR spectrum of complex 5.1 in CH₂Cl₂ (Table 5.2) exhibits two strong bands at 1592 and 1535 cm⁻¹ due to the vibrations of the nitrosyl and η²-acyl ligands. The 1535 cm⁻¹ band is assigned to the ν_{CO} of CpW(NO)(η²-C{O}-p-tolyl)(p-tolyl) by analogy to the labeling studies done by Neil Dryden.⁶ The ν_{CO} value falls well within the range generally observed for η²-acyls (1625-1453 cm⁻¹),¹ and thus 5.1 is formulated as the 18-electron species, CpW(NO)(η²-C{O}-p-tolyl)(p-tolyl).

The ¹H NMR spectroscopic properties of 5.1 (Figure 5.1) are also consistent with its formulation as a singly-inserted species. As expected, there are two different hydrocarbyl group environments for the complex corresponding to the aryl and acyl ligands, with the set of hydrocarbyl signals shifted to lower field being assigned to the acyl ligand due to the deshielding effect of the electron-withdrawing carbonyl group.¹⁴
5.4.1.2 X-ray Crystallographic Analysis of CpW(NO)(C\{O\})CH\_2CMe\_2Ph(CH\_2CMe\_2Ph)

A number of stable transition-metal acyl complexes have been synthesized and structurally characterized, and the acyl ligand has been found to coordinate to the metal in either a monohapto, M(\(\eta^1\)-C\{O\}R), or a dihapto, M(\(\eta^2\)-C\{O\}R), fashion.\(^{15}\) In order to establish the nature of the acyl linkage in CpW(NO)(C\{O\})CH\_2CMe\_2Ph(CH\_2CMe\_2Ph), the complex was subjected to a single-crystal X-ray crystallographic analysis.\(^{16}\) Regrettably, two overlapping chemically equivalent, but crystallographically independent, molecules caused severe refinement problems of the molecular structure. Consequently, the most reliable information that can be extracted from the X-ray crystallographic study is the atom connectivity which establishes (Figure 5.2) that the acyl ligand is indeed coordinated to the tungsten atom in an \(\eta^2\) fashion.

Figure 5.1 300 MHz \(^1\)H NMR spectrum of CpW(NO)(\(\eta^2\)-C\{O\}-p-toly1)(p-toly1) (5.1) in C\(_6\)D\(_6\).
Figure 5.2 The solid-state molecular structure of CpW(NO)(η²-C(O)CH₂CMe₂Ph)
(CH₂CMe₂Ph). Atoms are refined isotropically and drawn as open circles; H atoms are omitted for clarity. Only one view of the disordered overlapping molecules is shown.

The intramolecular metrical parameters (Table 5.4) of CpW(NO)(η²-C(O)CH₂CMe₂Ph)
(CH₂CMe₂Ph) generally resemble those determined for other η²-acyl complexes of the Group 6 metals. It has a short W-C_{acyl} bond of 2.01 Å. The W-O separation of 2.21 Å is indicative of a single bond. Since the acyl group functions as a three-electron donor ligand through its C and O atoms, the complex is best viewed as an 18-electron electronically and coordinatively saturated species.
Table 5.4. Selected Bond Lengths and Bond Angles for 
CpW(NO)(\eta^2-C{O}CH_2CMe_2Ph)(CH_2CMe_2Ph).a

<table>
<thead>
<tr>
<th>bond lengths (Å)</th>
<th>bond angles (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W - C(30)</td>
<td>O(2) - W - C(30)</td>
</tr>
<tr>
<td>W - C(19)</td>
<td>O(2) - W - C(19)</td>
</tr>
<tr>
<td>W - O(2)</td>
<td>C(19) - W - C(30)</td>
</tr>
<tr>
<td>C(30) - O(2)</td>
<td>C(19) - W - N</td>
</tr>
<tr>
<td>W - N</td>
<td>C(30) - W - N</td>
</tr>
<tr>
<td>N - O(1)</td>
<td>O(2) - W - N</td>
</tr>
<tr>
<td></td>
<td>O(1) - N - W</td>
</tr>
</tbody>
</table>

a These parameters were all subject to restraints during refinement and therefore no e.s.d.s are given.

MoCl(\eta^2-C\{O\}CH_2SiMe_3)(CO)(PMe_3)_3 has been prepared by Carmona’s group, not by CO insertion, but by the nucleophilic attack of Me_3SiCH_2^- on a terminal CO ligand of MoCl_2(CO)_2(PMe_3)_3.\(^{17}\) The dihapto acyl species has been structurally characterized. Carmona calculates a value of \(\Delta_{(Mo-O)-(Mo-C)}\) in MoCl(\eta^2-C\{O\}CH_2SiMe_3)(CO)(PMe_3)_3 of 0.30 Å which he compares to the value of \(\Delta_{(Mo-O)-(Mo-C)}\) found in other \(\eta^2\)-acyl organometallic compounds. The values range from 0.44 Å for Ru(\eta^2-C\{O\}CH_3)(I)(CO)(PPh_3)_2\(^{18}\) to 0.09 Å for Cp_2Zr(\eta^2-C\{O\}CH_3)(CH_3).\(^{19}\) Carmona believes that this value is an indicator of the strength of the \(\eta^2\) interaction. If \(\Delta_{(Mo-O)-(Mo-C)}\) is high, the \(\eta^2\) interaction is weak and the reverse migration reaction may occur. On the other hand, if \(\Delta_{(Mo-O)-(Mo-C)}\) is small, as in Cp^*^2ThCl(C\{O\}CH_2CMe_3) (0.07 Å), there is a larger contribution from the oxycarbene resonance structure (II). Early-transition metals are oxophilic and therefore

\[\begin{align*}
&M-C-R \\
&\text{I} \\
&M\overset{\text{O}}\leftarrow C\rightarrow R \\
&\text{II}
\end{align*}\]
the M-O interaction is strong enough to make the acyl ligand more like an oxycarbene than an \( \eta^2 \)-acyl. The value of \( \Delta_{(\text{Mo-O})-(\text{Mo-C})} \) for \( \text{CpW(NO)(C\{O\}CH}_2\text{CMe}_2\text{Ph})(\text{CH}_2\text{CMe}_2\text{Ph}) \) is 0.20 Å; therefore we would expect the interaction between the metal and acyl to be strong, and the resonance form 1 to dominate.

It is important to note from this structure that the oxygen of the acyl ligand is positioned trans to the NO ligand. This configuration stabilizes the interaction between the \( \sigma \)-donating acyl and the strongly \( \pi \)-accepting NO ligand.

### 5.4.1.3 The Unique Case of \( R = \text{CH}_2\text{Ar} \)

The reactions of the bis(benzyl) complexes, \( \text{Cp'}\text{M(NO)(CH}_2\text{Ar})_2 \) [\( \text{Ar} = \text{C}_6\text{H}_5, \text{C}_6\text{H}_4-4-\text{Me} \)], with CO do not proceed as depicted in eq 5.6, but rather lead to the reductive elimination of ketone and formation of the well-known dicarbonyl nitrosyl products as summarized in eq 5.7.

\[
\begin{align*}
\text{M} & \quad \text{CO (1 atm)} & \quad \text{M} \quad \text{N} \\
\text{R} & \quad \text{R} & \quad \text{OC} \\
\text{N} & \quad \text{O} & \quad \text{R} \quad \text{R} \\
\end{align*}
\]

These conversions occur slowly in benzene at 1 atm and ambient temperatures, but are quite rapid at higher pressures of CO (e.g. 30 atm). The workup of the reactions where \( R = \text{CH}_2\text{Ph} \) are particularly difficult for three reasons. Firstly, the dicarbonyl nitrosyl complex is extremely soluble in 1,3-diphenylacetone. Secondly, \( \text{(PhCH}_2)_2\text{CO} \) is a pale yellow liquid that is difficult to purify. Finally, mixtures of the two independently air-stable product complexes are not themselves air-stable.\(^{20}\) The work-up of the reaction solutions resulting from the treatment of \( \text{Cp}^*\text{Mo(NO)(CH}_2\text{C}_6\text{H}_4-4-\text{Me})_2 \) with CO is significantly easier because the resulting ketone, \( (4-\text{Me-C}_6\text{H}_4\text{CH}_2)_2\text{CO} \), can be crystallized from pentane.
The organometallic dicarbonyl nitrosyl products and 1,3-diphenylacetone have been identified by comparison of their spectroscopic properties to those exhibited by authentic samples. The identity of (4-Me-C₆H₄CH₂)₂CO has been established by IR, MS, ¹H and ¹³C NMR spectroscopies and by elemental analysis (Tables 5.1 - 5.3). A partial IR spectrum of the reaction mixture of Cp*Mo(NO)(CH₂C₆H₄-4-Me)₂ and carbon monoxide is shown in Figure 5.3. It clearly shows the ν(NO) (1663 cm⁻¹) and two ν(CO)'s (2000 cm⁻¹ and 1930 cm⁻¹) of the dicarbonyl nitrosyl complex, as well as weaker bands at 1726, 1713, and 1515 cm⁻¹ due to (4-Me-C₆H₄CH₂)₂CO.

We believe that reaction 5.7 proceeds via an intermediate acyl alkyl complex. However, unlike the other Cp'W(NO)(η²-C(O)R)(R) complexes isolated, the transient Cp'M(NO)(C{O}CH₂Ar)(CH₂Ar) species evidently eliminate (ArCH₂)₂CO spontaneously in the presence of excess CO. Since the Cp'M(NO)(CH₂Ar)₂ reagent complexes are prepared from Cp'M(NO)(CO)₄⁷ reactions 5.7 may be incorporated into a stoichiometric synthetic cycle as shown in Scheme 5.1.

The reductive elimination of ketone in this system is significant because organometallic reactions leading to the formation of new carbon-carbon bonds have an important place in synthetic organic chemistry.²¹ Reductive elimination is one of the most common ways to construct carbon-carbon bonds. The increasing importance of catalytic C-C bond-forming reactions between acyl and alkyl moieties makes the understanding of the fundamental coupling step important.
Figure 5.3 Partial IR spectrum (2195 - 1330 cm\(^{-1}\)), as a Nujol mull, of the mixture from the reaction between Cp*Mo(NO)(CH\(_2\)C\(_6\)H\(_4\)-4-Me\(_2\))\(_2\) and CO.
5.4.2 Step 2: Formation of the Bis(acyl) Complexes

Neil Dryden\textsuperscript{6} showed that exposure of a C\textsubscript{6}H\textsubscript{6} solution of Cp\textsuperscript{*}W(NO)(\eta\textsuperscript{2}-C\{O\}-p-tolyl) (p-tolyl) to elevated pressures (e.g. 30 atm) of CO results in the formation of an 18-electron 1:1 adduct, i.e.,

\[
\text{CO (30 atm)} \quad \text{Cp}^*\text{W(NO)}(\eta^2\text{-C\{O\}R})(\text{R}) \quad \text{Cp}^*\text{W(NO)(C\{O\}R)(R)(CO)}
\]

\[R = p\text{-tolyl}\]

The formulation of the red-orange product of reaction 5.8 as the CO adduct is based on a terminal CO stretch at 1970 cm\textsuperscript{-1} evident in its Nujol mull IR spectrum.\textsuperscript{22} This adduct is only stable under CO pressure, otherwise it slowly reverts to Cp\textsuperscript{*}W(NO)(\eta\textsuperscript{2}-C\{O\}-p-tolyl)(p-tolyl). The current work has shown that Cp\textsuperscript{*}W(NO)(\eta\textsuperscript{2}-C\{O\}CH\textsubscript{2}CMe\textsubscript{2}Ph)(CH\textsubscript{2}CMe\textsubscript{2}Ph) also forms an adduct under CO pressure. The IR spectrum of a Nujol mull of a sample of the reaction mixture taken to dryness in vacuo exhibits a terminal CO stretch at 2000 cm\textsuperscript{-1}. A strong band at 1733 cm\textsuperscript{-1} is attributed to the \(\nu\text{NO}\), and the existence of the \(\eta\textsuperscript{1}\)-acyl ligand in the 1:1 adduct is indicated by a CO stretch at 1606 cm\textsuperscript{-1}.\textsuperscript{4, 23} The terminal CO is labile and, as a result, all attempts to crystallize this new material afford only the organometallic reactant.

In order to confirm the hypothesis that the monoacyl complexes were sufficiently electron-deficient to form a 1:1 adduct with Lewis bases, I investigated the possibility of forming a phosphine adduct with one of the acyl alkyl compounds. Interestingly, treatment of CpW(NO)(\eta\textsuperscript{2}-C\{O\}CH\textsubscript{2}CMe\textsubscript{2}Ph)(CH\textsubscript{2}CMe\textsubscript{2}Ph) with an excess of PMe\textsubscript{3} does not produce the metal-centered adduct, CpW(NO)(\eta\textsuperscript{1}-C\{O\}CH\textsubscript{2}CMe\textsubscript{2}Ph)(CH\textsubscript{2}CMe\textsubscript{2}Ph)(PMe\textsubscript{3}), but rather the ylide complex, CpW(NO)(C\{O\}PMe\textsubscript{3})CH\textsubscript{2}CMe\textsubscript{2}Ph)(CH\textsubscript{2}CMe\textsubscript{2}Ph) (5.4). The ylide ligand in 5.4 may be described as the acyl phosphonium ion (Me\textsubscript{3}P)C\{O\}(CH\textsubscript{2}CMe\textsubscript{2}Ph).
Reaction 5.9 is rapid in CH$_2$Cl$_2$. Although the reaction is quantitative, the yields of 5.4 are moderate (63%) because of the lability of the PMe$_3$ ligand in solution (vide infra). Complex 5.4, having less solubility in organic solvents than its precursor complex, is best crystallized from CH$_2$Cl$_2$/hexanes mixtures.

The mass spectrum of complex 5.4 shows first loss of CO, and then loss of CO and PMe$_3$. The IR spectrum of 5.4 as a Nujol mull is complex. The assignment of $\nu_{NO}$ is difficult because of the presence of phenyl stretching bands. It is taken to be at 1493 cm$^{-1}$ because of the strength of this band and because it is expected to be significantly lower than the $\nu_{NO}$ of 1582 cm$^{-1}$ in CpW(NO)(C{O}CH$_2$Me$_2$Ph)(CH$_2$Me$_2$Ph).

The existence of the ylide ligand in 5.4 is indicated by two spectroscopic features, namely a singlet (no W satellites observed) at 22.3 ppm in the $^{31}$P NMR spectrum due to the ylide PMe$_3$ fragment, and a doublet at 58.14 ppm ($^1J_{CP} = 45.1$ Hz) in the $^{13}$C{$^1$H} NMR spectrum of the complex due to the ylide carbon (Table 5.3). In solution, complex 5.4 exists in equilibrium (K = 0.43 at 23 °C in C$_6$D$_6$) with CpW(NO)(C{O}CH$_2$Me$_2$Ph)(CH$_2$Me$_2$Ph)$^{24}$ and free PMe$_3$ as evidenced by the $^1$H NMR spectrum of isolated 5.4. If the reaction is performed in an NMR tube with an excess of PMe$_3$, the $^1$H NMR spectrum exhibits peaks due to only 5.4 (quantitative) and the excess PMe$_3$ (Figure 5.4). A similar spectrum results if a sample of 5.4 is dissolved in C$_6$D$_6$ and then excess PMe$_3$ is added. Thus, in solution, under conditions of excess PMe$_3$ the ylide is
Figure 5.4 A partial view of the 300 MHz $^1$H NMR spectrum (C$_6$D$_6$) of
CpW(NO)(C(0){PMe$_3$}CH$_2$Me$_2$Ph)(CH$_2$Me$_2$Ph) (5.4) in the presence of excess PMe$_3$. 
stable. Thus, the tendency for dissociation of the PMe₃ from complex 5.4 lowers the yield of this quantitative reaction.

This type of reactivity for an electrophilic dihaptoacyl group has been observed previously for the related CpMo(NO)(I)(η²-C{O}-p-tolyl) complex.²⁵ Hersh finds that this acyl species reacts with PMe₃ highly stereospecifically to form CpMo(NO)(I)(η²-C{O}{PMe₃}-p-tolyl). He obtained an X-ray crystal structure of this complex to confirm the structure of the η²-ylide ligand. It is not unreasonable to assume, based on the spectroscopic data of 5.4, that the geometry of its ylide ligand is similar to that in CpMo(NO)(I)(η²-C{O}{PMe₃}-p-tolyl).

Upon exposure to CO at higher pressures, the perhydrocyclopentadienyl tungsten monoacyl alkyl complexes undergo insertion of a second equivalent of CO, thereby affording novel bis(acyl) complexes (eq 5.10).¹²
The bis(acyl) complexes probably result from initially formed CO adducts of the type, 
\[ \text{CpW(NO)}(\eta^1-\text{C\{O\}alkyl})(\text{alkyl})(\text{CO}) \], 
undergoing insertion into the remaining M-C\_alkyl bond.

5.4.3 Reactivity Trends

With the completed set of reactions we can make some generalizations about these CO insertion reactions. The fact that only the cyclopentadienyl alkyl complexes undergo multiple insertions of CO can be rationalized on both steric and electronic grounds. For steric reasons, 
\[ \text{CpW(NO)}(\text{CH}_2\text{CMe}_2\text{Ph})_2 \] 
will insert two equivalents of CO and \[ \text{Cp}^*\text{W(NO)}(\text{CH}_2\text{CMe}_2\text{Ph})_2 \] 
will not, presumably because the W center is more sterically accessible in the former compound. For electronic reasons, M-C\_alkyl bonds are weaker than M-C\_aryl linkages and can thus be more readily cleaved during migratory insertion reactions. Unlike the first insertion of CO (eq 5.6) which is driven primarily by the Lewis acidity of the starting bis(hydrocarbyl) complex, the second insertion evidently depends on the relative bond strengths of the remaining W-C bond since the 18-electron monoacyl reactant is not particularly Lewis acidic. In other words, the rate of the second insertion reaction (eq 5.10) depends principally on the relative bond strengths of a W-sp\(^2\) vs 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 been able to isolate \[ \text{CpW(NO)}(\text{C\{O\}alkyl})_2 \] 
complexes but no \[ \text{CpW(NO)}(\text{C\{O\}aryl})_2 \] 
species during this work.

5.4.4 Electrochemical Study of \[ \text{CpW(NO)}(\text{C\{O\}CH}_2\text{CMe}_2\text{Ph})_2 \]

A cyclic voltammogram of \[ \text{CpW(NO)}(\text{C\{O\}CH}_2\text{CMe}_2\text{Ph})_2 \] in THF (Figure 5.6) exhibits one irreversible reduction wave at -1.83 V vs. Ag wire. This indicates that some structural change occurs upon the addition of an electron. The CV of \[ \text{CpW(NO)}(\text{C\{O\}CH}_2\text{CMe}_2\text{Ph})_2 \] shows no oxidation features to the solvent limit, however a peak at +0.36 V appears after the potential has been scanned past the reduction peak. This return oxidation peak is presumably due to the oxidation of the product obtained from the reduction of \[ \text{CpW(NO)}(\text{C\{O\}CH}_2\text{CMe}_2\text{Ph})_2 \].
In attempts to induce the reductive elimination of a diketone, 
CpW(NO)(C{O}CH₂CMe₂Ph)₂ was treated with Na/Hg in THF. The result of this reaction was 
the decomposition of the starting material to an number of unidentifiable products.

5.4.5 Related Systems

Stable acyl alkyl complexes are rare. The paucity of isolated acyl alkyl complexes is due to 
the strong tendency for these species to undergo reductive elimination of the acyl and alkyl 
ligands to form ketones. For instance, the rhenium acyl complex, CpRe(CO)₂(C(O)Me)(Me) 
undergoes reductive elimination of acetone thermally.²⁷ Cp⁴Ta(Me)₄ reacts with CO to afford 
the η²-acetone complex, Cp⁴Ta(Me)₂(η²-C{O}Me₂), which releases acetone under oxidizing 
conditions.²⁸ Cp⁴Rh(CO)(Ph)(Me) reacts with CO to produce acetophenone and the rhodium 
dicarbonyl complex.²⁹ (dppe)FeR₂ reacts with CO to produce (dppe)Fe(CO)₃ and R₂CO.⁴ The
carbonylation of many late transition-metal alkyl complexes also leads to the formation of aldehydes, ketones and diketones.\textsuperscript{21} The classic experiments of catalytic C-C bond-forming reactions between acyl and alkyl groups have been carried out by Yamamoto and involve the late transition-metal complexes, $L_2MR_2$ ($M = \text{Pd, Pt}$).\textsuperscript{30} It is speculated that bis(acyl) intermediates are involved when diketones are formed since CO insertion into acyl-metal bonds are energetically unfavorable.\textsuperscript{31} Eisenberg has reported that an A-frame Rh complex upon carbonylation produces either acetone or 2,3-butanedione depending on the pressure of carbon monoxide (i.e. double carbonylation is possible).\textsuperscript{32}

The closest analogues to $\text{CpM(NO)(η^2-\{O\}\{R\})R}$ are the valence isoelectronic $\text{Cp}_2M'(\eta^2-\{O\}\{R\})R$ ($M' = \text{Zr, Hf}$) complexes.\textsuperscript{19} Unlike our monoacyl complexes, the Group 4 species undergo rapid decarbonylation processes. $\text{Cp}_2M'(\eta^2-\{O\}\{CH_2\text{Ph}\})\{CH_2\text{Ph}\}$ ($M' = \text{Zr, Hf}$) have been isolated, however $\text{Cp}_2\text{Ti(CH}_2\text{Ph)}_2$ reacts with CO to produce $\text{Cp}_2\text{Ti(CO)}_2$ and 1,3-diphenylacetone.\textsuperscript{33} It has also been recently reported that pentane solutions of $\text{Cp}_2\text{Zr(CH}_2\text{Ph)}_2$ react with CO to produce $\text{Cp}_2\text{Zr(CO)}_2$ and 1,3-diphenylacetone through $\text{Cp}_2M'(\eta^2-\{O\}\{CH_2\text{Ph}\})\{CH_2\text{Ph}\}$ intermediates.\textsuperscript{34}

### 5.5 Epilogue and Future Work

These studies have shown that the products obtained from the carbonylation of various $\text{Cp'W(NO)R}_2$ complexes are very dependent upon the nature of the ancillary ligands and the experimental conditions employed. The nature of the cyclopentadienyl ligand determines the extent of the reactivity, with only the Cp complexes inserting a second equivalent of CO. The nature of the hydrocarbyl group influences the rate of the reaction such that the greater Lewis acidity of the diaryl complexes results in their forming monoacyl products faster than do the related dialkyl complexes. However, only the monoacyl alkyl complexes possess a sufficiently weak M-C σ bond to undergo a second insertion of CO to form bis(acyl) species. The nature of the hydrocarbyl ligand also plays an influential role in the case when $R = \text{CH}_2\text{Ar}$ in that putative reductive elimination of ketone occurs from the undetectable monoacyl intermediate complex.
The steric and electronic factors mitigating this set of reactions allows us, in principle, the opportunity to fine tune the reaction conditions so as to obtain specific carbonylation products. The first step towards attaining this goal was achieved when we determined that the insertions of CO into the asymmetric complexes Cp*W(NO)(R)(R') occur regioselectively.\textsuperscript{26} We have now begun investigating the reactions of CO analogues such as CNCMe\textsubscript{3} with these dialkyl and acyl alkyl systems.

### 5.6 References and Notes


(16) The X-ray crystallographic analysis of CpW(NO)(\eta^2-C\{O\}CH_2CMe_2Ph)(CH_2CMe_2Ph) was performed by Drs. A. Riesen and F. W. B. Einstein at Simon Fraser University, Burnaby, B.C., Canada. Crystal data for CpW(NO)(\eta^2-C\{O\}CH_2CMe_2Ph)(CH_2CMe_2Ph): orthorhombic, space group P2_12_12_1, a = 9.158 (3) Å, b = 14.603 (4) Å, c = 17.230 (6) Å, Z = 4, R = 0.068.


(20) It was found that a Et_2O solution of authentic Cp*Mo(NO)(CO)_2 and authentic (ArCH_2)_2CO decomposed to insoluble tan solids upon exposure to air.


(22) In the IR, terminal CO stretches range from 2100 - 1800 cm\(^{-1}\). Nakamoto, K. Infrared and Raman Spectra of Inorganic and Coordination Compounds; John Wiley and Sons, Inc.; New York, NY, 1986; p 261.

(23) Reference 2, p 107.
(24) $^1$H NMR data for CpW(NO)(C{O}CH$_2$Me$_2$Ph)(CH$_2$Me$_2$Ph) in C$_6$D$_6$: $\delta$ 7.66 (d, 2H, o-ArH, $^3$J$_{HH}$ = 7.5 Hz), 7.27 (d, 2H, o-ArH, $^3$J$_{HH}$ = 7.5 Hz), 7.25 (t, 2H, m-ArH, $^3$J$_{HH}$ = 7.5 Hz), 7.15 (t, 2H, m-ArH, $^3$J$_{HH}$ = 7.5 Hz), 7.09 (t, 2H, p-ArH, $^3$J$_{HH}$ = 7.5 Hz), 7.00 (t, 2H, p-ArH, $^3$J$_{HH}$ = 7.5 Hz), 4.53 (s, 5H, C$_5$H$_5$), 3.21 (d, 1H, C(0)CH$_A$H$_B$, $^2$J$_{HH}$ = 15.0 Hz), 2.71 (d, 1H, WCH$_A$H$_B$, $^2$J$_{HH}$ = 12.9 Hz), 2.69 (d, 1H, C(O)CH$_A$H$_X$, $^2$J$_{HH}$ = 15.0 Hz), 2.65 (d, 1H, WCH$_A$H$_B$, $^2$J$_{HH}$ = 12.9 Hz), 1.89, 1.80, 1.30, 1.13 (s, 4 x 3H, C(CH$_3$)$_2$Ph)


(26) Debad, J. D.; Legzdins, P.; Batchelor, R. J.; Einstein, F. W. B. Organometallics 1993, 12, 2094.

(27) Goldberg, K. I.; Bergman, R. G.; Organometallics 1987, 6, 430.


