LOW-VALENT AND LOW-COORDINATE TITANIUM AND MOLYBDENUM COMPLEXES SUPPORTED WITH BULKY AMIDO LIGANDS

by

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This doctoral thesis has been examined by a Committee of the Department of Chemistry as follows:

Professor Richard R. Schrock Chairman

Professor Christopher C. Cummins Thesis Supervisor

Professor Alan Davison
To Wendy

I love you,
Not only for what you are,
But for what I am
When I am with you.

I love you,
Not only for what
You have made of yourself,
But for what
You are making of me.

Roy Croft
According to convention there is a sweet and a bitter, a hot and a cold, and according to convention there is order. In truth there are atoms and a void.

Democritus (400 B.C.)
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Abstract

Chapter I: Heteroleptic Titanium(III) and -(IV) Complexes with Bulky Ancillary Ligands

Partially deuterated bulky N-tert-alkylanilide ligands for the study of low-valent and low-coordinate paramagnetic transition metal complexes were prepared. Using dimethylamide protecting groups, removable with methyl iodide, a wide variety of titanium(IV) complexes of the general formulation Ti(N[R]Ar)\textsubscript{a}(OA\textsuperscript{r})\textsubscript{b}(X)\textsubscript{c} (Ar' = 2,6-disubstituted aryl, X = dimethylamide, alkyl or halide, a + b + c = 4) were prepared. Various substitutions on the N[R]Ar ligand set allowed for steric and electronic tuning of the titanium center. The heteroleptic Ti(III) alkyl complex Ti(N[R]Ar)\textsubscript{2}(CH[SiMe\textsubscript{3}]\textsubscript{2}) was prepared from Ti(N[R]Ar)\textsubscript{2}(μ-Cl)\textsubscript{2}:Li(TMEDA) and was characterized by X-ray crystallography. Initial reactivity of this alkyl complex was explored.

Chapter II: Molybdenum(V) and -(VI) Chalcogenide Complexes

The terminal Mo(V) chalcogenido complexes EMo(N[R]Ar)\textsubscript{3} (E = O, S, Se and Te) were prepared from the reaction of Mo(N[R]Ar)\textsubscript{2} with pyridine N-oxide, S\textsubscript{8}, Se and Te/PEt\textsubscript{3}. The complexes were studied by EPR, SQUID magnetometry, cyclic voltammetry and single crystal X-ray diffraction. The Mo-O and Mo-S bond dissociation enthalpies were experimentally determined to be 155.61 ± 1.6 and 104.35 ± 1.2 kcal/mol respectively. Thermolysis of the Mo(V) complexes resulted in tert-butyl radical elimination and formation of the terminal Mo(VI) chalcogenido complexes EMo(NAr)(N[R]Ar)\textsubscript{2}. The
selenido and tellurido derivatives were studied by selenium and tellurium NMR spectroscopy. A first-order decay was measured for the thermolysis reaction for both the oxo and sulfido complexes. The reactivity of Mo(N[R]Ar)_3 with a wide variety of chalcogen atom donor reagents was examined.

Chapter III: Activation of a Molybdenum Nitride Derived from Molecular Nitrogen


Chapter IV: Group 6 Complexes with a Bulky Amide Ligand Containing β-Hydrogens-Synthesis with Mechanistic Implications


Thesis Supervisor: Professor Christopher C. Cummins

Title: Professor of Chemistry
Biographical Note

Adam Reid Johnson was born in New Haven, Connecticut, lived in Medford, Massachusetts for a short time, and was raised in Upper Arlington, Ohio. He graduated from Upper Arlington High School in 1989. He earned a B. A. from Oberlin College and graduated phi beta kappa with High Honors in Chemistry in 1993. He was awarded the Jewett Prize (1991), the Dow Scholarship (1992-3), the Holmes Prize (1993) and received an Honorable Mention in the National Science Foundation Fellowship Competition (1993). He was a National Science Foundation Summer Intern at the University of California, Irvine (1991). He has taught courses in group theory and advanced inorganic chemistry, and supervised laboratory instruction in general and organic chemistry. He has presented papers at local, regional and national American Chemical Society meetings. Subsequent to receiving his Ph. D., Adam will begin postdoctoral research in the laboratory of Ken Raymond at the University of California, Berkeley. His career goal is to teach inorganic and general chemistry at an undergraduate institution with a strong research focus. His hobbies include zymurgy, running, backpacking, cooking and reading. In 1996, he married Wendy Lynne Waggener.

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<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>A</td>
<td>EPR Coupling Constant</td>
</tr>
<tr>
<td>Å</td>
<td>Angstrom (10^-10 m)</td>
</tr>
<tr>
<td>1-Ad</td>
<td>1-Adamantyl</td>
</tr>
<tr>
<td>2-Ad</td>
<td>2-Adamantyl</td>
</tr>
<tr>
<td>Anal.</td>
<td>Analysis (Elemental)</td>
</tr>
<tr>
<td>Ar</td>
<td>Aryl or Argon or 3,5-C_6H_3Me_2</td>
</tr>
<tr>
<td>Ar_F</td>
<td>2,5-C_6H_3FMe</td>
</tr>
<tr>
<td>atm</td>
<td>Atmosphere</td>
</tr>
<tr>
<td>br</td>
<td>Broad</td>
</tr>
<tr>
<td>Bz</td>
<td>Benzyl, CH_2C_6H_5</td>
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<tr>
<td>c_{ij}</td>
<td>Coefficient of Atomic Orbital j in Molecular Orbital i</td>
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<tr>
<td>CACAO</td>
<td>Computer Aided Composition of Atomic Orbitals</td>
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<td>Calculated</td>
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<tr>
<td>CCD</td>
<td>Charge Coupled Device</td>
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<td>cm^{-1}</td>
<td>Wavenumber</td>
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<td>Doublet or Days</td>
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<tr>
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<td>Degrees</td>
</tr>
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<td>DME</td>
<td>1,2-Dimethoxyethane</td>
</tr>
<tr>
<td>dmpe</td>
<td>1,2-Bis(dimethylphosphino)ethane</td>
</tr>
<tr>
<td>d^n</td>
<td>Number of d-Electrons</td>
</tr>
<tr>
<td>E</td>
<td>Element (Usually a Group 16 Element) or Energy</td>
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<tr>
<td>EHC</td>
<td>Extended Hückel Calculation</td>
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<td>Gauss</td>
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<td>Gas Chromatography-Mass Spectrometry</td>
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<td>Planck's constant</td>
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<td>Hours</td>
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(20)
\[ H \]

Hamiltonian

\[ H_{ii} = \int \phi_i H \phi_i \, d\tau \]
Energy of Atomic Orbital \( \phi_i \) (Ionization Energy or Coulomb Integral)

\[ H_{ij} = \int \phi_i H \phi_j \, d\tau \]
Interaction Energy Between atomic orbitals \( \phi_i \) and \( \phi_j \) (Resonance Integral)

\(^1\)H
Proton

\(^2\)H
Deuteron

HOMO
Highest Occupied Molecular Orbital

HRMS
High Resolution Mass Spectrometry

Hz
Hertz (sec\(^{-1}\))

\( i \)-Pr
iso-Propyl

IR
Infra-Red

\( n \)\( J_{xy} \)
n-Bond Coupling Constant Between Atom \( x \) and \( y \)

\( k \)
Boltzmann's constant

K
Degrees Kelvin

\( k_f \)
Rate Constant

L
Neutral Two Electron Donor Ligand

LUMO
Lowest Unoccupied Molecular Orbital

M\(^+\)
Parent Ion

\( m \)
Multiplet or \( Meta \)

Me
Methyl

MO
Molecular Orbital

MOAN
Molecular Orbital ANalysis

MS
Mass Spectrometry

NMR
Nuclear Magnetic Resonance

Np
Neopentyl

nph
Neophyl, \( \text{CH}_2\text{CMe}_2\text{Ph} \)

\( o \)
Ortho

ORTEP
Oak Ridge Thermal Ellipsoid Plot

OTf
Triflate, \( \text{CF}_3\text{SO}_3^- \)

\( p \)
Para

Ph
Phenyl

ppm
Parts Per Million

py
Pyridine

q
Quartet

R
Generic Alkyl Group

[\( R \)]
\( \text{C(\text{CD}_3)_2\text{CH}_3} \)

(21)
\( [\text{R}_{\text{ph}}] \)  \( \text{C(CD}_3\text{)}_2\text{C}_6\text{H}_5 \)

s  Singlet or Spin Quantum Number

sept  Septet

\( S_{ij} = \int \phi_i \phi_j \text{ d}\tau \)  Overlap Integral Between \( \phi_i \) and \( \phi_j \)

silox  \( \text{OSi(tert-Bu)}_3 \)

SOMO  Singly Occupied Molecular Orbital

SQUID  Superconducting QUantum Interference Device

T  Absolute Temperature

t  Triplet

\( \text{t-Bu} \)  \( \text{tert-Butyl} \)

THF  Tetrahydrofuran

TIP  Temperature Independent Paramagnetism

TLA  Three Letter Acronym

TMEDA  Tetramethylethylenediamine

TMS  Tetramethylsilane

UV-vis  Ultra Violet-Visible

VT  Variable Temperature (as in VT-NMR)

X  Anionic One Electron Donor Ligand

\( \chi \)  Magnetic Susceptibility

\( \delta \)  Chemical Shift in ppm Downfield From Zero

\( \Delta H^\ddagger \)  Enthalpy of Activation

\( \Delta V_{1/2} \)  Peak Width at Half Height

\( \Delta S^\ddagger \)  Entropy of Activation

\( \varepsilon \)  Extinction Coefficient

\( \eta^\ddagger \)  \( \chi \)-Hapto

\( \lambda_{\text{max}} \)  Wavelength with Highest Absorbance

\( \mu \)  Magnetic Moment, or Bridging Ligand

\( \mu_B \)  Bohr Magneton

\( \mu_{\text{eff}} \)  Effective Magnetic Moment

\( \mu_L \)  Microliter

\( \nu_{\text{xy}} \text{ or } \nu(X) \)  Vibrational Band for an XY Bond or X-Group

\( \theta \)  Weiss Constant (K)

\( \psi_k \)  k'th Molecular Orbital

\( \phi_i \)  i'th Atomic Orbital

\( \zeta_x \)  Effective Nuclear Charge for Atom X (Exponential Term in Normalized Radial Atomic Orbital Function)
Chapter I: Heteroleptic Titanium(III) and -(IV) Complexes

with Bulky ancillary Ligands*

Section 1.1: Introduction.

Cyclopentadienyl complexes of titanium and the other group four elements are being intensely studied due to the wide variety of chemical transformations they mediate. One of the most important of these is the Ziegler-Natta polymerization of ethylene and propylene, and there is much synthetic effort towards the development of more effective catalysts for this reaction. There are many other uses for titanium reagents including hydrogenation and reductive coupling of organic substrates. A major focus of current research in this area is the development of new ligands capable of enhancing the inherent reactivity of the metal center. Noteworthy are the $C_2$-symmetric ansa-metalloccenes originally developed by Brintzinger and Cp ligands with pendant amide groups which alter the electronic environment at the metal center relative to titanocene-based reagents. One mode of reactivity for these reagents is through the Lewis acidic metal center generated by the formation of an open coordination site.

In order to develop reagents and catalysts with significantly improved or different properties, transition metal complexes with N- or O-donor ancillary ligands are currently under investigation. One feature common to these ligands is their steric bulk, which stabilizes reactive, low-valent complexes by preventing dimerization or oligimerization. The reactivity of the metal center should be enhanced relative to metalloocene complexes due to the enforced low coordination number and decreased electron count at the metal center. The ligand silox ($t$-Bu$_3$SiO$^-$) stabilizes a wide variety of early transition metal complexes, while bulky 2,6-$di$-alkyl substituted aryloxide ligands and benzamidinate ligands are also employed with a good deal of success. However, amides are the most common ligand used, due in large part to the increased steric protection offered by the additional alkyl group on nitrogen relative to oxygen. Bulky amide ligands such as $t$N(SiMe$_3$)$_2$, $t$N(Ph)$_2$, $t$N(Cy)$_2$ and $t$N(i-Pr)$_2$ have all been used successfully to generate low coordinate transition metal complexes. These low coordinate
complexes are generally quite reactive, mediate such reactions as carbon-carbon bond formation,\textsuperscript{26} reductive coupling,\textsuperscript{22,41} carbonyl insertion\textsuperscript{17} and hydrogenation,\textsuperscript{17} and stabilize reactive organic fragments.\textsuperscript{18}

A significant problem with the ligands which have been used so far is a direct consequence of the low-coordinate environment they stabilize. Low-valent and low-coordinate complexes are often paramagnetic, and are therefore difficult to study spectroscopically due to the line broadening effect of paramagnetic materials on proton NMR signals. Deuterium NMR of paramagnetic materials can theoretically give peaks which are 42 times sharper than the corresponding proton signals;\textsuperscript{42,43} therefore, ligands with deuterium incorporation are desirable. Unfortunately, it is neither easy nor cheap to substitute deuterium into standard amide ligands. A novel bulky amide ligand type, the \textit{N-tert}-alkyl anilide,\textsuperscript{44} addresses this problem. This ligand readily stabilizes molecules with low coordination numbers and oxidation states,\textsuperscript{45-54} mimics the \textit{N(SiMe}_3\textit{)}\textsubscript{2} ligand both electronically (the \textit{pK}_a of aniline and bis(trimethylsilyl)amine are both \textasciitilde 25) and sterically, and allows for simple incorporation of a relatively inexpensive deuterium label. These ligands are readily prepared in multi-gram quantities in only a few steps, and, like \textit{N(SiMe}_3\textit{)}\textsubscript{2}, are not susceptible to low-energy decomposition pathways such as \textbeta-hydrogen elimination or cyclometallation. However, the biggest advantage to using this ligand type is the inherent electronic tunability due to the commercial availability of a wide variety of inexpensive anilines.

The homoletic titanium(III) tris-anilide complex is monomeric in the solid state.\textsuperscript{55} It is a powerful one electron reductant, capable of abstracting halogen atoms from transition metal complexes\textsuperscript{56} and organic substrates.\textsuperscript{57} It also adds to terminal oxo groups in transition metal complexes, forming the novel "titanoxy" ligand.\textsuperscript{53,55} A heteroleptic titanium(III) alkyl complex should exhibit one electron reactivity similar to the tris-anilide, but the metal-carbon bond in the alkyl complex might also be reactive. Although rare, there are examples of heteroleptic complexes in the field of low-coordinate chemistry, including
W(silox)$_2$(N-t-Bu)$_2$.\textsuperscript{21} Two-electron chemistry of metal-carbon bonds is also well
precedent,$\textsuperscript{2}$ but three-electron chemistry, two from the metal-carbon bond plus one from
the unpaired electron on the metal center, is not. Titanium(III) alkyl complexes would be
expected to exhibit one, two and three electron chemistry, given the proper substrates.

This chapter describes the synthesis and characterization of a Ti(III) alkyl complex
stabilized with two N-tert-alkyl anilide ligands, steric and electronic constraints for the
stability of Ti(III) alkyl species in general, and initial reactivity studies demonstrating the
potential for one, two and three electron processes involving the single electron in tandem
with the reactive metal-carbon bond. In addition, alternate synthetic pathways are
presented which, although they do not lead to stable Ti(III) complexes, demonstrate the
inherent electronic tunability of the N-tert-alkyl anilide ligand. The syntheses in this
chapter make extensive use of a recently developed dimethylamide protecting group
strategy.$\textsuperscript{58}$ The dimethylamide "place holder" is replaced with an iodide by treatment with
methyl iodide. This strategy prevents oversubstitution and/or reduction of titanium halide
starting materials, and seems general in scope for the synthesis of otherwise inaccessible
metal iodide complexes.$\textsuperscript{59}$ Much of the work described in this chapter has appeared in
print.$\textsuperscript{58,60,61}$

Section 1.2: Synthesis of N-tert-alkyl Anilides

(i) HN[R]Ar

Several synthetic methods have been developed and optimized for the N-tert-alkyl
anilide ligand.$\textsuperscript{44,61}$ Hunter$\textsuperscript{62}$ prepared N-tert-buty1 aniline in low yield by methylating
phenylacetone imine.$\textsuperscript{63}$ This procedure is outlined in Scheme 1.1 for the synthesis of the
N[R]Ar ligand ($R = C(\text{CD}_3)$_2CH$_3$; $Ar = 3,5$-$C_6H_3Me_2$). Distilled 3,5-dimethylaniline is
added to acetone-$d_6$ in the presence of 4 Å sieves. To prevent significant proton
incorporation from adventitious water, the reaction is carried out under a partial vacuum.
The crude reaction mixture is monitored directly by $^1$H NMR, and the reaction takes from one to four days to go to completion. Removal of the sieves and the excess acetone yields a pale yellow oil (ArN=C(CD$_3$)$_2$, 1.1) in essentially quantitative yield.

![Chemical structure](image)

**Scheme 1.1: Synthesis of the N[R]Ar Framework**

The final conditions used for the methylation of 1.1 to give HN[R]Ar (1.2) are a result of extensive optimization. The synthesis is best accomplished by slowly adding a solution of the imine to three equivalents of a just thawed solution of methyllithium. After 18 hours of stirring, the reaction solution is poured over ice to quench the excess methyllithium. The separated organic fraction is a 1:1 mixture of 1.2 and ArN=C(CD$_3$)(CD$_2$H). Methyllithium deprotonates 1.1 to the extent of about 50% under these conditions; the aqueous quench regenerates the imine. The deuterium isotope effect
significantly slows this competing side reaction relative to the unlabeled material, where the yield of the desired addition product is only 9%. The undesired imine is chemically converted back to 3,5-dimethylaniline by the addition of strong aqueous acid, and the two amines are then separated on an alumina column. Complex 1.2 is recovered from the aqueous phase by extraction, and isolated in yields of 40 to 60%.

Deprotonation of 1.2 is straightforward. Addition of n-butyllithium to a cold solution of the amine results in a viscous yellow oil after solvent evaporation, but the addition of ether precipitates a fine white microcrystalline powder. An X-ray crystal structure of Et₂O-LiN[R]Ar (1.3) confirms the dimeric nature of the product shown in Scheme 1.1.⁶⁴

(ii) HN[R]ArF⁵⁴

The related ligand, originally prepared by Stokes, having a 2-fluoro-5-methyl substituted aryl group, is prepared similarly to 1.1, but starting instead with 2-fluoro-5-methylaniline.⁵⁴ ArF=N=CC(CD₃)₂ (1.4) is isolated in 73% yield. The methylation step to generate HN[R]ArF (1.5) proceeds smoothly, in 87% yield, without the formation of any deprotonated enamine. As deuterium is not required for good yields of the methylated product (the synthesis of the fully protiated derivative, HN[t-Bu]Ph, is also straightforward and high yielding) this is most likely a result of the reduced electron density at nitrogen due to the ortho fluorine.⁴⁵,⁶⁵ Deprotonation of 1.5 with n-butyllithium followed by the addition of ether forms Et₂O-LiN[R]ArF (1.6) in 73% yield.

(iii) HN[Rₚₖ]Ar

A third ligand, with significantly increased steric bulk, is prepared by addition of phenyllithium to imine 1.1. There are no appreciable side products observed in this reaction, and the desired aniline, HN[Rₚₖ]Ar (1.7), is isolated in 74% yield after an
aqueous quench. Deprotonation of the aniline with \( n \)-butyllithium followed by the addition of ether affords \( \text{Et}_2\text{O-LiN}[\text{R}_{\text{ph}}]\text{Ar} \) (1.8) in 42% yield.

These three anilide ligands are used in metathesis reactions on the \( \text{Ti(NMe}_2\text{)}_x\text{Cl}_{4-x} \) nucleus to generate most of the complexes discussed in this chapter. Their use offers the ability for rational steric and electronic tuning of the titanium center due to the different steric and electronic profiles of the ligands. Two bulky alkoxide ligands are also used: 2,6-di-\textit{iso}-propylphenoxide (\( \text{OA}'' \)) and 2,6-di-\textit{tert}-butylphenoxide (\( \text{OA}''' \)). For quick reference, the five ligands and their abbreviations are shown in Figure 1.1.

![Ligand Structures](image)

**Figure 1.1:** The Ligands used for Stabilization of Titanium Complexes
Section 1.3: Ti(IV) Complexes with N[R]Ar

(i) Attempted Synthesis of TiCl₂(N[R]Ar)₂

ClTi(N[R]Ar)₃ is prepared from TiCl₄(THF)₂⁶⁶ and three equivalents of lithium amide 1.₃.⁵⁸ Reduction of the chloride in benzene forms the homoleptic Ti(III) species Ti(N[R]Ar)₃ in good yield.⁵⁵ In order to allow for alkyl group incorporation on titanium prior to reduction, the dihalide complex TiCl₂(N[R]Ar)₂ is a reasonable initial synthetic goal. Treating TiCl₄(THF)₂ with two equivalents of 1.₃ forms a blood red solution, but analysis of the reaction mixture by ¹H NMR spectroscopy shows both significant side product formation and decomposition. There is evidence for the oversubstituted product ClTi(N[R]Ar)₃, which may also arise through a ligand-swapping reaction similar to the conproportionation chemistry that is known for other titanium amides.⁶⁷ The dichloride only crystallizes from the crude reaction mixture in very low yield and it has not been possible to separate it from the side products. The dichloride (1.₃₁) is prepared by a substantially different route as discussed in Section 1.₈. The presence of extra, potentially reducible or substitutable halides in the starting tetrachloride complex does not allow for selective addition of only two anilide groups, but instead suggests the use of a protecting group strategy.

(ii) Synthesis of TiI₂(N[R]Ar)₂ (1.₁₀)

It is quite easy to prepare the dichloride complex TiCl₂(NMe₂)₂ by conproportionation of TiCl₄ and Ti(NMe₂)₄ in hexane at elevated temperature.⁶⁷ Treating this complex with two equivalents of 1.₃ in ether forms the mixed tetraamide species Ti(NMe₂)₂(N[R]Ar)₂ (1.₉) as shown in Scheme 1.₂. Using dimethylamide groups as place holders prevents oversubstitution by the N[R]Ar ligand. This oily complex is not isolated or purified, but excess methyl iodide reacts with the dimethylamide groups over a 40 hour period, quaternizing them to [NMe₄]I. Methyl iodide does not react with the
remaining N[R]Ar ligands under these conditions, and the dark brown crystalline complex TiI₂(N[R]Ar)₂ (1.10) is isolated in 60% yield. The ortho and para resonances in the ¹H NMR spectrum, which appear at 7.07 and 6.86 ppm, are good spectroscopic handles for monitoring reactions involving the N[R]Ar ligand. Me₃SiI has been used similarly to remove dimethylamido groups from molybdenum and tungsten.⁶⁸ With a dihalide complex prepared, the next goal is the selective monoalkylation of the species, leaving one iodide which can be removed by reduction.

\[
\begin{align*}
\text{Me}_2\text{N}-\text{Ti} & \quad \text{NMe}_2 \\
\text{NMe}_2 & \quad 2 \text{Et}_2\text{O} \cdot \text{LiN[R]Ar} \\
\text{Cl} & \quad -2 \text{LiCl} \\
\text{Me}_2\text{N}-\text{Ti} & \quad \text{NMe}_2 \\
\text{N[R]Ar} & \quad 24 \text{MeI, Et}_2\text{O} \\
& \quad -2 \text{NMe}_4\text{I}
\end{align*}
\]

(1.9)

\[
\begin{align*}
\text{R} & \quad \text{Ti} \quad \text{N[R]Ar} \\
\text{N[R]Ar} & \quad \text{LiR} \\
\text{I} & \quad -\text{LiI} \\
\text{R} & \quad \text{CH}_2\text{SiMe}_3 \quad (1.11) \\
\text{R} & \quad \text{CH}_2\text{CMe}_2\text{Ph} \quad (1.12)
\end{align*}
\]

Scheme 1.2: Synthesis and Reactivity of TiI₂(N[R]Ar)₂

(iii) Alkylation of 1.10

A strong alkylating reagent is required to derivatize diiodide 1.10, as it does not react cleanly or at all with Grignard or dialkylmagnesium reagents. Attempted alkylation with neopentyllithium causes the rapid appearance of a short lived green color, followed by

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decomposition as monitored by $^1$H NMR spectroscopy. The green color is reminiscent of Ti(N[R]Ar)$_3$, suggesting reduction. However, the resulting complex "Ti(N[R]Ar)$_2$I" could readily disproportionate or dimerize, and is not expected to be stable. Reduction of the diiodide 1.10 with sodium amalgam in benzene forms sodium iodide, but no green color is observed. Analysis of the crude reaction mixture by $^1$H NMR spectroscopy shows at least three unknown, diamagnetic products.

Trimethylsilylmethyllithium reacts cleanly with 1.10 in a cold ether solution, forming the alkyl complex Ti(N[R]Ar)$_2$(I)(CH$_2$SiMe$_3$) (1.11). However, the complex is oily, preventing isolation or purification of the dark red material. $^1$H NMR spectroscopy shows the material to be fairly pure, contaminated with a small amount of free aniline 1.2. The para and ortho proton NMR resonances appear at 7.00 and 6.83 ppm respectively, and there is a 1:2 ratio of alkyl to anilide, suggesting that monoalkylation occurs selectively. Reduction of the crude material with sodium amalgam in benzene, as in the preparation of Ti(N[R]Ar)$_3$, causes the formation of sodium iodide, but no green color is observed. A $^2$H NMR spectrum does not show any resonances around 4 ppm, the region expected for a Ti(III) complex. Reducing the complex with sodium amalgam in THF causes a vivid olive green color to appear, but this color fades rapidly to brown. Proton NMR spectroscopy of the crude material shows at least five products.

Complex 1.10 also reacts with LiCH$_2$CMe$_2$Ph (neophyl lithium) in a cold ether solution generating the alkyl complex Ti(N[R]Ar)$_2$(I)(CH$_2$CMe$_2$Ph) (1.12). The ortho and para proton resonances appear at 7.15 and 7.11 ppm respectively, and again the monoalkylation product is generated selectively. However, this complex is also a dark red oil like 1.11, preventing purification. Similar disappointing results are obtained when 1.12 is treated with sodium amalgam in benzene: no paramagnetic products are observed although sodium iodide is formed. These results suggest that, although reduction of a Ti(IV) alkyl halide complex is thermodynamically feasible, either steric or electronic tuning is required in order to make an isolable Ti(III) alkyl complex.
Section 1.4: Ti(IV) Complexes with N[R]ArF

The instability of Ti(III) alkyl complexes generated with the N[R]Ar ligand could be due to the strong electron donating properties of the anilide ligand on the reduced metal center. The 2-fluoro-5-methyl anilide derivative (N[R]ArF) should be more electron withdrawing due to the ortho fluorine. Additionally, complexes with this ligand are typically more crystalline and therefore easier to isolate and purify. Both the enhanced crystallinity and the altered electronic environment are apparent when attempting to duplicate the synthesis of diiodide 1.10 with the N[R]ArF ligand.

(i) Synthesis of Ti(N[R]ArF)_2(I)(NMe_2) (1.14)

Dichloride TiCl_2(NMe_2)_2 reacts with two equivalents of Et_2O-LiN[R]ArF (1.6) in a chilled ether solution, forming Ti(N[R]ArF)_2(NMe_2)_2 (1.13) as a dark yellow crystalline solid (Scheme 1.3). This complex is significantly more crystalline than the N[R]Ar derivative 1.9. Although there is no longer a clear spectroscopic handle as with the ortho and para protons in the N[R]Ar ligand, the reactions depicted in Scheme 1.3 are readily monitored by ^1H NMR spectroscopy by observing the dimethylamide resonance, which appears at 3.075 ppm in 1.13.

The mixed tetraamide 1.13 reacts with methyl iodide in a manner analogous to that observed for 1.9. Addition of 10 equivalents of methyl iodide to 1.13 causes a slow color change to bright red over a period of 18 hours. The [NMe_4]I is removed by filtration, and the product is purified by crystallization from ether. Proton NMR spectroscopy shows a dimethylamide group with a resonance at 3.057 ppm in a one to two ratio with the N[R]ArF ligands, showing that the product Ti(N[R]ArF)_2(I)(NMe_2) (1.14) is only monosubstituted. Suitable conditions for synthesis of the diiodide complex have not been found. This result makes sense from an electronic standpoint. The ortho fluorine substituent, through an inductive electron withdrawing effect, makes the titanium center more electrophilic, thereby increasing Ti-N π interactions. With a decreased lone pair...
density on the dimethylamide nitrogen, it is less nucleophilic, and less likely to react with methyl iodide. When the first dimethylamide is replaced with an iodide, the remaining dimethylamide has an even stronger Ti-N π interaction, rendering the lone pair unavailable for subsequent reaction. This suggests that the N[R]ArF ligand behaves as desired; the electron withdrawing ligand should help stabilize the Ti(III) oxidation state.

\[ \text{Scheme 1.3: Ti(IV) Complexes with the N[R]ArF Ligand} \]
(ii) Alkylation of 1.14

Complex 1.14 reacts cleanly with one equivalent of LiCH₂SiMe₃ in a chilled pentane solution. After removing lithium iodide by filtration, the mustard yellow alkyl complex Ti(N[R]ArF)₂(CH₂SiMe₃)(NMe₂) (1.15) crystallizes in 70% yield from pentane. The dimethylamide resonance appears at 3.08 ppm in the ¹H NMR spectrum of 1.15.

It is possible to remove the remaining dimethylamide group from 1.15 using the methyl iodide reaction, but the choice of solvent is important. Although the reaction does proceed slightly in ether, it is much faster and goes to completion in THF. A large excess of methyl iodide is also required. The substitution of the iodide in 1.14 for the alkyl in 1.15 increases the electron density on titanium, decreases the Ti-N π interaction, and allows for cleavage of the dimethylamide. The iodide complex, Ti(N[R]ArF)₂(I)(CH₂SiMe₃) (1.16), is isolated as a thick orange-red oil which resists crystallization. The corresponding alkylation of 1.14 with neophyllolithium proceeds to give an impure oily compound, and the reaction of this mixture with methyl iodide does not lead to isolable products.

Reduction of the impure alkyl complex 1.16 with sodium amalgam in toluene darkens the solution to deep brown. Analysis of the crude reaction mixture by ²H NMR spectroscopy shows only small amounts of paramagnetic material. Reduction of the complex in DME gives similar results. The dimethylamide iodide complex 1.14 also does not react cleanly with sodium amalgam in benzene. Proton NMR analysis of the crude reaction mixture shows significant decomposition. No diagnostic green color is ever observed when complexes with the N[R]ArF ligand are reduced, suggesting that the ortho fluorine is incompatible with the reactive metal center. There is additional evidence to support this conclusion. Although ClTi(N[R]ArF)₃ can be made, reduction of the complex with sodium amalgam leads to marked decomposition. Attempts to synthesize Mo(N[R]ArF)₃ (which is never observed) from MoCl₃(THF)₃ and two equivalents of lithium amide 1.6, by analogy to the preparation of Mo(N[R]Ar)₃, result in the formation
of the orthometallated Mo(IV) complex shown in Figure 1.2. The incompatibility of an ortho fluorine with Ti(III) is not surprising in retrospect, as Ti(N[R]Ar)_3 is known to be a powerful halogen atom abstractor. Ti(N[R]Ar)_3 abstracts chlorine from chlorobenzene or chloroform, bromine from bromobenzene and iodine from iodobenzene or methyl iodide, but does not abstract fluorine from fluorobenzene. However, the N[R]Ar_F ligand is known to coordinate in a bidentate fashion, with N and F donation, and the proximity of the strongly electrophilic titanium center may allow the aryl fluorine to be activated in an intramolecular reaction.

\[
\begin{align*}
\text{Ar}_F[\text{R}]\text{N-Mo} & \cdots \text{N}[\text{R}]\text{Ar}_F \\
\text{[N}[\text{R}]\text{Ar}_F
\end{align*}
\]

![Figure 1.2: Orthometallation of the N[R]Ar_F ligand in a Mo(III) complex](image)

Section 1.5: Ti(IV) Complexes with N[R]Ar and OAr'

A way to decrease electron density at the titanium center without using a fluorinated ligand is by using aryloxide ligands. This is due both to the increased electronegativity of oxygen relative to nitrogen, and to the lower number of electron donating alkyl groups on the ligating atom. There are many examples of early transition metal complexes with O-donor ligands, including the three-coordinate Ti(III) complex Ti(OAr")_3. Clearly, 2,6-dialkyl-substituted phenoxides are capable of providing a good deal of steric protection to a metal center. However, to generate a Ti(III) complex with both an aryloxide and a less bulky alkyl substituent, substantial steric protection would be required at the remaining coordination site. Using the N[R]Ar ligand in conjunction with 2,5-di-iso-propylphenoxide (OAr') should provide enough steric protection to support titanium alkyl
complexes. In related work, Rothwell has synthesized titanium complexes with bulky aryloxide ligands and dimethylamide ligands.\textsuperscript{24}

(i) Synthesis of $\text{Ti(N}[\text{R}][\text{Ar}](\text{OAr'})\text{(I)}_2$ (1.19)

$\text{TiCl(NMe}_2\text{)}_3$ is prepared similarly to $\text{TiCl}_2\text{(NMe}_2\text{)}_2$ by conproportionation of $\text{TiCl}_4$ and $\text{Ti(NMe}_2\text{)}_4$ in the appropriate ratio.\textsuperscript{67} Treating the monochloride with one equivalent of lithium amide \textbf{1.3} in ether leads to rapid substitution and a color change to green-brown. The mixed tetraamide complex $\text{Ti(N}[\text{R}][\text{Ar}](\text{NMe}_2\text{)}_3$ (1.17) is a mobile brown oil, but the synthetic transformation is clean according to $^1\text{H}$ NMR spectroscopy (Scheme 1.4). The \textit{para} and \textit{ortho} hydrogen resonances appear at 6.65 and 6.58 ppm respectively, while the dimethylamido resonance appears at 2.91 ppm. A single dimethylamide group is selectively cleaved by adding one equivalent of 2,6-di-\textit{iso}-propylphenol to \textbf{1.17} in ether; the dimethylamine side product simply evaporates away. There is no obvious color change, and $\text{Ti(N}[\text{R}][\text{Ar}](\text{OAr'})\text{(NMe}_2\text{)}_2$ (1.18) is obtained as a thick dark brown oil after removing the solvent. Again, $^1\text{H}$ NMR spectroscopy shows that the transformation is clean and essentially quantitative. The ligand \textit{para} and \textit{ortho} resonances appear at 6.68 and 6.59 ppm, while the resonance corresponding to the two remaining dimethylamide groups has shifted downfield to 3.04 ppm, suggesting a reduced electron density on titanium. The two remaining dimethylamide groups are removed using the standard deprotection protocol by dissolving \textbf{1.18} in THF, adding 10 equivalents of methyl iodide and stirring at room temperature for nine hours. The deep red diiodide $\text{Ti(N}[\text{R}][\text{Ar}](\text{OAr'})\text{(I)}_2$ (1.19) crystallizes from ether in 65\% overall yield from the starting tris-dimethylamide complex.

(ii) Alkylation of 1.19

Complex \textbf{1.19} is alkylated with $\text{LiCH}_2\text{SiMe}_3$ in chilled hexane, causing a rapid color change to light orange and the formation of a white precipitate. Although the reaction appears quantitative and clean by $^1\text{H}$ NMR spectroscopy, it has not been possible to

(37)
crystallize the material due to its extreme solubility in hydrocarbon solvents. The $^1$H NMR spectrum is consistent with the proposed chiral-at-metal Ti(IV) complex Ti(N[R]Ar)(OAr')(CH$_2$SiMe$_3$)(I) (1.20); the diastereotopic methylene group appears as a doublet of doublets at 2.24 and 1.22 ppm, and the diastereotopic $iso$-propyl methyl groups appear as a doublet of doublets at 1.38 and 1.22 ppm.

Scheme 1.4: Synthesis of Chiral-at-Metal Ti(IV) Complexes
The corresponding neophyl complex, Ti(N[R]Ar)(OAr')(CH₂CMe₂Ph)(I) (1.21) is prepared by adding LiCH₂CMe₂Ph to a chilled solution of 1.19 in hexane. Proton NMR spectroscopy again shows the reaction to be clean and essentially quantitative, but the alkyl complex is isolated in only 49% yield by crystallization from pentane due to the extreme hydrocarbon solubility of the complex. Complex 1.21 also exhibits diastereotopic resonances in the ¹H NMR spectrum: the methylene protons appear as two doublets at 2.35 and 2.07 ppm, the iso-propyl methyls appear as two doublets at 1.36 and 1.21 ppm, and the neophyl methyls appear as two singlets at 1.32 and 1.24 ppm.

The results obtained with complexes 1.11 and 1.12 suggest carrying out reductions in a polar, coordinating solvent in order to increase the rate. Other researchers have observed that reductions in non-coordinating solvents lead to decomposition or disproportionation reactions.²⁸,⁷¹ Both alkyl complexes 1.20 and 1.21 are reduced with sodium amalgam in either THF or DME, causing a color change to olive green over a 10 minute period. Deuterium NMR analysis of the reaction mixture shows a resonance at 4.6 ppm which rapidly decreases in area; after one hour at room temperature the reaction solution is brown and ²H NMR spectroscopy shows only resonances in the diamagnetic region. The reduced species have a longer lifetime than those observed in complexes without aryloxo ligation, but they are still too unstable to be isolated. It is possible to store solutions of the green material for several hours at -35 °C, but they gradually become murky brown and ¹H NMR spectra indicate significant decomposition.

Ti(N[R]Ar)₃ reacts with NMo(O-t-Bu)₃ at room temperature, forming the "titanoxy" species NMo(O-t-Bu)₂{OTi(N[R]Ar)₃} with expulsion of a tert-butyl radical.²³ A Ti(III) alkyl complex should react similarly, suggesting a means of characterizing the reduced species by trapping it with the molybdenum complex. Reducing complex 1.20 with sodium amalgam in DME forms a green solution, but after NMo(O-t-Bu)₃ is added, analysis of the crude material by ¹H NMR spectroscopy is disappointing. There are no resonances due to the SiMe₃ fragment, suggesting that the alkyl group has been lost,
presumably as TMS. The spectrum is messy, suggesting that decomposition rather than addition to the Mo-O linkage is the primary reaction pathway. The neophyl derivative 1.21 behaves similarly under these conditions.

**Section 1.6: Ti(IV) Complexes with N[R_{ph}]Ar and OAr''**

The paramagnetic green Ti(III) materials are slightly longer lived with aryloxide ligation, but still decompose rapidly, precluding their isolation or characterization. Although the mode of decomposition of the reduced species is unknown, larger ligands would help prevent intermolecular pathways. The chemistry described in this section uses the bulkier amide N[R_{ph}]Ar and the bulkier aryloxide 2,6-di-tert-butylphenoxide (OAr'').

(i) **Synthesis of Ti(N[R_{ph}]Ar)(OAr'')(I)(NMe_{2}) (1.24)**

Treating TiCl(NMe_{2})_{3} with Et_{2}O-LiN[R_{ph}]Ar (1.8) in THF forms a greenish brown solution. After rigorous solvent removal by repeated lyophylization from benzene, Ti(N[R_{ph}]Ar)(NMe_{2})_{3} (1.22) is isolated as a greenish-brown powder in 83% yield (Scheme 1.5). The dimethylamide resonance in the proton NMR spectrum appears at 2.77 ppm, while the resonance of the aryl methyls of the N[R_{ph}]Ar ligand appears at 1.88 ppm. The phenyl substituent on the N[R_{ph}]Ar ligand gives better crystallinity properties to the mixed tetraamide complex as compared to the N[R]Ar derivative 1.17.

Complex 1.22 reacts with 2,6-di-tert-butylphenol in a manner analogous to that in the preparation of 1.18, causing a color change to reddish orange after about three hours. The reaction is slow as determined by ^1H NMR spectroscopic monitoring, and requires approximately 20 hours for complete substitution. Ti(N[R_{ph}]Ar)(OAr'')(NMe_{2})_{2} (1.23) is obtained in 83% yield as an orange powder. The dimethylamide resonance at 3.02 ppm in the ^1H NMR spectrum is shifted downfield relative to that in 1.22, while the aryl methyl resonance appears at 1.91 ppm. The NMR data are consistent with monosubstitution on titanium with the aryloxide ligand.

(40) References begin on page 81
Scheme 1.5: Cyclometallation of a 2,6-di-tert-Butyl phenoxide Ligand
Chapter I: Heteroleptic Titanium(III) and - (IV) Complexes with Bulky Ancillary Ligands

Cleaving a dimethylamide from complex 1.23 with methyl iodide at room temperature is straightforward but sluggish. 10 equivalents over an 18 hour period results in essentially no conversion, but with a large excess of methyl iodide the reaction goes to completion in about 48 hours, generating Ti(N[R_ph]Ar)(OAr")(I)(NMe₂) (1.24) in 95% isolated yield. The complex is obtained as an orange microcrystalline powder from a chilled pentane solution. The dimethylamide resonance appears at 2.86 ppm in the ³¹H NMR spectrum, while the aryl methyl resonance is found at 2.18 ppm. It is not possible to remove the dimethylamide group from 1.24 using methyl iodide at room temperature, and attempts to do so by extended thermolysis result in significant decomposition. Apparently the substitution of phenyl for methyl in the N[R_ph]Ar ligand leads to enhanced electrophilicity at titanium, strengthening the Ti-N π interaction to the dimethylamide. Complex 1.24 is reduced with sodium amalgam, but no green color is observed and a ²H NMR spectrum shows only diamagnetic materials.

(ii) Cyclometallation of OAr"

Complex 1.24 is readily alkylated with neopentyllithium in a chilled pentane/ether solution. The color of the complex changes from red to yellow after five minutes, and monitoring by proton NMR spectroscopy indicates a clean conversion. However, it has not been possible to isolate this material as a crystalline solid. As the complex, presumed to be Ti(N[R_ph]Ar)(OAr")(CH₂CMe₃)(NMe₂) (1.25), retains a dimethylamide functionality, the methyl iodide deprotection protocol should effect an amide for iodide replacement, which would be expected to yield a more crystalline complex. However, when this is attempted, no reaction is observed by ³¹H NMR spectroscopy at room temperature in either ether or THF after several days. Heating the reaction mixture in a sealed reaction bomb results in significant decomposition. The major product crystallizes from the crude reaction mixture in low yield, and its ³¹H NMR spectrum is indicative of
C-H bond activation of one of the tert-butyl groups on the phenoxide ligand with loss of the alkyl group. Cyclometallation of the OAr" ligand has been reported by Rothwell.\textsuperscript{72-74}

The cyclometallation of 1.25 is much cleaner when methyl iodide is omitted from the thermolysis reaction. Simply heating the complex at 65 °C in THF for several hours causes the loss of the neopentyl group, presumably as neopentane, and C-H bond activation of one aryloxide tert-butyl group, cleanly forming the cyclometallated complex Ti(N[R\textsubscript{ph}]Ar)(O-2,6-C\textsubscript{6}H\textsubscript{3}[CMe\textsubscript{3}](CH\textsubscript{2}CMe\textsubscript{2}-))(NMe\textsubscript{2}) (1.26). The oily complex has not been purified for full characterization. Removing the dimethylamide group from 1.26 is accomplished by adding 10 equivalents of methyl iodide and heating at 70 °C for 21 hours. Although there is no color change, [NMe\textsubscript{4}]I is observed and no dimethylamide resonance is observed in the \textsuperscript{1}H NMR spectrum of the product. Yellow-orange crystals of Ti(N[R\textsubscript{ph}]Ar)(O-2,6-C\textsubscript{6}H\textsubscript{3}[CMe\textsubscript{3}][CMe\textsubscript{2}CH\textsubscript{2}-])(I) (1.27) are obtained from a chilled pentane solution in 62% overall yield from 1.24 by this two-step one-pot procedure. The aryl methyl resonance appears at 2.20 ppm in the \textsuperscript{1}H NMR spectrum. Spectroscopic confirmation of the chiral-at-metal complex is found in the diastereotopic titanium bound methylene, which displays two doublets at 1.47 and 0.83 ppm.

Complex 1.27 is a somewhat bulkier derivative of complexes 1.20 and 1.21, although the cyclometallation of the aryloxide ligand significantly reduces the steric protection of the titanium center relative to the original design. Reducing 1.27 with sodium amalgam in ether gives rise to a persistent green color; the product exhibits a \textsuperscript{2}H NMR signal at approximately 4 ppm. The green material has not been isolated in pure form as it is oily, and decomposes slowly even at -35 °C, preventing further characterization. This complex, which contains amide, aryloxide and alkyl ligation of Ti(III), is quite long lived though, and remains a promising candidate for further study.

Other synthetic pathways into mixed amide-aryloxide ligation of titanium alkyl complexes have not yet been successful. Titanium (IV) complexes with either N[R]Ar and
OAr" or N[R\text{_{ph}}]Ar and OAr' ligands are not well characterized as they tend to be produced as impure oils, and no further work in this area has been attempted.

Section 1.7: A Ti(III) Complex with N[R_{ph}]Ar

Electronic stabilization of short-lived Ti(III) complexes with electron withdrawing aryloxide ligands leads to significantly longer lifetimes relative to amide complexes and allows for their observation by $^2$H NMR spectroscopy. The complexes may require more steric protection of the metal center than the single O-bound substituent can offer, however. Complexes analogous to 1.11 or 1.12 with the N[R_{ph}]Ar ligand would have that increased steric protection when reduced to Ti(III). Additionally, the lesser degree of substitution observed in the reaction of methyl iodide with 1.23 compared to the reaction with 1.18 suggests an electron withdrawing effect of the N[R_{ph}]Ar ligand relative to the N[R]Ar ligand. However, the reduction of transition metal complexes with alkali metals sometimes leads to decomposition of the desired reduced species through salt mediated disproportionation or other pathways.\textsuperscript{28,71} This may be one reason why the titanium (III) complexes with the other ligand sets are not stable. A related example is seen in tungsten chemistry.\textsuperscript{56} Reduction of WCl\textsubscript{4}(THF)\textsubscript{2} with sodium amalgam leads to W\textsubscript{2}Cl\textsubscript{7}⁻ or W\textsubscript{2}Cl\textsubscript{6}, depending on the conditions.\textsuperscript{56} Repeating the reduction using the halogen abstracting reagent Ti(N[R]Ar)\textsubscript{3} allows for isolation of WCl\textsubscript{3}(THF)\textsubscript{3}. However, there would be a low thermodynamic driving force for using Ti(N[R]Ar)\textsubscript{3} to reduce a Ti(IV) alkyl complex. Therefore, it seems reasonable to start at Ti(III), removing the reduction step from the synthesis of the desired Ti(III) alkyl complex.

TiCl\textsubscript{3}(THF)\textsubscript{3}\textsuperscript{66} reacts with two equivalents of lithium amide 1.8 in the presence of a large excess of TMEDA as shown in Scheme 1.6. The addition causes a rapid color change from bright blue to olive green. After removing the solvent, only one equivalent of lithium chloride is filtered away from the green solution. Pale green needles are obtained from a cold ether solution, and this material exhibits a broad $^2$H NMR resonance at 4.84
ppm. Complex 1.28 is believed to have the formulation Ti(N[R\text{ph}]Ar)_2(\mu-Cl)_2Li(TMEDA), analogous to the structurally characterized Ti(N[Cy]_2)_2(\mu-Cl)_2Li(TMEDA) which is prepared by a similar route.\textsuperscript{39} However, if a small amount of crystallized 1.28 is treated with excess CDCl\textsubscript{3} and examined by \textsuperscript{1}H NMR spectroscopy, three equivalents of TMEDA are observed. Rigorous evaporation of solid 1.28 causes a color change to dark brown, and significant decomposition occurs. Dark blood-red Ti(N[R\text{ph}]Ar)_2(Cl)_2 (1.29) is prepared in excellent yield by dissolving 1.28 in CHCl\textsubscript{3} and filtering away one equivalent of LiCl. The complex is purified by vapor diffusion of pentane into toluene followed by crystallization at -35 \textdegree C. This complex, analogous to 1.11, has not been investigated further.

\begin{center}
\textbf{Scheme 1.6: Synthesis of Ti(N[R\text{ph}]Ar)_2Cl\textsubscript{2} from the "Ate" Complex Ti(N[R\text{ph}]Ar)_2(\mu-Cl)_2Li(TMEDA)_3}
\end{center}
Section 1.8: A Ti(III) Alkyl Complex with N[R]Ar

(i) Synthesis of Ti(N[R]Ar)$_2$(μ-Cl)$_2$·Li(TMEDA) (1.30)

The electron withdrawing ability of the N[R$_{ph}$]Ar ligand is not required for stabilization of Ti(III) complexes using this method; the synthesis of the N[R]Ar derivative of "ate" complex 1.28 is directly analogous. Two equivalents of lithium amide 1.3 are added to a THF/TMEDA solution of TiCl$_3$(THF)$_3$, and bright green needles of Ti(N[R]Ar)$_2$(μ-Cl)$_2$·Li(TMEDA) (1.30) are recovered in 57% yield by crystallization from pentane (Scheme 1.7). Complex 1.30 is well behaved in that it does not retain excess TMEDA, but is extraordinarily air and water sensitive. It, like complex 1.28, is unstable under vacuum, turning brown, decomposing and becoming diamagnetic. It exhibits a fairly sharp $^2$H NMR resonance at 3.81 ppm. A measurement of the magnetic susceptibility by the Evans method$^{75}$ gives a value of 2.22 $\mu_B$; this value is typical for $d^1$ complexes obtained by this technique. SQUID magnetic susceptibility data have not been obtained due to the extreme air and moisture sensitivity of the complex. An EPR spectrum of 1.30 in toluene at room temperature shows a single feature at $g = 1.95$. The spectrum taken at 103 K is shown in Figure 1.3. The spectrum is approximately axial with broad linewidths (~25 G) which merge $g_1$ and $g_2$ into a single feature. The $g$ values of 1.980, 1.964 and 1.930 are obtained by simulation of the spectrum.$^{76}$ The elemental analysis results deviate slightly from the calculated values, most likely due to the partial incorporation of THF for TMEDA in the solvation sphere around lithium. The stoichiometry of the complex is verified by treating a small sample of 1.30 with CDCl$_3$. Only a single equivalent of TMEDA is observed in the $^1$H NMR spectrum.
Figure 1.3: EPR spectrum (103 K, toluene) of Ti(N[R]Ar)$_2$(μ-Cl)$_2$Li(TMEDA) (1.30) with $g_1 = 1.980$, $g_2 = 1.964$, $g_3 = 1.930$. 
Scheme 1.7: Synthesis of the Stable Ti(III) Alkyl Complex Ti(N[R]Ar)₂(CH[SiMe₃]₂)
Complex 1.30 reacts with an excess of chloroform, liberating one equivalent of LiCl and generating the dichloride complex Ti(N[R]Ar)2(Cl)2 (1.31), directly analogous to complexes 1.29 and 1.10. The original preparation of 1.31 from TiCl4(THF)2, which is not synthetically viable, is described in detail in Section 1.3.

(ii) Alkylation of 1.30

The alkylation of 1.30 with standard alkylating agents is not straightforward. Addition of one equivalent of LiCH2SiMe3 to a chilled pentane solution of the "ate" complex results in clean conversion to a single diamagnetic product which shows a one to one ratio of ligand to alkyl resonances in the 1H NMR spectrum. Two equivalents of lithium chloride are recovered from the reaction mixture. If diiodide 1.10 is treated with two equivalents of LiCH2SiMe3, a lightening of the solution to yellow is observed over the course of one hour, and lithium iodide is formed. An orange-yellow oily solid that is isolated from the reaction mixture in high yield has 1H NMR resonances which correspond to the product of 1.30 with one equivalent of the alkyllithium reagent. The complex is therefore formulated as Ti(N[R]Ar)2(CH2SiMe3)2 (1.32). A similar oily product, the dark brown Ti(N[R]Ar)2(CH2CMe2Ph)2 (1.34), is obtained upon alkylation of either 1.10 with two equivalents of LiCH2CMe2Ph or 1.30 with one equivalent; the NMR spectra are identical for both sets of conditions. These findings are in line with related work which uses the N(Cy)2 ligand; alkylation of Ti(N[Cy])2(μ-Cl)2Li(TMEDA) with LiCH2SiMe3 results in disproportionation to the Ti(IV) dialkyl and an unknown Ti(II) species.77 As with these results, the fate of the Ti(N[R]Ar)2 fragment which forms during the alkylation of 1.30 is not known.

(iii) Synthesis of Ti(N[R]Ar)2(CH[SiMe3]2) (1.34)

Clearly, extremely bulky ligands would be required to shut down this supposed disproportionation pathway for standard alkyl groups. However, the bulky alkyl group

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CH(SiMe₃)₂, which has a similar steric profile to the amide N(SiMe₃)₂, also offers a good deal of steric protection to the metal center; Ti(CH[SiMe₃]₂)₃ is quite stable. Treating 1.30 with LiCH(SiMe₃)₂ causes a color change to deep green, and two equivalents of LiCl are recovered. The resulting complex, Ti(N[R]Ar)₂(CH[SiMe₃]₂) (1.34), is isolated in good yield as a dark green crystalline solid. This complex is extremely halogen, moisture and air sensitive, has a fairly sharp ²H NMR resonance at 3.97 ppm, and the Evans method magnetic susceptibility measurement gives a value of 2.21 μₜ for the magnetic moment. The SQUID magnetic susceptibility data for 1.34 from 5 to 300 K and a fit to the Curie-Weiss law (μ = 1.66 μₜ; θ = -0.19 K) are shown in Figure 1.4. The data indicate simple paramagnetic behavior over the entire temperature range. An EPR spectrum of 1.34 in toluene at room temperature has an isotropic g value of 1.95; the spectrum taken at 95 K (Figure 1.5) is axial, with the g values of 1.997, 1.962 and 1.918 obtained through simulation of the spectrum.

An X-ray diffraction study performed on a suitable crystal confirms the three-coordinate nature of the alkyl complex. Tables 1.1 and 1.2 give selected bond lengths and angles and Table 1.3 lists the positional parameters and B(eq). An ORTEP diagram of the structure is shown in Figure 1.6. One anilide ligand is engaged in an η³ interaction of N2, C21 and C26 with the titanium center, reminiscent of that type of interaction in some benzyl complexes. The Ti-N2 bond length is increased by 0.045 Å relative to the Ti-N1 distance. The bond alternation that is observed in the aromatic ring in the anilide containing N2 is typical for complexes with semi-localized π electrons. The structure is similar to that observed for Ti(N[R]Ar)₃, where two of the three anilide ligands are coordinated in an η³ manner.
Figure 1.4: SQUID magnetic susceptibility data for solid Ti(N[R]Ar)$_2$(CH[SiMe$_3$]$_2$) (1.34) from 5 to 300 K fit to the Curie-Weiss law ($\mu = 1.66 \mu_B$, $\theta = -0.19$ K)
Figure 1.5: EPR spectrum (97 K, toluene) of Ti(N[R]Ar)₂(CH[SiMe₃]₂) (1.34) with \( g₁ = 1.997 \), \( g₂ = 1.962 \), \( g₃ = 1.918 \).
Figure 1.6: ORTEP diagram of Ti(N[R]Ar)₂(CH[SiMe₃]₂) (1.34) with thermal ellipsoids drawn at the 30% probability level
**Table 1.1: Selected Bond Lengths (Å) for Ti(N[R]Ar)₂[CH(SiMe₃)₂] (1.34).**

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**Table 1.2: Selected Bond Angles (°) for Ti(N[R]Ar)₂[CH(SiMe₃)₂] (1.34).**

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### Table 1.3: Positional Parameters and B(eq.) for the Non-Hydrogen Atoms of Ti(N[R]Ar)_2[CH(SiMe)_3]_2 (1.34).

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</tbody>
</table>

The complex is best regarded as an 11 e⁻ complex; N1 donates 3 e⁻ (1 σ + 1 π interaction), N2 and C1 donate 1 e⁻ each in a σ sense, and the C21-C26 π interaction adds an additional 2 e⁻. The titanium carbon bond length of 2.137(7) Å is short relative to those in (η⁷-C₇H₇)(DMPE)TiEt₈ and Cp*₂TiCH₂C(CH₃)₃ (2.211 and 2.231 Å respectively), both relatively electronically saturated relative to 1.34, and slightly longer than that in [PhC(NSiMe₃)₂]₂TiMe (2.120(5) Å), but not significantly so. The Ti-C bond lengths in

(55) References begin on page 81
the related Ti(III) amide complexes \([\text{Ti(N-\text{-i-Pr})_2(\text{Ph})_2][\text{Li(TMEDA)}_2]}\) (2.173(5) and 2.210(5) Å) and \([\text{Ti(N[SiMe_3]_2)(CH_2Ph)_2][\text{Li(TMEDA)}_2]}\) (2.18(1) Å) are also similar.

(iv) **Interconversion of 1.34 and 1.10**

Complex 1.34 is readily oxidized by one electron as demonstrated by its reaction with iodine in benzene solution. The reaction mixture rapidly changes from deep dark green to dark orange-red, and iodide \(\text{Ti(N[R]Ar)_2(CH[SiMe_3]_2)(I)}\) (1.35) is isolated in 68% yield. The methyne proton on the alkyl group exhibits a proton NMR resonance at 3.47 ppm while the aryl methyl resonance appears at 2.18 ppm. Complex 1.34 also reacts rapidly with chlorinated organic solvents, presumably making the chloride homologue of 1.35. Complex 1.35 is also prepared by direct alkylation of 1.10 with \(\text{LiCH(SiMe_3)_2}\), although the reaction is exceedingly slow and occurs with some decomposition. Reduction of iodide 1.35 with sodium amalgam in benzene regenerates the titanium (III) complex 1.34 as determined by \(^2\text{H}\) NMR spectroscopy.

**Section 1.9: Reaction Chemistry of 1.34**

The potential for one-electron chemistry with alkyl 1.34 is large, as demonstrated in the previous section, and there is substantial related one-electron chemistry of low valent titanium.\(^{18,22,39,77}\) The sterically shielded metal-carbon bond is also expected to be reactive, especially since the titanium(III) complexes with the more typical bulky alkyl groups \(\text{CH}_2\text{SiMe}_3\) and \(\text{CH}_2\text{CMe}_2\text{Ph}\) are not isolable. Complex 1.35 should therefore react with a wide variety of unsaturated substrates, demonstrating one, two and even three electron chemistry.

(i) **Benzonitrile**

When 1.34 is treated with one equivalent of benzonitrile, the solution becomes dark blue. The complex thus formed is believed to be a nitrile adduct,
Ti(N[R]Ar)_2(CH[SiMe_3]_2)(NCPh) (1.36), and has a ^2H NMR resonance at 4.67 ppm. This resonance gradually disappears over an 18 hour period while an orange precipitate forms. The solid is collected in 82% yield (Scheme 1.8). The orange powder is essentially insoluble in pentane or ether, and is purified by recrystallization from hot THF.

The resonance of the methyne proton on the alkyl group appears at 1.44 ppm in the ^1H NMR, and the aryl methyl resonance is at 2.16 ppm. The ^1H NMR spectrum of the product has a one to one ratio of alkyl to nitrile resonances, and the solubility properties suggest a dimeric formulation: [Ti(N[R]Ar)_2(CH[SiMe_3]_2)(NCPh)]_2 (1.37). Low-valent titanium complexes are known to mediate both nitrile and ketone coupling reactions.\textsuperscript{18,22,41}

(ii) Trimethylsilylazide

Organoazides react with suitable substrates to make imido ligands, delivering the R-N fragment to the metal with subsequent loss of N\textsubscript{2}.\textsuperscript{45,82-84} These reagents sometimes donate nitrogen atoms to especially reactive metal complexes.\textsuperscript{47} Delivery of a nitrogen atom to 1.35 should result in alkyl group migration to form the Ti(IV) imide complex Ti(N[R]Ar)_2(NCH[SiMe_3]_2) by formal insertion of the nitrogen atom into the metal carbon bond. However, the reaction of Me_2SiN_3 with the alkyl complex results in significant decomposition with the formation of multiple intractable products, even when starting the reaction at temperatures below -100 °C.
Scheme 1.8: Reaction Chemistry of Ti(N[R]Ar)$_2$(CH[SiMe$_3$]$_2$)
In an attempt to temper the reactivity of 1.35 with azide reagents, the three-coordinate titanium center is masked by the addition of several equivalents of tert-butylnitrile. This results in a lightening of the reaction solution to very pale green, but no subsequent reaction occurs. The adduct is formulated analogously to 1.36, but Ti(N[R]Ar)₂(CH[SiMe₃]₂)(NCCMe₃) (1.38) has not been isolated in pure form as the nitrile ligand is labile. When Me₃SiN₃ is added to the adduct at -35 °C, the solution gradually changes to an orange-yellow color over about two hours. A light orange powder is obtained in 37% yield by recrystallization from pentane. Proton NMR spectroscopy suggests that the product is formed high yield, but it is very soluble in organic solvents. NMR evidence is consistent with the desired imide complex, with the methyne proton resonance appearing at 2.50 ppm and the aryl methyl resonance appearing at 2.21 ppm in the ¹H NMR spectrum. However, the complex exhibits a strong IR stretch at 2107 cm⁻¹, indicative of an azido functionality. Elemental analysis data are consistent with the formulation of the product as the terminal azide Ti(N[R]Ar)₂(CH[SiMe₃]₂)(N₃) (1.39). It has not yet been possible to convert azide 1.39 to the desired alkyl imide complex either through thermolysis or photolysis; these conditions instead lead to considerable decomposition.

Section 1.10: Conclusion

In general, the synthetic goals outlined at the beginning of this chapter have been met. A heteroleptic titanium(III) alkyl complex stabilized with amide ligands containing a deuterium spectroscopic handle has been synthesized, and its initial reactivity has been presented. However, in order to stabilize the alkyl complex enough to allow for its isolation and characterization, the unique alkyl group CH(SiMe₃)₂ must be used. This alkyl is large, preventing dimerization and disproportionation, but limits the approach of reagents to the titanium center. Also, the inductive electron withdrawing effect of two
silicon substituents on the α-carbon may significantly reduce the Ti-C bond reactivity. As a result of these limitations, the reactivity of 1.35 is essentially identical to Ti(silo)₃ or the more recently prepared Ti(N[R]Ar)₃. More work needs to be done in this area to develop the three-electron chemistry initially envisioned for such complexes.

A large number of new organometallic complexes of both Ti(III) and Ti(IV) with N-tert-alkyl anilide ligation have been prepared, such as the alkyls prepared from Ti(N[R]Ar)₂(I)₂ (1.10) and Ti(N[R]ArF)₂(NMe₂)(I) (1.14) as well as the chiral-at-metal C-, N-, O-, and I- ligated species 1.20, 1.21 and 1.27. The steric requirements for titanium(III) alkyl complexes have been explored through the synthesis of these derivatives, showing that too little steric protection leads to decomposition, while too much leads to cyclometallation.

Additionally, the use of dimethylamide groups as protecting groups, or coordination site place holders, has proven to be an incredibly useful synthetic technique for the selective delivery of ancillary ligands to a titanium center. The dimethylamide is readily removed with methyl iodide, leaving a halide for further chemical modification. This protocol allows for the synthesis of molecular species, for example, Ti(N[R]Ar)₂(I)₂ (1.10), which cannot be accessed in synthetically useful amounts through normal means. The extensive use of this transformation demonstrates an attractive feature of the N[R]Ar ligand set: electronic tunability. This is seen in the substituent effects on the degree of completion of dimethylamide group replacement in the reactions of 1.9, 1.13, 1.15, 1.18, and 1.23 with methyl iodide. From these reactions, the relative electron donating ability of the ligand set is determined to decrease in the order Ti(N[R]Ar)₂ ≈ Ti(N[R]Ar)(OAr') > Ti(N[Rₘₙ]Ar)(OAr") > Ti(N[R]ArF)₂, as measured by electrophilicity at titanium.

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Section 1.11: Experimental

1.11.1 General Considerations

Unless otherwise stated, all operations were performed in a Vacuum Atmospheres dry box under an atmosphere of purified nitrogen, or using standard Schlenk techniques. Anhydrous diethyl ether, tetrahydrofuran, and toluene were purchased from Mallinckrodt; 1,2-dimethoxyethane was obtained from Fisher Scientific; benzene was purchased from J. T. Baker; n-pentane and n-hexane were purchased from EM Science. The ethereal solvents (diethyl ether, tetrahydrofuran, 1,2-dimethoxyethane) were distilled, under nitrogen, from purple sodium benzophenone ketyl. The aliphatic hydrocarbons and benzene were distilled, under nitrogen, from very dark blue to purple sodium benzophenone ketyl solubilized with a small quantity of tetrugyme. Toluene was refluxed over molten sodium for at least two days, then distilled under nitrogen. Chloroform was refluxed over potassium carbonate for at least two days before being distilled under nitrogen. Distilled solvents were transferred under vacuum into bombs before being pumped into a Vacuum Atmospheres dry box. Benzene-$d_6$ was degassed and dried over blue sodium benzophenone ketyl and transferred under vacuum into a storage vessel. Chloroform-$d$ was degassed and dried over 4 Å sieves. Tetramethylethlenediamine (TMEDA), methyl iodide and trimethylacetonitrile were degassed and distilled from calcium hydride. 2,6-di-iso-propylphenol was degassed and distilled. 2,6-di-tert-butylphenol was crystallized from diethyl ether. 4 Å sieves and alumina were dried in vacuo overnight at a temperature above 150 °C. ArF$_2$N=C(CD$_3$)$_2$ (1.4),$^{54}$ HN[R]ArF (1.5),$^{54}$ Et$_2$O-LiN[R]ArF (1.6),$^{54}$ TiCl$_3$(THF)$_3$, $^{66}$ TiCl(NMe$_2$)$_3$, $^{67}$ Ti(Cl)$_2$(NMe$_2$)$_2$, $^{67}$ and LiCH(SiMe$_3$)$_2$$^{85}$ were prepared by standard procedures. Other chemicals were used as received. Magnetic susceptibilities were measured by NMR techniques.$^{75}$ $^1$H and $^{13}$C NMR spectra were recorded on Varian XL-300, Varian Unity-300 or Brucker AC-250 spectrometers. Chemical shifts are reported with respect to internal solvent (7.15 ppm and 128.0 ppm).

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2H chemical shifts are reported with respect to external C6D6. Infrared measurements were carried out on a Bio-Rad FTS-135 spectrometer. UV-vis spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer. EPR spectra were recorded on a Brucker ESP-300 spectrometer in sealed quartz tubes in toluene at either ambient temperature or low temperature by using a liquid nitrogen cooled nitrogen stream. Spectra were simulated using the program EPR-NMR. CHN analyses were performed by Oneida Research Services. Melting points were obtained in sealed glass capillaries and are uncorrected.

1.11.2 SQUID Magnetic Measurements

Measurements were made using a Quantum Design SQUID magnetometer. The magnetometer uses the MPMSR2 software (Magnetic Property Measurement System Revision 2). Data were recorded at a field strength of 5000 G. Gel caps (Gelatin Capsule #4 Clear) and straws were ordered from Quantum Design, Inc. Samples of 1.34 for magnetic measurements were placed into a gel cap and Parafilm was inserted above it to keep it in place. The loaded gel cap was mounted in a straw, and the straw was placed in an airtight vessel for transport to the magnetometer. After inserting the sample, the field and temperature were adjusted to 5000 G and 5 K, respectively. Once the temperature had equilibrated and the field was stable, the sample was centered. This was done by running a full length DC scan, adjusting the position automatically, and then recentering using a DC centering scan. During the run, measurements were taken over the following temperature ranges with the indicated increments: 5-10 K (one data point every 1 K), 12-20 K (one data point every 2 K), 23-50 (one data point every 3 K), 55-100 (one data point every 5 K), 110-200 (one data point every 10 K), 220-300 (one data point every 20 K). The run required approximately 5 h.

The data for 1.34 fit the Curie-Weiss law in the temperature range 5-300 K (R = 0.99999). The calculated curve (Figure 1.4) is the best least-squares fit of the observed
susceptibility data to the equation $\chi_M(\text{obs}) = ((\mu^2)/(7.997584 \times (T-\theta)))-C$. The value of $\mu$ obtained in this manner was 1.66 $\mu_B$, to be compared with the spin-only value for one unpaired electron, 1.73 $\mu_B$. In the least-squares fit, carried out using the General curve-fitting routine included with the program Kaleidagraph, both $\theta$ and $C$ were treated as variable parameters. The obtained value of $\theta$, the Weiss constant, was $-0.195$ K. The value of the constant $C$, included to represent the sum of all temperature-independent contributions to the total observed susceptibility, including the diamagnetic correction and t.i.p., was $-2.41 \times 10^{-4}$.

1.11.3 Synthesis of Complexes

(i) ArN=C(CD$_3$)$_2$ (1.1)$^{44}$ By the method of Eaton,$^{63}$ freshly distilled 3,5-dimethylaniline (48.24 g, 398.1 mmol), 4 Å molecular sieves (dried under vacuum at $>140$ °C overnight, 90 g), and acetone-$d_6$ (200 mL, 2.72 mol) were added to a 500 mL round bottom flask and placed under a partial vacuum at 4 °C for 4 days with occasional stirring. The molecular sieves were removed by filtration of the reaction mixture through a sintered glass frit, and the excess acetone-$d_6$ was removed by vacuum transfer leaving the desired imine as a pale yellow oil. More imine was obtained by immersing the sieves in pentane (100 mL) overnight followed by filtration and removal of solvent under vacuum. Yield: 64.60 g (97%). $^1$H NMR (300 MHz, C$_6$D$_6$): $\delta$ = 6.60 (s, 1H, para); 6.44 (s, 2H, ortho); 2.15 (s, 6H, aryl CH$_3$). $^{13}$C NMR (75 MHz, C$_6$D$_6$): $\delta$ = 166.66 (C(CD$_3$)$_2$); 152.65 (ipso); 138.41 (meta); 124.72 (aryl); 117.51 (aryl); 27.60 (CD$_3$); 21.37 (aryl CH$_3$); 19.40 (CD$_3$). High resolution mass spec. Calcd. mass (167.158), measured mass (167.158).
(ii) **HN[R]Ar (1.2)**: A solution of MeLi (1.4 M in diethyl ether, 300 mL, 420 mmol) in a 500 mL Erlenmeyer flask was frozen solid in a liquid nitrogen filled cold well and allowed to thaw until magnetic stirring was just possible. A solution of ArN=C(CD₃)₂ (1.1, 26.00 g, 155.7 mmol) in diethyl ether (ca. 20 mL) at -35 °C was added via pipet over 10 minutes. The reaction mixture was allowed to stir for 18 hours, at which point it was quenched by removing the flask from the glove box to a fume hood, and carefully pouring the reaction mixture onto ice (500 mL) in a 1 L Erlenmeyer flask. The mixture was extracted with hexanes (2 x 150 mL) and flushed through a column of oven dried alumina (2 x 25 cm). The column was washed with hexanes to give a total volume of 950 mL. The solvent was removed under vacuum resulting in a canary yellow oil. This oil was shown (by ¹H NMR spectroscopy) to be a 1:1 mixture of ArN=C(CD₃)(CD₂H) and the desired product. Water (200 mL) was added to the oil, and with vigorous stirring, concentrated HCl (25 mL) was added via pipet over a 10 minute period. A large quantity of a white flocculent precipitate formed. Stirring was continued for 3 hours, at which point the pH of the solution was brought to 12-14 with a concentrated NaOH solution (~ 5 M). The mixture was extracted with hexanes (2 x 200 mL) and flushed through a column of oven dried alumina (2 x 25 cm). Additional hexanes were used to wash the column to give a total volume of 800 mL. The solvent was removed in vacuo leaving a yellow oil. The oil was used as prepared, or distilled (45 °C, ~10⁻¹ torr). Yield 15.54 g (55%). M.p. ~30 °C. ¹H NMR (300 MHz, C₆D₆): δ = 6.43 (s, 1H, para); 6.33 (s, 2H, ortho); 3.06 (s, 1H, NH); 2.18 (s, 6H, aryl CH₃); 1.16 (s, 3H, C(CD₃)₂CH₃). ¹³C NMR (75 MHz, C₆D₆): δ = 147.53 (s, ipso); 138.19 (q, meta); 120.62 (d, aryl); 115.96 (d, aryl); 50.74 (s, C(CD₃)₂CH₃); 30.08 (q, C(CD₃)₂CH₃); 29.56 (m, C(CD₃)₂CH₃); 21.70 (q, aryl CH₃). MS (70 eV): m/z(%) = 183.2(37)[M⁺]. High resolution mass spec. Calcd. mass (183.189), measured mass (183.189). Anal. Calcd. for C₁₂H₁₃D₆N: C, 78.62; H, 10.45; N, 7.64. Found: C, 78.12; H, 10.77; N, 7.16.
(iii) $\text{Et}_2\text{O} \cdot \text{LiN}[\text{R}]\text{Ar}$ (1.3): A solution of HN(R)Ar (1.2, 13.5 g, 73.7 mmol) in pentane (100 mL) was frozen solid in a liquid nitrogen filled cold well and allowed to thaw until magnetic stirring was just possible. A solution of $n$-BuLi (49 mL, 1.6 M in hexane, 78 mmol) was slowly added via pipet over a 10 minute period. The reaction mixture was stirred for 5 hours, at which point the volume was reduced to 60 mL and diethyl ether (8.30 g, 112 mmol, 1.6 eq.) was added, forming a white precipitate. The volume was further reduced to 30 mL, and the product was collected by filtration and dried under vacuum. Yield 13.0 g (96%). $^1\text{H}$ NMR (300 MHz, C$_6$D$_6$): $\delta = 6.54$ (s, 2H, ortho); 6.13 (s, 1H, para); 3.17 (q, 4H, OCH$_2$CH$_3$); 2.30 (s, 6H, aryl CH$_3$); 1.60 (s, 3H, C(CD$_3$)$_2$CH$_3$); 0.95 (t, 6H, OCH$_2$CH$_3$). $^{13}$C NMR (75 MHz, C$_6$D$_6$): $\delta = 159.48$ (ipso); 138.24 (meta); 116.42 (aryl); 113.47 (aryl); 65.34 (OCH$_2$CH$_3$); 52.13 (C(CD$_3$)$_2$CH$_3$); 31.72 (C(CD$_3$)$_2$CH$_3$); 31.00 (C(CD$_3$)$_2$CH$_3$); 22.14 (aryl CH$_3$); 14.87 (OCH$_2$CH$_3$).

(iv) HN[R$_{ph}$]Ar (1.7): Phenyl lithium (145 mL of a 1.8 M solution in cyclohexane/ether, 261 mmol) was frozen solid in a liquid nitrogen cooled cold well and allowed to thaw. Just as the solution began stirring, (CD$_3$)$_2$C=NAr (1.1, 15.4 g, 92.2 mmol) in Et$_2$O (20 mL) at -35 °C was added. The reaction mixture was stirred for 23 hours and then slowly poured over ice (~300 mL) in a 1 L Erlenmeyer flask. The organic layer was separated and the aqueous layer was extracted with petroleum ether (~200 mL). The organics were run through a column of alumina (2 x 25 cm) and the solvent was removed in vacuo leaving a thick brown oil (1, 16.75 g, 68.3 mmol, 74%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.50$ (d, 2H); 7.32 (t, 2H); 7.20 (m, 1H); 6.25 (s, 1H, para); 5.98 (s, 2H, orthos); 3.92 (s, 1H, NH); 2.10 (s, 6H, ArCH$_3$).

(v) $\text{Et}_2\text{O} \cdot \text{LiN}[\text{R}_{ph}]\text{Ar}$ (1.8): HN[R$_{ph}$]Ar (1.7, 16.75 g, 68.25 mmol) was dissolved in pentane (60 mL) and chilled to -35 °C. n-Butyllithium (47 mL of a 1.6 M solution in hexanes, 75.7 mmol) was added via pipet as the solution was stirred. A thick brown oil
precipitated 20 minutes after the addition. Addition of Et₂O (5.50 g, 74.3 mmol) caused the formation of a white precipitate which was collected on a frit (2, 9.24 g, 28.45 mmol, 42%). ¹H NMR (300 MHz, C₆D₆): δ = 7.6 (br s, 2H); 7.15 (br s, 2H); 7.05 (s, 1H); 6.38 (br s, 2H); 5.95 (br s, 1H); 3.10 (q, 4H, O(CH₂CH₃)₂); 2.05 (br s, 6H, ArCH₃); 0.94 (t, 6H, O(CH₂CH₃)₂).

(vi) Ti(N[R]Ar)₂I₂ (1.10): Ti(NMe₂)₂Cl₂ (0.40 g, 1.96 mmol) was slurried in ether (10 mL) and cooled to -35 °C. Et₂O·LiN[R]Ar (1.3, 1.02 g, 3.88 mmol) was added all at once to the stirred solution, which immediately became a mustard yellow color. The reaction mixture was stirred overnight and then filtered to remove LiCl, leaving Ti(N[R]Ar)₂(NMe₂)₂ (1.9). Methyl iodide (6.78 g, 24 eq) was added to the dark yellow solution, and a white precipitate (Me₄NI) formed immediately. After 43 hours, solvent and excess methyl iodide were removed in vacuo. The solid was extracted with pentane (10 mL) and the solution was filtered. The [NMe₄]I was washed with an additional 10 mL portion of pentane, and the combined pentane extractions were stored at -35 °C for 24 hours yielding a dark brown/black crystalline solid. The remaining solution was reduced in volume to ca. 2 mL and stored at -35 °C overnight yielding more dark solid (0.88 g, 1.17 mmol, 60%). M.p. 114-6 °C; ¹H NMR (250 MHz, C₆D₆): δ 7.07 (s, 4H, ortho); 6.86 (s, 2H, para); 2.11 (s, 12H, ArCH₃); 1.39 (s, 6H, C(CD₃)₂CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 138.693, 134.076, 132.132, 130.903, 67.555, 29.880, 29.5, 21.344; MS (70 eV): m/z(%): 666.2 (5.19). Anal. Calcd for C₂₄H₂₄D₁₂N₂I₂Ti: C, 43.26; H, 5.45; N, 4.20. Found: C, 43.24; H, 5.60; N, 4.13.

(vii) Ti(N[R]Ar)₂(I)(CH₂SiMe₃) (1.11): Ti(N[R]Ar)₂I₂ (1.10, 0.3000 g, 0.4504 mmol) was dissolved in ether (15 mL) and frozen. Upon thawing, a solution of LiCH₂SiMe₃ (0.0424 g, 0.4504 mmol) in ether (5 mL) was added dropwise. The solution gradually changed to a light brown red color with a white precipitate. After stirring for one
hour, the solvent was removed in vacuo and the residue was extracted with pentane. The solution was filtered and reduced in volume to a dark red brown oil (0.29 g) which was ~95 % pure by $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 7.00$ (s, 2H, para); 6.832 (s, 4H, ortho); 2.340 (s, 12 H, ArCH$_3$); 1.736 (s, 2H, CH$_2$); 1.307 (s, 6H, CCH$_3$(CD$_3$)$_2$); -0.134 (s, 9H, SiMe$_3$). Reduction in benzene gave no observable paramagnetic products although NaI was observed. Reduction in THF caused the formation of a vivid olive green solution which turned brown during the workup (< 50 minutes). $^1$H NMR of the isolated material showed at least 5 products.

(viii) Ti(N[R]Ar)$_2$(I)(nph) (1.12): Ti(N[R]Ar)$_2$I$_2$ (1.10, 0.4995 g, 0.7498 mmol) was dissolved in pentane (30 mL) and cooled to -30 °C. Neophyl lithium (0.1055 g, 0.7528 mmol) was added as a solid. The solution changed to a red-brown color with a white precipitate in five minutes. After stirring for one hour, the solution was filtered and reduced in volume to a dark red oil (0.40 g) which was ~90 % pure by $^1$H NMR (250 MHz, CDC$_3$): $\delta = 7.17$ (m, 5H, aryl); 7.149 (s, 4H, ortho); 7.107 (s, 2H, para); 2.3 (s, 2H, CH$_2$); 2.253 (s, 12H, ArCH$_3$); 1.455 (s, 6H, CH$_2$C(CH$_3$)$_2$Ph); 1.334 (s, 6H, CCH$_3$(CD$_3$)$_2$). Reduction with sodium amalgam in benzene gave no observable paramagnetic products although NaI was observed.

(ix) Ti(N[R]ArF)$_2$(NMe$_2$)$_2$ (1.13): A solution of Et$_2$O·LiN[R]ArF (3.00 g, 11.24 mmol) in ether (20 mL) at -30 °C was added to a stirring slurry of Ti(NMe$_2$)$_2$Cl$_2$ (1.16 g, 5.61 mmol) in ether (40 mL) at -30 °C. The solution changed from brown-red to yellow with a large amount of white precipitate. The reaction was stirred for 14 hours at 30 °C. Lithium chloride was removed by filtration through glass fibers to €e a dark yellow solution, which was evaporated in vacuo and reconstituted in pentane (15 mL). Very large yellow-orange crystals were collected in two crops (2.20 g, 4.33 mmol, 77.2%). M.p. 127-129 °C. $^1$H NMR (300 MHz, C$_6$D$_6$): $\delta = 6.98$ (d, 1H, aryl); 6.90 (dd, 1H, aryl);
6.65 (m, 1H, aryl); 3.075 (br s, 6H, NMe₂); 2.220 (s, 3H, ArMe); 1.068 (s, 3H, C(CD₃)₂CH₃). ¹³C NMR (75 MHz, CDCl₃): δ = 158.252 (d, J_CF = 239 Hz, C₁); 138.297 (d, ²J_CF = 12.9 Hz, C₂); 134.16 (d, J_CH = 159 Hz, C₆ or C₄); 131.640 (s, C₅); 125.343 (d, J_CH = 158.9, C₄ or C₆); 114.902 (dd, J_CF = 23.4 Hz, J_CH = 160.1 Hz, C₃); 60.796 (s, NC(CD₃)₂CH₃); 45.146 (q, J = 131 Hz, NMe₂); 29.797 (q, J = 125.1 Hz, NC(CD₃)₂CH₃); 29.3 (m, CD₃); 20.855 (q, J = 126.3, ArMe). Anal. Calcd. for C₂₆H₃₀D₁₂N₄F₂Ti: C, 61.40; H, 8.32; N, 11.02. Found C, 61.76; H, 8.73; N, 11.06.

(x) Ti(N[R]ArF)₂(I)(NMe₂) (1.14): To a stirring yellow solution of Ti(N[R]ArF)₂(NMe₂)₂ (1.13, 1.91 g, 3.76 mmol) in THF (40 mL) was added MeI (5.63 g, 39.6 mmol). The reaction mixture slowly changed to a bright cherry red over 18 hours. ¹H NMR spectroscopy was used to determine the extent of reaction by monitoring the disappearance of the dimethylamido peak at 3.075 ppm. The THF was removed in vacuo, and the red solid remaining was reconstituted in ether (10 mL). [NMe₄]I was removed by filtration through glass fibers, and the red solution was concentrated to a minimum amount. Two crops of crystals were collected (1.58 g, 2.67 mmol, 71%). M.p. 115-118 °C. ¹H NMR (300 MHz, C₆D₆): δ = 6.933 (m, 1H, aryl); 6.830 (dd, 1H, aryl); 6.637 (m, 1H, aryl); 3.057 (s, 6H, NMe₂); 2.057 (s, 6H, ArMe); 1.392 (s, 6H, C(CD₃)₂CH₃). ¹³C NMR (75 MHz, C₆D₆): δ = 132.59 (s, para); 115.93 (d, ²J_CF = 23.2 Hz, ipso); ortho and metas broadened into baseline; 63.62 (s, NC(CD₃)₂CH₃); 49.00 (s, NMe₂); 30.106 (s, C(CD₃)₂CH₃); 29.589 (m, C(CD₃)₂CH₃); 20.652 (s, ArMe). Anal. Calcd. for C₂₄H₂₄D₁₂F₂N₃Ti: C, 48.74; H, 6.14; N, 7.10. Found: C, 48.98; H, 6.44; N, 6.98.

(xi) Ti(N[R]ArF)₂(CH₂SiMe₃)(NMe₂) (1.15): Ti(N[R]ArF)₂(I)NMe₂ (1.14, 0.5011 g, 0.8473 mmol) was dissolved in pentane (25 mL) and cooled to -30 °C. LiCH₂SiMe₃ (0.85 mL, 1 M in pentane, 0.85 mmol) was added dropwise to the stirring solution. Precipitation of LiI with a concomitant color change to yellow orange occurred.
over three hours. LiI was removed with a medium frit, and the resulting dark yellow oil was lyophilized from benzene (4 mL) leaving a solid which was recrystallized from pentane (2 mL). Mustard yellow sheets were collected in two crops (0.33 g, 0.60 mmol, 70%). M.p. 68-71 °C. \(^1\)H NMR (250 MHz, C\(_6\)D\(_6\)): \(\delta = 6.92\) (m, 1H, aryl); 6.87 (d, 1H, aryl); 6.65 (m, 1H, aryl); 3.08 (s, 6H, NMe\(_2\)); 2.12 (s, 6H, ArMe); 1.31 (s, 6H,C(CD\(_3\))\(_2\)CH\(_3\)); 1.19 (s, 2H, CH\(_2\)SiMe\(_3\)); 0.11 (s, 9H, Si(CH\(_3\))\(_3\)). \(^{13}\)C NMR (75 MHz, C\(_6\)D\(_6\)): \(\delta = 157.934\) (d, \(J_{CF} = 242.4\) Hz, C\(_2\)); 135.863 (s, aryl); 134.098 (s, aryl); 132.502 (s, aryl); 127.214 (s, aryl); 115.894 (s, aryl); 61.587 (s, C(CD\(_3\))\(_2\)CH\(_3\) or CH\(_2\)SiMe\(_3\)); 61.521 (s, C(CD\(_3\))\(_2\)CH\(_3\) or CH\(_2\)SiMe\(_3\)); 46.563 (s, NMe\(_2\)); 30.262 (s, NC(CD\(_3\))\(_2\)CH\(_3\)); 29.75 (m, NC(CD\(_3\))\(_2\)CH\(_3\)); 20.769 (s, ArMe); 3.408 (s, SiMe\(_3\)). Anal. Calcd. for C\(_{28}\)H\(_{35}\)D\(_12\)N\(_3\)F\(_2\)SiTi: C, 60.95; H, 8.59; N, 7.62. Found: C, 61.18; H, 8.53; N, 7.37.

(xii) Ti(N[R]ArF\(_2\))\(_2\)(I)(CH\(_2\)SiMe\(_3\)) (1.16): Ti(N[R]ArF\(_2\))(NMe\(_2\))\(_2\)(CH\(_2\)SiMe\(_3\)) (1.15, 0.21 g, 0.38 mmol) was dissolved in THF (ca. 10 mL). MeI (1.08 g, 7.61 mmol, 30 eq.) was added and the solution was stirred for 22 hours. A white precipitate was observed and the solution changed from golden yellow to orange-red. The NMe\(_4\)I was removed by filtration, the solvent was removed in vacuo, and the resulting oil was triturated with hexane to give a thick orange oil (0.20 g, 0.32 mmol, 84%). \(^1\)H NMR (250 MHz, C\(_6\)D\(_6\)): \(\delta = 6.6-6.8\) (m, 6H, aryl); 2.11 (s, 6H, ArMe); 1.38 (br s, 8H, NC(CD\(_3\))\(_2\)CH\(_3\) and CH\(_2\)SiMe\(_3\)); 0.143 (s, CH\(_2\)Si(CH\(_3\))\(_3\)).

(xiii) Ti(N[R]Ar)(OAr\(_e\))(I\(_2\)) (1.19): TiCl(NMe\(_2\))\(_3\) (1.64 g, 7.63 mmol) was dissolved in Et\(_2\)O (40 mL) and chilled to -35 °C. Et\(_2\)O-LiN[R]Ar (1.3, 2.00 g, 7.60 mmol) was added as a solid causing a color change to greenish brown in about 30 seconds. After three hours, LiCl was removed by filtration and the solvent was removed in vacuo yielding a mobile dark brown oil (Ti(N[R]Ar)(NMe\(_2\))\(_3\), 1.17, 2.81 g) which was judged to be ~95% pure by \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 6.65\) (s, 1H, para); 6.58 (s, 2H,
ortho); 2.91 (s, 18H, NMe2); 2.28 (s, 6H, ArMe); 1.16 (s, 3H, C(\text{CD}_{3})_{2}CH_{3}). The oil was dissolved in fresh Et2O (5 mL). To it was added a solution of 2,6-diisopropylphenol (1.35 g, 7.58 mmol) in Et2O (5 mL). The resulting solution was stirred for 18 hours and then the solvent was removed in vacuo yielding a thick dark brown oil (Ti(N[R]Ar)(OAr')(NMe2))2, 1.18, 4.29 g) which was judged to be ~95% pure by 1H NMR (250 MHz, CDCl3): δ = 7.02 (d, 2H, OAr' meta); 6.8 (t, 1H, OAr' para); 6.68 (s, 1H, para); 6.59 (s, 2H, ortho); 3.45 (sep, 2H, CH(CH3)2); 3.04 (s, 12H, NMe2); 2.25 (s, 6H, ArMe); 1.19 (m, 15H, NC(\text{CD}_{3})_{2}CH_{3} and CH(CH3)2). The oil was dissolved in THF (50 mL) at 30 °C. MeI (10.70 g, 75.4 mmol) was added and the reaction mixture was stirred for nine hours. The reaction mixture gradually turned from dark brown to a blood red color. THF was removed in vacuo, and the resulting solids were triturated three times with hexane. [NMe4]I was removed by filtration, solvent was removed in vacuo, and the resulting solid was recrystallized from ether to give bright red/purple faceted crystals. Second and third crops were collected from pentane as dark red crystals (3.28 g, 4.96 mmol, 65%). M.p. 130-134 °C. 1H NMR (300 MHz, CDCl3): δ = 7.21 (br s, 1H, aryl); 7.09 (br s, 2H, aryl); 7.08 (s, 2H, aryl); 7.07 (s, 1H, aryl); 3.66 (m, 2H, CH(CH3)2); 2.38 (s, 6H, ArMe); 1.33 (s, 3H, C(\text{CD}_{3})_{2}CH_{3}); 1.27 (d, 12H, CH(CH3)2).

13C NMR (75 MHz, CDCl3): δ = 165.329 (s), 139.185 (s), 138.366 (d), 133.330 (d), 132.004 (d), 131.943 (s), 124.037 (d), 123.194 (d), 69.877 (s, C(\text{CD}_{3})_{2}CH_{3}); 29.375 (q, C(\text{CD}_{3})_{2}CH_{3}); 28.9 (m, C(\text{CD}_{3})_{2}CH_{3}); 27.1925 (d, CH(CH3)2); 23.8621 (q, CH(CH3)2); 21.2091 (q, ArMe). Anal. Calcd. for C24H29D6NOI2Ti: C, 43.59; H, 5.33; N, 2.12. Found: C, 43.98; H, 5.47; N, 1.92.

(xiv) Ti(N[R]Ar)(OAr')(CH2SiMe3)(I) (1.20): To a stirring solution of Ti(N[R]Ar)(OAr')I2 (1.19, 0.3004 g, 0.4545 mmol) in hexane (10 mL) at -35 °C was added LiCH2SiMe3 (0.0428 g, 0.4546 mmol) in hexane (5 mL). The solution rapidly turned orange with the formation of a white precipitate. The reaction was stirred for 20
minutes, filtered, and concentrated to a minimum volume. Tiny micro crystals were obtained in low yield, though the reaction appeared quantitative by NMR. \(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta = 7.1\) (m, 6H, aryls); 3.72 (sep, 2H, CH(CH\(_3\))\(_2\)); 2.39 (s, 6H, ArMe); 2.24 (d, 1H, CH\(_{Ha HB SiMe_3}\)); 1.38 (d, 6H, CH(CH\(_3\))\(_2\)); 1.22 (m, 7H, CH(CH\(_2\))\(_2\) and CH\(_{Ha HB SiMe_3}\)); 1.10 (s, 3H, C(CD\(_3\))\(_2\)CH\(_3\)); -0.09 (s, 9H, SiMe\(_3\)).

(xv) Ti(\(N[R]Ar\))(OAr')\((CH_2CMe_2Ph)\)(I) (1.21): Ti(\(N[R]Ar\))(OAr')I\(_2\) (1.19, 1.04 g, 1.57 mmol) was dissolved in hexane (25 mL) and chilled to -30 \(^\circ\)C. Neophyllithium (0.2205 g, 1.573 mmol) was added, causing an immediate color change to a light red brown. After 15 minutes of stirring, LiI was removed as a gray solid with a frit. The mother liquor was pumped to dryness in vacuo, leaving a thick orange-red oil. The oil was lyophilized from benzene and crystallized from pentane to give red orange waxy crystals (0.5161 g, 49.3%). M.p. 75-77 \(^\circ\)C. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.3\) (br s, 1H, ortho); 7.05 (m, 9H, aryl); 6.7 (br s, 1H, ortho); 3.82 (sep, 2H, CH(CH\(_3\))\(_2\)); 2.41 (br s, 6H, ArMe); 2.35 (d, 1H, CH\(_{Ha HB C(CH_3)_2Ph}\)); 2.07 (d, 1H, CH\(_{Ha HB C(CH_3)_2Ph}\)); 1.36 (d, 6H, CH(CH\(_3\))\(_2\)-a); 1.32 (s, 3H, CH\(_{Ha HB C(CH_3)_2Ph}\)); 1.24 (s, 3H, CH\(_{Ha HB C(CH_3)_2Ph}\)); 1.09 (s, 3H, C(CD\(_3\))\(_2\)CH\(_3\)); 1.21 (d, 6H, CH(CH\(_3\))\(_2\)-b).

(xvi) Ti(\(N[R_ph]Ar\))(NMe\(_2\))\(_3\) (1.22): TiCl(NMe\(_2\))\(_3\) (1.50 g, 6.97 mmol) was dissolved in THF (50 mL) and chilled to -35 \(^\circ\)C. Et\(_2\)O-Li[N(R\(_ph\)]Ar (2, 2.27 g, 6.98 mmol) was added as a powder. The solution changed from brown to a darker greenish brown. The reaction mixture was stirred for 12 hours, and the solvent was removed in vacuo. The mixture was reconstituted in pentane (~50 mL) and filtered through a frit, leaving a yellow brown solution which was evaporated to dryness, leaving a thin oil. Lyophilization twice from benzene to remove residual THF followed by recrystallization from pentane (8 mL) afforded a greenish brown powder (2.445 g, 5.76 mmol, 82.6%). M.p. 32.5-33.5 \(^\circ\)C. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.21\) (d, 2H); 7.06 (t, 2H); 6.95

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(t, 1H); 6.29 (s, 1H); 5.96 (s, 2H); 2.77 (s, 18H, NMe2); 1.88 (s, 6H, ArMe). 13C NMR (75 MHz, CDCl3): δ = 151.056, 148.716, 136.578, 127.64, 126.44, 125.48, 124.09, 123.57, 45.09, 30.64, 21.46. MS (70 eV): \( m/z (\%) \): 424(0.9)\( [M^+] \). Anal. Calcd. for C23H32D6N4Ti: C, 65.08; H, 9.02; N, 13.20. Found: C, 65.29; H, 9.02; N, 13.17.

(xvii) Ti(N[Rph]Ar)(OAr")(NMe2)2 (1.23): Ti(N[Rph]Ar)(NMe2)3 (1.22, 1.4274 g, 3.3622 mmol) was dissolved in Et2O (20 mL) and cooled to -35 °C in a round bottom flask. 2,6-Di-tert-butylphenol (0.6937 g, 3.362 mmol) was dissolved in Et2O (10 mL), cooled to -35 °C and then added to the solution. The greenish brown reaction mixture changed to a reddish orange color after three hours. 1H NMR spectroscopy at this point showed considerable starting material. After 19.5 hours of reaction, the solvent was removed in vacuo to give a bright cherry red foam. The foam was redissolved in pentane (about 3 mL), resulting in crystallization of the desired product as an orange powder at room temperature. A second crop of powder resulted upon cooling a concentrated solution for several days at -35 °C (1.626 g, 2.7766 mmol, 82.6%). M.p. 130-131 °C. 1H NMR (300 MHz, CDCl3): δ = 7.593 (d, 2H, J = 7.58 Hz); 7.3450 (t, 2H, J = 7.56 Hz); 7.25 (t, 3H, J = 7.8 Hz); 6.799 (t, 1H, J = 7.8 Hz); 6.5057 (s, 1H, para); 6.4372 (s, 2H, ortho); 3.0153 (s, 12H, NMe2); 1.9116 (s, 6H, ArMe); 1.4842 (s, 18H, C(CH3)3). 13C NMR (75 MHz, CDCl3): δ = 164.565 (s), 150.438 (s), 146.383 (s), 140.229 (s), 138.920 (s), 127.922 (d), 126.513 (d), 125.745 (d), 125.254 (d), 124.379 (d), 120.755 (d), 119.236 (d), 65.8920 (s, C(CD3)2C6H5), 47.9519 (q, NMe2), 35.4817 (s, C(CH3)3), 31.6 (m, CD3), 31.0918 (q, C(CH3)3), 21.5033 (q, ArMe). MS (70 eV): \( m/z (\%) \): 585(0.5)\( [M^+] \). Anal. Calcd. for C35H47D6N3OTi: C, 71.77; H, 9.12; N, 7.17. Found: C, 72.25; H, 8.94; N, 6.75.

(xviii) Ti(N[Rph]Ar)(OAr")(I)(NMe2) (1.24): Ti(N[Rph]Ar)(OAr")(NMe2)2 (1.23, 0.7363 g, 1.257 mmol) was dissolved in Et2O (45 mL) and cooled to -35 °C in a
round bottom flask. MeI (1.92 g, 13.5 mmol) was added, the flask was stoppered, and the reaction was stirred overnight. Monitoring by $^1$H NMR showed almost no conversion to product. It was thought that MeI was escaping from the stoppered flask. The reaction mixture was transferred to a glass reaction bomb, additional MeI was added and the reaction was stirred (and monitored by $^1$H NMR) for 48 hours. A large amount of white precipitate formed, but there was no noticeable color change. The solvent was then removed in vacuo, the product extracted with pentane, and [NMe$_4$I was removed by filtration through a medium frit. The solution was concentrated down to about 4 mL, when small microcrystals became apparent in the solution. Cooling overnight at -35 °C yielded a cake of orange microcrystalline powder (0.7952 g, 1.189 mmol, 94.6 %). M.p. 57-9 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.4$ (tm, $J = 5.4$ Hz, 2H); 7.331 (d, $J = 7.8$ Hz, 2H); 7.237 (dm, $J = 4.2$ Hz, 3H); 6.912 (t, $J = 7.8$ Hz, 1H); 6.850 (s, 1H, para); 6.408 (s, 2H, ortho); 2.859 (s, 6H, NMe$_2$); 2.180 (s, 6H, ArMe); 1.620 (s, 18H, C(CH$_3$)$_3$). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 165.424$, 144.226, 142.433, 138.998, 137.546, 129.049, 128.891, 127.820, 127.145, 126.979, 125.765, 120.894, 68.955 (C(CD$_3$)$_3$C$_6$H$_5$), 49.836 (NMe$_2$), 35.730 (C(CH$_3$)$_3$), 32.414 (C(CH$_3$)$_3$), 31.0 (CD$_3$), 21.101 (ArMe). MS (70 eV): m/z(%): 667.9 (0.19)[M$^+$. Anal. Calcd for C$_{33}$H$_{41}$D$_6$IN$_2$OTi: C, 59.29; H, 7.09; N, 4.19. Found: C, 58.98; H, 7.34; N, 3.88.

(xix) Ti(N[R$_{ph}$]Ar)(O-2,6-C$_6$H$_3$CMe$_3$)[CH$_2$CMe$_2$-])(I) (1.27): A solution of Ti(N[R$_{ph}$]Ar)(OAr")(I)(NMe$_2$) (1.24, 1.3206 g, 1.9752 mmol) in pentane (40 mL) was chilled to -40 °C. Neopentyllithium (0.1543 g, 1.9761 mmol) was added as a solution in ether. The reaction mixture changed from red to yellow over about five minutes. After the solution was stirred for 18 hours, the yellow brown solution was filtered to remove lithium iodide. Proton NMR spectroscopy showed a relatively clean conversion to the desired alkyl complex Ti(N[R$_{ph}$]Ar)(OAr")(CH$_2$CMe$_3$)(NMe$_2$) (1.25), but crystallization proved to be impossible. The ether was removed in vacuo and THF (40 mL) was added.
The mixture was heated at 65 °C for two hours. Proton NMR spectroscopy showed 50% conversion to the cyclometallated dimethylamide compound Ti(N[R\text{ph}]Ar)(O-2,6-C\text{6}H\text{3}[CMe\text{3}][CH\text{2}CMe\text{2}-])(NMe\text{2}) (1.26). Further heating at 65 °C gave a clean conversion. The THF was removed \textit{in vacuo} and ether (60 mL) and MeI (2.90 g, 20.4 mmol, 10.3 eq) were added. No reaction occurred at room temperature, so the mixture was heated to 70 °C for 21 hours. A precipitate was observed, but there was no color change. A proton NMR spectrum showed no starting dimethylamide peak. Solvent was removed \textit{in vacuo} leaving a solid, which was reconstituted in pentane. [NMe\text{4}]I was removed by filtration and the solution was concentrated to a minimum volume. Crystals were obtained after storage overnight at -35 °C (0.7668 g, 1.230 mmol, 62.3%). M.p. 102-103 °C. \textsuperscript{1}H NMR (300 MHz, CDCl\text{3}): \delta = 7.78 (d, J = 7.59 Hz, 2H); 7.393 (t, J = 7.04 Hz, 2H); 7.295 (t, J = 6.7 Hz, 1H); 7.174 (d, J = 7.71 Hz, 1H); 7.0235 (d, J = 7.71 Hz, 1H); 6.90 (s, 1H, para); 6.879 (t, J ~ 10 Hz, 1H); 6.708 (s, 2H, ortho); 2.202 (s, 6H, ArMe); 1.470 (d, J = 11.7 Hz, 1H, CH\text{2}-a); 1.320 (s, 9H, C(CH\text{3})\text{3}); 0.9836 (s, 6H, C(CH\text{3})\text{2}Ar); 0.833 (d, J = 11.7 Hz, CH\text{2}-b). \textsuperscript{13}C NMR (125 MHz, CDCl\text{3}): \delta = 162.818, 146.038, 143.338, 139.764, 139.345, 136.051, 130.326, 129.281, 127.914, 126.766, 124.759, 124.577, 122.270, 122.070, 65.842, 46.410, 35.304, 32.578, 32.046, 30.603, 28.2, 25.455, 21.202. 15.259. Anal. Calcd for C\text{31}H\text{34}D\text{6}INOTi: C, 59.72; H, 5.47; N, 2.25. Found: C, 60.19; H, 6.98; N, 1.92.

(xx) Ti(N[R\text{ph}]Ar)\textsubscript{2}(Cl)\textsubscript{2} (1.29): TiCl\textsubscript{3}(THF)\textsubscript{3} (1.00 g, 2.70 mmol) and TMEDA (1.94 g, 16.7 mmol) were added to THF (100 mL) to form a bright blue solution. Et\textsubscript{2}O-Li(N[R\text{ph}]Ar) (1.76 g, 5.41 mmol) was added causing the solution to become olive green. The solvent was removed \textit{in vacuo}, the solids were reconstituted in ether and filtered to remove LiCl. Yellow green crystals of Ti(N[R\text{ph}]Ar)\textsubscript{2}(\mu-Cl)\textsubscript{2}Li(TMEDA)\textsubscript{3} (1.28) were collected from a concentrated solution at -35 °C (2.28 g, 2.37 mmol, 87.7%). \textsuperscript{2}H NMR (46 MHz, C\text{6}H\text{6}): \delta(\Delta v\textsubscript{1/2}): 4.84(46.5). A large excess of chloroform (1.48 g)
was added to an olive green ether solution of the solid (0.17 g, 0.18 mmol). The solution turned blood red. Proton NMR spectroscopy showed three equivalents of TMEDA. The solvent was removed in vacuo and the product was extracted with benzene. The solution was filtered through glass fibers and evaporated to dryness yielding a dark red microcrystalline powder (0.10 g, 0.16 mmol, 91%). The red solid was recrystallized by vapor diffusion of pentane into toluene followed by cold storage overnight. M.p. 155-160 °C (dec). $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.45$ (d, 4H, phenyl ortho); 7.28 (m, 6H, phenyl meta, para); 6.56 (s, 2H, para); 5.62 (s, 4H, ortho); 1.93 (s, 12H, ArMe). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 147.700$, 143.119, 137.286, 128.699, 127.812, 126.841 (may be 2 carbons), 123.475, 71.2 (C(CD$_3$)$_2$Ar); 28.7 (CD$_3$); 21.094 (ArMe). Anal. Calcd. for C$_{34}$H$_{28}$D$_{12}$Cl$_2$N$_2$Ti: C, 67.22; H, 6.64; N, 4.61. Found: C, 67.00; H, 6.69; N, 4.28.

(xxi) Ti(N[R]Ar)$_2$(μ-Cl)$_2$Li(TMEDA) (1.30): Cl$_3$Ti(THF)$_3$ (1.00 g, 2.70 mmol) was slurried in THF (100 mL). TMEDA (1.92 g, 6.13 eq) was added, forming a blue solution. A solution of Et$_2$O-LiN[R]Ar (1.43 g, 5.44 mmol) was dissolved in THF (50 mL) and added, causing a rapid color change to bright green. After five minutes, the green color faded to olive. The THF was removed in vacuo and the resulting oil was triturated twice with pentane, extracted with pentane and filtered to remove LiCl. The solution was stored at -30 °C overnight, giving bright green needles (0.93 g, 56.9%). M.p. 137-138 °C. $^2$H NMR (46 MHz, C$_6$H$_6$): $\delta(\Delta v_{1/2}) = 3.809(18.5)$. $\mu_{\text{eff}}$ (300 MHz, C$_6$D$_6$, 25 °C) 2.219 μB. Uv-vis (hexane): $\lambda_{\text{max}}(\epsilon)$ 780 nm (188 M$^{-1}$cm$^{-1}$). EPR (298 K, toluene): $g = 1.95$. EPR (103 K, toluene): $g_1 = 1.980$, $g_2 = 1.964$, $g_3 = 1.930$; this spectrum is approximately axial with broad linewidths (~25 G) that merge $g_1$ and $g_2$ into one feature. Anal. Calcd for C$_{34}$H$_{40}$D$_{12}$Cl$_2$N$_2$LiTi: C, 59.40; H, 8.64; N, 9.24. Found: C, 58.97; H, 8.44; N, 8.46.

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(xxii) Ti(N[R]Ar)_2(Cl)_2 (1.31): A small amount of Ti(N[R]Ar)_2(μ-Cl)_2Li(TMEDA) (1.30) was added to CDCl₃, causing the solution to turn red. ¹H NMR (250 MHz, CDCl₃): δ = 6.877 (s, 2H, paras); 6.363 (s, 4H, orthos); 2.262 (s, 12H, ArMe); 1.263 (s, 6H, d₆-t-Bu); 2.389 (s, 4H, TMEDA methylene); 2.20 (s, 12H, TMEDA methyls).

(xxiii) Ti(N[R]Ar)_2(CH₂SiMe₃)₂ (1.32): To a solution of Ti(N[R]Ar)_2I₂ (1.10, 0.101 g, 0.152 mmol) in pentane was added a solution of LiCH₂SiMe₃ (0.0297 g, 0.315 mmol) to give a final volume of 10 mL. The solution immediately changed from dark brown to orange, and became yellow over the period of one hour. The solution was filtered and solvent was removed in vacuo to yield an orange/yellow semi-solid which was judged to be ~95% pure by ¹H NMR (0.0751 g, 0.128 mmol, 84%). ¹H NMR (300 MHz, C₆D₆): δ = 6.958 (s, 4H, ortho), 6.77 (s, 2H, para), 2.243 (s, 12H, ArMe), 1.595 (s, 4H, CH₂SiMe₃), 1.344 (s, 6H, CCH₃(CD₃)₂), 0.180 (s, 18H, SiMe₃). ¹³C NMR (75 MHz, CDCl₃): δ = 144.821 (s, ipso), 137.358 (q, ²J = 6.5 Hz, meta), 129.511 (d, J = 156.7 Hz, ortho), 127.577 (d, J = 142.1, para), 79.867 (t, J = 106.8 Hz, CH₂), 60.872 (s, CCH₃(CD₃)₂), 30.483 (q, J = 127.2 Hz, CCH₃(CD₃)₂), 29.992 (m, CCH₃(CD₃)₂), 21.285 (q, J = 125.8 Hz, ArMe), 2.474 (q, J = 117.9 Hz, SiMe₃).

(xxiv) Ti(N[R]Ar)_2(CH₂CMe₂Ph)₂ (1.33): To a solution of Ti(N[R]Ar)_2I₂ (1.10, 0.100 g, 0.150 mmol) in pentane was added a solution of LiCH₂CMe₂Ph (0.0425 g, 0.303 mmol) to give a final volume of 10 mL. The solution immediately turned from dark brown to yellow and changed to a brownish red color over one hour. The solution was filtered and solvent was removed in vacuo to yield a dark brown oil which was judged to be ~95% pure by proton NMR (0.0968 g, 0.1426 mmol, 95%). ¹H NMR (300 MHz, C₆D₆): δ = 7.24 (m, 6H, alkyl ortho/meta); 7.07 (m, 2H, alkyl para); 6.985 (s, 4H, ortho); 6.787 (s, 2H, para); 2.248 (s, 12H, ArMe); 1.839 (s, 4H, CH₂CMe₂Ph); 1.334 (s, 6H,
CCH$_3$(CD$_3$)$_2$; 1.266 (s, 12H, CH$_2$C(CH$_3$)$_2$Ph). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta =$ 153.211 (s, alkyl ipso); 146.700 (s, ipso); 137.502 (q, $^2J = 5.9$ Hz, meta); 129.947 (d, $J = 164.6$ Hz); 127.645 (d, $J = 161.1$ Hz); 127.567 (d, $J = 160$ Hz); 125.418 (d, $J = 157$ Hz); 124.696 (d, $J = 160.0$ Hz); 107.206 (t, $J = 110.3$ Hz, CH$_2$CMMe$_2$Ph); 60.832 (s, CCH$_3$(CD$_3$)$_2$); 43.787 (s, CH$_2$CMMe$_2$Ph); 32.777 (q, $J = 125.4$ Hz, CH$_2$C(CH$_3$)$_2$Ph)); 32.520 (q, $J = 124.5$ Hz, CCH$_3$(CD$_3$)$_2$); 30.044 (m, CCH$_3$(CD$_3$)$_2$); 21.322 (q, $J = 126.4$ Hz, ArMe).

(xxv) Ti(N[R]Ar)$_2$(CH[SiMe$_3$])$_3$ (1.34): Ti(N[R]Ar)$_2$(μ-Cl)$_2$Li(TMEDA) (1.30, 1.1385 g, 1.8770 mmol) in pentane (50 mL) was cooled to -35 °C. LiCH(SiMe$_3$)$_2$ (0.3123 g, 1.877 mmol) was added as a solid. The reaction mixture became dark green on addition. The reaction was stirred for 15 minutes, and then filtered to remove LiCl (0.1348 g, 3.186 mmol, 1.7 eq). The resulting dark green solution was concentrated to about 20 mL and stored at -35 °C. Dark green block-like crystals were obtained in two crops (0.7755 g, 1.356 mmol, 72.3 %). M.p. 134-135 °C. $^2$H NMR (46 MHz, C$_6$H$_5$): $\delta =$ 3.968; $\Delta\nu_{1/2}$ 17.9 Hz. $\mu_{\text{eff}}$ (300 MHz, C$_6$D$_6$, 25 °C) 2.213 μ$_{\text{B}}$. UV-Vis (ether): $\lambda_{\text{max}}(\varepsilon)$ = 663 nm (407 M$^{-1}$cm$^{-1}$). EPR (298 K, toluene): $g = 1.95$. EPR (95 K, toluene): $g_1 = 1.997; g_2 = 1.962; g_3 = 1.918$. Anal. Calcd. for C$_{31}$H$_{43}$D$_{12}$N$_2$Si$_2$Ti: C, 65.10; H, 9.69; N, 4.90. Found: C, 65.36; H, 9.76; N, 4.67.

(xxvi) Ti(N[R]Ar)$_2$(CH[SiMe$_3$])$_2$(I) (1.35): Ti(N[R]Ar)$_2$(CH[SiMe$_3$])$_2$ (1.34, 0.4034 g, 0.7054 mmol) was dissolved in benzene (5 mL). Iodine (0.0900 g, 0.3546 mmol, 0.5 eq) was slurried in benzene (5 mL) and the slurry was added to the alkyl. The reaction mixture became dark orange-red. The solvent was removed in vacuo giving a light orange powder. Crystals were obtained from a concentrated ether solution (0.3329 g, 0.4764 mmol, 67.5 %). M.p. 175-176 °C. $^1$H NMR (300 MHz, C$_6$D$_6$): $\delta =$ 6.938 (br d, $J = 71.9$ Hz, 4H, ortho); 6.710 (s, 2H, para); 3.466 (s, 1H, CH(SiMe$_3$)$_2$); 2.184 (s, 12H,
ArMe); 1.404 (s, 6H, C(CD$_3$)$_2$CH$_3$); 0.393 (s, 18H, SiMe$_3$). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 145.972$ (s, ipso), 137.682 & 137.085 (s, meta), 128.594 & 127.971 (d, ortho and meta); 112.023 (d, para), 104.010 (d, $J = 90.6$ Hz, CH(SiMe$_3$)$_2$); 65.306 (s, C(CD$_3$)$_2$CH$_3$); 30.394 (q, C(CD$_3$)$_2$CH$_3$); 30.074 (m, C(CD$_3$)$_2$CH$_3$), 21.274 (q, ArMe), 5.857 (q, SiMe$_3$). Anal. Calcd. for C$_{31}$H$_{43}$D$_{12}$N$_2$Si$_2$Ti: C, 53.28; H, 7.93; N, 4.01. Found: C, 53.66; H, 7.90; N, 3.84. **Alternate preparation from 1.10:** Alkylation of Ti(N[R]Ar)$_2$I$_2$ with LiCH(SiMe$_3$)$_2$ in pentane was exceedingly slow, and led to some decomposition. However, the major product after 48 hours was complex 1.35.

(xxvii)  [Ti(N[R]Ar)$_2$(CH(SiMe$_3$)$_2$)(NCPH)$_2$] (1.37):

Ti(N[R]Ar)$_2$(CH(SiMe$_3$)$_2$) (1.34, 0.4257 g, 0.7444 mmol) was dissolved in ether (20 mL) and cooled to -35 ºC. Benzonitrile (100 mL, 0.7534 mmol) was added over approximately 5 minutes causing a rapid color change to the deep dark blue of Ti(N[R]Ar)$_2$(CH(SiMe$_3$)$_2$(NCPH) (1.36). $^2$H NMR (46 MHz, Et$_2$O): $\delta(\Delta\nu_{1/2}) = 4.671(20), 1.86(17)$. The diamagnetic peak grew in noticeably over a 10 minute period. After 17 hours of stirring, an orange powder which precipitated was collected on a frit (0.4212 g, 0.6130 mmol, 82%). The powder was essentially insoluble in pentane and ether but could be recrystallized from hot THF. M.p. 180 ºC (dec). $^1$H NMR (300 MHz, C$_6$D$_6$): $\delta = 8.039$ (br s, 2H); 7.28 (m, 8H); 6.587 (s, 4H); 6.397 (br s, 8H); 2.159 (s, 24H, ArMe); 1.439 (s, 2H, CH(SiMe$_3$)$_2$); 1.210 (s, 12H, C(CD$_3$)$_2$CH$_3$); 0.443 (s, 36H, SiMe$_3$). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 173.115$ (s, C=N); 148.112 (s); 143.462 (s); 135.773 (s); 129.878 (d); 129.441 (d); 128.037 (d); 127.458 (d); 127.140 (d); 77.206 (d, CH(SiMe$_3$)$_2$); 62.380 (s, C(CD$_3$)$_2$CH$_3$); 30.628 (q, C(CD$_3$)$_2$CH$_3$); 30.065 (m, C(CD$_3$)$_2$CH$_3$); 21.408 (q, ArMe); 6.181 (q, SiMe$_3$). Anal. Calcd. for C$_{76}$H$_{96}$D$_{24}$N$_6$Si$_4$Ti$_2$: C, 67.61; H, 8.96; N, 6.22. Found: C, 68.05; H, 9.26; N, 6.13.
(xxviii) \( \text{Ti}([R]\text{Ar})_2(\text{CH}[\text{SiMe}_3]_2)(\text{N}_3) \) (1.39): \( \text{Ti}([R]\text{Ar})_2(\text{CH}[\text{SiMe}_3]_2) \) (1.34, 0.7124 g, 0.1.245 mmol) was dissolved in pentane (40 mL). tert-Butyl nitrile (575 mL, 5.20 mmol, 4 eq) was added, causing a color change to a light green. Trimethylsilylazide (230 mL, 0.1.733 mmol, 1.4 eq) was then added and the solution was stirred overnight (after about 2 hours the solution changed to an orange/yellow color). The pentane was removed in vacuo, and the waxy solid thus obtained was recrystallized from pentane to give a light orange powder (0.2852 g, 0.4645 mmol, 37%). M.p. 147-148 °C (dec. with bubbling). \(^1\)H NMR (300 MHz, C\(_6\)D\(_6\)): \( \delta = 6.839 \) (br s, 4H, ortho); 6.708 (s, 2H, para); 2.50 (s, 1H, CH(SiMe\(_3\))\(_2\)); 2.213 (s, 12H, ArMe); 1.251 (s, 6H, C(CD\(_3\))\(_2\)CH\(_3\)); 0.222 (s, 18H, SiMe\(_3\)). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta = 146.815 \) (s, ipso); 137.629 (s, meta); 128.247 (d, \( J = 157.3 \) Hz); 128.201 (d, \( J = 157.4 \) Hz); 98.1749 (d, \( J = 90.85 \) Hz, CH(SiMe\(_3\))\(_2\)); 63.6716 (s, C(CD\(_3\))\(_2\)CH\(_3\)); 30.3523 (q, \( J = 125.9 \) Hz, C(CD\(_3\))\(_2\)CH\(_3\)); 29.8439 (m, C(CD\(_3\))\(_2\)CH\(_3\)); 21.3200 (q, \( J = 126.4 \) Hz, ArMe); 4.2006 (q, \( J = 118.2 \) Hz, SiMe\(_3\)). IR (16 scans, 2.0 cm\(^{-1}\), THF): \( \nu(\text{N}_3) \) 2107 cm\(^{-1}\). Anal. Calcd for C\(_{31}\)H\(_{43}\)D\(_{12}\)N\(_5\)Si\(_2\)Ti: C, 60.64; H, 9.03; N, 11.41. Found: C, 60.75; H, 9.07; N, 11.05.

1.11.4 X-ray Structure of Ti([R]Ar)\(_2\)(CH[SiMe\(_3\)]\(_2\)) (1.34). A crystal of approximate dimensions 0.50 × 0.23 × 0.20 mm was obtained from a chilled ether solution. The crystal was mounted on a glass fiber. Data were collected at −86 °C on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. A total of 4774 reflections were collected to a 2θ value of 44.9 °, 4446 of which were unique (R\(_{\text{int}}\) = 0.098); equivalent reflections were merged. The structure was solved by direct methods. Non-hydrogen atoms were refined anisotropically, except C26 which was refined isotropically. The final cycle of least-squares refinement was based on 2735 observed reflections (I > 3.00σ(I)) and 320 variable parameters and converged (largest parameter shift was 0.01 times its esd) with R = 0.075 and R\(_w\) = 0.065. A final difference Fourier map showed no chemically significant features. Crystal data: a = 10.644(2) Å, b =
10.844(2) Å, c = 16.718(4) Å, V = 1713(2) Å³, α = 100.48(3) °, β = 95.86(3) °, γ = 113.11(3) °, space group P1 (No. 2), Z = 2, \( M_r = 571.92 \) for \( \text{C}_{31}\text{H}_{43}\text{D}_{12}\text{N}_{2}\text{Si}_{2}\text{Ti} \), and \( \rho(\text{calcd}) = 1.109 \text{ g/cm}^3 \). See Tables 1.1 and 1.2 for metrical parameters, Table 1.3 for positional parameters and U(eq), and Figure 1.5 for an ORTEP diagram.
References


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Chapter II: Molybdenum(V) and -(VI) Chalcogenide Complexes*
Section 2.1: Introduction

Transition metal complexes with a terminal chalcogen atom in the coordination sphere currently are being studied in order to develop new chalcogen atom transfer reagents. The field of oxygen atom transfer has been reviewed, but there is much less precedent for the transfer of the heavier chalcogens. Transition metal complexes of the heavier chalcogens are rare, and their chemistry is dominated by single bonding. Complexes which support double bonding to tellurium have only recently become available, but since that time, other complexes containing the terminal tellurido functionality have appeared. Further study of chalcogenido complexes may uncover novel reactivity and interesting periodic trends. A variety of synthetic routes to the tellurolate anion (RTe⁻) are being examined by Arnold, and these groups can be converted to the terminal telluride by using appropriate procedures. Elemental tellurium inserts into a lithium alkyl bond to form the lithium tellurolate, which is used in substitution reactions to generate transition metal tellurolates. HTeSi(SiMe₃)₃ reacts with Zr(Bz)₄ to liberate toluene and generate Zr(TeSi[SiMe₃]₃)₄. Addition of the bridging phosphine dmpe initially forms Zr(TeSi[SiMe₃]₃)₄(dmpe) and then Zr(Te)(TeSi[SiMe₃]₃)₂(dmpe)₂ with the loss of Te(Si[SiMe₃]₃)₂. Tellurium also inserts into transition metal-alkyl bonds. Cp₂ScR reacts with elemental Te to give the tellurolate Cp₂ScTeR. The corresponding reaction with Cp*₂TiH results in the loss of dihydrogen, and a complex with a μ₂ bridging tellurium between two Cp*₂Ti centers is the isolated product. A similar reaction occurs between Cp*₂Ta(H)(CH₂) and tellurium in the presence of PMe₃. Tellurium adds across the metal carbon double bond to form the tantalum adduct of telluroformaldehyde, Cp*₂Ta(η²-CH₂Te)(H), which is stable at room temperature. Heating above 130 °C causes a tautomerization to form the methyl telluride complex Cp*₂Ta(Te)(Me). The corresponding addition reaction does not occur with O and S atom sources, although Cp*₂TaH₃ reacts with Se to form the cyclo-diselenide Cp*₂Ta(η²-Se₂)(H). This species reacts with MeI at 80 °C to give the selenide iodide.
Cp*₂Ta(Se)(I).²⁰ Cp*₂Zr(CO)₂ reacts with Se to give the terminal Zirconium(IV) chalcogenide Cp*₂Zr(Se)(CO).²¹

V(N₃N) (N₃N = [Me₃SiNCH₂CH₂]₃N) reacts with a variety of oxo donors (propylene oxide, pyridine-N-oxide, N₂O, DMSO) to generate the oxo; S₈ and episulfides to generate the sulfido; elemental Se to generate the selenide; and trimethylphosphine telluride to generate the terminal telluride, which is only observed spectroscopically.¹⁰ V(N₃N) does not react with elemental tellurium, however. TaCl₂(N₃N) reacts with two equivalents of either LiSeSi(SiMe₃)₃ or LiTeSi(SiMe₃)₃ to generate ETa(N₃N) and E(Si[SiMe₃]₃).¹⁴ Sharp bands for the selenide (507 cm⁻¹) and telluride (460 cm⁻¹) are observed in the Raman spectrum.

The periodic trends of the chalcogenide series on a variety of transition metals are being studied by Parkin. In group four, Cp*₂M(CO)₂ (M = Zr, Hf) reacts with elemental sulfur, selenium or tellurium in the presence of pyridine at 80-100 °C to give the terminal chalcogenide pyridine complex Cp*₂M(E)(py). The telluride reacts with N₂O to give the oxo complex.¹¹,²² Mo(PMe₃)₄ reacts with H₂S, H₂Se, Se and Te to give the trans-dichalcogenide complexes Mo(E)₂(PMe₃)₄,¹⁶ and W(PMe₃)₄(H)(η²-CH₂PMe₂) reacts with H₂S, H₂Se and Te to give, again, the trans species W(E)₂(PMe₃)₄.⁵ Neither the corresponding tungsten nor molybdenum oxo complex has been made.

Mo(N[R]Ar)₃ (2.1, R = C(CD₃)₂CH₃, Ar = 3,5-C₆H₃Me₂) is an extremely reactive three-coordinate trigonal planar complex.²³ The complex is a powerful three electron reductant, capable of reducing dinitrogen²⁴ and effecting nitrogen atom transfer from Mo(N)(O-t-Bu)₃.²⁵ Interest in chalcogenide chemistry with complex 2.1 stems from the unusual selectivity in its reaction with N₂O, giving exclusively the terminal nitrido and nitrosyl complexes NMo(N[R]Ar)₃ and (ON)Mo(N[R]Ar)₃ rather than the terminal oxo complex OMo(N[R]Ar)₃.²³ There are a number of examples of N₂O acting as an O-atom donor,²⁶-²⁹ and this makes thermochemical sense as the N-N bond dissociation enthalpy is 84.4 kcal-mol⁻¹ while the N-O enthalpy is only 38.6 kcal-mol⁻¹,³⁰,³¹ and the liberation of

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dinitrogen is entropically favorable. There are therefore only a few examples of N-N bond cleavage in N₂O.³¹-³³ In the molybdenum tris-anilide system, the reverse cleavage is rationalized by the fact that two strong Mo-N triple bonds are formed in the products, but it seems counterintuitive that the Mo(V) oxo complex is not formed, thereby liberating dinitrogen. This species is never observed even in small quantities during the reaction, a fact initially attributed to thermodynamic or kinetic instability.

This chapter describes the preparation and characterization of the entire series of paramagnetic Mo(V) terminal chalcogenido complexes with the N[R]Ar ancillary ligand environment, definitively showing that the terminal oxo species is not an unstable complex. This is the first full series of terminal chalcogenido complexes of molybdenum, although a partial series does exist.¹⁶ Estimates of the Mo-O and Mo-S bond dissociation enthalpies determined by calorimetry and further verified by high level theoretical calculations further demonstrate the high stability of these Mo(V) d¹ complexes. All four complexes undergo a thermal C-N bond homolysis reaction, generating a series of diamagnetic Mo(VI) chalcogenide complexes. Extensive studies examining chalcogen atom abstraction from a wide variety of organic and inorganic substrates are also described.

Section 2.2: Mo(V) Chalcogenide Complexes

(i) Synthesis and Characterization of OMo(N[R]Ar)₃ (2.2)

Simple mixing of the reactive d¹ complex Ti(N[R]Ar)₃ with the vanadium oxo complex OV(O-t-Bu)₃ forms the heterodinuclear μ-oxo species (Ar[R]N)₃TiOV(O-t-Bu)₃ in good yield.³⁴ With the more reducing Mo(N[R]Ar)₃ (2.1) the reaction should lead to complete atom transfer, generating the terminal Mo(V) oxo species OMo(N[R]Ar)₃ (2.2). Simple mixing of ethereal solutions of the two reagents in fact leads to a marked color change to dark brown. Examination of the reaction mixture by ²H NMR spectroscopy shows a single peak at approximately 7.2 ppm, indicative of a d¹ species in this system.³⁵
Unfortunately, the resulting vanadium product is not easily separated from the molybdenum complex, though fractional crystallization does lead to a purified fraction of the oxo complex. The putative \([\text{V(O-\text{r-Bu})}_3]\) fragment is an intractable dark oil which exhibits four to five broad resonances in its \(^1\text{H}\) NMR spectrum and no signal by \(^{51}\text{V}\) NMR spectroscopy. EI-MS is inconclusive, as the compound has not been entirely purified, and the molecular ion is intermediate between the \(\text{V(III)}\) complex and the corresponding dimer \(\text{V}_2(\text{O-\text{r-Bu}})_6\). For preparative scale reactions to generate \(\text{2.2}\), pyridine \(\text{N-oxide}\) serves as an efficient oxo donor (Scheme 2.1). Addition of the solid reagent to a solution of \(\text{2.1}\) causes a rapid color change to reddish brown in a matter of minutes. The complex is highly crystalline and is isolated from ether in yields in excess of 70%.

Compound \(\text{2}\) exhibits a single resonance in the \(^2\text{H}\) NMR spectrum at 7.6 ppm in toluene with a peak width at half height of 30 Hz. The corresponding \(^1\text{H}\) NMR spectrum exhibits only two resonances in the range ± 100 ppm: 7.2 ppm for the tert-butyl group, and 0 ppm for the aryl methyl group. The other resonances are apparently too broad to be observed. The complex has a strong infrared stretch at 893 cm\(^{-1}\) attributable to \(\nu_{\text{Mo-O}}\). Labeling the complex with \(^{18}\text{O}\) has not yet been attempted. An Evans method\(^{36}\) measurement of \(\mu_{\text{eff}}\) gives a value of 2.19 \(\mu_\text{B}\), higher than the spin only value of 1.73 \(\mu_\text{B}\) as is typical for \(d^1\) complexes using this method.\(^{37}\) The magnetic susceptibility data of solid \(\text{2.2}\) determined over the temperature range 5 to 300 K using a SQUID magnetometer are consistent with simple paramagnetic behavior, obeying the Curie law over the entire temperature range. The data and least squares fit, shown in Figure 2.1, give a value for \(\mu\) of 1.66 \(\mu_\text{B}\), corresponding well to the expected spin only value of 1.73 \(\mu_\text{B}\). A room temperature EPR spectrum of \(\text{2.2}\) in toluene gives an isotropic \(g\) value of 1.96 with a six line coupling pattern to the \(s = 5/2\) nuclei \(^{95}\text{Mo}\) and \(^{97}\text{Mo}\) of 35.7 Gauss. This six line pattern is approximately 25% of the area of the central peak, reflecting the natural abundance of \(^{95/97}\text{Mo}\).\(^{38}\) Due to the similar gyromagnetic ratios of the two \(s = 5/2\) molybdenum nuclei, separate couplings are not seen, nor are they expected.\(^{16,38}\) A frozen

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glass EPR spectrum in toluene shows a poorly resolved rhombic spectrum with g values of 1.990, 1.967 and 1.937 (Figure 2.2); the g values are obtained through simulation of the spectrum.\textsuperscript{39} The corresponding couplings to \textsuperscript{95}Mo and \textsuperscript{97}Mo are not resolved in this spectrum. An ORTEP diagram of complex 2.2 derived from single crystal X-ray data is shown in Figure 2.3. Pertinent bond distances and angles are given in Tables 2.1 and 2.2, and positional parameters and U(eq.) are listed in Table 2.3. The molybdenum oxygen bond distance of 1.706(2) Å in 2.2 is at the long end of the range typical for Mo(V) oxo complexes.\textsuperscript{6} The other bond distances are typical, although the arrangement of the three anilide ligands is unique in that the complex is neither pseudo-\textit{C}$_{3}$ nor pseudo-\textit{C}_{5}, the two common arrangements for tris-anilide complexes. As seen from the O-Mo-N-C\textit{(tert)} dihedral angles (Table 2.2) one anilide is tilted by about 40°, larger by 10-20° than that usually seen in anilide complexes of this sort,\textsuperscript{23,34,37,40} one by 3° and the third by 62°. This third anilide ligand also is slightly pyramidalized towards the site trans to the oxo ligand, with the sum of the angles about nitrogen being 356.2°. The other two nitrogen atoms are planar. Although the three anilide ligands are quite different in the solid state, in solution there is no differentiation on the \textsuperscript{2}H NMR timescale.
Scheme 2.1: Preparation of Mo(V) Chalcogenide Complexes
Figure 2.1: SQUID magnetic susceptibility data for solid OMo(N[R]Ar)₃ (2.2) from 5 to 300 K fit to the Curie law (μ = 1.66 μₜ).
Figure 2.2: EPR spectrum (100 K, toluene) of O\textit{Mo(N[R]Ar)}$_3$ (2.2) with $g_1 = 1.990$, $g_2 = 1.967$, $g_3 = 1.937$. 
Figure 2.3: ORTEP diagram of OMo(N[R]Ar)₃ (2.2) with ellipsoids at the 30% probability level.
Table 2.1: Selected Bond Lengths (Å) for OMo(N[R]Ar)₃ (2.2).

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Table 2.2: Selected Bond Angles (°) for OMo(N[R]Ar)₃ (2.2).

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Table 2.3: Positional Parameters \((x \times 10^4)\) and \(U(\text{eq.})\) \((\text{Å}^2 \times 10^3)\) for the Non-Hydrogen Atoms of OMo(N[R]Ar)_3 (2.2).

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(ii) Synthesis and Characterization of S\text{Mo}(N[R]Ar)_3 (2.3)

It is also possible to synthesize homologues of oxo complex 2.2 with the heavier elements of group 16, starting with sulfur. An ethereal solution of Mo(N[R]Ar)_3 (2.1) reacts with a slight excess of elemental sulfur to give a dark greenish brown solution (Scheme 1.1). Monitoring the reaction by $^2$H NMR spectroscopy shows that all the starting material is consumed over approximately an 18 hour period, being converted to a single product. The excess sulfur is removed by filtration, and the terminal sulfido complex S\text{Mo}(N[R]Ar)_3 (2.3) is obtained by recrystallization from ether in 63% yield. Complex 2.1 also reacts with ethylene sulfide to give complex 2.3; the reaction is complete in only a few minutes.

The $^2$H NMR spectrum of 2.3 in ether exhibits a single resonance at 6.5 ppm with a peak width at half height of 22 Hz. The corresponding $^1$H NMR spectrum exhibits two broad resonances: one at 6.0 ppm for the tert-butyl group and one at 1.1 ppm for the aryl methyl group. As is the case with the oxo species, none of the other resonances are observed. The complex has a strong infrared stretch due to $\nu_{\text{Mo-S}}$ at 492 cm$^{-1}$. The solution magnetic susceptibility measurements again give an anomalously high value for $\mu_{\text{eff}}$ of 2.21 $\mu_B$. A measurement of the magnetic susceptibility by SQUID magnetometry from 5 to 300 K is again consistent with simple paramagnetic behavior. A fit of the data to the Curie law gives $\mu = 1.63 \mu_B$; the data and fit are shown in Figure 2.4. An EPR spectrum of 2.3 at room temperature in toluene gives an isotropic g value of 1.96 with coupling to the $s = 5/2$ nuclei $^{95/97}$Mo of 28.5 Gauss. A frozen glass EPR spectrum in toluene shows a rhombic pattern with g values of 1.996, 1.970 and 1.922 (Figure 2.5). In this spectrum, the anisotropic couplings to $g_1$ and $g_3$ are partially resolved as 25 G and 54 G respectively. Again, these assignments are obtained through spectrum simulation.$^{39}$
Figure 2.4: SQUID magnetic susceptibility data for solid \( \text{SMo(N[\text{R}]Ar)_3} \) (2.3) from 5 to 300 K fit to the Curie law \( (\mu = 1.63 \mu_B) \)
Figure 2.5: EPR spectrum (100 K, toluene) of SMo(N[R]Ar)_3 (2.3) with \( g_1 = 1.996, g_2 = 1.970, g_3 = 1.922, A_1 = 25 \text{ G} \) and \( A_3 = 54 \text{ G} \).
Chapter II: Molybdenum(V) and -(VI) Chalcogenide Complexes

An X-ray crystal structure determination on complex 2.3 shows it to have pseudo-\( C_3 \) symmetry, and an ORTEP diagram of the structure is shown in Figure 2.6. Selected bond lengths and angles are listed in Tables 2.4 and 2.5, and positional parameters and \( U(\text{eq.}) \) are given in Table 2.6. The molybdenum sulfur distance is 2.1677(12) Å. This distance is 0.09 Å shorter than those reported for \( d(\text{Mo-S}) \) in \( \text{trans-Mo(S)}_2(\text{PR}_3)_4 \),\(^{16} \) but this is best explained by the increased Mo-S π bonding possible in 2.3 relative to the bis sulfide complex. \( \text{Mo(S)}_2(\text{PR}_3)_4 \) has at most a Mo-S double bond, while complex 2.3 has a Mo-S bond order of 2.5 (see Section 2.3 for further details). Tungsten complexes with doubly bonded sulfur exhibit bond distances on the order of 2.25 Å, while those with a bond order of 2.5 to sulfur have lengths near 2.19 Å.\(^5 \) As Mo and W have similar radii, this places the Mo-S bond distance in 2.3 in the 2.5 bond order regime. The other bond distances in the sulfide complex are normal. The pseudo-\( C_3 \) arrangement of the anilides is identical to that seen in the \( d^{11} \) tris anilide complex Cl(Nb(N[R]Ar)_3.\(^{41} \) Two of the anilides engage in a π stacking arrangement with the tert-butyl groups splayed away from the center of the molecule, while the third is oriented in a more typical upright arrangement with a S-Mo-N-C(\text{tert}) dihedral angle of 7° and is nearly bisected by the pseudo-mirror plane.
Figure 2.6: ORTEP diagram of SmO\(_2\)(N[R]Ar)_3 (2.3) with ellipsoids at the 30% probability level.
Table 2.4: Selected Bond Lengths (Å) for SMo(N[R]Ar)₃ (2.3).

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Table 2.5: Selected Bond Angles (°) for SMo(N[R]Ar)₃ (2.3).

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### Table 2.6: Positional Parameters (x 10⁴) and U(eq.) (Å² x 10³) for the Non-Hydrogen Atoms of SMo(N[R]Ar)₃ (2.3).  

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</tbody>
</table>

(102) References begin on page 184
(iii) **Synthesis and Characterization of SeMo(N[R]Ar)₃ (2.4)**

Synthesis of the terminal selenide complex is straightforward. Again, simple mixing of a solution of Mo(N[R]Ar)₃ (2.1) and excess elemental selenium results in a slow color change over about 11 hours to dark brown (Scheme 2.1). The excess selenium is removed by filtration and the product, SeMo(N[R]Ar)₃ (2.4), is collected by crystallization from ether in 80% yield.

The §H NMR spectrum of 2.4 in ether exhibits a single resonance at 7.0 ppm, with a peak width at half height of 31 Hz. The ¹H NMR spectrum is similar to those observed for complexes 2.3 and 2.2, with resonances at 6.5 ppm for the tert-butyl group and -1.5 ppm for the aryl methyl group. The complex exhibits a fairly strong peak at 342 cm⁻¹ in the Far-IR spectrum which is due to νMo-Se. Measurement of the magnetic moment by SQUID magnetometry from 5 to 300 K gives a μ value of 1.75 μB and a θ value of -1.45 K when fit to the Curie-Weiss Law; the SQUID data and fit are presented in Figure 2.7. An EPR spectrum of 2.4 in toluene at room temperature exhibits an isotropic g value of 1.97, with isotropic coupling to ⁹⁵Mo and ⁹⁷Mo of 30.5 G. The frozen glass EPR spectrum has well resolved g values of 2.030, 1.986 and 1.899 (Figure 2.8). The separation allows the anisotropic couplings for g₁ and g₃ to be observed at 29 and 48 G respectively. The g values and A couplings are verified by simulation.³⁹ Complex 2.4 is isostructural to the sulfide 2.3, with pseudo-C₃ symmetry, as determined by single crystal X-ray diffraction; an ORTEP diagram is shown in Figure 2.9. Selected bond distances and angles are listed in Tables 2.7 and 2.8, and positional parameters and U(eq.) are listed in Table 2.9. The Mo-Se distance is 2.3115(6) Å. Tungsten complexes with bond orders of two to selenium have W-Se bond distances of approximately 2.38 Å while those with a bond order of 2.5 have bond lengths near 2.32 Å,⁵ suggesting a bond order of 2.5 in the selenide complex.
Figure 2.7: SQUID magnetic susceptibility data for solid SeMo(N[R]Ar)₃ (2.4) from 5 to 300 K fit to the Curie-Weiss law (μ = 1.75 μₜ; θ = -1.45 K)
Figure 2.8: EPR spectrum (100 K, toluene) of SeMo(N[R]Ar)$_3$ (2.4) with $g_1 = 2.030$, $g_2 = 1.986$, $g_3 = 1.899$, $A_1 = 29$ G and $A_3 = 48$ G.
Figure 2.9: ORTEP diagram of SeMo(N[R]Ar)\textsubscript{3} (2.4) with ellipsoids at the 30\% probability level.
### Chapter II: Molybdenum(V) and -(VI) Chalcogenide Complexes

#### Table 2.7: Selected Bond Distances (Å) for SeMo(N[R]Ar)₃ (2.4).

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<td>N1-C17</td>
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<td>N3-C37</td>
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#### Table 2.8: Selected Bond Angles (°) for SeMo(N[R]Ar)₃ (2.4).

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(107) References begin on page 184
### Table 2.9: Positional Parameters (x 10^4) and U(eq.) (Å² x 10^3) for the Non-Hydrogen Atoms of SeMo(N[R]Ar)₃ (2.4).

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(iv) Synthesis and Characterization of TeMo(N[R]Ar)_3 (2.5)

The synthesis of the terminal telluride completes the series of Mo(V) chalcogenido complexes (Scheme 2.1).⁴² Treating Mo(N[R]Ar)_3 (2.1) with a slight excess of elemental tellurium in ether causes an extremely slow conversion to dark brown TeMo(N[R]Ar)_3 (2.5) as shown by ^2H NMR spectroscopy. After 72 hours at room temperature, there is significant decomposition, on the order of 35%, as well as about 5% unreacted 2.1. In order to circumvent the slow reaction time, a soluble form of tellurium is required. Phosphine tellurides effectively deliver tellurium atoms to appropriate substrates,⁸¹⁰,⁴³ and compound 2.1 does not react with triethyl phosphine as shown by ^2H NMR spectroscopy, so triethyl phosphine telluride seems a good delivery agent. Rather than synthesizing the phosphine telluride directly, a catalytic amount of phosphine (ca. 15 mol%) is added to the reaction mixture of 2.1 and tellurium, resulting in conversion to the desired telluride 2.5 over approximately 18 hours. When prepared this way, there is typically about 12% decomposed, diamagnetic material as determined by ^2H NMR spectroscopy. After removing the solvent and phosphine by evaporation, the reaction mixture is extracted with THF and filtered to remove excess tellurium. The telluride complex is much less soluble in ether than the lighter homologues but recrystallizes from ether in 73% yield.

The ^2H NMR spectrum of 2.5 exhibits a single resonance at 8.1 ppm with a peak width at half height of 23 Hz. The ^1H NMR spectrum is unsurprising, with resonances at 8 ppm for the tert-butyl group and -2 ppm for the aryl methyl group. A determination of the magnetic moment by SQUID magnetometry gives a μ value of 1.86 μB and a θ value of -5.1 K when fit to the Curie-Weiss law over the temperature range 5-170 K. The data and fit are shown in Figure 2.10. The frozen glass EPR spectrum is very well resolved as seen in Figure 2.11, with g values and their associated A (⁹⁵,⁹⁷Mo) couplings (G) of 2.130 (28), 1.970 (24) and 1.850 (48). The best simulation of this spectrum is obtained using the values g₁ = 2.1302, A₁ = 25, g₂ = 1.9717, A₂ = 22, g₃ = 1.8481 and A₃ = 41. The isotropic spectrum shows a g value of 1.98, but is extremely broad and obscures the
smaller peaks due to the $s = 5/2$ nuclei. Complex 2.5 is isostructural to complexes 2.3 and 2.4, with pseudo-$C_5$ symmetry relating the two parallel and $\pi$-stacked aryl rings. An ORTEP diagram of the structure is shown in Figure 2.12, selected bond distances and angles are listed in Tables 2.10 and 2.11 and positional parameters and $U(eq.)$ for the structure are given in Table 2.12. The Mo-Te distance is $2.5353(6)$ Å, and all other bond distances are normal. Tungsten complexes with bond orders of two to Te have bond lengths of around $2.60$ Å, while those with a bond order of 2.5 have lengths of $2.53$ Å, indicating the higher bond order in complex 2.5.

Table 2.10: Selected Bond Distances (Å) for TeMo(N[R]Ar)_3 (2.5).

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<td>Mo-N3</td>
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Table 2.11: Selected Bond Angles (°) for TeMo(N[R]Ar)_3 (2.5).

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Figure 2.10: SQUID magnetic susceptibility data for solid TeMo(N[R]Ar)₃ (2.5) from 5 to 170 K fit to the Curie-Weiss law (μ = 1.86 μ_B; θ = -5.1 K)
Figure 2.11: EPR spectrum (100 K, toluene) of TeMo(N[R]Ar)_3 (2.5) with $g_1 = 2.130$, $g_2 = 1.970$, $g_3 = 1.850$, $A_1 = 28 \text{ G}$, $A_2 = 24 \text{ G}$ and $A_3 = 48 \text{ G}$.  

(112) References begin on page 184
Figure 2.12: ORTEP diagram of TeMo(N[R]Ar)_3 (2.5) with ellipsoids at the 30% probability level.
### Table 2.12: Positional Parameters (x 10^4) and U(eq.) (Å² x 10^3) for the Non-Hydrogen Atoms of TeMo(N(NR)Ar)_3 (2.5).

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(v) Cyclic Voltammetry

The cyclic voltammetry data for the four Mo(V) chalcogenide complexes are shown in Table 2.13. The $E_{1/2}$ values for the electrochemically reversible oxidations, obtained in CH$_2$Cl$_2$ with saturated Bu$_4$NPF$_6$ as the supporting electrolyte, are reported relative to the Fc/Fc$^+$ couple. The data clearly show that the oxo complex 2.2 is a more powerful reductant than the other chalcogenide complexes; this result is supported by experimental data. There is no reaction when [Mo(O)(N[R]Ar)$_3$][OTf] 2.12 (see section 2.5) is mixed with a solution of the other chalcogenide complexes 2.3-2.5. It is not possible to test the reverse reaction of adding a cationic chalcogenide species to 2.2, as the heavier cations are not isolable.

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<th>Species</th>
<th>$E_{1/2}$ rel. to Fc/Fc$^+$ (V)</th>
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(vi) Thermochemistry

Estimates of the solution bond dissociation enthalpies for both the Mo-O and the Mo-S bonds in complexes 1.2 and 1.3 are determined based on thermochemical experiments carried out by Steve Nolan and Scafford Serron at the University of New Orleans; details are presented in the experimental section. The heat of reaction of 2.1 with pyridine $N$-oxide (equation 2.1) is $-83.5 \pm 1.4$ kcal·mol$^{-1}$. The bond dissociation enthalpy of pyridine $N$-oxide (equation 2.2) is $72.11 \pm 0.67$ kcal·mol$^{-1}$. Combination of these two values (equation 2.3 = eq. 2.2 - eq. 2.1) leads to the bond dissociation enthalpy for the Mo-O bond in 2.2 of $155.6 \pm 1.6$ kcal·mol$^{-1}$.  

(115) References begin on page 184
2.1) \( \text{Mo(N[R]Ar)}_3 + \text{py-O} \rightarrow \text{OMo(N[R]Ar)}_3 + \text{py} \); \( \Delta H_r = -83.5 \pm 1.4 \text{ kcal\cdot mol}^{-1} \)
2.2) \( \text{py-O} \rightarrow [\text{O}] + \text{py} \); \( \Delta H_r = 72.11 \pm 0.67 \text{ kcal\cdot mol}^{-1} \)
2.3) \( \text{OMo(N[R]Ar)}_3 \rightarrow [\text{O}] + \text{Mo(N[R]Ar)}_3 \); \( \Delta H_r = 155.6 \pm 1.6 \text{ kcal\cdot mol}^{-1} \)

Similarly, the heat of reaction of 2.1 with ethylene sulfide (equation 2.4) is \( 45.2 \pm 1.2 \text{ kcal\cdot mol}^{-1} \). The heat of reaction of ethylene sulfide to give ethylene and sulfur atoms (equation 2.5) is calculated to be \( 59.15 \pm 0.33 \text{ kcal\cdot mol}^{-1} \). Finally, combination of the two reactions (equation 2.6 = eq. 2.5 - eq. 2.4) leads to the bond dissociation enthalpy for the Mo-S bond in 2.3 of \( 104.4 \pm 1.2 \text{ kcal\cdot mol}^{-1} \).

2.4) \( \text{Mo(N[R]Ar)}_3 + \text{SC}_2\text{H}_4 \rightarrow \text{SMo(N[R]Ar)}_3 + \text{C}_2\text{H}_4 \); \( \Delta H_r = -45.2 \pm 1.2 \text{ kcal\cdot mol}^{-1} \)
2.5) \( \text{SC}_2\text{H}_4 \rightarrow [\text{S}] + \text{C}_2\text{H}_4 \); \( \Delta H_r = 59.15 \pm 0.33 \text{ kcal\cdot mol}^{-1} \)
2.6) \( \text{SMo(N[R]Ar)}_3 \rightarrow [\text{S}] + \text{Mo(N[R]Ar)}_3 \); \( \Delta H_r = 104.4 \pm 1.2 \text{ kcal\cdot mol}^{-1} \)

The small contribution due to solvation effects is accounted for where possible; the heat of solvation of complex 2.1, which is included in the above calculations, is \( 8.9 \pm 0.2 \text{ kcal\cdot mol}^{-1} \). A major assumption which must be made in the above interpretation is that the measured heats of reaction in equations 2.1 and 2.4 correspond closely to the bond dissociation enthalpies of interest. This seems reasonable, as the only bonds being made or broken during the reaction are element-chalcogen bonds. Changes in enthalpy on structural reorganization from the \( C_3 \) symmetric 1.1 to the pseudo-\( C_5 \) symmetric chalcogenide complexes are expected to be on the order of \( 6 \text{ kcal\cdot mol}^{-1} \).
The value for the Mo-O bond dissociation enthalpy in complex 1.2 of 155 kcal·mol\(^{-1}\) represents one of the strongest transition metal-oxo bond strengths known when compared to an extensive list tabulated by Holm for the purposes of investigating biological oxo transfer.\(^{51}\) There are many fewer data corresponding to metal-sulfur interactions, so it is assumed that the Mo-S bond in complex 1.3 is comparably strong.

Section 2.3: Theoretical Description of Mo(V)-E Complexes

(i) Extended Hückel MO Analysis

The electronic structures of the Mo(V) chalcogenides are examined through an extended Hückel analysis using the computer program CACAO.\(^{52,53}\) Further discussion of this method is presented in Appendix I of this thesis. The calculations are simplified by using the model complex SMo(NH\(_2\))\(_3\). The ground state structure of Mo(NH\(_2\))\(_3\) is known to be of \(C_{3h}\) symmetry from high level theoretical calculations.\(^{54}\) By bringing in a sulfur atom at an appropriate distance (2.168 Å), an interaction diagram between the two entities in the point group \(C_3\) is constructed. This diagram is shown in Figure 2.13. The Cartesian coordinates used for the calculations are shown in Table 2.14. The lowest energy orbitals (4a and 3e) are primarily Mo-N in plane bonding. Orbital 4e is a mixture of Mo-E and Mo-N \(\pi\) bonding, and 5a is Mo-E \(\sigma\) bonding. Orbital 6a is a ligand based lone pair consisting of in-phase in-plane p orbitals on all three nitrogenos and 5e is the metal based \(d_{xy}\) and \(d_{x^2-y^2}\). The 6e orbital is a singly occupied degenerate Mo-E \(\pi^*\) orbital. A CACAO generated diagram of this degenerate orbital set, MO 14 and 15, is shown in Figure 2.14. Orbitals 7e and 7a are empty, and correspond to Mo-N \(\pi^*\) and Mo-E \(\sigma^*\) interactions respectively. The net Mo-S bond order predicted from these calculations is 2.5, in agreement with the structural data given in Section 2.2.
Figure 2.13: Diagram in $C_3$ for the Interaction of Mo(NH$_2$)$_3$ in $C_{3h}$ with a sulfur atom at 2.168 Å.
Table 2.14: Cartesian Coordinates for SMo(NH₂)₃ in C₃v.

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<th>z</th>
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</thead>
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<td>0.000</td>
<td>0.000</td>
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<td>0.000</td>
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<td>H12</td>
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<td>0.156</td>
<td>0.827</td>
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<td>0.000</td>
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<tr>
<td>H31</td>
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<td>-2.294</td>
<td>-0.827</td>
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<td>H32</td>
<td>-1.144</td>
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<tr>
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<td>0.000</td>
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Table 2.15: Cartesian Coordinates for SMo(NH₂)₃ with coordinates derived from X-ray data (pseudo-C₃v).

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<tr>
<td>S</td>
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<td>0.000</td>
<td>2.168</td>
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</table>
Figure 2.14: The singly occupied degenerate HOMO (orbitals 14 and 15) in $C_3$ for the calculated structure of Mo(NH$_2$)$_3$ ($C_{3h}$) with a sulfur atom at 2.168 Å.
This $C_3$ symmetric structure would be expected to undergo a Jahn-Teller type distortion in order to break the degeneracy of the partially filled $\pi^*$ orbital, and in fact, this is what is observed in the crystal structures of the four chalcogen complexes, which approximate $C_s$ symmetry. An interaction diagram of $\text{SMo(NH}_2\text{)}_3$ constructed using coordinates derived from the X-ray structure of complex 2.3 is shown in Figure 2.15. The Cartesian coordinates used for the calculations are listed in Table 2.15. Most of the orbitals in this diagram roughly correspond to the same type of interaction as in the $C_3$ diagram. The largest difference is the singly occupied 6e orbital from the $C_3$-symmetric structure which splits significantly in energy upon distorting to the $C_s$ geometry. The orbital partner which lowers in energy and is half filled is primarily Mo-E $\pi^*$ in character, MO 15 in Figure 2.16, while the partner which rises in energy and remains empty is primarily Mo-N $\pi^*$ in character, MO 14 in Figure 2.16. This analysis helps to explain the experimentally observed distortion. In pseudo-$C_s$ symmetry, the unpaired electron is able to occupy an orbital with minimal Mo-N $\pi^*$ character, reducing the unfavorable interaction with the strongly electron-donating nitrogen lone pairs which exist before the distortion.
Figure 2.15: Interaction diagram for the model complex SMo(NH₂)₃ derived from the X-ray coordinates of SMo(N[R]Ar)₃ (2.3).
Figure 2.16: The LUMO (orbital 14) and SOMO (orbital 15) for the model complex SMo(NH$_2$)$_3$ derived from the X-ray coordinates of SMo(N[R]Ar)$_3$ (2.3).
(ii) **Density Functional Calculations**

Quantum chemical calculations have been carried out on the model complexes EMo(NH$_2$)$_3$ by Jamal Musaev and Keiji Morokuma at Emory University in order to further elucidate the electronic and geometrical structures as well as thermodynamic parameters of the EMo(N[R]Ar)$_3$ complexes. These calculations use the hybrid density functional B3LYP method$^{56-58}$ in conjunction with the double-$\zeta$ plus polarization quality basis set lanl2dz + d$_E$ ($\alpha_d = 0.85$, 0.503, 0.364 and 0.252 for O,$^{59}$ S, Se and Te atoms,$^{60}$ respectively), which for heavy atoms (S, Se, Te and Mo) uses the Hay and Wadt effective core potential (ECP) including the relativistic effects for Mo and Te.$^{61,62}$ All calculations were performed by the GAUSSIAN-94 package.$^{63}$

Gradient-corrected density functional methods such as B3LYP are quite reliable both in geometry and in energies.$^{54,64,65}$ For instance, the B3LYP method describes the geometry of the model complex ($\mu$-N$_2$[Mo(N(HNCH$_2$CH$_2$)$_3$)])$_2$ very well in comparison with the experimental structure of the real system ($\mu$-N$_2$[Mo(N(t-BuMe$_2$SiNCH$_2$CH$_2$)$_3$)])$_2$, with the N-N distance of 1.22 Å (calculated) vs. 1.20 Å (X-ray), the Mo-N (trans to N$_2$) distance of 2.30 Å (calculated) vs. 2.29 Å (X-ray) and the other Mo-N distances of 1.97 Å (calculated) vs. 2.01 Å (average, X-ray).$^{66}$

As mentioned previously, the ground state of the Mo(NH$_2$)$_3$ complex is the quartet A' state in $C_{3h}$ symmetry with three unpaired electrons in the [d$_{xz}$ and d$_{yz}$] (e") and sd$_\sigma$ (a') orbitals. The doublet A' state is calculated to be about 14.5 kcal·mol$^{-1}$ higher.$^{54}$ In $C_3$ symmetry, the addition of an O, S, Se or Te atom in the $^3S$ state with two unpaired electrons to the quartet Mo(NH$_2$)$_3$ gives the doublet EMo(NH$_2$)$_3$ complex with a Mo-E bonding interaction consisting of one $\sigma$- and a net 1.5 $\pi$-component. The interaction diagram obtained is qualitatively identical to the one calculated from extended Hückel methods shown in Figure 2.13.
Chapter II: Molybdenum(V) and -(VI) Chalcogenide Complexes

(iii) **Density Functional Structures**

The Jahn-Teller effect should distort the structure from a $C_3$ symmetry into one of the two $C_5$ conformations **A** or **B**, shown in Figure 2.17. Both conformations distort from $C_3$ symmetry to $C_5$ symmetry, but conformation **A** has one horizontal amide and two vertical amides, while conformation **B** has one vertical amide and two horizontal amides. The primary orbital considerations for this type of distortion are demonstrated in Figures 2.13-2.16. Geometry optimization on the model complexes EMo(NH$_2$)$_3$ converges to the conformation **A** for all four E ligands.

![Diagram showing two possible conformations](image)

**Figure 2.17:** Two Possible Conformations of $C_5$ EMo(NH$_2$)$_3$ Resulting from Jahn-Teller Distortion of the $C_3$ Structure.
OMo(NH$_2$)$_3$ is calculated to have $C_1$ symmetry, albeit only slightly distorted from $C_5$, with a doublet A ground state, while the other homologues are calculated to have true $C_5$ symmetry with a doublet A" ground state. The Cartesian coordinates of the calculated structures are given in Tables 2.16-2.19 for the four chalcogen complexes. PLUTO diagrams of the calculated structures are shown in Figures 2.18-2.21. Pertinent bond distances are presented in Table 2.20. The conformation B is not a local minimum, though the energy of B relative to that of A is less than 2 kcal-mol$^{-1}$.

**Table 2.16**: Cartesian Coordinates for OMo(NH$_2$)$_3$

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**Table 2.17**: Cartesian Coordinates for SMo(NH$_2$)$_3$

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Table 2.18: Cartesian Coordinates for SeMo(NH₂)₃ calculated at the B3LYP/lanl2dz + dE level.

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</tr>
<tr>
<td>H21</td>
<td>-0.612744</td>
<td>2.165538</td>
<td>-1.547989</td>
</tr>
<tr>
<td>H22</td>
<td>-0.612993</td>
<td>-2.164159</td>
<td>-1.549909</td>
</tr>
<tr>
<td>N3</td>
<td>-1.184854</td>
<td>-1.625677</td>
<td>-0.900086</td>
</tr>
<tr>
<td>H31</td>
<td>-2.135465</td>
<td>1.989536</td>
<td>-0.815950</td>
</tr>
<tr>
<td>H32</td>
<td>-2.135638</td>
<td>-1.988591</td>
<td>-0.817604</td>
</tr>
<tr>
<td>Se</td>
<td>1.724824</td>
<td>-0.000043</td>
<td>0.042173</td>
</tr>
</tbody>
</table>

Table 2.19: Cartesian Coordinates for TeMo(NH₂)₃ calculated at the B3LYP/lanl2dz + dE level.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>0.923899</td>
<td>0.000010</td>
<td>-0.020664</td>
</tr>
<tr>
<td>N1</td>
<td>1.683733</td>
<td>-0.000049</td>
<td>1.769876</td>
</tr>
<tr>
<td>H11</td>
<td>1.782080</td>
<td>-0.847408</td>
<td>2.331885</td>
</tr>
<tr>
<td>H12</td>
<td>1.781527</td>
<td>0.847081</td>
<td>2.332324</td>
</tr>
<tr>
<td>N2</td>
<td>1.517578</td>
<td>-1.623813</td>
<td>-0.90599</td>
</tr>
<tr>
<td>H21</td>
<td>0.943622</td>
<td>-2.158933</td>
<td>-1.556052</td>
</tr>
<tr>
<td>H22</td>
<td>0.943636</td>
<td>2.159192</td>
<td>-1.555754</td>
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<td>N3</td>
<td>1.517624</td>
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<td>-0.905306</td>
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<td>H31</td>
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<td>-0.841796</td>
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<tr>
<td>H32</td>
<td>2.474027</td>
<td>-1.976698</td>
<td>-0.841701</td>
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<tr>
<td>Te</td>
<td>-1.581449</td>
<td>-0.000002</td>
<td>0.024707</td>
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</tbody>
</table>

Table 2.20: Calculated Bond distances (Å) at the B3LYP lanl2dz + dE level of theory for the complexes Mo(NH₂)₃ and EMo(NH₂)₃ where E = O, S, Se and Te.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Symmetry, Ground State</th>
<th>Mo-E</th>
<th>Mo-N₁</th>
<th>Mo-N₂</th>
<th>Mo-N₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(NH₂)₃</td>
<td>C₃h, ⁴A'</td>
<td>---</td>
<td>1.980</td>
<td>1.980</td>
<td>1.980</td>
</tr>
<tr>
<td>OMo(NH₂)₃</td>
<td>C₁, ²A</td>
<td>1.715</td>
<td>1.956</td>
<td>1.956</td>
<td>1.960</td>
</tr>
<tr>
<td>SMo(NH₂)₃</td>
<td>Cₛ, ²A&quot;</td>
<td>2.162</td>
<td>1.949</td>
<td>1.947</td>
<td>1.947</td>
</tr>
<tr>
<td>SeMo(NH₂)₃</td>
<td>Cₛ, ²A&quot;</td>
<td>2.302</td>
<td>1.946</td>
<td>1.944</td>
<td>1.944</td>
</tr>
<tr>
<td>TeMo(NH₂)₃</td>
<td>Cₛ, ²A&quot;</td>
<td>2.506</td>
<td>1.945</td>
<td>1.942</td>
<td>1.942</td>
</tr>
</tbody>
</table>

The experimental structures for the complexes EMo(N[R]Ar)₃ have the B conformation for E = S, Se and Te, and a distorted B conformation for E = O. This discrepancy between theory and experiment is attributable mainly to the steric effect of the bulky N[R]Ar ligands which could reasonably overshadow the small electronic energy difference between the two conformations. This steric effect would also be expected to

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enforce significant differences in bond angles, and therefore, only bond distances in the calculated structures have any real meaning.

Table 2.20 shows that addition of an O, S, Se or Te atom should shorten the Mo-N distance by 0.02-0.03 Å from 1.98 Å in $C_{3h}$ Mo(NH$_2$)$_3$. The calculated Mo-N distances are in good agreement with those observed experimentally. The distance between Mo and the added O, S, Se and Te atom is calculated to be 1.715, 2.162, 2.302, and 2.506 Å, which is in excellent agreement with the experimental values, 1.706, 2.168, 2.312 and 2.535 Å.

(iv) Density Functional Bond Energies

As seen in Table 2.21, the EMo(NH$_2$)$_3$ binding energies calculated at the B3LYP/lan12dz + $d_E$ level are 140.2, 94.1, 82.5 and 64.5 kcal·mol$^{-1}$ for E = O, S, Se and Te, respectively. At this level of theory, the calculated values for OMo(NH$_2$)$_3$ and SMo(NH$_2$)$_3$ are 10% smaller than the experimentally determined ones, 155.6 ± 1.6 and 104.3 ± 1.2 kcal·mol$^{-1}$, respectively. The errors, in part due to the approximations used in the calculations and in part due to the difference between the real and model systems, are expected to be systematic. Therefore, the SeMo(N[R]Ar)$_3$ and TeMo(N[R]Ar)$_3$ bond energies are best estimated by scaling up the calculated values for SeMo(NH$_2$)$_3$ and TeMo(NH$_2$)$_3$ by 10% to be 91 and 71 kcal·mol$^{-1}$, respectively.

Table 2.21: The calculated and experimental EMoL$_3$ binding energies (in kcal/mol), where E = O, S, Se, and Te and L = NH$_2$ (calculated) and N[R]Ar (experimental, R = C(CD$_3$)$_2$CH$_3$ and Ar = 3,5-Me$_2$C$_6$H$_3$).

<table>
<thead>
<tr>
<th>E</th>
<th>Symmetry, Ground State</th>
<th>B3LYP lan12dz + $d_E$</th>
<th>Best estimated$^a$</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>$C_1$, $^2A$</td>
<td>140.2</td>
<td>--</td>
<td>155.61 ± 1.6</td>
</tr>
<tr>
<td>S</td>
<td>$C_{5v}$, $^2A''$</td>
<td>94.1</td>
<td>--</td>
<td>104.35 ± 1.2</td>
</tr>
<tr>
<td>Se</td>
<td>$C_{5v}$, $^2A''$</td>
<td>82.5</td>
<td>91.0</td>
<td>----</td>
</tr>
<tr>
<td>Te</td>
<td>$C_{5v}$, $^2A''$</td>
<td>64.5</td>
<td>71.0</td>
<td>----</td>
</tr>
</tbody>
</table>

a) See text for more detail.
Figure 2.18: PLUTO diagram of the calculated structure for OMo(NH₂)₃ (C₁, ²A) at the B3LYP/lanl2dz + dₑ level.
Figure 2.19: PLUTO diagram of the calculated structure for SMo(NH$_2$)$_3$ ($C_s$, $^2A''$) at the B3LYP/lanl2dz + d$_E$ level.
Figure 2.20: PLUTO diagram of the calculated structure for SeMo(NH$_2$)$_3$ ($C_s$, $^2A''$) at the B3LYP/lanl2dz + d$_E$ level.
Figure 2.21: PLUTO diagram of the calculated structure for TeMo(NH$_2$)$_3$ (C$_s$, 2A") at the B3LYP/lanl2dz + d$_E$ level.
(v) Population Analysis and Metal-Ligand Bond Character

The above mentioned trends in the energies and geometries of the calculated complexes are best explained in terms of the electronegativity and the size of valence s and p orbitals of the O, S, Se and Te atoms. The atomic electronegativity decreases in the order O > S > Se > Te, and the size of valence s and p orbitals increases in the same order. Therefore, the electrostatic character of the Mo-E bond decreases and its covalent character increases in the order of E: O-S-Se-Te. As seen in Table 2.22 in the Mulliken population analysis, both the positive charge of the metal center, +1.35, +1.16, +1.10, and +1.04 e, and the absolute value of the negative charge of the atom E, -0.46, -0.38, -0.32, and -0.29 e, decrease in the same order, confirming that the ionic character of the Mo-E bond decreases in the above order. At the same time, the overlap population Q between the Mo and E atoms, 0.68, 0.81, 0.86 and 0.87 e increases in the same order, confirming that the covalent character of the Mo-E bond increases in this order.

<table>
<thead>
<tr>
<th></th>
<th>Z*</th>
<th>Q(X-Mo)</th>
<th>Spin Density</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E</td>
<td>Mo</td>
<td>E</td>
</tr>
<tr>
<td>O</td>
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<td>+1.35</td>
<td>0.68</td>
</tr>
<tr>
<td>S</td>
<td>-0.38</td>
<td>+1.16</td>
<td>0.81</td>
</tr>
<tr>
<td>Se</td>
<td>-0.32</td>
<td>+1.10</td>
<td>0.86</td>
</tr>
<tr>
<td>Te</td>
<td>-0.29</td>
<td>+1.04</td>
<td>0.87</td>
</tr>
</tbody>
</table>

The Mulliken spin density in Table 2.22 confirms that the unpaired electron in the Mo-E π* orbital is localized more on the molybdenum atom. The extent of localization decreases as the ligand E goes down the periodic table. As E changes in this order, the lower electronegativity of E as well as the larger Mo dπ-E pπ overlap increases the contribution of the E pπ orbital in the π* orbital, resulting in more delocalization and smaller spin density on molybdenum.
Section 2.4: Mo(VI) Chalcogenide Complexes

(i) Synthesis and Characterization of OMo(NAr)(N[R]Ar)\textsubscript{2} (2.6)

Prolonged thermolysis of the Mo(V) oxo complex 2.2 at temperatures exceeding 65 °C leads to disappearance of the starting material and clean appearance of a new diamagnetic product as determined by \textsuperscript{1}H and \textsuperscript{2}H NMR spectroscopies. The color of the solution also changes from dark brown to a very light yellow-brown. When the reaction is carried out in C\textsubscript{6}D\textsubscript{6} and the volatiles are examined by \textsuperscript{1}H NMR spectroscopy, isobutylene, isobutane and hexamethylethane are observed. Close examination of the reaction by \textsuperscript{2}H NMR spectroscopy shows the presence of isobutylene at around 4.8 ppm. The fact that these organic products are observed in both the deuterium and the proton NMR spectra leads to the conclusion that the reaction in question is tert-butyl radical elimination of a d\textsubscript{6-tert}-butyl group.\textsuperscript{67-69} Recent reports describe a similar type of reaction involving tert-butyl radical elimination from a tert-butoxy group.\textsuperscript{35} Scheme 2.2 shows the reaction in question. Carrying out the thermolysis reaction on a large scale results in formation of the oxo imide species 2.6. Unfortunately, this complex proves to be an oil, contaminated with 5-10% HN[R]Ar, which resists purification. Carrying out the thermolysis reaction at higher temperatures leads to shorter reaction times, but the resulting product is less pure: there is a higher degree of free aniline production, and higher temperatures cause a disproportionation reaction (see below for details).
Scheme 2.2: Preparation of Mo(VI) Chalcogenide Complexes through Radical C-N Bond Homolysis
1H NMR spectroscopy is not sufficient to distinguish between two possible structures, the oxo imide OMo(NAr)(N[R]Ar)$_2$, or the aryloxo nitrido species NMo(OAr)(N[R]Ar)$_2$ which could result from the migration of an aryl group. The migration of an N-bound substituent to oxygen is preceded in a related system. Other characterization data (HRMS, $^{13}$C NMR) are consistent with either connectivity. Hydrolysis of the isolated material followed by analysis by GC-MS shows HN[N[R]Ar and H$_2$NAr, but no HOAr, consistent with the formulation of 2.6 as OMo(NAr)(N[R]Ar)$_2$. Complex 2.6 reacts with benzaldehyde to the extent of about 10% to the products shown in Scheme 2.3 suggesting a terminal oxo ligand in 2.6. Both imine PhC(H)=NAr and the dioxo complex O$_2$Mo(N[R]Ar)$_2$ 2.12 (see section 2.5) are observed spectroscopically (see experimental section for details). Prolonged storage of complex 2.6 at room temperature, or thermolysis of the complex in solution at high temperatures leads to disproportionation of 2.6 to a mixture of 2.6, 2.12 and the presumed bis-imide complex Mo(NAr)$_2$(N[R]Ar)$_2$. This reaction appears to be an equilibrium mixture, with $K_{eq} \approx 1$. The most convincing evidence obtained for the formulation of the product as the oxo imide is the intense IR stretch at 913 cm$^{-1}$ due to $\nu_{Mo-O}$. This band is at slightly higher energy than the stretch observed for oxo complex 2.2, as would be expected for the increase in oxidation state of the molybdenum center.
Scheme 2.3: Reactions of OMo(NAr)(N[R]Ar)₂ (2.6)

(ii) Synthesis and Characterization of SMo(NAr)(N[R]Ar)₂ (2.7)

Thermolysis of sulfide 2.3 causes a color change from dark brown to a much lighter reddish brown (Scheme 2.2). The reaction also results in the formation of
isobutylene, isobutane and hexamethylethane (observed by $^1$H and $^2$H NMR spectroscopy) due to tert-butyl radical elimination from the Mo(V) complex. The sulfide imide 2.7 is recrystallized from ether as an orange powder in 84% yield.

Again, spectroscopic evidence does not differentiate between the two possible connectivities (sulfide imide or thiophenoxide nitride). Crystals suitable for an X-Ray diffraction experiment have not been obtained. Complex 2.7 reacts with benzaldehyde and spectroscopic evidence for gradual production of the imine PhC(H)=NAr in small quantities suggests that the sulfide is terminal like the oxo ligand in 2.6. Prolonged thermolysis of the complex leads primarily to decomposition. The complex exhibits a strong stretch in the IR at 506 cm$^{-1}$ which has a slightly higher $\nu_{\text{Mo-S}}$ than that observed for the Mo(V) sulfide complex 2.3, supporting the proposed terminal sulfide formulation.

(iii) **Synthesis and Characterization of SeMo(NAr)(N[R]Ar)$_2$ (2.8)**

Thermolysis of selenide 2.4 at 65 °C for 22 hours gives a diamagnetic product, as determined by $^1$H NMR spectroscopy, generating isobutane, isobutylene and hexamethylethane as side products (Scheme 2.2). The color of the reaction mixture changes from dark brown to a lighter red-orange. The selenide imide 2.8 is orangeish brown in color and is isolated in 64% yield as a powder.

Spectroscopic evidence is consistent with its formulation as the terminal chalcogenide imide like complexes 2.6 and 2.7. Investigation of the complex by $^{77}$Se NMR spectroscopy shows a broad resonance at 1923.4 ppm ($\Delta \nu_{1/2} = 46.2$ Hz); molybdenum satellites are not observed. The $^{77}$Se NMR chemical shifts for transition metal selenides are extremely dependent on the chemical environment, but there are some general trends. Terminal selenides exhibit resonances appearing between 800 and 2400 ppm,$^{5,14,70}$ with the majority falling in the 1900-2300 ppm range.$^{5,16}$ Alkyl selenides have resonances in the region from 200 to 1100 ppm,$^{71-74}$ although this latter number is of a very deshielded complex. The chemical shift in 2.8 is therefore more consistent with a

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terminal selenido than an organoselenolate functionality. The complex exhibits a strong peak in the Far-IR at 355 cm\(^{-1}\), attributable to \(v_{\text{Mo-Se}}\), which is at slightly higher energy than that observed for the Mo(V) selenide, lending further support to the formulation as a terminal selenide.

(iv) Synthesis and Characterization of TeMo(NAr)(N[R]Ar\(_2\)) (2.9)

Telluride 2.5 eliminates a tert-butyl radical at 65 °C to generate a diamagnetic product which is much more thermally sensitive than the lighter homologues (Scheme 2.2). Prolonged heating gives rise to peaks in the NMR spectrum suggesting a disproportionation reaction similar to that seen for the oxo complex 2.6 in Scheme 2.3. This decomposition reaction occurs at a rate comparable to product formation, and there is also substantial formation of free HN[R]Ar. As a consequence, the thermolysis is only carried out for about five hours at 65 °C. The reaction (as monitored by \(^2\)H NMR spectroscopy) is approximately 80% complete after this time period. Recrystallization of TeMo(NAr)(N[R]Ar\(_2\)) (2.9) from ether gives a dark brown powder in around 40% yield, but it has not been obtained analytically pure.

Spectroscopic evidence is analogous to that reported for 2.6, 2.7 and 2.8, consistent with its formulation as the terminal telluride imide. The complex exhibits an extremely broad \(^{125}\)Te NMR resonance at 2459.3 ppm (\(\Delta v_{1/2} = 250\) Hz) and Mo satellites are not observed. Terminal tellurides tend to have \(^{125}\)Te chemical shifts in the window from 2700\(^8\) to 3300\(^16\) ppm, though they can appear below this region.\(^\text{14}\) Alkyl tellurides of tin\(^75\) and iron\(^76\) have chemical shifts of approximately -1200 ppm. There is a scarcity of tellurium NMR data in the literature, but it is possible to correlate selenium and tellurium chemical shifts in related systems.\(^5\) The chemical shift for 2.9 is more consistent with a terminal telluride function than an aryltellurolate. The complex exhibits a strong peak in the Far-IR at 291 cm\(^{-1}\), which is at slightly higher energy for \(v_{\text{Mo-Te}}\) than that observed for the Mo(V) telluride, lending further support to the terminal telluride formulation.
(v) General Features of Mo(VI) Chalcogenide Complexes

The molybdenum(VI) chalcogenide imide complexes 2.6-2.9 are quite unreactive. For example, 2.6 fails to react with even the strained or activated unsaturated hydrocarbons shown in Scheme 2.3. The chemistry of these molecules remains to be explored further.

The thermolysis of Mo(V) chalcogenide complexes to give Mo(VI) chalcogenide imide complexes takes advantage of the stability of the tert-butyl radical. This relatively high degree of stability also explains the ease of tert-butyl radical ejection from tert-butoxide ligands.\(^{35}\) Alternatively, this reaction shows a potential weakness of the N[R]Ar ligand framework. The ejection of tert-butyl radicals from the N[R]Ar ligand to form aryl imides is also an observed decomposition pathway in niobium chemistry. The Nb(III) reduction product of ClNb(N[R]Ar)\(_3\) is not isolated or even spectroscopically observed as it decomposes via a tert-butyl radical expulsion to give the Nb(IV) dimer [Nb(N[R]Ar)\(_2\)(\(\mu\)-NAr)]\(_2\).\(^{41}\) The thermolysis reaction represents a new synthesis of imides that, although not expected to be general in scope, may have some synthetic utility.

(vi) Kinetics of C-N Bond Homolysis

Measuring the kinetics of the thermolysis reactions (Scheme 2.2) by UV-visible spectroscopy has been hampered by the lack of suitable absorption differences between the starting materials and products, and also by the presumed disproportionation reaction of the chalcogenide imide complexes at higher temperatures. The deconvolution of UV-vis spectroscopic data using suitable computer programs has been unsuccessful.\(^{77}\)

The kinetics of the thermolysis reaction of oxo 2.2 are determined between 65 °C and 105 °C by monitoring the disappearance of the starting material relative to an internal sealed reference capillary of D\(_2\)O/THF by \(^2\)H NMR spectroscopy (see experimental section for details). The reaction is cleanly first order over this temperature range, and the observed first order rate constants are given in Table 2.23. An Eyring plot of the data is
shown in Figure 2.22, clearly showing a good fit to first order kinetics. The first order activation parameters derived from the fit are shown in Table 2.24. The $\Delta H^\dagger$ value of 28.85 ± 0.07 kcal·mol$^{-1}$ suggests bond breaking in the transition state, while the $\Delta S^\dagger$ value of 3.10 ± 0.08 cal·mol$^{-1}$·K$^{-1}$ is very small and not indicative of a substantial entropy contribution to the rate.

**Table 2.23: Kinetics of EMo(N[R]Ar)$_3$ Decomposition.**

<table>
<thead>
<tr>
<th>T (K)</th>
<th>k ($x \times 10^5$ sec$^{-1}$)</th>
<th>T (K)</th>
<th>k ($x \times 10^4$ sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>335.9</td>
<td>0.586 ± 0.067</td>
<td>339.1</td>
<td>1.32 ± 0.27</td>
</tr>
<tr>
<td>345.7</td>
<td>1.86 ± 0.37</td>
<td>348.5</td>
<td>3.86 ± 0.62</td>
</tr>
<tr>
<td>355.7</td>
<td>6.50 ± 2.09</td>
<td>355.9</td>
<td>8.94 ± 1.87</td>
</tr>
<tr>
<td>365.8</td>
<td>22.8 ± 4.0</td>
<td>366.0</td>
<td>20.1 ± 3.8</td>
</tr>
<tr>
<td>377.0</td>
<td>67.4 ± 10.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 2.24: Heats (kcal·mol$^{-1}$) and enthalpies (cal·mol$^{-1}$·K$^{-1}$) of activation for the thermolysis of EMo(N[R]Ar)$_3$.**

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta H^\dagger$</th>
<th>$\Delta S^\dagger$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMo(NRAr)$_3$</td>
<td>28.85 ± 0.07</td>
<td>3.10 ± 0.08</td>
</tr>
<tr>
<td>SMo(NRAr)$_3$</td>
<td>24.39 ± 0.13</td>
<td>-4.53 ± 0.06</td>
</tr>
</tbody>
</table>

References begin on page 184
Figure 2.22: Logarithmic least-squares fit of first-order rate constants \( \ln (k_r \cdot T^{-1}) \) versus reciprocal temperature \( [K\cdot1] \) using the Eyring equation \( \ln (k_r \cdot T^{-1}) = -\Delta H^\ddagger \cdot R^{-1} \cdot T^{-1} + C \) for the thermal conversion of OMo(N[R]Ar)_3 (2.2) and SMo(N[R]Ar)_3 (2.3) to OMo(NAr)(N[R]Ar)_2 (2.6) and SMo(NAr)(N[R]Ar)_2 (2.7) with tert-butyl radical loss. Data are shown with 95% confidence limit intervals.
The kinetics of the thermolysis reaction leading to 2.7 are determined over the temperature range from 65 °C to 95 °C in an analogous manner. The reaction is cleanly first order over this temperature range, but the rate is too fast to be measured accurately using this method above 95 °C. The observed first order rate constants are approximately an order of magnitude larger than those for the oxo thermolysis, and the two sets of numbers are compared in Table 2.23. An Eyring plot of the data is given in Figure 2.22, clearly showing a good fit to first order kinetics. The first order activation parameters derived from the fit are shown in Table 2.24. The \( \Delta H^\ddagger \) value of 24.39 ± 0.13 kcal·mol\(^{-1}\) suggests bond breaking in the transition state. The \( \Delta S^\ddagger \) value of -4.53 ± 0.06 cal·mol\(^{-1}\)·K\(^{-1}\) is opposite in sign to the one measured for the oxo thermolysis reaction, but again, it is very small and not indicative of substantial entropy contribution to the rate.

(vii) **Extended Hückel Description of Thermolysis**

The thermolysis reaction is readily examined in more detail by carrying out extended Hückel calculations on a model complex which undergoes plausible deformations along the reaction coordinate. This analysis sheds light on mechanistic aspects of the reaction, despite the limited attempts to find a minimum energy surface. Step one in this simplistic scheme is the \( C_5 \) symmetric SMo(NH\(_2\))\(_3\), with one vertical amide and two horizontal amides, derived from slight distortions of the experimentally determined solid state structure. Steps two through ten retain \( C_5 \) symmetry, but one N-H bond on the unique amide is gradually lengthened along the original NH vector to 2 Å, suggesting its loss as a radical, while the Mo-N-H angle for the remaining hydrogen is increased from 107° to 180°. The Cartesian coordinates of step one and step ten used for these calculations are given in Table 2.25 and 2.26. This simplistic pathway ignores any changes in the pertinent Mo-N distance, and assumes that all other atoms in the molecule remain stationary. It is expected that the molecule represented in step ten would undergo significant distortions to lower its energy, but these distortions are ignored in this analysis.
Table 2.25: Cartesian Coordinates used in Extended Hückel calculations for step one of the model transformation of SMo(NH2)3 to SMo(NH)(NH2)2.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
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<td>1.767</td>
<td>0.000</td>
<td>0.889</td>
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<td>2.751</td>
<td>0.000</td>
<td>0.616</td>
</tr>
<tr>
<td>H12</td>
<td>1.607</td>
<td>0.000</td>
<td>0.616</td>
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<tr>
<td>N2</td>
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<td>-1.644</td>
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<td>-2.167</td>
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Table 2.26: Cartesian Coordinates used in Extended Hückel calculations for step ten of the model transformation of SMo(NH2)3 to SMo(NH)(NH2)2.

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<td>1.588</td>
<td>0.720</td>
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<tr>
<td>H22</td>
<td>-0.660</td>
<td>2.603</td>
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<tr>
<td>N3</td>
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<td>-1.644</td>
<td>0.438</td>
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<tr>
<td>H31</td>
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<tr>
<td>H32</td>
<td>-1.929</td>
<td>-2.603</td>
<td>0.720</td>
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<tr>
<td>S</td>
<td>0.000</td>
<td>0.000</td>
<td>-2.167</td>
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</table>

Despite the simplistic model, mechanistic conclusions are obtained which give a deeper understanding of the reaction pathway than the single headed arrow mechanism that is usually drawn for a radical elimination reaction. A Walsh diagram depicting the transformation is shown in Figure 2.23. The total energy of the system is shown as a dashed line in the Figure, which rises to a maximum in step seven and then begins dropping. However, as mentioned previously, the model complex described by step ten should undergo significant distortions to lower its energy. In Step one, the interaction diagram is, not surprisingly, essentially identical to that shown in Figure 2.15. During the course of this reaction coordinate, all of the orbitals depicted in the interaction diagram
remain unchanged in either directionality or energy except orbitals 10, 13, 15, 22, 24 and 26 of Step one, which make significant changes in these areas. Orbital 10 starts as an N-H σ* orbital in the upright amide, and drops substantially in energy, becoming a Mo-N π* orbital in step ten. Orbital 13 is primarily a Mo-N π* orbital to the two horizontal amides, but gains some Mo-N π* to the upright amide at the expense of a Mo-N σ* interaction, thereby lowering its energy. Orbital 15, which in step one contains the unpaired electron in a Mo-E and Mo-N π* interaction, drops in energy along the reaction coordinate as it gains a significant amount of electron density on the departing hydrogen atom, suggesting its departure as a radical. Two orbitals representing the starting and ending points of this transformation are shown in Figure 2.24a. Orbital 22 is a Mo-N σ orbital in step one, and it transforms into a Mo-N π interaction by step ten, thereby raising slightly in energy. Two orbitals which show this transformation are shown in Figure 2.24b. Orbital 24 is a Mo-N σ interaction to all three nitrogens in step one, but loses most of the σ interaction to the upright amide nitrogen by step ten, and raises only slightly in energy. Finally, orbital 26 starts in step one as a N-H σ orbital in the upright amide which changes into a Mo-N σ orbital in step ten while slightly increasing its energy. Two orbitals which show this transformation are depicted in Figure 2.24c.

Mechanistically, this analysis suggests that the tert-butyl radical elimination reaction depicted in Scheme 2.2 involves the smooth transfer of a metal based electron into a carbon centered orbital. As this orbital becomes filled, it supports the formation of a new Mo-N π bond at the expense of the Mo-N σ bond, and a new Mo-N σ bond at the expense of the N-C σ bond which is lost with the loss of an alkyl radical. This is in agreement with the observed thermochemical parameters presented in Table 2.24 which suggest bond-breaking in the transition state and a minimal entropy contribution. In the experimental system, the preferred (more stable) radical to be lost is the tert-butyl radical, which explains the selectivity in the thermolysis reaction for formation of an aryl imide rather than a tert-butyl imide.
Figure 2.23: Walsh diagram for the model transformation of $\text{EMo}(\text{NH}_2)_3$ to $\text{EMo(NH)}(\text{NH}_2)_2$. See text for further details.
Figure 2.24: a) Orbital 15 of step one transforms from a Mo based π* orbital to a hydrogen radical. b) Orbital 22 of step one transforms from a Mo-N σ bond to a Mo-N π bond. c) Orbital 26 of step one transforms from a N-H σ bond to a Mo-N σ bond. See text for further details.
Section 2.5: Oxidation of OMo(N[R]Ar)₃ (2.2)

(i) One Electron Oxidants

OMo(N[R]Ar)₃ is oxidized to a Mo(VI) cation with either ferrocenium triflate \([((C_5H_5)_2Fe(O_3SCF_3))\] or iodine to generate the corresponding triflate \([OMo(N[R]Ar)₃][OTf]\) (2.10) or iodide complex \([OMo(N[R]Ar)₃][I]\) (2.11) (Scheme 2.4). Adding FcOTf to a solution of the oxo 2.2 causes the slow precipitation of an orange brown solid over 15 hours. This complex is isolated in 71% yield. The IR spectrum of this complex shows a strong peak at 972 cm⁻¹ for the \(ν_{Mo-O}\) stretch, and peaks indicative of an ionic rather than a covalently bound triflate. Adding one-half equivalent of iodine to 2.2 causes rapid precipitation of an orange solid which is isolated in 88% yield. This complex exhibits a strong stretch in the IR spectrum at 975 cm⁻¹, ascribable to \(ν_{Mo-O}\). Both complexes decompose slightly during recrystallization (THF, CH₂Cl₂); the iodide is especially sensitive to decomposition in solution, precluding its analysis by \(^{13}\)C NMR spectroscopy. As a result, combustion analytical data are poor.

The syntheses of cations of 2.3, 2.4, and 2.5 by similar methodology is not possible, as mentioned in Section 2.2.v, as the salts are unstable. The complex \([SMo(N[R]Ar)₃][OTf]\) is spectroscopically observable but it is not isolable. Addition of either ferrocenium triflate or iodine to the telluride complex 2.5 results in rapid decomposition. Presumably the cationic species forms and decomposes rapidly to unknown products.
Scheme 2.4: Oxidations of OMo(N[R]Ar)$_3$ (2.2)

(ii) Dioxygen: Synthesis of O$_2$Mo(N[R]Ar)$_2$ (2.12)

Treating OMo(N[R]Ar)$_3$ with 1.1 equivalents of dioxygen causes a gradual color change from dark brown to a much darker brown (Scheme 2.4). After approximately 12 hours, the reaction mixture is deep red-brown. Analysis of the reaction mixture by $^1$H NMR spectroscopy shows the formation of HN[R]Ar and O$_2$Mo(N[R]Ar)$_2$ (2.12) in an approximate two to one molar ratio. The dioxo complex 2.12 is crystallized away from the aniline in low yield as bright yellow crystals. The complex exhibits two strong ν$_{Mo-O}$ peaks in the IR at 943 and 920 cm$^{-1}$, which correspond well to those reported in the literature for the related dioxo complex O$_2$Mo(O-$t$-Bu)$_2$.\textsuperscript{80} The use of excess dioxygen is essential; if OMo(N[R]Ar)$_3$ is treated with one half equivalent of dioxygen over a similar time period, $^2$H NMR spectroscopy shows approximately 50% starting oxo complex. Complex 2.12 also forms, non-reproducibly and in low yield, from the reaction of oxo 2.2 with Me$_2$SO, or from the reaction of 2.1 with dioxygen. This reactivity is starkly
different than that observed in the analogous chromium system. Cr(N[R]Ar)\textsubscript{2} reacts immediately with even a large excess of dioxygen to generate O\textsubscript{2}Cr(N[R]Ar)\textsubscript{2} in essentially quantitative yield\textsuperscript{81}. The reaction of \textbf{2.1} with dioxygen is complex, generating OMo(N[R]Ar)\textsubscript{3} and O\textsubscript{2}Mo(N[R]Ar)\textsubscript{2} in some cases, but in general resulting in complete destruction of the Mo(N[R]Ar)\textsubscript{3} framework with formation of HN[R]Ar. The reaction of oxo imide \textbf{2.6} with benzaldehyde to generate the dioxo complex \textbf{2.12} is described in detail in section 2.4.

**Section 2.6: Reactions of Mo(N[R]Ar)\textsubscript{3} With Chalcogen Donors**

(i) **Carbon Dioxide**

From the list of bond enthalpies tabulated by Holm\textsuperscript{51}, a prediction of the thermodynamic favorability of an oxo transfer reaction is possible. For example, since the bond strength of the oxo ligand in \textbf{2.2} is 155 kcal·mol\textsuperscript{-1}, and the oxo bond strength in Me\textsubscript{2}SO is 87 kcal/mol, \textbf{2.2} should be able to deoxygenate Me\textsubscript{2}SO with $\Delta H_r$ of 68 kcal·mol\textsuperscript{-1}. To this end, a variety of potential chalcogen atom donors are allowed to react with Mo(N[R]Ar)\textsubscript{3} in an attempt to map out thermodynamic favorability and its relation to kinetic barriers. Several reactions of \textbf{2.1} which are thermodynamically feasible have turned out to be kinetically non-viable (Scheme 2.5). There is no reaction of \textbf{2.1} with CO\textsubscript{2} (either 1 eq, 10 eq or 1 atm) in a sealed reaction bomb, even though this reaction should be exothermic by almost 30 kcal·mol\textsuperscript{-1}.  

(150)
Scheme 2.5: Oxygen Donors Unreactive towards Mo(N[R]Ar)₃ (2.2)

(ii) Triphenylphosphine Oxide

The reaction of 2.1 with Ph₃PO is enthalpically downhill by 22 kcal·mol⁻¹, but again, no reaction is observed. In this case, it may be the steric bulk of the two reactants which prevents oxo transfer. As a control experiment, oxo 2.2 and Ph₃P are mixed and no reaction is observed.

(iii) tert-Butyl Isocyanate

The deoxygenation of MeNCO with 2.1 is calculated to be exothermic by 46 kcal·mol⁻¹. When 2.1 is treated with the related t-BuNCO, only a very small amount of oxo 2.2 and Mo(NC-t-Bu)(N[R]Ar)₃ are observed over a 24 hour time period. The latter isonitrile adduct is detected by ²H NMR spectroscopy, and is presumably analogous to the known (OC)Mo(N[R]Ar)₃.⁸²

(iv) Dimethylsulfone

The enthalpy for the reaction of 2.1 with Me₂SO₂ is calculated to be favorable by 43 kcal·mol⁻¹. This reaction is intriguing, in that the second deoxygenation of the oxidant
(deoxygenation of Me₂SO) is more favorable at 68 kcal·mol⁻¹ as mentioned previously. Therefore, for each molecule of Me₂SO₂ which reacts, two equivalents of OMo(N[R]Ar)₃ are expected. However, over a 48 hour period, there is essentially no oxygen atom transfer from Me₂SO to 2.1. The lack of reactivity for Me₂SO₂ is likely due to its insolubility in hydrocarbon solvents in which 2.1 is soluble.

(v) Dimethylsulfoxide

Some oxygen atom donors do react with complex 2.1, and these are shown in Scheme 2.6. Mo(N[R]Ar)₃ is thermodynamically capable of deoxygenating Me₂SO as predicted at the beginning of this section. Simply treating 2.1 with Me₂SO forms a dark brown product in about 10 minutes. ²H NMR spectroscopy shows greater than 90% conversion to oxo 2.2.

(vi) Nitrogen Dioxide

Complex 2.1 is thermodynamically competent to reduce NO₂, with a reaction enthalpy of -82 kcal·mol⁻¹. When Mo(N[R]Ar)₃ is treated with 0.5 equiv. NO₂, the color changes to brown over a 10 minute period. Examination of the reaction mixture shows the clean production of the oxo complex 2.2, as well as the known terminal nitrosyl complex (ON)Mo(N[R]Ar)₃²³ in a 1:1 molar ratio as determined by both ²H and ¹H NMR spectroscopies.
\[
\begin{align*}
\text{Ar[R]N} & \xrightarrow{\text{Me}_2\text{SO}} \text{Mo}^{\text{III}} \text{N}[\text{R}]\text{Ar} + \text{OMo(N[R]Ar)}_3 + [\text{Me}_2\text{S}] \\
\text{(2.2)} & \quad \text{(2.3)}
\end{align*}
\]

\[
\begin{align*}
\text{Ar[R]N} & \xrightarrow{\text{NO}_2} \text{Mo}^{\text{III}} \text{N}[\text{R}]\text{Ar} + 0.5 \text{OMo(N[R]Ar)}_3 + 0.5 \text{(ON)Mo(N[R]Ar)}_3 \\
\text{(2.2)} & \quad \text{(2.3)}
\end{align*}
\]

\[
\begin{align*}
\text{Ar[R]N} & \xrightarrow{\text{SO}_2} \text{Mo}^{\text{III}} \text{N}[\text{R}]\text{Ar} + \frac{2}{3} \text{OMo(N[R]Ar)}_3 + \frac{1}{3} \text{SMo(N[R]Ar)}_3 \\
\text{(2.2)} & \quad \text{(2.3)} \quad \text{(2.4)}
\end{align*}
\]

**Scheme 2.6:** Oxygen Donors Reactive towards Mo(N[R]Ar)_3 (2.2)

(vii) **Sulfur Dioxide**

Complex 2.1 is also thermodynamically competent to remove one oxygen from SO_2 with an enthalpy of reaction of -24 kcal·mol\(^{-1}\). Mo(N[R]Ar)_3 reacts with 0.6 equivalent of gaseous SO_2 to give an immediate color change to dark brown. Analysis of the reaction mixture by \(^2\)H NMR spectroscopy shows clean conversion to the oxo complex 2.2 and the sulfide complex 2.3 in a two to one molar ratio. This reaction is a rare example of clean activation of SO_2 to give sulfido and oxo ligands where the fate of all the reactants and product distribution is known.\(^{83-85}\) Oxidation of the crude reaction mixture with iodine shows conversion to the oxo iodide 2.11 and the decomposition product is observed when 2.3 is oxidized with iodine.
(viii) **Carbon Disulfide: Synthesis of** $(N[R]Ar)_3\text{Mo}(\mu-\text{CS})\text{Mo}(N[R]Ar)_3$ (2.13)

Addition of one equivalent of $\text{CS}_2$ to $\text{Mo}(N[R]Ar)_3$ results in a rapid darkening of the solution to greenish brown (Scheme 2.7). Analysis of the reaction mixture by $^2\text{H}$ NMR spectroscopy at this point shows complete conversion of the starting material to two products, paramagnetic $\text{SMo}(N[R]Ar)_3$ (2.3) and diamagnetic $(N[R]Ar)_3\text{Mo}(\mu-\text{CS})\text{Mo}(N[R]Ar)_3$ (2.13) in a 1:1 molar ratio. Separation of the two complexes is difficult; the best analytical data for 2.13 are given in the experimental section. Activation of $\text{CS}_2$ by transition metals is the subject of a fairly dated review, but this article does not describe the formation of bridging thiocarbonyl complexes, though some are known. The complex does not have a distinct band in its IR spectrum corresponding to $\nu_{C\cdot\cdot\cdot S}$. The stretching frequency for this functional group is expected to be in the range 1150-1230 cm$^{-1}$. Proton NMR spectroscopy shows two distinct ligand environments corresponding to the inequivalent halves of the molecule. The thiocarbonyl carbon is strongly deshielded, appearing at 293.51 ppm in the $^{13}\text{C}$ NMR spectrum.

![Scheme 2.7: Synthesis of $(Ar[N]N)_3\text{Mo}(\mu-\text{CS})\text{Mo}(N[R]Ar)_3$ (2.13)](image-url)
A single crystal X-ray structural determination of bridging thiocarbonyl complex 2.13 is of marginal quality due to a disordered tert-butyl group in the molecule (modeled with 1/2 occupancy at two positions), as well as two disordered diethyl ether molecules in the asymmetric unit, but it clearly shows the atomic connectivity. Selected bond lengths and angles are given in Tables 2.27 and 2.28, positional parameters and U(eq.) are listed in Table 2.29, and an ORTEP diagram is shown in Figure 2.25. The μ-CS linkage is clearly bent at sulfur, with a C-S-Mo(2) angle of 130.5(5)° indicative of lone pair character on sulfur. The sulfur is presumed to act as a 1σ-, 1π-donor of 3 e- to molybdenum, forcing the Mo(IV) center to be low spin d² and diamagnetic. The Mo(1)-C-S angle of 162.7° is approximately linear, indicative of sp hybridization at carbon. The Mo-C bond distance of 1.751(12) Å and the Mo-S bond distance of 2.289(3) Å are similar to those reported for (η⁶-C₆H₅Me)(CO)₂Cr(μ-CS)Cr(CO)₅, where the Cr-C bond distance is 1.747(5) Å and the Cr-S distance is 2.486(2) Å. This chromium complex is the only other structurally characterized end to end bridging thiocarbonyl complex found in a search of the Cambridge Structural Database.

The bond lengths in 2.13 are indicative of Mo-C triple bonding and Mo-S single bonding. The molecule is unique in that it exhibits the two most common arrangements for the N[R]Ar ligand in a single molecule. There is a pseudo-C₃ symmetric half, that containing Mo(1) and the carbon atom, and a pseudo-C₅ symmetric half, that containing Mo(2) and the sulfur atom. The dihedral angles between the Mo-C and N-C vectors are 18.0, 23.0 and 32.5°, while the corresponding angles to the Mo-S vector are 1.0, 38.8 and 50.8°. This type of arrangement seems to be general. Molecules which have a molybdenum in a high formal oxidation state (i.e. no lone pairs or unpaired electrons) like NMo(N[R]Ar)₃,¹⁴ (ON)Mo(N[R]Ar)₃²³ or PMo(N[R]Ar)₃⁹⁰ have pseudo-C₃ propeller arrangements of the anilide ligands. Meanwhile, molecules which have unpaired electrons, like the Mo(V) chalcogenido complexes, or lone pairs have pseudo-C₅ symmetry.
Table 2.27: Selected Bond Distances (Å) for (Ar[R]N)$_3$Mo(μ-CS)Mo(N[R]Ar)$_3$ (2.14).

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Table 2.28: Selected Bond Angles (°) for (Ar[R]N)$_3$Mo(μ-CS)Mo(N[R]Ar)$_3$ (2.14).

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Figure 2.25: Partial ORTEP diagram of \((\text{Ar}[R]N)_3\text{Mo}(\mu-\text{CS})\text{Mo(N[R]Ar)}_3\) (2.14) with ellipsoids at the 30% probability level (two disordered solvent molecules have been removed for clarity).
Extended Hückel calculations performed on the model complex $(\text{H}_2\text{N})_3\text{Mo}(\mu-\text{CS})\text{Mo(\text{NH}_2)_3}$ with coordinates derived from the X-ray structure, give the electronic structure of the $\mu$-CS linkage. The Cartesian coordinates used for the calculations are listed in Table 2.30. CACAO$^{52,53}$ drawings of some pertinent orbitals are shown in Figure 2.26. The second and third HOMOs, of which only one is shown (MO 32), are Mo-C $\pi$ bonding and C-S $\pi^*$, with a weaker Mo-S $\pi$ interaction. This result is consistent with the experimentally observed short Mo-C bond and long C-S bond. The HOMO (MO 31) is best described as an lone pair on sulfur, as expected from the bent structure. The LUMO (MO 30) is largely Mo-S $\pi^*$, while the second and third LUMOs (of which only one is shown, MO 29) are mostly Mo-C $\pi^*$ in character.

Table 2.30: Cartesian Coordinates for $(\text{H}_2\text{N})_3\text{Mo}(\mu-\text{CS})\text{Mo(\text{NH}_2)_3}$ with coordinates derived from X-ray data.

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Figure 2.26: Frontier molecular orbitals calculated for (Ar[R]N$_2$)Mo(μ-CS)Mo(N[R]Ar)$_3$ (2.14). Orbitals 29 and 30 are unoccupied, while orbitals 31 and 32 are filled.
(ix) Diphenyl Diselenide: Synthesis of (PhSe)Mo(N[R]Ar)_3 (2.14)

Addition of one half equivalent Ph_2Se_2 to Mo(N[R]Ar)_3 results in the formation of a brilliant blue-green diamagnetic complex, (PhSe)Mo(N[R]Ar)_3 (2.14), which is isolated in 72% yield, Scheme 2.8. The complex exhibits an extremely broad ^77Se NMR chemical shift of 1006.3 ppm (Δν_1/2 = 600 Hz). This chemical shift falls in the predicted region for alkyl selenides,^71-74 though it is towards the low-field end of the range. The diamagnetism of the molecule suggests that the Mo-Se-C vector is bent, as seen in the Mo-S-C angle in 2.13, but no structural data is available for the selenolate complex.

Scheme 2.8: Synthesis of (PhSe)Mo(N[R]Ar)_3 (2.14)

Section 2.7: Conclusion

This chapter addresses the question of the stability of Mo(V) chalcogenido complexes with N[R]Ar ligation initially raised by the reaction of Mo(N[R]Ar)_3 with N_2O. Theoretical and experimental observations suggest that the Mo-E bond is very strong. Theoretical calculations explain the Jahn-Teller distortion of the chalcogenide complexes from C_3 symmetry to pseudo-C_5 symmetry in the observed structures. The complexes are, in fact, quite stable, but do undergo a C-N bond homolysis at elevated temperatures, resulting in tert-butyl radical elimination and the formation of Mo(VI) chalcogenide imide complexes. A mechanistic analysis of this thermolysis reaction suggests smooth transfer of the unpaired electron into an N-H σ* orbital, causing a rearrangement of the complex and
the formation of a new Mo-N π bond. The reaction, or lack thereof, of a variety of chalcogenido donors with Mo(N[R]Ar)_3 lays the groundwork for chalcogen atom transfer reactions with this system. The potential for Mo(N[R]Ar)_3 to act as a chalcogen atom acceptor is generally high for the donors which have been tested.

Section 2.8: Experimental

2.8.1 General Considerations

General experimental details are as described in Chapter I. Ether was dried according to a procedure by Grubbs. Other solvents were distilled, under nitrogen, from sodium benzophenone ketyl. Toluene which was used for EPR spectroscopy was vacuum transferred from tert-butyl lithium. Mo(N[R]Ar)_3 was prepared by standard procedures. Other chemicals were purified and dried by standard procedures or used as received. Magnetic susceptibilities were measured by NMR spectroscopy. ¹H and ¹³C NMR spectra were recorded on Varian XL-300, Varian Unity-300 or Brucker AC-250 spectrometers. Chemical shifts are reported with respect to internal solvent (7.15 ppm and 128.0 ppm). ²H chemical shifts are reported with respect to external C₆D₆. ⁷⁷Se NMR spectra were recorded on a Varian Unity-300 or a Varian VXR-500 spectrometer and are referenced to Me₂Se (0 ppm) by comparing to external PhSeSePh (CDCl₃, 460 ppm). ¹²⁵Te NMR spectra were recorded on a Varian VXR-500 spectrometer and referenced to Me₂Te (0 ppm) by comparing to external TeCl₄ (HCl/H₂O, 1237 ppm). EPR spectra were recorded on a Brucker ESP-300 spectrometer in sealed quartz tubes in toluene at either ambient temperature or low temperature by using a liquid nitrogen cooled nitrogen stream. Spectra were simulated using the program EPR-NMR. Infrared measurements were carried out on a Bio-Rad FTS 135 spectrometer. Far-IR measurements were carried out on a Mattson Instruments IR-10110 spectrometer. UV-vis spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer. Electrochemical
measurements were carried out at room temperature in a glove box with \(-1 \times 10^{-3}\) M methylene chloride solutions containing saturated \(n\)-Bu$_4$NPF$_6$ as the supporting electrolyte. The standard three electrode system consisted of platinum working and counter electrodes with a silver reference electrode. Platinum electrodes were pretreated by polishing with diamond paste. Potentials are referred to the ferrocene/ferrocenium couple.\textsuperscript{45,95} CHN analyses were performed by Oneida Research Services (Whitesboro, NY) or Microlytics (South Deerfield, MA). Melting points were obtained in sealed glass capillaries and are uncorrected.

\subsection*{2.8.2 SQUID Magnetic Measurements}

Data were acquired as reported in Chapter I using a Quantum Design SQUID magnetometer.\textsuperscript{37} The calculated curves are the best least-squares fits of the observed susceptibility data to either the Curie Law, with the equation \(\chi_\text{M}(\text{obs}) = ((\mu^2)/(7.997584 \times (T)) - C)\), or the Curie Weiss law, with the equation \(\chi_\text{M}(\text{obs}) = ((\mu^2)/(7.997584 \times (T - \theta))) - C\).

\subsection*{2.8.3 Kinetics Measurements}

A sample of OMo(N[R]Ar)$_3$ or SMo(N[R]Ar)$_3$ (ca. 0.02 M in C$_6$H$_6$) was placed in an NMR tube along with a sealed capillary filled with a D$_2$O/THF solution (1:20 by weight). The tube was flame sealed and stored at 4 °C. Constant temperature oil baths were employed for the thermolysis reaction. NMR tubes were placed in the oil bath for a measured time interval, and then immediately placed in an ice water slurry. The decay of starting material was measured by comparing integrals of peaks in the $^2$H NMR spectrum. The oxo peak was integrated from 9.2 ppm to 5.2 ppm, the sulfido peak was integrated from 7.8 to 4.8 ppm, and the D$_2$O peak was integrated from 3.6 to 4.6 ppm (relative to external C$_6$D$_6$). The tubes were then replaced in the oil bath and this process was repeated for 3 to 4 half lives. Plots of [oxo (or sulfido) area]/[D$_2$O area] versus time were obtained.
and fit to the equation \( Y = M_1 + M_2 \exp(-M_3 \cdot X) \). Alternatively, linear fits could be obtained from plots of \( \ln(\text{relative area}) \) versus time. The measured first order rate constants \((M_3)\) are reported with their respective 95% confidence intervals. Activation parameters were obtained from the relation of the derived first order rate constants with temperature using the following equations: 
\[
\ln(k_r \cdot T^{-1}) = -\Delta H^\ddagger + R \cdot T^{-1} + C; \quad \text{and} \quad \Delta S^\ddagger = \Delta H^\ddagger \cdot T^{-1} + R \cdot \ln(h \cdot k_r \cdot k^{-1} \cdot T^{-1})
\]
where \( h \) is Planck's constant, \( k \) is Boltzmann's constant and \( T \) is absolute temperature.

2.8.4 Synthesis of Complexes

(i) \( \text{OMo(N[R]Ar)}_3 \) (2.2): \( \text{Mo(N[R]Ar)}_3 \) (2.1, 0.5844 g, 0.9090 mmol) was dissolved in ether (15 mL) and pyridine-\( N \)-oxide (0.1014 g, 0.9467 mmol) was added. The slurry was stirred for 3.5 hours, at which time all the oxidant had dissolved and the solution had turned dark brown. The solvent was removed, the product was extracted with fresh ether and the solution was filtered. Crystallization from ether yielded dark brown faceted crystals (0.4311 g, 0.6543 mmol, 72%). M.p. 134-135 °C (dec.). \( ^2 \text{H NMR (46 MHz, toluene): } \delta = 7.62; \Delta v_{1/2} = 30 \text{ Hz.} \) \( ^1 \text{H NMR (300 MHz, C}_6\text{D}_6): \delta = \sim 7.2 \) (br s, 9H, C(CD\(_3\))\(_2 CH_3\)), 0.0895 (br s, 18H, ArMe). IR (benzene/KBr, 2 cm\(^{-1}\)): \( \nu_{\text{Mo-O}} = 891 \text{ cm}^{-1}. \) UV/Vis (ether): \( \lambda_{\text{max}}(\epsilon) = 212(53000). \) EPR (toluene, 25 °C): \( g = 1.96, \)
\( A(95/97\text{Mo}) = 35.7 \text{ G; (toluene, 101 K): } g_1 = 1.990, g_2 = 1.967, g_3 = 1.937. \) MS (70 eV): \( m/z(\%): 654.5(3.8)[M^+]. \) \( \mu_{\text{eff}} \) (300 MHz, C\(_6\)D\(_6\), 22.6 °C): 2.19 \( \mu_B. \) SQUID (5-300K): \( \mu = 1.664 \mu_B. \) CV (CH\(_2\)Cl\(_2\)/Bu\(_4\)NPF\(_6\)): \( E_{1/2} = -0.92 \text{ V.} \) Anal. Calcd. for C\(_{36}\)H\(_{39}\)D\(_{15}\)MoN\(_3\)O: C, 65.93; H, 8.30; N, 6.41. Found: C, 66.22; H, 8.50; N, 6.19.

(ii) \( \text{SMo(N[R]Ar)}_3 \) (2.3): \( \text{Mo(N[R]Ar)}_3 \) (2.1, 0.4303 g, 0.6693 mmol) in ether (6 mL) was added to a slurry of S\(_8\) (0.0322 g, 0.1255 mmol, 1.5 eq) in ether (5 mL) causing a rapid color change to purple and then brown after about five minutes. The reaction was
stirred overnight and the ether was removed in vacuo. The product was extracted with pentane, the solution was filtered, and crystals were obtained from ether (3 mL) at -35 °C (0.2865 g, 0.4245 mmol, 63%). M.p. 110-112 °C (dec.). 2H NMR (46 MHz, ether): δ = 6.545; Δν1/2 = 22.0 Hz. 1H NMR (300 MHz, C6D6): δ = ~6.0 (br s, 9H, C(CD3)2CH3), ~3.1 (br s, 18H, ArMe). IR (benzene/KBr, 2 cm⁻¹): νMo-S = 491 cm⁻¹. EPR (toluene, 25 °C): g = 1.96 A(95,97Mo) = 28.5 G; (toluene, 107 K): g1 = 1.996, A1(95/97Mo) = 25 G, g2 = 1.970, g3 = 1.922, A3(95/97Mo) = 54 G. MS (70 eV): m/z (%): 671 (0.22)[M+]. μeff (300 MHz, C6D6, 22.3 °C): 2.21 μB. SQUID (5-300K): μ = 1.630 μB. CV (CH2Cl2/Bu4NPF6): E1/2 = -0.73 V. Anal. Calcd. for C36H42D12MoN3S: C, 64.64; H, 8.14; N, 6.28. Found: C, 64.94; H, 8.31; N, 6.23.

(iii) SeMo(N[R]Ar)3 (2.4): Mo(N[R]Ar)3 (2.1, 0.5008 g, 0.7790 mmol) and Se (0.0810 g, 0.790 mmol) were combined in ether (10 mL) and the resulting mixture was stirred for 11 hours. The solution was filtered to remove excess Se and the filtrate was concentrated. Three crops of crystals were collected from ether at -35 °C (0.4519 g, 0.6260 mmol, 80.4%). M.p. 128-130 °C. 2H NMR (46 MHz, Et2O): δ = 7.036; Δν1/2 = 30.7 Hz. 1H NMR (300 MHz, C6D6): δ = ~6.5 (br s, 9H, C(CD3)2CH3), -1.412 (br s, 18H, ArMe). IR (benzene/polyethylene, 2 cm⁻¹): νMo-Se = 342 cm⁻¹. EPR (toluene, 25 °C): g = 1.97, A(95/97Mo) = 30.5 G; (toluene, 98 K): g1 = 2.030, A1(95/97Mo) = 29 G, g2 = 1.986, g3 = 1.899, A3(95/97Mo) = 48 G. UV/Vis (Ether): λ(ε) = 403(6270); 487(2410). MS (70 eV): m/z (%): 658.2(18.11)[M+ - d6-tert-Bu]. SQUID (5-300 K): μ = 1.75 μB; θ = -1.45 K. CV (CH2Cl2/Bu4NPF6): E1/2 = -0.64 V. Anal. Calcd. for C36H36D18MoN3Se: C, 59.90; H, 7.54; N, 5.82. Found: C, 60.25; H, 7.41; N, 5.68.

(iv) TeMo(N[R]Ar)3 (2.5): Mo(N[R]Ar)3 (2.1, 0.5035 g, 0.7832 mmol) and Te (0.1188 g, 0.9310 mmol) were mixed in ether (10 mL). PEt3 (20 μl, 0.14 mmol, 0.17 eq) was then added and the solution was stirred for 18 hours. The solution gradually turned a
dark brown color. The ether was removed in vacuo, the product was extracted with THF, and the extract was filtered. The product was recrystallized from ether (ca. 25 mL) at -35 °C (2 crops, 0.4422 g, 0.5739 mmol, 73%). M.p. 127-128 °C (dec.). 2H NMR (46 MHz, ether): δ = 8.120; Δν1/2 = 22.9 Hz. 1H NMR (300 MHz, C6D6): δ = ~8 (br s, 9H, NC(CD3)2CH3), -1.9 (br s, 18H, ArMe). IR (benzene/polyethylene, 2 cm⁻¹): νMo-Te = 286 cm⁻¹. EPR (toluene, 25 °C): g = 1.977; (toluene, 105 K): g₁ = 2.130, A₁(95/97Mo) =28 G, g₂ = 1.970, A₂(95/97Mo) = 24 G, g₃ = 1.850, A₃(95/97Mo) = 48 G. UV-Vis (ether): λmax(ε) = 486(6314). MS (70 eV): m/z(%): 707.3(38.24)[M+ -d₆-tert-Bu]. SQUID (5-180 K): χ = 1.86 μB; θ = -5.1 K. CV (CH2Cl2/Bu4NPF6): E1/2 = -0.63 V. Anal. Calcd. for C36H42D12MoN3Te: C, 56.12; H, 7.06; N, 5.45. Found: C, 56.50; H, 7.33; N, 5.17.

(v) OMo(NAr)(N[Ar]Ar)₂ (2.6): OMo(N[Ar]Ar)₃ (2.2, O.4422 g, 0.6879 mmol) was heated at 65 °C in benzene (10 mL) until the dark brown color faded to a much lighter yellow (ca. 5 days). Solvent was removed in vacuo yielding a yellow oil in quantitative yield. Proton NMR spectroscopy showed it to be approximately 85-90% pure, contaminated with HN[Ar]Ar. 1H NMR (300 MHz, C6D6): δ = 6.912 (s, 4H, orthos); 6.885 (s, 2H, paras); 6.712 (s, 2H, imide orthos); 6.52 (s, 1H, imide para); 2.139 (s, 12H, ArMe); 2.026 (s, 6H, imide ArMe); 1.340 (s, 6H, C(CD3)2CH3). 13C NMR (75 MHz, CDCl3): δ = 156.365 (s, NAr ipso); 150.510 (s, N[Ar]Ar ipso); 137.712 (s, NAr meta); 137.560 (s, N[Ar]Ar meta); 128.304 (d, JCH = 158.2, N[Ar]Ar ortho); 127.373 (d, JCH = 155.0, NAr ortho); 120.702 (d, JCH ~160, NAr para); 120.008 (d, JCH = 160.7, N[Ar]Ar para); 60.555 (s, NC(CH3)2CD3); 31.496 (q, JCH = 125.9, C(CD3)2CH3); 30.990 (m, NC(CD3)2CH3); 21.237 (q, JCH = 126.1, N[Ar]Ar ArMe); 21.14 (q, JCH ~126, NAr ArMe). IR (benzene/KBr, 2 cm⁻¹): νMo-O = 913 cm⁻¹. MS (70 eV): m/z(%): 594.3(1.77)[M⁺]. HRMS (70 ev): calcd. mass (597.3370); found mass (597.3371).
(vi) **PhCHNAr** for spectroscopic characterization: Benzaldehyde (8.12 g, 76.5 mmol) and 3,5-dimethylaniline (10.23 g, 84.43 mmol) were mixed in benzene (30 mL) and heated to reflux for 6 hours. Water was collected with a Dean-Stark trap (1.2 mL, .87 eq) yielding a thick yellow oil (16.22 g) which was 95% pure by $^1$H NMR spectroscopy. $^1$H NMR (300 MHz, C$_6$D$_6$): $\delta = 8.284$ (s, 1H, N=CHC$_6$H$_5$); 7.923 (m, 2H, phenyl); 7.196 (m, 3H, phenyl); 6.946 (s, 2H, aryl ortho); 6.786 (s, 1H, aryl para); 2.223 (s, 6H, ArMe). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 159.934$ (d, $J_{CH} = 158.2$, aryl para); 152.176 (d, $^2J_{CH} = 9.7$, ipso); 138.795 (q, $^2J_{CH} = 5.8$, aryl meta); 136.446 (s, ipso); 131.288 (dt, $^1J_{CH} = 160.6$, $^2J_{CH} = 7.7$, phenyl para); 128.800 (d, $J_{CH} = 163.8$, phenyl meta); 127.729 (d, $J_{CH} = 155.2$, ortho); 118.753 (d, $J_{CH} = 157.5$, ortho); 113.204 (d, $J_{CH} \sim 170$, N=CHC$_6$H$_5$); 21.3884 (q, $J_{CH} = 126.5$, ArMe). MS (70 eV): $m/z$(%): 209.2(100)[M$^+$]. HRMS (70 ev): calcd. mass (209.1205); found mass (209.1204).

(vii) **SMo(NAr)(N[R]Ar)$_2$ (2.7):** SMo(N[R]Ar)$_3$ (2.3, 0.1640 g, 0.2430 mmol) was dissolved in benzene (10 mL) and heated at 62.5 °C in a sealed bomb for 25 hours. The solution changed from dark brown to reddish brown. The benzene was removed in vacuo and an orange powder was obtained by recrystallization from Et$_2$O (0.1250 g, 0.2043 mmol, 84.1%). M.p. 183-4 °C. $^1$H NMR (300 MHz, C$_6$D$_6$): $\delta = 7.204$ (s, 2H, N[R]Ar para); 7.15 (s, 4H, N[R]Ar orthos); 6.710 (s, 2H, NAr orthos); 6.587 (s, 1H, NAr para); 2.145 (s, 12H, N[R]Ar ArMe); 2.041 (s, 6H, NAr ArMe); 1.310 (s, 6H, C(CD$_3$)$_2$CH$_3$). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 157.545$ (s, NAr ipso); 151.53 (s, N[R]Ar ipso); 138.27 (s, NAr meta); 137.87 (s, N[R]Ar meta); 129.77 (d, $J_{CH} = 150.6$ Hz, ortho); 128.60 (br d, $J_{CH} = 156.6$ Hz, ortho); 127.711 (d, $J_{CH} = 155.6$ Hz, para); 119.87 (d, $J_{CH} = 162.3$ Hz, para); 62.385 (s, C(CD$_3$)$_2$CH$_3$); 31.957 (q, $J_{CH} = 126.5$ Hz, C(CD$_3$)$_2$CH$_3$); 31.447 (m, C(CD$_3$)$_2$CH$_3$); 21.481 (q, $J_{CH} = 126.7$ Hz, NAr and N[R]Ar ArMe). IR (benzene/KBr, 2 cm$^{-1}$): $\nu_{Mo-S} = 506$ cm$^{-1}$. MS (70 eV): $m/z$(%):
613(44.1)[M+]. Anal. Calcd. for C\textsubscript{32}H\textsubscript{33}D\textsubscript{12}MoN\textsubscript{3}S: C, 62.82; H, 7.41; N, 6.87. Found: C, 63.11; H, 7.56; N, 6.76.

(viii) SeMo(NAr)(N[R]Ar)\textsubscript{2} (2.8): SeMo(N[R]Ar)\textsubscript{3} (2.4, 0.6377 g, 0.8834 mmol) and benzene (30 mL) were loaded into a sealable glass reaction bomb which was then evacuated to autogenic pressure. The mixture was heated at 65 °C for 22 hours at which point the solution had changed from the dark brown initial color to a red-orange color. The benzene was removed in vacuo, and the product was precipitated from ether (~15 mL) at -35 °C as a finely divided orange brown powder in two crops (0.3733 g, 0.5667 mmol, 64%). M.p. 201.5-202 °C. \textsuperscript{1}H NMR (300 MHz, C\textsubscript{6}D\textsubscript{6}): δ = 7.304 (2H, aryl); 7.15 (4H, N[R]Ar orthos); 6.713 (2H, aryl); 6.601 (1H, NAr para); 2.145 (12H, N[R]Ar ArMe); 2.052 (6H, NAr ArMe); 1.290 (6H, C(CD\textsubscript{3})\textsubscript{2}CH\textsubscript{3}). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}): δ = 157.243 (s, NAr ipso); 150.940 (s, N[R]Ar ipso); 138.027 (q, J\textsubscript{CH} = 6.14 Hz, NAr meta); 137.613 (q, J\textsubscript{CH} = 4.03 Hz, N[R]Ar meta); 129.454 (d, J\textsubscript{CH} = 153.1 Hz, aryl); 128.612 (br m, N[R]Ar ortho); 127.438 (d, J\textsubscript{CH} = 155.1 Hz, aryl); 119.225 (d, J\textsubscript{CH} = 163.2 Hz, aryl); 62.20 (s, C(CD\textsubscript{3})\textsubscript{2}CH\textsubscript{3}); 31.517 (q, J\textsubscript{CH} = 126.6 Hz, C(CD\textsubscript{3})\textsubscript{2}CH\textsubscript{3}); 31.0 (m, C(CD\textsubscript{3})\textsubscript{2}CH\textsubscript{3}); 21.101 (q, J\textsubscript{CH} = 126.2 Hz, NAr and N[R]Ar ArMe). \textsuperscript{77}Se NMR (57.292 MHz, CDCl\textsubscript{3}, pw = 15 μsec, d\textsubscript{1} = 1 sec, 16000 scans): δ = 1923.4; Δν\textsubscript{1/2} = 46.2 Hz. IR (benzene/polyethylene, 2 cm\textsuperscript{-1}): ν\textsubscript{Mo-Se} = 355 cm\textsuperscript{-1}. UV/Vis (ether): λ\textsubscript{max} (ε) = 292(17700 M\textsuperscript{-1} cm\textsuperscript{-1}). MS (70 eV): m/z (%): 660(5)[M+]. Anal. Calcd. for C\textsubscript{32}H\textsubscript{33}D\textsubscript{12}MoN\textsubscript{3}Se: C, 58.35; H, 6.89; N, 6.38. Found: C, 58.79 H, 6.94; N, 6.24.

(ix) TeMo(NAr)(N[R]Ar)\textsubscript{2} (2.9): TeMo(N[R]Ar)\textsubscript{3} (2.5, 0.5085 g, 0.6600 mmol) was dissolved in benzene (25 mL) in a reaction bomb which was then evacuated to autogenic pressure. The solution was heated at 65 °C for 5 hours; no color change was observed. The benzene was removed in vacuo leaving a fine dark red-brown powder (0.3712 g, 0.5248 mmol, 80%) which was contaminated with about 5% HN[R]Ar. The

(169) References begin on page 184
complex could be recrystallized from ether in low yield (~40%). M.p. 194.5-195.5 °C. 

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.3$ (br s, 2H, N[R]Ar ortho a); 7.032 (s, 2H, aryl); 6.916 (s, 1H, NAr para); 6.886 (s, 2H, aryl); 6.4 (br s, 2H, N[R]Ar ortho b); 2.350 (s, 6H, NAr ArMe); 2.278 (s, 12H, N[R]Ar ArMe); 1.131 (s, C(CD$_3$)$_2$CH$_3$). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 157.624$ (s, N Ar ipso); 149.799 (N[R]Ar ipso); 138.412 (q, $^2$J$_{CH} = 5.8$ Hz, NAr meta); 137.947 (q, $^2$J$_{CH} = 5.7$ Hz, N[R]Ar meta); 131.2 (br d, $J_{CH} = 125$ Hz, N[R]Ar ortho a); 129.548 (d, $J_{CH} = 155$ Hz, aryl); 127.776 (d, $J_{CH} = 155$ Hz, aryl); 127.0 (br d, $J_{CH} = 125$ Hz, N[R]Ar ortho b); 119.116 (d, $J_{CH} = 162$ Hz, aryl); 62.6735 (s, C(CD$_3$)$_2$CH$_3$); 31.4322 (q, $J_{CH} = 126.2$ Hz, C(CD$_3$)$_2$CH$_3$); 30.9061 (m, C(CD$_3$)$_2$CH$_3$); 21.2830 (q, $J_{CH} = 127.1$ Hz, N[R]Ar ArMe); 21.2226 (q, $J_{CH} = 126.6$ Hz, NAr ArMe).

$^{125}$Te NMR (158 MHz, CDCl$_3$, pw = 12 μsec, $d_1 = 1$ sec, 28000 scans): $\delta = 2459.3$; $\Delta V_{1/2} = 250$ Hz. IR (benzene/polyethylene, 2 cm$^{-1}$): $\nu_{Mo-Te}$ = 291 cm$^{-1}$. UV/Vis (ether): $\lambda_{max}(\epsilon) = 327(13700)$. MS (70 eV): $m/z(\%)$: 705.2(70)[M$^+$]. Anal. Calcd. for C$_{32}$H$_{33}$D$_{12}$Mo$_3$N$_7$Te: C, 54.34; H, 6.41; N, 5.94. Found: C, 51.30; H, 6.42; N, 5.39.

(x) [OMo(N[R]Ar)$_3$]OTf (2.10): OMo(N[R]Ar)$_3$ (2.2, 0.0996 g, 0.1512 mmol) in ether was added to a slurry of FcOTf (0.0512 g, 0.1528 mmol) in ether to give a total volume of 5 mL. The solution was stirred for 15 hours, at which point the solution was brown and an orange brown precipitate was observed. The solid was collected on a frit and washed with ether; the washings were colorless (0.0865 g, 0.1071 mmol, 71%). The complex decomposed fairly rapidly in solvents in which it was soluble, precluding purification by recrystallization. The reported analysis is of isolated and washed material. M.p. 100-101 °C (dec). 

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.094$ (s, 3H, para); 5.5 (br s, 6H, ortho); 2.221 (br s, 18H, ArMe); 1.428 (br s, 9H, C(CD$_3$)$_2$CH$_3$). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta = -83.417$. $^{13}$C NMR (125 MHz, CDCl$_3$): 148.083, 139.397, 131.501, 125.394 (ipso), 70.547 (C(CD$_3$)$_2$CH$_3$), 31.227 (C(CD$_3$)$_2$CH$_3$), 30.739 (C(CD$_3$)$_2$CH$_3$), 21.56 (ArMe). IR (Nujol/KBr 2 cm$^{-1}$): 1601.8, 1266.1(ionic triflate), 79
1221.8, 1146.4, 1111.1, 1031.1 (ionic triflate), \textsuperscript{79} \text{971.8} (v_{\text{Mo-O}}), 698.8, 637.3, 570.7, 474.0. Anal. Calcd. for C\textsubscript{37}H\textsubscript{36}D\textsubscript{18}F\textsubscript{3}MoN\textsubscript{3}O\textsubscript{4}S: C, 55.00; H, 6.74; N, 5.20. Found: C, 56.67; H, 6.94; N, 4.89.

(xi) \[\text{OMo(N[R]Ar)}_3\] [I] (2.11): To a solution of OMo(N[R]Ar)\textsubscript{3} (2.2, 0.0999 g, 0.1516 mmol) in ether was added iodine (0.0199 g, 0.0784 mmol, 0.52 eq) in ether to give a total volume of 5 mL. An orange precipitate formed immediately. The solution was stirred for 15 hours, at which point the solution was colorless. The orange solid was collected on a frit and washed with ether; the washings were colorless (0.1042 g, 0.1326 mmol, 87.5\%). The complex decomposed fairly rapidly in solvents in which it was soluble, precluding characterization by \textsuperscript{13}C NMR spectroscopy and purification by recrystallization. The reported analysis is of isolated and washed material. M.p. 95-97 °C (dec). \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta = 7.079\) (s, 3H, para); 5 (br s, 6H, ortho); 2.214 (br s, 18H, ArMe); 1.428 (br s, 9H, C(CD\textsubscript{3})\textsubscript{2}CH\textsubscript{3}). IR (Nujol/KBr 2 cm\textsuperscript{-1}): 1602.1, 1582.8, 1285.0, 1147.6, 1110.8, 1051.3, 1030.6, 974.5(v_{\text{Mo-O}}), 939.1, 886.3, 701.1, 696.2. Anal. Calcd. for C\textsubscript{36}H\textsubscript{36}D\textsubscript{18}IMoN\textsubscript{3}O: C, 55.03; H, 6.93; N, 5.35. Found: C, 54.17; H, 6.99; N, 5.14.

(xii) \[\text{O}_2\text{Mo(N[R]Ar)}_2\] (2.12): OMo(N[R]Ar)\textsubscript{3} (2.2, 0.2198 g, 0.3336 mmol) was dissolved in ether (15 mL) in a reaction bomb and dioxygen (45.96 mL, 150 torr, 0.3712 mmol, 1.11 eq) was added. After 80 minutes, the reaction mixture was dark brown. After 14 hours, the reaction mixture was a rich dark red brown. An aliquot was examined by \textsuperscript{1}H NMR spectroscopy, showing the presence of O\textsubscript{2}Mo(N[R]Ar)\textsubscript{2} and HN[R]Ar in a 1:2 molar ratio as the major products. Examination of the reaction mixture by \textsuperscript{1}H NMR spectroscopy showed the consumption of all paramagnetic material. The solvent was removed \textit{in vacuo} and the resulting oily solid was dissolved in a minimum of hexane (ca. 2 mL). A dark brown solid was collected, which could be recrystallized from hexane.
yielding a dark golden yellow solid (0.0410 g, 0.0832 mmol, 25%). M.p. 129-130 °C.  
\(^1\)H NMR (300 MHz, C\(_6\)D\(_6\)): \(\delta = 6.761\) (s, 4H, ortho); 6.666 (s, 2H, ortho); 2.074 (s, 12H, ArMe); 1.227 (s, 6H, CCH\(_3\)(CD\(_3\))\(_2\)). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 148.390\) (s, ipso); 138.369 (s, meta); 128.855 (d, \(J_{CH} = 154.3\) Hz, para); 127.602 (d, \(J_{CH} = 158.0\) Hz, ortho); 61.54 (s, CCH\(_3\)(CD\(_3\))\(_2\)); 30.976 (q, \(J_{CH} = 126.4\) Hz, CCH\(_3\)(CD\(_3\))\(_2\)); 30.611 (m, CCH\(_3\)(CD\(_3\))\(_2\)); 21.476 (q, \(J_{CH} = 126.4\) Hz, ArMe). IR (benzene, 2 cm\(^{-1}\)): \(v_{Mo-O} =\) 943, 920 cm\(^{-1}\). MS (70 eV): \(m/z\)%: 491.8(17.6)[M\(^+\)]. Anal. Calcd. for C\(_{24}\)H\(_{24}\)D\(_{12}\)MoN\(_2\)O\(_2\): C, 58.52; H, 7.37; N, 5.69. Found: C, 58.74; H, 7.36; N, 5.64.

(xiii) (N[R]Ar\(_3\))Mo(\(\mu\)-CS)Mo(N[R]Ar\(_3\)) (2.13): CS\(_2\) (50 \(\mu\)L, 0.5187 mmol, 0.66 eq) was added to a solution of Mo(N[R]Ar\(_3\)) (2.1, 0.5034 g, 0.7831 mmol) in ether (25 mL). The solution rapidly turned a dark greenish brown color. \(^2\)H NMR spectroscopy at this point showed a 1:1 molar ratio of the terminal sulfide complex and the bridging thiocarbonyl complex. Solvent was removed \textit{in vacuo} leaving a foamy solid which was dissolved in ether (~3 mL). Upon standing for about 30 seconds, a dark solid began to precipitate. More ether was added to fully dissolve the solid (~10 mL), and the solution was stored at -35 °C. The first crop of solid was >95% diamagnetic but additional crops were contaminated with sulfide 2.3 (as determined by \(^2\)H NMR spectroscopy) (0.1640 g, 0.1233 mmol, 47%). M.p. 139-140 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 6.711\) (s, 3H, para(a)); 6.5681 (s, 3H, para(b)); 6.455 (br s, 6H, ortho(a)); 5.718 (s, 6H, ortho(b)); 2.199 (s, 18H, ArMe(a)); 2.112 (s, 18H, ArMe(b)); 1.285 (br s, 18H, C(CD\(_3\))\(_2\)CH\(_3\)). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 293.51\) (br s, \(\mu\)-CS); 153.42 (br s, ipso(a)); 151.10 (s, ipso(a)); 136.20 (m, meta(a)); 136.00 (m, meta(b)); 131.02 (d, \(J = 158.7\) Hz, aryl); 127.67 (d, \(J = 158.4\) Hz, aryl); 126.96 (d, \(J = 153.8\) Hz, aryl); 126.39 (d, \(J = 152.9\) Hz, aryl); 63.57 (br s, CCH\(_3\)(CD\(_3\))\(_2\)(a)); 61.30 (s, CCH\(_3\)(CD\(_3\))\(_2\)(b)); 33.69 (q, \(J = 125.4\) Hz, C(CD\(_3\))\(_2\)CH\(_3\)(a)); 33.01 (m, C(CD\(_3\))\(_2\)CH\(_3\)(a)); 31.99 (q, \(J = 125.5\) Hz, C(CD\(_3\))\(_2\)CH\(_3\)(b)); 31.33 (m, C(CD\(_3\))\(_2\)CH\(_3\)(b)); 21.69 (q, \(J = 125.9\) Hz, ArMe(a)); 21.60 (q, \(J = 125.7\) Hz, (172) References begin on page 184
ArMe(b)). UV/Vis (ether): \( \lambda(\epsilon) = 363(27300); 438(9660); 582(3090) \). Anal. Calcd. for C\(_{73}H_{72}D_{36}Mo2N\_6S: \) C, 65.93; H, 8.19; N, 6.32. Found: C, 64.74; H, 8.18; N, 6.18.

(xiv) (PhSe)Mo(N[R]Ar\(_3\)) (2.14): Diphenyldiselenide (0.1273 g, 0.4078 mmol, 0.52 eq) was dissolved in ether (10 mL) and added to a solution of Mo(N[R]Ar\(_3\)) (2.1, 0.5063 g, 0.7876 mmol) in ether (20 mL). The solution rapidly changed to a dark green-blue color. The solvent was removed in vacuo, and the resulting blue-green solid was recrystallized from ether (0.4520 g, 0.5657 mmol, 71.8%). M.p. 141-142 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 8.09 \) (d, \( J = 7.5 \) Hz, 2H, Ar); 7.38 (t, \( J = 7.4 \) Hz, 2H, Ar); 7.29 (t, \( J = 7.2 \) Hz, 1H, Ar); 6.48 (s, 3H, N[R]Ar para); 6.05 (br s, 6H, N[R]Ar ortho); 2.10 (s, 18H, ArMe); 1.25 (s, 9H, C(CD\(_3\))\(_2\)CH\(_3\)). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta = 152.03 \) (s, N[R]Ar ipso); 148.5 (s, ipso); 136.04 (s, N[R]Ar ortho); 133.72 (d, \( J = 159.8 \) Hz, aryl); 128.33 (d, \( J = 158.5 \) Hz, aryl); 127.57 (br d, aryl); 126.62 (d, \( J = 154.4 \) Hz, aryl); 125.35 (d, \( J = 159.8 \) Hz, aryl); 62.67 (s, C(CD\(_3\))\(_2\)CH\(_3\)); 31.11 (q, \( J = 127.6 \) Hz, C(CD\(_3\))\(_2\)CH\(_3\)); 30.62 (m, C(CD\(_3\))\(_2\)CH\(_3\)); 21.652 (q, \( J = 126.2 \) Hz, ArMe). \(^{77}\)Se NMR (95.4 MHz, CDCl\(_3\), pw = 8 µsec, d\(_1\) = 1 sec, 14400 scans): \( \delta = 1006.3; \Delta v_{1/2} \sim 600 \) Hz. UV/Vis (ether): \( \lambda(\epsilon) = 255(5000); 421(5970); 582(2490) \). Anal. Calcd. for C\(_{42}H_{41}D_{18}MoN\_3Se: \) C, 63.14; H, 7.44; N, 5.26. Found: C, 63.38; H, 7.67; N, 5.28.

2.8.5 Other Reactions

(i) Reaction of 2.1 with SO\(_2\): Mo(N[R]Ar\(_3\)) (0.0219 g, 0.0341 mmol) was dissolved in ether (5 mL) in an evacuated reaction bomb. SO\(_2\) (0.50 mL, 0.020 mmol, 0.58 equiv) was added via syringe, causing a rapid color change to dark brown. Examination of the reaction mixture by \(^2\)H NMR spectroscopy showed the presence of the oxo complex 2.2 (\( \delta = 7.41 \)) and the sulfido complex 2.3 (\( \delta = 6.46 \) ppm) in

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approximately a 2:1 ratio. The peaks were not baseline resolved, preventing an accurate integral to be obtained.

(ii) Reaction of 2.1 with NO₂: Mo(N[R]Ar)₃ (0.0203 g, 0.0316 mmol) was dissolved in ether (5 mL) in an evacuated reaction bomb. NO₂ (0.42 mL, 0.017 mmol, 0.54 equiv) was added via syringe, causing a color change to pale tan-brown over a 10 minute period. Examination of the reaction mixture by ²H NMR spectroscopy showed the presence of the oxo complex 2.2 (δ = 7.57) and diamagnetic material (δ = 2.16) in a 1:1 molar ratio. The solvent was removed in vacuo and the reaction mixture was examined by ¹H NMR spectroscopy, clearly showing that the only diamagnetic product was (ON)Mo(N[R]Ar)₃.

(iii) Reaction of 2.1 with OSMe₂: Mo(N[R]Ar)₃ (0.0201 g, 0.0313 mmol) was dissolved in ether (3 mL) and OSMe₂ (2.5 µL, 0.0352 mmol, 1.1 equiv) was added. After 10 minutes, the reaction mixture was dark brown in color. Examination of the reaction mixture by ²H NMR spectroscopy showed Mo(N[R]Ar)₃ 2.1 (δ = 63.95) and OMo(N[R]Ar)₃ 2.2 (δ = 7.59) in a 1:9 molar ratio.

(iv) Reaction of 2.1 with OPPh₃: Mo(N[R]Ar)₃ (0.0400 g, 0.0622 mmol) and OPPh₃ (0.0260 g, 0.0934 mmol, 1.5 equiv) were dissolved in toluene (5 mL) under an atmosphere of Ar and stored at -35 °C for 24 hours. The solution was then warmed to room temperature. Analysis of the reaction mixture by ²H NMR spectroscopy showed the presence of Mo(N[R]Ar)₃ (δ = 62.99), OMo(N[R]Ar)₃ (δ = 7.1) and diamagnetic material (δ = 1.53) in a 5:2:1 ratio. Analysis of the reaction mixture by ³¹P NMR showed the presence of OPPh₃ (δ = 25.00). The reaction was stirred at room temperature for 24 hours, at which point the ²H NMR spectrum showed the presence of Mo(N[R]Ar)₃ (δ = 63.27), an unknown paramagnetic material (δ = 23.46), OMo(N[R]Ar)₃ (δ = 7.22) and
diamagnetic material ($\delta = 1.49$) in a 3:1:1:1 ratio. The $^{31}$P NMR again only showed the presence of OPPh$_3$ ($\delta = 25.00$). Analysis of the reaction mixture by $^1$H NMR showed primarily HN[R]Ar.

(v) Reaction of 2.1 with CO$_2$: Mo(N[R]Ar)$_3$ (0.0500 g, 0.0778 mmol) was dissolved in ether (ca. 5 mL) in a reaction bomb and CO$_2$ (ca. 25 mL, 1 atm, 1.0 mmol, 13 equiv) was added. After 1 hour at 0 °C, the reaction mixture was examined by $^2$H NMR spectroscopy, showing Mo(N[R]Ar)$_3$ ($\delta = 64$) and OMo(N[R]Ar)$_3$ ($\delta = 7.5$) in an 18:1 molar ratio. The reaction was repeated and allowed to react at 0 °C for 24 hours. Examination of the reaction mixture by $^2$H NMR showed Mo(N[R]Ar)$_3$ ($\delta = 63.6$), (OC)Mo(N[R]Ar)$_3$ ($\delta = 10.0$),$^{97}$ OMo(N[R]Ar)$_3$ and other material ($\delta = 7.8$) and diamagnetic material ($\delta = 2.13$) in approximately a 20:1:10:20 ratio.

(vi) Reaction of 2.1 with tert-BuNC: Mo(N[R]Ar)$_3$ (0.0204 g, 0.0317 mmol) was dissolved in ether (3 mL) and tert-BuNC (3.5 µL, 0.0309 mmol, 0.97 equiv) was added causing a rapid color change to dark red/brown. Analysis of the reaction mixture by $^2$H NMR spectroscopy showed a peak at 11.1 ppm corresponding to the adduct Mo(CN-tert-Bu)(N[R]Ar)$_3$.

(vii) Reaction of 2.1 with tert-BuNCO: Mo(N[R]Ar)$_3$ (0.0217 g, 0.0338 mmol) was dissolved in tert-BuNCO (0.75 g) and the reaction mixture was stirred for 24 hours. Examination of the reaction mixture by $^2$H NMR spectroscopy showed Mo(N[R]Ar)$_3$ ($\delta = 64.7$), paramagnetic material ($\delta = 29.4$ and 26.4), Mo(CN-tert-Bu)(N[R]Ar)$_3$ ($\delta = 11.6$), OMo(N[R]Ar)$_3$ ($\delta = 7.8$) and diamagnetic material ($\delta = 2.9$-3) in a 60:1:5:1:3:10 ratio.

(viii) Reaction of 2.1 with O$_2$SMe$_2$: Mo(N[R]Ar)$_3$ (0.0211 g, 0.0328 mmol) was dissolved in THF (2 mL) and O$_2$SMe$_2$ (0.0030 g, 0.0319 mmol, 0.97 equiv) was added.
The reaction mixture was stirred for 48 hours, at which point is was examined by \(^2\text{H} \) NMR spectroscopy, showing Mo(N[R]Ar)\(_3\) (\(\delta = 64.3\)) and diamagnetic material (\(\delta = 2.2\) to 1.8) in a 5:1 ratio, along with a tiny amount of OMo(N[R]Ar)\(_3\) (\(\delta = 7.5\)).

(ix) **Reaction of 2.2 with PPh\(_3\)**: OMo(N[R]Ar)\(_3\) (0.0480 g, 0.0729 mmol) was dissolved in toluene and PPh\(_3\) (0.0400 g, 0.153 mmol, 2.1 equiv) was added. The reaction was stirred for 24 hours, at which point examination by \(^2\text{H} \) NMR spectroscopy showed only the starting oxo complex. Examination of the reaction by \(^{31}\text{P} \) NMR spectroscopy showed only PPh\(_3\) (\(\delta = -4.41\)).

(x) **Reaction of 2.2 with OSMMe\(_2\)**: OMo(N[R]Ar)\(_3\) (0.0312 g, 0.0474 mmol) was dissolved in ether (5 mL) and OSMMe\(_2\) (8.5 mL, 0.12 mmol, 2.5 equiv) was added. The reaction was stirred for 20 hours, at which point it was examined by \(^2\text{H} \) NMR spectroscopy, showing the presence of a significant amount of starting oxo complex. The reaction was stirred an additional 48 hours, at which point the reaction solution was red-brown. Analysis of the reaction mixture by \(^1\text{H} \) NMR spectroscopy showed HN[R]Ar and O\(_2\)Mo(N[R]Ar)\(_2\) in a 3.5:1 ratio.

(xi) **Reaction of 2.1 with O\(_2\)**: Mo(N[R]Ar)\(_3\) (0.2200 g, 0.3422 mmol) was dissolved in ether (10 mL) and dioxygen (8.5 mL, 0.35 mmol, 1.0 eq) was added slowly over a 2 minute period. The solution became dark blue for about 10 seconds, and then green. After 30 seconds, the solution was dark brown. A \(^2\text{H} \) NMR spectrum obtained at this point showed the presence of 1 part OMo(N[R]Ar)\(_3\) and 2 parts diamagnetic material. A \(^1\text{H} \) NMR spectrum of the material showed five products: O\(_2\)Mo(N[R]Ar)\(_2\), HN[R]Ar, and OMo(N[R]Ar)\(_3\) in a 2:1:1 molar ratio, as well as two additional unidentified products.
(xii) **Thermolysis of OMo(NAr)(N[R]Ar)_2:** OMo(NAr)(N[R]Ar)_2 (ca. 0.015 g) was dissolved in C_6D_6 (ca. 1 mL) and sealed in an NMR tube. The mixture was heated at 110 °C for 82 hours, at which point it was examined by ^1H NMR spectroscopy. Three products were observed: O_2Mo(N[R]Ar)_2, OMo(NAr)(N[R]Ar)_2 and a product corresponding to Mo(NAr)_2(N[R]Ar)_2 in a 1:2:1 molar ratio.

(xiii) **Reaction of 2.6 with benzaldehyde:** OMo(NAr)(N[R]Ar)_2 (0.0471 g, 0.0788 mmol) and benzaldehyde (0.080 mL, 0.787 mmol, 10 eq) were dissolved in ether (3 mL) and stirred at room temperature for 72 hours. ^1H NMR showed primarily starting material, but also a small amount of O_2Mo(N[R]Ar)_2 and PhC(H)=NAr.

(xiv) **Reaction of 2.1 with PEt₃:** Several hundred milligrams of Mo(N[R]Ar)_3 were dissolved in C_6D_6 (1.5 mL) and triethylphosphine (ca. 10 μL) was added. Analysis of the reaction mixture by ^2H NMR spectroscopy showed only starting tris- anilide 2.1.

**2.8.6 Thermodynamic Measurements**

(i) **General Considerations.** All manipulations involving organomolybdenum complexes were performed under inert atmospheres of argon in a Vacuum Atmospheres glovebox containing less than 1 ppm oxygen and water. Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80) which was periodically calibrated using the TRIS reaction⁹⁸ or the enthalpy of solution of KCl in water.⁹⁹ The experimentally determined enthalpies for these two standard calibration reactions are the same within experimental error as the literature values. This calorimeter has been previously described¹⁰⁰ and typical procedures are described below. Experimental enthalpy data are reported with 95% confidence limits.
(ii) \( ^2 \text{H} \) NMR titrations. Prior to the calorimetric experiments, an accurately weighed amount (± 0.1 mg) of the molybdenum complex was placed in an NMR tube and toluene was subsequently added. The solution was titrated with a large excess of the reagent of interest. The reactions were monitored by \( ^2 \text{H} \) NMR spectroscopy and the reactions were found to be rapid, clean, and quantitative under experimental calorimetric conditions. These conditions are necessary for accurate and meaningful calorimetric results and were satisfied for the molybdenum reactions investigated with pyridine N-oxide and ethylene sulfide. Only reactants and products were observed in the course of the NMR titration.

(iii) Calorimetric Measurement for Preparation of 2.2. The mixing vessels of the Setaram C-80 were cleaned, dried in an oven maintained at 120 °C, and then taken into the glovebox. A 20-30 mg sample of 2.1 was accurately weighed into the lower vessel, and it was closed and sealed with 1.5 mL of mercury. Four mL of a stock solution of pyridine N-oxide [0.5 g of pyridine N-Oxide in 25 mL of toluene] was added and the remainder of the cell was assembled, removed from the glovebox and inserted in the calorimeter. The reference vessel was loaded in an identical fashion with the exception that no organomolybdenum complex was added to the lower vessel.

After the calorimeter had reached thermal equilibrium at 30.0 °C (about 1.5 hrs), the calorimeter was inverted thereby allowing the reactants to mix. After reaching thermal equilibrium, the vessels were removed from the calorimeter, taken into the glovebox, opened, and analyzed using \( ^1 \text{H} \) NMR spectroscopy. Conversion to OMo(N[R]Ar)\(_3\) was found to be quantitative under these reaction conditions. The enthalpy of reaction, \(-74.6 \pm 1.2 \) kcal/mol represents the average of five individual calorimetric determinations. The enthalpy of solution of 2.1 was then added to this value to obtain a value of \(-83.5 \pm 1.4 \) kcal/mol for all species in solution.
(iv) Calorimetric Measurement for Preparation of 2.3. The mixing vessels of the Setaram C-80 were cleaned, dried in an oven maintained at 120 °C, and then taken into the glovebox. A 20-30 mg sample of 2.1 was accurately weighed into the lower vessel, and it was closed and sealed with 1.5 mL of mercury. Four mL of a stock solution of ethylene sulfide [0.5 g of ethylene sulfide in 25 mL of toluene] was added and the remainder of the cell was assembled, removed from the glovebox and inserted in the calorimeter. The reference vessel was loaded in an identical fashion with the exception that no organomolybdenum complex was added to the lower vessel.

After the calorimeter had reached thermal equilibrium at 30.0 °C (about 1.5 hrs), the calorimeter was inverted thereby allowing the reactants to mix. After reaching thermal equilibrium, the vessels were removed from the calorimeter, taken into the glovebox, opened, and analyzed using $^1$H NMR spectroscopy. Conversion to $\text{SMo(N[R]Ar}_3$ was found to be quantitative under these reaction conditions. The enthalpy of reaction, $-36.3 \pm 1.2$ kcal/mol represents the average of five individual calorimetric determinations. The enthalpy of solution of 2.1 was then added to this value to obtain a value of $-45.2 \pm 1.2$ kcal/mol for all species in solution.

(v) Calorimetric Measurement of Enthalpy of Solution of 2.1. In order to consider all species in solution, the enthalpies of solution of 2.1 had to be directly measured in the solvents utilized. This was performed by using a similar procedure as the one described above with the exception that no chalcogen reagent was added to the reaction cell. This enthalpy of solution represents the average of three individual determinations and is $8.9 \pm 0.2$ kcal/mol in toluene.
2.8.7 X-ray Structural Determination

(i) O\textsubscript{Mo}(N[R]Ar)\textsubscript{3} (2.2)

A black needle of approximate dimensions 0.8 x 0.5 x 0.2 mm was obtained from a chilled ether solution. The crystal was mounted on a glass fiber. Data collection was carried out on a Siemens Platform goniometer with a CCD detector at 188 K using Mo K\textalpha radiation (\(\lambda = 0.71073\ \text{Å}\)). The total data collected were 7169 reflections (-10 \(\leq h \leq 10,\ -11 \leq k \leq 10,\ -22 \leq l \leq 21\)), of which 4915 were unique (\(R_{\text{int}} = 0.0309\)). Corrections applied: Semi-empirical from psi-scans. The structure was solved by direct methods (SHELXTL V5.0, G. M. Sheldrick and Siemens Industrial Automation, Inc., 1995) in conjunction with standard difference Fourier techniques. Least-squares refinement based upon \(R^2\) converged with residuals of \(R_1 = 0.0341,\ wR_2 = 0.0959,\) and GOF = 1.053 based upon \(I > 2\sigma(I)\). All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated (\(d_{C-H} = 0.96\ \text{Å}\)) positions. The residual peak and hole electron density was 0.446 and -0.558 e \(\text{Å}^{-3}\). Crystal data: triclinic, \(a = 9.8974(12)\ \text{Å}, b = 9.9883(14)\ \text{Å}, c = 20.254(2)\ \text{Å}, V = 1760.9(4)\ \text{Å}^3, \alpha = 95.745(10)^\circ, \beta = 92.324(8)^\circ, \gamma = 117.356(8)^\circ,\) space group P1, \(Z = 2,\ \mu = 0.402\ \text{mm}^{-1}, M_r = 640.76\) for \(C_{36}H_{54}MoN_3O,\ \rho(\text{calcd}) = 1.208\ \text{g/cm}^3,\) and \(F(000) = 682.\) See Tables 2.1 and 2.2 for metrical parameters, Table 2.3 for positional parameters and \(U(\text{eq}),\) and Figure 2.3 for an ORTEP diagram.

(ii) S\textsubscript{Mo}(N[R]Ar)\textsubscript{3} (2.3)

A black needle of approximate dimensions 0.55 x 0.23 x 0.11 mm was obtained from a chilled ether solution. The crystal was mounted on a glass fiber. Data collection was carried out on a Siemens Platform goniometer with a CCD detector at 188 K using Mo K\textalpha radiation (\(\lambda = 0.71073\ \text{Å}\)). The total data collected were 13213 reflections (-15 \(\leq h \leq 15,\ -14 \leq k \leq 7,\ -22 \leq l \leq 22\)), of which 5098 were unique (\(R_{\text{int}} = 0.0570\)).
Absorption corrections were applied. The structure was solved by direct methods (SHELXTL V5.0, G. M. Sheldrick and Siemens Industrial Automation, Inc., 1995) in conjunction with standard difference Fourier techniques. Least-squares refinement based upon $F^2$ converged with residuals $R_1 = 0.0527$, $wR_2 = 0.1015$, and GOF = 1.168 based upon $I > 2\sigma(I)$. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated ($d_{\text{C-H}} = 0.96 \, \text{Å}$) positions. The residual peak and hole electron density was 0.376 and -0.709 e Å$^{-3}$. Crystal data: monoclinic, $a = 13.9099(8)$ Å, $b = 12.8972(8)$ Å, $c = 19.9860(12)$ Å, $V = 3580.4(4)$ Å$^3$, $\alpha = 90^\circ$, $\beta = 93.0580(10)^\circ$, $\gamma = 90^\circ$, space group P2$_1$/c, $Z = 4$, $\mu = 0.451$ mm$^{-1}$, $M_r = 656.82$ for C$_{36}$H$_{54}$MoN$_3$S, $\rho(\text{calcd}) = 1.219$ g/cm$^3$, and $F(000) = 1396$. See Tables 2.4 and 2.5 for metric parameters, Table 2.6 for positional parameters and U(eq), and Figure 2.6 for an ORTEP diagram.

(iii) SeMo(N[R]Ar)$_3$ (2.4)

A black needle of approximate dimensions 0.75 x 0.32 x 0.22 mm was obtained from a chilled ether solution. The crystal was mounted on a glass fiber. Data collection was carried out on a Siemens Platform goniometer with a CCD detector at 188 K using Mo K\(\alpha\) radiation ($\lambda = 0.71073$ Å). The total data collected were 12674 reflections (-14 $\leq k \leq 14$, -22 $\leq l \leq 15$), of which 5075 were unique ($R_{\text{int}} = 0.0379$). Corrections applied: Semi-empirical from psi-scans. The structure was solved by direct methods (SHELXTL V5.0, G. M. Sheldrick and Siemens Industrial Automation, Inc., 1995) in conjunction with standard difference Fourier techniques. Least-squares refinement based upon $F^2$ converged with residuals of $R_1 = 0.0391$, $wR_2 = 0.0976$, and GOF = 1.285 based upon $I > 2\sigma(I)$. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated ($d_{\text{C-H}} = 0.96 \, \text{Å}$) positions. The residual peak and hole electron density was 0.394 and -0.501 e Å$^{-3}$. Crystal data: monoclinic, $a = 13.9372(7)$ Å, $b = 12.8821(7)$ Å, $c = 19.9510(10)$ Å, $V = 3577.4(3)$ Å$^3$, $\alpha = 90^\circ$, $\beta = 92.9060(10)^\circ$, $\gamma = 90^\circ$, $\mu = 0.451$ mm$^{-1}$, $M_r = 656.82$, $Z = 4$, $\rho(\text{calcd}) = 1.219$ g/cm$^3$, and $F(000) = 1396$. See Tables 2.4 and 2.5 for metric parameters, Table 2.6 for positional parameters and U(eq), and Figure 2.6 for an ORTEP diagram.

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90°, space group P2\(_1\)/c, Z = 4, \(\mu = 1.411\) mm\(^{-1}\), \(M_r = 703.72\) for C\(_{36}\)H\(_{54}\)MoN\(_3\)Se, 
\(\rho(\text{calcd}) = 1.307\) g/cm\(^3\), and F(000) = 1468. See Tables 2.7 and 2.8 for metrical parameters, Table 2.9 for positional parameters and U(eq), and Figure 2.9 for an ORTEP diagram.

(iv) \(\text{TeMo(N[R]Ar)}_3\) (2.5)

A black needle of approximate dimensions 0.65 x 0.48 x 0.23 mm was obtained from a chilled ether solution. The crystal was mounted on a glass fiber. Data collection was carried out on a Siemens Platform goniometer with a CCD detector at 188 K using Mo K\(\alpha\) radiation (\(\lambda = 0.71073\) Å). The total data collected were 14461 reflections (-12 \(\leq\) h \(\leq\) 15, -14 \(\leq\) k \(\leq\) 11, -22 \(\leq\) l \(\leq\) 22), of which 5182 were unique (\(R_{\text{int}} = 0.0295\)). No Absorption corrections were applied. The structure was solved by direct methods (SHELXTL V5.0, G. M. Sheldrick and Siemens Industrial Automation, Inc., 1995) in conjunction with standard difference Fourier techniques. Least-squares refinement based upon \(F^2\) converged with residuals of \(R_1 = 0.0256\), \(wR_2 = 0.0634\), and GOF = 1.008 based upon \(I > 2\sigma(I)\). All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated (\(d_{\text{C-H}} = 0.96\) Å) positions. The residual peak and hole electron density was 0.399 and -0.359 e Å\(^{-3}\). Crystal data: monoclinic, \(a = 14.108(2)\) Å, \(b = 12.762(3)\) Å, \(c = 20.083(4)\) Å, \(V = 3612.2(13)\) Å\(^3\), \(\alpha = 90°, \beta = 92.558(11)°, \gamma = 90°\), space group P2\(_1\)/c, Z = 4, \(\mu = 1.181\) mm\(^{-1}\), \(M_r = 752.36\) for C\(_{36}\)H\(_{54}\)MoN\(_3\)Te, \(\rho(\text{calcd}) = 1.383\) g/cm\(^3\), and F(000) = 1540. See Tables 2.10 and 2.11 for metrical parameters, Table 2.12 for positional parameters and U(eq), and Figure 2.12 for an ORTEP diagram.

(v) \((\text{N[R]Ar)}_3\text{Mo(\mu-CS)}\text{Mo(N[R]Ar)}_3\cdot 2\text{Et}_2\text{O}\) (2.13)

A greenish brown needle of approximate dimensions 0.40 x 0.21 x 0.18 mm was obtained from a chilled ether solution. The crystal was mounted on a glass fiber. Data collection was carried out on a Siemens Platform goniometer with a CCD detector at 188 K.
using Mo Kα radiation ($\lambda = 0.71073 \, \text{Å}$). The total data collected were 11885 reflections
(-16 ≤ h ≤ 13, -16 ≤ k ≤ 12, -22 ≤ l ≤ 20), of which 7493 were unique ($R_{int} = 0.0673$).
Corrections applied: semi-empirical from psi-scans. The structure was solved by direct
methods (SHELXTL V5.0, G. M. Sheldrick and Siemens Industral Automation, Inc.,
1995) in conjunction with standard difference Fourier techniques. Least-squares
refinement based upon $F^2$ converged with residuals of $R_1 = 0.1035$, $wR_2 = 0.2107$, and
GOF = 1.209 based upon $I > 2\sigma(I)$. All non-hydrogen atoms were refined anisotropically,
and hydrogen atoms were placed in calculated ($d_{C\cdot H} = 0.96 \, \text{Å}$) positions. The residual
peak and hole electron density was 0.920 and -0.512 e Å$^{-3}$. Crystal data: triclinic, $a =
14.6441(3) \, \text{Å}$, $b = 15.2700(2) \, \text{Å}$, $c = 20.5956(4) \, \text{Å}$, $V = 4150.44(13) \, \text{Å}^3$, $\alpha =
89.1990(10)^{\circ}$, $\beta = 77.8370(10)^{\circ}$, $\gamma = 67.6530(10)^{\circ}$, space group $P\overline{1}$, $Z = 2$, $\mu = 0.372$
mm$^{-1}$, $M_r = 1432.76$ for $\text{C}_8\text{H}_{11}\text{Mo}_2\text{N}_6\text{O}_2\text{S}$, $\rho(\text{calcd}) = 1.146$ g/cm$^3$, and $F(000) =
1526$. See Tables 2.27 and 2.28 for metrical parameters, Table 2.29 for positional
parameters and U(eq), and Figure 2.25 for an ORTEP diagram.
References

22) Howard, W. A.; Parkin, G. Organometallics 1993, 12, 2363-2366.

(184) References begin on page 184


41) Fickes, M. G.; Cummins, C. C., Unpublished Results.

42) As polonium is radioactive, it is not generally included in the chalcogen series. See reference 12 for a similar disclaimer from Gerard Parkin.


44) All CV experiments were carried out by Marc Johnson.


46) Thermochemical experiments were carried out in collaboration with Steve Nolan and Safford Serron at the University of New Orleans.


50) Unpublished Results by Clark Landis at the University of Wisconsin communicated by Christopher Cummins.


55) Quantum calculations were carried out in collaboration with Jamal Musaev and Keiji Morokuma at Emory University.


(185) References begin on page 184
Chapter III: Activation of a Molybdenum Nitride

Derived from Molecular Nitrogen
**Section 3.1: Introduction**

Mo(N[R]Ar)$_3$ (2.1, R = C(CD$_3$)$_2$CH$_3$, Ar = 3,5-C$_6$H$_3$Me$_2$) reacts with dinitrogen at -35 °C to form a dimer with a dinitrogen bridge.$^{1,2}$ Warming the complex results in clean N-N bond scission, forming the tetrahedral NMo(N[R]Ar)$_3$ (3.1). Extensive experimental investigation and theoretical calculations have been reported on the mechanism and structures of the intermediates proposed in this unique reaction.$^{3-5}$ The cleavage reaction can be made to occur at room temperature by the addition of NMo(O-t-butyl)$_3$ or elemental sodium, but turnover numbers are very low.$^{6,7}$ This mild and efficient fixation of dinitrogen could in principle be made catalytic if an efficient means for regeneration of the paramagnetic complex 2.1 were found. This regeneration would result in the productive formation of "fixed" nitrogen-containing molecules, with ammonia being an obvious potential target.

Potential regenerative pathways include N-atom transfer,$^{8,9}$ and nitrene transfer,$^{10,11}$ either to a transition metal complex or an organic substrate. A more elegant approach involves stepwise alkylation of the nitride, with the hopeful generation of a labile amine complex. Addition of Lewis acidic substrates to transition metal nitrides to form imido ligands is preceded for many electrophilic reagents such as boron trihalides,$^{12}$ Ph$_3$C$^+$,$^{13}$ PhC(O)Cl,$^{13}$ trifluoroacetic anhydride,$^{14}$ chlorotrimethylsilane,$^{15}$ methyl iodide$^{13,16-18}$ and others.$^{15,19,20}$ This chapter describes initial experiments designed to activate the molybdenum nitride functionality in 3.1 by methylation with methyl iodide. Also reported are the reactions of 2.1 with a variety of amines. The experiments are designed to explore the compatibility or reactivity of 2.1 with these reagents, as they would be likely targets for "fixed" nitrogen containing molecules. Related chemistry concerning the activation of a coordinated phosphorus atom in PMo(N[R]Ar)$_3$ has recently been reported.$^{21,22}$
Section 3.2: Activation of a Molybdenum Nitride

(i) Synthesis and Characterization of Mo(NMe)(N[R]Ar)₃ (3.3)

Nitrido 3.1, which is obtained from the reaction of tris-anilide 2.1 with dinitrogen or mesityl azide, is methylated by stirring in neat methyl iodide for a period of 14 hours. This reaction was first carried out by Catalina Laplaza. Removal of the excess methyl iodide results in a dark orange material, [Mo(NMe)(N[R]Ar)₃][I] (3.2) which is insoluble in hydrocarbon solvents (Scheme 3.1). The complex is purified by pentane diffusion into THF, and is isolated in greater than 90% yield. The salt is unstable in solution for long periods of time (more than a few hours) but is stable indefinitely in the solid state at -35 °C.

The ¹H NMR spectrum of 3.2 exhibits a resonance at 5.15 ppm which is attributed to the methyl imide functionality. The methyl imide carbon resonance cannot be definitively assigned from the ¹³C NMR spectrum taken in chloroform as it appears to overlap the aryl methyl resonance at 21.55 ppm. The ¹³C NMR spectrum taken in THF shows some separation of the two resonances, but the complex decomposes more rapidly in THF, precluding an analysis of the spectrum. The methyl imide ¹³C NMR chemical shift is substantially different from those observed in [OsCp(CH₂SiMe₃)₂(NMe)][I], with a resonance at 61.5 ppm (CD₂Cl₂),¹⁶ and [Os(NMe)(CH₂SiMe₃)₄], with a resonance at 46.2 ppm (C₆D₆).¹⁷
Scheme 3.1: Stepwise activation of dinitrogen to give a methylimide complex

Treatment of the cationic complex 3.2 with cobaltocene (one equivalent) results in the immediate formation of a dark brown solution and a bright yellow solid (CoCp₂I) which are separated by filtration (Scheme 3.1). The neutral methyl imide complex 3.3 is isolated quantitatively by dissolution in a minimum of pentane followed by precipitation with acetonitrile. The complex is purified by recrystallization and isolated in ca. 50% yield. The low isolated yield is due to the extreme solubility of the complex and does not reflect low conversion to the desired complex or decomposition; the reaction is quantitative as measured by $^2$H NMR spectroscopy.

Methyl imide 3.3 exhibits a single resonance in the $^2$H NMR spectrum at 7.867 ppm, which corresponds well to chemical shifts observed in other $d^1$ molybdenum complexes with the N[R]Ar ligand framework. The methyl resonance appears at -51.3 ppm in the $^1$H NMR spectrum. The magnetic moment of the complex as measured by NMR techniques is found to be 1.95 $\mu_B$, in good agreement with the spin-only value.
of 1.73 $\mu_B$. An EPR spectrum of the complex in toluene at room temperature shows an isotropic g value of 1.949. The spectrum exhibits a six line coupling pattern which is approximately 25% of the area of the central peak, reflecting the natural abundance of the $s = \frac{5}{2}$ nuclei $^{95}$Mo and $^{97}$Mo ($A(^{95,97}$Mo) = 37 G). Due to the similar gyromagnetic ratios of the two molybdenum nuclei, separate couplings to both $^{95}$Mo and $^{97}$Mo are not seen. The frozen glass spectrum (102 K) exhibits a rhombic pattern, shown in Figure 3.1, with g values of 1.976, 1.956 and 1.915, but the anisotropic coupling constants are not well resolved.

(ii) Attempted Synthesis of $\text{Mo(}N\text{Me}_2\text{)(N[R]Ar}_3\text{)}$

Further functionalization of the methyliminido fragment in 3.3 with additional methyl iodide could result in the formation of $[\text{Mo(}N\text{Me}_2\text{)(N[R]Ar}_3\text{)}][\text{I}]$, one step closer to removing the dinitrogen derived nitrogen atom in a productive fashion. Complex 3.3 reacts with excess methyl iodide in a fashion similar to that used for the synthesis of 3.2, but examination of the reaction mixture by $^1$H NMR spectroscopy after a 15 hour period shows only the presence of cationic 3.2. Methyl iodide acts as an oxidant rather than as an electrophile in this case. The fate of the methyl radical equivalent which must form in this reaction is unknown. This result is unexpected, as from a molecular orbital point of view, the methyl imide should have nucleophilic character. However, in this case the steric environment of the pocket formed by the tert-butyl groups dominates the reaction chemistry, blocking approach of an electrophile to the imide and forcing an electron transfer event.
Figure 3.1: EPR spectrum (97 K, toluene) of Mo(NMe)(N[R]Ar)₃ (3.3) with \( g_1 = 1.976, g_2 = 1.956, g_3 = 1.915 \).
Chapter III: Activation of a Molybdenum Nitride Derived from Molecular Nitrogen

Cationic complex 3.2 also reacts with dimethylmagnesium. However, rather than addition of the methyl group to form the dimethylamide complex, reduction occurs, forming the neutral methyl imide 3.3. Again, the electron transfer process suggests that the imide functionality is sterically protected.

(iii) Synthesis and Characterization of IMo(N[R]Ar)₃ (3.4)

Another potential entry into the Mo(IV) dimethylamide complex is through metathesis from a Mo(IV) halide complex. Initial experiments in this area were carried out by Catalina Laplaza. The iodide, IMo(N[R]Ar)₃ (3.5), is prepared by simple addition of one half equivalent iodine to the tris anilide 2.1 (Scheme 3.2). The addition results in a rapid color change from dark red to very dark green. The complex is obtained by crystallization from ether in 83% yield.

![Scheme 3.2: Oxidation of Mo(N[R]Ar)₃ (2.1) with Iodine](image)

The ¹H NMR spectrum of 3.4 exhibits unusually sharp resonances, and the ²H NMR resonance for the d₆-tert-butyl group is solvent dependent, appearing at 8.97 ppm in ether and 6.36 ppm in benzene. Variable temperature Evans method magnetic susceptibility measurements are suggestive of a spin equilibrium process. Although the data are poor, the measured susceptibilities are so low that the diamagnetic correction factor dominates, a clear temperature dependence of μₑffective is observed (Figure 3.2).
Figure 3.2: Temperature dependence of the Evans method magnetic susceptibility of complex 3.4.
Examination of the iodide complex by SQUID magnetometry over the temperature range from 5 to 350 K, shows large fluctuations in the data over a temperature of 220 K. The SQUID data from 5 to 220 K to are presented in Figure 3.3, clearly showing a decrease in paramagnetism as measured by $\chi$ at low temperature. The dependence of $\mu$ on temperature, which is calculated from the $\chi$ values, is shown in Figure 3.4. The complex exhibits paramagnetic behavior at all temperatures, but $\mu$ approaches zero at 0 K. At 200 K, the complex is about 15% in the $s = 2$ state, with the remainder in the spin-paired state. It is not possible to accurately measure magnetic behavior of the complex above room temperature because the complex decomposes rapidly to unknown products when heated. Attempts to fit the data to suitable spin equilibrium models have not been successful,\textsuperscript{30} due perhaps to the low absolute concentration of triplet spin of 15% which is observed at 220 K. EPR spectra taken at room temperature and 101 K also support a spin equilibrium. Both spectra exhibit a primary $g$ value of 1.98, with features at $g = 2.03$ and 1.95, but the intensity of the low temperature spectrum is significantly reduced; the room temperature spectrum is shown in Figure 3.5.

When iodide 3.4 and lithium dimethylamide are mixed no reaction is readily observed at room temperature, and the color of the reaction solution does not change from dark green. Monitoring the reaction after 45 minutes by $^1$H NMR spectroscopy shows unreacted starting material, tris anilide 2.1 and free HN[R]Ar, as well as decomposition products. This suggests that reduction of rather than substitution on 3.4 is the dominant mode of reactivity, a result which is also attributed to the substantial steric protection of the Mo center. There is no reaction of iodide 3.4 with the BH$_3$ adduct of dimethylamine in the presence of triethylamine as a base, as determined by $^1$H NMR spectroscopy.
Figure 3.3: SQUID magnetic susceptibility data of complex 3.4 from 5 to 220 K.
Figure 3.4: Magnetic susceptibility of complex 3.4 obtained from SQUID measurements from 5 to 220 K.
Figure 3.5: EPR spectrum (28 °C, toluene) of IMo(N[R]Ar)₃ (3.4) (See text for further details).
Section 3.3: Reactions of Mo(N[R]Ar)₃ (2.1) with Amines

Neither methylation of the methyl imide 3.3 nor metathesis from iodide 3.4 are productive routes into a dimethylamide complex. Therefore, the reaction of tris anilide 2.1 with a variety of amine reagents is examined in order to explore the steric and/or electronic constraints on this system with regard to the eventual synthetic goal of productive nitrogen fixation.

(i) 2-Methylaziridine

2-Methylaziridine reacts with 2.1 (Scheme 3.3); however, this does not result in the formation of Mo(NH)(N[R]Ar)₃, which is the expected product. Instead, nitrido 3.1 is formed, as well as an equivalent of propylene which is detected by ¹H NMR spectroscopy.¹¹ Free HN[R]Ar is also observed to be produced with time. No evidence for dihydrogen is observed in the ¹H NMR spectrum, and there are no observable side products, so it seems likely that the hydrogen atom is delivered to an N[R]Ar fragment resulting from some sacrificial quantity of tris-anilide complex 2.1.

(ii) 7-Amino-7-aza-benzonorbornadiene

Tris anilide 2.1 also reacts with 7-amino-7-aza-benzonorbornadiene³²,³³ (Scheme 3.3), generating an equivalent each of nitrido 3.1 and anthracene as determined by ¹H NMR spectroscopy. Approximately one equivalent of free HN[R]Ar also grows in with time, suggesting again that the hydrogen atom in the starting amine reacts with some sacrificial quantity of complex 2.1. Repeating the reaction with the deuterated amine gives similar results. Analysis of the reaction mixture by ²H NMR spectroscopy shows the presence of DN[R]Ar at about 3.0 ppm.
Scheme 3.3: Successful nitrogen atom transfer from organic amines to Mo(N[R]Ar)₃ (2.1).

(iii) Ammonia

Complex 2.1 reacts with one equivalent of ammonia, freshly distilled from sodium. This reaction results in complete decomposition of the starting complex 2.1, with formation of almost 90% free HN[R]Ar. A very small amount of nitrido 3.1 is detected in
the reaction mixture. This suggests that hydrogenation or protonation of 3.1 would not result in clean formation of ammonia, counter to a predicted result.34

(iv) N-Methylaziridine

There is no reaction of complex 2.1 with a variety of other amines (Scheme 3.4). Complex 2.1 does not react with N-methyl aziridine to generate methyl imide complex 3.3 directly. In fact, mixing of the two reagents for 24 hours does not result in any consumption of starting material. Neither heating the reaction at 55 °C for two hours nor irradiation with UV light for 90 minutes effects the transformation. The fact that no reaction occurs suggests that tertiary amines are not capable of bonding to the tris anilide. This is most likely due to a steric effect; however, the electronic effects of a nucleophile binding to 2.1 should be considered as well. Bringing in a lone pair as a σ donor to the tris anilide would force a high-spin to low-spin conversion of complex 2.1 in order to access an empty σ-type orbital. This transformation is not very favorable as the calculated energy gap between the ground quartet (4A') and first excited doublet (2A') state for Mo(NH2)3 is 14-28 kcal·mol−1.35 There should therefore be an electronic barrier to amine binding as well as a steric barrier. It has been shown previously that triethylphosphine does not react with 2.1.24,25 This result suggests that if an tertiary amine complex of Mo(N[R]Ar)3 were prepared, it would be labile and the amine would be lost, regenerating free tris anilide 2.1.

(v) Azetidine

Complex 2.1 also does not react with azetidine. This amine would be expected to react similarly to 2-methylaziridine on a steric basis, generating nitride 3.1. However, there does not appear to be any reaction with the four-membered amine. The reduced strain energy in this molecule may be the cause for reduced reactivity, as the two amines have similar steric profiles.
1) \( N\)-methylaziridine  
25 °C, 18 h

2) \textit{tert}-butylamine  
25 °C, 19 h

3) triethylamine  
25 °C, 18 h

4) diethylamine  
25 °C, 24 h

5) azetidine  
25 °C, 18 h

\[
\text{Ar[R]N—Mo} \xrightarrow{\text{N[R]Ar}} \text{N[R]Ar} \quad > 90\% \text{ No Reaction}
\]

\textbf{Scheme 3.4:} Unsuccessful nitrogen atom transfer from organic amines to \( \text{Mo(N[R]Ar)}_3 \) (2.1).

\textbf{(vi) \textit{tert}-Butylamine, Triethylamine and Diethylamine}

There is no reaction of tris anilide 2.1 with one equivalent of either \textit{tert}-butyl amine, triethylamine or diethylamine over a period of 24 hours. The lack of reactivity with triethylamine is not surprising based on the lack of reactivity of 2.1 with triethylphosphine as mentioned in Section 2.8.

\textbf{(viii) General Trends}

The above results suggest reactivity for only a select class of amines with tris-anilide 2.1. Tertiary amines seem to be prohibited from reaction on a steric ground; the bulky \textit{tert}-butyl groups of the N[R]Ar ligand protect the molybdenum center from incoming amine reagents. Secondary amines are capable of delivering a nitrogen atom to 2.1 if the
organic fragment which must be lost is stabilized. Reorganization of 2-methylaziridine to generate propylene, or 7-amino-7-aza-benzonorbornadiene to generate anthracene, with the concomitant ejection of the [NH] fragment, occurs only through the π system, with minimal reorganization energy. Azetidine does not react because the 1,3-diradical which would form is a high-energy species which must undergo reorganization through the σ system (a 1,2-hydrogen shift) to generate propylene. Ammonia is in a special class by itself: its small size allows approach of the Mo and N atoms, and the hydrogen atoms which are lost can be transferred to N[R]Ar fragments, resulting in complete decomposition of the tris-anilide fragment.

Section 3.4: Conclusion

It is possible to begin conversion of a dinitrogen derived N-atom on a molybdenum complex to a more useful, "fixed" state. Methylation of the nitrido functionality in 3.1 results in clean, high yield formation of the methyl imide cation, which is reduced to the neutral complex with cobaltocene. It has not yet been possible to further derivatize the imido function, nor is it yet possible to observe clean metathesis reactions with the iodide 3.4. The reactions, or lack thereof, which are observed between tris anilide complex 2.1 and a variety of amines suggest that there is a large steric barrier to reaction in the pocket at the metal center. The electronic rearrangement required to bind an amine to the molybdenum center also presents an additional barrier. Small amines such as ammonia or 2-methylaziridine are permitted to approach the complex, and those with stabilized leaving groups like 2-methylaziridine or 7-aza-dibenzonorbornadiene deliver a nitrogen atom. These results do support the idea that if a way is found to derivatize the nitrido functionality to a neutral amine complex, perhaps by making the nitride and imide functionalities more nucleophilic through changing the basal ligand set, it would be labile, resulting in regeneration of the tris anilide complex 2.1.
Section 3.5: Experimental

3.5.1 General Considerations

General experimental details are as described in Chapters I and II. Solvents were dried and deoxygenated according to previously published procedures.\textsuperscript{36} Diethyl ether was dried according to a procedure by Grubbs.\textsuperscript{37} Methyl iodide was distilled from CaH\textsubscript{2} and stored over sieves at -35 °C. 7-Amino-7-azabenzonorbornadiene,\textsuperscript{32,33} Mo(N[R]Ar)\textsubscript{3},\textsuperscript{1} and NMo(N[R]Ar)\textsubscript{3},\textsuperscript{1} were prepared according to published procedures. Iodine was sublimed prior to use. N-methyl aziridine was prepared from N-methylaminoethanol.\textsuperscript{10,38} Other chemicals were purified and dried via standard procedures\textsuperscript{39} or used as received.

Magnetic susceptibilities were measured by NMR spectroscopy.\textsuperscript{26} NMR spectra were recorded on Varian XL-300, Varian Unity-300 or Varian VXR-500 spectrometers. Chemical shifts are reported with respect to internal solvent. $^2$H chemical shifts are reported with respect to external C\textsubscript{6}D\textsubscript{6}. EPR spectra were recorded on a Brucker ESP 300 spectrometer in sealed quartz tubes in toluene at either ambient temperature or low temperature by using a liquid nitrogen cooled nitrogen stream. SQUID data were acquired as reported previously\textsuperscript{36} using a Quantum Design SQUID magnetometer. CHN analyses were performed by Oneida Research Services (Whitesboro, NY) or Microlytics (South Deerfield, MA). Melting points were obtained in sealed glass capillaries and are uncorrected.

3.5.2 Synthesis of Complexes

(i) [Mo(NMe)(N[R]Ar)\textsubscript{3}][I] (3.2). NMo(N[R]Ar)\textsubscript{3} (3.1, 0.1556 g, 0.2369 mmol) was dissolved in methyl iodide (4.0 mL) and stirred for 14 hours. The color of the reaction solution gradually changed from dark brown/orange to dark yellow. The excess iodomethane was removed \textit{in vacuo}, resulting in a dark solid material which was insoluble
in pentane and only slightly soluble in ether. The material dissolved in THF (ca. 1 mL) and was precipitated by the addition of pentane (ca. 15 mL) (0.1740 g, 0.2178 mmol, 92%). The compound is slightly unstable in both THF and CDCl<sub>3</sub> solution. M.P. 110 °C (dec). 1H NMR (300 MHz, CDCl<sub>3</sub>): δ = 6.989 (s, 3H, para); 5.620 (s, 6H, ortho); 5.151 (s, 3H, NCH<sub>3</sub>); 2.163 (s, 18H, ArMe); 1.255 (s, 9H, C(CD<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>). 13C NMR (125 MHz, CDCl<sub>3</sub>): δ = 145.46 (s, ipso); 138.72 (q, 2J<sub>CH</sub> = 6 Hz, meta); 130.88 (d, J = 155.6 Hz, para); 128.55 (d, J = 160.2 Hz, ortho); 68.22 (s, C(CD<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>); 32.10 (q, J = 126.7 Hz, C(CD<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>); 31.44 (m, C(CD<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>); 21.55 (q, J = 122.07 Hz, ArMe and NMe). Calcd for C<sub>37</sub>H<sub>39</sub>D<sub>18</sub>IMoN<sub>4</sub>: C, 55.63; H, 7.19; N, 7.01. Found: C, 56.13; H, 7.64; N, 6.53.

(ii) Mo(NMe)(NRAr)<sub>3</sub> (3.3). [Mo(NMe)(N[R]Ar)<sub>3</sub>][I] (3.2, 0.1740 g, 0.2178 mmol) was dissolved in THF (3.5 mL) and CoCp<sub>2</sub> (0.0409 g, 0.2163 mmol, 0.99 eq) in THF (1.5 mL) was added. The solution rapidly changed color to dark brown. The THF was removed in vacuo and the resulting solid was extracted with benzene, leaving behind a yellow solid which was filtered away (CoCp<sub>2</sub>I). After filtration, the solvent was removed from the filtrate in vacuo. The solid obtained was dissolved in a minimum of pentane (ca. 1 mL) and acetonitrile (2 mL) was added, causing precipitation of a dark solid in essentially quantitative yield. Analytically pure material was obtained by recrystallization of the solid obtained from a cold ether solution (ca. 1.5 mL) (0.0753 g, 0.1121 mmol, 52%). M.p. 111-112 °C. 2H NMR (46 MHz, ether) δ = 7.867; Δν<sub>1/2</sub> = 34.3 Hz. 1H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ = 7 (br s), 0.107 (br s, 18 H, ArMe), 0 (br s), -51.258 (br s, 3H, NMe). MS (70 eV): m/z(%): 670(8.8)[M+]. μ<sub>eff</sub> (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): 1.95 μ<sub>B</sub>. EPR (toluene, 285 K): g <sub>1</sub> = 1.949, A<sub>95.97</sub>Mo = 37 G. EPR (toluene, 102 K): g<sub>1</sub> = 1.976, A<sub>1</sub>(95/97Mo) = 25 G, g<sub>2</sub> = 1.956, g<sub>3</sub> = 1.915. Anal. Calcd for C<sub>37</sub>H<sub>39</sub>D<sub>18</sub>MoN<sub>4</sub>: C, 66.14; H, 8.55; N, 8.34. Found: C, 66.30; H, 8.70; N, 8.36.
(iii) IMo(N[R]Ar)\(_3\) (3.4). Iodine (0.0706 g, 0.2782 mmol, 0.51 eq) in ether (5 mL) was added to Mo(N[R]Ar)\(_3\) (1, 0.3494 g, 0.5435 mmol) in ether (10 mL) causing a rapid color change to deep green. The solution was stirred for 30 minutes, and the solvent was removed \textit{in vacuo}. The product was obtained by recrystallization from ether (0.3461 g, 0.4496 mmol, 82.7%). M.p. 122-124 °C. \(^2\)H NMR (46 MHz, ether): \(\delta = 8.97; \Delta v_{1/2} = 10.62\) Hz. \(^2\)H NMR (46 MHz, C\(_6\)H\(_6\)): \(\delta = 6.363; \Delta v_{1/2} = 11\) Hz. \(^1\)H NMR (300 MHz, C\(_6\)D\(_6\)): \(\delta = 6.58\) (9H, C(CD\(_3\))\(_2\)CH\(_3\)), 4.618 (6H, ortho), 3.558 (3H, para), 1.154 (18H, ArMe). EPR (toluene, 25 °C): \(g = 1.97\) (features at \(g = 2.02\) and 1.95); (toluene, 101 K): \(g = 1.98\) (features at \(g = 2.03\) and 1.95). UV/Vis (ether): \(\lambda(e) = 255(21400); 607(2000)\). \(\mu_{\text{eff}}\) (300 MHz, C\(_6\)D\(_6\), 25 °C): 1.94 \(\mu_B\). MS (70 eV): \(m/z(\%) = 768.2(0.6)[M^+].\) Anal. Calcd for C\(_{36}\)H\(_{36}\)D\(_{18}\)MoN\(_3\)I: C, 56.17; H, 7.07; N, 5.46. Found: C, 56.15; H, 6.90; N, 5.34.

3.5.3 Other Reactions

(i) Reaction of 3.3 with methyl iodide. Mo(NMe)(N[R]Ar)\(_3\) (3.3, 0.0753 g, 0.1121 mmol) was dissolved in methyl iodide (2.0 mL) and the reaction mixture was stirred for 15 hours. The color of the reaction changed from dark brown to yellow orange over this time. The methyl iodide was removed \textit{in vacuo}. The resulting solid (0.0854 g, 0.1069 mmol, 95%) was determined to be [Mo(NMe)(N[R]Ar)\(_3\)][I] (3) by \(^1\)H NMR spectroscopy.

(ii) Reaction of 3.2 with Me\(_2\)Mg. [Mo(NMe)(N[R]Ar)\(_3\)][I] (3.2, 0.0854 g, 0.1069 mmol) was dissolved in THF (2 mL) and Me\(_2\)Mg (0.0044 g, 0.8093 mmol, 1.5 eq) in THF (2 mL) was added. The solution turned red brown on addition. The product obtained was determined to be Mo(NMe)(N[R]Ar)\(_3\) (3.3) by \(^1\)H and \(^2\)H NMR spectroscopy.
(iii) Reaction of 3.4 with LiNMe₂. IMo(N[R]Ar)₃ (3.4, 0.1506 g, 0.1956 mmol) was dissolved in THF (5 mL) and chilled to -35 °C. A solution of LiNMe₂ (0.0100 g, 0.196 mmol) in THF (3 mL) at -35 °C was added dropwise. The solution gradually changed to an olive green color over a 45 minute period. Solvent was removed in vacuo. Examination of the solid obtained by ¹H NMR spectroscopy showed the presence of Mo(N[R]Ar)₃, HN[R]Ar and IMo(N[R]Ar)₃, as well as decomposition products.

(iv) Reaction of 3.4 with BH₃NHMe₂. IMo(N[R]Ar)₃ (3.4, 0.0962 g, 0.125 mmol) was dissolved in ether (10 mL). BH₃-NHMe₂ (0.0081 g, 0.14 mmol, 1.1 eq) and NEt₃ (20 µL, 0.15 mmol, 1.2 eq) in ether (2 mL) was added to the solution of 3.4. No color change was observed. After 24 hours, the reaction mixture was examined by ¹H NMR spectroscopy, showing only starting material, as well as a small amount of HN[R]Ar.

(v) Reaction of 2.1 with 2-methylaziridine. Mo(N[R]Ar)₃ (2.1, 0.0138 g, 0.0215 mmol) was dissolved in C₆D₆ (ca. 1 mL) and 2-methylaziridine (freshly flushed through alumina, 1.6 µL, 0.023 mmol, 1.1 eq) was added via syringe. The reaction was monitored by ¹H NMR spectroscopy over about four hours, clearly showing the growth of peaks attributable to NMo(N[R]Ar)₃ (2), HN[R]Ar and propylene.

(vi) Reaction of 2.1 with 7-amino-7-aza-benzonorbornadiene. Mo(N[R]Ar)₃ (2.1, 0.0359 g, 0.0558 mmol) was dissolved in C₆D₆ (1.0 mL) and 7-amino-7-aza-benzonorbornadiene (0.0107 g, 0.0560 mmol, 1.00 eq) in C₆D₆ (0.5 mL) was added. The reaction was monitored by ¹H NMR spectroscopy after 40 minutes. At this time, there was a 4:2:1 ratio of Mo(N[R]Ar)₃ to NMo(N[R]Ar)₃ to HN[R]Ar. After 16 hours, the ratio was 1:5:3. This reaction was repeated using the deuterated amine, which was prepared by
multiple washings of the starting amine with D$_2$O in THF. Analysis of the reaction by $^2$H NMR after 24 hours showed the presence of DN[R]Ar.

(vii) **Reaction of 2.1 with ammonia.** Mo(N[R]Ar)$_3$ (2.1, 0.0290 g, 0.0451 mmol) was dissolved in C$_6$D$_6$ (ca. 1 mL) in an NMR tube with a ground glass joint. The tube was attached to a vacuum line, and degassed with three freeze-pump-thaw cycles. Ammonia (freshly stirred over sodium until blue, 3.1 mL, 300 torr, 0.052 mmol, 1.2 eq) was condensed into the NMR tube, which was then sealed. After 80 minutes, $^1$H NMR spectroscopy showed a 3:1 ratio of HN[R]Ar to Mo(N[R]Ar)$_3$ (2.1) and approximately 70% starting complex 2.1. After 48 hours, $^1$H NMR spectroscopy showed a greater than 10:1 ratio of HN[R]Ar to NMo(N[R]Ar)$_3$ (3.1), with essentially complete consumption of starting complex 2.1. The NMR tube contained a large amount of black insoluble solid after 48 hours, perhaps corresponding to (MoN)$_n$.$^{40}$

(viii) **Reaction of 2.1 with N-methylaziridine.** Mo(N[R]Ar)$_3$ (2.1, 0.0250 g, 0.0389 mmol) was dissolved in C$_6$D$_6$ (ca. 1 mL) and N-methylaziridine (5 μL) was added. The reaction mixture was sealed in an NMR tube and allowed to stand at room temperature overnight. $^1$H NMR spectroscopy showed no reaction after this time. The tube was heated at 55 °C for 2 hours, but a $^1$H NMR spectrum obtained after this time still showed no reaction. The tube was irradiated with UV light for 90 minutes, but $^1$H NMR spectroscopy showed no reaction had occurred.

(ix) **Reaction of 2.1 with azetidine.** Mo(N[R]Ar)$_3$ (2.1, 0.0163 g, 0.0254 mmol) was dissolved in C$_6$D$_6$ (1.5 mL) and azetidine (3.0 μL, 0.0495 mmol, 1.9 eq) was added. The tube was frozen and degassed and then flame-sealed. The reaction was monitored by $^1$H NMR spectroscopy after 40 minutes, and again after 18 hours, showing that no reaction had occurred.
(x) **Reaction of 2.1 with tert-butylamine.** Mo(N[R]Ar)$_3$ (2.1, 0.0269 g, 0.0418 mmol) was dissolved in ether (1 mL) and tert-butyl amine (5.0 µL, 0.048 mmol, 1.1 eq) was added. $^2$H NMR spectroscopy showed only the presence of starting 2.1 after 19 hours.

(xi) **Reaction of 2.1 with triethylamine.** Mo(N[R]Ar)$_3$ (2.1, 0.0220 g, 0.0342 mmol) was dissolved in C$_6$D$_6$ (1.5 mL) and trimethylamine (6.0 µL, 0.0817 mmol, 2.4 eq) was added. The reaction was monitored by $^1$H NMR spectroscopy after 18 hours, showing that no reaction had occurred.

(xii) **Reaction of 2.1 with diethylamine.** Mo(N[R]Ar)$_3$ (2.1, 0.0280 g, 0.0436 mmol) was dissolved in C$_6$D$_6$ (1.5 mL) and dimethylamine (5.5 µL, 0.053 mmol, 1.2 eq) was added. The reaction was monitored by $^1$H NMR spectroscopy after 24 hours, showing that no reaction had occurred.

**References**

Chapter III: Activation of a Molybdenum Nitride Derived from Molecular Nitrogen

23) Our laboratory is indebted to Marc Johnson for the discovery of and Jonas Peters for the implementation of this purification technique with the N[R]Ar ligand set.
25) Also see Chapter II of this Thesis.
32) The amine was prepared by Dan Minidola.

(210) References begin on page 209
Chapter IV: Group 6 Complexes with a Bulky Amide Ligand Containing β-Hydrogens - Synthesis with Mechanistic Implications
Section 4.1: Introduction

The field of low-valent, low-coordinate transition metal amide chemistry begins with the synthesis of $\text{Cr(N(i-Pr)_2)_3}$, and $(\text{ON})\text{Cr(N(i-Pr)_2)_3}$ by Bradley and coworkers. In recent years, these types of complexes have exhibited diverse and fundamentally interesting reactivity. The most common amide ligands used to stabilize low-coordinate complexes, such as $\text{-N(SiMe}_3\text{_2)}$, $\text{-N[R']Ar'}$ ($\text{R'} = \text{tert-alkyl}; \text{Ar'} = \text{aryl}$) and $\text{-N(C}_6\text{H}_5\text{)_2}$, lack $\beta$-hydrogens. The $\beta$-hydrogen elimination reaction is a well known and well documented decomposition pathway for metal alkyls and alkoxides, as well as late metal amides. Some early metal amide complexes, for example those with $\text{-N(Cy}_2\text{)}$ and $\text{-N(i-Pr)_2}$, exhibit reactivity involving formal activation of the $\beta$-hydrogen, but in general, the $\beta$-hydrogen elimination reaction is not common in metal-amide chemistry. Clearly, the presence of $\beta$-hydrogens in the monomeric complex $\text{Cr(N(i-Pr)_2)_3}$ does not render it unstable.

This chapter, which describes the synthesis of a variety of group six amide complexes with the $\text{-N[2-Ad]Ar}$ ligand ($\text{2-Ad = 2-Adamantyl}$, $\text{Ar = 3,5-C}_6\text{H}_3\text{Me}_2$), is part of an ongoing project towards understanding the steric and electronic factors which control the reactivity of low-valent and low-coordinate metal amide complexes, especially concerning the cleavage of dinitrogen and nitrous oxide by Mo(III). Substitution of bulkier tertiary alkyl groups for the tert-butyl group in the $\text{-N[R']Ar}$ ligand ($\text{R = C(CD}_3\text{)_2CH}_3$) causes substantial reactivity differences. For example, the ligands in $\text{Mo(N[1-Ad]Ar)_3}$ ($\text{1-Ad = 1-adamantyl}$) are too large to allow dimerization in the transition state required to cleave dinitrogen, thereby shutting down the reaction. Other researchers have recently reported chemistry with this ligand.

Interest in the 2-adamantyl ligand stems from the desire to activate metal-element triple bonds. The steric pocket surrounding the M-E linkage precludes approach of a reagent to the $\pi$-cloud, rendering it essentially unreactive. Only recently have the Mo-N and Mo-P triple bonds been chemically modified, but the addition reactions result in
essentially linear Mo-E-X linkages with no interaction between the molybdenum atom and the added group.\textsuperscript{37-39} By reducing the steric pocket protecting the Mo-E group, an increase in reactivity could be realized. This steric pocket would be reduced substantially by using a secondary alkyl substituent, but two potential problems are envisioned. First, a large decrease in steric protection could result in metal-metal triple bond formation,\textsuperscript{40-42} and second, the \( \beta \)-hydrogen could potentially be activated by the reactive Mo(III) center.

In addition to the above mentioned Cr(N(i-Pr)\textsubscript{2})\textsubscript{3}, there are several examples of low-coordinate metal amide or phosphide complexes with \( \beta \)-hydrogens, including Ti(N(i-Pr)\textsubscript{2})\textsubscript{3},\textsuperscript{43} Mo(N(i-Pr)\textsubscript{2})\textsubscript{3},\textsuperscript{44} V(N(i-Pr)\textsubscript{2})\textsubscript{3},\textsuperscript{29} V(P(cy)\textsubscript{2})\textsubscript{3},\textsuperscript{45} and Cr(P(cy)\textsubscript{2})\textsubscript{3},\textsuperscript{45} but none of these latter complexes are well characterized. Therefore, it is not possible to make predictions concerning the stability of a highly reactive Mo(III) complex with such an amide ligand. The 2-adamantyl substituent potentially exhibits an iso-propyl-like profile, in principle opening access to the Mo-E \( \pi \)-bond, but retains significant steric bulk, thereby preventing dimerization. The ligand is large and is not expected to significantly reduce the steric protection of the molybdenum center, but its use tests the compatibility of the reactive metal center with \( \beta \)-hydrogens, opening the door for future studies with other, less bulky secondary-alkyl anilide ligands.

Section 4.2: A New Bulky Ligand with \( \beta \)-hydrogens

(i) Synthesis of HN[2-Ad]Ar (4.1)

The synthesis of the aniline HN[2-Ad]Ar (4.1) is a trivial extension of the published procedure for HN[2-Ad]Ph.\textsuperscript{46} Simply heating 2-adamantanone with 2 equivalents each of formic acid and 3,5-dimethylaniline using Luekart conditions\textsuperscript{47} results in the formation of aniline 4.1 in essentially quantitative yield, given that unreacted starting materials are recovered. Carrying out the synthesis using the published procedure with a five hour reflux results in good product formation, but a substantial increase in yield is
realized when the reflux is extended to 24 hours. The amine is purified by crystallization from pentane. The $^1$H NMR spectrum of 4.1 shows the ortho and para hydrogen resonances at 6.25 and 6.41 ppm respectively, and a downfield resonance at 3.5 ppm which is due to the β-hydrogen; all other resonances are in the normal regions as expected.

(ii) Synthesis of LiN[2-Ad]Ar (4.2)

Deprotonation of 4.1 using $n$-butyllithium in a hydrocarbon solvent results in clean, quantitative formation of LiN[2-Ad]Ar (4.2), which precipitates directly from the reaction mixture. The lithium reagent is essentially insoluble in hydrocarbon solvents, but has good solubility in ether and THF. Isolation of the etherate of 4.2 has thus far been unsuccessful, as it has poor solubility properties, but it is not necessary to do so. The $^1$H NMR spectrum of 4.2 in THF-$d_8$ shows an upfield shift of the ortho and para resonances to 5.59 and 5.35 ppm respectively, while the β-hydrogen appears at 3.31 ppm.

Section 4.3: Complexes with N[2-Ad]Ar

(i) Synthesis of Cr(N[2-Ad]Ar)$_3$ (4.3)

It is desirable to first test the properties of this ligand in a system which is expected to be well behaved in the presence of β-hydrogens. Lithium amide 4.2 reacts with CrCl$_3$ in ether, following the standard procedure for the synthesis of Cr(N[R]Ar)$_3$ complexes (Scheme 4.1). After workup, the dark brown powdery material Cr(N[2-Ad]Ar)$_3$ (4.3) is isolated in 79% yield. The 2-adamantyl substituent significantly alters the solubility properties of the chromium complex relative to that with tert-butyl substitution. During filtration to remove LiCl from the crude reaction mixture, the filter cake must be washed with multiple portions of ether in order to fully dissolve 4.3. Crystallization of the complex is difficult, and the preferred method to obtain large quantities of material is by
slurrying it in pentane to wash away the major byproduct 4.1. This results in pure material, as shown by $^1$H NMR spectroscopy.

\[
\begin{align*}
3.0 \text{ LiN[2-Ad]Ar} \\
\text{CrCl}_3 \xrightarrow{\text{Et}_2\text{O, 4.5 h}} \text{Cr[N[2-Ad]Ar]} \\
\text{- 3.0 LiCl} \\
\text{Ar[2-Ad]N} \xrightarrow{1.5 \text{ NO}} \text{Cr[N[2-Ad]Ar]} \\
\text{Et}_2\text{O} \xrightarrow{20 \text{ min}} \text{O} \\
\text{N} \\
\text{Ar[R]N} \xrightarrow{\text{N[R]Ar}} \text{Cr[N[R]Ar} \\
\end{align*}
\]

(2.2)

(2.3)

**Scheme 4.1:** Chromium complexes with the $N$-2-adamantyl-3,5-dimethylanilide ligand

The resonances in the $^1$H NMR spectrum are extremely broad, and the only one that is definitively assigned is the aryl methyl resonance, appearing at -3.43 ppm. This is approximately where the aryl methyls appear in Cr(N[R]Ar)$_3$.\(^{49}\) A magnetic susceptibility measurement by the Evans method\(^ {50}\) shows three unpaired electrons; $\mu_{\text{eff}}$ is calculated to be 3.98 $\mu_B$, which is in good agreement with the spin-only value of 3.87 $\mu_B$.

(ii) **Synthesis of (ON)Cr(N[2-Ad]Ar)$_3$ (4.4)**

Complex 4.3 reacts with an excess of nitric oxide (Scheme 4.1), following the standard procedure,\(^ {48}\) to form the dark red diamagnetic derivative, (ON)Cr(N[2-Ad]Ar)$_3$.
(4.4) which is isolated in 80% yield by crystallization from ether. Crystals suitable for an X-ray diffraction study have not been obtained.

The $^1$H NMR spectrum of the complex shows ortho and para resonances at 5.67 and 6.72 ppm respectively, with a substantially deshielded $\beta$-hydrogen resonance of 4.65 ppm. Another of the adamantyl resonances appears downfield of the aryl methyl resonance at 2.24 ppm. The IR spectrum shows a strong stretch at 1668 cm$^{-1}$ due to $v_{N=O}$. It has not been possible to obtain complex 4.4 in analytically pure form, even after multiple recrystallizations; the best data are given in the experimental section. High resolution mass spectral data support the formulation proposed, and all characterization data are similar to those reported for (ON)Cr(N[R]Ar)$_3$.\textsuperscript{48}

(iii) Synthesis of Mo(N[2-Ad]Ar)$_3$ (4.5)

The synthesis of the supposedly more reactive molybdenum complex, Mo(N[2-Ad]Ar)$_3$ (4.5), is also straightforward. Treating MoCl$_3$(THF)$_3$ with a deficiency of LiN[2-Ad]Ar (4.2), using standard procedures,\textsuperscript{16} forms the desired tris-anilide complex (Scheme 4.2). The dark orange material has to be separated from an unknown dark brown impurity. This is best accomplished by allowing a fairly concentrated solution to stand at room temperature for several hours; the dark material is then simply be filtered away. Crystallization of the desired complex is difficult to initiate: solutions become supersaturated at -35 °C without significant formation of solid material. Induction of crystallization in a concentrated solution at room temperature followed by cooling to -35 °C results in the best yields. Similar solubility properties are observed with the related 1-adamantyl ligand.\textsuperscript{33,35}
Scheme 4.2: Molybdenum complexes with the N-2-adamantyl-3,5-dimethylanilide ligand

The $^1$H NMR spectrum of 4.5 is much better resolved than that of the chromium derivative 4.3, although the resonances are still extremely broad. The aryl methyl resonance appears at -3.00 ppm. An Evans method magnetic susceptibility measurement is consistent with 3 unpaired electrons ($\mu_{\text{eff}} = 3.88 \mu_B$). The increased steric bulk of the 2-adamantyl substituent relative to the tert-butyl substituent manifests itself during recrystallization of 4.5. Extended storage of the purified material at -35 °C does not result in a deep purple color, and no diamagnetic material is observed to appear by $^1$H NMR spectroscopy, suggesting that the intermolecular dinitrogen cleavage reaction is shut down in this system. This result is also observed with the 1-adamantyl derivative.

Crystals suitable for X-ray diffraction are obtained from a chilled ether solution. An ORTEP diagram of 4.5 is shown in Figure 4.1, pertinent bond lengths and angles are listed in Tables 4.1 and 4.2, and positional parameters and U(eq) are listed in Table 4.3. The average Mo-N distance is 1.99 Å, the N-Mo-N angles are ca. 120°, the Mo-N-C$_{ipso}$ angles are ca. 110°, and the Mo-N-C$_{\alpha}$ angles are ca. 130°. All metrical data are similar to
those observed with the related tert-butyl derivative. The 2-adamantyl groups do not exhibit either the expected pseudo-iso-propyl or pseudo-cyclohexyl geometries, but instead are rotated by about 90° from these positions, creating a chiral C₃ propeller with significant intermeshing of the alkyl substituents. Interconversion of the two chiral rotamers is not observed spectroscopically; the adamantyl groups appear to be related by mirror symmetry on the NMR time scale.

**Table 4.1.** Selected Bond Lengths (Å) for Mo(N[2-Ad]Ar)₃ (4.5).

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**Table 4.2.** Selected Bond Angles (°) for Mo(N[2-Ad]Ar)₃ (4.5).

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(218) References begin on page 240
Figure 4.1: ORTEP diagram of Mo(N[2-Ad]Ar)₃ (4.5) with ellipsoids drawn at the 30% probability level.
Table 4.3: Positional Parameters \((x \times 10^4)\) and \(U(\text{eq.})\) \((\AA^2 \times 10^3)\) for the Non-Hydrogen Atoms of Mo\(\text{N}[2-\text{Ad}]\text{Ar}_3\) (4.5).

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(iv) Synthesis of PMo(N[2-Ad]Ar)₃ (4.6)

In order to chemically characterize 4.5, a diamagnetic triply-bonded derivative analogous to those obtained with Mo(N[R]Ar)₃ is desired. Treating a solution of 4.5 with a large excess of P₄ generates the phosphide complex, PMo(N[2-Ad]Ar)₃ (4.6) in moderate yield (Scheme 4.2). Using only 1.4 equivalents of [P], the standard preparation,¹⁵ results in significant formation of free aniline 4.1, which is also the major contaminant in the preparation using a large excess of phosphorus. Separation of the two complexes is extremely difficult, especially given the poor solubility properties of complexes with the 2-adamantyl ligand as discussed previously. Precipitation of 4.6 from a methylene chloride solution with acetonitrile is the only way to obtain good yields of material. However, even after multiple recrystallizations from toluene, the material is not analytically pure. The best analytical data are given in the experimental section. The observed proton NMR spectrum is typical for diamagnetic complexes with the N[2-Ad]Ar ligand environment; the ortho and para protons have resonances at 5.99 and 6.65 ppm respectively, while the β-hydrogen appears at 4.70 ppm. The ³¹P NMR spectrum has a single resonance at the extremely downfield position of 1215 ppm. This is the usual region for phosphide (P³⁻) signals.¹⁵,³⁷,³⁸,⁵¹ The high resolution mass spectrum supports the formulation presented.

A crystal suitable for X-ray diffraction is obtained from a chilled ether solution. An ORTEP diagram of 4.6 is shown in Figure 4.2, pertinent bond lengths and angles are
listed in Tables 4.4 and 4.5, and positional parameters and U(eq) are listed in Table 4.6. The Mo-P vector of the molecule sits on a three-fold axis, and the Mo-P bond length of 2.106(3) Å is comparable to those observed in other phosphido complexes.\textsuperscript{15,38,51} The Mo-N distance is 1.987(6) Å. The phosphido complex is approximately tetrahedral, with a P-Mo-N angle of 102.6(2)° and an N-Mo-N' angle of 115.35(11)°. The most significant distortion in the molecule is the Mo-N-C111 angle of 136.2(4)°, increased by an average of 7° from complex 4.5. This results in a compression of the C11-N-C111 angle by an average of 6° from the starting tris-anilide complex. This distortion is necessary to allow room for the phosphido fragment. The N-α-carbon vector of the 2-adamantyl group is displaced by 5° from the Mo-P vector, a significantly smaller angle than that usually observed for pseudo-C\textsubscript{3} symmetric complexes using the N[R]Ar ligand environment; these angles are typically 20-30°.\textsuperscript{15,38,52,53} This is due to the large steric requirement of the 2-adamantyl group when oriented sideways in a C\textsubscript{3} propeller.

| Table 4.4. Selected Bond Lengths (Å) for PMo(N[2-Ad]Ar)\textsubscript{3} (4.6). |
|-----------------|-----------------|-----------------|-----------------|
| Mo-P            | 2.106(3)        | Mo-N            | 1.987(6)        |
| N-C11           | 1.441(9)        | N-C111          | 1.488(9)        |

| Table 4.5. Selected Bond Angles (°) for PMo(N[2-Ad]Ar)\textsubscript{3} (4.6). |
|-----------------|-----------------|-----------------|-----------------|
| N-Mo-N'         | 115.35(11)      | P-Mo-N          | 102.6(2)        |
| Mo-N-C11        | 110.2(4)        | Mo-N-C111       | 136.2(4)        |
| C11-N-C111      | 110.9(6)        | P-Mo-N-C111     | 5.0             |
| P-Mo-N-C111     | 152.0           |                 |                 |
Figure 4.2: ORTEP diagram of PMo(N[2-Ad]Ar)₃ (4.6) with ellipsoids drawn at the 30% probability level.
Table 4.6: Positional Parameters (x 10^4) and U(eq.) (Å^2 x 10^3) for the Non-Hydrogen Atoms of PMo(N[2-Ad]Ar)_3 (4.6).

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Section 4.4: Reactions of Mo(N[2-Ad]Ar)_3 (4.5)

(i) Mesityl Azide, Synthesis of NMo(N[2-Ad]Ar)_3 (4.7)

The nitride of 4.5, NMo(N[2-Ad]Ar)_3 (4.7), is prepared by using mesityl azide as the nitrogen atom source (Scheme 4.3). Spectroscopically, the reaction generates an equivalent of free aniline 4.1, but it is possible to isolate the nitride complex in low yield and in pure form by multiple recrystallizations from ether. The ^1H NMR resonances due to the N[2-Ad]Ar ligand protons are grossly similar to those observed in the chromium nitrosyl 4.4 and in the molybdenum phosphide derivative 4.6.
Scheme 4.3: Reactions of Mo(N[2-Ad]Ar)₃
(ii) Nitric Oxide, Synthesis of (ON)Mo(N[2-Ad]Ar)₃ (4.8)

Complex 4.5 also reacts with an excess of nitric oxide, cleanly generating the nitrosyl complex (ON)Mo(N[2-Ad]Ar)₃ (4.8) after about 20 minutes (Scheme 4.4). The complex is isolated in approximately 70% yield by recrystallization from THF, and the ¹H NMR resonances of this complex are again grossly similar to those observed in complexes 4.4 and 4.6.

(iii) Nitrous Oxide

When tris a.lide complex 4.5 is treated with one to two equivalents of nitrous oxide, added via syringe to a Schlenk flask containing 4.5 as is typical for the transformation,¹⁶ no reaction is observed except for the generation of small amounts of free aniline 4.1. Adding 2.6 equivalents of nitrous oxide to complex 4.5 using rigorous air-exclusion gas transfer techniques shows less than 5% conversion to the diamagnetic nitride and nitrosyl complexes 4.7 and 4.8 after 35 minutes (Scheme 4.3), as shown by ¹H NMR spectroscopy. When the reaction is repeated with approximately 50 equivalents of nitrous oxide (1 atm), and allowed to react for 60 minutes before removing the solvent, ¹H NMR spectroscopy shows approximately 90% conversion to 4.7 and 4.8, with a detectable quantity (ca. 5%) of 4.5 (Scheme 4.3).

(iv) Comparison of Molybdenum Complexes

It is now possible to compare the reactivity of three different molybdenum complexes with different steric environments: Mo(N[R]Ar)₃ (2.1), Mo(N[1-Ad]Ar)₃ (4.9) and Mo(N[2-Ad]Ar)₃ (4.5). Mo(N[1-Ad]Ar)₃ is prepared analogously to complex 4.5 using the lithium anilide LiN[1-Ad]Ar.³²,⁵⁴ Complex 2.1 reacts with either dinitrogen¹⁴ or mesityl azide¹⁶ to give NMo(N[R]Ar)₃ (3.1); nitric oxide to give

(226)  References begin on page 240
(ON)Mo(N[R]Ar)₃;¹⁶ and nitrous oxide to give a 1:1 ratio of nitride and nitrosyl complexes.¹⁶

As discussed previously, Mo(N[1-Ad]Ar)₃ does not react with dinitrogen at reduced temperature to give a deep purple µ-dinitrogen complex. This is believed to be due to the deeper steric pocket which prohibits a two-atom bridge between two molybdenum centers.³² Mo(N[1-Ad]Ar)₃ does react with mesityl azide, however, initially forming a purple color which fades to tan brown over a few minutes. Analysis of the product by ¹H NMR spectroscopy shows diamagnetic material corresponding to NMo(N[1-Ad]Ar)₃ with similar aryl resonances to nitride 3.1. Mo(N[1-Ad]Ar)₃ also reacts with nitric oxide, rapidly changing color from orange red to very pale yellow. Proton NMR spectroscopy shows diamagnetic resonances consistent with (ON)Mo(N[1-Ad]Ar)₃. Finally, Mo(N[1-Ad]Ar)₃ reacts rapidly with 0.5 equivalents of nitrous oxide, and ¹H NMR shows the formation of a 1:1 mixture of the corresponding nitride and nitrosyl complexes. Under no conditions (solvent, temperature, number of equivalents of N₂O) could this ratio be altered.

The reaction chemistry of Mo(N[2-Ad]Ar)₃ (4.5) with mesityl azide and nitric oxide, and its lack of reaction with dinitrogen at reduced temperatures is analogous to the 1-adamantyl derivative 4.9. The increased steric bulk is evident in the substantially slower reaction observed with nitrous oxide. Further details of this reaction are presented in Section 4.5.

Section 4.5: Competition Experiments between Mo(N[R]Ar)₃ (2.1) and Mo(N[2-Ad]Ar)₃ (4.5)

(i) Background

In the original report concerning the cleavage of the N-N bond in nitrous oxide,¹⁶ there are no data to either support or refute the postulate that the reaction requires two molybdenum centers. Since that time, the dinitrogen cleavage reaction has been intensely
studied, and it is known that two molybdenum centers are required.\textsuperscript{14,31,55} It is not yet possible to measure the kinetics of the nitrous oxide reaction due to the extremely fast rate. Even with the 1-adamantyl substituent, the reaction is extremely rapid and always generates equimolar amounts of nitride and nitrosyl complexes 4.8 and 4.9. When the 2-adamantyl derivative 4.5 reacts with nitrous oxide, it also does so to form equimolar quantities of nitride and nitrosyl 4.10 and 4.11. All this taken together suggests that the N-N cleavage in the nitrous oxide reaction also requires two molybdenum centers. However, as the new data shows that tris anilide 4.5 does not react with nitrous oxide on the usual timescale of the reaction, it should be possible to detect the presence of free nitric oxide during the reaction of Mo(N[R]Ar)\textsubscript{3} with N\textsubscript{2}O, thereby determining whether any of the N-N bonds in N\textsubscript{2}O are cleaved by a single Mo(N[R]Ar)\textsubscript{3} center.

(ii) Nitric Oxide

First, a competition study between 4.5 and 2.1 for NO must be carried out in order to see if it is possible for 4.5 to compete for free NO in solution. As it turns out, the 2-adamantyl derivative does compete to the extent of about 20% for free NO (Scheme 4.4). Equimolar amounts of both Mo(III) starting materials are loaded into a reaction bomb, and a deficiency of NO is injected through a septum. Analysis of the reaction mixture by \textsuperscript{1}H NMR spectroscopy after 20 minutes shows a 3:1 ratio of (ON)Mo(N[R]Ar)\textsubscript{3} and nitrosyl 4.8, along with significant amounts of both starting tris anilide complexes.
Scheme 4.4: Competition of molybdenum tris-anilides for NO

(ii) Nitrous Oxide

Next, equimolar quantities of 4.5 and 2.1 are treated with a deficiency of N$_2$O. After stirring for 35 minutes, the reaction mixture is analyzed by $^1$H NMR spectroscopy. The only observed diamagnetic complexes are the nitride and nitrosyl complexes with the -N[R]Ar ligand (Scheme 4.5). This result strongly suggests that there is no free nitric oxide present in solution during the course of the nitrous oxide reaction, which points to a bimolecular cleavage pathway like that observed in the dinitrogen cleavage reaction. The fact that no diamagnetic complexes with the N[2-Ad]Ar ligand are observed indicates that there is no mixed-bimetallic N$_2$O cleavage; the only productive cleavage pathway is when two Mo(N[R]Ar)$_3$ molecules react together with one nitrous oxide molecule. These results also shed some light on the increased steric requirements of the 2-adamantyl group relative to the 1-adamantyl. Use of N[2-Ad]Ar not only shuts down intermolecular chemistry along a two-atom bridge (N$_2$), but significantly slows intermolecular reactions along a three-atom bridge (N$_2$O).
Scheme 4.5: Competition of molybdenum tris-anilides for $N_2O$

Section 4.7: Conclusion

Use of the 2-adamantyl substituent on an anilide ligand allows for the synthesis and characterization of both chromium (as expected) and molybdenum (as hoped) -(III) and -(VI) complexes. There appear to be no inherent problems of $\beta$-hydrogens with the reactive Mo(III) center. The fact that complex 4.5 reacts fairly rapidly with nitric oxide but does not react similarly with nitrous oxide allows for the determination of free NO in the $N$-$N$ bond cleavage reaction of nitrous oxide mediated by Mo(N[R]Ar)$_3$. No free NO is observed, strongly suggesting an intramolecular reaction similar to that observed in the cleavage of dinitrogen. The significantly increased steric environment around a metal center with the 2-adamantyl ligand may be useful in other systems where more steric protection is required.
Section 4.8: Experimental

4.8.1 General Considerations

General experimental details are as described in Chapters I, II and III. Solvents were dried and deoxygenated according to previously published procedures. Diethyl ether was dried according to a procedure by Grubbs. P₄ was purified by recrystallization from toluene. MoCl₃(THF)₃ and Mo(1-Ad)Ar were prepared via standard procedures. Other chemicals were purified via standard procedures or used as received. Magnetic susceptibilities were measured by NMR spectroscopy. NMR spectra were recorded on Varian XL-300, Varian Unity-300 or Varian VXR-500 spectrometers. Chemical shifts are reported with respect to internal solvent. CHN analyses were performed by Oneida Research Services (Whitesboro, NY) or Microlytics (South Deerfield, MA). Melting points were obtained in sealed glass capillaries and are uncorrected.

4.8.2 Synthesis of Complexes

(i) HN[2-Ad]Ar 4.1. 3,5-dimethylaniline (33.4 mL, 268 mmol, 2.01 eq.), formic acid (10.4 mL of a 95-98% solution, ca. 2 eq.) and 2-adamantanone (20.06 g, 133.5 mmol) were heated at 95-100 °C for 24 hours. Concentrated HCl (70 mL) was then added and the solution was heated at 95 °C for one hour. A copious amount of white solid appeared. The reaction mixture was diluted with water (100 mL), and the white solid was collected on a frit. The filtrate contained the hydrochloride of 3,5-dimethylaniline. The filter cake was washed with water (100 mL) and 3,5-dimethylaniline was recovered from the filtrate by adding concentrated NaOH solution (ca. 5 M) until the pH was ~14, at which point a yellow oil appeared. The aqueous layer was washed with ether (2 x 150 mL) and the solvent was removed in vacuo to yield a yellow oil (22 mL, 176 mmol). The filter cake

(231) References begin on page 240
was then washed with ether (2 x 100 mL), removing unreacted 2-adamantanone, which was recovered by removing the ether in vacuo (9.82 g, 73.5 mmol). The filter cake was slurried in water (200 mL) and ether (200 mL), and NaOH (12 g) was added to neutralize the hydrochloride. The organic layer was separated and the aqueous layer was washed with ether (2 x 200 mL). The combined organics were washed with saturated aqueous sodium chloride (200 mL) and saturated aqueous sodium bicarbonate (200 mL). The combined aqueous layers were then extracted with ether (200 mL). The combined organics were evaporated, resulting in a white solid (14.9 g, 58.3 mmol, 43.7%). The solid was recrystallized from pentane at -35 ºC in five crops (13.67 g, 53.54 mmol, 40%). M.p. 57-58 ºC. ¹H NMR (500 MHz, C₆D₆): δ = 6.412 (s, 1H, para); 6.252 (s, 2H, ortho); 3.636 (s, 1H, NH); 3.502, (s, 1H, β-H); 2.222 (s, 6H, ArMe); 1.948 (s, 2H); 1.614-1.802 (m, 10H); 1.4 (d, 2H). ¹³C NMR (76 MHz, CDCl₃): δ = 147.406 (s, ipso); 138.733 (q, ²JCH = 5Hz, meta); 118.634 (d, J = 156 Hz, aryl); 110.818 (d, J = 153 Hz, aryl); 56.592 (d, J = 134 Hz, adamantyl-α); 37.683 (t, J = 127 Hz); 37.365 (t, J = 127 Hz); 31.652 (d, J = 135 Hz); 31.541 (t, J = 128 Hz); 27.431 (d, J = 135 Hz); 27.296 (d, J = 135 Hz); 21.432 (q, J = 126 Hz, ArMe). MS (70 ev): m/z(%): 255(100)[M⁺]. Anal. Calcd. for C₁₈H₂₅N: C, 84.65; H, 9.87; N, 5.48. Found: C, 84.94; H, 10.03; N, 5.52.

(ii) LiN[2-Ad]Ar (4.2). HN[2-Ad]Ar (4.1, 10.30 g, 40.33 mmol) was dissolved in pentane (50 mL) and cooled to -35 ºC. n-Butyllithium (28 mL of a 1.6 M solution, 44.8 mmol, 1.1 eq.) was added via syringe over about a 5 minute period, causing the precipitation of a fine white powder. The solid was collected on a frit and dried in vacuo to constant weight (10.19 g, 38.99 mmol, 97%). ¹H NMR (500 MHz, C₄D₈O): δ = 5.590 (s, 2H, ortho); 5.349 (s, 1H, para); 3.306 (s, 1H, β-H); 2.150 (m, 2H); 1.962 (s, 6H, ArMe); 1.87 (s, 2H); 1.83 (m, 4H); 1.716 (s, 3H); 1.38 (d, 2H); 1.28 (m, 1H). ¹³C NMR (126 MHz, C₄D₈O): δ = 161.868 (s, aryl ipso); 137.093 (s, meta); 110.629 (br d, J = 149.73 Hz, ortho); 107.743 (d, J = 143.85 Hz, para); 62.323 (d, J = 126.83, β-C);
39.841 (t, J = 124.09); 39.294 (t, J = 125.46); 34.018 (t, J = 125.46); 33.971 (d, J = 130.96); 29.718 (d, J = 130.49); 22.595 (q, J = 123.93, ArMe).

(iii) Cr(N[2-Ad]Ar)₃ (4.3). LiN[2-Ad]Ar (4.2, 1.8083 g, 6.9196 mmol, 2.73 eq) was dissolved in ether (60 mL) and frozen solid. CrCl₃ (0.4018 g, 2.537 mmol) was added as a solid and the reaction was stirred for 3.5 hours. The solution changed from colorless to dark brown as the solids reacted and dissolved. LiCl and excess CrCl₃ were removed by filtration through celite. The filter cake was washed with ether (10 x 25 mL) until the washings were essentially colorless, and the solvent was removed from the filtrate in vacuo. The dark solid obtained was slurried in ether (15 mL) and stored at -35 °C overnight. Two crops were obtained (0.7230 g, 1.0095 mmol, 43%). Two additional crops were obtained from pentane (0.6664 g, 0.8175 mmol, 36%). Low yields of analytically pure material were obtained by recrystallization from ether. M.p. 268-269 °C. 

¹H NMR (300 MHz, C₆D₆): δ = 7.67 (~6H); Δν₁/₂ = ~300; 3.883 (~12H); Δν₁/₂ = 370; 2.241 (~6H); 3.427 (6H, ArMe); Δν₁/₂ = 700. MS (70 eV): m/z(%): 814(0.27)[M⁺]. 


(iv) (ON)Cr(N[2-Ad]Ar)₃ (4.4). To a dark brown stirring solution of Cr(N[2-Ad]Ar)₃ (4.3, 0.3371 g, 0.4135 mmol) in ether (40 mL) was added NO (15 mL, 0.614 mmol, 1.5 eq) via syringe. The solution changed to red orange over a 10 minute period. The ether was removed in vacuo and the solid was redissolved in a minimum of ether and cooled to -35 °C to yield dark red faceted crystals in three crops (0.2796 g, 0.3308 mmol, 80%). M.p. 200-205 °C (dec). 

¹H NMR (300 MHz, CDCl₃): δ = 6.715 (s, 3H, para); 5.666 (br s, 6H, orthos); 4.651 (s, 3H, β-H); 2.238 (br s, 6H); 2.092 (s, 18H, ArMe); 1.842 (br s, 15H); 1.75 (m, 15H); 1.32 (m, 6H). 

¹³C NMR (76 MHz, CDCl₃): δ = 153.762 (s, ipso); 136.837 (q, ²JCH = 6 Hz, meta); 127.370 (d, J = 154 Hz); 126.458 (d,
Chapter IV: Group 6 Complexes with a Bulky Amide Ligand Containing β-Hydrogens

\( J = 157 \, \text{Hz} \); 75.984 (d, \( J = 118 \, \text{Hz} \), adamantyl-\( \alpha \)); 38.151 (t, \( J = 130 \)); 37.897 (t, \( J = 130 \)); 34.596 (d, \( J = 133 \, \text{Hz} \)); 31.097 (t, \( J = 126 \, \text{Hz} \)); 27.732 (d, \( J = 130 \, \text{Hz} \)); 27.621 (d, \( J = 130 \, \text{Hz} \)); 21.385 (q, \( J = 126 \, \text{Hz} \), ArMe). IR (ether, 2 cm\(^{-1}\)): ν\(_{\text{NO}}\) = 1668 cm\(^{-1}\). MS (70 eV): \( m/z(\%) \): 844(0.22)[M\(^+\)]. HRMS (EI, 70 eV): calcld \( \text{m}_{\text{ass}} \): 844.51123. Found mass: 844.511(2) Anal. Calcd for \( \text{C}_{54}\text{H}_{72}\text{CrN}_{4}\text{O} \): C, 76.74; H, 8.59; N, 6.63. Found: C, 75.55; H, 9.12; N, 6.11.

(v) \( \text{Mo(N[2-Ad]Ar)}_3 \) (4.5). LiN[2-Ad]Ar (4.2, 3.8001 g, 14.541 mmol, 2.02 eq) was slurried in ether (100 mL) and frozen solid. The frozen solution was allowed to thaw, and when magnetic stirring was just possible, MoCl\(_3\)(THF)\(_3\) (3.0200 g, 7.2145 mmol) was added. The solution was stirred vigorously for 4.5 hours, during which time the solution turned dark brown. The reaction mixture was filtered through celite, and the filter cake was washed with ether (2 x 20 mL) until the washings were colorless. The filtrate was evaporated *in vacuo*, redissolved in ether (35 mL) and allowed to stand at room temperature overnight. A dark precipitate was removed by filtration, and the filtrate was reduced in volume and stored at room temperature until crystallization initiated. The saturated solution was then stored overnight at -35 °C. The solid powdery material was collected on a frit and washed with cold pentane (3 x 5 mL) yielding dark orange material. A second crop was obtained by a similar crystallization from pentane (15 mL) (2.279 g, 2.653 mmol, 64%). M.p. 211-212 °C. \(^1\)H NMR (300 MHz, C\(_6\)D\(_6\)): \( \delta(\Delta v_{1/2}) = 12.818(71) \) (6H); 9.288(148) (6H); 5.299(-300); 3.534(109); 1.962(-300); -2.995(124) (18H, ArMe); -47.64(193) (3H). MS (70 eV): \( m/z(\%) \): 861.1(6.6)[M\(^+\)]. \( \mu_{\text{eff}} \) (300 MHz, C\(_6\)D\(_6\)): 3.875 \( \mu_\text{B} \). Anal. Calcd for \( \text{C}_{54}\text{H}_{72}\text{MoN}\text{N} \): C, 75.49; H, 8.45; N, 4.89. Found: C, 74.96; H, 8.63; N, 4.70.

(vi) \( \text{PMo(N[2-Ad]Ar)}_3 \) (4.6). Mo(N[2-Ad]Ar)\(_3\) (4.5, 0.5212 g, 0.6067 mmol) was dissolved in toluene (10 mL) and P\(_4\) (0.0861 g, 0.695 mmol, 4.58 eq [P]) was added.

(234) References begin on page 240
The reaction mixture was stirred for one hour, at which point the solvent was removed in vacuo. The solids obtained were dissolved in ether (20 mL) and filtered, removing a dark brown-orange solid (ca. 90 mg). The filtrate was evaporated to dryness and dissolved in methylene chloride (5 mL). Acetonitrile (10 mL) was added, causing precipitation of a brown solid, which was collected on a frit. This process was repeated with the filtrate, resulting in a second crop of material (0.2896 g, 0.3254 mmol, 54%). M.p. 223-224 °C (dec). 1H NMR (500 MHz, C6D6): δ = 6.654 (s, 3H, para), 5.987 (s, 6H, ortho); 4.700 (s, 3H, β-H); 3.129 (s, 6H); 2.086 (s, 18H, ArMe); 1.937 (m, 12H); 1.800 (br m, 6H); 0.931 (s, 12H); 1.413 (d, 6H). 13C NMR (126 MHz, CDCl3): 149.942 (s, ipso); 137.058 (q, 2JCH = 5.8 Hz, meta); 128.327 (d, J = 152.94 Hz, ortho); 127.150 (d, J = 147.89 Hz, para); 79.395 (d, J = 138.28 Hz, adamantyl-α); 38.675 (t, J = 128.44); 38.205 (t, J = 127.06); 35.319 (d, J = 130.50 Hz); 30.827 (t, J = 126.38 Hz); 28.108 (d, J = 132.33); 27.825 (d, J = 132.79 Hz); 21.570 (q, J = 126.07 Hz, ArMe). 31P NMR (203 MHz, CDCl3): δ (Δν1/2) = 1215.46(86). MS (70 eV): m/z(%): 891.8(0.72)[M+]. HRMS (EI, 70 eV): calcd mass: 891.451793. Found mass: 892.451(2) Anal. Calcd for C54H72MoN3P: C, 72.87; H, 8.15; N, 4.72. Found: C, 73.64; H, 7.92; N, 4.34.

(vii) NMo(N[2-Ad]Ar)3 (4.7): Mo(N[2-Ad]Ar)3 (4.5, 0.4747 g, 0.5525 mmol) was dissolved in ether (10 mL) and chilled to -35 °C. Mesityl azide (90 mL, .6186 mmol, 1.1 eq) was dissolved in Et2O (15 mL) and chilled to -35 °C. The Molybdenum solution was added to the azide solution over a 15 minute period. The solution turned purple and then changed to brown over a five minute period. After one hour of stirring, the solvent was removed in vacuo. Two crops of tan-brown powder were obtained from a concentrated ether solution at -35 °C (0.1648 g, 0.1887 mmol, 34 %). M.p. 235-40 (dec). 1H NMR (300 MHz, CDCl3): δ = 6.730 (s, 3H, para); 6.708 (s, 6H, ortho); 3.898 (s, 3H, β-H); 2.490 (s, 6H); 2.082 (s, 18H, ArMe); 2.000 (d, 6H), 1.84 (d, 12 H); 1.72 (m, 6H); 1.36 (d, 6H) 1.273 (6H). 1H NMR (300 MHz, C6D6): δ = 6.886 (s, 3H, para);
6.031 (s, 6H, ortho); 4.29 (s, 3H, β-H); 2.96 (s); 2.35 (m); 2.097 (s, 18H, ArMe); 1.851 (s); 1.682 (s); 1.52 (m). $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 151.951 (s, ipso); 137.731; 127.268; 127.125; 72.733; 38.414; 38.215; 32.327; 30.921; 28.540; 27.677; 21.632. IR (benzene, 2 cm$^{-1}$): 1600, 1585 cm$^{-1}$.

(viii) (ON)Mo(N[2-Ad]Ar)$_3$ (4.8): Mo(N[2-Ad]Ar)$_3$ (4.5, 0.6658 g, 0.7750 mmol) was dissolved in ether (10 mL) and NO (21 mL, 0.8594 mmol, 1.1 eq) was added via syringe. The reaction mixture was stirred for 20 minutes and the solution turned much lighter brown orange color. The solvent was removed in vacuo and the remaining solid was dissolved in ca. 10 mL THF with stirring. Two crops of powdery solid were collected (0.4800 g, 0.5399 mmol, 70%). M.p.: 280-285 (dec). $^1$H NMR (300 MHz, CDCl$_3$): δ = 6.770 (s, 3H, para); 5.779 (s, 6H, ortho); 4.190 (s, 3H, β-H); 2.162 (s, 6H); 2.100 (s, 18H, ArMe); 1.902-1.697 (m, 30 H); 1.40 (d, 6H). $^1$H NMR (300 MHz, C$_6$D$_6$): δ = 6.884 (s, 3H, para); 6.092 (s, 6H, ortho); 4.579 (s, 3H, β-H); 2.638 (s, 6H). 2.10 (m, 9H); 2.080 (s, 18H, ArMe); 1.866 (s, 12H); 1.7-1.5 (m, 15H). $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 148.943 (s, ipso); 137.929 (q, $^2J_{CH} = 7.72$ Hz, ortho); 128.119 (d, $J = 151.5$ Hz, para); 127.515 (d, $J = 157.5$ Hz, meta); 75.536 (d, $J \sim 145$Hz, adamantyl-α); 38.361 and 38.194 (t, $J = 128.3$ Hz); 33.835 (d, $J = 132.8$ Hz); 31.019 (d, $J = 130.6$ Hz); 28.260 (d, $J = 139.0$ Hz); 27.897 (d, $J = 134.1$ Hz), 21.714 (q, $J = 125.9$ Hz, ArMe). IR (benzene, 2cm$^{-1}$): 1604, 1582 cm$^{-1}$. Anal. calcd for C$_{54}$H$_{72}$MoN$_4$O: C,72.95; H, 8.16; N, 6.30. Found: C, 72.63; H, 8.43; N, 5.80.
4.8.3 Other Reactions

(i) Reaction of 4.5 with N₂. Several hundred milligrams of Mo(N[2-Ad]Ar)₃ were dissolved in ether (ca 10 mL) and stored at -35 °C overnight; there was no observed color change. ¹H NMR spectroscopy showed only starting tris-anilide 4.5.

(ii) Reaction of 4.5 with N₂O. a) 2.6 equiv: Mo(N[2-Ad]Ar)₃ (4.5, 0.0177 g, 0.0206 mmol) was dissolved in toluene (5 mL) and removed from the glove box in a reaction bomb. The solution was degassed with 2 freeze-pump-thaw cycles, and nitrous oxide was added (3.1 mL, 320 torr, 2.6 eq). The reaction was stirred for 35 minutes, at which point the solvent was removed in vacuo. A ¹H NMR spectrum showed less than 5% conversion to the nitrido (4.7) and nitrosyl (4.8) complexes, with greater than 95% starting tris-anilide. b) 50 equiv: Mo(N[2-Ad]Ar)₃ (4.5, 0.0174 g, 0.0203 mmol) was dissolved in toluene (5 mL) and removed from the glove box in a reaction bomb. The solution was degassed, and nitrous oxide was added (~25 mL, 1 atm, ~1 mmol, ~50 eq). The reaction was stirred for 60 minutes, at which point the solvent was removed in vacuo. ¹H NMR spectroscopy showed greater than 90% conversion to 4.7 and 4.8 as well as about 5% starting tris-anilide.

(iii) Competition of 4.5 with 2.1 for NO. Mo(N[R]Ar)₃ (2.1, 0.0280 g, 0.0326 mmol) and Mo(N[2-Ad]Ar)₃ (4.5, 0.0231 g, 0.0359 mmol) were dissolved in toluene (5 mL) and removed from the glove box in a reaction bomb. The solution was evacuated, and nitric oxide was added to the head space through a septum (0.45 mL, 0.018 mmol). The gas was admitted to the bomb by opening the stopcock, and the reaction mixture was stirred for 20 minutes, at which point the solvent was removed in vacuo. ¹H NMR spectroscopy showed (ON)Mo(N[R]Ar)₃ and (ON)Mo(N[2-Ad]Ar)₃ 4.7 in a 4:1 molar ratio.
(iv) **Competition of 4.5 with 2.1 for N₂O.** Mo(N[R]Ar)³ (2.1, 0.0252 g, 0.0392 mmol) and Mo(N[2-Ad]Ar)₃ (4.5, 0.0323 g, 0.0376 mmol) were dissolved in toluene (5 mL) and removed from the glove box in a reaction bomb. The solution was degassed with 3 freeze-pump-thaw cycles, and nitrous oxide was added (3.1 mL, 120 torr, 0.020 mmol, 0.51 eq based on Mo(N[R]Ar)₃). The reaction was stirred for 35 minutes, at which point the solvent was removed *in vacuo.* ¹H NMR spectroscopy showed NMo(N[R]Ar)₃ and (ON)Mo(N[R]Ar)₃ as the only diamagnetic products.

4.8.4 **X-ray Structural Determination**

(i) **Mo(N[2-Ad]Ar)₃ (4.5).** A dark orange needle of approximate dimensions 0.57 x 0.37 x 0.19 mm was obtained from a chilled ether solution. The crystal was mounted on a glass fiber. Data collection was carried out on a Siemens Platform goniometer with a CCD detector at 183 K using Mo Kα radiation (λ = 0.71073 Å). The total data collected were 20644 reflections (-13 ≤ h ≤ 13, -21 ≤ k ≤ 11, -24 ≤ l ≤ 25), of which 7395 were unique (R_int = 0.0300). Corrections applied: semi-empirical from psi-scans. The structure was solved by direct methods (SHELXTL V5.0, G. M. Sheldrick and Siemens Industrial Automation, Inc., 1995) in conjunction with standard difference Fourier techniques. Least-squares refinement based upon F² converged with residuals of R₁ = 0.0443, wR₂ = 0.1164, and GOF = 1.242 based upon I > 2σ(I). All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated (d_C-H = 0.96 Å) positions. The largest residual peak and hole electron density was 0.476 and -0.259 e·Å⁻³. Crystal data: monoclinic, a = 11.761(3) Å, b = 19.737(5) Å, c = 22.761(5) Å, V = 5170(2) Å³, α = 90°, β = 101.89(2)°, γ = 90°, space group P2₁/n, Z = 4, μ = 0.294 mm⁻¹, M_r = 923.13 for C₅₈H₇₂MoN₃O, ρ(calcd) = 1.186 g/cm³, and F(000) = 1540. See Tables 4.1 and 4.2 for metrical parameters, Table 4.3 for positional parameters and U(eq), and Figure 4.1 for an ORTEP diagram.
(ii) PMo(N[2-Ad]Ar)₃ (4.6). A yellow parallelepiped of approximate dimensions 0.31 x 0.25 x 0.22 mm was obtained from a chilled ether solution. The crystal was mounted on a glass fiber. Data collection was carried out on a Siemens Platform goniometer with a CCD detector at 183 K using Mo Kα radiation (λ = 0.71073 Å). The total data collected were 18823 reflections (-42 ≤ h ≤ 41, -42 ≤ k ≤ 41, -42 ≤ l ≤ 42), of which 2424 were unique (R_int = 0.0382). Corrections applied: semi-empirical from psi-scans. The structure was solved by direct methods (SHELXTL V5.0, G. M. Sheldrick and Siemens Industrial Automation, Inc., 1995) in conjunction with standard difference Fourier techniques. Least-squares refinement based upon F² converged with residuals of R₁ = 0.0868, wR₂ = 0.2662, and GOF = 1.257 based upon I > 2σ(I). All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated (d_C-H = 0.96 Å) positions. The residual peak and hole electron density was 1.512 and -0.492 e·Å⁻³. Crystal data are Rhombohedral, a = b = c = 38.3067(6) Å, V = 5033.71(14) Å³, α = β = γ = 18.6720(10)°, space group R̅3c, Z = 4, μ = 0.329 mm⁻¹, M_r = 890.10 for C₅₈H₇₂MoN₃P, ρ(calcd) = 0.881 g/cm³, and F(000) = 1896. See Tables 4.4 and 4.5 for metrical parameters, Table 4.6 for positional parameters and U(eq), and Figure 4.2 for an ORTEP diagram.
References

36) The steric shielding sometimes shifts substitution chemistry, forcing electron transfer, as described in Chapter III.
39) Also See chapter III of this thesis.
51) Johnson, M. J. A.; Cummins, C. C., Unpublished Results.
53) Also see chapter II of this thesis.
Appendix I: Instructions for Extended Hückel Calculations And Orbital Visualization Using the Computer Programs EH and CACAO
Section 1: Introduction

CACAOn1,2 (Computer Aided Composition of Atomic Orbitals) is a collection of FORTRAN programs intended for the calculation and subsequent visualization of molecular orbitals at the extended Hückel level of theory. The original programs (CDNT, ICON and FMO) originate from the work of Hoffmann; the computational algorithms have not been substantially changed.3-5 New features include the automatic recognition and assignment of molecular symmetry, assignment of Mulliken symbols to each MO, fragment molecular orbital (FMO) analysis routines enabling the construction of Walsh diagrams, and a substantially improved user interface. The program can generate localized pictures of MOs similar to those seen in textbooks,7 but is also capable of presenting a delocalized and more realistic picture. Generally, the extended Hückel method gives a good approximation of the shapes of molecular orbitals, but the absolute energies of the orbitals are best obtained by higher levels of theory. However, it is possible to gain significant insight to chemical reactivity of a molecule by investigating the frontier orbital set.8

This document is meant as a clear and general introduction to CACAOn as the manual included with the program is not very easy to understand for a beginning user. Advanced features not found in this document are found in the manual. What follows in this section is a brief review of basic quantum mechanics in order to present a simple introduction to the extended Hückel method. A full discussion is clearly beyond the scope of this document, and more advanced understanding is readily available in one of many suitable texts.9-11

One of the most common ways to derive molecular orbitals is the linear combination of atomic orbitals (LCAO) approximation. The procedure is as follows for the creation of an extended π system in a conjugated carbon chain. Each π MO is written as a sum of the appropriate normalized atomic orbitals (in this case, p_z) of the various atoms in the

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molecule. This is summarized mathematically by the following equations, where \( \psi_k \) is the k'th molecular orbital, \( \phi_i \) is the i'th atomic orbital, and \( c_{ij} \) is a constant:

\[
\psi_k = \sum c_{ik} \phi_i \quad \text{the composition of MO}_k
\]

\[
\int \phi_i \phi_j \, d\tau = 1 \quad \text{the normalization of each } p_z \text{ orbital}
\]

The energy of the k'th molecular orbital, \( \psi_k \), is found by solving the wave equation

\[
(H - E)\psi_k = 0
\]

where \( H \) is the Hamiltonian. The LCAO expression for \( \psi_k \) is introduced, giving

\[
\sum c_{ik}(H - E)\phi_i = 0
\]

This expression is expanded and manipulated to give a series of linear equations, one for each \( \psi_k \). The first such equation (for \( \psi_1 \)) is

\[
c_{11}\int \phi_1(H - E)\phi_1 \, d\tau + c_{21}\int \phi_1(H - E)\phi_2 \, d\tau + \ldots + c_{11}\int \phi_1(H - E)\phi_1 \, d\tau = 0
\]

To simplify notation, the following definitions are introduced:

\[
H_{ii} = \int \phi_i H \phi_i \, d\tau
\]

\[
H_{ij} = \int \phi_i H \phi_j \, d\tau
\]

\[
S_{ij} = \int \phi_i \phi_j \, d\tau
\]

\( H_{ii} \) gives the energy of the atomic orbital \( \phi_i \) (the Coulomb integral), \( H_{ij} \) gives the energy of interaction between a pair of atomic orbitals \( \phi_i \) and \( \phi_j \) (the Resonance integral), and \( S_{ij} \) is the overlap integral between \( \phi_i \) and \( \phi_j \). The equation is now written as:

\[
c_{11}(H_{11} - ES_{11}) + c_{21}(H_{12} - ES_{12}) + \ldots + c_{11}(H_{11} - ES_{11}) = 0
\]

Similar equations are written for \( \psi_2 \) through \( \psi_k \), and the secular determinant for this series of equations is:

\[
\begin{vmatrix}
H_{11} - ES_{11} & H_{12} - ES_{12} & \ldots & H_{1i} - ES_{1i} \\
H_{21} - ES_{21} & H_{22} - ES_{22} & \ldots & H_{2i} - ES_{2i} \\
\vdots & \vdots & \ddots & \vdots \\
H_{i1} - ES_{11} & H_{i2} - ES_{12} & \ldots & H_{ii} - ES_{ii}
\end{vmatrix} = 0
\]
Appendix I: Instructions for Extended Hückel Calculations Using CACAO

Solving this secular determinant gives values for \( c_{ij} \). Since the atomic orbitals are normalized, each \( S_{ii} = 1 \). However, solving this series of equations without further simplification is difficult. This expression is substantially simplified by using the Hückel approximations, which are: \( S_{ij} = 0 \); and \( H_{ij} = 0 \) unless the \( i \)'th and \( j \)'th orbitals are on adjacent atoms. These simplifications make some sense, as most chemical bonds can be thought of in a localized fashion. The further simplifications of setting all remaining \( H_{ii} = 0 \) and \( H_{ij} = \beta \) is often made. This means that the energy of interaction of any orbital with a like orbital is set to an arbitrary zero point, and that between any \( i \) and \( j \) atom is of the same energy. Again, for an extended \( \pi \) MO, this makes sense. This results in a simpler secular determinant, which is more easily solved:

\[
\begin{bmatrix}
1 & -E & \beta & 0 & \ldots & 0 & 1 \\
1 & \beta & -E & \beta & \ldots & 0 & 1 \\
1 & 0 & \beta & -E & \ldots & 0 & 1 \\
1 & : & : & : & \ldots & : & 1 \\
1 & 0 & 0 & \ldots & \beta & -E & 1
\end{bmatrix} = 0
\]

For more complicated molecules (naphthalene for example), symmetry considerations are employed to reduce a large matrix to several smaller irreducible matrices.

The above matrix is derived for a linear chain of carbon \( p_z \) orbitals in a conjugated system, and obviously is substantially different for one which would be derived for a transition metal complex. For example, each different kind of ligand or metal \( s, p, d \) and hybrid orbital has a different \( H_{ii} \), and every possible interaction between each type of orbital would have a different \( H_{ij} \) term. Solving a determinant for even a relatively simple coordination complex is much more difficult than a simple extended \( \pi \) system, as the matrices involved are quite large, but the basic principles and simplifications remain the same as in this specific case.
Section 2: Program Architecture

There are two basic programs included in the CACAO package: EHC (Extended Hückel Calculation) which is the mathematical workhorse, and CACAO, which is the user controlled orbital visualization program. Also included in the package is a plotting program (PRINTGL), which is a third party shareware program. Two DOS batch files (pl.bat and plotf.bat) are used to allow CACAO to communicate with the plotting program.

EHC initially calculates Cartesian coordinates from the input internal coordinates. Alternatively Cartesian coordinates can be input directly. From the coordinates, MO calculation ensues, and the program can generate a wide variety of numerical output (wavefunction coefficients, energy levels, Mulliken population analysis, etc.). The program uses a modified version of the Wolfsberg-Helmholz formula, with a double-\(\zeta\) expansion of d orbitals. The parameters which the program uses are stored in the data file param.dat (this file can be modified if desired, see the manual for more details), with definitions are as follows:

\[\text{SYM, NE, NS, } \zeta_s, H_{ss}, NP, \zeta_p, H_{pp}, \text{ND, } H_{dd}, \zeta d_1, C_1, \zeta d_2, C_2\]

(where \text{SYM} = atomic symbol, \text{NE} = number of valence electrons in the neutral atom, \text{NS}, \text{NP}, \text{ND} = quantum numbers for s, p and d orbitals, \(\zeta_s, \zeta_p\) = exponents for s and p orbitals, \(\zeta d_1, \zeta d_2\) = exponents for the double expansion of d orbitals, \(C_1, C_2\) = coefficients for double expansion, \(H_{ss}, H_{pp}, H_{dd}\) = valence orbital ionization energy for s, p, d orbitals)

Sample parameters for an s, p and d block element are:

\[\text{H, 1, 1, 1.300, -13.60}\]
\[\text{C, 4, 2, 1.625, -21.40, 2, 1.625, -11.40}\]
\[\text{MO, 6, 5, 1.960, -8.34, 5, 1.900, -5.24 , 4, 4.540, -10.50, .5899, 1.900 .5899}\]

It is not yet possible to use f block elements or orbitals with EHC, though a later version of the program should have this capability. The program identifies the correct molecular point group and each MO is assigned the correct Mulliken label. It is possible to carry out
MO analysis at a variety of steps in order to generate the necessary information for the construction of Walsh diagrams. It is also possible to perform fragment analysis, allowing the subsequent construction of an interaction diagram between two molecular fragments. EHC always generates two output files for each input file (file.in): file.cor (the Cartesian coordinates derived for the molecule) and file.bin (binary data for MO construction). A third file, file.out, is a message file, which contains the desired numerical output, or error messages. The output files are not required for use of CACAO and they should periodically be deleted from the hard drive as they can be large. The maximum number of atoms per molecule is 125; the maximum number of orbitals per molecule is 500; the maximum number of steps in a Walsh diagram is 20; the maximum number of free variables is 10. These facts should be kept in mind during the generation of input files. More detailed information can be found in the CACAO manual.

CACAO takes the information present in file.bin and file.cor and generates either a Walsh or interaction diagram, depending on the type of input file, and pictures of the molecular orbitals. It is also allows viewing of the numerical output that is output to the file.out file, but this information is recalculated during the interactive session from the file.bin file (which is why the file.out files can be deleted). At the start of an interactive session, CACAO presents a list of available data sets. Once a data set is selected, the generation of diagrams and orbitals begins. The program is user friendly and menu driven. The user is asked questions that allow two or more choices which can usually be answered with Y(es), N(o) or a numerical input. Striking return chooses the default option, which is identified by DEF. Be careful to read the menus as inputting a negative number often makes the program choose an alternative pathway. The types of options which are selected include such things as maximum and minimum energies for a window, view orientation of a molecule, which MO to draw, and the resolution of the MO grid. The instruction manual for CACAO contains descriptions of more advanced features.

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PRINTGL is a shareware program which enables better interaction between the DOS/Windows environment and a printer. There is a lengthy manual for this program, but in general, no options need to be changed. The major options are set through the interface programs. . .

pl.bat and plotf.bat, which are two DOS batch files that allow communication between CACAO and PRINTGL. When a diagram is printed from CACAO, the program activates pl.bat, which determines several options and then activates plotf.bat, which sends the options through a command line to PRINTGL. When viewing a diagram or orbital in CACAO, typing P plots the graphics on the printer. Typing S gives a sub-menu, allowing either plotting to the printer, or saving to a Postscript file. This latter option is useful for the generation of high-quality output on a laser printer.

Section 3: DOS Navigation

For those familiar with UNIX, using DOS will be a nightmare. Many of the commands for DOS and UNIX are similar enough that if you have been using UNIX for a while, you will be unable to use DOS. However, there are only a few commands in DOS that are required for successful use of the CACAO package. Remember, file names and directory names are limited by 8 characters, and files can have at most a 3 character extension (?????????.??)

Directory hierarchy:  To move up a level, type cd ..
To move down a level, type cd \<directory name>
. is defined as the current level, while .. is the next higher

Directories:  md \<directory name> creates a new sub-directory
rd \<directory name> removes a directory.

File listings:  dir gives a file listing in the current directory
dir /w gives a file listing "widened" out

list continues . . .
**Wild cards:**
* is the general wild card, dir *.in will find all files with the extension .in
dir * .in/w "widens" the directory
? is a one letter wild card, dir ??.in will find file.in,
fill.in etc.

**File creation:**
For the purposes of CACAO, the edit command creates files

**File editing:**
After typing edit, the edit program is run. This program is very easy to use, is menu driven and utilizes the mouse. Anyone capable of using a Mac will be able to use the editor.

**File removal:**
del <file name>.<extension> will remove the selected file
del *.out will delete all output files
del file.* will delete file.in, file.out etc.
del *.* will delete ALL files in the current directory

**File renaming:**
rename file.in input.in will rename the file "file.in" to the new name "input.in"

**File moving:**
move c:\moan\file.in c:\moan\adam will move the file "file.in" from the moan directory to the adam subdirectory of the moan directory.

### Section 4: Program Installation

If the program is already installed, this process will not need to be repeated! To install the program, move to the DOS prompt, (c:\> and create a subdirectory called moan (Molecular Orbital ANalysis) (c:\> md .\moan). Move to this subdirectory (c:\> cd .\moan) and copy the file cacao40.exe from the floppy to this subdirectory. This file is a self extracting file. To use it, type (c:\moan\>cacao40.exe -d). This will create a variety of files including cacao.exe, eh.exe, param.dat, manual.doc, as well as a "files" subdirectory of moan, which will include a variety of sample input files. Two batch files are created in this process, pl.bat and plotf.bat; however, it should be noted that the files automatically created by cacao40.exe WILL NOT WORK. The correct forms of the .bat files are included at the end of this manual. Manual.doc is a word for Windows file. This file may be deleted. The CACAO manual has been translated to a Macintosh format on the lab computer. More detailed instructions for installation are found in the manual.
PRINTGL also needs to be installed, if it is not already. To the c:\moan\ subdirectory, copy rsunzip.exe and printgld.zip. Then, type c:\moan\>rsunzip printgld.zip. Following installation, printgld.zip and cacao40.exe may be deleted from the hard drive, as they are no longer needed.

Section 5: Use of Program

It is highly recommended that each user create a sub-directory for files. The number of files in the moan directory expands exponentially with use of the program. It is very easy to create files, and therefore it becomes very difficult to find desired files when needed, especially given the eight character limit on file names! Within each sub-directory, further sub-directories may be created, so that all Walsh diagram files are kept separate from all interaction diagram files or each molecule has its own sub-directory, for example. Therefore, at the moan prompt type:

c:}\moan\ > md \.<your name>

Then, type c:\moan\ > cd \.<your name>

to move into your subdirectory. The next portion of the instruction manual describes the creation of input files in detail. This is a simplified discussion from what appears in the manual.doc file, but clearly describes the input file creation for basic features of the program. More advanced features are described in the manual.

Section 6: Creation of Input Files

Introduction. There are three types of input file. The first is derived from X-ray crystal coordinates, the second is derived by using internal coordinates, and the third generates a Walsh diagram. This third type requires the use of internal coordinates. Three sample input files, xray.in, inter.in and walsh.in will be created in this section, with detailed line-by-line instructions for their modification. Remember, the numbers of spaces in the input file is very important. Therefore, the tilde (~) is used in this document to show
the correct numbers of spaces in each line. In general, to avoid problems, start with a working input file and modify it rather than creating a new one from scratch.

Crystal Data

This type of input file is useful when only a quick and dirty MO visualization of a specific molecule is required, without the possibility for Walsh diagrams or easy changing of the model. To generate the Cartesian coordinates, follow the following procedure. Port the X-ray data to Chem 3-D. Remove all extraneous atoms (i.e. convert N[R]Ar to NH₂). Do this by deleting all carbons and hydrogens in the molecule except the ipso carbon and the quaternary carbon of the tert-butyl. Select these two atoms and change them to H's. Select one N-H bond and change its bond length to a suitable one (ca. 1 Å) using the $ key combination (from the Build menu). Repeat for all N-H's. Next, it is a very good idea to center and orient the molecule for ease of viewing later on in CACAO. Select the central metal atom, and center it (from the View menu). Shift-click on a second atom (a nitrogen) and move it to the z-axis. Finally, shift-click on a third atom and move it to the x-z plane. Finally, from the Windows pull down menu, highlight the model, bringing up a sub menu. Select the Cartesian coordinates option which will bring up a window with atoms and x,y,z coordinates. Select this text and print it (from the file menu) or remember it. What follows is a description of an X-ray input file in detail.

line 1: title line
Mo(S)(NH2)3 from x-ray coordinates

Be as specific as possible. DOS only allows an 8 letter title for file names, and it becomes difficult to remember what names like "walslh1a.in vs. mowalshb.in" are. The title line is readily accessible from CACAO during an interactive session.

line 2: general parameter directive
~11~0DIST~1~0~0

Be careful to use the required number of spaces. Each integer is given three spaces to occupy, and each space not used by either a number or a negative sign must be present.

References begin on page 281
The first number is the total number of Real atoms (not counting dummy atoms which are only used with internal coordinates or for Walsh diagram input files, as discussed later). Mo(S)(NH₂)₃ has 11 atoms. The second number is the molecular charge. This will usually be 0. **HELPFUL TIP:** the calculated molecular charge, which is the last piece of information printed by the FMO part of EHC in the file.out file, should be equal to the value input in this line. If it is not, the calculation is most likely wrong, and the geometry of the molecule should be rechecked. DIST causes the EH program to generate output consisting of coordinates and interatomic separations. This field may be left blank if desired; add four spaces. The first number after the DIST card is the POPUL card. This field may be blank (three spaces), which will cause the MO occupation to be automatic, where electrons go into the lowest orbitals in order as usual. The unpairing of electrons (if it occurs) is done if the energy difference between two frontier orbitals is <0.1 eV. POPUL = 0 causes the HOMO to be doubly occupied even if there is an empty MO (LUMO) with the same energy. If POPUL is negative, its absolute value is taken as the imposed number of unpaired electrons. If POPUL is positive (not recommended), the electron population of each MO must be specified independently. In general, POPUL should be 0 or -n. The next two integers are used only in the generation of Walsh diagrams, and should be zero in this case.

**line 3: Keywords**

-EL-WF-RO-NC

These keywords control the output for the MO calculations. Choose one or more of the following two letter words in any order. If this line is not present, output is limited to EL, total energy, reduced overlap and net charges.

- DI = distances (ignored if DIST card is present in line 2)
- WF = wave functions
- OV = overlap matrix
- OP = overlap population matrix
- RO = reduced overlap matrix
- CM = charge matrix
- RC = reduced charge matrix
- EL = energy levels

References begin on page 281
NC = net charges  
HM = Hückel matrix  
DM = density matrix  
OD = overlap deletion matrix (requires additional parameter line, see the manual)  
MP = Molecular orbital reduced overlap population matrix (also requires additional parameter line)  

**line 4: Cartesian coordinates**  
**CELL  1,1,1,90,90,90.**  

CELL alerts EHC to expect Cartesian coordinates. The next 6 numbers are A, B, C, α, β, γ, and should be set as above (1,1,1,90,90,90).

**lines 5.1-5.n: coordinates**  
~S~-.000000,~-.000000,~-.2.1680  

Input the atoms one through n (where n is the number of atoms defined in line 2) keeping the following points in mind. Elements must be two digits and in all caps. If the element is only one digit, precede it with a space (i.e., ~S = sulfur, MO = molybdenum, CL = chlorine, ~C = carbon). The three numbers are x, y, and z. To avoid FORTRAN problems, keep the number of digits after the decimal point to 4 or 5, and include a comma after each number. Although it is not necessary to use commas, there must then be exactly six digits after the decimal point and the correct number of spaces between numbers. Be safe; use commas.

**line 6: FMO directive**  
**FMO**  

This card alerts the eh program to carry out a fragment MO analysis. If this card is absent and any other lines are present, the program will exit with an error message. If this card and other lines are absent, the program will attempt to generate Walsh diagram with zero variables and zero steps (from line 2). This will result in the generation of a Walsh diagram with the input molecule twice (step 1 and 2). It is not possible to view an interaction diagram this way since no FMO analysis is done, but it is possible to view the molecular orbitals. To generate an interaction diagram, this card must be present.
line 7: FMO keywords
   ~OP~RO~CM~TO~NC

These keywords are like those in line three. Choose one or more to select the output of the FMO calculations. If these keywords are not present, the output is limited to the overlap population and reduced overlap matrices for fragments.

DI = distances
WF = wavefunctions
OV = overlap matrix (between atomic orbitals)
TO = transformed overlap (between FMO's)
OP = overlap population between FMO's
CM = charge matrix
EL = energy levels
RO = reduced overlap matrix for fragments
RC = reduced charge matrix

line 8: Fragment definition
   ~~2~~1~10

The first integer is the number of fragments. This should always be two. Other numbers will be accepted, but then it is not possible to view MOs. The second integer is the number of atoms in the first fragment. In this example, the terminal sulfur is one fragment, so the first number is 1, and the Mo(NH$_2$)$_3$ is the second fragment, so the second number is 10. The two integers should add up to the total number of atoms in line two. It is highly recommended that the atoms of fragment one precede the atoms of fragment two during their original definition in lines 5.1-5.n. If a non-standard numbering scheme for the fragments is required, consult the manual.

line 9a-9b. Information about the fragments
   ~~0~EL~WF~CM

The first integer is the charge of fragment a/b. The sum of these numbers should add to the total charge given in line two. The two-letter words following the charge control the output, and the keywords available are the same as those given in line three. It is important to not hit return (enter) following the final keyword in line 9b. EHC ends with an error message if there is a blank line at the end. If return is accidentally pressed, or if a new line appears magically at the end of your input file, select the blank text with the mouse and
delete it using shift-delete in the editor. If all has gone well, a working input file for a truly exciting molecule has just been created (This author takes no responsibility for boring molecules). A sample, working input file is reproduced here:

XRAY.IN

Mo(S)(NH2)3~from~x-ray~coordinates
~11~~ODIST~~1~~0~~0
~EL~WF~RO~NC
CELL~~1.,1.,1.,90.,90.,90.
~S~~.000000,~~.000000,~~2.1680
MO~~.000000,~~.000000,~~.0000
~N~~1.612000,~~1.023000,~~.461000
~N~~1.694000,~~.796000,~~.531
~N~~.000000,~~1.76200,~~.89500
~H~~1.52700,~~2.00700,~~.74700
~H~~2.57900,~~.759000,~~.23400
~H~~1.67400,~~1.60900,~~1.15900
~H~~2.63300,~~.48200,~~.25500
~H~~1.280000,~~1.62300,~~1.90600
~H~~1.0400,~~2.739000,~~.5950
FMO
~OP~RO~CM~TO~NC
~~2~~1~~10
~~0~EL~WF~CM
~~0~EL~WF~CM

Internal Coordinates

It is usually easier to generate an input file using internal coordinates, and it is essential that this is done in order to construct a Walsh diagram. Also, EHC sometimes has a difficult time seeing symmetry which is present in a molecule when the molecule is input with Cartesian coordinates. By using internal coordinates, the symmetric parts of the molecule can be defined to be mathematically identical, allowing EHC to see the full symmetry. As an example, when Mo(NH2) is modeled in D3h using mathematically derived Cartesian coordinates (accurate to 6 decimal places), EHC does not see the molecule in D3h, but instead, C5. By using internal coordinates, it is very easy to create the input file, and EHC picks the correct point group. Although a bit mentally challenging at first, the internal coordinate system becomes logical after a few misfires, and for modeling
complexes in idealized symmetries, the input file can be created from a simple line drawing in a few minutes. Most of the file lines are similar to those discussed previously for the X-ray input file.

**line 1:** title line as before
(H2N)3MoNMo(SH)3~from~x~ray~structure~using~internal~coordinates

**line 2:** line 2: general parameter directive as before
~18~~0DIST~0~~0~~0

**line 3:** Keywords
~~EL~WF~RO~NC

**line 4:** internal coordinates, first atom at the origin
0.,0.,0.,MO

This first atom sits on the origin by definition. The atom may be a dummy atom, if that makes it easier to define the molecule (for example, a bimetallic molecule with no central atom). If that is the case, or if at any point a dummy atom is required, (as will be true for the generation of Walsh diagrams) use the symbol DU. If the origin atom is a dummy atom, its number by default is -1, the next real atom created should be atom number 1.

**line 5:** Atom 2
~1,2,~N~1.771,~0,0

The format of these lines is as follows. The new atom being created has six variables which need to be defined. These are (in order): the pointing atom (atom n-1, the atom it is coming from), the atom #, the symbol, a distance (from atom n-1), an angle $\alpha$ (defined as the angle between the three atoms n-2, n-1, and n) and a torsion angle $\tau$ (the dihedral between the planes defined by n-3/n-2/n-1 and n-2/n-1/n). Note that atom n-1 is not necessarily the atom preceding atom n in the list (lines 5.1-5.n). Similarly, atom n-2 is the atom which points to atom n-1, and is not necessarily the atom directly preceding atom n-1. Since this is only the second atom, atoms n-2 and n-3 are undefined. Therefore, two reference vectors are required. In CACAO, these two vectors are defined as the -z axis and the +x axis respectively. Therefore atom two is 1.771 Å from atom 1, with an angle of 0° from the -z axis, and an angle of 0° away from the +x axis.
Appendix I: Instructions for Extended Hückel Calculations Using CACAO

**Line 6: Atom 3**  
~1,3,~N~1.977,~105.93,~120

This line places a nitrogen (atom 3) 1.977 Å from atom one (Mo). Atom n-2 and n-3 are still not defined, so the α angle of 105.93 refers to the -z axis, and the τ angle of 120 refers to the +x axis.

**Line 7: Atom 4**  
3,4,~H~0.96,~133.8,~26.2~

This line places a hydrogen 0.96 Å from atom 3 (N). The atom n-2 exists (Mo), but atom n-3 does not, so the reference vector is taken to be the -z axis (the first reference vector needed to define an atom is always taken to be the -z axis, a second vector, if required, is the +x axis). The Mo-N-H angle is defined as 133.8 ° by the first angle descriptor, and the Mo-N-H plane is bent away from the -z axis by 26.2 °.

It will probably be helpful at this point to look at Figure AI.1, which gives a more explicit depiction of the angles and lengths involved. The input lines and the corresponding resultant distances and angles are shown. A₁ is at the origin and A₂ is 1.25 Å away along the -z axis. A₃ is 1.47 Å from A₂, bent 90° from -z (placing it momentarily on the +x axis) and then bent an additional -90° from +x, placing it on the +y axis. A τ angle of +90° from +x would have placed A₃ on the -y axis. The τ angle is a simple rotation angle from +x (or sometimes -z, as above) until the n-4 atom is defined. A₄ and A₅ are 0.85 Å from A₃, with an A₂-A₃-A₄₅ angle of 120°. The τ angle in this case does refer to a dihedral angle. In order to determine the correct sign for this angle, hold a book, with its spine down along the A₂-A₃ vector. τ will be positive if the right side of the book opens when moving to A₄, while τ will be negative if the left side of the book opens when moving to A₅. Generally, (and especially with Cₙ or Dₙ-symmetric molecules) the absolute sign of τ is not important, as long as all related atoms are given identical signs of τ. Investigation of models derived from internal coordinates will allow familiarity with the coordinate system and reference vectors.
Appendix I: Instructions for Extended Hückel Calculations Using CACAO

Figure AI.1: Description of Internal Coordinates in CACAO.

Lines 8-12: FMO directive, FMO keywords, fragment definition and information
FMO
~OP-RO-CM~TO-NC
~~2~11~~7
~~0~EL~WF~CM
~~0~EL~WF~CM

After inputting all the atoms from one to the total number assigned in line two, the rest of the input file is identical to that discussed previously for the X-ray input file (except, of course, the number of atoms in fragments one and two). The whole input file is reproduced here:

INTER.IN

(H2N)3MoNMo(SH)3~from~x-ray~structure~using~internal~coordinates
~~18~~0DIST~0~~0~~0
~~EL~WF~RO~NC
0,0,0,M0
~~1,2,~N~1.771,~0,0
~~1,3,~N~1.977,~105.93,~0
~~1,4,~N~1.977,~105.93,~120
~~1,5,~N~1.977,~105.93,~240
3,6,~H~0.96,~133.8,~26.2~
3.7, -H~0.96, ~111.7, ~212
4.8, -H~0.96, ~133.8, ~26.2
4.9, -H~0.96, ~111.7, ~212
5.10, -H~0.96, ~133.8, ~26.2
5.11, -H~0.96, ~111.7, ~212
-2.12, MO~1.882, ~180, ~0
12.13, -S~2.308, ~93.71, ~78.87
12.14, -S~2.308, ~93.71, ~198.87
12.15, -S~2.308, ~93.71, ~318.87
13.16, -H~0.96, ~115.5, ~159.9
14.17, -H~0.96, ~115.5, ~159.9
15.18, -H~0.96, ~115.5, ~159.9
FMO
-OP~RO~CM~TO~NC
~2~11~7
~0~EL~WF~CM
~0~EL~WF~CM

Walsh Diagrams

The final type of input file is one which generates data for a Walsh diagram. The use of internal coordinates is required, and for the most part, the input file remains the same as discussed previously. However, several changes are made. First, sets of atoms are assigned to groups, and these groups are rotated and translated relative to internally derived vectors defined with dummy atoms. Second, the general parameter directive line is changed to reflect the number of variables and steps in the diagram. Third, the values which the variables take is inserted as a new line between the general parameter directive and the MO keywords. Fourth, one or more of the internal coordinates is flagged to become a variable parameter. Keep in mind the fact that molecular symmetry MUST remain constant during the course of the molecular event. This may require slight distortions in either bond lengths (ca. 0.001 Å) or angles (ca. 0.1°) in the initial and final steps.

line 1: title line as usual
Mo(NH2)3~rotation~of~one~amide

line 2: general parameter directive
~10~0DIST~0~1~10
This line lets the EHC program know that there are 10 atoms, the net charge is 0, the DIST card is on, and that the POPUL card is set to zero. The final two values are the number of variables (1) and the number of steps (10) in the Walsh diagram. If more than one internal coordinate is to take the same value (i.e., two bonds lengthening at the same rate), then the number of variables is still one; however, more than one coordinate will take the different values.

**line 3: step values for the variable**
0.1,20,40,60,80,100,120,140,160,179.9

These are the values that the variable parameter will take.

**line 4: keywords as before**
~EL~CM~NC~RO

**line 5a-n: Internal coordinates as before**
0.,0.,0.,MO
~1,2,~N~1.96,90.,90,1
~1,3,~N~1.96,90.,-30.,2
~1,4,~N~1.96,90.,-150,3
~2,5,~H~1.10,~120,0,1
~2,6,~H~1.10,~120,180,1
~3,7,~H~1.10,~120,0,2
~3,8,~H~1.10,~120,180,2
~4,9,~H~1.10,~120,0,3
~4,10,~H~1.10,~120,180,3
~1,-1,DU~3,90,90,1

In general, the coordinates are the same as before. However, each atom which potentially will be moved during the distortion is assigned to a group. In this example, atom one (Mo) is a member of group zero (the default), atom two (N) is a member of group one, and atom -1 (DU) is also a member of group one. Any atom not specifically assigned to a group is considered a member of group zero. Each group is a rigid object which can be moved or rotated while keeping relative bond lengths and angles constant. All other parameters are the same as discussed previously.
line 6: group rotation parameter
GR1~2~1~1000,.0.

In this example, group one (GR1) is rotated about the axis defined by atom 2 and atom -1 by a variable parameter. Note that the dummy atom should be a member of the same group. The 1000 card alerts EHC that the coordinate to be varied is the rotation angle, and the final zero is a non-changing (in this example) translational value. To look at a Walsh diagram for rotating all three amides at the same time, two additional dummy atoms need to be defined;

1,-2,DU~3,90,-30,2 (this defines dummy atom -2)
~1,-3,DU~3,90,-150,3 (this defines dummy atom -3)

and add two lines to the end of the input file:

GR2~3~2~1000,.0. (rotate group 2 about the 3/-2 vector)
GR3~4~3~1000,.0. (rotate group 3 about the 4/-3 vector)

The number of variables in the general parameter directive does not need to be changed, as all three variable parameters take the same value at each step. If, instead of a group rotation, a group translation is desired, the input file could look something like this:

Mo(NH2)3~translation~of~one~amide
~10~0DIST~0~1~10
1.96,1.97,1.98,1.99,2.00,2.02,2.04,2.06,2.08,2.10
~EL~CM~NC~RO
0,.0,.0,.MO
~1,2,~N~1000,90,.90,1
~1,3,~N~1.96,90,.30,.2
~1,4,~N~1.96,90,.150,3
~2,5,~H~1.10,~120,0,1
~2,6,~H~1.10,~120,180,1
~3,7,~H~1.10,~120,0,2
~3,8,~H~1.10,~120,180,2
~4,9,~H~1.10,~120,0,3
~4,10,~H~1.10,~120,180,3

This input file would move nitrogen 2 from 1.96 to 2.10 Å over 10 steps. Since H5 and H6 are defined from N2, the hydrogens will move with it. Alternatively, you could use the group translation parameter like before (after defining an appropriate dummy atom of
course). The "1000" variable card in the definition of N2 would need to be changed back to 1.96 like the other nitrogen atoms.

```
~1,-1,DU=3.90,-150,1
GR1~1~1~~~0,1000.
```

This group translation parameter tells EHC to move group one along the 1/1 vector by the variable amount. If two variables are desired, for example, if one amide is rotated and lengthened, the input file would look something like this (note, lines three and four are the values taken for variables one and two respectively):

```
Mo(NH2)3~translation~and~rotation~of~one~amide
~10~0DIST~0~2~10
1.96,1.97,1.98,1.99,2.00,2.02,2.04,2.06,2.08,2.10
0.1,20,40,60,80,100,120,140,160,179.9
-EL~CM~NC~RO
0.,0.,0.,MO
~1,2,~N~1.96,90.,90,1
~1,3,~N~1.96,90.,~30.,2
~1,4,~N~1.96,90.,~150,3
~2,5,~H~1.10,~120,0,1
~2,6,~H~1.10,~120,180,1
~3,7,~H~1.10,~120,0,2
~3,8,~H~1.10,~120,180,2
~4,9,~H~1.10,~120,0,3
~4,10,~H~1.10,~120,180,3
GR1~1~1~2000,1000
```

This input file moves group one along the vector 1/1 by the first variable, while rotating group one about the 1/1 vector by the second variable. It should be clear that accurate definition of dummy atoms is critical for the desired molecular event to occur. The Walsh diagram input file used in the interactive session which follows is reproduced here:

```
WALSH.IN
```

```
Mo(NH2)3~rotation~of~one~amide
~10~0DIST~0~1~10
0.1,20,40,60,80,100,120,140,160,179.9
-EL~CM~NC~RO
0.,0.,0.,MO
~1,2,~N~1.96,90.,90,1
~1,3,~N~1.96,90.,~30.,2
```

(262) References begin on page 281
-1.4,~N~1.96,90.,~150,3
-2.5,~H~1.10,~120,0,1
-2.6,~H~1.10,~120,180,1
-3.7,~H~1.10,~120,0,2
-3.8,~H~1.10,~120,180,2
-4.9,~H~1.10,~120,0,3
-4.10,~H~1.10,~120,180,3
-1,-1,DU~3,90,90,1
GR1~2~1~1000,0.

There are additional commands and options for the input files which are not discussed in this document. For example, it is possible to do an FMO calculation during multiple steps of a Walsh diagram. For detailed instructions on these more advanced features, consult the manual.

Section 7: Explicit instructions for running EHC and CACAO

After the creation of the input file, all of the hard work is done. Now comes the fun part. The general procedure for running the program is as follows. At the c:\moan\subdir\> prompt, where the input files are located, type;
c:\moan\subdir\> eh . file

The command "eh" runs the EHC program. The "." tells EHC that the input files are in the current directory (c:\moan\subdir\). The "file" is the filename of the input file, without the "in" extension. This command, if no errors are encountered in the input file, will activate the eh program which generates file.bin, file.cor and file.out files. From time to time, it is a good idea to delete the file.out files, as they are not needed by CACAO, and only serve to provide information about the calculations to the user. What follows is a transcribed interactive session, giving an idea of the types of messages that will be seen on the screen while using EHC and CACAO. What appears on the screen will appear in this font. This includes any user-typed characters. Any commentary about the session (which would not actually appear on the screen) will be in this font. At any point where a default is taken, there will be no character typed after a menu, as the default character is the
return key. In anticipation of problems with the input file, this session starts with several error messages which occur when faulty input files are used. This session assumes that there are three input files (created earlier in this document), with the titles inter.in, xray.in, walsh.in, in the adam subdirectory of moan. It would be most beneficial at this point to follow along with the interactive session using CACAO with the three sample input files described above, in order to begin gaining familiarity with the program.

**Interactive Session**

**Possible Error messages**

C:\MOAN\ADAM\eh . inter

C:\MOAN\ADAM\ECHO OFF

-------- DOSVER

MS-DOS Version 6.22

1 file(s) copied

C:\MOAN\ADAM\EHC >inter.out

C:\MOAN\ADAM\ECHO OFF

1 file(s) copied

File not found - C:\MOAN\TEMP\FP

0 file(s) copied

******************************************************************************

Q = Exit
C = Run CACAO
K = Edit the current input file (inter.in)
O = Edit the current output file (inter.OUT)

choose an option[Q,C,K,O]?o

Notice that the program eh can run the editor from within. Alternatively, select option "q" to exit, and then type C:\moan\adam> edit inter.out. The following are the contents of inter.out. Notice that the file contains the line which contains the error.

ERROR IN CARD. (Check Format).
2 18 ODIST 0 0 0
2Stop - Program terminated.

This first file has an incorrect number of spaces in the first line. A second common error is forgetting to put a space before a one letter element. The contents of inter.out if this occurs is:

ELEMENT N MUST BE DEFINED BY THE USER
2Stop - Program terminated.
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Element N is undefined, as eh is looking for element ~N. Another common error is forgetting a comma. If no comma is placed where one should be, the contents of inter.out are:

ERROR IN CARD. (Check Format).
$4A9, H 0.96 111.7, 212$
2Stop - Program terminated.

Sometimes, the inter.out file has no contents. If this is the case, there should be an error message generated by eh on the screen. An example of this type of session is:

C:\MOAN\ADAM>eh . xray

C:\MOAN\ADAM>ECHO OFF

-------- DOSVER

MS-DOS Version 6.22

1 file(s) copied
C:\MOAN\ADAM>EHC >xray.out

run-time error F6103: READ\"\moan\INPUT\" - invalid REAL

C:\MOAN\ADAM>ECHO OFF

1 file(s) copied
File not found - C:\MOAN\TEMP3WF

0 file(s) copied

*******************************************************************************

Q = Exit
C = Run CACAO
K = Edit the current input file (xray.in)
O = Edit the current output file (xray.OUT)

choose an option [Q,C,K,O]?

The output file is blank, your only clue is the "invalid real" error message. This error message occurs because FORTRAN expected an integer with a certain number of characters, and one was missing. There will be a line in the input file without a comma or without the correct number of spaces. What follows is a long interactive session, in which all three files (xray, inter and walsh) are calculated, and subsequently viewed. This will demonstrate most of the options available in CACAO. Normally most of the defaults would be taken, and not all options would be explored.

X-ray session

C:\MOAN\ADAM>eh . xray

C:\MOAN\ADAM>ECHO OFF

-------- DOSVER

MS-DOS Version 6.22

1 file(s) copied
C:\MOAN\ADAM>EHC >xray.out

C:\MOAN\ADAM>ECHO OFF

1 file(s) copied
1 file(s) copied

Q = Exit
C = Run CACAO
K = Edit the current input file (xray.in)
O = Edit the current output file (xray.OUT)

choose an option [Q, C, K, O]? C

Note that in the event of a successful run, three files will be copied. Typing C runs CACAO:

* CARLO MEALLI and DAVIDE N. PROSERPIO
* C.A.C.A.O. (Version 4.0, April 1994)
* (Computer Aided Composition of Atomic Orbitals)
* Ref.: JOURNAL of the CHEMICAL EDUCATION (1990, 67, 399)

1) INTER  2) WALSH  3) XRAY

The above files contain suitable CACAO datasets.
Select one of them by number (=N).
(CR=Escape this menu, L=List Files again, -N=Show Title of Nth Set) -1

Your 4 options here are N, CR (return), L, -N. Typing -1 gives the title line from inter.in, a helpful feature as the number of suitable datasets grows:

------------------------------------------------------------------------- TITLE FOR INTER-----------------------
(H2N)3MoNMo(SH)3 from x-ray structure using internal coordinates
-------------------------------------------------------------------------

The above files contain suitable CACAO datasets.
Select one of them by number (=N).
(CR=Escape this menu, L=List Files again, -N=Show Title of Nth Set) -2
------------------------------------------------------------------------- TITLE FOR WALSH---------------------
Mo(NH2)3 rotation of one amide
-------------------------------------------------------------------------

The above files contain suitable CACAO datasets.
Select one of them by number (=N).
(CR=Escape this menu, L=List Files again, -N=Show Title of Nth Set) -3
------------------------------------------------------------------------- TITLE FOR XRAY----------------------
Mo(S)(NH2)3 from x-ray coordinates
-------------------------------------------------------------------------

The above files contain suitable CACAO datasets.
Select one of them by number (=N).
(CR=Escape this menu, L=List Files again, -N=Show Title of Nth Set) L

Now, typing L gives the list again.

1) INTER  2) WALSH  3) XRAY

The above files contain suitable CACAO datasets.
Select one of them by number (=N).
(CR=Escape this menu, L=List Files again, -N=Show Title of Nth Set) 3

(266) References begin on page 281
Interaction Diagram / MO drawings? (Any char. / CR=return) j

Option three was used to select the X-ray data file. Then, typing any character causes
the program to begin the interaction diagram generation:

DATASET = XRAY

Strike Return to use the following default settings:

Energy Interval =  -25.0     3.0 eV
Minimum FMO contribution = 2.0%
Draw all MOs within the given range (i.e., no selection by symmetry or number)
Use the highest resolution between quasi-degenerate levels

Otherwise, start entering MINIMUM ENERGY (M=menu) -16
                     MAXIMUM ENERGY -8
Minimum FMO Contribution (DEF=2.0%)   
Magnify resolution between quasi-degenerate levels? [Def=Y]
do you wish to select orbitals? (Def=N)

The diagram generated by these settings is shown in Figure A1.2. It is printed by
typing P from the menu reproduced below. Alternatively, it can be written to a file by
typing S, and then F. The menu bar shown below will also be below the diagram on the
screen.

+0=Exit/1=New diagr./2=MO draw.s/3=Mullik/P,S=Prn/-N=get Nth Diag ( 1: 1)3

Typing "3" selects a Mulliken analysis of the molecule (first will be orbital 16, followed
by fragment 13 of orbital 16):

Numerical results for:       XRAY
Enter threshold for orbital contribution to the various MOs (DEF=1.0%)
enter MO number (max. = 31) [CR = EXIT] 16
MO 16[ 16a ] E(eV) = -13.217 FILLED - Total Levels= 31
         S 1 px  31% (+) FMO 13 (FRG 1)  5% (+)
         S 1 py  2% (-) FMO 16 (FRG 1)  51% (+)
         N 3 px  3% (+) FMO 17 (FRG 1)  3% (+)
         N 3 py  30% (-) FMO 18 (FRG 1)  5% (+)
         N 4 py  5% (-) FMO 30 ( 3 in FRG 2) 2% (-)
         N 4 px  11% (+) FMO 29 ( 2 in FRG 2) 31% (+)
         N 5 px  16% (-)
one MO # OR one or two FMO(s) [negative] OR Atom # and At. Orb. type (eg: 1, px)
[CR/E/Z = EXIT/Energies/Mulliken Analysis] -13
FMO 13[ 15a ] E(eV) = -9.638 EMPTY - Total Levels= 27
MO 1 px  3% (+)/MO 1 xz 82% (+)/MO 1 yz 2% (-)/ N 2 px 4% (-)/
N 3 py  2% (-)/ N 3 pz  2% (-)/
Electrons in FMO 13 = .215 ** Ov.Pop. with other FMOs:
<* | 29>= 1 <* | 30>= 15
>> FMO 13 contributes to the following MOs:
   12 [32% (+)] 13 [ 9% (-)] 14 [48% (+)] 16 [ 5% (+)] 18 [ 3% (+)]
   21 [ 2% (-)]

Return goes back to the interaction diagram and menu. Selecting two goes to the MO
drawings:
Figure AI.2: Interaction Diagram for X-Ray Input File
Appendix I: Instructions for Extended Hückel Calculations Using CACAO

***the interaction diagram will be above this menu now***
+0=Exit/1=New diag./2=MO draw.s/3=Mullik/F,S=Prn/-N=get Nth Diag ( 1: 1)2

DATASET = XRAY

Atoms shown as Symbols, Numbers or Balls? [Codes=1/2/3]
If Code is NEGATIVE, only the STRUCTURE is drawn (no MO) [DEF=3, M=Menu] 1

Like the menu says, 1 uses atomic symbols, 2 uses the atom number and 3 uses a ball to represent the atom. Typing the negative integer only draws the molecule, no orbitals will be drawn. This is useful to quickly inspect the model:

Options: Perspective and other Details? (DEF=N) y

In general, keep the defaults (DEF) here. The options are:

perspective value? (DEF= 15.00)
draw stereo pictures? (DEF=N)
1=atoms&bonds /2=bonds only /3=atoms only /4=no structure - (DEF=1)
tolerance on bond distances [D=R1+R2+TOL] (DEF= .40)

View direction [down X (=1, Y= hor.) (=1, Z= hor.)]
[down Y (=2, Z= hor.) (=2, X= hor.)]
[down Z (=3, X= hor.) (=3, Y= hor.)]

Multiple views (max 1 MO) [down: X&Y (=4); X&Z (=5); Y&Z (=6); Z&X&Y (=7)]
[M=menu, DEF = 3] -2
Rotation angle about Y? (DEF= .00)
Rotation angle about X? (DEF= .00) 20
Rotation angle about Z? (DEF= .00)

In general, if the molecule is centered with one amide nitrogen along the x-axis, this will result in a good view:

plot FMOs? [DEF=N] y
MO energies, occ., symmetries for: $\text{Mo(S(NH}_2)_3$ from x-ray coordina ST. 1

Pointgroup: C1 Total Energy = -574.7108

<table>
<thead>
<tr>
<th>Energy</th>
<th>Occupancy</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>33.152</td>
<td>1.00</td>
<td>331a</td>
</tr>
<tr>
<td>21.942</td>
<td>0.00</td>
<td>428a</td>
</tr>
<tr>
<td>20.288</td>
<td>0.00</td>
<td>725a</td>
</tr>
<tr>
<td>2.087</td>
<td>0.00</td>
<td>1022a</td>
</tr>
<tr>
<td>-8.687</td>
<td>0.00</td>
<td>1319a</td>
</tr>
<tr>
<td>-13.217</td>
<td>0.00</td>
<td>1616a</td>
</tr>
<tr>
<td>-13.812</td>
<td>0.00</td>
<td>1913a</td>
</tr>
<tr>
<td>-14.975</td>
<td>0.00</td>
<td>2210a</td>
</tr>
<tr>
<td>-16.577</td>
<td>0.00</td>
<td>257 a</td>
</tr>
<tr>
<td>-20.754</td>
<td>0.00</td>
<td>284 a</td>
</tr>
<tr>
<td>-28.326</td>
<td>0.00</td>
<td>311a</td>
</tr>
</tbody>
</table>

enter MO number to analyze in terms of FMOs. Otherwise:
CR=only FMO drawings / Alph.char.=show levels again / Z = MO composition

Hitting return here allows visualization of the fragment M0's:

text up to a max. of 12 FMO # that you wish to visualize
CR=end --- Alph. char.=show FMO levels

first fragment. pointgroup: C1

<table>
<thead>
<tr>
<th>Energy</th>
<th>Occupancy</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.443</td>
<td>0.00</td>
<td>127a</td>
</tr>
<tr>
<td>5.789</td>
<td>0.00</td>
<td>424a</td>
</tr>
<tr>
<td>2.369</td>
<td>0.00</td>
<td>721a</td>
</tr>
<tr>
<td>-5.034</td>
<td>0.00</td>
<td>1018a</td>
</tr>
<tr>
<td>-9.638</td>
<td>0.00</td>
<td>1315a</td>
</tr>
<tr>
<td>-13.422</td>
<td>0.00</td>
<td>1612a</td>
</tr>
<tr>
<td>-14.974</td>
<td>0.00</td>
<td>199 a</td>
</tr>
<tr>
<td>-16.575</td>
<td>0.00</td>
<td>226 a</td>
</tr>
</tbody>
</table>

(269) References begin on page 281
Appendix I: Instructions for Extended Hückel Calculations Using CACAO

Show: 1st frag. again /2nd frag. /Select FMOs (1/2/CR)
   Enter FMO number(s) [CR=end / Alph.Char.=show FMO levels] 15
   Enter FMO number(s) [CR=end / Alph.Char.=show FMO levels]

The following defaults are set for:
Wavefunction Surface Value (WSV= .060)
Plot Margin ( .00)
Atomic Orbital Contraction Coefficient ( 1.50)
Minimum Wavefunction Coefficient ( .0001)
Two-dimensional Plot? (No)

redefine any of the above? (DEF=N, M=menu) y

again, usually take the default here:

Value of Wavefunction (WSV) at the plotted MO Surface? (DEF= .060)
Plot Margin (use PM=0.0 if some contours are not closed) [DEF= .000]
AO Contraction Coefficient [=x in the expression exp(-xr)]
   (enter 1.0 for No Contraction) [DEF= 1.5]
Minimum Wavefunction coeff. (Cij) to be considered [DEF=0.0001]
Two-Dimensional plot (no MO contraction)? [DEF=N]

Enter two Keys for Grid Finess and Mode
FINESS=Index between 1 (highest resol., slow) and 9 (lowest resol., fast)
MODE= one of the Key Characters listed below:
N (or blank)= Normal (molecule rotated, faster)
M= same as N with double grid points
P= Observation point rotated (slower)
S= same as P with double grid points
X= MO envelopes only
[Defaults: CR= 5, N --- Any Alph.Char.= 5,X]
Select atomic orbital contributions to MOs?
[DEF=Y / Z = examine MO compositions) z

The MO compositions of the orbital can be examined by typing z:

Numerical results for: XRAY
Enter treshold for orbital contribution to the various MOs (DEF=1.0%)
enter MO number (max. = 31) [CR = EXIT] 15
Mo(S)(NH2)3 from x-ray coordina Pointgroup: Cl
MO 15[ 17a ] E(eV) = -9.806 FILLED - Total Levels= 31
     S 1 py  4%(-)  FMO 11 (FRG 1) 12%(+)
     MO 2 x2y2 51%(-)  FMO 15 (FRG 1) 82%(+)
     MO 2 yz  37%(+)  FMO 29 ( 2 in FRG 2) 4%(-)
one MO # OR one or two FMO(s) [negative] OR Atom # and At.Orb. type (eg: 1,px)
[CR/E/Z = EXIT/Energies/Mulliken Analysis]
Select atomic orbital contributions to MOs?
[DEF=Y / Z = examine MO compositions)

Atoms can be excluded from the MO calculation or display:

Atom  S 1- Enter CODE (0/1/2 for Incl./Excl/Show only), RANGE (opt.)= Highest
        atom number of the given type to which the CODE applies (A=all) a
Atom MO 2- Enter CODE (0/1/2 for Incl./Excl/Show only), RANGE (opt.)= Highest
        atom number of the given type to which the CODE applies (A=all) a
Atom  N 3- Enter CODE (0/1/2 for Incl./Excl/Show only), RANGE (opt.)= Highest
        atom number of the given type to which the CODE applies (A=all) a
Atom  H 6- Enter CODE (0/1/2 for Incl./Excl/Show only), RANGE (opt.)= Highest

(270) References begin on page 281
atom number of the given type to which the CODE applies (A=all) a

Scale for the hard copy of the drawing:
Scale=1cm./Ang. \ Drawings rescaled to fit one page \ User Scale \ [1.2]3, DEF=2
P=Proceed / R=Repeat Questions / S=Symmetry Redef. / M=Main Menu (DEF=P)

*CACAO*CACAO*CACAO*CACAO*CACAO*CACAO*CACAO*CACAO*CACAO*CACAO*
C  C  A
A  A
C  CALCULATION IN PROGRESS! Wait and See 1 Plot(s) C
A  A
O  O
*CACAO*CACAO*CACAO*CACAO*CACAO*CACAO*CACAO*CACAO*CACAO*CACAO*

The FMO diagram obtained is shown in figure A1.3 The normal menu is below the diagram. Typing 2 allows the drawing of a new MO:

+0=Exit/1=New diagr./2=MO draw.s/3=Mullik/P,S=Prn/-N=get Nth Diag ( 1: 1)2

DATASET =  XRAY

Atoms shown as Symbols, Numbers or Balls? [Codes=1/2/3]
If Code is NEGATIVE, only the STRUCTURE is drawn (no MO) [DEF=3, M=Menu] 1

Options: Perspective and other Details? (DEF=N)

View direction  [down X (=1, Y= hor.) (=1, Z= hor.)]
[down Y (=2, Z= hor.) (=2, X= hor.)]
[down Z (=3, X= hor.) (=3, Y= hor.)]

Multiple views (max 1 MO) [down: X&Y (=4); X&Z (=5); Y&Z (=6); 2&X&Y (=7)]
[M=mnu, DEF = 3] -2
Rotation angle about Y? (DEF= .00)
Rotation angle about X? (DEF= .00) 20
Rotation angle about Z? (DEF= .00)

plot FMOs? [DEF=N] The following defaults are set for:
Wavefunction Surface Value (WSV= .060)
Plot Margin (.00)
Atomic Orbital Contraction Coefficient (1.50)
Minimum Wavefunction Coefficient ( .0001)
Two-dimensional Plot? (No)

redefine any of the above? (DEF=N, M=menu) N

MO energies, occup., symmetries for: $\text{Mo(S)(NH}_2\text{)}_3$ from x-ray coordina ST. 1
pointgroup: C1 total energy = -574.7108

  1[31a ]  33.152 (.0)  2[30a]  27.269 (.0)  3[29a]  23.220 (.0)
  4[28a]  21.942 (.0)  5[27a]  6.019 (.0)  6[26a]  5.423 (.0)
  7[25a]  5.088 (.0)  8[24a]  2.371 (.0)  9[23a]  2.309 (.0)
 10[22a]  2.087 (.0) 11[21a]  -8.172 (.0) 12[20a]  -8.535 (.0)
 31[ 1a ]  -28.326 (2.0)

(271)  References begin on page 281
Figure AI.3: FMO Diagram for X-Ray Input File
Appendix I: Instructions for Extended Hückel Calculations Using CACAO

Enter MO number for plot 1 (if < 0 the MO phase is inverted).
[E=show levels again /CR=end input /Z=examine MO composition /M=menu] 2
Enter MO number for plot 2 (if < 0 the MO phase is inverted).
[E=show levels again /CR=end input /Z=examine MO composition /M=menu]

Typing "2" indicated that MO #2 is selected (orbitals are numbered from high to low energy, orbital #2 is empty). Up to 6 MO's can be visualized at one time without loss of too much resolution:

Enter two Keys for Grid Finess and Mode

FINESS=Index between 1 (highest resol., slow) and 9 (lowest resol., fast)
MODE= one of the Key Characters listed below:

N (or blank)= Normal (molecule rotated, faster)
M= same as N with double grid points
P= Observation point rotated (slower)
S= same as P with double grid points
X= MO envelopes only
[Defaults: CR= 5,N --- Any Alph.Char.= 5,X]
Select atomic orbital contributions to MOs?
[DEF=Y / Z = examine MO compositions] N
Scale for the hard copy of the drawing:
Scale= $\text{lcm./Ang. \ Drawings rescaled to fit one page \ User Scale [1\2\3, DEF=2]}
P=Proceed / R=Repeat Questions / S=Symmetry Redef. / M=Main Menu (DEF=P)]

The MO obtained is shown in Figure A1.4. The normal menu will be below. To quit the session, simply type Q and return. The next session uses the input file inter.in. As the two sessions have identical options, fewer comments will be given. To run CACAO, type "eh ." with no file name:

Internal Coordinates Session

C:\MOAN\ADAM=EH
C:\MOAN\ADAM=ECHO OFF
-------- DOSVER
MS-DOS Version 6.22

******************************************************************************
* CARLO MEALLI and DAVIDE M. PROSERPIO                           *
* C.A.C.A.O. (Version 4.0, April 1994)                             *
* (Computer Aided Composition of Atomic Orbitals)                   *
* Ref.: JOURNAL of the CHEMICAL EDUCATION (1990,67,399)             *
******************************************************************************

1) INTER  2) WALSH  3) XRAY

The above files contain suitable CACAO datasets.
Select one of them by number (=N).
(CR=Escape this menu, L=List Files again, -N=Show Title of Nth Set) 1
Interaction Diagram / MO drawings ? (Any char. / CR=return) J

(273) References begin on page 281
MO = 2 \quad (30a) \quad E = 27.269

Figure AI.4: MO Diagram for X-Ray Input File
Appendix I: Instructions for Extended Hückel Calculations Using CACAO

DATASET = INTER

Strike Return to use the following default settings:

Energy Interval = -25.0 3.0 eV
Minimum FMO contribution = 2.0%
Draw all MOs within the given range (i.e., no selection by symmetry or number)
Use the highest resolution between quasi-degenerate levels

Otherwise, start entering MINIMUM ENERGY (M=menu)

The interaction diagram thus obtained is shown in Figure A1.5.

+0=Exit/1=New diagr./2=MO draw.s/3=Mullik/P,S=Pzn/N=get Nth Diag ( 1: 1) 2
DATASET = INTER

Atoms shown as Symbols, Numbers or Balls? [Codes=1/2/3]
If Code is NEGATIVE, only the STRUCTURE is drawn (no MO) [DEF=3, M=Menu] 1

Options: Perspective and other Details? (DEF=N)

View direction
[down X (=1, Y= hor.) (=1, Z= hor.]
[down Y (=2, Z= hor.) (=2, X= hor.]
[down Z (=3, X= hor.) (=3, Y= hor.]

Multiple views (max 1 MO) [down: X&Y (=4); X&Z (=5); Y&Z (=6); Z&X&Y (=7)]
[M=menu, DEF = 3] -2
Rotation angle about Y? (DEF= .00)
Rotation angle about X? (DEF= .00) 20
Rotation angle about Z? (DEF= .00)
plot FMOs? [DEF=N]

The following defaults are set for:
Wavefunction Surface Value (WSV= .060)
Plot Margin (.00)
Atomic Orbital Contraction Coefficient (1.50)
Minimum Wavefunction Coefficient (.0001)
Two-dimensional Plot? (No)

redefine any of the above? (DEF=N, M=menu)

MO energies, occup., symmetries for: $(HZN)_3 MoNH2(SH)3 from x-ray str. 1
pointgroup:c3 total energy = -1003.7394
1[ 19a ] 54.932( .0) 2[ 18e ] 54.888 ( .0) 3[ 18e ] 54.888 ( .0)
4[ 18a ] 43.288 ( .0) 5[ 17e ] 30.827 ( .0) 6[ 17e ] 30.827 ( .0)
7[ 17a ] 27.679 ( .0) 8[ 16a ] 17.295 ( .0) 9[ 16e ] 15.950 ( .0)
10[ 16e ] 15.950 ( .0) 11[ 15e ] 7.681 ( .0) 12[ 15e ] 7.681 ( .0)
13[ 15a ] 6.781 ( .0) 14[ 14e ] 5.826 ( .0) 15[ 14e ] 5.826 ( .0)
16[ 14a ] 5.407 ( .0) 17[ 13a ] 4.174 ( .0) 18[ 13e ] -8.030 ( .0)
55[ 1a ] -28.512(2.0)

(275) References begin on page 281
Figure AI.5: Interaction Diagram for Internal Coordinates Input File
Appendix I: Instructions for Extended Hückel Calculations Using CACAO

Enter MO number for plot 1 (if <0 the MO phase is inverted).
[E=show levels again /CR=end input /Z=examine MO composition /M=menu] 26
Enter MO number for plot 2 (if <0 the MO phase is inverted).
[E=show levels again /CR=end input /Z=examine MO composition /M=menu]

Enter two Keys for Grid Finess and Mode

FINES$=Index between 1 (highest resol., slow) and 9 (lowest resol., fast)
MODE= one of the Key Characters listed below:

N (or blank)= Normal (molecule rotated, faster)
M= same as N with double grid points
P= Observation point rotated (slower)
S= same as P with double grid points
X= MO envelopes only
[Defaults: CR= 5,N --- Any Alph.Char.= 5,X]
Select atomic orbital contributions to MOs?
[DEF=Y / Z = examine MO compositions] n

Scale for the hard copy of the drawing:
Scale=1cm./Ang. \Drawings rescaled to fit one page \\User Scale [1\2\3, DEF=2]
P=Proceed / R=Repeat Questions / S=Symmetry Redef. / M=Main Menu (DEF=P)]

The MO diagram obtained is shown in Figure A1.6. Finally, the last session shows the generation of a Walsh diagram:

Walsh diagram Session

C:\MOAN\ADAM=eh
C:\MOAN\ADAM=ECHO OFF
--------- DOSVER
MS-DOS Version 6.22

****************************************************************************=
* CARLO MEalli and DAVIDE M. PROSERPIO                                *
* C.A.C.A.O.  (Version 4.0, April 1994)                             *
* (Computer Aided Composition of Atomic Orbitals)                 *
* Ref.: JOURNAL of the CHEMICAL EDUCATION (1990,67,399)          *
****************************************************************************=

1) INTER       2) WALSH       3) XRAY

The above files contain suitable CACAO datasets.
Select one of them by number (=N).
(CR=Escape this menu, L=List Files again, -N=Show Title of Nth Set) 2
Walsh Diagram / MO drawings ? (Any char. / CR=return) k

References begin on page 281
MO=26 \quad (10e) \quad E= -9.940

Figure AI.6: MO Diagram for Internal Coordinates Input File
Appendix I: Instructions for Extended Hückel Calculations Using CACAO

\[
\text{DATASET = WALSH}
\]

Strike Return to use the following default settings:

Energy interval = -25.0 \quad 3.0 \text{ eV}.
Total energy plotted with the scale of the MO levels
Steps in the original order
Draw all MOs within the given range (i.e., no selection by symmetry or number)

Otherwise, start entering MINIMUM ENERGY (M=menu)

To zoom in on the energy, reverse the order of the steps or change the defaults, enter a minimum energy here, otherwise hitting return goes to the Walsh diagram, which is shown in Figure A1.7.

+0=Exit/1=New diagr./2=MO draw.s/3=Mullik/P,S=Prn/-N=get Nth Diag ( 1: 1)2

\[
\text{DATASET = WALSH}
\]

Atoms shown as Symbols, Numbers or Balls? [Codes=1/2/3] If Code is NEGATIVE, only the STRUCTURE is drawn (no MO) [DEF=2, M=Menu]

Options: Perspective and other Details? (DEF=N)

View direction
\[
\begin{align*}
\text{down X} &= \{-1, Y \text{ hor.}\} \
\text{down Y} &= \{-2, Z \text{ hor.}\} \
\text{down Z} &= \{-3, X \text{ hor.}\}
\end{align*}
\]

Multiple views (max 1 MO)
\[
\begin{align*}
\text{down} : X&Y = \{4\}; X&Z = \{5\}; Y&Z = \{6\}; Z&X&Y = \{7\}\n\end{align*}
\]

[M=menu, DEF = 3] - ?
Rotation angle about Y? (DEF= .00)
Rotation angle about X? (DEF= .00) 20
Rotation angle about Z? (DEF= .00)

There are 10 computed steps in the file. Enter the number of a single step to visualize some of its MOs. Otherwise, the evolution of one MO over the steps can be monitored CR to select the steps one by one
A= Include all Steps

Typing return here allows for the selection of some of the steps:

The following defaults are set for:
Wavefunction Surface Value (WSV=.060)
Plot Margin (.00)
Atomic Orbital Contraction Coefficient (1.50)
Minimum Wavefunction Coefficient (.0001)
Two-dimensional Plot? (No)

redefine any of the above? (DEF=N, M=menu)

MO energies, occup., symmetries for: $\text{Mo(NH}_2)_3$ rotation of one a\text{-}ide ST. 1
\[
\begin{align*}
\mu_{\text{Intgroup}} &\text{C}_2 \\
\text{total energy} &= \text{-470.1742} \\
1[13b] &= 22.585(\text{.0}) \\
4[12b] &= 2.254(\text{.0}) \\
7[11b] &= -.004(\text{.0}) \\
10[9b] &= -4.560(\text{.0}) \\
13[8a] &= -10.208(\text{.0}) \\
16[6b] &= -13.354(\text{2.0}) \\
19[5a] &= -14.905(\text{2.0}) \\
22[3b] &= -16.626(\text{2.0}) \\
25[2a] &= -27.302(\text{2.0}) \\
2[14a] &= 22.585(\text{.0}) \\
5[12a] &= 2.254(\text{.0}) \\
8[10a] &= -.114(\text{.0}) \\
11[9a] &= -8.480(\text{.0}) \\
14[7b] &= -10.232(1.0) \\
17[6a] &= -13.776(2.0) \\
20[4b] &= -14.905(2.0) \\
23[2b] &= -16.626(2.0) \\
26[1b] &= -27.902(2.0) \\
3[13a] &= 15.979(\text{.0}) \\
6[11a] &= 1.327(\text{.0}) \\
9[10b] &= -.114(\text{.0}) \\
12[8b] &= -8.480(\text{.0}) \\
15[7a] &= -10.232(2.0) \\
18[5b] &= -13.776(2.0) \\
21[4a] &= -15.187(2.0) \\
24[3a] &= -16.655(2.0) \\
27[1a] &= -28.098(2.0)
\end{align*}
\]
Figure AI.7: Walsh Diagram
Appendix I: Instructions for Extended Hückel Calculations Using CACAO

enter the number of a single MO to be drawn at 10 different steps
[Z=examine MO compositions - M=menu] 14

Enter two Keys for Grid Finess and Mode

FINESS=Index between 1 (highest resol., slow) and 9 (lowest resol., fast)
MODE= one of the Key Characters listed below:

N (or blank)= Normal (molecule rotated, faster)
M= same as N with double grid points
P= Observation point rotated (slower)
S= same as P with double grid points
X= MO envelopes only

[Defaults: CR= 5,N --- Any Alph.Char.= 5,X]
Select atomic orbital contributions to MOS?
[DEF=Y / Z = examine MO compositions] n

Scale for the hard copy of the drawing:
Scale=1cm./Amg. \Drawings rescaled to fit one page \User Scale [1\2\3, DEF=2]
P=Proceed / R=Repeat Questions / S=Symmetry Redef. / M=Main Menu (DEF=P)]

Several of the 18 orbitals observed are shown in Figure A1.8. This ends the interactive
session. There are other features to be explored with this program, but the important
and most useful ones have been covered. The best way to become familiar with the
program is by making some models and looking at some orbitals. Thanks for reading!

References

2) Mealli, C.; Proserpio, D. M. CACAO (Computer Aided Composition of Atomic
Orbitals); 4.0 ed.Florence (Italy), 1994.
7) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. Orbital Interactions in Chemistry;
8) See, for example, Chapter II of this thesis.
10) Cotton, F. A. Chemical Applications of Group Theory; third ed.; John Wiley and
11) Karplus, M.; Porter, R. N. Atoms and Molecules; Benjamin/Cummings Publishing
12) Mealli, C.; Proserpio, D. M.; Fachinetti, G.; Funaioli, T.; Fochi, G.; Zanazzi, P.
14) The molecule described in this section was originally prepared by Aaron Odom.

References begin on page 281
Figure AI.8: Some MOs Corresponding to Walsh Diagram
Section 8: DOS Batch Files

The DOS batch files included with CACAO for interfacing with printgl, are defective. Corrected batch files are included in this addendum.

pl.bat

@ECHO off
REM pl.bat
IF ""=="%1" GOTO HELP
:BEGIN
IF "MOAN"=="%1" GOTO DIAGRAM
IF "moan"=="%1" GOTO DIAGRAM
IF "CACAO"=="%1" GOTO CACAO
IF "cacao"=="%1" GOTO CACAO
IF "OUT"=="%1" GOTO PRINTOUT
IF "out"=="%1" GOTO PRINTOUT
IF "ALL"=="%1" GOTO PRINTALL
IF "all"=="%1" GOTO PRINTALL
IF "%2"=="" GOTO PS2
GOTO PS1
:PS2
CALL PLOTF %1 253
GOTO END
:PS1
CALL PLOTF %1 %2
GOTO END
:CACAO
IF "P"=="%2" GOTO PSCAC
IF "p"=="%2" GOTO PSCAC
IF "F"=="%2" GOTO PSCAC
IF "f"=="%2" GOTO PSCAC
FOR %%F IN (%moan\CACAO*.hgl) DO CALL PLOTF %%F
GOTO END
:PS2
ECHO POSCRIPT
FOR %%F IN (%moan\CACAO*.HGL) DO COPY %%F %moan\cacao*.tem
FOR %%F IN (%moan\CACAO*.HGL) DO CALL PLOTF %%F %2 R
FOR %%F IN (%moan\CACAO*.HGL) DO COPY %%F %moan\cacao*.ps
FOR %%F IN (%moan\CACAO*.TEM) DO COPY %%F %moan\cacao*.hgl
FOR %%F IN (%moan\MOAN*.hgl) DO CALL PLOTF %%F
GOTO END
:PS2
ECHO POSCRIPT
FOR %%F IN (%moan\moan*.HGL) DO COPY %%F %moan\moan*.tem
FOR %%F IN (%moan\moan*.HGL) DO CALL PLOTF %%F %2 R
FOR %%F IN (%moan\moan*.HGL) DO COPY %%F %moan\moan*.ps
FOR %%F IN (%moan\moan*.TEM) DO COPY %%F %moan\moan*.hgl
FOR \%\%F IN \{\moan\moan*.TEM\} DO ERASE \%\%F
GOTO END

:PRINTOUT
IF NOT EXIST \moan\CACAO.OUT GOTO NOPRINTOUT
PRINT \moan\CACAO.OUT
GOTO END

:NOPRINTOUT
ECHO ********** The file \moan\CACAO.OUT does not exist. ******
ECHO.
GOTO END

:PRINTALL
IF "P"=="%2" GOTO PSTITUTO
IF "p"=="%2" GOTO PSTITUTO
IF "F"=="%2" GOTO PSTITUTO
IF "f"=="%2" GOTO PSTITUTO
FOR \%\%F IN \{\moan\CACAO*.hgl\} DO CALL PLOTF \%\%F 253 R
FOR \%\%F IN \{\moan\moan*.hgl\} DO CALL PLOTF \%\%F 253 R
GOTO PRINTOUT

:PSTITUTO
ECHO  POSTSCRIPT ALL
FOR \%\%F IN \{\moan\CACAO*.HGL\} DO COPY \%\%F \moan\cacao*.tem
FOR \%\%F IN \{\moan\CACAO*.HGL\} DO CALL PLOTF \%\%F %2 R
FOR \%\%F IN \{\moan\CACAO*.HGL\} DO COPY \%\%F \moan\cacao*.ps
FOR \%\%F IN \{\moan\CACAO*.TEM\} DO COPY \%\%F \moan\cacao*.hgl
FOR \%\%F IN \{\moan\moan*.TEM\} DO ERASE \%\%F
FOR \%\%F IN \{\moan\moan*.HGL\} DO COPY \%\%F \moan\moan*.tem
FOR \%\%F IN \{\moan\moan*.HGL\} DO CALL PLOTF \%\%F %2 R
FOR \%\%F IN \{\moan\moan*.HGL\} DO COPY \%\%F \moan\moan*.ps
FOR \%\%F IN \{\moan\moan*.TEM\} DO COPY \%\%F \moan\moan*.hgl
FOR \%\%F IN \{\moan\moan*.TEM\} DO ERASE \%\%F
GOTO PRINTOUT

:HELP
ECHO  -------------------------------------------------------------
ECHO  Two parameters are required:
ECHO  1) any of the keywords below.
ECHO  2) the output device:
ECHO  (blank=normal printer, P=Postcr. Printer, F=Postcr. File)
ECHO  *******
ECHO  ---- Keywords ------
ECHO  ALL = PRINT ALL DRAWINGS AND NUMERIC OUTPUT
ECHO  OUT = PRINT ONLY NUMERIC OUTPUT
ECHO  MOAN = PRINT ONLY THE EXISTING WALSH or INTERACTION DIAGRAMS
ECHO  CACAO = PRINT ALL THE EXISTING CACAO DRAWINGS
ECHO  FILENAME = PRINT THE SPECIFIED FILE (ex. CACAO1 or MOAN2)

:END

plotf.bat

@echo off
REM plotf.bat
IF "P"=="%2" GOTO POSTSCRIPT
IF "p"=="%2" GOTO POSTSCRIPT

(284)  References begin on page 281
IF "F"="%2" GOTO POSTSCRIPT
IF "f"="%2" GOTO POSTSCRIPT
IF "R"="%3" GOTO ALL
IF NOT EXIST \moin\%1.hgl GOTO NOFILE3
REM definition of the printer: /FA=deskjet, /FL=laserjet (or see Printgl manual)
PRINTGLD \moin\%1.hgl /d1/fa~\mf.9/ao0,0/o1/cok
GOTO END
:NOFILE3
ECHO ERROR: FILE \moin\%1.hgl DOESN'T EXIST
ECHO.
GOTO END
:NOFILE2
ECHO ERROR: FILE \%1 DOESN'T EXIST
ECHO.
GOTO END
:POSTSCRIPT
IF "R"="%3" GOTO TUTTI
IF NOT EXIST \moi...\%1.hgl GOTO NOFILE1
IF "P"="%2" GOTO STAMPANTE1
IF "p"="%2" GOTO STAMPANTE1
PRINTGLD \moin\%1.hgl /d\%1.out/fs~\mf.9/ao0,0/o1
GOTO END
:STAMPANTE1
echo printer
PRINTGLD \moin\%1.hgl /d1/fa~\mf.9/ao0,0/o1/cok
GOTO END
:NOFILE1
ECHO ERROR: FILE \moin\%1.hgl DOESN'T EXIST
ECHO
GOTO END
:TUTTI
IF NOT EXIST \%1 GOTO NOFILA
IF "P"="%2" GOTO STAMPANTE
IF "p"="%2" GOTO STAMPANTE
COPY \%1 \moin\pippo
ERASE \%1
\print\PRINTGLD pippo /FS /AO0,0 /M1. /O1 /LF7.60,10.87 /XSFU /CKBMGRYCKB /WB /D\%1
erase pippo
GOTO END
:STAMPANTE
echo printer
\print\PRINTGLD \%1 /FS /AO0,0 /M1. /O1 /LF7.60,10.87 /XSFU /WB /CKBMGRYCKB
GOTO END
:NOFILA
ECHO ERROR: FILE \%1 DOESN'T EXIST
Appendix II: Raw Kinetics and SQUID Data
Table AII.1: Kinetics Data for the Decomposition of OMo(N[R]Ar)$_3$ (2.2) and SMo(N[R]Ar)$_3$ (2.3)

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>$k_r$</th>
<th>Temp (K)</th>
<th>$k_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>335.95</td>
<td>6.1609E-06</td>
<td>339.05</td>
<td>1.4168E-04</td>
</tr>
<tr>
<td>335.95</td>
<td>5.6257E-06</td>
<td>339.05</td>
<td>1.3314E-04</td>
</tr>
<tr>
<td>335.95</td>
<td>5.7852E-06</td>
<td>339.05</td>
<td>1.2008E-04</td>
</tr>
<tr>
<td>345.65</td>
<td>1.9740E-05</td>
<td>343.35</td>
<td>2.2059E-04</td>
</tr>
<tr>
<td>345.65</td>
<td>1.6940E-05</td>
<td>343.35</td>
<td>2.0670E-04</td>
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<tr>
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<td>355.55</td>
<td>5.8206E-05</td>
<td>343.35</td>
<td>2.3535E-04</td>
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<td>348.45</td>
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<td>4.1490E-04</td>
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<td>9.3965E-04</td>
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<td>376.95</td>
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<td>375.35</td>
<td>3.1737E-03</td>
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<td>376.95</td>
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<td>375.35</td>
<td>3.9610E-03</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Avg. Temp (K)</th>
<th>Avg. $k_r$</th>
<th>Avg. Temp (K)</th>
<th>Avg. $k_r$</th>
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</thead>
<tbody>
<tr>
<td>335.95</td>
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<td>3.8600E-04</td>
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<td>8.9365E-04</td>
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<td>376.95</td>
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<td>365.95</td>
<td>2.0107E-03</td>
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</tbody>
</table>

(287)
Table AII.2: SQUID magnetic data for Ti(N[AR]Ar)\(_2\)CH[SiMe\(_3\)]\(_2\) (1.31), OMo(N[AR]Ar)\(_3\) (2.2) and SMo(N[AR]Ar)\(_3\) (2.3).

<table>
<thead>
<tr>
<th>Ti(N[AR]Ar)(_2)CH[SiMe(_3)](_2)</th>
<th>OMo(N[AR]Ar)(_3)</th>
<th>SMo(N[AR]Ar)(_3)</th>
</tr>
</thead>
<tbody>
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<td>TEMP</td>
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<td>Temp (K)</td>
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<tr>
<td>6</td>
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</tr>
<tr>
<td>6.98</td>
<td>0.04805512</td>
<td>6.98</td>
</tr>
<tr>
<td>7.97</td>
<td>0.0422427</td>
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</tr>
<tr>
<td>8.97</td>
<td>0.03762058</td>
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<tr>
<td>9.98</td>
<td>0.03394181</td>
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</tr>
<tr>
<td>11.99</td>
<td>0.02837201</td>
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<tr>
<td>14.01</td>
<td>0.0243435</td>
<td>14</td>
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<tr>
<td>16.02</td>
<td>0.02134613</td>
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</tr>
<tr>
<td>18.04</td>
<td>0.0190043</td>
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<tr>
<td>20.07</td>
<td>0.01712206</td>
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<td>23.11</td>
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<td>26.07</td>
<td>0.0132717</td>
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<tr>
<td>80.07</td>
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<tr>
<td>85.09</td>
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<td>85.1</td>
</tr>
<tr>
<td>90.1</td>
<td>0.00409697</td>
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</tr>
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<td>95.11</td>
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<td>100.13</td>
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<td>100.1</td>
</tr>
<tr>
<td>110.16</td>
<td>0.00337123</td>
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</tr>
<tr>
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<tr>
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</tr>
<tr>
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<td>138.82</td>
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</tr>
<tr>
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</tr>
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<tr>
<td>180.2</td>
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</tr>
</tbody>
</table>
### Table AII.2 continued.

<table>
<thead>
<tr>
<th>Ti(N[R]Ar)₂(CH[SiMe₃])₂</th>
<th>OMo(N[R]Ar)₃</th>
<th>SMo(N[R]Ar)₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEMP</td>
<td>χ</td>
<td>Temp (K)</td>
</tr>
<tr>
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</tr>
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<td>220.18</td>
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<td>220.15</td>
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<tr>
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<td>0.00160104</td>
<td>240.15</td>
</tr>
<tr>
<td>260.16</td>
<td>0.00148385</td>
<td>260.16</td>
</tr>
<tr>
<td>280.14</td>
<td>0.00138235</td>
<td>280.17</td>
</tr>
<tr>
<td>300.21</td>
<td>0.00129042</td>
<td>300.16</td>
</tr>
</tbody>
</table>

### Table AII.3: SQUID magnetic data for SeMo(N[R]Ar)₃ (2.4), TeMo(N[R]Ar)₃ (2.5) and IMo(N[R]Ar)₃ (3.4).

<table>
<thead>
<tr>
<th>SeMo(N[R]Ar)₃</th>
<th>TeMo(N[R]Ar)₃</th>
<th>IMo(N[R]Ar)₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp (K)</td>
<td>χ</td>
<td>Temp (K)</td>
</tr>
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<td>5</td>
</tr>
<tr>
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</tr>
<tr>
<td>6.99</td>
<td>0.04627807</td>
<td>6.99</td>
</tr>
<tr>
<td>7.98</td>
<td>0.04145898</td>
<td>7.99</td>
</tr>
<tr>
<td>8.98</td>
<td>0.03749608</td>
<td>8.97</td>
</tr>
<tr>
<td>9.98</td>
<td>0.03425008</td>
<td>9.96</td>
</tr>
<tr>
<td>11.98</td>
<td>0.02917384</td>
<td>11.99</td>
</tr>
<tr>
<td>13.98</td>
<td>0.02541295</td>
<td>14</td>
</tr>
<tr>
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Acknowledgments

As this is the section of the thesis that will most frequently be read (perhaps the only section to be read), it is the hardest section to write. There are so many people who deserve recognition here that I could not possibly begin to mention them all, and for any omissions, I apologize outright. During the last four years I have experienced both the happiest and the darkest moments of my life, and there have been times that I did not feel I had the strength to carry on, either emotionally or physically. For helping me through these tough times I wish to specifically thank my parents, Lee and Ann, my brother Karl, my extended family, and most importantly, my wife Wendy, to whom this thesis is dedicated. For giving me a solid foundation in the field of chemistry, I wish to thank the faculty at Oberlin College, especially Marty Ackermann and Norm Craig. Marty's genuine love of inorganic chemistry rubbed off on me, at least a little bit, and his treasured mentoring role continues to this day. I would also like to thank my former mentors, Ken Shea, Regina Wang and Rolf Wagner, for allowing me to learn from and with you. For getting the Cummins lab off the ground and being wonderful friends and co-workers, the other members of the "first five" deserve special recognition: Aaron Odom (not Greg Fu), Marc Johnson (screwdriver), Mike Fickes (grain bag) Sheree Stokes (Lybia), and yes, I include Jonas Peters (flatbread) as an honorary member of this group. The five of you have helped me in innumerable ways, not only in the loaning (giving) of starting materials, but also by sharing your unique viewpoints on chemistry and life in general. I will truly miss you and your company. Much of the chemistry described in this thesis is based on work carried out by our first UROPs Catalina Laplaza and Paulus Wanandi; I hope they continue to do well. The newest members of the group, Jane Brock and Dan Mindiola probably don't understand any of the rest of us very well; we have all spent far too much time together. I wish the two of you well in the continuation of your studies. I also want to specifically thank: Fred, for finding that first apartment, reminding me of OC days, and helping me out in the lab way back when; Doug, for teaching me everything I know about EPR; Aaron and Bill, for putting up with my X-ray questions; Marc, for your Ti-support (and lately Mo-support) and much needed editing help (!); Mike, for many helpful suggestions and needed discussions; and the Schrock and Fu labs, for indirectly (and sometimes directly) giving me chemicals, information, and interesting reading material. To anyone else whom I fail to mention specifically, I apologize, but it has been a long two weeks. Finally, it goes without saying that my research advisor, Kit Cummins, deserves a lot of credit for the contents of this thesis. Kit has a love of and skill in chemistry that is truly astonishing. I will certainly always remember the conversations we have had, and hope to someday approach your level of chemical knowledge. Most of my understanding of and excitement about group theory comes from close interactions with you in the classroom and the lab. But, if I have learned anything at all from you, it is the importance of "telling a story," and preferably an interesting one. I hope that I have done so in the preceding pages, and I intend to carry that thought with me as I continue on in chemistry.