Synthetic Approaches to New Three Coordinate Group 6 Compounds: Chromium Alkenyls, Molybdenum Thiolates and Tungsten Amides

by

Jane Brock Greco

Submitted to the Department of Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry at the MASSACHUSETTS INSTITUTE OF TECHNOLOGY

May 2001

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April 17, 2001

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Abstract

A series of alkenyl (-C[Ad]Ar) and thioalkenyl (-SC[Ad]Ar, Ad=2-adamantylidene, Ar=3,5-Me2C6H3, 4-tBuC6H4, 3,5-(C6H5)2C6H3, 3,5-(4-tBu-C6H4)2C6H3) ligands have been prepared. The alkenyl ligands are synthesized by bromination and dehydrohalogenation of an adamantyl olefin to yield an alkenyl bromide. The Grignard reagent, derived from the bromide, is used either as a transmetallation reagent, or reacted with elemental sulfur to form a magnesium thiolate, (THF)2Mg(SC[Ad]Ar)2. The magnesium thiolate can be protonated to give a free thiol, oxidized to afford a disulfide or reacted with CITi(O'Pr)3 to give the titanium reagent, Ti(SC[Ad]Ar)(O'Pr)3.

Treatment of CrCl3 with an alkenyl Grignard reagent forms the Cr(III) complex, (THF)Cr(C[Ad]ArMe)3. While this compound reacts with pyridine to give (py)-Cr(C[Ad]ArMe)3, it fails to react with THT or PEt3. (THF)Cr(C[Ad]ArMe)3 can be oxidized with I2 or PhSSPh, however, the oxidation products are thermally unstable and disproportionate back to (THF)Cr(C[Ad]ArMe)3. Reactivity with nitric oxide is also discussed.

Molybdenum nitrides of the form N≡Mo(SC[Ad]Ar)3 have been prepared by reaction of Ti(SC[Ad]Ar)(O'Pr)3 with N≡Mo(O'Bu)3. The nitride reacts with Mo(N[R]ArMe)3 to give (μ-N)[Mo(SC[Ad]Ar)3]2. Reaction of (THF)2Mg(SC[Ad]Ar)3 with MoCl3(THF) in diethyl ether leads to the formation of a molybdenum-molybdenum triply bonded compound, Mo2(SC[Ad]Ar)6, while performing the same reaction in THF followed by addition of pyridine leads to the isolation of (py)Mo(SC[Ad]Ar)3.

A series of tungsten nitrides with amide ligands, NEW(NMe2)3, N=W(N[iPr]-ArMe)2(NMe2), and N=W(N[iPr]ArMe)3 have been synthesized by the reaction of a titanium or zirconium amide reagent with NEW(OtBu)3. Nitride N≡W(N[iPr]-ArMe)3 has been compared to the molybdenum analogue N≡Mo(N[iPr]ArMe)3 on the basis of crystal structure data and Density Functional Theory calculations. Treatment of N≡W(NMe2)3 with Mo(H)(η2-Me2C=NArMe)(N[iPr]ArMe)2 leads to formation of (Me2N)3W(μ-N)Mo(N[iPr]ArMe)3. Reaction of (Me2N)3W(μ-N)Mo(N[iPr]-
ArMe)₃ with other small molecules leads to the transfer of the nitride atom from tungsten to molybdenum. However, in the case of the larger nitride, N=W(N[dPr]-ArMe)₃, the bridging nitride formed with Mo(H)(η²-Me₂C=NArMe)₂(N[dPr]-ArMe)₂ is present in solution in equilibrium with the starting materials.

The rate of proton transfer self exchange of [C≡Mo(N[R]ArMe)]⁻ with HC≡Mo-(N[R]ArMe)₃ has been measured by line shape kinetics in the ¹³C NMR and found to be 7 x 10⁶ M⁻¹ s⁻¹. This very fast proton transfer rate has been used, in conjunction with solution and solid state NMR studies and DFT calculations, to develop a bonding picture for the carbide anion in which the lone pair on the carbon is localized in a nonbonding s orbital.

Thesis Supervisor: Christopher C. Cummins
Title: Professor of Chemistry
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## 0.1 Biographical Sketch

Jane was born Jane Ruth Brock on December 28, 1973 in Tucson, Arizona to Gerald and Ruth Brock. She grew up in Arden Hills, Minnesota and Falls Church, Virginia. She graduated from George Mason High School in June 1992. Deciding to pursue her interests in science and mathematics, she decided to attend the California Institute of Technology. At Caltech, she was blessed with many social and academic opportunities. She was able to pursue undergraduate research through the Summer Undergraduate Research Fellowship program in the laboratories of Professor Erik Carreira and Professor John Bercaw. In the Carreira group she worked on the resolution of a chiral ligand, and in the Bercaw group she worked on preparing a new derivative of an aminoborollide ligand. Jane was awarded a NSF predoctoral fellowship, and chose
to pursue her doctoral studies at the Massachusetts Institute of Technology. Upon her arrival at MIT, she was fascinated by the world of three coordinate compounds, and began research in the laboratory of Professor Kit Cummins. During her time at MIT, she met and married fellow chemist George Greco. After graduation, Jane will pursue postdoctoral studies with Dr. Gilbert Gonzales at the Massachusetts General Hospital. She will be using MRI and solid state NMR to examine dementia in SIV-infected monkeys.

0.2 List of Publications:


0.3 List of Abbreviations Used in the Text

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<td>2-dimensional nuclear magnetic resonance spectroscopy</td>
</tr>
<tr>
<td>Å</td>
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</tr>
<tr>
<td>1Ad</td>
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<td>2-Adamantylidene group</td>
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Ph  phenyl ring, -C₆H₅
ppm  parts per million
py  pyridine
R  C(CD₃)₂CH₃ or tert-butyl -C(CH₃)₃
RT  room temperature
s  singlet
SQUID  superconducting quantum interference device
T  temperature
t  triplet
'tBu  tertiary butyl C(CH₃)₃
THF  TetraHydroFuran
TMEDA  TetraMethylEthyleneDiAmine
TREN  triamidoamine, N(CH₂CH₂NH₂)₃
μₚ  effective magnetic moment
μₚ  Bohr magneton
UV  ultraviolet
VT  Variable Temperature
Vis  visible portion of the electromagnetic spectrum
X  Generic ligand
Chapter 1

Synthesis of Sterically Encumbering Alkenyl Fragments for the Stabilization of Three Coordinate Metal Centers

1.1 Introduction

Three coordinate transition metal complexes stabilized by sterically encumbering ligands have been shown to undergo a wide variety of novel chemical transformations. Indeed Mo(N[R]ArMe)$_3$ (R=C(CD$_3$)$_2$CH$_3$ or tBu, Ar$_{Me}$=aryl) is able to cleave N$_2$ and N$_2$O to form the terminal nitride N≡Mo(N[R]Ar$_{Me}$)$_3$. Mo(N[R]Ar$_{Me}$)$_3$ has also been used as a platform for the synthesis of new triply bonded functional groups including a terminal phosphide$^6$ and a terminal carbide.$^7$ This unique reactivity can be understood in terms of the electronic structure of the compound. In trigonal sym-
Figure 1-1: Schematic diagram illustrating the propensity of MX$_3$ (M=Cr, Mo, W) compounds to form metal-element triple bonds. The electronic structure of a three coordinate $d^3$ system is illustrated on the left, and a group 15 element is illustrated on the right.

metry, the $d$ electrons are split into three levels: low lying $a_1'$ ($d_{z^2}$) and $e''$ ($d_{yz}$, $d_{xz}$) sets and a higher lying $e'$ set ($d_{xy}$, $d_{x^2-y^2}$). Group 6 compounds in the +3 oxidation state have three electrons in the $a_1'$ and $e''$ set, a configuration isolobal with the nitrogen atom. As illustrated in Fig 1-1, it is possible to form a strong triple bond to a nitrogen atom consisting of a $\sigma$ bond from the $a_1'$ set to the nitrogen $p_z$ orbital and two $\pi$ bonds from the $e''$ set to the nitrogen $p_x$ and $p_y$ orbitals. However, in the case of complexes containing smaller ancillary ligands such as dimethyl amide and tert-butoxide, this electronic structure manifests itself in the formation of metal-metal triple bonds of the type X$_3$M=MX$_3$ (M=Mo, W).$^{8-12}$ The electronic structure of three coordinate compounds has been reviewed from both a ligand field theory and a Density Functional Theory (DFT) perspective.$^{13-15}$

Chromium compounds of the form CrX$_3$ are relatively stable.$^1$ One reason for this stability is that the three low lying metal orbitals are half filled. Furthermore, as first row metal complexes they have less propensity to form metal-metal multiple bonds. Not surprisingly, CrX$_3$ compounds are known for a wide variety of ligand donor sets, including amides,$^{16-22}$ siloxides,$^{23}$ alkyls,$^{24-26}$ and phosphides,$^{27}$ although
later reports have questioned whether the chromium tris-phosphide compound was correctly characterized. In addition to three coordinate compounds, there are examples of (THF)CrX₃ compounds containing aryl or alkenyl ligands, which may be considered as "masked" three coordinate compounds. Examples of MoX₃ compounds are much more limited, the only examples being those containing anilido ligands. Notably, there are no examples of W(III) three coordinate compounds. An example of a W(IV) three coordinate compound is W(OSiᵗBu₃)₂(NᵗBu) synthesized by Wolczanski and Eppley. Another related class of compounds are the trigonally symmetric compounds of triamidoethylamine (TREN) ligands studied extensively in the Schrock group.

While actual examples of three coordinate Group 6 compounds are limited, theoretical studies have been undertaken in order to assess the role of ligand and metal on the scission of the dinitrogen molecule. It is therefore of interest to expand the family of Group 6 three coordinate compounds in order to understand the effect of the ligand donor set and metal on reactivity. In other words, will all MoX₃ compounds with the appropriate steric considerations cleave N₂ or is there a specific electronic feature of the anilide ligand that allows the cleavage to occur? Will tungsten also effect this transformation? What are the steric and electronic requirements that allow nitrogen atom transfer between metals? Theoretical calculations have suggested that good π donors are important for dinitrogen cleavage, suggesting that the reaction is endothermic for H, Cl, and methyl, and that tungsten would be a better metal for N₂ cleavage than molybdenum. Steric effects also play an important role in the formation of μ-N₂ complexes. It has been shown that while Mo(N[¹Ad]ArMe)₃ is able to form dinitrogen complexes, the (ArMe[¹Ad]N)₃Mo-N≡N-Mo(N[¹Ad]ArMe)₃ intermediate necessary for dinitrogen cleavage cannot be formed for steric reasons. Therefore, it is necessary that the steric properties be tuned such that it is possible to form a μ-N₂ complex while preventing the formation of a M-M triple bond.

Furthermore, it is of interest to explore the effect of ligand donor set on the reactivity and electronic structure of N≡MX₃. After Mo(N[R]ArMe)₃ cleaves dinitrogen, N≡Mo(N[R]ArMe)₃ is formed. At this time, it is not possible to regenerate Mo(N-
Figure 1-2: An ideal catalytic cycle in which dinitrogen is first cleaved, and the resulting nitride is functionalized to regenerate the Mo(III) species. While dinitrogen cleavage has been realized for a number of systems,\textsuperscript{3,4,37-42} there are no reports of being able to remove the nitrido nitrogen functionality and regenerate the starting material.

\[ [\text{R}]\text{ArMe}]_3 \text{from N=Mo(}[\text{R}]\text{ArMe}]_3, \] which would be necessary to complete an ideal catalytic cycle in which dinitrogen could be converted into an amine as shown in Fig 1-2. Productive reactions of molybdenum (VI) nitrides with protic reagents to form functionalized nitrogen moieties are limited, and appear to be very dependent on the ligand donor set. Herrmann and coworkers prepared N=MoNp\textsubscript{3} and reacted it with a variety of acids to convert the nitrido functionality into an imido functionality.\textsuperscript{43} The reactivity of this molecule has been reported to contrast with that of N=MoMes\textsubscript{3}.\textsuperscript{44} The Dehnicke group was able to completely protonate the nitride ligand of both N=MoCl\textsubscript{3} and N=Mo(O\textsuperscript{t}Bu)\textsubscript{3} with ethylene glycol, forming ammonia and Mo(OC\textsubscript{2}H\textsubscript{4}O)\textsubscript{3}.\textsuperscript{45} This result is in contrast with Chisholm’s observation that treatment of N=Mo(O\textsuperscript{t}Bu)\textsubscript{3} with isopropanol leads only to alcoholysis of the ligands.
However, the reaction of alcohols is also very dependent on the metal; treatment of N≡W(OtBu)₃ with isopropanol leads to W(O'Pr)₆ and NH₃.⁴⁶

In addition to reactions with protons, molybdenum (VI) nitrides have been functionalized with other electrophiles. Stirring N≡Mo(N[R]ArMe)₃ in neat MeI leads to [MeNMo(N[R]ArMe)₃]I.⁴⁷ Furthermore, [MeNMo[N(CH₂CH₂NSiMe₃)₃][OTf] has been formed from the corresponding nitride and methyl triflate. However, further treatment of the imide with methyl magnesium bromide leads to methylation of the molybdenum rather than the nitride.⁴⁸ A wide variety of electrophiles including the trityl cation and benzoyl chloride have been reported to react with N≡Mo(S₂CNEt₂)₃ to form the corresponding imides.⁴⁹

In light of the desire to form a nitride from N₂ that could be activated preferentially to the ligands, synthetic efforts have focused on the generation of three coordinate tungsten amides, three coordinate chromium alkenyl compounds, and three coordinate molybdenum thiolate compounds. Tungsten amides were appealing in that it is predicted that dinitrogen cleavage by a three coordinate tungsten would be fast, and that the corresponding nitride is predicted to be more polar, and hence more reactive than the corresponding molybdenum nitrides. Alkenyl compounds were of interest in that the metal-alkenyl bond is believed to be strong, and a chromium tetrakis-alkenyl compound has been reported to be stable to hydrolysis.⁵⁰ Thiolate ligands are appealing in that the pKₐ values for thiols are low, suggesting that the corresponding thiolate ligands should be much less susceptible to protonolysis than amide ligands.

One approach to address the effect of ligand donor set on dinitrogen cleavage and nitrido activation is to use Mo(N[R]ArMe)₃ to abstract a nitride from N≡MX₃, and examine the course of the reaction. Using this approach, Catalina Laplaza demonstrated that Mo(N[R]ArMe)₃ would abstract the nitride from N≡Mo(OtBu)₃, and the “Mo(OtBu)₃” generated would then participate in dinitrogen cleavage.³⁷ Aaron Odom and Theo Agapie were able to prepare (⁴AdS)₃Mo(μ-N)Mo(N⁴Bu)Ph. However, the breakup of this fragment did not appear to involve dinitrogen cleavage.⁵¹ Finally, Marc Johnson’s results on the breakup of (μ-N)[Mo(NMe₂)₃]₂ seem to sug-
Figure 1-3: Alkenyl fragment

gest that dinitrogen cleavage is occurring in the system.\textsuperscript{52} Nitrogen atom abstraction from tungsten nitrides is detailed in Chapter 4.

In order to further our understanding of the electronic and reactivity properties of three coordinate compounds, it was of interest to use sterically encumbering ligands in order to isolate new three coordinate species. This chapter will focus on the design and the synthesis of sterically encumbering alkenyl and thioalkenyl ligands as well as ligand transfer reagents. Chapter 2 will focus on the chromium alkenyl complexes, whereas Chapter 3 will focus on molybdenum thioalkenyl compounds.

\section*{1.2 Results and Discussion}

\subsection*{1.2.1 Design of New Sterically Encumbering Ligands}

We were interested in designing a robust, sterically encumbering ligand fragment. Specifically, the use of -SiMe\textsubscript{3} and -C\textsubscript{6}F\textsubscript{5} groups that often serve as components of ligands in organometallic chemistry was avoided due to their frequent involvement in reaction chemistry. Secondly, \(\beta\)-hydrogens were avoided in order to prevent the possibility of \(\beta\)-hydrogen elimination. Furthermore, it has been observed that the -NRAr\textsubscript{Me} ligand can decompose by the loss of a \textsuperscript{4}Bu substituent.\textsuperscript{53} Therefore, the alkenyl fragment that was designed features both a relatively strong C=C double bond and a C-C\textsubscript{aryl} bond. The alkenyl fragment is shown in Fig 1-3.

The fragment features a 2-adamantyl group for steric protection, and an aryl
Figure 1-4: Retrosynthetic analysis for the synthesis of alkenyl bromides.

group to allow for structural modularity. Changing the substitution pattern on the aryl ring will change both the steric and solubility properties of the ligand. While the primary function of the double bond is to provide ligand robustness, it was also of interest to determine if the double bond would be able to donate electron density into the metal center.

1.2.2 Preparation of the Ligands

Synthetic Strategy

The alkenyl bromide (Fig 1-4) was an appealing target in that it is easily transformed into a Grignard reagent for subsequent transmetallation reactions. There are limited methods for the synthesis of trisubstituted vinyl bromides. One synthetic method is the addition of alkyl halides to acetylenes. This method has had limited use, and in general produces a mixture of isomers. Furthermore, it is not a suitable route to a vinyl bromide with an adamantyl group. Therefore the chosen strategy was to prepare the olefin, brominate and dehydrohalogenate. The symmetric nature of the adamantyl substituent eliminates concerns about olefin stereochemistry, and the high pKₐ of the adamantyl H eliminates concerns of olefin isomerization. Hence, the first step is the synthesis of the adamantyl olefin.
Preparation of Adamantyl Olefins

There are limited known routes to adamantyl olefins. Both the phenyl and the p-tolyl derivatives are literature compounds. The methyl group of the p-tolyl derivative has been further elaborated for pharmaceutical purposes. Olah and coworkers reported that adamantanone was an unsuitable ketone for Wittig reactions, undergoing two electron reduction to 2-adamantanol rather than formation of the olefin. They later reported a procedure for the synthesis of adamantyl olefins involving the addition of an alkyl lithium to the ketone, followed by low temperature quenching with thionyl chloride. In their report, they concluded that for the substrates they tried, only trace amounts of olefins were formed when the alkyl lithium reagent was replaced with an alkyl Grignard reagent. However, these results do not seem to apply to the formation of aryl substituted adamantyl olefins. It has been reported that the reaction of (4-methylbenzylic) Grignard reagent with 2-adamantanone yields the alcohol, which is subsequently dehydrated to the olefin by refluxing with a catalytic amount of the p-toluenesulfonic acid. A second method for the synthesis of aryl substituted adamantyl olefins developed by the Olah group consists of the one carbon homologation of adamantanone to form the adamantyl epoxide, followed by addition of an aryl cuprate and dehydration.

In this work, the two different strategies for the synthesis of the adamantyl olefin used were the Wittig reaction, and the addition of an aryl lithium to adamantyl
epoxide. The family of substituted olefins that was prepared is shown in Fig 1-5. Initial efforts focused on the preparation of HC[Ad]ArMe (1). The ready availability of mesitylene made this a logical choice of starting material. Mesitylene was brominated using N-bromosuccinamide in CCl₄,⁶₀ and then treated with PPh₃. Deprotonation with lithium diisopropyl amide (LDA) followed by refluxing the resulting ylide with 2-adamantanone in THF allowed isolation of olefin 1 in approximately 50% yield (Fig 1-6). It was also possible to prepare HC[Ad]ArBu (2) from commercially available α-bromo(4-Bu)toluene using the same methodology.

The desire to prepare ligands containing more sterically encumbering aryl groups required an alternative synthesis of the olefins as the necessary α-bromo toluenes were more difficult to prepare than the corresponding substituted aryl bromides. Hart reported the synthesis of 3,5-diphenyl bromobenzene in two steps from the very inexpensive 2,4,6-tribromoaniline.⁶¹ The amino group was first converted to an iodide using the Sandmeyer reaction (NaNO₂ in HCl followed by KI) and the resulting 2,4,6-tribromiodobenzene underwent a double benzyne reaction with phenyl magnesium bromide to yield the desired product. This methodology has been extended to the synthesis of 3,5-di-(4'Bu)phenyl bromobenzene⁶² and we wished to extend it to 3,5-dimesityl bromobenzene. The first provides greater solubility, and the second a much greater steric encumbrance due to the inability of the aryl rings to align with one another.

Unfortunately, 3,5-dimesityl bromobenzene proved difficult to synthesize. After removing the mesityl iodide byproduct by vacuum distillation, the resulting mixture
still contained two major products. These products could only be separated by silica gel column chromatography with hexanes as the eluent. While one of the products was the desired material, the other product was 6-mesityl-1,3-dibromobenzene formed as the result of improper regioselectivity in the reaction of mesitylmagnesium bromide with the first benzyne intermediate (Fig 1-7).

With these fragments in hand it was possible to turn to the synthesis of the olefins. The published cuprate procedure used adamantyl epoxide as the limiting reagent with a ten fold excess of the diaryl cuprate. While the procedure worked well when the aryl fragment was phenyl, it was not acceptable to use a large excess of our very precious terphenyl bromides. Therefore, we sought to use a 1:1 ratio of the epoxide and the aryl fragment. Initial experiments involved addition of the aryl Grignard reagent to the expoxide followed by quenching with thionyl chloride. Very low yields were obtained. Since the reaction was a two step sequence it was desirable to determine which step was problematic. In order to do this, the reaction was quenched with NH$_4$Cl to afford the alcohol. It was found that when the aryl bromide was converted to a Grignard reagent, and the epoxide was added, that the resulting product was the result of a rearrangement from the expected alcohol. This observed alcohol (Fig 1-8) was identified by a distinctive doublet at $\delta$ 5.2 ppm in the $^1$H NMR integrating to one proton. This signal represents the proton on the carbon containing the -OH group; it is a doublet due to coupling to an adamantyl H. When rearrangement does not occur (see Fig 1-9), there is a singlet at 3.0 ppm representing...
the two methylene protons. Undergraduate Han-Sen Soo has since taken advantage of this rearrangement to prepare similar alcohols from aryl Grignard reagents and subsequently oxidize the alcohol to the corresponding ketone. The ketones are being explored as enolate ligands, and the alcohol can also be dehydrated to the olefin. The rearrangement of the alcohols appeared to be specific for the Grignard reagents; if the aryl bromides were converted to aryl lithium reagents (by addition of two equiv of tBuLi) rather than to aryl Grignard reagents, no rearrangement occurred. The alcohols were dehydrated by refluxing in benzene with a catalytic amount of p-toluenesulfonic acid to afford the corresponding olefins. For 3,5-dimesityl phenyl, the olefin HC[Ad]ArMes (3) was formed in 33% yield from the aryl bromide, and the representative synthesis is illustrated in Fig 1-9.

This procedure worked well for the synthesis of HC[Ad]ArPh (4) and HC[Ad]-Ar(But)Ph (5). The yields in these cases were better than for 3, but remain around 50%. Furthermore, 2 could be prepared from (4-tert-butyl) bromobenzene using this methodology. The advantage of this procedure is that it does not generate a large amount of triphenylphosphine oxide waste that must be separated from the desired product in Wittig reactions.
Preparation of Alkenyl Bromides

With the olefins in hand, it was possible to prepare the alkenyl bromides. The olefin was brominated with elemental bromine in CH$_2$Cl$_2$, followed by reaction with KO'Bu in THF. Representative of this methodology is the synthesis of BrC[Ad]ArMe (6), formed in 78% yield, illustrated in Fig 1-10. This methodology worked well for the synthesis of BrC[Ad]Ar$_{Bu}$ (7), BrC[Ad]Ar$_{Ph}$ (8) and BrC[Ad]Ar$_{(Bu)}$Ph (9) in 100%, 64%, and 72% yields, respectively. While these substrates worked well, bromination of 3 led to at least two products, which were difficult to separate by either crystallization or column chromatography. Hence, it was not feasible to continue work with the 3,5-mesityl substituted ligand.
Preparation of Alkenyl Transfer Reagents

The simplest method for the transfer of an alkenyl fragment to a transition metal center is to form a Grignard reagent from the alkenyl bromide followed by a trans-metallation reaction with a transition metal halide. The Grignard reagents were formed by stirring the alkenyl bromide in THF with magnesium turnings. For the 3,5-dimethyl Grignard reagent (10) the material was isolated and characterized. However, for the remaining substituent patterns, the Grignard reagents were formed in situ. Heating was required to initiate Grignard formation with the alkenyl bromides, and it appeared that it was necessary to perform the reactions in THF.

Preparation of Thiolate Transfer Reagents

One limitation to the alkenyl ligands is the lack of significant π donor ability, the consequences of which will be detailed in Chapter 2. Sulfur was an appealing ligand donor atom in that the corresponding thiolates have a low pKa, and hence the ligands are less likely to be removed by protic reagents, while maintaining strong π donor properties. It is difficult to use tertiary alkyl thiolates as ligands due to their propensity to lose an alkyl radical and form a metal sulfide. Aryl thiolates are less likely to lose a ligand radical because of the higher heats of formation of the corresponding radical associated with the $sp^2$ hybridized center. We reasoned that since the alkenyl fragment also possessed an $sp^2$ hybridized carbon, that rupture of the C-S bond was unlikely to occur. Indeed, the heats of formation for tBu, phenyl and vinyl radicals are 8.7, 78.6 and 70.4 kcal/mole, respectively. One concern with vinyl groups is that the ligand could exist as a mixture of the two tautomeric forms, thioenol and thioketone, as depicted in Fig 1-11. However, in general this equilibrium is known to lie far toward the thioenol form.

A traditional method for the synthesis of aryl thiolates is the insertion of sulfur into the carbon-magnesium bond of an aryl Grignard reagent. In the case of alkenyl Grignard reagents, careful control of the reaction conditions was very important to avoid the formation of thioethers (formed from the reaction of the magnesium thio-
Figure 1-11: Two possible tautomeric forms of the sulfur ligand, the thioenol form and the thioketone form. The only product detected is the thioenol. The carbon signals for the double bond, identified using 2-D NMR experiments, are denoted in the figure.

late and an additional equivalent of Grignard reagent$^{65}$ and disulfides. The optimum conditions were the addition of $1/8$ equiv of $S_8$ to a dilute, rapidly stirring, thawing solution of the Grignard reagent in diethyl ether. It was then necessary to separate the desired magnesium thiolate from MgBr$_2$, olefin, thioether, and disulfide byproducts. Due to the low solubility of the magnesium reagents, it was difficult to separate them from MgBr$_2$. The original experiments with the 3,5-dimethyl substituted ligand were carried out with (THF)$_2$Mg(SC[Ad]ArMe)(Br) (11). However, the amount of THF and excess MgBr$_2$(THF)$_x$ could vary between different preparations of the compound. Hence, it was decided that it was best to isolate bis-thiolate magnesium reagents, even at the possible expense of yield. In order to remove MgBr$_2$ salts, dioxane was added to the reaction mixture and large amounts of THF were used to solubilize the magnesium thiolates. In this way, (THF)$_2$Mg(SC[Ad]ArMe)$_2$ (12), (THF)$_2$Mg(SC[Ad]ArBu)$_2$ (13), and (THF)$_2$Mg(SC[Ad]ArPh)$_2$ (14) were isolated in moderate yield. Even when large amounts of THF were used to solubilize the magnesium thiolate, some magnesium thiolate was still filtered away with the MgBr$_2$(dioxane)$_x$ polymer. This thiolate could be recovered as a free thiol by quenching the precipitate with aqueous NH$_4$Cl or dilute HCl and extracting the organic material into CH$_2$Cl$_2$. The solubility properties of the 3,5-(4-tert-butyl)phenyl derivative, (THF)$_2$Mg(SC[Ad]Ar(Bu)Ph)$_2$, were very poor. Therefore, this material was generated in situ, and used directly for the
preparation of the titanium reagent (*vide infra*).

With the magnesium thiolates in hand, it was possible to synthesize a variety of ligand transfer reagents as well as identify NMR resonances of possible decomposition products (Fig 1-12). The free thiol, formed by protonation of the magnesium thiolate with a dilute acid, is not only a likely decomposition product, but can also be used to transfer the fragment to a transition metal by thiolysis of amide and alkoxide ligands. It was also of interest to identify the free thiol as the thioenol, rather than the thioketone, tautomer. Protonation reactions were used to afford free thiols HSC[Ad]ArMe (15), HSC[Ad]ArBu (16), and HSC[Ad]ArPh (17). These thiols were all identified as existing in the thioenol form by a peak corresponding to loss of a SH in the mass spectrum, a fragmentation that would not be observed in the case of the thioketone, and a sharp singlet in the $^1$H NMR at 2.5 ppm, representing the SH proton. If this resonance represented the adamantyl H of the thioenol, it would be a multiplet due to coupling to other protons in the adamantyl ring system. In order to unambiguously identify the thioenol form, as well as to assign the $^{13}$C NMR spectra, and hence identify the resonances for the double bond, a series of 2D experiments were performed on 16. The first, an HMQC spectrum, correlates resonances for directly bonded carbon and hydrogen atoms. The lack of a cross peak for the $^1$H NMR resonance at 2.5 ppm conclusively identifies this as the SH proton. The HMBC spectrum correlates resonances for protons and carbons separated by two or three bonds. Hence, the resonance at 2.5 ppm in the $^1$H spectra correlates to $^{13}$C resonances at 116.7 and 145.1 ppm. These $^{13}$C resonances are therefore identified as the double bond. The resonance at 145.1 ppm can be further identified as being part of the adamantyl moiety by the presence of cross peaks with the adamantyl hydrogen resonances at 2.78 and 3.30 ppm.

Loss of a disulfide fragment is a common side reaction in high oxidation state thiolate chemistry. It was of interest to identify the product which would be formed through this potential decomposition pathway. Furthermore, the reaction of disulfide linkages with Mo(CO)$_6$ is a route to the formation of Mo(III) compounds containing sulfur ligands. A common method for the synthesis of disulfides is oxidation of
the thiolate salts. Indeed oxidation of 11 with I₂ yields the corresponding disulfide, ArMe[Ad]CSSC[Ad]Ar₆. Disulfide formation is quite facile; allowing hexane solutions of the 16 and 17 to stir in air will lead to the formation of the corresponding disulfides over the course of several hours.

It was also of interest to prepare titanium transfer reagents. Previous workers have shown that alkoxide ligands on molybdenum will transfer to titanium while transferring a thiolate fragment to molybdenum.⁵¹ The titanium reagents were prepared by addition of the magnesium thiolate to CITi(O’Pr)₃ to form the titanium thiolates. The synthesis of Ti(SC[Ad]Ar₆)(O’Pr)₃ (18) was complicated by the initial isolation of the compound as an oil. Only after weeks in concentrated hydrocarbon solution did this material begin to crystallize as a solid. Although much of the material in Ti(SC[Ad]ArBu)(O’Pr)₃ (19) and Ti(SC[Ad]ArPh)(O’Pr)₃ (20) was also initially isolated as an oil, these compounds were easier to isolate as solids. Using this method, Ti(SC[Ad]Ar(Bu)Ph)(O’Pr)₃ (21) was also prepared.

1.3 Conclusions

Presented here is the synthesis of a large number of alkenyl and thioalkenyl fragments differing in their substituent pattern on the aryl ring. The substituents have been chosen to vary both the steric and solubility properties of the ligands, as well as to provide recognizable patterns in the ¹H NMR. This work substantially increases the number of adamantyl olefins that have been synthesized, and represents the first examples of trisubstituted alkenyl bromides with adamantyl substituents. These very hindered alkenyl bromides can be used to form Grignard reagents, which can serve as alkenyl ligand transfer reagents as discussed in chapter 2. The thioenol ligand, the synthesis of which has been detailed in this chapter, represents a new type of thiol ligand utilizing an sp² hybridized center not part of an aryl thiolate. The magnesium thiolates have been synthesized by careful control of reaction conditions. These magnesium thiolates, as well as the free thiols, disulfides, and titanium reagents
Figure 1-12: Reaction pinwheel showing the synthesis of magnesium thiolates, and the subsequent synthesis of free thiols, disulfides and titanium transfer reagents.
prepared in this chapter will be used ligand transfer reagents for the synthesis of molybdenum thiolate compounds, the chemistry of which is the subject of chapter 3.

1.4 Experimental Procedures

1.4.1 General Procedures

The following compounds were prepared by literature procedures: adamantyl epoxide,\textsuperscript{67} 1 bromo-3,5-diphenyl benzene,\textsuperscript{61} and α-bromomesitylene.\textsuperscript{60} All other reagents were obtained from standard sources and used as received. When noted, standard glove box and Schlenk techniques for the manipulations of air sensitive reactions were used. Solvents used for air sensitive manipulations were dried by the method of Grubbs,\textsuperscript{68} or by distillation from Na/benzophenone (THF). Dioxane was distilled over Na/benzophenone or purchased from Aldrich as anhydrous grade and stored over molecular sieves. Hexamethyldisiloxane was dried over molecular sieves. NMR spectra were obtained on Varian VXR-500, Varian XL-300, Varian Unity-300 or Varian Mercury 300 instruments. Chemical shifts are reported in ppm, and coupling constants in hertz. Proton chemical shifts are referenced to the residual C\textsubscript{6}D\textsubscript{5}H resonance at 7.15 ppm or to the residual CHCl\textsubscript{3} resonance at 7.27 ppm, carbon chemical shifts are referenced to the C\textsubscript{6}D\textsubscript{6} resonance at 128.39 ppm or the CDCl\textsubscript{3} resonance at 77.23, and phosphorus chemical shifts are referenced to external phosphoric acid at 0 ppm. Melting points were obtained on a Mel Temp II and are uncorrected. High resolution mass spectra were obtained by Li Li by electron impact. Elemental analysis (C, H) were performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany. The \textsuperscript{1}H and \textsuperscript{13}C NMR spectra are assigned as illustrated in the following diagram:
1.4.2 Preparation of Adamantyl Olefins

3,5-Dimethylbenzylphosphonium bromide

A 2 L flask was charged with α-bromomesitylene (124.9 g, 0.627 mol, 1 equiv), PPh₃ (164.5 g, 0.627 mol, 1 equiv) and toluene (1 L). The mixture was refluxed overnight, cooled, and filtered. The product was washed with toluene (300 mL) and petroleum ether (300 mL) to yield the phosphonium salt (258.86 g, 0.561 mol, 89%) as a white powder. $^1$H NMR (CDCl₃) δ 2.05 (s, 6H, m), 5.19 (d, J=14.2 Hz, 2H, benzylic H), 6.54 (s, 2H, j), 6.82 (s, 1H, l), 7.67 (m, 15H, phenyl). $^{13}$C NMR (CDCl₃) δ 21.29 (m), 117.87, 118.57, 129.43, 129.48, 130.21, 130.31, 134.60, 134.68, 135.10, 135.12, 138.54. $^{31}$P (CDCl₃) δ 23.5.

Preparation of HC[Ad]ArMe (1)

The phosphonium salt from α-bromomesitylene and PPh₃ (176 g, 0.38 mol) was dissolved in dry THF (650 mL) in the glove box. Lithium diisopropylamide (200 mL, 2M in THF/heptane/ethylbenzene, 0.40 mol) was added to the reaction mixture and
the mixture was stirred for 10 min. 2-Adamantanone (57.3 g, 0.38 mol) was added and the slurry was refluxed for 18 h under N₂. The mixture was cooled, concentrated and extracted with diethyl ether (4 × 400 mL). The combined extracts were concentrated to give a light yellow solid which was recrystallized from boiling methanol. Two crops of crystals were collected and dried in vacuo to yield 1 (48.3 g, 0.191 mol, 50%) as colorless crystals. ¹H NMR (C₆D₆) δ 1.6-2.0 (m, 12H, a-d), 2.18 (s, 6H, m), 2.50 (s, 1H, f), 3.36 (s, 1H, e), 6.34 (s, 1H, olefin H), 6.74 (s, 1H, l), 6.99 (s, 2H, j). ¹³C NMR (CDCl₃) δ 21.57 (m), 28.67 (b), 31.10 (f), 32.59 (e), 37.459 (a), 39.26 (d), 40.16 (c), 117.32 (h), 126.67 (j), 127.55 (l), 137.58 (k), 138.48 (g), 151.26 (i). m.p. 78 °C

Preparation of HC[Ad]Ar₄Bu (2) via Phosphonium Salt

Triphenyl phosphine (115 g, 0.44 mol, 1.1 equiv) and 4-tert-butylbenzyl bromide (100 g, 0.44 mol, 1.1 equiv) were combined in toluene (500 mL) and the reaction was refluxed overnight. The reaction was cooled and filtered. A white solid was collected and washed with toluene and petroleum ether. NMR confirms the identity of the phosphonium salt: ¹H NMR (CDCl₃) δ 1.23 (s, 9H, n), 5.19 (J=13.8 hz, d, 2H, benzylic H), 6.98 (d, 4H, j and k), 7.11-7.77 (m, 15H, Ph). ³¹P NMR (CDCl₃) 24.3. In the glove box, the phosphonium salt was slurried in THF (500 mL) and lithium diisopropyl amide (220 mL, 2.0 M solution, 0.44 mol, 1.1 equiv) was added. This was allowed to stir for 10 min, followed by addition of adamantanone (60 g, 0.40 mol, 1.0 equiv). The reaction was refluxed overnight under N₂. The THF was concentrated, and the reaction was extracted into OEt₂ (1 L). The ethereal extracts were concentrated and recrystallized from MeOH to yield 2 (30 g, 0.11 mmol, 28%) as colorless crystals. ¹H NMR (C₆D₆) δ 1.24 (s, 9H, n), 1.73-1.94 (m, 12H, a-d), 2.47 (s, 1H, f), 3.34 (s, 1H, e), 6.35 (s, 1H, olefin H), 7.29 (s, 4H, j and k). ¹³C NMR (C₆D₆) δ 29.38 (b), 32.02 (n), 33.21 (f), 34.97 (m), 37.94 (e), 39.759 (a), 40.67 (d), 41.84 (c), 118.225 (h), 125.746 (j or k), 129.906 (j or k), 136.257 (i), 148.992 (g), 151.066 (l). m.p. 63 °C. HRMS: Calculated: 280.2191, Found: 280.2186.
Large Scale Synthesis of 2,4,6-tribromiodobenzene

2,4,6-tribromoaniline (150 g, 0.46 mmol, 1.0 equiv) was slurried in concentrated HCl (300 mL) and cooled in an ice bath. NaNO₂ (35 g, 0.51 mmol, 1.1 equiv) was dissolved in water (200 mL) and added dropwise. Meanwhile, in a 5 L flask, KI (110 g, 0.66 mmol, 1.4 equiv) was dissolved in water (1.5 L). The aniline solution was transferred to a separatory funnel with a glass wool filter and the diazonium salt solution was added dropwise to the KI solution. The reaction was allowed to stir overnight. The following morning CH₂Cl₂ (1 L) was added, followed by Na₂S₂O₃. The organic layer was separated and partially concentrated. Several crops of light orange crystals (130 g, 0.29 mmol, 63%) were collected from CH₂Cl₂. The material is clean by ¹H NMR (CDCl₃, δ 7.71 ppm) m.p. matches lit 108 °C.⁶⁹

3,5-Dimesityl Bromobenzene

In the glove box Mg (5.1 g, 210 mmol, 3.4 equiv) was slurried in THF (100 mL). A solution of 2-bromomesitylene (40.6 g, 200 mmol, 3.2 equiv) in THF (250 mL) was prepared. About 20% of this solution was added, and initiation of the Grignard reaction was observed. The remaining bromide solution was added at such a rate to maintain a gentle reflux, and then allowed to stir an additional 1 hr. A solution of 2,4,6 tribromiodobenzene (27.2 g, 62 mmol, 1.0 equiv) in THF (125 mL) was prepared and added dropwise to the Grignard solution over the course of 2 h. The reaction was then refluxed overnight under N₂. The reaction was cooled, and poured onto ice. Dilute HCl was added, followed by extraction of the organic layer with OEt₂. The ethereal extracts were concentrated, followed by extraction between petroleum ether and water. The organic layer was concentrated and subjected to purification by column chromatography on silica gel using hexanes as an eluent. The fractions containing product were concentrated and recrystallized from hexanes to yield 3,5-dimesityl bromobenzene (2.5 g, 6.4 mmol, 10%) as colorless crystals. ¹H NMR (CDCl₃) δ 2.09 (s, 12H, q), 2.36 (s, 6H, r), 6.90 (s, 1H, l), 6.96 (s, 4H, o), 7.31 (s, 2H, j). ¹³C NMR (CDCl₃) δ 21.03 (q), 21.33 (r), 122.56 (i), 128.26 (o), 129.38 (l),
130.55 (j), 135.76 (n), 137.08 (p), 137.58 (m), 143.30 (k). The second major product of the reaction (eluting from the column before the desired 3,5-dimesityl bromobenzene) has been identified as 1,3-dibromo (6-mesityl) benzene. \( ^1H \) NMR (CDCl\(_3\)) \( \delta \) 1.940 (s, 6H), 2.156 (s, 3H), 4.08 (s, 1H), 6.05 (s, 2H), 7.21 (s, 1H), 7.27 (s, 1H) \(^{13}C\) NMR (CDCl\(_3\)) \( \delta \) 19.44, 22.17, 53.12, 60.85, 115, 117, 124.2, 132.3, 138.3, 147, 149.9, 154.0 Mass spec (from gc): 354

**Preparation of HC[Ad]Ar\(_{\text{Mes}}\) (3)**

In the glove box, 3,5-dimesityl bromobenzene (2.90 g, 7.38 mmol, 1.0 equiv) was dissolved in cold diethyl ether (40 mL). tert-butyllithium (1.6 M in pentane, 8.6 ml, 14.7 mmol, 1.99 equiv) was added and the solution allowed to stir for 2.5 h. Adamantyl epoxide (1.27 g, 7.75 mmol, 1.05 equiv) was added, and the reaction was allowed to stir overnight. The reaction was brought out of the glove box, and poured onto aqueous NH\(_4\)Cl (100 ml), and extracted into additional diethyl ether (2 x 100 mL). The organic extracts were concentrated to give the expected alcohol. \(^1H\) NMR (CDCl\(_3\)) \( \delta \) 1.5-1.9 (m, 12 H, a-d), 2.06 (s, 12 H, q), 2.19 (d, 2H, e,f), 2.34 (s, 6H, r) 2.662 (s, 1 H, OH), 3.059 (s, 2 H, CH\(_2\)), 6.837 (s, 1 H, l), 6.948 (s, 4 H, o), 6.999 (s, 2 H, j) The alcohol was dissolved in benzene (75 mL), and p-tolunesulfonic acid (290 mg, 1.68 mmol, 0.23 equiv) was added. The solution was refluxed overnight with a Dean-Stark trap. It was concentrated, extracted between NaHCO\(_3\)/petroleum ether, dried over MgSO\(_4\), filtered and concentrated. The residue was then recrystallized twice from boiling methanol to yield olefin 3 (1.13 g, 2.46 mmol, 33 %) in two crops of colorless crystals. \(^1H\) NMR (CDCl\(_3\)) \( \delta \) 1.8-2.0 (m, 12H, a-e), 2.08 (s, 12H, q), 2.326 (s, 6H, r), 2.503 (s, 1H, f), 3.158 (s, 1H, e), 6.230 (s, 1 H, olefin H), 6.722 (s, 1H, l), 6.943 (s, 6H, o and j).

**Preparation of HC[Ad]Ar\(_{\text{Mes}}\) from the Grignard Reagent**

In the glove box, 3,5-dimesityl bromobenzene (4.08 g, .010 mole, 1.0 equiv) was dissolved in THF and Mg powder was added. The solution was allowed to stir overnight.
The solvent was removed, and the residue was dissolved in diethyl ether. The solution was cooled to \(-35 \, ^\circ\text{C}\) and adamantyl epoxide (1.70 g, 0.010 mol, 1.0 equiv) was added. The solution was allowed to stir for 4 days, brought out of the glove box and poured onto aqueous NH\(_4\)Cl. The reaction was extracted into OEt\(_2\), and the ethereal layers were separated and tried over MgSO\(_4\). The reaction was purified by silica gel column chromatography with 10:1 hexanes/ethyl acetate as the eluent. Examination of the \(^1\)H NMR of the purified product suggests that the alcohol has rearranged to give the product shown in Fig 1-8. \(^1\)H NMR (C\(_6\)D\(_6\)) \(\delta\) 1.4-2.0 (m, 14H, a-e), 1.99 (s, 12H, q), 2.23 (s, 6H, r), 2.48 (broad s, ad H or alcohol, 1H), 4.64 (d, methylene, 1H), 6.67 (s, 1H, \(\alpha\)), 6.88 (s, 4H, o), 7.01 (s, 2H, j). This alcohol can be refluxed with p-toluenesulfonic acid in benzene in order to generate 3 with spectroscopic properties matching those obtained in the above procedure.

Preparation of HC[Ad]ArPh (4)

In the glove box, 3,5-diphenyl bromobenzene (8.00 g, 25.9 mmol, 1 equiv) was dissolved in OEt\(_2\) (200 mL) and chilled in the cold well. A solution of tert-butyl lithium (30 mL, 1.7 M in pentane, 51.0 mmol 2.0 equiv) was added and the solution was allowed to stir 4 h. Adamantyl epoxide (4.46 g, 27.2 mmol 1.05 equiv) was added and the solution was allowed to stir an additional 16 h. The solution was brought out of the box, and poured onto an aqueous solution of NH\(_4\)Cl. The layers were separated, and the aqueous layer was extracted with additional diethyl ether. The combined ethereal extracts were dried over MgSO\(_4\), filtered and concentrated. The residue was redissolved in benzene (125 ml), p-toluenesulfonic acid was added, and the mixture was refluxed 5 hours with a Dean Stark trap. The reaction was cooled and concentrated. The residue was extracted between CH\(_2\)Cl\(_2\) and aqueous NaHCO\(_3\). The organic layer was separated and concentrated, followed by recrystallization from hexanes to yield 4 (5.41 g, 14.4 mmol, 55%) as light orange crystals. \(^1\)H NMR (C\(_6\)D\(_6\)) \(\delta\) 1.72-1.93 (m, 12H, a-d), 2.51 (s, 1H, f), 3.38 (s, 1H, e), 6.41 (s, 1H, olefin H), buried under C\(_6\)D\(_6\) (probably a doublet, 2H, p), 7.24 (t, 4H, o), 7.58 (d, 4H, n, probably
also 2H for j under this peak), 7.71 (s, 1H, l). $^1$H NMR (CDCl$_3$) δ 28.70 (b), 32.80 (f), 37.46 (e), 39.35 (a), 40.21 (d), 41.28 (c), 117.07 (h), 123.76 (j or l), 126.70 (j or l), 127.35 (p or n), 127.38 (p or n), 128.86 (o), 139.40 (g), 141.44 (k or m), 141.60 (k or m), 152.28 (i). m.p. 122 °C. HRMS: Calculated: 376.2191, Found: 376.2186.

3,5-Bis(4-tert-butylphenyl) Bromobenzene

In the glove box, Mg powder (12 g, 374 mmol, 6.4 equiv) was slurried in THF. (4-tert-butyl-1-bromobenzene) (41 g, 192 mmol, 3.3 equiv) was dissolved in THF. 20% of this solution was added, and the solution was heated until initiation of the Grignard occurred. The Grignard solution was decanted off the Mg turnings into a Schlenk flask. 2,4,6 tribromoiodobenzene (24 g, 58 mmol, 1.0 equiv) was dissolved in THF (100 ml). This solution was added dropwise to the Grignard solution over four hours. The reaction was then brought out of the box and allowed to reflux under N$_2$ for 1.5 hours. It was cooled and poured onto ice (200 mL). Concentrated HCl was added, and the THF was partially removed by concentration. The product was extracted twice into CH$_2$Cl$_2$; the organic layer was separated and concentrated. The residue was subjected to vacuum distillations, and a pink material was removed. Hexane (200 ml) was added, and the solution was stored in the fridge overnight. The following morning 3,5-bis-(4-tert-butylphenyl) bromobenzene (12.95 g, 53% yield) was obtained as a white crystalline material. Additional crops of material could be collected. $^1$H NMR (CDCl$_3$) δ 1.39 (s, 18H, r), 7.49 (d, 4H, n or o), 7.56 (d, 4H, n or o), 7.69 (s, 2H, j), 7.72 (s, 1H, l). $^{13}$C NMR (CDCl$_3$) δ 31.56 (r), 34.81 (q), 123.36 (i), 124.73 (l), 126.10 (n or o), 127.05 (n or o), 128.72 (j), 137.11 (m), 143.64 (k), 151.24 (p). m.p.: 124-126 °C HRMS: Calculated: 420.1452, Found: 420.1453.

Preparation of HC[Ad]Ar(Bu)Ph (5)

In the glove box, a solution of 3,5-bis(4-tert-butylphenyl) bromobenzene (9.14 g, 21.7 mmol, 1.0 equiv) was dissolved in OEt$_2$ (100 mL) and frozen in the cold well. tert-Butyllithium (25.6 mL, 1.7 M, 43.5 mmol) was added to the thawing solution. The
reaction was allowed to stir and warm for 1.5 h. At this point, adamantyl epoxide (3.57 g, 21.7 mmol, 1.0 equiv) was added and the solution was allowed to stir overnight. The reaction was brought out of the glove box, and poured onto aqueous NH₄Cl, leading to the formation of a large amount of precipitate. This mixture was stirred for 2 h, and the organic layer was separated. The aqueous layer was washed with CH₂Cl₂ (50 mL) and this was combined with the ethereal extract. The combined organic layers were concentrated to a foam. The foam was redissolved in benzene (100 mL) and p-toluenesulfonic acid (220 mg, 1.28 mmol, .05 equiv) was added. The mixture was refluxed for 12 h attached to a Dean-Stark trap. The reaction was then cooled and concentrated to a foam. The foam was boiled in MeOH (100 mL) which led to the formation of a white solid which was collected and recrystallized from hexanes (5.4 g, 11.3 mmol, 52% yield). 

$$^1$$H NMR (C₆D₆) δ 1.27 (s, 18H, r), 1.7-1.9 (m, 12H, a-d), 2.5 (s, 1H, f), 3.5 (s, 1H, e), 6.46 (s, 1H, olefin H), 7.37 (d, 4H, o or n), 7.65 (d, 4H, o or n), 7.68 (s, 2H, j), 7.88 (s, 1H, l).

### 1.4.3 Preparation of Vinyl Bromides

**Preparation of BrC[Ad]ArMe (6)**

Olefin 1 (58.4 g, 0.23 mol) was dissolved in CH₂Cl₂ (500 mL) in a 1 L Schlenk flask. Bromine (13 mL, 40.7 g, 0.25 mol, 1.1 equiv) was dissolved in CH₂Cl₂ to give a total volume of 100 mL. The bromine solution was slowly added to the stirring olefin solution. *This reaction is very exothermic.* The reaction mixture was stirred for 1.5 h, concentrated, and brought into the glove box. Dry THF (500 mL) was added and the solution was chilled. To the chilled solution was added KOtBu (32 g, 0.29 mol, 1.25 equiv) and the flask was closed and allowed to stir overnight under N₂ on the Schlenk line. The resulting mixture was concentrated and subjected to an aqueous (400 mL)/ethereal (400 mL) workup. The ethereal layer was then washed with water (200 mL) and the combined aqueous layers were washed with OEt₂ (100 mL). The combined ethereal extracts were dried with MgSO₄ and concentrated. The resulting
crude solid was then recrystallized from boiling methanol (2 L). The crystalline product was then collected and dried in vacuo overnight to yield 6 (59.6 g, 0.18 mol, 78 %) as colorless crystals. ¹H NMR (C⁶D₆) δ 1.5-1.9 (m, 12H, a-d), 2.07 (s, 6H, m), 2.85 (s, 1H, f), 3.55 (s, 1H, e), 6.68 (s, 1H, l), 7.07 (s, 2H, j). ¹³C NMR (C⁶D₆) δ 21.62 (m), 28.46 (b), 36.28 (f), 37.19 (e), 38.51 (a), 38.87 (d), 39.40 (c), 112.01 (h), 127.67 (j), 130.13 (l), 138.32 (g or k), 141.47 (g or k), 147.74 (i). m. p. 103 ºC.

**Preparation of BrC[Ad]ArBu (7)**

Olefin 2 (43.6 g, 0.156 mol, 1.0 equiv) was dissolved in CH₂Cl₂ (500 mL). A solution of bromine (8 mL, 0.156 mol, 1.0 equiv) in CH₂Cl₂ (50 mL) was prepared. This solution was added slowly to the stirring solution of olefin. After five minutes, the solution was concentrated. The residue was brought into the glove box, slurried in THF (200 mL) and chilled. KOᵗBu (22 g, 0.196 mol, 1.25 equiv) was added, and the reaction was allowed to stir overnight under N₂. The reaction was concentrated and the residue was extracted between OEt₂ and water. The layers were separated and the OEt₂ layer was partially concentrated, and the solid was collected by filtration and dried to yield 7 (56 g, 0.156 mol, 100 %) as colorless crystals. ¹H NMR (C⁶D₆) δ: 1.16 (s, 9H, n), 1.4-1.9 (m, 12H, a-d), 2.86 (s, 1H, e), 3.53 (s, 1H, f), 7.20 (d, 2H, j or k), 7.37 (d, 2H, j or k). ¹³C NMR δ 28.52 (b), 31.80 (n), 35.01 (m), 36.31 (f), 37.25 (e), 38.72 (a), 38.91 (d), 39.48 (c), 111.87 (h), 125.89 (j or k), 129.70 (j or k), 138.69 (i), 148.04 (g), 151.06 (l). m.p. 159-160 ºC. HRMS:Calculated: 358.1296, Found: 358.1291.

**Preparation of BrC[Ad]ArPh (8)**

Olefin 4 (5.15 g, 13.7 mmol, 1.0 equiv ) was dissolved in CH₂Cl₂ (75 mL). Bromine (0.35 mL, 6.85 mmol, 0.5 equiv) was added, and the reaction was allowed to stir 5 min. The reaction was concentrated to an orange oily residue, which was brought into the glove box. The residue was dissolved in dry THF (50 mL) and KOᵗBu (2.30g, 20.5 mmol, 1.5 equiv) was added and the flask was immediately evacuated, brought
out of the glove box and allowed to stir overnight under N₂. The suspension was quenched with H₂O (50 mL) and the THF was removed. The reaction was extracted into CH₂Cl₂ (2 × 75 mL). The combined organic layers were concentrated and the solid was recrystallized from OEt₂ to provide 8 (4.0 g, 8.78 mmol, 64%) as light orange crystals. ¹H NMR (C₆D₆) δ 1.45-1.94 (m, 12H, a-d), 2.91 (1H, s, f), 3.57 (1H, s, e), d buried in C₆D₆, 7.20 (t, 4H, o), 7.46 (d, 4H, n), 7.70 (s, 1H, l), 7.72 (s, 2H, j). ¹³C NMR (C₆D₆) δ 28.39 (b), 36.44 (f), 37.12 (e), 38.63 (a), 38.85 (d), 39.35 (c), 111.18 (h), 126.44 (j or l), 127.70 (j or l), 128.01 (p or n), 128.14 (p or n), 129.47 (o), 141.51 (g), 142.56 (k or m), 142.94 (k or m), 148.94 (i). m.p. 138 °C. HRMS: Calculated: 454.1296, Found: 454.1291.

Preparation of BrC[Ad]Ar(Bu)Ph (9)

Olefin 5 (5.4 g, 11.3 mmol, 1.0 equiv) was dissolved in CH₂Cl₂ (50 mL). Elemental bromine (0.30 mL, 5.9 mmol, 0.52 equiv) was added and the solution was concentrated. The foam was brought into the glove box, dissolved in THF (50 mL), and KO'Bu (1.68 g, 15.0 mmol, 1.33 equiv) was added. The reaction was removed from the glove box, and allowed to stir 2 h under N₂, followed by addition of H₂O (100 mL). The THF was removed, and the white solid was collected. This solid was washed with hexanes (10 mL), methanol (10 mL) and additional hexane (10 mL) and dried overnight under vacuum to yield 9 (4.59 g, 8.09 mmol, 72%) as a white powder. ¹H NMR (C₆D₆) δ 1.25 (s, 18 H, r), 1.5-2.0 (m, 12H, a-d), 3.0 (s, 1H, f), 3.6 (s, 1H, e), 7.33 (d, 4H, n or o), 7.55 (d, 4H, n or o), 7.82 (s, 2H, j), 7.89 (s, 1H, l). ¹³C NMR (C₆D₆) δ 28.61 (b), 31.99 (n), 35.08 (m), 36.66 (f), 37.33 (e), 38.88 (a), 39.07 (d), 39.61 (c), 111.66 (h), 126.43 (l), 126.67 (n or o), 127.74 (n or o), 128.00 (j), 139.09 (g), 142.76 (m), 143.20 (k), 149.06 (i), 151.11 (p). m.p. 205 °C. HRMS: Calculated: 566.2548, Found: 566.2541.
1.4.4 Preparation of Alkenyl Transfer Reagents

Preparation of 3,5-Dimethyl Grignard Reagent (10)

Vinyl bromide 6 (38.05 g, 0.114 mol, 1.0 equiv) was dissolved in dry THF (200 mL) and 10 mL of the solution was cannula-transferred onto Mg turnings (6 g, 0.25 mol, 2.19 equiv). The reaction mixture was heated until initiation began. Initiation is observable when an autoreflux is maintained with slow addition of the vinyl bromide solution. After the reaction had initiated, the cannula transfer was completed and the reaction mixture was refluxed for 1 h, cooled, and brought into the glove box. The reaction mixture was filtered through a Büchner funnel to remove excess Mg with additional THF (100 mL) and concentrated to yield a yellow oil. The oil was slurried in pentane (100 mL) to give a white solid, which was collected on a filter frit to yield 10 (52.05 g, 91%) as a white powder. One- pulse $^1$H NMR spectroscopy indicated the product to be a mixture of Mg(C[Ad]ArMe)(Br)(THF)$_x$ (δ 2.25 for aryl methyl H) and Mg(C[Ad]ArMe)$_2$(THF)$_x$ (δ 2.31 for aryl methyl H).

1.4.5 Preparation and Characterization of Magnesium Thiolates, Free Thiols and Disulfides

Synthesis of (THF)$_2$Mg(SC[Ad]ArMe)(Br) (11)

In the glove box Grignard reagent 10 (2.62 g, 5.6 mmol, 1 equiv) and S$_8$ (167 mg, 0.65 mmol, 0.12 equiv) was slurried in just melted OEt$_2$ (50 mL). The reaction was allowed to warm and stirred for 1 h. The reaction was filtered, and the solid was washed with pentane (20 mL) to yield 11 (2.01 g, 4.0 mmol, 71%) as a white powder. $^1$H NMR (C$_6$D$_6$) δ 1.29 (s, THF), 1.5-2.1 (12H, a-d), 2.29 (s, 6H, m), 2.8 (br s, 1H, f), 3.74 (s, THF), 3.82 (s, 1H, e), 6.68 (s, 1H, l), 7.48 (s, 2H, j).
Preparation of \((\text{THF})_2\text{Mg(SC}[\text{Ad}]\text{Ar}_\text{Me})_2\) (12)

In the glove box bromide 6 (4.164 g, 12.6 mmol, 1.0 equiv) was dissolved in THF (50 mL) and Mg turnings (996 mg, 41 mmol, 3.25 equiv) were added. The flask was heated until initiation of the Grignard reaction occurred. The reaction was allowed to stir 3 h, and filtered to remove Mg. The reaction was concentrated, slurried in OEt\(_2\) (150 mL), and the solution was frozen in the cold well. The reaction was removed from the cold well, and as soon as the ethereal solution was melted, S\(_8\) (405.4 mg, 2.11 mmol, 0.167 equiv) was added to the rapidly stirring solution. The reaction was allowed to stir 2 h, dioxane was added (10 mL) and the reaction was allowed to stir an additional 36 h. The mixture was filtered through a bed of celite, and the solid was extracted into additional THF (75 mL) and filtered. The filtrate was concentrated and slurried in pentane (50 mL) to form a white solid. This solid was collected to yield 12 (2.817 g, 3.8 mmol, 60%) as a white powder. This procedure did not remove all the 12 from the celite layer, the solid that was trapped in the celite could be quenched with aqueous NH\(_4\)Cl and the organic material extracted in CH\(_2\)Cl\(_2\) to yield additional HSC[Ad]Ar\(_{\text{Me}}\).

\(^1\)H NMR (C\(_6\)D\(_6\)) \(\delta\) 1.231 (br s, 8H, bound THF), 1.7-2.3 (m, 24H, a-d), 2.90 (s, 2H, f), 3.43 (br s, 8H, bound THF), 4.30 (br s, 2H, e), 6.67 (s, 2H, I), 7.32 (s, 4H, j).

Preparation of Ar\(_{\text{Me}}[\text{Ad}]\text{CSSC}[\text{Ad}]\text{Ar}_\text{Me}\)

In the glove box Grignard reagent 10 (5.11 g, 10.9 mmol, 1.0 equiv) was added rapidly to a stirring solution of S\(_8\) (326 mg, 1.27 mmol, 0.12 equiv) in just melted OEt\(_2\). The solution was allowed to stir 2 h, brought out of the box and I\(_2\) was added until the solution remained dark. The OEt\(_2\) solution was extracted with aqueous sodium thiosulfate, and the organic layer was separated and concentrated to yield Ar\(_{\text{Me}}[\text{Ad}]\text{CSSC}[\text{Ad}]\text{Ar}_\text{Me}\) (2.88 g, 5.1 mmol, 94%) as a light orange solid. \(^1\)H NMR (C\(_6\)D\(_6\)) \(\delta\) 1.61-1.93 (m, 24H, a-d), 2.23 (s, 12H, m), 2.84 (s, 2H, f), 3.77 (s, 2H, e), 6.80 (s, 2H, I), 7.10 (s, 4H, j). \(^{13}\)C NMR (C\(_6\)D\(_6\)) \(\delta\) 21.93 (m), 21.87 (b), 36.27 (f), 36.98 (e), 37.53 (a), 40.08 (d), 40.42 (c), 126.78, 128.63, 129.31, 137.61, 141.15, 154.30. HRMS:
Preparation of \( \text{HSC[Ad]ArMe} \) (15)

Magnesium thiolate \((\text{THF})_2\text{Mg(SC[Ad]ArMe})_2\) was brought out of the glove box and partitioned between aqueous \(\text{NH}_4\text{Cl}\) and \(\text{CH}_2\text{Cl}_2\). The organic layer was separated and concentrated to yield 15 as a colorless oil that eventually solidified to a white solid. \(^1\text{H} \text{NMR (C}_6\text{D}_6) \delta 1.5-2.0 \text{ (m, 12H, a-d)}, \ 2.58 \text{ (s, 1H, SH)}, \ 2.80 \text{ (s, 1H, f)}, \ 3.34 \text{ (s, 1H, e)}, \ 6.72 \text{ (s, 1H, l)}, \ 7.04 \text{ (s, 2H, j)}. \ ^{13}\text{C NMR (C}_6\text{D}_6) \delta 21.71 \text{ (m), 21.89 (b), 35.48 (f), 36.21 (e), 37.42 (a), 39.03 (d), 39.70 (c), 116.92 (h), 125.94 (j), 129.30 (l), 128.35 (k), 144.17 (g), 145.10 (i)}. \ \text{HRMS: Calculated: 284.1599 Found: 284.1593}

Preparation of \((\text{dioxane})_2\text{Mg(SC[Ad]ArBu})_2\) (13)

In the glove box, bromide 7 (7.76 g, 21.6 mmol, 1.0 equiv) was dissolved in THF (40 mL) and Mg powder (2 g, 82.3 mmol, 3.8 equiv) was added. The reaction was gently heated until a darkening of the solution indicated initiation of the Grignard reaction. The reaction was allowed to stir 2 h, filtered to remove excess Mg, and concentrated. The residue was slurried in OEt\(_2\) (150 mL), and chilled in the cold well until nearly frozen. The reaction was rapidly stirred and \(\text{S}_8\) (692 mg, 2.7 mmol, 0.125 equiv) was added all at once. After 1 h, dioxane (50 mL) was added and the reaction was allowed to stir overnight. The mixture was filtered through celite, and the solid was washed with THF (200 mL) and reduced in volume to 20 mL. Two crops of solid were collected and washed with pentane to yield 13 (3.71 g, 4.87 mmol, 45%) as a white powder. \(^1\text{H NMR (C}_6\text{D}_6) \delta 1.27 \text{ (s, 18H, n)}, \ 1.6-2.2 \text{ (m, 24H, a-d)}, \ 2.9 \text{ (s, 2H, f)}, \ 3.32 \text{ (s, 8H, dioxane), 4.05 (s, 2H, e), 7.38 (d, 4H, j or k), 7.9 (d, 4H, j or k)}

Preparation of \(\text{HSC[Ad]ArBu}\) (16)

In the glove box, bromide 7 (3.57 g, 9.9 mmol, 1.0 equiv) was dissolved in THF (50 mL), Mg powder (996 mg, 41 mmol, 4.1 equiv) was added and the solution was brought to reflux to initiate the Grignard reaction. The reaction was then allowed to
stir 2 h, filtered to remove excess Mg powder and concentrated. The solid was slurried in OEt₂ (100 mL) and cooled in the cold well until nearly frozen. S₈ (312.4 mg, 1.22 mmol, 0.123 equiv) was added all at once to the rapidly stirring solution. The reaction was filtered and concentrated to an orange oily residue. The residue was slurried in pentane (40 mL) and the pentane was decanted. The solid removed from filtrated and the pentane insoluble material was combined with the solids obtained during filtration, brought out of the glove box and partitioned between aqueous NH₄Cl (100 mL) and CH₂Cl₂ (50 mL × 2). The organic layer was separated, and concentrated to yield 16 (1.482 g, 4.740 mmol, 45%) as a white powder. From the pentane solution that was decanted, (THF)₂Mg(SC[Ad]ArBu)₂ (582.3 mg, 0.74 mmol, 15%) was obtained as a white powder. ¹H NMR (C₆D₆) δ 1.21 (s, 9H, n), 1.5-1.9 (s, 12H, a-d), 2.53 (s, 1H, SH), 2.78 (s, 1H, f), 3.30 (s, 1H, e), 7.24 (d, 2H, j or k), 7.33 (d, 2H, j or k). ¹³C NMR (C₆D₆) δ 28.71 (b), 31.87 (n), 34.92 (m), 35.43 (f), 36.31 (e), 37.49 (a), 39.06 (d), 39.75 (c), 116.73 (h), 125.93 (j or k), 128.99 (j or k), 141.29 (i), 145.51 (g), 150.18 (l). HRMS: Calculated: 312.1910, Found: 312.1906.

Characterization of ArBu[Ad]CSSC[Ad]ArBu

Upon allowing solutions of HSC[Ad]ArBu to stand in air, the solutions will take on a blue-purple color. Upon concentration and recrystallization from petroleum ether, a white solid is isolated. ¹H NMR (C₆D₆) δ 1.55 (s, 18H, n), 1.5-2.0 (m, 24H, a-d), 2.8 (s, 2H, f), 3.8 (s, 2H, e), 7.31 (d, 4H, j or k), 7.41 (d, 4H, j or k). ¹³C NMR: (C₆D₆) δ 28.93 (b), 32.00 (n), 35.05 (m), 36.33 (f), 36.97 (e), 37.67 (a), 40.00 (d), 40.32 (c), 125.43 (j or k), 125.67 (j or k), 130.38 (h), 137.77 (i), 150.13 (g), 156.95 (l). m.p. 211-212 °C. HRMS: Calculated: 622.3670, Found: 622.3670.

Characterization of ArBu[Ad]CSC[Ad]ArBu

The pentane washing from preparation of 13 were concentrated and brought out of the box. The material was recrystallized from petroleum ether. The white solid was pure ArBu[Ad]CSC[Ad]ArBu. ¹H NMR (C₆D₆) δ 1.25 (s, 18H, n), 1.56-1.85 (m, 24H,
a-d), 2.86 (s, 2H, f), 3.75 (s, 2H, e), 7.38 (d, 4H, j or k), 7.44 (d, 4H, j or k). $^{13}$C NMR (C$_6$D$_6$): $\delta$ 28.94 (b), 32.03 (n), 35.09 (m), 36.43 (f), 36.98 (e), 37.63 (a), 40.08 (d), 40.21 (c), 125.50 (j or k), 126.63 (j or k), 130.62 (h), 138.15 (i), 150.01 (g), 154.10 (l). m.p.: 174 °C. HRMS: Calculated: 590.3946, Found: 590.3958.

**Synthesis of (THF)$_2$Mg(SC[Ad]ArPh)$_2$ (14)**

In the glove box, vinyl bromide 8 (3.935 g, 8.64 mmol, 1.0 equiv) was dissolved in THF (100 mL) and Mg powder (300 mg, 12.3 mmol, 1.4 equiv) was added. The slurry was heated until the mixture darkened and boiled, and then stirred 2 h. The reaction was filtered and concentrated to yield a white powder. The powder was slurried in OEt$_2$ (100 mL) and cooled in the cold well until the solution began to freeze. It was removed from the cold well and stirred rapidly, then S$_8$ (277.6 mg, 1.08 mmol, 0.125 equiv) was added all at once. After 2 h, the solution was filtered to collect a white solid. The solid was redissolved in THF (100 mL) and dioxane (5 mL) was added. The mixture was allowed to stir an additional 2 h, filtered through celite and concentrated to yield a yellow oil. The oil was slurried in pentane (75 mL) until a white solid formed. The solid was collected to yield white 14 (3.29 g, 3.34 mmol, 77 %) as a white solid. While spectroscopic data for this compound is difficult to interpret, clean reactivity was observed from this material.

**Characterization of HSC[Ad]ArPh (17)**

The thiol was formed by protonation of (THF)$_2$Mg(SC[Ad]ArPh)$_2$ with aqueous NH$_4$-Cl, followed by extraction into dichloromethane. Separation of the organic layer followed by concentration yielded 17. $^{1}$H NMR (C$_6$D$_6$) $\delta$ 1.5-2.0 (s, 12H, a-d), 2.61 (s, 1H, SH), 2.86 (s, 1H, f), 3.38 (s, 1H, e), 7.17 (t, 2H, p), 7.24 (t, 4H, o), 7.54 (d, 4H, n), 7.70 (s, 2H, j), 7.74 (s, 1H, l). $^{13}$C NMR (C$_6$D$_6$) $\delta$ 28.65 (b), 35.69 (f), 36.35 (e), 37.39 (a), 39.05 (d), 39.68 (c), 116.52 (h), 125.59 (j or l), 127.05 (j or l), 128.00 (p or n), 129.50 (p or n), 141.72 (g), 142.95 (k or m), 145.21 (k or m), 146.52 (i).
Characterization of HSC[Ad]Ar(Bu)Ph

Ti(SC[Ad]ArBu)(O1Pr)3 was brought out of the box, and extracted between CH2Cl2 and water. The solution was filtered, and the organic layer was separated and concentrated. Recrystallization from hexane yielded HSC[Ad]Ar(Bu)Ph. 1H NMR (C6D6) δ 1.26 (s, 18H, r), 1.5-2.0 (s, 12 H, a-d), 2.65 (s, 1H, SH), 2.93 (s, 1H, f), 3.39 (s, 1H, e), 7.36 (d, 4H, n or o), 7.61 (d, 4H, n or o), 7.78 (s, 2H, j), 7.91 (s, 1H, l).

Characterization of Ar(Bu)Ph[Ad]CSSC[Ad]Ar(Bu)Ph

Oxidation of HSC[Ad]Ar(Bu)Ph with I2 led to the formation of Ar(Bu)Ph[Ad]CSSC[Ad]-Ar(Bu)Ph. 1H NMR (CD) δ 1.27 (s, 18H, r), 1.50-2.0 (s, 12H, a-d), 2.94 (s, 1H, f), 3.97 (s, 1H, e), 7.37 (d, 4H, n or o), 7.65 (d, 4H, n or o), 7.85 (s, 2H, j), 7.90 (s, 1H, f).

1.4.6 Preparation of Titanium Transfer Reagents

Preparation of Ti(SC[Ad]ArMe)(O1Pr)3 (18)

A solution of CITi(O1Pr)3 (26 mg, 0.10 mmol, 1.0 equiv) was prepared in OEt2 and frozen in the cold well. Upon thawing it was added to a melting slurry of (THF)2Mg(SC[Ad]ArMe)(Br) (54 mg, 0.10 mmol, 1.0 equiv) in OEt2 (10 mL). The reaction was allowed to stir 30 min, at which time dioxane (1 mL) was added, and the reaction was allowed to stir an additional 2 h. The reaction was filtered through celite and concentrated to yield 18 (46 mg, 0.090 mmol, 90 %) as a light yellow oil. 1H NMR (C6D6) δ 1.19 (d, 18H, isopropyl H), 1.71-2.18 (m, 6 H, a-d), 2.23 (s, 6H, m), 3.04 (s, 1H, f), 4.04 (s, 1H, e), 4.43 (q, 3H, isopropyl methine), 6.76 (s, 1H, l), 7.30 (s, 2H, j ). 13C NMR (C6D6) δ 21.88 (m), 26.99 (isopropyl CH3), 29.03 (b), 36.08 (f), 36.55 (e), 37.78 (a), 39.40 (d), 40.22 (c), 79.34 (methine C), 125.54 (j or k), 127.69 (j or k), 137.50 (i), 146.14 (g), 147.88 (l). Elemental Analysis: Calculated for C28H44SO3Ti: C, 66.12; H, 8.72. Found: C, 66.89; H, 9.12.
Preparation of Ti(SC[Ad]ArBu)(O'Pr)₃ (19)

Magnesium thiolate (THF)₂Mg(SC[Ad]ArBu)₂ (582.3 mg, 0.74 mmol, 0.5 equiv) was slurried in pentane (5 ml) and ClTi(O'Pr)₃ (389.7, 1.50 mmol, 1.0 equiv) in pentane (5 mL) was added. The reaction was stirred 1.5 h, and dioxane (2 mL) was added. The reaction was stirred an additional 3 h, filtered through a bed of celite and concentrated. Several crops of 19 (503 mg, 0.94 mmol, 63%) were collected as a light yellow solid. ¹H NMR (C₆D₆) δ 1.17 (d, 18H, isopropyl H), 1.24 (s, 9H, n), 1.6-2.2 (m, 12H, a-d), 3.05 (s, 1H, f), 4.01 (s, 1H, e), 4.4 (m, 3H, methine H), 7.30 (d, 2H, j or k), 7.61 (d, 2H, j or k). ¹³C NMR (C₆D₆) δ 27.10 (isopropyl CH₃), 29.10 (b), 32.03 (n), 34.07 (m), 36.12 (f), 36.88 (e), 37.86 (a), 39.44 (d), 40.28 (c), 78.99 (methine C), 101.00 (h) 125.34 (j or k), 129.61 (j or k), 143.23 (i), 148.31 (g), 149.08 (l) Anal. Calculated for C₃₀H₄₈SO₃Ti: C, 67.14; H, 9.02. Found: C, 67.07; H, 9.39.

Preparation of Ti(SC[Ad]ArPh)(O'Pr)₃ (20)

In the glove box, magnesium thiolate 14 (2.47 g, 2.51 mmol, 1.0 equiv) was added to a solution of ClTi(O'Pr)₃ (1.38 g, 5.30 mmol, 2.11 equiv) in OEt₂ (25 mL). After 1 h dioxane (5 mL) was added and the reaction was allowed to stir an additional 3 h. It was filtered through celite and concentrated to a yellow oil. The oil was dissolved in pentane, filtered and cooled to −35 °C to collect several crops of 20 (2.335 g, 3.69 mmol, 74%) were collected as a light yellow powder. ¹H NMR (C₆D₆) δ 1.11 (d, 18H, isopropyl methyl), 1.6-2.2 (m, 12H, a-d), 3.060 (s, 1H, f), 4.1 (s, 1H, e), 4.36 (quintet, 3H, methine H), 7.15 (d, 2H, under benzene, p), 7.23 (t, 4H, o), 7.65 (d, 4H, n), 7.74 (s, 1H, l), 7.956 (s, 2H, j). ¹³C NMR (C₆D₆) δ 27.12 (isopropyl CH₃), 29.13 (b), 36.26 (f), 36.50 (e), 37.71 (a), 39.37 (d), 40.15 (c), 79.34 (methine C), 124.68 (h), 126.03 (j or l), 127.04 (j or l), 127.80 (p or n), 127.85 (p or n), 128.68 (o), 129.43 (g), 142.32 (k or m), 147.25 (k or m), 148.7 (i) Anal. Calculated for C₃₈H₄₈SO₃Ti: C, 72.12; H, 7.65. Found: C, 72.38, H, 7.88.
Preparation of Ti(SC[Ad]Ar(Bu)Ph)(OiPr)₃ (21)

Bromide 9 (3.27 g, 5.76 mmol, 1.0 equiv) was dissolved in THF (30 mL). Mg powder (360 mg, 12.8 mmol, 2.2 equiv) was added, and the solution was brought to reflux. After initiation of the Grignard reaction, the mixture was allowed to stir 2 h, filtered and concentrated. The residue was redissolved in diethyl ether (100 mL), and frozen in the cold well. Upon melting, S₈ (185 mg, 0.72 mmol, 0.125 equiv) was added to the rapidly stirring reaction. The reaction was allowed to stir 2 hr, reduced in volume to 50 mL, and filtered. The mother liquor was concentrated, and dissolved in pentane (20 mL). ClTi(OiPr)₃ (1.50 g, 5.76 mmol, 1.0 equiv) was added and the reaction was allowed to stir 2 h. Dioxane (2 ml) was added, the reaction was filtered through celite and concentrated to yield 21 as a yellow oil in ca. 90% purity. ¹H NMR (C₆D₆) δ 1.18 (br s, 18H, isopropyl CH₃), 1.26 (s, 18H, r), 3.17 (s, 1H, f), 4.10 (s, 1H, e), 4.43 (s, 3H, methine H), 7.38 (d, 4H, n or o), 7.75 (d, 4H, n or o), 7.94 (s, 1H, l), 8.06 (s, 2H, j).
Chapter 2

Synthesis and Reactivity of Chromium tris-Alkenyl Compounds

A portion of this material has been published: Brock, J. R.; Odom, A. L., Klei, S. R., Cummins, C. C. Organometallics. 1999, 18, 1360.

2.1 Introduction

In setting out to explore the utility of the alkenyl fragment, -C[Ad]ArMe, developed in Chapter 1 as a ligand, initial experiments were focused on chromium compounds. Chromium (III)-tris-ligand complexes are stabilized by the half filled $d^3$ configuration, in which there is one electron in each of the three low lying metal orbitals. In addition, CrCl$_3$ is commercially available and serves as a convenient starting material. Indeed, three coordinate chromium complexes exist for a wide variety of ligand donor types including amide,$^{16-22}$ phosphide,$^{27}$ siloxide,$^{23}$ and alkyl ligands.$^{24-26}$ Of
related interest are the (THF)CrX₃ compounds that have been prepared with aryl²⁹ and alkenyl ligands.₃⁰,₅₀ A smaller alkenyl ligand, -C[CMₑ₂]Ph, has previously been used in the context of chromium chemistry. However, the limited steric bulk of this compound proved to be problematic. While (THF)Cr(C[CMₑ₂]Ph)₃ was isolated and characterized by elemental analysis, this compound is thermally unstable at room temperature and disproportionates to the crystallographically characterized Cr(C[CMₑ₂]Ph)₄ species.₃⁰,₅₀ Hence, it was of interest to explore a more sterically encumbering alkenyl ligand in the context of chromium chemistry in order to isolate and study the reactivity of a CrR₃(THF) species.

There are very few reports in the literature on the reactivity of three coordinate chromium and “masked” three coordinate chromium compounds with hydrocarbyl ligands. Complexes prepared with alkyl ligands include Cr(2,2,3-trimethylbicyclo-[2.2.1]hept-1-yl)₃ prepared by Bower,²⁶ and Cr(CH[SiMe₃]₂)₃ prepared by Lappert.²⁴ Lappert reported that Cr(CH[SiMe₃]₂)₃ did not react with pyridine and generated unstable compounds upon treatment with NO or Ph₃CCl.²⁴,²⁵ While (THF)Cr(Mes)₃ was originally prepared in 1966, the reactivity of this compound has been poorly explored. It has been used to study isocyanide insertion⁷⁰ and as a polymerization catalyst.⁷¹ Finally, the reactivity of (THF)Cr(C[CMₑ₂]Ph)₃ has been limited by its propensity to disproportionate to Cr(C[CMₑ₂]Ph)₄, although (tmeda)Cr([CMe₂]Ph)₃ has also been prepared.³⁰,₅₀ It was therefore expected that the use of more sterically encumbering -C[Ad]Arₘ ligand would allow for the isolation of three coordinate species without concern about disproportionation reactions.
Figure 2-1: Treatment of CrCl₃ with 10 gave 22-THF in 68% yield (Ar = 3,5-Me₂C₆H₃, Ad = 2-adamantylidene).

2.2 Results and Discussion

2.2.1 Synthesis and Characterization of

(THF)Cr(C[Ad]ArMe)₃

The preparation of the chromium tris-alkenyl compound, (THF)Cr(C[Ad]ArMe)₃ (22-THF), was straightforward, as illustrated in Fig 2-1. Reaction of the Grignard reagent 10 with anhydrous CrCl₃ in diethyl ether (Fig 2-1) led to a bright blue mixture. Addition of dioxane to this mixture, followed by filtration, and partial removal of volatiles, provided 22-THF in a 68% yield as blue crystals. The THF molecules coordinated to the Grignard reagent are the source of the THF that binds to the chromium center. The compound is paramagnetic and exhibits a magnetic moment of 3.67 μₜ in the solid state, as measured by SQuID magnetometry. This moment is indicative of a high spin \( d^3 \) system. The visible spectrum of 22-THF in C₆H₆ consists of a single broad band at \( \lambda \) 590 nm (ε 1300 M⁻¹cm⁻¹).

The solid state structure of (THF)Cr(C[Ad]ArMe)₃ is shown in Fig 2-2. The THF is located in a pocket comprised of the three aryl rings. The Cr–C bond distances are 2.039(7), 2.048(6), and 2.055(7) Å. These distances compare well with the value of 2.07(1) Å determined for Cr(CH[SiMe₃]₂)₃.²⁵ In comparing the Cr–C
Figure 2-2: Drawing of (THF)Cr(C[Ad]ArMe)₃ (22-THF) (35% probability ellipsoids). Selected distances (Å) and angles (°): Cr(1)-O, 2.174(4); Cr(1)-C(1), 2.039(7); Cr(1)-C(2), 2.048(6); Cr(1)-C(3), 2.055(7); Cr(1)-C(1)-C(2), 104.7(3); Cr(1)-C(1)-C(3), 112.3(3); C(2)-Cr(1)-C(3), 106.0(3); C(1)-Cr(1)-O, 97.3(2); C(2)-Cr(1)-O, 130.4(2); C(3)-Cr(1)-O, 105.6(2).
bond distances to those found in other chromium alkenyl compounds, the bond distances are similar to those in Cr(C[CMe₂]Ph)₄ (2.049(12), 2.027(13), 2.032(13) and 2.033(11) Å)³⁰ but shorter than the corresponding distances in the significantly more electron rich Cr(CMe=CH₂)₂(C₃H₅)-(PMe₃)₂ (2.113(5) Å).⁷² The C=C bond distances are unexceptional and are 1.347(9), 1.323(8) and 1.349(9) Å.

The issue of donation of π electron density from the double bond into empty metal orbitals, or conversely π-backbonding, has been investigated previously by comparison of the solid state structures of Cr(C[CMe₂]Ph)₄ and Sn(C[CMe₂]Ph)₄. The authors concluded that there is a lengthening of the C=C double bonds in the chromium structure compared to the tin structure.⁵⁰ However, the differences in the bond lengths are not significant using the 3σ criteria. In order to address the question of Cr–C π-bonding in 22-THF, Professor Cummins performed density functional theory (DFT) calculations⁷³–⁷⁵ on the hypothetical molecule Cr(OMe₂)(vinyl)₃ (24) using the core bond angles from the X-ray structure of 22-THF. These calculations, the results of which are summarized in Table 2.1, revealed that the C=C overlap population is reduced from that found in ethylene, consistent with partial transfer of electron density from Cr into the C=C π* orbital. It must be noted, however, that the calculated structure of 24 represents only an approximation to the full structure of 22-THF, such that any electronic consequences of steric effects are lost within the context of this analysis.

### 2.2.2 Reaction of (THF)Cr(C[Ad]ArMe)₃ with Lewis Bases

Inasmuch as some three-coordinate chromium(III) complexes do not display pronounced Lewis acidity, a noteworthy feature of the structure of 22-THF is the presence of a THF molecule coordinated to the chromium center. The Cr–O bond length of 2.174(4) Å is similar to the Cr–O bond length of 2.225(10) Å found for Cr(Ph)₃(THF)₃⁷⁶ and is longer than the Cr–O bond lengths in CrCl₃(THF)₃.⁷⁷ Siloxide and amide ancillary ligands have led to THF-free three-coordinate chromium(III) derivatives, even when prepared with THF as the reaction solvent.¹⁶⁻²³ In con-
Table 2.1: Results of DFT calculations on hypothetical \textbf{24}. Constraints used for geometry optimization: quartet state, all Cr-C bond lengths equal, all C=C bond lengths equal, all core bond angles same as found by X-ray for \textbf{22-THF}. Average overlap populations (o.p.) or Hirschfield charges are provided where relevant. Results of similar calculations on ethylene, ethane, and planar trimethylchromium are included for comparison.

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Contrast, chromium(III) derivatives of non-$\pi$-donor ligands contain a bound base, such as (THF)Cr(Mes)$_3$ and (THF)Cr(C[CM$_2$]Ph)$_3$,\textsuperscript{29,30,50} except for Cr(CH[SiMe$_3$]$_2$)$_3$, which was reported not to react with pyridine.\textsuperscript{24,25}

Addition of pyridine addition to a pentane solution of (THF)Cr(C[Ad]Ar$_{Me}$)$_3$ resulted in rapid precipitation of (py)Cr(C[Ad]Ar$_{Me}$)$_3$ (\textbf{22-py}) as dark blue needles (Fig 2-3). Pyridine adduct \textbf{22-py} exhibits physical properties similar to those of the THF adduct \textbf{22-THF}, with a magnetic moment of 3.83 $\mu_B$ in the solid state and a single band in the visible spectrum ($\lambda$ 585 nm, $\varepsilon$ 1600 M$^{-1}$cm$^{-1}$, C$_6$H$_6$). The THF ligand was not displaced by an excess of PEt$_3$, $N,N'$-tetramethylethylenediamine (TMEDA), or tetrahydrothiophene (see Fig 2-3).

The Lewis acidity exhibited by the Cr(C[Ad]Ar$_{Me}$)$_3$ fragment (\textbf{22}) can be attributed to the lack of $\pi$-donation by the ligands, resulting in a low electron count on the chromium center. Chromium \textit{tris}-amide compounds have (in $C_{3v}$ symmetry) a formal electron count of 13e$^-$, with two of the available nitrogen lone-pair orbitals having the proper symmetry for interaction with low-lying empty metal orbitals. In
Figure 2-3: Reaction of (THF)Cr(C[Ad]ArMe)₃ with σ-donors, demonstrating the formation of the pyridine adduct and the lack of reactivity with triethyl phosphine, tetramethylethylenediamine, and tetrahydrothiophene.
contrast, the fragment 22 has a formal electron count of $9e^-$. Even so, the reactivity of 22-THF with Lewis bases evidently can be attenuated by steric factors: THF and pyridine are able to fit into the ‘pocket’ comprised of the aryl substituents, while TMEDA and PEt$_3$ do not displace THF.

2.2.3 Oxidation of (THF)Cr(C[Ad]Ar$_{Me}$)$_3$

We were interested in the oxidation behavior of the Cr(III) alkenyl fragment. Electrochemical measurements on (THF)Cr(C[Ad]Ar$_{Me}$)$_3$, performed by Dr. Luis Baraldo, demonstrated a reversible oxidation at 100 mV referenced to the ferrocene/ferrocnium couple. Furthermore, it has been found that in the case of complexes containing small alkenyl ligands, CrX$_3$ fragments disproportionate to stable Cr(IV) species.$^{50}$ Hence, it was of interest to determine the chemical stability of the Cr(IV) oxidation state. Initial experiments were focused on oxidation with I$_2$. Treatment of blue (THF)Cr(C[Ad]Ar$_{Me}$)$_3$ with 1/2 equiv of I$_2$ led to the immediate formation of a red solution. However, this solution turned green, and then reacquired its initial blue color. Monitoring this reaction by $^1$H NMR revealed the formation of a new peak, presumably corresponding to ICr(C[Ad]Ar$_{Me}$)$_3$, which is then replaced by the peaks diagnostic of (THF)Cr(C[Ad]Ar$_{Me}$)$_3$ when the solution color returned to blue. In addition, there was a significant amount of free ligand, and diene, Ar$_{Me}$[Ad]CC[Ad]Ar$_{Me}$ (23), in the final mixture. Diene 23 was independently synthesized and fully characterized during attempts to form niobium-tris-alkenyl compounds. A possible mechanism consistent with this observation is formation of 22-I, which subsequently ejects a ligand radical to form ICr(C[Ad]Ar$_{Me}$)$_2$. The latter could then disproportionate to form 22. It has previously been found that impure samples of ICr(N[R]Ar$_{Me}$)$_2$ disproportionate to form Cr(N[R]Ar$_{Me}$)$_3$.$^{78}$ This speculative mechanism is shown in Fig 2-4. Compound 22-THF was also oxidized with 1/2 equiv of PhSSPh to produce the new red species, (PhS)Cr(C[Ad]Ar$_{Me}$)$_3$ (22-SPh). Its crystals were grown from pentane, and the crystal structure shown in Fig 2-5 was obtained. This structure proved to be of poor quality. Nevertheless, it nicely illustrates the connectivity pattern in the
Figure 2-4: Possible mechanism explaining observations for the reaction of (THF)-Cr(C[Ad]ArMe)\(_3\) with 1/2 equiv I\(_2\). After addition of I\(_2\) a red solution is formed, however, this solution turns green, presumably signifying the loss of a ligand. The solution then regains spectroscopic properties of (THF)Cr(C[Ad]ArMe)\(_3\) and olefin and diene are present in the \(^1\)H NMR.
Table 2.2: Nitrosyl stretching frequency for a variety of four coordinate chromium nitrosyls

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu_{NO}$, cm$^{-1}$</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(ON)Cr(N['Pr]$_2$)(CH$_2$Ph)$_2$</td>
<td>1634</td>
<td>a</td>
</tr>
<tr>
<td>(ON)Cr(N['Pr]$_2$)$_3$</td>
<td>1641</td>
<td>b</td>
</tr>
<tr>
<td>(ON)Cr(C[Ad]ArMe)$_3$</td>
<td>1656</td>
<td>This work</td>
</tr>
<tr>
<td>(ON)Cr(N(C(D$_3$)$_2$CH$_3$)3,5-Me$_2$C$_6$H$_3$)$_3$</td>
<td>1662</td>
<td>c</td>
</tr>
<tr>
<td>(ON)Cr(N['Pr]$_2$)(CH$_2$SiMe$_3$)$_2$</td>
<td>1670</td>
<td>a</td>
</tr>
<tr>
<td>(ON)Cr(2,6-dimethylpipеридиde)$_3$</td>
<td>1673</td>
<td>b</td>
</tr>
<tr>
<td>(ON)Cr(CH[SiMe$_3$]$_2$)$_3$</td>
<td>1672</td>
<td>d</td>
</tr>
<tr>
<td>(ON)Cr(N(C(D$_3$)$_2$CH$_3$)3,5-C$_6$H$_3$(CF$_3$)$_2$)$_3$</td>
<td>1673</td>
<td>c</td>
</tr>
<tr>
<td>(ON)Cr(N['Pr]$_2$)(O$t$Bu)$_2$</td>
<td>1683</td>
<td>b</td>
</tr>
<tr>
<td>(ON)Cr(N[SiMe$_3$]$_2$)$_3$</td>
<td>1698</td>
<td>b</td>
</tr>
<tr>
<td>(ON)Cr(O$t$Bu)$_3$</td>
<td>1707</td>
<td>b</td>
</tr>
<tr>
<td>(ON)Cr(O'Pr)$_3$</td>
<td>1720</td>
<td>b</td>
</tr>
</tbody>
</table>


new product. Unfortunately, (PhS)Cr(C[Ad]ArMe)$_3$ was thermally unstable as well. A red pentane solution of 22-SPh kept at room temperature for several hours turned blue due to the formation of Cr(C[Ad]ArMe)$_3$.

2.2.4 Reactivity of (THF)Cr(C[Ad]Ar$_{Me}$)$_3$ with Nitric Oxide

The reactivity of (THF)Cr(C[Ad]Ar$_{Me}$)$_3$ with nitric oxide was explored in order to draw a comparison with known chromium-nitrosyl chemistry. A large number of (ON)CrX$_3$ compounds have been prepared. In a classic paper, Bradley correlated the nitrosyl stretching frequency of a series of compounds of general formula (ON)CrX$_3$ with the $\pi$ donor ability of the ligands.$^{79}$ The N-O stretching frequencies of these compounds, as well as those of other complexes synthesized since then, are summarized in Table 2.2. Addition of 1 equiv of NO gas to a cold ethereal solution of (THF)Cr(C[Ad]Ar$_{Me}$)$_3$ led to the formation of a brown solution. Spectral data suggested that the product is best formulated as (ON)Cr(C[Ad]Ar$_{Me}$)$_3$. Indeed, there is a single set of ligand resonances in the $^1$H NMR spectrum as well as a strong band in
Figure 2-5: Structural determination of (PhS)Cr(C[Ad]ArMe)_3. Both an ORTEP diagram (35% probability ellipsoids) and a ball and stick drawing derived from the crystal structure coordinates are shown. Selected Bond lengths (Å) and angles (°): Cr(1)-C(1) 2.028 (16), Cr(1)-C(2) 2.042 (14), Cr(1)-C(3) 2.010 (14), Cr(1)-S(1) 2.249 (5), Cr(1)-S(1)-C(4) 102.05 (49).
the infrared spectrum at 1656 cm\(^{-1}\). As can be seen from Table 2.2, the position of this band is at a much lower frequency than one would expect for a compound with ligands of limited \(\pi\)-donor ability. However, it is consistent with the infrared band for the transiently generated \((ON)Cr(CH[SiMe_3]_2)_3\). This data suggests the nitrosyl stretching frequencies for compounds ligated with hydrocarbons do not correlate with the \(\pi\) donor ability of the ligands, and may indicate a bent nitrosyl.

Unfortunately, \((ON)Cr(C[Ad]ArMe)_3\) proved to be thermally unstable. This observation is consistent with a report that the nitrosyl complex formed from \(Cr(CH-[SiMe_3]_2)_3\) was also unstable.\(^{25}\) During the course of this work, Legzdins prepared \((ON)Cr(N[Pr]_2)-(CH_2SiMe_3)_2\) and found this compound to be thermally robust. He postulated that one \(\pi\)-donor was necessary to donate electron density into the \(\pi^*\) orbital of the linear nitrosyl ligand.\(^{80,81}\)

Decomposition of the N-O linkage in molybdenum and tungsten cyclopentadienyl-containing compounds has been extensively studied by Legzdins.\(^{82-89}\) His group has found that the N-O linkage is cleaved through reduction,\(^{87}\) under certain transmetalation conditions,\(^{83,84}\) and thermolysis.\(^{88}\) In addition, it was found that the nitrosyl linkage could be hydrolyzed by water.\(^{86}\) Most of these decomposition reactions led to multiple products. Bridging nitrides and metal oxo species were among the commonly encountered products.

It was difficult to determine the decomposition pathway of \((ON)Cr(C[Ad]ArMe)_3\). After decomposition, all of the chromium containing products proved to be paramagnetic. The only resonances observable in the \(^1\)H NMR spectrum were those attributable to olefin 1 and diene 23. Formation of the diene could occur via reductive elimination of two ligands, or loss of a ligand radical followed by subsequent coupling with a second ligand radical. The decomposition of \((ON)Cr(C[Ad]ArMe)_3\) could be followed by monitoring the depletion of the \((ON)Cr(C[Ad]ArMe)_3\) resonances in the \(^1\)H NMR spectrum, or the decrease in the intensity of the nitrosyl stretching band in the infrared spectrum. Qualitatively, it was found that the decomposition was more rapid in solvents that are better Lewis bases, such as THF or pyridine.

To further understand the decomposition of \((ON)Cr(C[Ad]ArMe)_3\), one decom-
Figure 2-6: ORTEP drawing of the molecule (25) crystallized from the decomposition of \((\text{ON})\text{Cr(C[Ad]ArMe})_3\). (35% probability ellipsoids). Selected distances (Å) and angles (°): Cr(1)-O(1), 1.810(4); Cr(1)-O(2), 1.806(4); Cr(1)-N(1), 1.843(5); Cr(1)-C(3), 2.041(6); Cr(1)-Cr(2), 2.648(1); Cr(2)-O(1), 1.806; Cr(2)-O(2), 1.810(4); Cr(2)-N(2), 1.837(5); Cr(2)-C(6), 2.035(6); Cr(1)-O(1)-Cr(2), 94.17(17); Cr(1)-O(2)-Cr(2), 94.18(18)

position product (25) was crystallographically characterized. Brown crystals were obtained upon allowing a hydrocarbon solution of \((\text{ON})\text{Cr(C[Ad]ArMe})_3\) to stand at room temperature over the course of weeks. These crystals were analyzed by X-ray diffraction and the structure obtained is shown in Fig 2-6. In this structure the nitrosyl fragment has been cleaved to produce an oxo moiety, and two of the alkenyl groups have migrated to the nitrogen atom to form an amide ligand. The \(\text{Cr(\mu-O_2})\text{Cr core has previously been observed in } (\mu-\text{O})_2[(\text{Cp}^*\text{CrO})]_2\). The chromium-bridging oxygen bond distances found in \((\mu-\text{O})_2[(\text{Cp}^*\text{CrO})]_2\) (1.817(4), 1.813(4) Å) are very
similar to those found in 25. The Cr-N bond lengths are typical for Cr-amide bonds.91

One possible mechanism for the formation of 25 would be insertion of the nitric oxide into the Cr-C bond, followed by N-O bond cleavage. There is literature precedent for the addition of NO to metal-carbon bonds.92,93 Very recently, Legzdins has reported that the attempted synthesis of (ON)Cr(N[Pr]2)(o-tolyl)2 led instead to the crystallographically characterized OCr(N[Pr]2)(No-tolyl) (o-tolyl).82 The proposed mechanism was insertion of the nitric oxide into the carbon-aryl bond, followed by cleavage of the NO bond. Unfortunately, in our case it was not feasible to identify any 1H NMR signals that could be attributed to 25, which made further characterization difficult. In order to ascertain that the obtained structure did indeed represent a significant portion of the bulk crystals, the remaining crystals were subjected to an aqueous/organic work-up, and the organic products were characterized by GC-MS. It was expected that the amide ligand would hydrolyze to the ketone, which was detected in the GC-MS along with olefin.

2.2.5 Reactivity of (THF)Cr(C[Ad]ArMe)3 with Other Small Molecules

The reactivity of (THF)Cr(C[Ad]ArMe)3 with a large variety of small molecules, including MesN3, CO, tBuNC, MeCN, ethylene and dioxygen was examined. While most reactions were rapid, it appeared that multiple paramagnetic products were formed. These products were difficult to characterize because they were paramagnetic and did not show any broadened signals in the paramagnetic regions of the 1H NMR spectrum. Evidence for small molecule insertion into the Cr-C bond was obtained from the analysis of organic products. For example, in the reaction of 22-THF with CO, ArMe[Ad]C-C(O)-C[Ad]ArMe, was isolated and characterized from the reaction mixture. In addition, it was found that 22-THF did not react with N2O or P4.
2.3 Conclusions

Reported in this section is the synthesis and crystallographic characterization of the "masked" three coordinate compound, (THF)Cr(C[Ad]ArMe)₃. Reactions with nitric oxide and oxidizing agents led to the formation of thermally unstable compounds. The diene 23 was present in all of the reaction mixtures. A ligand radical, once ejected from the metal complex, can either abstract H⁺ from solvent or couple with a second radical. An alternative pathway for the formation of the diene is the reductive elimination of two ligands. Furthermore, reactions with small molecules were complicated by insertion reactions into the Cr-C bond. Therefore, it can be concluded that in order to stabilize low coordinate compounds in high oxidation states, good π donors are necessary. Therefore, the alkenyl fragment was incorporated into a thioalkenyl ligand, the chemistry of which is the subject of the following chapter.

2.4 Experimental Procedure

2.4.1 General Procedures

Standard glove box and Schlenk techniques for the manipulation of air sensitive materials were used. Solvents were dried by distillation from the appropriate drying agents, or by drying with a column of alumina, as first developed by Grubbs.¹ H NMR spectra were obtained in C₆D₆ and referenced to residual C₆D₅H resonance at 7.15 ppm on Varian XL-300, Varian Unity-300 instruments. Infrared spectra were recorded on a Bio-Rad 135 Series FTIR spectrometer. UV-Vis spectra were obtained on a Hewlett-Packard 8453 Diode-array spectrometer. The elemental analyses (C,H,N) were obtained by Microlytics, Deerfield, MA. SQUID magnetic measurements were performed by Steve Klei on a Quantum Design SQuID magnetometer using MPMSR2 software. The data were measured at 1000 G field strength. The samples were loaded in #4 gelatin capsules and suspended in plastic straws. The sample was secured in the gel cap with a square of parafilm. The measurements were done from 5 to 300 K.
with data points taken every 5 K. The sample was centered and corrected for diamagnetism using Pascal’s constants and background from similar runs without sample. The effective magnetic moment, \( \mu_{\text{eff}} \), was determined by fitting the data to the Curie-Weiss Law. X-Ray diffraction data was collected on a Siemens Platform goniometer with a Charge Coupled Device (CCD) detector, and structures were typically solved by direct methods. Solution magnetic susceptibilities were determined by \(^1\)H NMR at 300 MHz using the method of Evans.\(^ {94,95}\)

### 2.4.2 Preparation of (THF)Cr(C[Ad]Ar\text{Me})\(_3\) (22-THF)

Vinyl Grignard reagent 10 (12.9 g, 26 mmol, 3.0 equiv) and anhydrous CrCl\(_3\) (1.7 g, 11 mmol, 1.25 equiv) were slurried in diethyl ether (500 mL). The suspension was allowed to stir for 48 hours. Dioxane (10 mL) was added and the reaction mixture was allowed to stir for two additional hours, and then the solid was allowed to settle. The mixture was filtered through celite, washed with diethyl ether (40 mL) and concentrated to about 100 mL. After standing for 2 hours at RT, blue crystals of 22-THF (5.1 g, 5.8 mmol, 68\%) were collected and dried under vacuum. \( \mu_{\text{eff}} \) (SQuID)=3.68 \( \mu_B \). UV-Vis spectrum (C\(_6\)H\(_6\)) \( \lambda \) 590 nm (\( \varepsilon \) 1300 M\(^{-1}\)cm\(^{-1}\)). Anal. Calcd. for C\(_{61}\)H\(_{77}\)CrO: C, 83.42; H, 8.84. Found: C, 83.33 H, 8.99.

### 2.4.3 Preparation of (py)Cr(C[Ad]Ar\text{Me})\(_3\) (22-py)

Chromium compound 22-THF (183.3 mg, 0.209 mmol, 1 equiv) was dissolved in pentane (15 mL). A solution of pyridine (104 mg, 1.31 mmol, 6.3 equiv) in pentane (2 mL) was added dropwise and the reaction vial was allowed to stand for 2 h. Filtration of the reaction mixture afforded 22-py (150 mg, 0.169 mmol, 81\%) as analytically pure dark blue needles. \( \mu_{\text{eff}} \) (SQuID)=3.83 \( \mu_B \). Anal. Calcd. for C\(_{62}\)H\(_{74}\)CrN: C, 84.12; H, 8.43; N, 1.58. Found: C, 83.81; H, 8.30; N, 1.30.
2.4.4 Treatment of \(\text{THF})\text{Cr(}\text{C[Ad]Ar}_{\text{Me}}\text{)}_3\) (22-THF) with Neutral Ligands

In a typical experiment, a stock solution of 22-THF (118.8 mg, 0.0135 M) and ferrocene (144 mg, 0.077 M) was prepared in 10 mL of \(\text{C}_6\text{D}_6\). A portion of this solution (0.6 mL) was transferred to the NMR tube, and the appropriate amount of reagent was added via microliter syringe: pyridine (2 equiv): quantitative THF release, TMEDA (1.0 equiv or 5.0 equiv): no THF release, Tetrahydrothiophene: (1.0 equiv or 5.0 equiv): no THF release, triethyl phsosphine: (1.0 equiv or 5.0 equiv) no THF release.

2.4.5 Preparation of \(\text{PhS})\text{Cr(}\text{C[Ad]Ar}_{\text{Me}}\text{)}_3\)

Chromium compound 22-THF (56 mg, 0.064 mmol, 1 equiv) was dissolved in \(\text{C}_6\text{H}_6\) and a solution of PhSSPh (7 mg, 0.5 equiv) in \(\text{C}_6\text{H}_6\) was added. The reaction mixture turned green and was allowed to stir for 30 min. The solvent was removed, and the residue was redissolved in pentane, and stored at \(-35^\circ\text{C}\) resulting in the formation of very dark red crystals. These crystals, dissolved in \(\text{C}_6\text{D}_6\) gave a diagnostic peak in the \(^1\text{H}\text{ NMR at 10 ppm.}\) The crystals were used for a single crystal X-Ray diffraction study. Upon allowing the mother liquor to stir for 5 hr in pentane, the solution turned blue.

2.4.6 Attempted Preparation of \(\text{ON})\text{Cr(}\text{C[Ad]Ar}_{\text{Me}}\text{)}_3\)

Chromium compound 22-THF (86 mg, 0.098 mmol, 1.03 equiv) was dissolved in pentane (10 mL) and cooled to \(-78^\circ\text{C}\) in a Schlenk flask. Nitric oxide gas (2.31 mL, 0.095 mmol, 1 equiv) was added via syringe and the flask was evacuated after allowing the solution to stir for 1 min. \(^1\text{H NMR (C}_6\text{D}_6\) δ 1.67-2.4 (m, 36 H, ad-H), 2.16 (s, 18H, aryl me), 3.95 (s, 3H, ad H), 6.28 (s, 6H, o-H), 6.74 (s, 3H, p-H) IR (THF): 1656 cm\(^{-1}\) (very strong, NO), 1596 cm\(^{-1}\).
2.4.7 Preparation of $\text{Ar}_\text{Me}[\text{Ad}]\text{C-C[Ad]}\text{Ar}_\text{Me}$ (23)

Grignard reagent $10$ (430 mg, 0.86 mmol, 1.8 equiv) was slurried in pentane (10 mL) and $\text{NbCl}_4(\text{THF})_2$ (163 mg, 0.47 mmol, 1.0 equiv) was added as a solid. The reaction was allowed to stir overnight, followed by the addition of $\text{OEt}_2$ (20 mL) and dioxane (4 mL). The reaction was allowed to stir an additional 30 min, and then filtered through Celite. The mother liquor was concentrated, extracted into toluene (10 mL), filtered, and concentrated. The material was then extracted into pentane (10 mL), followed by $\text{OEt}_2$ (10 mL). The volume of the ethereal fraction was reduced to 4 mL, and the solution was allowed to stand at $-35 \, ^\circ\text{C}$. Colorless crystals of 23 were collected. $^1\text{H}$ NMR ($\text{C}_6\text{D}_6$): $\delta 1.6-2.0$ (m, 24H, ad H), $2.16$ (s, 12H, aryl me), $2.85$ (s, 2H, ad H), $3.49$ (s, 2H, ad H), $6.73$ (s, 2H, $p$-H), $6.90$ (s, 1H, $o$-H). GC/MS:502.

2.4.8 Crystal Structure Determinations

$(\text{THF})\text{Cr}([\text{Ad}]\text{Ar}_\text{Me})_3$ (22-THF)

$\text{C}_{61}\text{H}_{77}\text{CrO}$, $M_W = 878.23$, triclinic $P\overline{1}$, $a = 11.3534$ (10) Å, $b = 11.6451$ (10) Å, $c = 20.165$ (2) Å, $\alpha = 76.556(2)$ °, $\beta = 77.9370$ °, $\gamma = 73.5660$ (10) °, $V = 2457.5$ (4) Å$^3$, $Z = 2$, $D_{\text{calc}} = 1.187$ Mg/m$^3$, absorption coefficient .274 mm$^{-1}$, $F(000) = 950$, number of reflections collected 7262, number of independent reflections 4531, GOF = 1.234, $R = .0762$, $wR_2 = .1372$.

$(\text{PhS})\text{Cr}([\text{Ad}]\text{Ar}_\text{Me})_3$ (22-SPh)

$\text{C}_{63}\text{H}_{74}\text{CrS}$, $M_W = 883.28$, monoclinic, $P2/c$, $a = 21.2748(19)$ Å, $b = 11.9058(11)$ Å, $c = 23.1145(20)$ Å, $\alpha = 90$ °, $\beta = 106.802$ (2) °, $\gamma = 90$ °, $V = 5604.81$ Å$^3$, $Z = 4$, $D_{\text{calc}} = 1.047$ Mg/m$^3$, $F(000) = 2160$, GOF = 1.139, $R = .1756$, $wR_2 = .5240$. 

70
\((\mu-O)_2[Cr(N(C[Ad]ArMe)_2)(C[Ad]ArMe)]_2\) (25)

\(C_{123}H_{103}Cr_2N_2O_2, \ M_W = 1813.71, \) triclinic, \(P\bar{1}, \ a = 12.9542(20) \ \text{Å}, \ b = 15.0252 \ (29) \ \text{Å}, \ c = 27.7029 (85) \ \text{Å}, \ \alpha = 84.652(14) ^\circ, \ \beta = 84.261 \ (30) ^\circ, \ \gamma = 78.084 \ (13) ^\circ, \ V = 5234.84 \ (4) \ \text{Å}^3, \ Z = 2, \ D_{\text{calc}} = 1.151 \ \text{Mg/m}^3, \ F(000) = 1970.0, \ \text{GOF} = 1.294, \ R = .0982, \ wR_2 = .2543.\)
Chapter 3

Studies Directed Toward the Isolation of a Molybdenum-
\textit{tris}-Thiolate Fragment

3.1 Introduction

The enzyme nitrogenase is competent to produce ammonia at room temperature and pressure from protons and electrons, whereas the commercial Haber-Bosch process requires temperatures of 400 °C and pressures of 250 atmospheres to produce ammonia from dinitrogen and hydrogen. Hence, great attention has been devoted to the developing a greater understanding of the enzyme’s function. \superscript{96} The crystal structure of nitrogenase, reported in 1992, reveals two inorganic cofactors, a molybdenum-iron (FeMoco) cluster (See Fig 3-1) which is believed to serve as the active site for the reduction of dinitrogen, and an iron-sulfur cluster (P cluster) which is believed to be important for electron transfer within the protein. \superscript{97-99} More recently a higher resolution (1.6 Å) structure has been reported, and the authors compared the bonding in
different oxidation states of the cluster. In some forms of nitrogenase the molybdenum in FeMoco is replaced with vanadium or iron. FeMoco has an empirical formula MoFe$_7$S$_9$, and features a single molybdenum atom ligated by three inorganic bridging sulfides. A molecule of homocitrate, and a protein histidine residue complete the coordination sphere of the molybdenum atom. The MoFe cluster was first isolated from the protein matrix in 1977, however, the isolated cluster is not catalytically competent to reduce dinitrogen, and has not been crystallographically characterized. Furthermore, the mechanism of dinitrogen reduction at FeMoco has been the subject of lively debate.

Inorganic chemists have been involved in the study of nitrogen fixation, both through the design of metal complexes for dinitrogen activation, and the synthesis of model compounds for FeMoco. Dinitrogen activation has been the subject of much study, and is the subject of many reviews. Notable developments include the cleavage of dinitrogen by Mo(N[R]Ar$_{Me}$)$_3$; dinitrogen cleavage has more recently been reported by Floriani for a niobium-calixarene system, and by Cloke for a vanadium bis-amido system. Furthermore, Fryzuk has been able to crystallize a zirconium compound containing both coordinated dinitrogen and dihydrogen.

Sulfur ligation has long been important in the study of dinitrogen activation. In an early series of papers, Chatt and Dilworth made extensive use of molybdenum-tris-dithiocarbamate compounds in order to study dinitrogen functionalization in a
While most groups no longer believe that the molybdenum center is involved in initial dinitrogen binding and reduction, some still hold that the dinitrogen reduction chemistry is completely centered at molybdenum, with the rest of the Fe-S cluster simply serving as the “perfect” ligand for molybdenum. Very recent calculations have considered the possibility of dinitrogen binding to molybdenum. Detailed spectroscopic measurements seem to indicate that inhibitory CO binding takes place at one of the iron atoms, however, others working with the isolated cofactor find the binding location inconclusive.

There have been extensive studies, in particular from the Holm and Coucouvanis groups, devoted to synthesis of model complexes for FeMoco. The Holm group has prepared a cluster \([(\text{Meida})\text{MoFe}_3\text{S}_4\text{Cl}_2](\mu_2-\text{S})(\text{Fe}_4\text{S}_4\text{Cl}_3)^{4-}\) (Meida=N-methylimidoacetate(2-)) that mimics the composition (MoFe$_7$S$_9$) of FeMoco. They have also prepared a series of symmetric clusters (ie Mo$_2$Fe$_6$S$_9$) as structural analogues, some of which contain aryl oxide and aryl thiolate ligands instead of chloride ligands. The Coucouvanis group has prepared clusters containing MoFe$_3$S$_4$ frameworks that are able to reduce hydrazine to ammonia and dimethylidiazene to methylamine but are unable to reduce dinitrogen. The observation that the molybdenum center of these model complexes is involved in the reduction of hydrazine, presumably an intermediate in the dinitrogen reduction pathway, has led to their proposed mechanism in which the dinitrogen molecule initially binds in the iron region of the iron-sulfur cluster, where it is reduced to a hydrazine molecule. The hydrazine molecule subsequently migrates to the molybdenum center where it is reduced to two molecules of ammonia. Supporting this mechanistic proposal is the observation of significant differences in Fe-Fe distances in model MoFe$_3$S$_3$ complexes differing by only two valence electrons, suggesting the metal-metal or the metal-sulfur bonds may contain the electrons needed for initial dinitrogen reduction. Calculations by Dance suggest that the iron region is indeed the site of N$_2$ binding.

Given the observation that three coordinate molybdenum will cleave dinitrogen, combined with the presence of molybdenum tris-sulfide in the active site of nitrogenase, we wished to embark upon the synthesis of a three coordinate molybdenum
tris-thiolate fragment. While model complexes for FeMoco in nitrogenase are plentiful, there are no examples of three coordinate molybdenum (III) thiolate complexes. Molybdenum dinitrogen complexes supported by thiolate ligands are rare, one example is a bis-dinitrogen molybdenum (0) complex with a macrocyclic thioether ligand providing four additional sulfur donor atoms. The use of thiolate ligands has been very limited in three coordinate chemistry, the only examples being iron-tris thiolates. We wished to consider this class of molecules in the context of the effect of ligand donor set on dinitrogen scission. Theoretical calculations suggested that good π donors are important for dinitrogen scission, although thiolates, which are strong π-donors have not been explicitly considered. Nitrosyl stretching frequencies provide some measure of the π-donor ability of ligands. A comparison of the nitrosyl stretching frequency of two related compounds, [Mo(O'Pr)₃NO]₂ and [Mo(S'Ad)₃NO]₂ reveals them to be very similar, 1640 cm⁻¹ and 1642 cm⁻¹, respectively. Furthermore, it is expected that the nitride would be easier to activate in a nitrido-molybdenum-tris-thiolate molecule than in the nitrido-molybdenum-tris-amido complexes due to the low pKₐ values for thiols. In considering the pKₐ values of protonated ligands in DMSO, the pKₐ values for thiophenol, phenol, and diphenylamine are 10.3, 18.0 and 24.95, respectively. Notable in sulfur ligation is the ability to protically remove a nitride while leaving the ligands intact. Treatment of N≡Mo(S₂CNEt₂)₃ with H₂NOSO₃H and NaBF₄ in methanol led to the formation of a formal Mo(S₂CNEt₂)₃³⁺ fragment, which coordinates two molecules of N≡Mo-(S₂CNEt₂)₃ as additional ligands. Theo Agapie and Aaron Odom examined the chemistry of the transient “Mo(S₁Ad)₃” fragment via nitrogen atom transfer from N≡Mo(S₁Ad)₃ to Mo(N[₄Bu]Ph)₃. They were able to form (ON)Mo(S₁Ad)₃ and Mo₂(S₁Ad)₆ from the addition of NO or benzonitrile to (₁AdS)₃Mo(μ-N)Mo(N[Bu]-Ph)₃. However, no evidence of dinitrogen chemistry was detected.

In order to more carefully examine the chemistry of molybdenum-tris-thiolates, we wished to design sterically encumbering ligands to facilitate the isolation of a molybdenum-tris-thiolate fragment. Popular in the chemistry of metal thiolates are
Figure 3-2: Schematic illustration of the placement of steric bulk in the 2,6 aryl phenyl thiolate ligands and the thioalkenyl ligands discussed in this chapter.

2,6-diaryl aryl thiolates.\textsuperscript{139,140} However, the close proximity of the substituent aryl group allows for the formation of metal-$\eta^6$-aryl interactions, which have been documented in a number of electron deficient systems.\textsuperscript{141-144} Power has recently reported the crystal structure of a molybdenum tris-thiolate fragment using 2,6-dimesityl phenyl thiolate. However, a strong interaction between the molybdenum and the mesityl ring shuts down the reactivity of this compound, and it is reported to be unreactive towards N\textsubscript{2} and N\textsubscript{2}O.\textsuperscript{145} Therefore it was important to design a sterically encumbering ligand in which the steric bulk is directed away from, rather than toward the metal center. The ligand used in this chapter is a thioalkenyl ligand, the synthesis of which has been documented in Chapter 1. Fig 3-2 schematically illustrates the difference in placement of steric bulk between the 2,6 diaryl thiolate ligands and the alkenyl thiolate ligands. In this chapter, the synthesis of several nitrido-molybdenum-tris-thiolates is discussed, along with the nitrogen atom transfer chemistry of these species. Alternative methods of the installation of the thiolate ligand onto molybdenum, including reaction of the magnesium thiolate with MoCl\textsubscript{3}(THF)\textsubscript{3} and reactions of the free thiols with Mo(NMe\textsubscript{2})\textsubscript{4} are also discussed.
3.2 Results and Discussion

3.2.1 Synthesis of Molybdenum tris-thiolate Nitrides

A starting point for the study of the chemistry of molybdenum thiolate compounds is the synthesis of molybdenum nitrides. These were appealing initial targets in that they are they diamagnetic compounds that are the ideal products of dinitrogen cleavage reactions. An initial attempt to treat $\text{N=MoCl}_3$ with the magnesium thiolate, $(\text{THF})_2\text{Mg}(\text{SC}[\text{Ad}][\text{ArMe}])\text{(Br)}$ (11), led to the isolation of large amounts of disulfide $\text{ArMe}[\text{Ad}]\text{CSSC}[\text{Ad}][\text{ArMe}]$, and only small amounts of the desired $\text{N=Mo} (\text{SC}[\text{Ad}][\text{ArMe}])_3$ (26). However, titanium transfer reagents proved to be a facile method of transferring a thiolate unit to molybdenum. Treatment of $\text{N=Mo} (\text{O}^\text{Bu})_3$ with 3 equivalents of $\text{Ti} (\text{SC}[\text{Ad}][\text{ArMe}]) (\text{O}^\text{Pr})_3$ (18) led to clean formation of 26 (Fig 3-3). While $^1\text{H}$ NMR spectroscopy indicates that conversion is complete, the yield is only moderate (53%) due to the need to separate the desired molybdenum nitrides from three equivalents of titanium byproducts. This methodology, which had been used previously for the synthesis of $\text{N=Mo}(\text{S}^1\text{Ad})_3$, is quite general and was also used to prepare $\text{N=Mo} (\text{SC}[\text{Ad}][\text{ArBu}]_3$ (27), $\text{N=Mo} (\text{SC}[\text{Ad}][\text{ArPh}]_3$ (28), and $\text{N=Mo} (\text{SC}[\text{Ad}][\text{Ar(Bu)}][\text{Ph}])_3$ (29). The molybdenum nitrides were separated from the titanium alkoxide byproducts by precipitation with $\text{O} (\text{SiMe}_3)_2$.

A single crystal of 26 was grown from pentane and interrogated by single crystal
Figure 3-4: ORTEP diagram of nitride 26. The ellipsoids are at the 35 % probability level. Selected bond distances (Å) and angles (°): Mo(1)-N(1) 1.62(2), Mo(1)-S(1) 2.323 (5), Mo(1)-S(2) 2.319 (5), Mo(1)-S(3) 2.325 (5), N(1)-Mo(1)-S(1) 103.1 (5), N(1)-Mo(1)-S(2) 106.4 (6), N(1)-Mo(1)-S(3) 98.5(5), Mo(1)-S(1)-C(1) 106.8 (5), Mo(1)-S(2)-C(2) 110.8(6), Mo(1)-S(3)-C(3) 99.9(5).

X-Ray diffraction. The ORTEP diagram is shown in Fig 3-4. The structure does confirm the monomeric nature of the nitride and provide a sense of the orientation and steric constraints of the ligand. The sulfur ligands form a much more open pocket, and hence provide less steric protection near the metal center than the -N[R]ArMe ligands. Not only is sulfur a larger atom than nitrogen, resulting in longer metal-ligand bond distances, but the sulfur atom only has one substituent, whereas an amide ligand has two substituents on nitrogen. Space filling models comparing the steric protection provided by three thioalkenyl ligands to the steric protection provided by three anilide ligands are shown in Fig 3-5.

A notable feature of the nitrides is the dramatic color changes they undergo depending on temperature and solvent. Nitride 26 is generally isolated as a yellow compound, however, cooling pentane and diethyl ether solutions to -35 °C leads to
Figure 3-5: Space filling models, taken from X-Ray structure determinations of molybdenum nitrides, comparing the steric bulk provided by the -SC[Ad]ArMe and -N[R]Ph ligands, respectively. The view shown is looking down the nitride molybdenum vector. The nitride nitrogen has been removed in both models for clarity.
a bright emerald color. However, benzene and toluene solutions remain yellow upon cooling to $-35 \, ^\circ\mathrm{C}$. The color changes for 3,5-diphenyl derivative 28 are even more dramatic; it is isolated as a blue powder from $\text{O(SiMe}_3)_2$. Furthermore, 29 remains green even at RT in $\text{C}_6\text{D}_6$. Nitride 28 was examined by UV-Vis spectroscopy. A concentrated THF solution displays an absorbance at 680 nm, however, this band disappears much more rapidly upon dilution than expected by Beer's law. In diethyl ether, in which very pure samples of the nitride were only sparingly soluble, there was a band at 655 nm in which the extinction coefficient greatly increased upon lowering the temperature from 25 °C to 10 °C. In order to try to understand these changes, $^1\text{H}$ NMR spectra of 28 were obtained in toluene-$d_8$ over the temperature range 25 °C to $-50 \, ^\circ\mathrm{C}$, a temperature range in which the color of the solution in the NMR tube changed from yellow to green. While the signals began to broaden upon cooling, no new signals were observed. The nitrides are $d^0$ compounds, hence, there is no possibility of d-d transitions in these compounds.

The Hopkins group has studied molybdenum and tungsten alkylidyines and nitrides as nonlinear optical materials.\textsuperscript{146-148} It is noted that in nitrido tungsten tris-alkoxides, tert-butoxide containing materials are white, whereas 2,6-bis(isopropyl) phenoxide containing materials are red.\textsuperscript{149} This difference is most likely related to the W-N bonding: the butoxide compounds form linear polymers,\textsuperscript{150} and the phenoxide complex forms a W-N head to tail dimer.\textsuperscript{148} However, it seems unlikely that the color changes in the nitrido molybdenum thiolates synthesized in this chapter are due to the formation of Mo-N aggregates. The 3,5-dimethyl derivative is a monomer in the solid state, and the most striking color changes are observed for the larger terphenyl derivatives. The color is therefore assumed to be the result of ligand-metal charge transfer bands. The monomeric nature of nitride 26 is most likely due to steric effects since the metal center is still Lewis acidic. Addition of pyridine to an ethereal solution of 26 leads to the precipitation of $\text{N=Mo(SC[Ad]Ar}_\text{Me})_3\text{(py)}$. Examination of the $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of this compound demonstrates that the resonances for pyridine are shifted from those expected for pyridine in $\text{C}_6\text{D}_6$. 

3.2.2 Reaction of Molybdenum Nitrides with Mo(N[R]ArMe)₃

With the nitrides in hand, it was of interest to determine if the nitrido functionality could be transferred from 26 to Mo(N[R]ArMe)₃. Treatment of 26 with one equiv of Mo(N[R]ArMe)₃ led to the appearance of N≡Mo(N[R]ArMe)₃, however, there was also unreacted Mo(N[R]ArMe)₃ present. A green compound could be isolated from the reaction by precipitation from a pentane solution. Initial experiments were focused on quenching the isolated compound with mesityl azide, which led to the formation of 26 suggesting that the “Mo(SC[Ad]ArMe)₃” fragment was present in the mixture in some form. However, when the compound was quenched with NO, two compounds were formed. One of the compounds was assumed to be (ON)Mo(SC[Ad]ArMe)₃ based on a nitrosyl stretching frequency in the infrared (in THF solution) of 1676 cm⁻¹. The nitrosyl stretching frequency in this compound is higher, as expected, than the nitrosyl stretching frequency in (ON)Mo(N[R]ArMe)₃ (1604 cm⁻¹). The second compound was 26, suggesting that the green compound was not (ArMe[R]N)₃Mo(μ-N)Mo(SC[Ad]ArMe)₃, which would have been analogous to the (¹AdS)₃Mo(μ-N)Mo-(N[ıtBu]Ph)₃ synthesized by Aaron Odom, but rather (μ-N)[Mo(SC[Ad]ArMe)₃]₂ (Fig 3-6). Two different intermediates can be envisioned in this reaction sequence, either a free “Mo(SC[Ad]ArMe)₃” fragment or a bridging nitride (ArMe[R]N)₃Mo(μ-N)Mo(SC[Ad]ArMe)₃. However, in either case, it appears that reaction of the intermediate with an additional equivalent of nitride 26 is more rapid than formation of the intermediate.

3.2.3 Reaction of Magnesium Thiolates with MoCl₃(THF)₃

In order to isolate “Mo(SC[Ad]ArMe)₃” without the possibility of bridging nitride formation, we turned our attention to salt metathesis reactions with MoCl₃(THF)₃. Initial experiments focused on the reaction of (THF)₂Mg(SC[Ad]ArMe)(Br) (11) with MoCl₃(THF)₃ in diethyl ether. While no diamagnetic products were observed after filtration and concentration, upon allowing solutions to stand at −35 °C a diamagnetic red product crystallized. According to the ¹H NMR chemical shifts, this diamagnetic
Figure 3-6: Nitrogen atom transfer from \( \text{N} \equiv \text{Mo(SC}[\text{Ad}]\text{ArMe})_3 \) to \( \text{Mo(N}[\text{R}]\text{ArMe})_3 \).

The product did not correspond to free thiol or disulfide decomposition products, or the previously characterized 26. Elemental analysis revealed that the product had the empirical composition “\( \text{Mo(SC}[\text{Ad}]\text{ArMe})_3 \)” . The analysis, combined with the diamagnetic nature of the product reveals that the ligand was not large enough to prevent triple bond formation and the isolated product is \( \text{(ArMe}[\text{AdCS)3Mo ≡ Mo(SC}[\text{Ad]}\text{ArMe})_3} \). Several different methods have been reported for the preparation of molybdenum-molybdenum triple bonds supported by thiolate ligands. These methods include treatment of \( \text{Mo}_2(\text{StBu})_2(\text{NMe})_4 \) with \( \text{HS-(2,4,6-Me}_3\text{C}_6\text{H}_2}) \), \( 15^1 \) treatment of \( \text{MoCl}_4 \) with the sodium salt of 2,4,6-triisopropyl thiophenol in dimethoxyethane, \( 15^2 \) and treatment of \( \text{LiS}^1\text{Ad} \) with \( \text{Mo}_2\text{Cl}_6(\text{DME})_2 \). \( 5^1 \)

The product formed upon reaction of a thiolate source with \( \text{MoCl}_3(\text{THF})_3 \) was found to depend on reaction conditions. Reaction of \( \text{MoCl}_3(\text{THF})_3 \) in \( \text{OEt}_2 \) with \( (\text{THF})_2\text{Mg(SC}[\text{Ad}]\text{ArMe})_2 \) \( (12) \) gave clean formation of dimer 30. However, if the reaction was done in a THF/dioxane mixture, and pyridine was added after filtration to remove Mg salts, a paramagnetic compound, \( (\text{py})\text{Mo(SC}[\text{Ad}]\text{ArMe})_3 \) \( (31) \) was isolated, suggesting that a coordinated solvent molecule will prevent formation of the metal-metal triple bond (Fig 3-7). In order to control for the possibility that Mg
salts have a role in the formation of 31, MoCl₃(THF)₃ was reacted with the titanium transfer reagent 18 in THF, followed by addition of pyridine, which also leads to the formation of 31. Compound 31 is only sparingly soluble in pentane, allowing for easy separation from the titanium byproducts. Tin reagents have previously been used to transfer thiolate ligands to iron chlorides.¹⁵³

Due to the propensity of 3,5 dimethyl substituted alkenyl thiolate ligands to form molybdenum-molybdenum triple bonds, it was of interest to examine the effects of other aryl groups. Disappointingly, reaction of (THF)₂Mg(SC[Ad]ArBu)₂ (13) with MoCl₃(THF)₃ in diethyl ether led to the immediate formation of the molybdenum-molybdenum triply bonded compound. However, solvent choice is also very important for this reaction, since conducting the reaction in THF solution followed by addition of pyridine led to a yellow compound which was only sparingly soluble, but displayed broad resonances in the ¹H NMR, suggesting that a paramagnetic material had been obtained, possibly a mononuclear pyridine adduct analogous to 31.

The larger terphenyl ligands were designed to provide additional steric protection.
to prevent the formation of metal-metal triple bonds. Initial attempts at salt metathesis reactions between MoCl₅(THF)₃ and (THF)₂Mg(SC[Ad]ArPh)₂ led to a product that was too insoluble to separate from the magnesium salts. Titanium transfer reagents proved to be very useful in this regard. Treatment of three equivalents of Ti(SC[Ad]ArPh)₃ (20) with MoCl₃(THF)₃ in THF led to the formation of a bright red solution. The molybdenum compound was insoluble in OEt₂, therefore the titanium byproducts were easily removed by washing with OEt₂. However, the low solubility of this compound, even in THF after purification, made characterization difficult. It was possible to generate and use this material in situ. Treatment of a solution of “Mo(SC[Ad]ArPh)₃” with N≡Cr(OᵗBu)₃ led to the formation of N≡Mo(SC[Ad]ArPh)₃ (28).

### 3.2.4 Treatment of Mo(NMe₂)₄ with Free Thiols

We were interested in the synthesis of compounds of the type XMo(SC[Ad]Ar)₃ where X is a halide ligand. The halide would then be available for subsequent salt metathesis reactions, an ideal nucleophile being a dinitrogen anion. There are a couple of literature examples of molybdenum tetrathiolate complexes, including Mo(SC₆H₂-2,4,6 iPr)₄ prepared by the Schrock group,¹⁵₄ and Mo(SᵗBu)₄ prepared by Otsuka.¹⁵₅ A common method for the installation of thiolate ligands is thiolysis of dimethyl amide ligands. Hence, Mo(NMe₂)₄ was treated with a pentane solution of HSC[Ad]ArBu (16) which led to the formation of Mo(NMe₂)(SC[Ad]ArBu)₃ as a dark purple-red compound in moderate yield. This compound is paramagnetic with a $\mu_{\text{eff}}$ of 2.31 $\mu_B$. While this value is low for two unpaired electrons, Mo(IV) compounds with dimethyl amide ligands have been known to undergo a high spin-low spin equilibrium.⁴⁸

### 3.3 Conclusion

Herein the molybdenum chemistry of a new type of thiolate ligand, a thioalkenyl ligand, has been explored. With this ligand, we have been able to synthesize several
molybdenum thiolate species. The target molecule “Mo(SC[Ad]ArMe)3” has been generated in solution and trapped by donor ligands.

3.4 Experimental Procedures

3.4.1 General Procedures

The following compounds were prepared by literature procedures: N≡Mo(OtBu)3,46 N≡MoCl3,46 MoCl3(THF)3,156 Mo(NMe2)4.157 The synthesis of the thiolates and associated thiolate transfer reagents is given in Chapter 1. Standard glove box and Schlenk techniques for the manipulations of air sensitive reactions were used. Solvents used for air sensitive manipulations were dried by the method of Grubbs,68 or by distillation from Na/benzophenone (THF). Dioxane was distilled from Na/benzophenone or purchased from Aldrich as anhydrous grade and stored over molecular sieves. NMR spectra were obtained on Varian VXR-500, Varian XL-300, Varian Unity-300 or Varian Mercury 300 Instruments. Chemical shifts are reported in ppm, and coupling constants in hertz. Proton chemical shifts are referenced to the residual C6D5H resonance at 7.15 ppm and carbon chemical shifts are referenced to the C6D6 resonance at 128.39 ppm. Infrared spectra were recorded on a Bio-Rad 135 Series FTIR spectrometer and UV-Visible spectra were recorded on a Hewlett-Packard 8453 diode-array spectrometer. Elemental analysis (C, H, N) were performed by Microlytics, S. Deerfield, MA or H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany. X-Ray diffraction data was collected on a Siemens Platform goniometer with a Charge Coupled Device (CCD) detector, and structures were typically solved by direct methods. Solution magnetic susceptibilities were determined by 1H NMR at 300 MHz using the method of Evans.94,95 Diagram for assignment of NMR spectra:
3.4.2 Synthesis of Nitrido-Molybdenum-*tris*-thiolates

Synthesis of N≡Mo(SC[Ad]ArMe)₃ (26)

N≡Mo(O^†Bu)₃ (78.6 mg, 0.24 mmol, 1.0 equiv) was dissolved in diethyl ether. Titanium reagent 18 (376.4 mg, 0.74 mmol, 3.08 equiv) was dissolved in diethyl ether (8 mL). The titanium solution was added to the nitride solution which led to an immediate color change to orange-red. The reaction was allowed to stir 10 min and concentrated. Hexamethyldisiloxane (10 mL) was added to the reaction, and the solution was allowed to stir until a precipitate formed. The precipitate was filtered to yield 26 (122.3 mg, 0.13 mmol, 53%) as an orange solid. Nitride 26 is soluble in pentane, diethyl ether, and dichloromethane, but insoluble in acetonitrile. Pentane and diethyl ether solutions of 26 turn green when cooled to -35°C, however, toluene solutions remain yellow. ¹H NMR (C₆D₆) δ 1.5-2.1 (m, 36H, a-d), 2.20 (s, 18H, m), 2.8 (s, 3H, f), 3.41 (s, 3H, e), 6.75 (s, 3H, l), 7.30 (s, 6H, j). ¹³C NMR (C₆D₆) δ 22.02 (m), 28.78 (b), 36.14 (f), 36.93 (e), 37.53 (a), 39.20 (d), 39.88 (c), 102.98 (h), 127.72 (j), 129.93 (l), 138.83 (k), 143.76 (g), 149.07 (i). Elemental Analysis: Calculated for
C$_{57}$H$_{69}$MoNS$_3$: C, 71.29; H, 7.24; N, 1.46. Found: C, 71.50; H, 7.15; N, 1.25.

**Reaction of 26 with pyridine**

Pyridine was added to an ethereal solution of 26 leading to the formation of N≡Mo-(SC[Ad]Ar$_{Me}$)$_3$(py). $^1$H NMR (C$_6$D$_6$) $\delta$ 1.5-2.1 (m, 36H, a-d), 2.20 (s, 18 H, m), 2.84 (s, 3H, f), 3.42 (s, 3H, e), 6.625 (d, 2H, py), 6.75 (s, 3H, l), 6.95 (t, 1H, py), 7.27 (s, 6H, j) 8.48 (t, 2H, py). $^{13}$C NMR (C$_6$D$_6$) $\delta$ 22.01 (m), 28.80 (b), 36.11 (f), 36.90 (e), 37.55 (a), 39.55 (d), 39.90 (c), 123.83 (h), 127.78 (j), 128.68 (py), 129.79 (l), 135.65 (py), 138.70 (k), 143.74 (g), 148.96 (py), 150.77 (i).

**Reaction of (THF)$_2$Mg(SC[Ad]Ar$_{Me}$)(Br) with N≡MoCl$_3$**

Freshly prepared N≡MoCl$_3$(CH$_3$CN)$_4$ (219 mg, .89 mmol, 1.0 equiv) was reacted with (THF)$_2$Mg(SC[Ad]Ar$_{Me}$)(Br) (469 mg, .88 mmol, 1.0 equiv) in toluene. The reaction was allowed to stir 24 h, concentrated and extracted into OEt$_2$. Dioxane was added to the reaction, and the mixture was allowed to stand 30 min, and then filtered and concentrated. Examination of the solid by $^1$H NMR reveals the products to be 26 and Ar$_{Me}$[Ad]CS-SC[Ad]Ar$_{Me}$.

**Synthesis of N≡Mo(SC[Ad]Ar$_{Bu}$)$_3$ (27)**

Titanium reagent 19 (483.7 mg, 0.90 mmol, 2.36 equiv) was dissolved in OEt$_2$ (5 mL) and a solution of N≡Mo(OtBu)$_3$ (125.6 mg, 0.38 mmol, 1.0 equiv) in OEt$_2$ (10 mL) was added. The reaction was allowed to stir overnight, concentrated and extracted into O(SiMe$_3$)$_2$. A first crop of 27 (76.2 mg, 0.073 mmol, 24%) was obtained as a green powder. $^1$H NMR(C$_6$D$_6$) $\delta$ 1.23 (s, 27H, n), 1.5-2.2 (m, 36H, a-d), 2.85 (s, 3H, f), 3.43 (s, 3H, e), 7.37 (d, 6H, j or k), 7.61 (d, 6H, j or k). $^{13}$C NMR (C$_6$D$_6$) $\delta$ 28.74 (b), 31.78 (n), 34.99 (m), 36.11 (f), 37.05 (e), 37.48 (a), 39.28 (d), 39.87 (c), 126.40 (h), 128.68 (j or k), 129.74 (j or k), 141.07 (i), 149.90 (j), 150.44 (l).
Synthesis of N≡Mo(SC[Ad]ArPh)₃ (28)

Solid N≡Mo(O₄Bu)₃ (87.5 mg, 0.265 mmol, 1.0 equiv) was placed in a vial with a stir bar. The titanium transfer reagent 20 (505 mg, 0.798 mmol, 3.01 equiv) was dissolved in OEt₂ (10 mL) and added to the solid nitride. Upon addition, a change of color to blue-green was observed. The reaction was allowed to stir 30 min, and concentrated. O(SiMe₃)₂ was added to the resulting oil, and the slurry was stirred until precipitation of a powder occurred. The blue green powder was collected to yield 28 (302 mg, 0.226 mmol, 86 %). The material can be recrystallized from THF/pentane mixtures or from toluene/pentane mixtures. Although isolated as a blue powder, the compound forms yellow solution in THF, toluene and benzene. The UV-spectrum in THF (25°C) is sensitive to concentration: at 5.13 mM a band is present at 680 nm (absorbance=1.25), however, upon diluting this sample to 2.57 mM the band disappears. The compound is only sparingly soluble in OEt₂, and it was difficult to prepare a 3.2 mM solution. The absorbance at 655 nm was temperature dependent: at 25 °C the absorbance was 1.58, and when the solution was cooled to 10 °C the absorbance increased to 2.78. Warming the sample caused the absorbance of the sample to return to 1.57. ¹H NMR (C₆D₆) δ 1.4-2.0 (36H, m, a-d), 2.83 (s, 3H, f), 3.26 (s, 3H, e), (doublet under C₆D₆, 6H, p), 7.21 (t, 12H, o), 7.64 (d, 12H, n), 7.74 (s, 3H, l), 7.91 (s, 6H, j). Variable temperature ¹H NMR in toluene-d₈ over the temperature range 25 °C to −50 °C shows broadening of the aromatic resonances upon cooling the sample. ¹³C NMR (C₆D₆) δ 28.59 (b), 36.40 (f), 37.04 (e), 37.34 (a), 39.07 (d), 39.74 (c), 126.12 (j or l), 127.88 (j or l), 127.97 (p or n), 129.50 (p or n), 141.84 (k or m), 143.10 (k or m), 150.89 (i). Elemental Analysis: Calculated for C₈₇H₇₃MoNS₃: C, 78.41; H, 6.13; N, 1.05. Found C, 78.20; H, 6.16; N, 1.08.

3.4.3 Single crystal X-Ray Structure Determination of 26

C₅₇H₆₉MoNS₃, M_W = 960.25, triclinic P1̅, a = 12.455 (2) Å, b = 16.094 (2) (10) Å, c = 16.527 (2) Å, α = 65.169 (2) °, β = 75.596 (2) °, γ = 86.173 (2) °, V = 2862.3 (7) Å³, Z = 2, D_calc = 1.114 Mg/m³, absorption coefficient 0.371 mm⁻¹, F(000) =
1016, number of reflections collected 11869, number of independent reflections 8070, GOF = 1.110, $R = .1317$, $wR_2 = .3134$.

3.4.4 Reactions of Magnesium Thiolates with MoCl$_3$(THF)$_3$

Isolation of (Ar$_{Me}$[Ad]CS)$_3$Mo═Mo(SC[Ad]Ar$_{Me}$)$_3$ (30)

Magnesium thiolate (THF)$_2$Mg(SC[Ad]Ar$_{Me}$)$_2$ (12) (690 mg, .93 mmol, 1.4 equiv) was slurried in OEt$_2$ (5 mL). A slurry of MoCl$_3$(THF)$_3$ (292.8 mg, 0.70 mmol, 1.0 equiv) in OEt$_2$ (5 mL) was added to the magnesium reagent, and the reaction was allowed to stir 2 hr. Dioxane (1 mL) was added and the reaction was allowed to stir an additional 1.5 h, filtered through celite and concentrated. The material was extracted into pentane, filtered through celite and the mother liquor was allowed to stand at $-35 \degree C$. Two crops of 30 (185 mg, 0.11 mmol, 31%) were collected as red crystals. $^1$H NMR (C$_6$D$_6$) $\delta$ 1.5-2.2 (m, 72H, a-d), 2.29 (s, 36H, m), 2.91 (s, 6H, f), 3.24 (s, 6H, e), 6.75 (s, 6H, l), 7.01 (s, 12H, j). $^{13}$C NMR (C$_6$D$_6$) $\delta$ 22.20 (m), 29.02 (b), 36.91 (f), 36.94 (e), 39.46 (a), 39.96 (d), 128.30 (h), 128.68 (j), 129.01 (l), 137.48 (k), 143.08 (g), 150.37 (i). Elemental Analysis: Calculated for C$_{114}$H$_{138}$Mo$_2$S$_6$: C, 72.35; H, 7.35; Found: C, 71.71; H, 7.57.

Reaction of (THF)$_2$Mg(SC[Ad]Ar$_{Me}$)$_2$ with MoCl$_3$(THF)$_3$ in THF

Magnesium thiolate (THF)$_2$Mg(SC[Ad]Ar$_{Me}$)$_2$ (789 mg, 1.06 mmol, 1.47 equiv) was slurried in THF (10 mL) and a slurry of MoCl$_3$(THF)$_3$ (300 mg, 0.72 mmol, 1.0 equiv) was added. The reaction was allowed to stir 1.5 h, and dioxane (1 mL) was added. This reaction was allowed to stir an additional 2.25 h, filtered through a bed of celite and concentrated. The material was extracted in THF (10 mL) and pyridine (30 microliters, 0.37 mmol) was added. The volume was reduced to 8 mL and layered with pentane (4 mL). Two crops of precipitate (479 mg) were collected.
Synthesis of \((\text{ArBu[Ad]CS})_3\text{Mo=Mo(SC[Ad]ArBu)}_3\)

Magnesium reagent 13 (1.13 g, 1.4 equiv, 1.37 mmol) was slurried in OEt\(_2\) (40 mL) and partially frozen. MoCl\(_3\)(THF)\(_3\) (398 mg, 1.0 equiv, .95 mmol) was added as a solid to the melting solution. The reaction was allowed to stir for 30 min, at which point dioxane (15 mL) was added. After an additional 2 hours, the reaction was filtered through celite and concentrated. The material was then recrystallized from toluene to yield Mo\(_2\)(SC[Ad]ArBu)\(_6\) (156 mg, 0.082 mmol, 17 %) as two crops of red crystals. \(^1\)H NMR (CD\(_6\)) \(\delta\) 1.31 (s, 54H, n), 1.63-2.10 (m, 72H, a-d), 2.96 (s, 6H, f), 3.24 (s, 6H, e), 7.36 (2 overlapping doublets, 24 H, j and k). \(^{13}\)C NMR (C\(_6\)D\(_6\)) \(\delta\) 29.15 (b), 32.11 (n), 35.01 (m), 37.34 (f), 37.74 (e), 39.56 (a), 40.02 (d), 125.34 (j or k), 130.26 (j or k), 135.62 (h), 140.81 (i), 149.42 (j), 151.47 (l). Elemental Analysis: Calculated: C, 73.43; H, 7.92. Found: C, 73.56; H, 7.85.

Reaction of 20 with MoCl\(_3\)(THF)\(_3\)

MoCl\(_3\)(THF)\(_3\) (119 mg, 0.28 mmol, 2.9 equiv) was slurried in THF (2 mL). A solution of titanium reagent 20 (517 mg, 0.82 mmol, 1.0 equiv) in THF (8 mL) was added to the molybdenum. The slurry was allowed to stir 1 h, at which point it was a homogeneous, red solution. The solution was concentrated, and slurried in OEt\(_2\) (10 mL) and stirred for 30 min, then the rose-colored insoluble material (269 mg, ) as a rose-colored powder.

3.4.5 Reactions of Free Thiols with Mo(NMe\(_2\))\(_4\)

Synthesis of \((\text{Me}_2\text{N})\text{Mo(SC[Ad]ArBu)}_3\)

Mo(NMe\(_2\))\(_4\) (315 mg, 1.15 mmol, 1.0 equiv) was dissolved in pentane (20 mL). A slurry of HSC[Ad]ArBu (1.097 mg, 3.51 mmol, 3.05 equiv) was prepared in pentane (40 mL). The thiol slurry was added to the molybdenum solution, and the reaction was allowed to stir 1 hr. Several crops of dark red-purple crystals were collected from pentane. \(^1\)H NMR: (C\(_6\)D\(_6\)) shows a broad peak at \(\delta\) 1.23 Magnetic Susceptibility
(Evan's Method): 2.31 $\mu_B$ Elemental Analysis: Calculated for $C_{65}H_{87}NMoS_3$: C, 72.66; H, 8.16; N, 1.30. Found: C, 72.75, H, 8.06, N, 1.23.
Chapter 4

Nitrogen Atom Transfer: A Strategy to Access the Chemistry of the Elusive "WX₃" Fragment

4.1 Introduction

In considering the chemistry of three coordinate compounds, there are a substantial number of three coordinate chromium(III) compounds. Three coordinate molybdenum (III) compounds are limited to the molybdenum tris-anilide complexes, which can be made with a variety of alkyl groups and substitution patterns on the aryl ring.¹,¹⁵ The only example of a three coordinate tungsten compound is the W(IV) compound, W(OSiBu₃)₂(N₃Bu), synthesized by Wolczanski.³¹ Molybdenum tris-anilide compounds have been able to cleave a wide variety of small molecules including dinitrogen and the N-N bond of nitrous oxide.²⁻⁵ Theoretical calculations indicate a lower barrier to dinitrogen cleavage for a hypothetical tungsten tris-amide fragment.³³ Furthermore, work in the related triamido ethyl amine (TREN) ligand system has
shown tungsten dinitrogen compounds to be further reduced than their molybdenum analogues. The tungsten complexes \([\text{N}_3\text{N}]\text{WCl} \) \((\text{N}_3\text{N})=(\text{RNCH}_2\text{CH}_2)_3\text{N}, \text{R} = \text{Np, aryl})\) have been prepared and reduced under N\(_2\) to the \(\mu-\eta^1,\eta^1\)-N\(_2\) complex, \([\text{N}_3\text{N}]\text{W}\text{N}=\text{N}_\text{W}[\text{N}_3\text{N}]^6\). The dinitrogen N-N bond length in the structurally characterized example with a neopentyl substituent is longer \((1.39(2) \text{ Å})\) than that for related molybdenum compounds.\(^{159}\) There are two structurally characterized molybdenum TREN bridging dinitrogen compounds with N-N bond lengths of 1.20 (2) Å for the \(^1\text{BuMe}_2\text{Si}^\) substituent and 1.186(7) Å for the 4-\(^1\text{Bu}-\text{C}_6\text{H}_4^\) derivative.\(^{158,160}\)

We are interested in systems in which a N\(_2\)-derived nitride could be further activated into useful nitrogen containing molecules. We were therefore intrigued by the demonstration by the Chisholm group that the nitride in N=\text{W}(\text{O}^4\text{Bu})\(_3\) is much more prone to protonolysis than the nitride in N=\text{Mo}(\text{O}^4\text{Bu})\(_3\).\(^{46}\) Treatment of the tungsten derivative with isopropanol leads to ammonia, whereas treatment of the molybdenum derivative with isopropanol leads to exchange of the tert-butoxide ligands with isopropoxide ligands. It is therefore expected that it should be easier to activate the nitride in the proposed N=W(N[R]ArMe\(_3\)) than in N=Mo(N[R]ArMe\(_3\)). However, to date efforts to synthesize a tungsten tris-anilido compound have proved unsuccessful.

One approach to the generation of three coordinate fragments that can not be directly synthesized is to use Mo(N[R]ArMe\(_3\)) to abstract the nitrogen from a N=MoX\(_3\) species and observe the chemistry of the transiently generated “MoX\(_3\)” species. This methodology has been used for N=Mo(O\(^4\)Bu)\(_3\),\(^{37}\) N=Mo(S\(^1\)Ad)\(_3\),\(^{51}\) and N=Mo(NMe\(_2\))\(_3\).\(^ {161}\) For both N=Mo(S\(^1\)Ad)\(_3\) and N=Mo(NMe\(_2\))\(_3\) the intermediate \(\mu\)-nitride has been isolated and crystallographically characterized. However, in the case of N=Mo(O\(^4\)Bu)\(_3\) the intermediates are formed only transiently. The “Mo(O\(^4\)Bu)\(_3\)” fragment derived from N=Mo(O\(^4\)Bu)\(_3\) has been shown to participate in dinitrogen cleavage from \(^{15}\)N\(_2\) labeling studies.\(^{37}\) Inconclusive evidence suggests that the N=Mo(NMe\(_2\))\(_3\) fragment is also able to participate in N\(_2\) cleavage.\(^{52}\) Therefore, nitrogen atom transfer was an appealing way to approach the chemistry of tungsten tris-amido fragments. While it is expected that the more reducing nature of tungsten would favor nitrogen atom transfer from molybdenum to tungsten, this electronic preference may be modulated.
by steric effects.

In this chapter the use of titanium and zirconium transfer reagents are employed to synthesize a series of tungsten nitrides with amide ligands. A survey of the known tungsten (VI) nitrides reveals very few compounds. The most prevalent compound is $\text{N=WCl}_3$ and its Lewis base adducts. There are three different routes to its synthesis: $\text{W(CO)}_6$ and $\text{NCl}_3$, $\text{WCl}_6$ and $\text{Me}_3\text{SiN}_3$, and $\text{WCl}_6$ and $\text{NaN}_3$. The properties of this compound, including the crystal structures in several different forms have been extensively studied. However, there have been few reports of using it as a starting material for the formation of other tungsten (VI) nitrides with non-chloride ligands. There is one report on the synthesis of $\text{N=W(NPh}_2)_3$ from $\text{N=WCl}_3$ and $\text{LiNPh}_2$. However, not only is the yield (12.3%) low, but the analysis results (the only characterization data given) are off by more than 1.6% in each of C, H, and N. A second well characterized tungsten (VI) nitride is $\text{N=W(OtBu)}_3$. This nitride is synthesized from the nitrile cleavage of $(\text{tBuO})_3\text{W=W(OtBu)}_3$, which results in $\text{N=W(OtBu)}_3$ and PhC=W(OtBu)$_3$. However, the cleavage of W-W triple bond with nitriles is not a general reaction, and the course of the reaction is very dependent on the electronic properties of the ligands. It has been shown that nitriles do not cleave $(\text{Me}_2\text{N})_3\text{W=W(NMe}_2)_3$ to give the corresponding $\text{N=W(NMe}_2)_3$. Tungsten nitrides with aryloxide ligands have also been synthesized by treatment of a tungsten alkylidyne with acetonitrile.

There are several examples of tungsten nitrides with TREN ligands. However, these nitrides are prepared by treatment of the tungsten-chlorides with sodium azide after the ligand is installed. Hence, these routes can not be utilized until the necessary tris-anilide tungsten precursors become available. As preliminary experiments with $\text{N=WCl}_3$ and $\text{LiNMe}_2$ gave an inseparable 2:1 mixture of products, with the minor product at the authentic chemical shift for $\text{N=W(NMe}_2)_3$, it was critical to look into other routes to the transfer of ligands. While salt metathesis reactions between an alkali or alkaline earth metal amide and a transition metal chloride remain a prevalent method of installing the amide functionality, other ligand transfer reagents have been used. Marc Johnson used Ti(NMe$_2$)$_4$ to transfer NMe$_2$ ligands to.
Figure 4-1: Non-alkali and alkaline earth metal amide metathesis routes to install amide ligands onto molybdenum nitride.

\[ \text{N} = \text{Mo}(O^t\text{Bu})_3 \] to yield \[ \text{N} = \text{Mo}(\text{NM}e_2)_3 \].\(^{161}\) This method has also been used to transfer thiolate ligands to \[ \text{N} = \text{Mo}(O^t\text{Bu})_3 \].\(^{51}\) In addition, Verkade has used tin to transfer TREN ligands to \[ \text{N} = \text{Mo}(O^t\text{Bu})_3 \] and \[ \text{O} = \text{V}(O^t\text{Bu})_3 \],\(^{175}\) and Kempe has used yttrium to transfer amide ligands to palladium.\(^{176}\) A few of these examples are illustrated in Fig 4-1. We wished to extend this methodology to the use of zirconium transfer reagents.

The synthesis of new tungsten nitrides has allowed for comparison of the molybdenum and tungsten analogues on the basis of crystal structure determinations, density functional theory calculations and reactivity studies. Furthermore, the preparation of several tungsten nitrides of different steric bulk has allowed for an examination of the steric influence on the nitrogen atom transfer reaction to three coordinate molybdenum.
4.2 Results and Discussion

4.2.1 Synthesis of Tungsten Amido Nitrides

Preparation of N=W(NMe$_2$)$_3$ (32)

Analogous to the preparation of N=Mo(NMe$_2$)$_3$, treatment of the insoluble N=W-(O$i^4$Bu)$_3$ with Ti(NMe$_2$)$_4$ in toluene, followed by recrystallization from boiling toluene provides N=W(NMe$_2$)$_3$ as colorless needles in 72% yield. This compound is insoluble in pentane and diethyl ether, but is sparingly soluble in THF and toluene. The N=W(NMe$_2$)$_3$ is much less soluble than N=Mo(NMe$_2$)$_3$, reminiscent of the situation between N=W(O$i^4$Bu)$_3$ and N=Mo(O$i^4$Bu)$_3$. This suggests that N=W(NMe$_2$)$_3$ is also an oligomeric compound. N=W(O$i^4$Bu)$_3$ has been shown to form a linear polymer in the solid state, consisting of short M=N bonds trans to long M-N dative bonds.$^{150}$

Formation of N=W(N[$^i$Pr]ArMe)$_3$ (33) from Titanium

It was of interest to form the more sterically encumbering N=W(N[$^i$Pr]ArMe)$_3$ (33). This compound represents the first fully characterized example of a tungsten complex containing anilido ligands. The formation of this compound will not only allow us to examine the effect of sterics on the possible transfer of a nitrogen atom from tungsten to molybdenum, but it will also allow us to examine the possibility of nitride activation in a more soluble system. Treatment of ClTi(O$i^4$Pr)$_3$ with (Et$_2$O)LiN[$^i$Pr]ArMe led to the formation of two products. Vacuum distillation of the reaction mixture removed Ti(O$i^4$Pr)$_4$ and left a major product which appears to be Ti(N[$^i$Pr]ArMe)$_2$(O$i^4$Pr)$_2$, based on the integration of $^1$H NMR resonances, although this remained an oil and was contaminated by impurities. Use of the oil effected the transfer of -N[$^i$Pr]ArMe groups to N=W(O$i^4$Bu)$_3$ to form N=W(N[$^i$Pr]ArMe)$_3$, albeit in irreproducible yield. A potential problem was the involvement of the isopropoxide ligands; it has been demonstrated that Ti(O$i^4$Pr)$_4$ is able to exchange ligands with N=W(O$i^4$Bu)$_3$. Purification was also difficult, as the N=W(N[$^i$Pr]ArMe)$_3$ is soluble in O(SiMe$_3$)$_2$ and it was
necessary to separate it from several equivalents of oily titanium alkoxide byproducts. Using titanium transfer chemistry it was possible to prepare enough material to obtain $^1$H and $^{13}$C NMR spectra, a single crystal suitable for an X-Ray diffraction study, elemental analysis and preliminary chemical reactivity. However, it was necessary to develop an alternative, reproducible method for the synthesis of $\text{N=W(N}[^{1}\text{Pr}]\text{ArMe)}_3$. Neither treatment of $\text{N=W(NMe}_2\text{)}_3$ with $\text{HN[^{1}\text{Pr}]ArMe}$ or treatment of $\text{N=WCl}_3$ with $(\text{Et}_2\text{O})\text{LiN[^{1}\text{Pr}]ArMe}$ led to the formation of any $\text{N=W(N}[^{1}\text{Pr}]\text{ArMe)}_3$ product.

**Use of Zirconium Transfer Reagents**

In order to take advantage of the larger atomic radius of zirconium and the decreased solubility of the alkoxide byproducts, it was of interest to examine the use of zirconium as an anilide transfer reagent. In a test reaction $\text{Zr(NMe}_2\text{)}_4$ was reacted with $\text{N=W(O}^{1}\text{Bu)}_3$ to form $\text{N=W(NMe}_2\text{)}_3$ under the same conditions that had been used for the successful synthesis of 32 from $\text{Ti(NMe}_2\text{)}_4$. However, in the case of zirconium it was more difficult to cleanly isolate 32.

The formation of a zirconium anilide transfer reagent proved trivial: treatment of $\text{ZrCl}_4$ with 4 equiv of $(\text{Et}_2\text{O})\text{LiN[^{1}\text{Pr}]ArMe}$ in cold diethyl ether led to the clean formation of $\text{Zr(N[^{1}\text{Pr}]ArMe)}_4$ (34) as a pale yellow crystalline compound. Reaction of 34 with $\text{N=W(O}^{1}\text{Bu)}_3$ led not to the formation of $\text{N=W(N[^{1}\text{Pr}]ArMe)}_3$, but rather to the formation of the heteroleptic nitride, $\text{N=W(O}^{1}\text{Bu)(N[^{1}\text{Pr}]ArMe)}_2$ (35). After the stoichiometry was properly adjusted to favor the compound that is formed, the product could be isolated in 60% yield. The remaining tert-butoxide ligand can be further transformed to allow for the formation of tris-amide complexes in which the steric bulk of the third ligand is varied, and other heteroleptic tungsten nitrides. Indeed, treatment of 35 with $\text{Ti(NMe}_2\text{)}_4$ leads to the formation of $\text{N=W(N[^{1}\text{Pr}]ArMe)}_2$($\text{NMe}_2$) (36). The original target, $\text{N=W(N[^{1}\text{Pr}]ArMe)}_3$, can be formed by treatment of 35 with $(\text{Et}_2\text{O})\text{LiN[^{1}\text{Pr}]ArMe}$. The synthesis of these compounds is summarized in Fig 4-2.

It was of interest to undertake a single crystal X-ray diffraction study of N=W(N[^3]Pr]ArMe)_3 in order to compare it to the structure of N=Mo(N[^3]Pr]ArMe)_3 obtained by Marc Johnson. An extensive body of literature has been devoted to the various oligomeric forms of tungsten (VI) nitrides. Schematic representations of these structures are shown in Fig 4-3. Without additional bases, N=W(O^1Bu)_3 crystallizes as a linear polymer,\(^{150}\) N=W(O-2,6-^1PrC\(_6\)H\(_3\))\(_3\) crystallizes as a square with two W=N units,\(^{148}\) N=W(OCH\(_2\)CF\(_3\))\(_3\) crystallizes as a trimer and N=WCl\(_3\) crystallizes as a square consisting of four N=WCl\(_3\) units.\(^{164}\) The determination of N=W(N[^3]Pr]ArMe)_3 as a monomer in the solid state represents the first such crystal structure determination.

Furthermore, the crystal structure determination allows for a comparison of the
metal-nitride bond lengths for Mo and W derivatives without the necessity of considering additional dative interactions. For example, Chisholm has analyzed the differences in the crystal structures of N≡Mo(OtBu)\textsubscript{3} and N≡W(OtBu)\textsubscript{3}, but this analysis is complicated by the presence of both short M≡N as well as long M-N dative bonds. Hence, while it was found that the N≡W bond length (1.740 (15) Å) is longer than the N≡Mo bond length (1.661(4) Å or 1.673(5) Å, depending on the isomorph), this difference may be only related to the stronger dative bonds (2.661 (15) Å for W, 2.883(8) or 2.844(5) for Mo) than to any difference intrinsic to the tungsten-nitride bond. The same conclusion can be drawn for the comparison of N≡WCl\textsubscript{3} and N≡MoCl\textsubscript{3}.

In the solvent free form, these are tetramers with short (W: 1.705(7) Å, Mo: 1.638(10) Å) and long (W: 2.085(7) Å, Mo: 2.143(10) Å) metal-nitrogen distances. Once again, the tungsten-nitride bond distances are longer for tungsten, however, this can once again be attributed to the stronger dative interaction. A comparison can also be made between tungsten and molybdenum derivatives in the OP\textsubscript{3}Cl\textsubscript{3} adducts of tungsten and molybdenum nitrides, which both crystallize as tetrameric squares. However, in this case, the four metal-nitride units are not related by symmetry, and both the short tungsten-nitride lengths, and the long tungsten nitride lengths span the corresponding molybdenum lengths.

The ORTEP diagram for N≡W(N[^Pr]ArMe)\textsubscript{3} is shown in Fig 4-4 and Table 4.1 summarizes the relevant bond distances and angles for both N≡W(N[^Pr]ArMe)\textsubscript{3} and N≡Mo(N[^Pr]ArMe)\textsubscript{3}. Inspection of the bond lengths and angles reveals there is very little crystallographic difference between the two molecules. While there are no crystallographically characterized examples, presumably the nitrides formed from the TREN ligands are monomeric due to donation from the apical nitrogen. Hence, two closely related molecules, [N(CH\textsubscript{2}CH\textsubscript{2}NSiMe\textsubscript{3})\textsubscript{2}(CH\textsubscript{2}CH\textsubscript{2}NCH\textsubscript{3})]Mo≡N and [(Me\textsubscript{3}Si-NCH\textsubscript{2}CH\textsubscript{2})\textsubscript{3}N]W≡N, can be compared on the basis of the \textsuperscript{15}N NMR signal of the nitride. There is a substantial change in chemical shift between the two derivatives. The chemical shift of the Mo compound is δ 866.08 and that of the tungsten compound chemical shift is δ 551.2 (\textsuperscript{1}J_{WN}=48 Hz). This clearly suggests that while the bond length may be similar, there is a substantial change in bonding in moving from
Figure 4-4: ORTEP diagram for $N=W(N^{[3]Pr}ArMe)_3$ with the ellipsoids shown at the 35% probability level. Selected bond distances and angles are given in Table 4.1.

Table 4.1: Comparison of bond distances (Å) and angles (°) for $N=Mo(N^{[3]Pr}ArMe)_3$ and $N=W(N^{[3]Pr}ArMe)_3$ derived from solid state X-Ray crystal structure determinations, and of $N=Mo(NH_2)_3$ and $N=W(NH_2)_3$ derived from Density Functional Theory calculations

<table>
<thead>
<tr>
<th></th>
<th>Mo$^{a, b}$</th>
<th>W$^c$</th>
<th>Mo$^d$</th>
<th>W$^e$</th>
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<td>$M-N_{nitride}$</td>
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<tr>
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<td>1.994(4)</td>
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</tr>
<tr>
<td>$N_{nitride}-M-N_{amide}$</td>
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<td>101.14(10)</td>
<td>103.7</td>
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<td></td>
<td>100.4(2)</td>
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$^b$N$=Mo(N^{[3]Pr}ArMe)_3$

$^c$N$=W(N^{[3]Pr}ArMe)_3$

$^d$N$=Mo(NH_2)_3$

$^e$N$=W(NH_2)_3$
4.2.3 Reactivity of Tungsten Nitrides with Electrophiles

Given the observation from the Chisholm group that the nitrido functionality could be removed by protonation in the case of $N=W(OtBu)_3$ but not in the case of $N=Mo-(O^tBu)_3$ it was of interest to study the reactivity of the new tungsten amido nitrides with electrophiles and protic reagents. Initial efforts focused on reaction of 32 with electrophiles Me$_3$SiCl and MeI. The products formed are only sparingly soluble in most dry organic solvents, and hence were difficult to fully characterize. There are two possible electrophilic sites on the molecule, either the amide lone pair or the nitride. Disappointingly, 1-adamantanol reacted with 32 to yield the sparingly soluble $N=W(O^tAd)_3$, rather than a product in which the nitrido nitrogen had been protically removed. Methyl iodide and trimethylsilyl chloride failed to react with $N=W(N[^Pr]ArMe)_3$, in which the amide nitrogen lone pairs are more sterically protected, suggesting that indeed the lone pair is a more reactive site than the nitride.

4.2.4 Density Functional Theory Calculation on Hypothetical Molybdenum and Tungsten Nitrides

In order to begin to understand the differences in bonding between molybdenum and tungsten nitrides, in light of the crystal structure determinations and reactivity studies, we performed DFT calculations on the hypothetical $N=Mo(NH_2)_3$ and $N=W(NH_2)_3$. These calculations can be viewed in light of the previous theoretical work on the bonding in metal nitrides. Hoffmann has used Extended Hückel Theory to analyze the bonding in $N=W(O^tBu)_3$ in the context of the oligomerization of this species. Frenking has used ab initio calculations on a large number of transition metal oxo and nitrido compounds. Finally, Schoeller found the formation of the tetramer, $(N=MeCl)_4$, more exothermic for tungsten as compared to molybdenum. Geometry optimization for $N=Mo(NH_2)_3$ and $N=W(NH_2)_3$ has been reported pre-
viously by Morokuma in his study on the rates of N₂ scission for molybdenum and tungsten nitrides, however, the bonding in the nitrides was not studied. The calculated bond lengths and angles for N≡Mo(NH₂)₃ and N≡W(NH₂)₃ compare well to the experimentally determined values for N≡Mo(N[NPr]ArMe)₃ and N≡W(N[NPr]-ArMe)₃ and are tabulated in Table 4.1. The HOMO of both molecules is an orbital of A₂ symmetry, which represents a combination of amide lone pairs that are not of the proper symmetry to π bond with the metal. Hence, consistent with the reactivity studies, unless this lone pair is protected by the steric bulk of the organic groups on the nitrogen, reactions occur at the amides. While it is not feasible to preferentially activate the nitride in the tungsten system, it is observed that N≡W(NMe₂)₃ is much less soluble than N≡Mo(NMe₂)₃ suggesting that the formation of oligomers is more thermodynamically preferred. Oligomers are most likely formed through interaction of the HOMO-2 and the LUMO+3, both of A₁ symmetry, which are depicted for both molybdenum and tungsten in Fig 4-5. While the σ-bonding orbital, HOMO-2, is similar in both cases, the σ-antibonding orbital, LUMO+3, has a larger lobe on the tungsten metal center than on the molybdenum metal center. This data suggests the tungsten fragment may be more Lewis acidic than the molybdenum fragment, which is consistent with the more favorable formation of oligomers.

4.2.5 Nitrogen Atom Transfer From N≡W(NMe₂)₃

Given the ability to synthesize N≡W(N[NPr]ArMe)₃ and N≡Mo(N[NPr]ArMe)₃, we wished to address two questions. First, could we transfer the nitrogen atom from tungsten to molybdenum? Secondly, could we isolate a new molecule formally derived from W(III)? The transfer outlined in the first question is intriguing, as we would expect a nitrogen atom to transfer from molybdenum to tungsten rather than vice versa. This expectation is based on both the greater reducing power of tungsten compared to molybdenum, and the greater strength of tungsten element bonds compared to molybdenum element bonds. Both of these statements are related to systematic changes that occur in moving down a triad of elements. The electrochemistry of many
Figure 4-5: Selected orbitals of $A_1$ symmetry for tris-amide nitrides. The orbitals for $\equiv\text{Mo}(\text{NH}_2)_3$ are shown on the left, and those for $\equiv\text{W}(\text{NH}_2)_3$ are shown on the right. The top orbitals are the LUMO+3, the $\sigma$-antibonding orbitals, and the bottom orbitals are the HOMO-2, the $\sigma$ bonding orbitals.
pairs of molybdenum and tungsten compounds can be used to support the more reducing nature of tungsten. As the tungsten metal center is more reducing, it should be more easily oxidized. Hence, in a comparison between the oxidation potentials for the molybdenum and tungsten derivatives of [(4-tBuC₆H₄NCH₂CH₂)₃N]M-N=N-M[4(NCH₂CH₂N-4-tBuC₆H₄)₃] it was found that it was 650 mV easier to oxidize the tungsten derivative than the molybdenum derivative. The greater strength of the tungsten-nitride bond compared to the molybdenum-nitride bond is evidenced from theoretical calculations and the lack of reactivity of X₃Mo=MoX₃ compounds compared to the corresponding tungsten triply bonded compounds.

Reaction of NEW(NMe₂)₃ with Mo(N[R]ArMe)₃

Initial nitrogen atom transfer reactions from NEW(NMe₂)₃ focused on Mo(N[R]-ArMe)₃ as the source of three coordinate molybdenum. The rapid formation of N≡Mo(N[R]ArMe)₃ upon treatment of NEW(NMe₂)₃ with Mo(N[R]ArMe)₃ suggested that indeed nitrogen atom transfer was occurring. Furthermore, the course of the transfer reaction was very dependent on the presence or absence of dinitrogen. The reaction was done both in the presence and absence of N₂, and ¹H NMR spectra were obtained. Comparison of these spectra allowed for the assignment of peaks belonging to (Me₂N)₃W(μ-N)Mo(N[R]ArMe)₃ and a dinitrogen dependent product, presumably (Me₂N)₃W-N≡N-Mo(N[R]ArMe)₃. The (Me₂N)₃W(μ-N)Mo(N[R]ArMe)₃ was one of several products in solution, and its lifetime was short, suggesting that isolation would be difficult. Both (Me₂N)₃W(μ-N)Mo(N[R]ArMe)₃ and (Me₂N)₃W-N≡N-Mo(N[R]ArMe)₃ decompose into a large number of tungsten containing products, many of them paramagnetic.

The reactivity of NEW(NMe₂)₃ with Mo(N[R]ArMe)₃ contrasts with that of N≡Mo(NMe₂)₃ and Mo(N[R]ArMe)₃. When N≡Mo(NMe₂)₃ was treated with Mo(N[R]-ArMe)₃, a mixture of N≡Mo(N[R]ArMe)₃, (Me₂N)₃Mo≡Mo(NMe₂)₃ and (μ-N)[Mo-(NMe₂)₃]₂ was formed. The latter compound was thermally unstable and broke up to yield (Me₂N)₃Mo≡Mo(NMe₂)₃ and N≡Mo(NMe₂)₃. However, in the case of the
Reaction of N≡W(NMe₂)₃ with Mo(H)(η²-Me₂C=NArMe)(N[Pr]ArMe)₂

Given the limited lifetime of the bridging nitride obtained with Mo(N[R]ArMe)₃, we turned our attention to the less sterically encumbering synthon for the three coordinate molybdenum, Mo(H)(η²-Me₂C=NArMe)(N[Pr]ArMe)₂. Reaction of N≡W(NMe₂)₃ with Mo(H)(η²-Me₂C=NArMe)(N[Pr]ArMe)₂ in THF yields a bright purple solution. The bridging nitride, (Me₂N)₃W(μ-N)Mo(N[Pr]ArMe)₃, can be isolated in moderate (61%) yield (see Fig 4-6). There are several competing side reactions that contribute to the low yield. Bridging nitride 37 competes with Mo(H)(η²-Me₂C=NArMe)(N[Pr]ArMe)₂ in reacting with N≡W(NMe₂)₃ (vide infra). The low solubility of N≡W(NMe₂)₃ in THF requires high dilution conditions in order to assure that all of the nitride is dissolved. In addition, compound 37 is thermally unstable and any N≡Mo(N[Pr]ArMe)₃ that is produced will react with any additional Mo(H)(η²-Me₂C=NArMe)(N[Pr]ArMe)₂ in solution to form (μ-N)[Mo(N[Pr]ArMe)₃]₂. Furthermore, it is necessary to perform this reaction in the absence of N₂, as crude samples of 37 are sensitive to N₂. However, once (Me₂N)₃W(μ-N)Mo(N[Pr]ArMe)₃ has been completely purified, it is no longer sensitive to N₂. The origin of this be-
behavior is discussed in the section on reactivity of 37 with N≡W(NMe₂)₃. The ¹H NMR spectrum of 37 shows four resonances at δ 3.2, 4.4 and 18.2 that each integrate to eighteen protons. Presumably these are the aryl methyls, isopropyl methyls (confirmed by preparing the compound that is deuterated in this position), and the dimethylamide methyls respectively. There is also a peak at δ 6.1 ppm that integrates to three protons, this could represent either the isopropyl methine or the para hydrogen. The magnetic susceptibility of 2.3 B. M. obtained by the Evans method is high, but still in the proper range for one unpaired electron.

**Crystal Structure of 37**

Crystals suitable for single crystal X-Ray diffraction were grown from a concentrated hexane solution under vacuum. The thermal ellipsoid diagram is shown in Fig 4-7. The molybdenum fragment consists of three amide nitrogens in a trigonal environment (sum of the Namide-Mo-Namide angles is 353.4°). The Mo-N_nitride vector is nearly perpendicular to this plane, the Namide-Mo-N_nitride angles are 95.7°, 96.4°, and 103.5°. The Mo-Namide distances are in the normal range. The tungsten environment is tetrahedral. The planes defined by two of the three dimethylamide ligands are parallel to the W-N-Mo vector, while the third plane is twisted perpendicularly. This twist is most likely evidence of a second order Jahn-Teller distortion. The two parallel fragments have W-Namide bond lengths of 1.938(6) and 1.940(6) Å, whereas the W-Namide bond length of the perpendicular fragment is 1.963(6) Å. These bond lengths are all statistically identical using the 3 σ criteria.

The bridging nitride is located closer to the tungsten metal center (1.811(6) Å) than to the molybdenum center (1.859(6) Å). It should be noted that W and Mo have similar atomic radii. Furthermore, as discussed earlier the metal-nitride bond lengths in N≡Mo(N[¹Pr]ArMe)₃ and N≡W(N[¹Pr]ArMe)₃ are nearly identical. The only other crystallographically determined bridging nitride with the Mo(N[¹Pr]Ar)₃ fragments is (µ-N)[Mo(N[¹Pr]ArMe)₃]₂. In this structure the bridging nitride lies on a crystallographic inversion center, with a Mo-N bond length of 1.8204 (4) Å.⁵² In
another related structure, \((\text{Me}_2\text{N})_3\text{Mo}(\mu-\text{N})\text{Mo}(\text{N}[\text{R}]\text{Ar}_\text{F})_3\) \((\text{Ar}_\text{F}=\text{4F-C}_6\text{H}_4)\) the two Mo-N bridging bond distances are 1.82(4) and 1.83(4) Å respectively. A third example of a bridging nitride, \((\text{AdS})_3\text{Mo}(\mu-\text{N})\text{Mo}(\text{N}[\text{tBu}]\text{Ph})_3\), is more unsymmetric than 37. In \((\text{AdS})_3\text{Mo}(\mu-\text{N})\text{Mo}(\text{N}[\text{tBu}]\text{Ph})_3\) the Mo-N nitride distance is 1.771(7) Å to the anilide fragment and 1.882(7) Å to the thiolate fragment.51

**Treatment of \((\text{Me}_2\text{N})_3\text{W}(\mu-\text{N})\text{Mo}(\text{N}[\text{Pr}]\text{Ar}_\text{Me})_3\) with Small Molecules**

The reaction of a large number of small molecules (\(^4\text{BuCN}, \text{MesCN}, \text{P}_4, \text{PhCN}, \text{MeCN}, \text{N}_2\text{O}, \text{NO}, \text{2,6-Me}_2\text{C}_6\text{H}_4-\text{NC}\)) with \((\text{Me}_2\text{N})_3\text{W}(\mu-\text{N})\text{Mo}(\text{N}[\text{Pr}]\text{Ar}_\text{Me})_3\) was surveyed in order to find an isolable compound derived from a W(III) fragment. These reactions led to the formation of \(\text{N}≡\text{Mo}(\text{N}[\text{Pr}]\text{Ar}_\text{Me})_3\) and multiple tungsten containing products. These results confirm the nitrogen atom was transferred from the more reducing metal center to the less reducing metal center. The transfer can be understood from a steric perspective. In Fig 4-8 space filling models derived from the crystal structure coordinates for 37 demonstrate the greater accessibility of the metal on the tungsten side of the molecule.

Unfortunately, for the small molecules examined it was not possible to isolate any tungsten containing products. The isolation of tungsten products is complicated by the formation of paramagnetic materials that are difficult to monitor by \(^1\text{H}\) NMR spectroscopy, and the presence of 1 equiv of \(\text{N}≡\text{Mo}(\text{N}[\text{R}]\text{Ar}_\text{Me})_3\) in the reaction mixture which must be removed during attempts to purify tungsten containing products. Furthermore, the dimethylamide ligands are most likely not large enough to stabilize the highly reactive tungsten compounds that are formed.

The reaction of 37 with PhCN was examined more closely. James Tsai has studied the reaction of \(\text{Mo}(\text{H})(\eta^2-\text{Me}_2\text{C}=\text{NAr}_\text{Me})(\text{N}[\text{Pr}]\text{Ar}_\text{Me})_2\) with PhCN in detail; depending on the reaction conditions two molecules of nitrile are coupled to form \((\text{Ar}_\text{Me}[\text{Pr}]\text{N})_3\text{MoNC}[\text{Ph}-\text{C}[\text{Ph}]]\text{NMo}(\text{N}[\text{Pr}]\text{Ar}_\text{Me})_3\) or one molecule of nitrile is split to form \(\text{PhC}≡\text{Mo}(\text{N}[\text{Pr}]\text{Ar}_\text{Me})_3\) and \((\mu-\text{N})[\text{Mo}(\text{N}[\text{Pr}]\text{Ar}_\text{Me})_3]_2\). Therefore, we could envision the tungsten center forming similar products. Examination of the \(^1\text{H}\)
Figure 4-7: Thermal ellipsoid representation of 37, from an X-ray study. Ellipsoids are at the 35 % probability level. Selected bond distances (Å) and angles (°): W(1)-N(7) 1.811, W(1)-N(4) 1.940(6), W(1)-N(5) 1.963(6), W(1)-N(6) 1.938(6), Mo(1)-N(7) 1.859 (6), Mo(1)-N(1) 1.980 (6) Mo(1)-N(2) 2.011 Mo(1)-N(3) 1.976(6), W(1)-N(7)-Mo(1) 176.3(4), N(7)-W(1)-N(4) 103.6(3), N(7)-W(1)-N(5) 115.7(3), N(7)-W(1)-N(6) 110.9, N(7)-Mo(1)-N(1) 96.4(2), N(7)-Mo(1)-N(2) 103.5(3), N(7)-Mo(1)-N(3) 95.7.
Figure 4-8: Space filling models derived from the crystal structure coordinates of 37. The view on the top is looking down the Mo-N-W axis, whereas the view on the bottom is looking down the W-N-Mo axis.
NMR spectra of the reaction of 37 with PhCN reveals there to be three diamagnetic products containing dimethylamide ligands, integration suggests that these products represent all of the NMe₂ containing products. However, the identity of these products remains unknown. One possible product, PhC≡W(NMe₂)₃, was independently synthesized from PhC≡W(OᵗBu)₃ and Ti(NMe₂)⁴, however, it was not one of the products of the reaction of PhCN with 37.

Treatment of (Me₂N)₃W(μ-N)Mo(N[Pr]ArMe)₃ with N≡W(NMe₂)₃

Notable in the chemistry of N≡Mo(NMe₂)₃ was the ability to form the bridging nitride (μ-N)[Mo(NMe₂)₃]₂, which was thermally unstable and disproportionated to (Me₂N)₃Mo≡Mo(NMe₂)₃ and N≡Mo(NMe₂)₃. We wished to form an analogous tungsten compound by treatment of N≡W(NMe₂)₃ with (Me₂N)₃W(μ-N)Mo(N[Pr]ArMe)₃. While reaction of the two reagents at low temperature did lead to the formation of a bright blue solution, the color quickly turned to brown. A green powder, 38, could be isolated from the solution by cooling an evacuated (to remove all N₂) Schlenk flask to −35 °C. The powder was characterized by a ¹H NMR spectra with resonances in a 4:2:2:1 ratio. The NMR spectra remained unchanged even after several recrystallizations. Given that there are an odd number of dimethyl amide ligands, and this a diamagnetic compound, there must be an odd number of nitride nitrogen atoms. Likely empirical formulations include W₃(NMe₂)₉N or W₃(NMe₂)₉N₃, although W₂(NMe₂)₉N would also lead to a diamagnetic compound. Compound 38 was very sensitive to N₂ and decomposed over several hours at room temperature in a dinitrogen atmosphere. The only diamagnetic compound produced in this decomposition is N≡W(NMe₂)₃. Integration of a ¹H NMR spectra of decomposed material against an internal standard suggested that one molecule of N≡W(NMe₂)₃ was produced for every molecule of 38 that decomposed.

X-Ray diffraction data collected on a crystal grown from a solution of 38 revealed a compound featuring four tungsten atoms and a variety of bridging nitride and amide ligands (39), shown in Fig 4-9. Compound 39 would not produce the expected 4:2:2:1
ligand resonance pattern in the $^1$H NMR spectrum, therefore, this structure must represent a paramagnetic decomposition product of 38. While no compounds have been isolated and definitively characterized by elemental analysis, due to their extreme thermal sensitivity, these results do shed light on the problems in the synthesis of $(\text{Me}_2\text{N})_3\text{W}(\mu-\text{N})\text{Mo}(\text{N}[^{1}\text{Pr}]\text{Ar}_\text{Me})_3$. Due to the fact that 37 and $\equiv\text{W}(\text{NM}e_2)_3$ are both present in the reaction flask during the synthesis of 37, some 38 is formed as a byproduct, and is visible in crude $^1$H NMR spectra. Under a $N_2$ atmosphere, 38 will release a molecule of $\equiv\text{W}(\text{NM}e_2)_3$, which will further decompose another molecule of $(\text{Me}_2\text{N})_3\text{W}(\mu-\text{N})\text{Mo}(\text{N}[^{1}\text{Pr}]\text{Ar}_\text{Me})_3$.

The chemistry detailed for the tungsten fragment is hence substantially different than that reported for the molybdenum fragment. Noteworthy, is the fact that no $(\text{Me}_2\text{N})_3\text{W}=\text{W}(\text{NM}e_2)_3$ is detected in any of the reactions described, whereas all of the reported transfers from molybdenum nitrides to $\text{Mo}(\text{N}[R]\text{Ar}_\text{Me})_3$ have formed some Mo-Mo triply bonded compounds.$^{37,51,161}$ This observation is counterintuitive, in the sense that metal-metal multiple bonds are generally stronger for third row compounds than second row compounds. However, the original synthesis of $(\text{Me}_2\text{N})_3$-
W≡W(NMe₂)₃ was reported to be problematic, product only being obtained when LiNMe₂ was reacted with WCl₄(OEt₂) that had been allowed to decompose.⁹ As later reports suggested that reduction of WCl₄ leads to NaW₂Cl₇,¹₈²,¹₈³ it appears that (Me₂N)₃W=W(NMe₂)₃ is synthesized only when the W-W triple bond has been preformed. This contrasts the situation for (Me₂N)₃Mo≡Mo(NMe₂)₃ which can be formed directly from MoCl₃ and LiNMe₂.⁸

One explanation for this difference in reactivity could be the relative abundance of the singlet and the triplet states. In going down the triad, chromium compounds will have the highest energy gap between the singlet and triplet states, whereas the tungsten compounds will have the smallest energy gap. Therefore, chromium-tris-amide compounds remain unreactive, with reactions limited to harsh reagents such as nitric oxide. Molybdenum-tris amide complexes are isolated in the triplet state (as confirmed by their magnetic moment), however, their rich reaction chemistry relies on the ability to access the singlet state. In a hypothetical tungsten tris amide complex, the singlet state is much more readily accessible, and the compounds rapidly decomposes through pathways other than triple bond formation. An alternative simpler explanation would be related to the reduction potentials: as tungsten compounds are the easiest in the triad to oxidize, they are expected to be the least stable in the +3 oxidation state, and they will find a pathway to increase their oxidation state faster than multiple bond formation can occur.

4.2.6 Treatment of N=W(N[iPr]ArMe)₃ with Mo(H)(η²-Me₂C=NArMe)(N[iPr]ArMe)₂

Treatment of the sterically more encumbering N=W(N[iPr]ArMe)₃ with Mo(H)(η²-Me₂C=NArMe)(N[iPr]ArMe)₂ led to the immediate formation of a bright purple solution. Purple crystals were easily grown from pentane. However, after washing these crystals with pentane and redissolving them in C₆D₆ a substantial amount of N=W(N[iPr]ArMe)₃ was present in the ¹H NMR. As the purple crystals are only
sparingly soluble in C₆D₆, it was possible to filter a precipitate off this NMR sample and redissolve the freshly washed precipitate. However, once again there was N≡W(N[^Pr]ArMe)₃ present in the reaction mixtures. There were also paramagnetic signals assignable to (ArMe[^Pr]N)₃W(μ-N)Mo(N[^Pr]ArMe)₃. These assignments are made on the basis of the chemical shifts for (Me₂N)₃W(μ-N)Mo(N[^Pr]ArMe)₃ and the fact that paramagnetic tungsten NMR signals are expected to be sharper than those for molybdenum on the basis of larger spin-orbit coupling. This suggests that while (ArMe[^Pr]N)₃W(μ-N)Mo(N[^Pr]ArMe)₃ may precipitate from solution as a solid, in solution an equilibrium is formed between the bridging nitride and the starting materials.

4.2.7 Electrochemical Studies on Bridging Nitrides

It was of interest to study the electrochemical behavior of the bridging nitrides, both in order to gain additional information into the electronic structure of the molecules as well as to predict the isolation of additional stable molecules containing the Mo(μ-N)W motif. Electrochemical studies on (Me₂N)₃W(μ-N)Mo(N[^Pr]ArMe)₃ (37) revealed a reversible oxidation at -1.47 V which is shown in Fig 4-10. This can be compared to the oxidation potential of -0.84 V measured for (μ-N)[Mo(N[^Pr]ArMe)₃]₂ by John-Paul Cherry. The effect of tungsten on the redox chemistry is clearly illustrated by the 630 mv change in oxidation potential. In scanning reductively there was a quasi-reversible reduction wave at -1.978 V, the location of the return wave was dependent on the scan rate. Reduction destroyed the reversible oxidation at -1.47 V, and replaced it with an irreversible oxidation at -1.43 V.

4.2.8 Chemical Oxidation with I₂

Given the observation of a reversible oxidation wave for (Me₂N)₃W(μ-N)Mo(N[^Pr]-ArMe)₃, we wished to chemically oxidize this species. Treatment of (Me₂N)₃W(μ-N)Mo(N[^Pr]ArMe)₃ with 0.5 equiv of I₂ led to an immediate color change to green
Figure 4-10: Cyclic voltamgram showing the reversible oxidation for \([(\text{Me}_2\text{N})_3\text{W}(\mu-\text{N})\text{Mo}(\text{N}[\text{Pr}]\text{ArMe})_3)[\text{I}]\). The compound is diamagnetic, with a 1:1 ratio of dimethyl amide and anilide ligands. Given this successful oxidation, we wished to examine the reactivity of I\(_2\) with \((\text{ArMe}[\text{Pr}]\text{N})_3\text{W}(\mu-\text{N})\text{Mo}(\text{N}[\text{Pr}]\text{ArMe})_3\). However, in this case it was not feasible to form an oxidized bridging species; treatment of the purple solutions of \((\text{ArMe}[\text{Pr}]\text{N})_3\text{W}(\mu-\text{N})\text{Mo}(\text{N}[\text{Pr}]\text{ArMe})_3\) with I\(_2\) yields a 1:1 mixture of N=W(NMe\(_2\))\(_3\) and IMo(NiPrAr)\(_3\), a green compound which had been previously characterized by James Tsai.

4.2.9 Electronic Structure of the Model

\((\text{H}_2\text{N})_3\text{Mo}(\mu-\text{N})\text{W}(\text{NH}_2)_3\)

The formation and reactivity of these unsymmetrical bridging nitrides raised several interesting issues that we wished to address from a theoretical point of view. Symmetrical \(\mu\)-nitrides in trigonal symmetry have an electronic structure shown schematically in Fig 4-11. The two group 6 metals with three anionic ligands contribute 3 electrons to the bonding in the bridging nitride, whereas the nitrogen atom contributes 5 electrons. Of these 11 electrons, 4 are used in the \(\sigma\) bonds, leaving 7 \(\pi\) electrons to be
Figure 4-11: Schematic representation of the $\pi$ orbitals for bridging nitrides $X_3M(\mu$-$N)MX_3$ where $M$ represents a group 6 metal.

distributed as illustrated in the doubly degenerate orbitals.

There were several questions that we wished to address in these calculations. First, will the calculations reproduce the crystallographically determined location of the nitride between the tungsten and the molybdenum atoms? How does the asymmetric nature (molybdenum and tungsten) nature of the bridging nitride affect the electronic structure? Will calculations reproduce the presumed Jahn-Teller distortion, or is the twisting of one amide ligand only related to steric and crystal packing forces? Finally, what can we learn about the electronics of the oxidized and reduced species?

Calculations were performed on the model compound, $(H_2N)_3Mo(\mu$-$N)W(NH_2)_3$, where both the anilide and dimethyl amide ligands were represented by $NH_2$ groups. Previous calculations in this group by Tom Baker on molybdenum methylidyne and carbide species have shown very similar results for the pairs of $HC\equiv Mo(NMe_2)_3$ and $HC\equiv Mo(NH_2)_3$ model complexes.\textsuperscript{184} Initial calculations were performed in $C_{3v}$ symmetry. The calculations yield very similar distances for the molybdenum and the tungsten to the bridging nitride: 1.83 Å for W and 1.84 Å for Mo. These distances can be compared to the crystallographically determined values of 1.81 Å (W-N distance) and 1.86 Å (Mo-N distance). The Mullikan overlap population (o.p.) provides one measure of the amount of bonding between two atoms. There is a larger overlap population between the bridging nitride and the tungsten atom (0.0774) than between the bridging nitride and the molybdenum atom (0.0570). For comparison, this represents substantially more bonding than found between the metals and their amide ligands. The $W$-$N_{amide}$ o.p. is 0.0113 and the $Mo$-$N_{amide}$ o.p. is 0.0119.
It was also of interest to examine the orbitals, to determine if the bonding picture in the unsymmetrical bridging nitride (Fig 4-12) was substantially different than our schematic representation for a symmetrical bridging nitride. The Mo-N-W π-bonding orbitals are illustrated in Fig 4-12. The partially occupied metal-based nonbonding orbital of E symmetry (middle) does contain more molybdenum character than tungsten character, the orbital in the x plane is 36.31% Mo $d_{xz}$ and 44.65% W $d_{xz}$. The HOMO and HOMO-1 orbitals are nonbonding amide-based orbitals of $A_2$ symmetry. The HOMO-2 and HOMO-3 energy levels are E sets with metal-amide based π-bonding, although the tungsten based π-bonding orbital does have a small amount of bridging nitride character in it. The Mo-N-W based π-bonding orbital (bottom), the x plane of which is substantially N $p_x$ in character, is also 16.29% W $d_{xz}$ and 12.27% Mo $d_{xz}$. Finally, there is only slightly more tungsten character in the Mo-N-W σ bond. This low lying orbital of $A_1$ symmetry, is mostly N $p_z$ in character, with 13.75% W $d_{z^2}$ and 13.14% Mo $d_{z^2}$ character. Hence, while the orbitals involved in bonding do slightly favor bonding to tungsten, there is not a large electronic preference. This observation is consistent with the reactivity studies which suggest that steric factors can determine the course of the nitrogen atom transfer reaction.

In order to begin to examine the electronic preference for a Jahn-Teller distortion, calculations were performed without symmetry constraints. Initial calculations did not indicate significant rotation of the amide ligand, but local minima can be problematic in this type of calculation. Due to the computational intensity of these calculations, it was not feasible to identify the absolute minimum.

Finally, we were interested in the electronic structure of the oxidized and reduced species. Notable was that oxidation with I$_2$ produced a diamagnetic compound, where according to our schematic representation we would expect a paramagnetic compound with two unpaired electrons. The diamagnetism can be attributed to the formation of localized W(VI)-Mo(IV) oxidation states given the asymmetric bridging nitride, or it can be attributed to binding of the I cation to change the electronic structure, or Jahn-Teller distortion of an amide to lower the symmetry from 3v. As very recent work has revealed diamagnetic compounds upon oxidation of ($\mu$-N)[Mo(N[6Pr]ArMe)$_3$]$\text{I}_2$ and
Figure 4-12: The W-N-Mo $\pi$ bonding orbitals. The orbitals were generated from a calculation on the $(\text{H}_2\text{N})_3\text{Mo}(\mu-\text{N})\text{W(NH}_3)_3$ anion. The tungsten atom is on the left, whereas the molybdenum atom is on the right.
(μ-P)[(Mo(N[1]Pr)ArMe)3]2 with FcOTf, this result can not be taken as conclusive evidence for the formation of a W(VI)-Mo(IV) bonding picture. Calculations were performed on the (H2N)3Mo(μ-N)W(NH2)3 cation, also in C3v symmetry. While these calculations suggested that the two unpaired electrons favor the molybdenum metal center, the molecular orbital is delocalized onto both tungsten and molybdenum.

4.3 Conclusion

In this chapter, zirconium anilide complexes have been used to transfer anilide ligands to tungsten to form N≡W(N[1]Pr)ArMe)3, a method that will most likely be useful for the formation of other anilido-containing tungsten complexes. The synthesis of several new tungsten nitrides containing amide ligands has allowed for the formation of bridging nitrides containing the Mo(μ-N)W motif. The transfer of a nitrogen atom is found to dependent on the steric constraints of the ligands on tungsten and molybdenum.

4.4 Experimental Procedures

The following materials were prepared by the literature procedure: Ti(NMe2)4, N≡W(OtBu)3,171 PhC≡W(OtBu)3,171 H[1]Pr)ArMe,41 (Et2O)LiN[1]Pr)ArMe,41 Mo(N[R]ArMe)3,5 and Mo(H)(η2-Me2C=NArMe)(N[1]Pr)ArMe)2.41 All manipulations were carried out using standard Schlenk and glove box techniques unless otherwise noted. Hexane, pentane, OEt2, CH2Cl2, toluene, and benzene were dried by the method of Grubbs68 and THF was distilled from Na/Benzophenone. Hexamethyldisiloxane was dried over 4Å molecular sieves. NMR spectra were obtained on Varian VXR-500, Varian XL-300, Varian Unity-300 or Varian Mercury 300 instruments. Chemical shifts are reported in ppm, and coupling constants are reported in hertz. Proton chemical shifts are referenced to the residual C6D5H resonance at 7.15 ppm and carbon chemical shifts are referenced to the C6D6 resonance at 128.39 ppm. Elemental analyses (C, H, N)
were performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany. X-Ray diffraction data was collected on a Siemens Platform goniometer with a Charge Coupled Device (CCD) detector, and were typically solved by direct methods. Solution magnetic susceptibilities were determined by \(^1\)H NMR at 300 MHz using the method of Evans. \(^94\) \(^95\) \(^1\)H and \(^{13}\)C NMR assignments are based on the following diagram:

![Diagram](image)

### 4.4.1 Synthesis of Group 4 Transfer Reagents

**Synthesis of Zr(N[^iPr]ArMe)\(_4\)** 34

\((\text{Et}_2\text{O})\text{LiN[^iPr]ArMe}\) (4.84 g, 19.9 mmol, 1.0 equiv) was slurried in \(\text{OEt}_2\) (30 mL) and the slurry was frozen. As the slurry melted, \(\text{ZrCl}_4\) (1.12 g, 4.8 mmol, 4.14 equiv) was added as solid, and the mixture was allowed to stir overnight. The following morning the reaction was concentrated, redissolved in pentane (20 mL), and filtered through a bed of celite. Partial concentration of the mother liquor, followed by cooling to \(-35\ ^\circ\text{C}\) led to the formation of colorless crystals. These crystals were collected to yield 34 (0.63 g, 1.03 mmol, 25%) as colorless crystals. The yield was not optimized, and is low due to loss of material in the salt layer. \(^1\)H NMR (\(\text{C}_6\text{D}_6\)) \(\delta\) 1.13 (d, 24H, 7), 2.26 (s, 24H, 5), 4.15 (septet, 4H, 6), 6.62 (s, 4H, 4), 6.80 (s, 8H, 2) \(^{13}\)C NMR (\(\text{C}_6\text{D}_6\)) \(\delta\) 22.22 (5 or 7), 23.91 (5 or 7), 52.60 (6), 125.06 (2), 125.55 (4), 138.39 (3), 148.91 (1).

Elemental Analysis: Calculated for \(\text{C}_{44}\text{H}_{69}\text{N}_4\text{Zr}\): C, 71.78; H, 8.22; N, 7.61. Found: C, 71.80; H, 8.65; N, 7.58.
4.4.2 Synthesis of N≡W(NMe₂)₃ (32)

Synthesis of N≡W(NMe₂)₃ from N≡W(OtBu)₃ and Ti(NMe₂)₄

N≡W(OtBu)₃ (2.08 g, 4.99 mmol, 1.0 equiv) was slurried in toluene (40 mL). A solution of Ti(NMe₂)₄ (838 mg, 3.74 mmol, 0.75 equiv) in toluene (40 mL) was added. It was stirred for 1 hr, brought to boiling, and filtered. The solution was cooled to -35 °C, and 32 (1.18 g, 3.57 mmol, 72%) was collected as colorless needles. ¹H NMR (C₆D₆) δ 3.325. ¹³C NMR (C₆D₆) δ 51.34. Elemental Analysis: Calculated for C₆H₁₈N₄W: C, 21.83; H, 5.50; N, 16.97. Found: C, 21.94; H, 5.49; N, 16.78.

Reaction of N≡WCl₃ and LiNMe₂

N≡WCl₃ (500 mg, 1.64 mmol, 1.0 equiv) was slurried in toluene (10 mL) and frozen. Upon melting, LiNMe₂ (250 mg, 4.9 mmol, 3.0 equiv) was added and the solution was allowed to stir overnight. The following morning the solution was brought to reflux, filtered while hot and then allowed to cool to -35 °C. A ¹H NMR of an aliquot of this reaction showed a large number of products in the baseline, and ca. a 2:1 ratio of peaks at δ 3.377 and δ 3.323, the later representing NEW(NMe₂)₃. Crystallization did not aid substantially in purifying the material.

Reaction of Zr(NMe₂)₄ and N≡W(OtBu)₃

A toluene solution of Zr(NMe₂)₄ (52.6 mg, 0.196 mmol, 0.75 equiv) was added to solid N≡W(OtBu)₃ (110.4 mg, 0.263 mmol, 1 equiv) and the mixture was allowed to stir. After 3 h the solution was concentrated to a white solid. ¹H NMR (C₆D₆) δ: 1.463 (Zr(OtBu)₄) and 3.295 (N≡W(NMe₂)₃) indicates that complete transfer occurred.

Reaction of HN[iPr]Ar with N≡W(NMe₂)₃

Method A: A solution of HN[iPr]ArMe in C₆D₆ was added to a stirring slurry of N≡W-(NMe₂)₃. ¹H NMR spectra were obtained after 15 min and 15 h and both spectra indicated that no reaction had occurred. Method B: HN[iPr]ArMe (165 mg, 1.01 mmol,
3 equiv) was weighed into a glass bomb. $N=W(NMe_2)_3$ (112 mg, .34 mmol, 1 equiv) was added as a solid. The mixture was heated in an oil bath at 70 °C for 3 h, and then allowed to stir an additional 36 h at RT. $^1H$ NMR ($C_6D_6$) reveals no formation of any anilide containing products (all H[N[Pr]ArMe]) and complete decomposition of $N=W(NMe_2)_3$.

4.4.3 Synthesis of Tungsten Nitrides Containing the
-N[Pr]ArMe Ligand

Synthesis of $N=W(N[Pr]ArMe)_2(OtBu)$ (35)

A solution of 34 (680 mg, 0.92 mmol, 0.50 equiv) in toluene (15 mL) was added to stirring $N=W(OtBu)_3$ (766 mg, 1.84 mmol, 1.0 equiv). The solution was gently heated until homogeneous, about 30 min. It was then allowed to stir for an additional 2 h, and concentrated. The yellow crystals were scraped onto a frit and washed with cold pentane (10 mL) to provide spectroscopically pure 35 (756 mg, 1.27 mmol, 69%). $^1H$ NMR ($C_6D_6$) δ 1.54 (d, 6H, 7), 1.65 (s, 9H, OC(CH$_3$)$_3$), 1.72 (D, 6H, 7), 1.97 (s, 12H, 5), 4.23 (quintet, 2H, 6), 6.35 (s, 2H, 4), 6.43 (s, 4H, 2). $^{13}C$ NMR ($C_6D_6$) δ 21.60 (5), 26.91 (7), 27.80 (7), 32.38 (OC(CH$_3$)$_3$), 63.23 (6), 78.84 (OC(CH$_3$)$_3$), 122.78 (2), 128.0 (4), 128.68 (3), 138.78 (1). Elemental Analysis: Calculated for $C_{26}H_{41}N_3OW$: C, 52.44; H, 6.94; N, 7.06. Found: C, 52.06; H, 7.34; N, 6.95.

Synthesis of $N=W(N[Pr]ArMe)_3$ (33)

A solution of (Et$_2$O)LiN[Pr]ArMe (198.5 mg, 0.82 mmol, 1.0 equiv) in OEt$_2$ (15 mL) was added to solid 35 (486 mg, 0.82 mmol, 1.0 equiv) and the mixture was allowed to stir overnight. It was then concentrated, extracted into a minimal amount of pentane and concentrated. It was once again extracted into pentane, filtered and cooled to −35 °C. A first crop of 33 (270 mg, 0.39 mmol, 48%) was collected as large colorless crystals. $^1H$ NMR ($C_6D_6$) δ 1.703 (d, 18 H, 7), 1.920 (s, 18H, 5), 4.490 (q, 3H, 6),

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6.306 (s, 6H, 2), 6.457 (s, 3H, 4) $^{13}$C NMR (C$_6$D$_6$) δ 21.64 (5), 27.10 (7), 65.72 (6), 124.53 (2), 124.69 (4), 138.55 (3), 151.25 (1).

**Synthesis of N=W(N[\textit{i}Pr]ArMe)$_2$(NMe$_2$)$_2$ (36)**

A solution of Ti(NMe$_2$)$_4$ (60.6 mg, 0.27 mmol, 0.26 equiv) in OEt$_2$ (6 mL) was added to solid 35 (585 mg, 1.02 mmol, 1.0 equiv). The solution was allowed to stir overnight, and concentrated. It was extracted into a minimal amount of O(SiMe$_3$)$_2$, filtered, and stored at -35 °C to collect two crops of 36 (293 mg, 0.52 mmol, 51%) as light yellow crystals. $^1$H NMR (C$_6$D$_6$) δ 1.67 (d, 6H, 7), 1.72 (d, 6H, 7), 1.98 (s, 12 H, 5), 3.23 (s, 6H, N(CH$_3$)$_2$), 4.26 (q, 2H, 6), 6.45 (s, 6H, 2 and 4). $^{13}$C NMR (C$_6$D$_6$) δ 21.71 (5), 26.69 (7), 27.83 (6), 53.93 (N(CH$_3$)$_2$), 64.22 (6), 124.22 (2), 126.78 (4), 138.94 (3), 150.71 (1). Elemental Analysis: Calculated for C$_{34}$H$_{38}$N$_4$W: C, 50.89; H, 6.76; N, 9.89. Found: C, 50.76; H, 6.66; N, 9.74.

**4.4.4 Reactivity of Tungsten Nitrides with Electrophiles**

**Reaction of 32 with 1-adamantanol**

Nitride 32 (67.3 mg, 0.204 mmol, 1.0 equiv) was slurried in diethyl ether (6 mL). A solution of 1-adamantanol (76.4 mg, 0.503 mmol, 2.46 equiv) was prepared in diethyl ether (6 mL) and added to the nitride slurry. Additional diethyl ether (6 mL) was added, and the entire reaction went into solution. The reaction was allowed to stir 2 h, and concentrated. Upon partial concentration, a white precipitate formed and was collected by filtration to give N=W(1Ad)$_3$. The $^1$H NMR featured broad peaks that were difficult to interpret. Elemental Analysis: Calculated for C$_{30}$H$_{45}$NO$_3$W: C, 55.30; H, 6.96; N, 2.15. Found: C, 54.50, H, 6.85, N, 2.20.
4.4.5 Reactions of $N=W(NMe_2)_3$ with $Mo(N[R]ArMe)_3$

$N=W(NMe_2)_3$ and $Mo(N[R]ArMe)_3$ under vacuum

$N=W(NMe_2)_3$ (20 mg, 0.061 mmol, 1.0 equiv) and $Mo(N[R]ArMe)_3$ (40 mg, 0.061 mmol, 1.0 equiv) were added to an NMR tube. The tube was evacuated and $C_6D_6$ was condensed in by vac transfer to give a bright green solution. The tube was flame sealed and the $^1H$ NMR spectra was monitored at regular intervals. 30 minutes: unreacted $Mo(N[R]ArMe)_3$ and a new product assigned as $(Me_2N)_3W(p-N)Mo(N[R]ArMe)_3$. The $^1H$ peaks for this compound are $\delta$ 19.5 (s, 18H, $N(CH_3)_2$), 6.5 (very broad, 18 H, 5), 5.0 (s, 3H, 4), 2.08 (s, 27 H, 9). There is also a small amount of $N=Mo(N[R]ArMe)_3$ and $HN[R]Ar$, and several more unidentified compounds in the $\delta$ 3.0 to $\delta$ 3.7 region. The solution was examined again at time = 2hr, 8hr, 20 hr, 28 hr, and 44 hr. The peaks assigned to $(Me_2N)_3W(\mu-N)Mo(N[R]ArMe)_3$ almost completely decayed over this period and were replaced by peaks belonging to $N=Mo(N[R]ArMe)_3$. At the end of the run, there was a small amount of unreacted $Mo(N[R]ArMe)_3$. The fate of the NMe$_2$ fragment was less clear. While peaks at $\delta$ 3.6 ppm and $\delta$ 3.5 ppm did increase during the run, at the end of the run there were approximately 25 peaks in the 2.5-4.8 region, none of which appeared to be significant.

$N=W(NMe_2)_3$ and $Mo(N[R]ArMe)_3$ under $N_2$.

$N=W(NMe_2)_3$ (93.8 mg, 0.284 mmol, 1.0 equiv) was dissolved in THF (8 mL) and chilled. $Mo(N[R]ArMe)_3$ (180.4 mg, 0.289 mmol, 1.0 equiv) was dissolved in THF (8 mL) and added to the cold solution of $N=W(NMe_2)_3$. The solution was concentrated, and a small amount of solid was dissolved in $C_6D_6$. The $^1H$ NMR showed paramagnetic peaks belonging to $Mo(N[R]ArMe)_3$ and those assigned to $(Me_2N)_3W(\mu-N)Mo(N[R]ArMe)_3$ above. There was also a third set of peaks that including resonances $\delta$ 19.7, 7.39 and 2.49 ppm. This species is tentatively assigned to be $(Me_2N)_3W=N-Mo(N[R]ArMe)_3$. The spectrum suggests that the compound assigned to $(Me_2N)_3W(\mu-N)Mo(N[R]ArMe)_3$ decays much more rapidly than the species
assigned to (Me₂N)₃W-N=N-Mo(N[R]ArMe)₃. At the end of the reaction, all of the detectable material is diamagnetic. The only -N[R]Ar ligand resonances are N≡Mo(N[R]ArMe)₃, and while there are a substantial number of NMe₂ containing products, the most intense resonance is at δ 3.330, which is the chemical shift for N≡W(NMe₂)₃.

4.4.6 Synthesis of Bridging Nitrides

Synthesis of (Me₂N)₃W(μ-N)Mo(N[Pr]ArMe)₃ (37)

Nitride 32 (630 mg, 1.91 mmol, 1.08 equiv) was dissolved in THF (100 mL) in a 250 mL Schlenk flask. A solution of Mo(H)(η²-Me₂C=NArMe)(N[Pr]ArMe)₂ (1.1 g, 1.77 mmol, 1.0 equiv) was prepared in THF (20 mL) and placed in a solid addition tube. The solid addition tube was fitted to the Schlenk flask, and the entire apparatus was evacuated. The molybdenum solution was added very quickly to the nitride solution, and the reaction was shaken, and immediately concentrated to remove THF. The purple solid was redissolved in hexane (75 mL), and filtered into a Schlenk flask. The flask was evacuated and stored at -35 °C. Two crops (980 mg, 1.07 mmol, 61%) of purple 37 were collected. ¹H NMR δ (C₆D₆) 3.16 (s, 18 H, 5), 4.3 (s, 18 H, 7), 6.17 (s, 3H, 4), 18.2 (s, 18H, N(CH₃)₂). Magnetism: Evans Method, C₆D₆: μeff=2.2μB. Elemental Analysis: Calculated for C₅₀H₇₀N₇MoW: C, 51.32; H, 7.29; N, 10.74. Found: C, 51.26; H, 7.35; N, 10.66.


Nitride 33 (270.6 mg, 0.39 mmol, 1.0 equiv) was dissolved in pentane (5 mL). A solution of Mo(H)(η²-Me₂C=NArMe)(N[Pr]ArMe)₂ (245.5 mg, 0.40 mmol, 1.03 equiv) in pentane (5 mL) was added to the nitride solution. The solution was transferred to a Schlenk flask, evacuated to removed N₂ and stored at -35 °C. Purple crystals of (ArMe[Pr]N)₃W(μ-N)Mo(N[Pr]ArMe)₃ (314 mg, 0.25 mmol, 64%) were collected. This compound has limited solubility, even in THF.
4.4.7 Reactivity of Bridging Nitrides

Treatment of \((\text{Me}_2\text{N})_3\text{W}(\mu\text{-N})\text{Mo}(\text{N}[^{\text{Pr}}]\text{ArMe})_3\) with I₂

Bridging nitride 37 (192.8 mg, 0.217 mmol, 1.0 equiv) was dissolved in diethyl ether (6 mL). A solution of I₂ (28 mg, 0.109 mmol, 0.5 equiv) was prepared in diethyl ether (6 mL). Both solutions were frozen, and upon melting the I₂ solution was added to the bridging nitride solution, leading to an immediate color change to green. The reaction was allowed to stir 5 min, and concentrated to give \(\left[(\text{Me}_2\text{N})_3\text{W}(\mu\text{-N})\text{Mo}(\text{N}[^{\text{Pr}}]\text{ArMe})_3\right][\text{I}]\). While the material can be purified by recrystallization from hexanes, it is thermally unstable and decomposes to \(\text{N}=\text{Mo}(\text{N}[^{\text{Pr}}]\text{ArMe})_3\) and \(\text{IMo}(\text{N}[^{\text{Pr}}]\text{ArMe})_3\).

\(^1\text{H} \text{NMR} (\text{C}_6\text{D}_6) \delta 1.27 (\text{d}, 18\text{H}, 7), 2.16 (\text{s}, 18\text{H}, 5), 3.50 (\text{s}, 18\text{H}, \text{N(CH}_3)_2), 6.60 (\text{s}, 3\text{H}, 4), 6.73 (\text{s}, 6\text{H}, 2). \ ^{13}\text{C} \text{NMR} (\text{C}_6\text{D}_6) \delta 21.84 (5), 23.32 (6), 52.68 (\text{N(CH}_3)_2), 63.53 (6), 125.82 (2), 127.27 (4), 138.03 (3), 155.14 (1).

4.4.8 Electrochemical Measurements on \((\text{Me}_2\text{N})_3\text{W}(\mu\text{-N})\text{Mo}(\text{N}[^{\text{Pr}}]\text{ArMe})_3\)

The electrochemical measurements were performed in THF solution containing the desired compounds and 0.5 M tetra-\text{n}-butylammonium hexafluorophosphate. A platinum disk (1.6 mm diameter, Bioanalytical systems), a platinum wire, and a silver wire were employed as the working electrode, the auxiliary, and the reference, respectively. The electrochemical response was collected with the assistance of an BAS CV-50W potentiostat. An IR drop correction was always employed due to the high resistance of the solutions. The potentials are measured against the ferrocenium/ferrocene couple at 0.0 V measured in the same solution. The scan rate was 100 mV/sec.

4.4.9 Synthesis of PhC≡W(\text{NMe}_2)_3

\text{PhC≡W(O'Bu)_3}(1.0 \text{ g}, 2.03 \text{ mmol, 1.0 equiv}) was dissolved in pentane (8 mL). A solution of \text{Ti(\text{NMe}_2)_4}(0.39 \text{ g}, 1.74 \text{ mmol, 0.86 equiv}) in pentane (2 mL) was added.
The reaction was allowed to stir 4 hrs, and a colorless precipitate was collected. The solution was partially concentrated to yield a second crop of material (Total yield: 0.64 g, 1.58 mmol, 78%) $^1$H NMR: (C$_6$D$_6$) δ 3.373 (s, 18 H, N(CH$_3$)$_2$), 6.91 (t, 1H, p-H), 7.20 (t, 2H, m-H), 7.33 (d, 2H, o-H). $^{13}$C NMR (C$_6$D$_6$) δ 50.175 (N(CH$_3$)$_2$), 125.85, 128.67, 130.73, 148.50, 276.73 (W≡CPh). Elemental Analysis: Calculated for C$_{13}$H$_{23}$N$_3$W: C, 38.53; H, 5.68; N, 10.41. Found: C, 38.64; H, 5.60; N, 10.33

4.4.10 X-Ray Crystal Structure Determinations

N=W(N[Pr]ArMe)$_3$ (33)

C$_{36}$H$_{57}$N$_4$O$_{0.5}$SiW, $M_w$=765.80, trigganol, $P_3$, $a$=14.973 (9) Å, $b$= 14.973 (9) Å, $c$ = 9.960 (8) Å, $\alpha$ = 90 $\beta$ = 90 $\gamma$ = 120 $V$=1934 (2) Å$^3$, $Z$=2, $D_{calc}$=1.315 g·cm$^{-3}$, absorption coefficient 3.046 mm$^{-1}$, $F(000)$=786, number of reflections collected: 7798, number of independent reflections: 1849, GOF=1.032, $R$=0.0402, $wR_2$=0.0905.

(Me$_2$N)$_3$W($\mu$-N)Mo(N[iPr]ArMe)$_3$ (37)

C$_{39}$H$_{66}$MoN$_7$W, $M_w$=912.78, monoclinic, $P2_1/n$, $a$=13.2395 (6) Å, $b$= 19.0223 (9) Å, $c$ = 17.1206 (8) Å, $\alpha$ = 90 $\beta$ = 99.8730 (10) $\gamma$ = 90 $V$=4247.9 (3) Å$^3$, $Z$=4, $D_{calc}$=1.427 g·cm$^{-3}$, absorption coefficient 3.035 mm$^{-1}$, $F(000)$=1860, number of reflections collected: 17008, number of independent reflections: 6095, GOF=1.268, $R$=0.0567, $wR_2$=0.0907.

4.4.11 Density Functional Theory Calculations

All calculations were performed using the Amsterdam Density Functional theory package. Calculations on (H$_2$N)$_3$Mo($\mu$-N)W(NH$_2$)$_3$ were performed on an Alpha/Linux machine employing Becke and Perdew gradient corrections (GGA) and the VWN local density approximation (LDA).$^{185-187}$ All atoms were treated relativistically, and calculations were spin unrestricted. Calculations on N≡W(NH$_2$)$_3$, N≡Mo(NH$_2$)$_3$, and
the \((H_2N)_3Mo(\mu-N)W(NH_2)_3\) cation used for the figure (but not the analysis) were performed on a PC running LINUX. Calculations employed the ZORA relativistic method,\textsuperscript{188} and the gradients are augmented with the gradient corrections due to Perdew and Wang (pw91).\textsuperscript{189}
Chapter 5

Insights into the Molecular Structure of a Terminal Carbide Anion including Fast Proton Transfer Self-Exchange Kinetics with its Conjugate Acid

5.1 Introduction

Small-molecule reductive cleavage reactions mediated by the three-coordinate molybdenum(III) complex Mo(N[R]ArMe)₃ have opened new pathways for the synthesis of molybdenum-element multiple bonds.¹,² A highlight in this regard has been the preparation and structural characterization of a carbidomolybdenum(VI) anion, in which the terminal carbide (formally C⁴⁻) ligand is derived from carbon monoxide.⁷
The anion in question, namely $[\text{C}=\text{Mo}(\text{N}[R]\text{Ar}_{\text{Me}})_3]^-$ (40), is of interest because it is an example of one-coordinate carbon bonded solely to a transition metal center. Other examples of molecules containing one-coordinate carbon are organic isonitriles, cyanide, and carbon monoxide. More recently, Templeton and coworkers have prepared a carbidotungsten (IV) anion.\textsuperscript{190} Other examples of CO cleavage by transition metals lead to the formation of bridging carbides.\textsuperscript{39,191–196}

In previous chapters, the effect of the ligand donor set (thiolate or amide) and metal (molybdenum or tungsten) on the electronic structure of metal (VI) nitrides has been examined. In this chapter we turn our attention to the isoelectronic 40, $\text{HC}=\text{Mo}(\text{N}[R]\text{Ar}_{\text{Me}})_3$ (41), and $\text{tBuC(O)}\text{OC}=\text{Mo}(\text{N}[R]\text{Ar}_{\text{Me}})_3$ (42). Physical methods have been used to probe the electronic structure of the molecules including single crystal X-ray diffraction, and solution and solid state Nuclear Magnetic Resonance spectroscopy. Furthermore, the rate of degenerate proton transfer between 40 and its conjugate acid 41 has been measured, and the rate was found to be very fast. This observation is noteworthy inasmuch as fast proton exchange rates are unusual for carbanions.\textsuperscript{197} With the aid of DFT calculations these results have been used to develop bonding pictures for the methylidyne and the carbide, both in relation to each other and in relation to the isoelectronic nitrides.

5.2 Results and Discussion

5.2.1 Molecular Structure of Methylidyne 41

A single-crystal X-Ray diffraction study of 41 was undertaken for comparison with the previously reported structure of $[\text{K(benzo-15-crown-5)}_2][40]$.\textsuperscript{7} A thermal ellipsoid plot of the structure of 41 is shown in Fig 5-1. The Mo=C bond length of 1.702(5) Å is statistically identical to the Mo=C bond length of 1.713(9) Å for $[\text{K(benzo-15-crown-5)}_2][40]$. There is little difference in the Mo-N bond lengths between the two structures: 1.964(4), 1.981(4) and 1.991(4) Å for 41 compared with 2.008(6), 2.010(7) and
Figure 5-1: Thermal ellipsoid representation of 41. Ellipsoids are at the 35% probability level. Selected bond distances (Å) and angles (°): Mo-C(1) 1.702(5), Mo-N(1) 1.981(4), Mo-N(2) 1.991(4), Mo-N(3) 1.964(4), C(1)-Mo-N(1) 102.4(2), C(1)-Mo-N(2) 101.7(2), C(1)-Mo-N(3) 101.6(2).

2.013(6) Å for [K(benzo-15-crown-5)₂][40]. Using the 3σ criterion, two of the three Mo–N bond lengths of 41 are equivalent to those found in [K(benzo-15-crown-5)₂][40]. While there is very little crystallographic difference between the two structures, it is difficult to draw conclusions about the Mo–C bond order based on crystallographic data alone. Such a situation has been encountered previously in a related system in which a shorter Mo–P bond length was observed for phosphorus monoxide complex (OP)Mo(N[R]ArMe)₃ than for terminal phosphide P≡Mo(N[R]ArMe)₃.¹⁹⁸
5.2.2 Solution $^{13}$C NMR Chemical Shifts and Relaxation Parameters

A detailed $^{13}$C NMR spectroscopic study of 40 and its precursor pivalate 42 and methylidyne 41 complexes was undertaken to accrue insight into the properties of the molybdenum-bound carbon atom and accordingly into the nature of the Mo–C bonding. This study was facilitated by the ease of incorporating a $^{13}$C label into the compounds through the use of 99% $^{13}$CO in the preparation of carbonyl complex (OC)Mo(N[R]ArMe)$_3$. Jonas Peters determined a very large downfield shift of 501 ppm for [K(2,2,2-crypt)][40]. The $^{13}$C NMR shift for the carbido carbon atom of [K(2,2,2-crypt)][40] was reported originally as δ 488 ppm, this value being in error due to chemical exchange with small amounts of methylidyne 41 present in the sample. It was therefore of interest to further examine the solution NMR parameters of 40 and related molecules, as well as to determine the rate of proton transfer self exchange (vide infra).

Known compounds with large downfield $^{13}$C NMR chemical shifts include the bridging cationic alkylidyines reported by Casey. Terminal phosphido and nitrido molybdenum tris-anilido compounds, isolobal with 40, display large downfield $^{31}$P and $^{15}$N NMR chemical shifts respectively. The downfield $^{13}$C NMR shift for [K(2,2,2-crypt)][40] is larger than that of other molecules incorporating a one-coordinate carbon atom, such as CO (δ 181), [CN]$^-$ (δ 168), and CNMe (δ 158). Not merely ascribable to the presence of negative charge is the dramatic downfield shift for the carbido carbon in 40, since the chemical shift difference of 213 ppm between the signal for [K(2,2,2-crypt)][40] and the corresponding signal for methylidyne 41 (δ 288) is substantially larger than the corresponding 49 ppm chemical shift difference between the signal for Me(CH$_2$)$_5$CCH (δ 70.7) and the corresponding lithiated derivative [Li][Me(CH$_2$)$_5$CC] (δ 118.8). Solid state NMR results in the next section demonstrate that the large downfield chemical shift is related to a large chemical shift anisotropy (CSA).

In order further to investigate the NMR parameters of the Mo–C multiply-bonded
compounds, and to optimize conditions for spectral data collection, it was of interest to measure the relaxation rates for the $^{13}$C-labeled carbon nuclei. The $T_1$ values were measured via the inversion-recovery (180-$\tau$-90) pulse sequence, in which the value of $\tau$ is varied. The peak intensities are a function of $\tau$ and were fit to an exponential curve in order to determine the value of $T_1$. All of the measured $T_1$ values are very short, which is particularly noteworthy for pivalate 42 and carbide $[K(2,2,2$-crypt)]$[40]$; compounds lacking protons on the $^{13}$C nuclei of interest, and hence having no $^1$H-$^{13}$C dipole-dipole relaxation mechanism. $^{205}$ Observed $T_1$ values are 0.97, 0.63, and 0.14 s for 42, 41 and $[K(2,2,2$-crypt)]$[40]$ at room temperature (ca. 25 °C) on an instrument operating at 500 MHz. Other compounds lacking dipole-dipole relaxation often have very long $^{13}$C $T_1$ values, an example being phenylacetylene, $HC=CoPh$, wherein the $\alpha$ and $\beta$ carbons have $T_1$ values of 9.3 and 132.0 s respectively. $^{206}$ Presumably, the very short $T_1$ values are ascribable to significant chemical shift anisotropy, although quadrupolar relaxation from the molybdenum most likely contributes the relaxation rate.

Upon dissolving $[K][40]$, which has been shown by a preliminary X-Ray diffraction study to exist as a solvent free dimer in the solid state, $^{207}$ in THF, two peaks are observed for the $^{13}$C labeled carbon, one at 489 ppm and the other at 501 ppm. Presumably, THF solvates some of the potassium ions leading to a mixture in solution of dimeric and monomeric THF-solvated species. Assuming that the peak at 489 ppm is the dimer and the peak at 501 ppm is the monomeric THF solvated carbide, it is possible to determine from $^{13}$C NMR integrations an equilibrium constant for the equation in Fig 5-2. The integrations in the $^{13}$C NMR spectrum are reliable measures of concentration because there is no nuclear Overhauser effect (nOe), due to the absence of protons directly bound to the $^{13}$C nucleus in question, and because the acquisition time employed (0.8 s) is greater than 5$T_1$ for both species. $^{205}$ At 0 °C, $K_{eq}$ is found to be 22.5 M$^{-1}$, and upon cooling the solution the equilibrium is found to favor the dimeric form. From the temperature dependence of $K_{eq}$ was determined $\Delta H = 13.3$ kJmol$^{-1}$ and $\Delta S = -23$ Jmol$^{-1}$K$^{-1}$. 

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5.2.3 Solid-State $^{13}$C NMR Spectra

In order to determine the chemical shift anisotropy, Gang Wu at Queens University obtained solid state $^{13}$C NMR spectra of ([K][40])$_2$, 41, and 42, which are shown in Figure 5-3. For all three compounds, the isotropic $^{13}$C chemical shifts observed in the solid state are in excellent agreement with data obtained from solution spectra. In each of the three solid-state $^{13}$C NMR spectra in Fig 5-3, the isotropic peak is flanked by a large number of spinning sidebands, indicating the presence of CSA. From stationary samples, the principal components of the chemical shift can be determined accurately as given in Table 5.1. As expected from their crystal structures, the $^{13}$C chemical shift tensors for the three compounds studied exhibit axial symmetry. The span of the $^{13}$C chemical shift tensor in ([K][40])$_2$, 806 ppm, is apparently the largest among diamagnetic compounds so far studied. It is clear also from Table 5.1 that the significant deshielding effect observed in ([K][40])$_2$ arises from the large paramagnetic shielding along directions perpendicular to the Mo≡C bond axis, i.e. $\delta_{11}$ and $\delta_{22}$. For ([K][40])$_2$ the difference between $\delta_{11}$ and $\delta_{22}$ is due to the aryl interactions with the unsolvated potassium. In contrast, the shielding along the Mo≡C bond, $\delta_{33}$, is similar for the three compounds studied here, indicating that the paramagnetic shielding contribution is negligible along the nearly cylindrical Mo≡C bond axis. Reminiscent
Table 5.1: Solid-State $^{13}$C NMR Data

<table>
<thead>
<tr>
<th></th>
<th>$\delta_{\text{iso}}$ $^a$</th>
<th>$\delta_{11}$ $^b$</th>
<th>$\delta_{22}$</th>
<th>$\delta_{33}$</th>
<th>$\Omega_{d}^{c}$</th>
<th>$1J_{\text{MoC}}^{e}$</th>
<th>$1K_{\text{MoC}}^{f}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$([\text{K}][40])_2$</td>
<td>504</td>
<td>788</td>
<td>742</td>
<td>-18</td>
<td>0.88</td>
<td>806</td>
<td>60</td>
</tr>
<tr>
<td>41</td>
<td>288</td>
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<td>437</td>
<td>-10</td>
<td>1.00</td>
<td>447</td>
<td>130</td>
</tr>
<tr>
<td>42</td>
<td>218</td>
<td>334</td>
<td>334</td>
<td>-13</td>
<td>1.00</td>
<td>347</td>
<td>208</td>
</tr>
</tbody>
</table>

- $^a$Chemical shifts are in ppm and are referenced to TMS.
- $^b$Chemical shift tensor components are reported to ±2 ppm.
- $^c$Skew = $3(\delta_{22} - \delta_{\text{iso}})/(\delta_{11} - \delta_{33})$.
- $^d$Span = $\delta_{11} - \delta_{33}$.
- $^e$J couplings are reported to ±5 Hz.
- $^f$The reduced indirect spin-spin coupling constant $K$ has units of $\text{NA}^{-2}\text{m}^{-3}$.

of the circumstance for phosphido compounds such as $\text{P}=\text{Mo(N[R]ArMe)}_3$, the observation of a remarkably large paramagnetic shielding in $([\text{K}][40])_2$ is suggestive of the presence of a low-lying Mo–C $\pi^*$ orbital.

### 5.2.4 Coupling Constants

While not visible in the solution $^{13}$C NMR, Gang Wu found satellite peaks due to the J-coupling to $^{95/97}$Mo nuclei in the solid state $^{13}$C NMR. The values of $1J_{\text{MoC}}$ were found to be 208, 130 and 60 (all ±5) Hz for pivalate 42, methylidyne 41, and carbide anion $([\text{K}][40])_2$, respectively. The $^{13}$C CP/MAS spectra obtained at a higher field strength, 11.75 T, confirmed the J-coupling constants. As there is little relevant literature for the comparison of $1J_{\text{MoC}}$ coupling constants, Gang Wu analyzed the data in terms of the relationship between Mo-C and W-P triple bonds. He found there to be a parallel diagonal relationship between the coupling constant and the chemical shift. Hence, it appears that there are similarities in the bonding in Mo-C and W-P triple bonds. As the W-P bonding has been analyzed in terms of one $\sigma$ and two $\pi$ bonds between the tungsten metal orbitals and the phosphorus $p$ orbitals, the bonding in the carbide is most likely similar. The measurement of the coupling constants is also important because one bond coupling constants can provide a rough approximation of the amount of s character in the bond.

The $1J_{\text{CH}}$ in methylidyne 41 can be observed from the splitting of the methylidyne
Figure 5-3: $^{13}$C MAS NMR spectra of (a) 42 (b) 41 and (c) ([K][40])$_2$. The spectra were obtained at 4.7 T. The isotropic peaks are indicated.
H resonance in the solution $^1$H NMR spectrum of $^{13}$C labelled compound, and is found to be 157 Hz. This is much smaller than is typically observed in sp hybridized compounds. Generally, $^1J_{\text{CH}}$ is seen to increase with increasing s character in the C-H bond. This can be estimated using the equation:

$$^1J_{\text{CH}} = 500(\%\text{s character in bond})$$

A typical $^1J_{\text{CH}}$ value for an sp-hybridized carbon center is ca. 250 Hz. For example, $^1J_{\text{CH}}$ values are 251 Hz and 269 Hz for phenylacetylene and hydrogen cyanide, respectively. The $^1J_{\text{CH}}$ value reported here for 41 is larger than that of 138 Hz reported for the related tungsten methyldyne, HC≡W((Me$_3$SiNCH$_2$CH$_2$)$_3$N)$_3$. Previously, it has been observed that $^1J_{\text{CH}}$ coupling constants in transition metal methyldyne species are small, the implication being that the C-H bond is poor in s character.

Care must be exercised in interpreting coupling constants only as a measure of the s character in the bond, as the assumptions used to derive the relationship between coupling constant and s character do not take relativistic effects into consideration.

Recent work from Hopkins group on the vibrational spectroscopy of methyldynes does corroborate the suggestion that the C-H bond of methyldynes are poor in s character.

The $^1J_{\text{MoC}}$ data implies a substantial decrease in s character in the Mo-C bond upon deprotonation, and the $^1J_{\text{CH}}$ data for the methyldyne implies that the C-H bond in the methyldyne is poor in s character, or conversely rich in p character. In order to form the four bonds (a triple bond to the molybdenum and a single bond to the hydrogen) of the methyldyne, the 3 p and 1 s orbitals on the carbon must be used. Presumably the hybrid orbital involved in the Mo-C sigma bonding in the methyldyne has a substantial amount of s character. However, upon deprotonation, only three of the carbon orbitals are needed for bonding, and the carbon center can rehybridize to bond to the molybdenum with only the $p_x$, $p_y$, and $p_z$, leaving a lone pair on carbon that is substantially s in character.

It was of interest to determine if the composition of the orbitals in other metal-element triply bonded systems changed in a similar manner upon addition of a sub-
stituent. In the case of the terminal phosphide, \( P\equiv Mo(N[R]ArMe)_3 \), addition of an oxygen atom to form \((OP)Mo(N[R]ArMe)_3 \) leads to a shortening of the Mo-P bond, although the bond order is decreased. One explanation is that Mo-P bond in the \((OP)Mo(N[R]ArMe)_3 \) must involve the s orbital on phosphorus, which is located closer to the metal center.\(^{52}\) The Schrock group has prepared a terminal phosphide of tungsten, \( P\equiv W(Me_3SiNCH_2CH_2)_3N \); methylation leads to an increase in the \( J_{WP} \) from 138 Hz to 784 Hz.\(^{48}\) This data also suggests the addition of the substituent results in a substantial increase in the amount of s character in the tungsten-phosphorus bond.

### 5.2.5 Proton Self-Exchange Kinetics

There is an extensive body of literature pertaining to the rates of proton-exchange reactions involving carbanions, and to the factors governing these rates. While proton-exchange reactions involving hydroxylic or amino functionalities typically are associated with diffusion-controlled rates, corresponding exchange rates for C-H groups are known to span ten orders of magnitude.\(^{214}\) It is accepted generally that proton transfer becomes slow when an anionic proton acceptor is capable of charge delocalization.\(^{197}\) The latter theory has been developed extensively by Bernasconi as the principle of non-perfect synchronization.\(^{214-216}\) The theory states that a product-stabilizing factor that develops after the transition state lowers \( k_0 \), the intrinsic rate constant, in the absence of a thermodynamic driving force. Examples of product stabilizing factors that may develop late along a reaction coordinate include resonance, charge delocalization and solvation. Considering [40]\(^{-}\) to be a unique carbanion, and in view of the attention devoted herein to the bonding and charge distribution in [40]\(^{-}\) along with its conjugate acid methylidyne 41, it was of interest to investigate proton-exchange rates involving this intriguing pair of complexes.

To determine the intrinsic rate of a proton transfer reaction, kinetic and thermodynamic factors must be separated. One approach is to measure the rate of transfer involving a variety of bases, thereby gaining information from which the intrinsic rate may be extracted. A more desirable method is to measure the rate of a self-
exchange reaction directly. Proton NMR spectroscopy often constitutes a convenient method for the interrogation of degenerate proton-transfer reactions, but $^{13}$C NMR spectroscopy has been employed also, for example, in a study concerning the rates of HCN/cyanide proton-exchange reactions in aqueous media.$^{217}$

Carbon-13 NMR spectroscopy proved to be suitable for the study of proton-exchange rates involving methylidyne $^{41}$ and carbide anion $^{40}$. NMR data obtained for [K(2,2,2-crypt)][$^{40}$] are indicative of rapid proton-transfer reactivity in the presence of trace amounts of methylidyne $^{41}$. This is why the originally reported $^{13}$C chemical shift for the same salt in THF was 482.8 ppm, the peak width $\Delta \nu_{1/2}$ having been given as 1400 Hz.$^{7}$ Acquisition of [K(2,2,2-cryptofix)][$^{40}$] spectra in the presence of small amounts of KCH$_2$Ph allowed for the limiting chemical shift for the carbido carbon of [K(2,2,2-cryptofix)][$^{40}$] to be determined as 501 ppm, the peak width in this case being relatively narrow ($\Delta \nu_{1/2} = 46$ Hz). Benzylpotassium in the previous experiment serves to scavenge traces of methylidyne $^{41}$. It is fortuitous that the chemical shifts for the $^{13}$C-labeled positions in carbide [K(2,2,2-cryptofix)][$^{40}$] and methylidyne $^{41}$ are so disparate, because this circumstance allows for very fast rates of proton exchange to be measured by line-shape analysis. Based on the 213 ppm separation in chemical shifts, coalescence of the two signals is expected when the exchange lifetime, $\tau$, is ca. $6 \times 10^{-6}$ s.

For a two-component system undergoing degenerate chemical exchange, the observed NMR spectrum depends on the lifetime of exchange $\tau$, the relative concentration of the two species, $T_2$ relaxation times, and the limiting chemical shift values.$^{218}$ In the present study, chemical shift and $T_2$ relaxation parameters were measured independently in the absence of exchange. Simulated spectra were produced using appropriate lineshape equations:$^{218}$

$$ v \propto \frac{(1 + \frac{\pi f_M}{T_{2C}} + \frac{\pi f_C}{T_{2M}})S + QR}{S^2 + R^2} $$

$$ Q = 2\pi \tau (\Delta \nu + f_M \delta \nu) $$
\[ S = \frac{\tau}{T_{2C}T_{2M}} + \frac{f_T}{T_{2M}} + \frac{f_C}{T_{2C}} - 4\pi^2 \tau \Delta \nu (\Delta \nu + \delta \nu) \]

\[ R = 2\pi \tau (\frac{\Delta \nu + \delta \nu}{T_{2M}} + \frac{\Delta \nu}{T_{2C}}) + 2\pi (\tau + f_3 \delta \nu) \]

where

- \( T_{2C} \) is the \( T_2 \) relaxation time for \([\text{K}(2,2,2\text{-crypt})][\text{40}]\).
- \( T_{2M} \) is the \( T_2 \) relaxation time for \( \text{41} \).
- \( f_C \) is the fraction of the sample that is \([\text{K}(2,2,2\text{-crypt})][\text{40}]\).
- \( f_C \) is the fraction of the sample that is \( \text{41} \).
- \( \tau \) is the lifetime of exchange.
- \( \delta \nu \) is the difference (in Hz) between the two resonances in the absence of chemical exchange.
- \( \Delta \nu \) is the difference (in Hz) between the chemical shift of the methylidyne and the frequency at which \( \nu \) is being calculated.

Relative concentrations of the two species as determined from experimental spectra were used as a starting point for the simulations, but the extreme sensitivity of carbide 40 to protonation by trace impurities necessitated the inclusion of this quantity as a variable parameter. Peak widths obtained from simulated spectra were compared to those observed experimentally, this procedure constituting the means for determination of the lifetime, \( \tau \). An example of an experimental spectrum with an overlaid calculated spectrum is shown in Fig 5-4.

At room temperature, the \( ^{13} \text{C} \) NMR spectra for an equimolar mixture of \([\text{K}(2,2,2\text{-cryptofix})][\text{40}] \) and 41 in THF exhibits coalescence behavior, such that the signal is too broad to be observed. Therefore, in order to be able to record a signal, samples for RT measurements were prepared with a high relative concentration of methylidyne or carbide. A calculated RT spectrum for a 1.5:1 mixture of 40:41 demonstrating the nearly flat simulated spectra is shown in Fig 5-5.

It was also of interest to determine the rate of proton transfer as a function of temperature. Spectra were obtained at \(-90 \, ^\circ\text{C} \) (Fig 5-6) and at \(-60 \, ^\circ\text{C} \) (Fig 5-7) which
In order to determine the value of $T$ from the experimental spectra, spectra were calculated and fit to the proper line width and peak position of the experimental spectrum. The data points obtained in the experimental measurement are represented by the light colored squares, where as the calculated spectra is represented by the solid line.

illustrate the sample approaching coalescence upon warming. These spectra were fit to calculated spectra generated using the line shape equations, and the calculated spectra are illustrated in Fig 5-5.

From the values for the lifetime of exchange, it was possible to determine a rate constant. Assuming that the reaction is first order in each reactant, the rate constant was obtained from the expression

$$k = 1/\tau[C]$$

where $[C]$ is the total concentration of both molybdenum containing species. This expression was developed by Wahl to extract rate constants for electron transfer reactions from $\tau$.\textsuperscript{219} The assumption that the rate constant is first order can be validated by preparing samples at different concentrations. Data obtained at several different total molybdenum concentrations, and several relative concentrations of 41 and $[K(2,2,2$-cryptofix)]$[40]$ are summarized Table 5.2. The rate constant obtained at 20 °C is $7 \times 10^6 \text{ M}^{-1} \text{s}^{-1}$. At -60 °C the rate constant shrinks to $4 \times 10^5 \text{ M}^{-1} \text{s}^{-1}$, and at -90 °C it is $1 \times 10^5 \text{ M}^{-1} \text{s}^{-1}$. The activation parameters obtained from the
Figure 5-5: Calculated spectra for a mixture of [K(2,2,2-crypt)][40] and 41 at different temperatures. The spectra are calculated for a total molybdenum concentration of 27 mM, and a ratio [K(2,2,2-crypt)][40]:41=1.5. At -90 °C the lifetime was calculated at $\tau = 4 \times 10^{-4}$ and at -60 °C the lifetime was calculated at $\tau = 9 \times 10^{-5}$. At room temperature $\tau = 5 \times 10^6$ (cross-hashed line). No spectrum was observed at this temperature.
Figure 5-6: Observed $^{13}$C NMR spectrum obtained at $-90 \, ^\circ\text{C}$ for a sample that was 9 mM in 41 and 18 mM in [40]$^-$. 
Figure 5-7: Observed $^{13}$C NMR spectrum obtained at $-60$ °C for a sample that was 9 mM in 41 and 18 mM in [40]$^-$. 
Arrhenius plot suggest $E_a = 17$ kJ/mole.

The rate of self exchange between $[\text{K}(2,2,2\text{-crypt})][40]$ and 41 is very fast for proton exchange in a carbon acid/base pair, suggesting that there is not an extensive amount of charge delocalization onto the ligands. In addition, solvent effects due to the use of THF could cause significant differences relative to the aqueous solutions normally used for proton transfer studies. The principle of nonperfect synchronization also is valid in the gas phase, suggesting that even without a strong solvent effect we would expect a slower rate if a significant amount of charge were being delocalized onto the ligands. The implication that the electron density remains localized in the Mo-C bond upon deprotonation is consistent with the solid state NMR data and the DFT calculations. The rates measured in this study are slower than those found for the analogous chemistry involving phenylacetylene, which by tritium tracer studies has been estimated to occur at the diffusion limit. Notably, the rates measured in this study for the exchange of $[\text{K}(2,2,2\text{-crypt})][40]$ and 41 are very close to those measured for hydrogen cyanide. A $^{13}$C NMR exchange study has found the self exchange rate constant for HCN/CN$^-$ to be $3.1 \times 10^6$ M$^{-1}$ s$^{-1}$ in an aqueous solution 1 M in NaClO$_4$. This value for the hydrogen cyanide self exchange rate constant is slightly higher than that obtained by Bedner and Jencks.

### 5.2.6 Density Functional Theory Calculations

In order to further study the bonding in $[\text{C}=\text{Mo}(\text{N}[\text{R}]\text{Ar}_\text{Me})_3]^-$ and HC=Mo(N[R]-Ar$_\text{Me}$)$_3$, Tom Baker performed DFT calculations. He studied the Mullikan overlap populations (OP) for a series of compounds including triplet $\text{H}_3\text{CMo}(\text{NH}_2)_3$, doublet
H₂CMo(NH₂)₃, singlet HC≡Mo(NH₂)₃, and singlet −[C≡Mo(NH₂)₃]. He found a gradual increase in the Mo-C OP across the series. However, he also found an increase in OP in the organic compounds C₂H₆, C₂H₄, C₂H₂, and [C₂H]−. Hence, it was concluded that the formal [C]⁴⁻ ligand is a stronger donor than the formal [CH]³⁻ ligand, regardless of whether the bonding is to an organic fragment or to a transition metal fragment.

It was enlightening to reexamine the calculations in light of our interpretation of the spectroscopic data. It was assumed that the chemical shift anisotropy is related to the presence of low lying π* orbitals. While DFT is limited in its ability to calculate the proper energy of unfilled orbitals, we do see the presence of low lying π* orbitals in the calculations. Furthermore, the energy gap between the σ and the π* orbital (3.32 eV) for −[C≡Mo(NH₂)₃] is substantially smaller than the gap of 7.12 eV found for HC≡Mo(NH₂)₃. This observation is consistent with the greater chemical shift anisotropy for ([K][C≡Mo(N[R]ArMe)₃])₂ compared to HC≡Mo(N[R]ArMe)₃. Finally, it was assumed that the coupling constant for ([K][40])₂ indicated that the molybdenum carbon bond was rich in p character, or conversely that the lone pair on the carbon was rich in s character. Indeed the calculations demonstrate a low lying orbital corresponding to the lone pair on the carbon consisting of 79.5 % C s character and only 1.08 % carbon p character.

5.2.7 The Isolobal Analogy: Comparison of the Carbide Anion to Nitrides

Having completed an extensive study of the bonding in the terminal carbide anion, it was of interest to compare the bonding in the carbide to the bonding in the molybdenum and tungsten nitrides which have been the subject of previous chapters. Notable in a comparison of the energy levels of the different species which have been calculated is the position of the nonbonding lone pairs on the amide nitrogen. In C₃ᵥ symmetry, the amide lone pairs decompose into an E and A₂ set. As there are no metal orbitals of A₂ symmetry, this irreducible representation of nitrogen lone pairs remains nonbonding. In N≡Mo(NH₂)₃, N≡W(NH₂)₃, and HC≡Mo(NH₂)₃, this orbital is the
HOMO, which in part illustrates the problem of functionalization of the terminal nitride. However, in the case of $-[\text{C}\equiv\text{Mo(NH}_2\text{)}_3]$, this representation is lower in energy than both the Mo-C $\sigma$ and $\pi$ bonds. Hence, protonation of the terminal functionality is relatively simple for the carbide anion. In the case of nitrides, electrophilic reagents tend to react at the ligand lone pairs rather than at the nitride. This is also true for the terminal phosphide, which has proved difficult to functionalize, and calculations have indicated the HOMO to be the nonbonding amide lone pairs.

5.3 Conclusions

Herein has been presented extensive characterization of the novel carbon base, $[40]^-$. While other one coordinate carbon bases exhibit similar $pK_a$ and proton transfer rate profiles, the electronic structure of this molecule clearly is more complex. The latter complexity has been unraveled in part via a combination of computational and solid-state NMR studies. It appears that while deprotonation of $41$ brings about minimal structural rearrangement, substantial changes in metal-carbon bonding become manifest. The rapid addition of a proton to the terminal carbon functionality is in stark contrast to terminal molybdenum and tungsten nitrides, in which functionalization of the nitride nitrogen is extremely difficult.

5.4 Experimental Procedures

5.4.1 General Considerations

All synthetic work and sample preparation was done in a Vacuum Atmospheres glove box using standard techniques for the manipulation of air sensitive compounds. The compounds were prepared according to literature procedures. All NMR samples for relaxation parameters and kinetic studies were contained in flame sealed tubes and interrogated using a Varian VXR-500 spectrometer. All samples were referenced to residual solvent protons, and spectra of samples in protio solvents were obtained without a lock. Density functional theory calculations were performed on an SGI Indy workstation using the Amsterdam Density Functional Package employing Becke
and Perdew gradient corrections (GGA) and the VWN local density approximation (LDA). A scalar relativistic correction was also included on the Mo, C, and N atoms. The molybdenum was treated using a triple zeta basis including polarizations with up to the 3d orbitals frozen. The carbon was also treated at the triple zeta level including polarizations with its 1s electrons frozen. Nitrogen was treated using a double zeta basis (with polarizations) and the 1s frozen core. Hydrogen was treated at the triple zeta level (with spin polarizations). All geometries were optimized in $C_{3v}$ symmetry. X-Ray data was collected on Siemens Platform goniometer with a charge coupled device (CCD) detector. The structure was solved by direct methods (ShelxtlV5.0, G. M. Sheldrick and Siemens Industrial Automation Inc, 1995).

5.4.2 X Ray Crystallographic Determination of 41

Colorless crystals were grown from a concentrated diethyl ether solution at -35 °C. The crystals were moved quickly from a vial and attached to a glass fiber.

$C_{37}H_{55}MoN_3$, $M_W=637.78$, monoclinic, $P2_1/n$, $a=11.256\ (2)$ Å, $b=17.278\ (7)$ Å, $c=18.626\ (7)$ Å, $\alpha=90\ \beta=100.18\ (2)\ \gamma=90\ \nu=3565(2)\ \AA^3$, $Z=4$, $D_{calc}=1.188\ \text{g-cm}^{-3}$, absorption coefficient $0.395\ \text{mm}^{-1}$, $F(000)=1360$, number of reflections collected: 14191, number of independent reflections: 5142, $GOF=1.115$, $R=0.0552$, $wR_2=0.1240$.

5.4.3 Solution $^{13}$C NMR Data

$[K][40]$ in THF

A 30 mM solution of $[K][40]$ was prepared by dissolving $[K][40]$ (33.9 mg) and benzyl potassium (9.5 mg) in THF (1.34 mL). The relative concentrations of $([K][40])_2$ and $[K(\text{thf})_x][40]$ were determined from $^{13}$C NMR integrations of the labelled carbon peaks at $\delta 501\ \text{ppm}$ and $\delta 488\ \text{ppm}$. For $2\ [K(\text{thf})_x][40] \Leftrightarrow ([K][40])_2$, $K_{eq}=[([K][40])_2]/([K(\text{thf})_x][40])]^2$. $K_{eq}$: $0^\circ\text{C}: 22.5\ M^{-1}$, $-10^\circ\text{C}: 27.3\ M^{-1}$, $-20^\circ\text{C}: 31.4\ M^{-1}$, $-30^\circ\text{C}: 44.3\ M^{-1}$, $-40^\circ\text{C}: 56\ M^{-1}$, $-50^\circ\text{C}: 84.5\ M^{-1}$. The data was then plotted as $1/T$ vs $\ln K$, to give $\Delta H=-6.7\ \text{KJ/mole}$ and $\Delta S=-23\ \text{J/mol K}$. For the fit, $R^2=0.99$. 

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\textbf{$T_2$ measurements for 41 and [K(2,2,2-crypt)][40]}

The $T_2$ measurements were calculated using the formula $T_2 = (W\pi)^{-1}$, where $W$ is the peak width at half height. Because of the extremely short values of $T_2$ obtained, the contribution from field inhomogeneities was ignored. \textbf{41} (30 mM in THF, 125 MHz): 20°C: 16 ms, 0°C: 37 ms, −20°C: 67 ms. [K(2,2,2-crypt)][40] (20 mM in THF with 8.6 mM BzK, 125 MHz): 20°C: 5.8 ms, 0°C: 7.5 ms, −20°C: 12 ms, −40°C: 17 ms.

\textbf{$T_1$ measurements}

$T_1$ measurements were performed by centering the transmitter on the peak of interest, measuring the 90 pulse angle and then using the inversion recovery (180°-90° pulse sequence and fitting the resulting peaks to an exponential curve. \textbf{42} (20°C, 68 mM in C$_6$D$_6$, 125 MHz): 0.97 s, \textbf{41} (15 mM in thf, 125 MHz): 20°C: 0.63 s, 0°C: 0.47 s, −20°C: 0.32 s, −40°C: 0.23 s, −60°C: 0.14 s. [K(2,2,2-crypt)][40] (14 mM in THF with 6 mM BzK and 5 mM 2,2,2 Kryptofix, 125 MHz): 20°C: 0.14 s, −90°C: 0.04 s.

\textbf{5.4.4 Proton Transfer Kinetics}

The following samples were prepared: \textbf{A}: 20 mM in [K(2,2,2-crypt)][40], 7 mM in 41. \textbf{B}: 11 mM in [K(2,2,2-crypt)][40], 19 mM in 41. \textbf{C}: 13 mM in [K(2,2,2-crypt)][40], 12 mM in 41. \textbf{D}: 13 mM in [K(2,2,2-crypt)][40], 2 mM in 41. For sample \textbf{A} the relative concentrations were determined by low temperature integrations. For the rest of these spectra these parameters were obtained from the spectral simulation. At 20°C and 0°C the measured values for $T_2$ were used. For the lower temperature spectra these were estimated at 0.04 s for the carbide and 0.1 s for the methylidyne.

Experimental spectrum:
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<th>δ</th>
<th>$\Delta_{1/2}(ppm)$</th>
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<td>-</td>
<td>292</td>
<td>11</td>
<td>$1 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
Appendix A

Development of a New Procedure for the Synthesis of the HN[R]ArMe Ligand in the Undergraduate Laboratory

A.1 Introduction

In 1998 it was decided to implement a new experiment on dinitrogen chemistry in the undergraduate laboratory. The goal was to have the students synthesize Mo(N-[R]ArMe)₃ (R=tBu or C(CD₃)₂CH₃, Ar=3,5-Me₂C₆H₃) and observe the subsequent dinitrogen scission brought about by species.²⁻⁴ However, in order to implement this experiment it was necessary to develop a cheap and efficient synthesis of HN[R]ArMe. Four possible synthetic routes to this molecule have been utilized, and are shown in Fig A-1

The published procedure for the synthesis of HN[R]ArMe (R=C(CD₃)₂CH₃) involves methylation of the corresponding imine, (CD₃)₂C=NAr.²²⁶,²²⁷ The imine is first prepared by condensation of 3,5-dimethyl aniline and d₆ acetone. The imine is subsequently treated with excess MeLi, and the reaction mixture is quenched by pouring onto ice. Column chromatography is used to separate the desired HN[R]ArMe from (CD₃)(CD₂H)C=NAr. The use of d₆-acetone is necessary in this synthesis in order to favor methylation of the imine over deprotonation of the imine based on the deuterium isotope effect. Problematic in this synthesis is the cost of the d₆-acetone,
which is used as the solvent for the formation of the imine. In addition, there are two equivalents of MeLi that must be quenched, a potentially dangerous operation for the undergraduate laboratory.

The second route to HN[R]ArMe (R=tBu) ligand was developed by Marc Johnson and other Cummins group members based on benzyne methodology. In this procedure tBuNHLi is prepared in tBuNH₂, and 2,4-dimethylbromobenzene is added. Mechanistically, dehydrohalogenation of the xylene leads to a benzyne intermediate, which is immediately quenched by tBuNH₂. Two different isomers are produced. The desired 3,5-dimethylaniline is the major product, and the isomers can be separated by recrystallization of the HCl salts. While this procedure is facile and inexpensive for the research lab, it is dangerous for the undergraduate lab. The tBuNHLi/tBuNH₂ slurry is formed by cannula transfer of tBuNH₂ to neat BuLi on the Schlenk line. Neat BuLi is potentially explosive if exposed to air, and precaution is necessary on cannula addition because of the large amount of heat and butane produced in the reaction.

The third route is based on Buchwald aryl amination methodology. A palladium catalyst with a phosphine ligand is able to couple an amine to an aryl bromide. Fürstner and coworkers have published a synthesis of HN[R]ArMe (R=tBu) using this methodology. However, this synthesis is rather expensive, in that the obtained yield is only 47 % and uses both chiral Binap and Pd₂(dba)₃. While these materials are only used catalytically, they are still quite expensive and without careful air-free manipulation the active Pd(0) species is quenched. Finally, it is necessary to use column chromatography to separate the desired product from the unreacted starting material.

Therefore, it was of interest to develop an efficient synthesis using the addition of tBuNH₂ to 2,4,6-trimethylpyrylium tetrafluoroborate. Preliminary experiments by Mircea Gheorghiu indicated this procedure would yield HN[R]ArMe (R=tBu) in reasonable yield. Optimization of this synthesis by the undergraduate students, followed by the subsequent scale up and utilization of this procedure are detailed herein.
Figure A-1: Outline of the different synthetic methodology available for the synthesis of the HN[R]ArMe molecule. In A an imine is formed and methylated, taking advantage of the deuterium isotope effect to favor methylation. Scheme B takes advantage of the benzyne reaction, followed by subsequent separation of the isomers that are formed. Buchwald amination technology forms the basis for the synthesis shown in C, whereas D takes advantage of addition of ¹⁴BuNH₂ to a pyrylium salt.
A.2 Results and Discussion

The first group of 5.33 students to attempt this laboratory experiment were given a procedure for the synthesis of HN[R]ArMe. The first step in the procedure was the synthesis of 2,4,6-trimethylpyrylium tetrafluoroborate following the literature procedure. The second step in the synthesis is the synthesis of the aniline itself. After completing the synthesis of HN[R]ArMe using the procedure described in the lab manual, the students were given several different variations to optimize the procedure. The students goal was to obtain the highest yield and purity with the least amount of waste. In addition, different procedures for the work up and purification of the reaction mixtures were examined to determine the simplest method to obtain pure material.

A.2.1 Optimization of the Synthesis of HN[R]ArMe

Each of the five groups of students was given different reaction condition variables with which to experiment. These variables included reaction temperature, addition rate of pyrylium salt solution, concentration of acetonitrile and number of equivalents of tBuNH₂ used. The temperature of the reaction seemed to have little effect on the chemical yield. The yield was found to be slightly higher at 0 °C than at -40 °C or room temperature. A significant factor in determining yield and purity was the addition rate of the pyrylium salt solution. The slower the addition rate the greater the purity of the product produced. One of the most significant byproducts formed was bis(3,5-dimethylphenyl)tert-butyl amine. Presumably, this product was formed when HN[R]ArMe rather than tBuNH₂ added to the pyrylium salt. A second modification that greatly improved the yield and purity was to replace the triethylamine with excess tBuNH₂. Indeed, using six equivalents of tBuNH₂ improved the yield and the purity. Furthermore, it was found that the yield substantially decreased upon decreasing the amount of acetonitrile used in a given scale reaction. Finally, a variety of procedures were examined for the purification of the compound. The work up procedure in the laboratory manual consisted of removing acetonitrile, performing
an aqueous/organic workup with CH₂Cl₂, and drying and concentrating the organic layer. However, it was found that petroleum ether was also a suitable solvent for the aqueous/organic extraction, and this change eliminated the use of halogenated solvents in the procedure. Several different techniques were tried for the further purification of the crude material, these included recrystallization of hydrochloride salt of HN[R]ArMe and running the crude solution of HN[R]ArMe through a column of alumina. These techniques did not work well, and it was determined that the best purification method was distillation. Vacuum distillation works very well on a large scale, but can be more problematic on a smaller scale.

While the synthesis of HN[R]ArMe was being optimized, a final group of students explored the possibility of using this synthetic route to form a deuterated ligand. In this procedure the deuterium is incorporated into the aryl methyl groups rather than the tert-butyl group, as in the procedure shown in Fig 1A. The deuterated compound is formed by refluxing the pyrillium salt in D₂O. The aniline is then synthesized using an analogous procedure to that for the synthesis of the undeuterated aniline. While most of the deuterium is incorporated into the aryl methyl groups, it does appear that some deuterium is incorporated into the aromatic ring.

After these tests were complete, the students met to develop an optimized procedure for the synthesis of this ligand. The synthetic procedure included doing the reaction at 0 °C with 6 equivalents of tBuNH₂ in 250 mL of acetonitrile on a 40 mmol scale using an 80 minute addition time. All five groups of students ran this procedure and determined the yield and purity of the crude product by GC/MS. The obtained results varied from 88-97 % yield, with a crude purity of 95% of higher.

A.2.2 Attempt at Waste Reduction on Pyrylium Salt Synthesis

One concern that was raised in the further development and scale up of this procedure was the large amount of waste that was generated in the synthesis of the pyrylium salt. The solvent for the reaction is 10 equivalents of acetic anhydride, which forms a large amount of acidic waste. Therefore, the second set of students was given the
task of trying to reduce the waste in the pyrylium salt synthesis. Several different procedures for the synthesis of the pyrylium salt were examined. These variations included reducing the number of equivalents of acetic anhydride used and using starting materials other than 4-hydroxy-4-methyl-2-pentanone. However, in each of these cases the decrease in yield outweighed the reduction in waste.

A.2.3 Scale up of HN[R]ArMe Synthesis

Given the success in the pyrylium salt methodology for the generation of HN[R]ArMe, it was of interest to use this procedure on a larger scale. Two changes were made for the large scale procedure. First, on large scale it was easier to do the addition at room temperature than to use a large ice bath. Secondly, it was found that the acetonitrile concentration was not that important, and it was feasible to increase the concentration up to the limit of the solubility of pyrrilium salt in acetonitrile. Therefore, while the scale was increased by 14.3 times, the amount of solvent was only increased by 8 times. Using this procedure and distilling the product under vacuum led to a 64% yield HN[R]ArMe. The higher yields obtained by the students were crude yields before distillation, with the purity being determined by GC/MS.

A.2.4 Synthesis of Mo(N[R]ArMe)₃ from the Aniline

The third group of students was able to duplicate the synthesis of HN[R]ArMe and proceed with the synthesis of Mo(N[R]ArMe)₃. While an error on the stoichiometry for the addition of BuLi first caused some problems, when this was corrected the students were able to synthesize (Et₂O)LiN[R]ArMe and Mo(N[R]ArMe)₃.

The following year this experiment was repeated. There were 12 groups of students over the course of the semester. In all cases the students were able to synthesize HN[R]ArMe and Mo(N[R]ArMe)₃. The most significant trouble that the students had was the crystallization of Mo(N[R]ArMe)₃ under vacuum. In some cases the ¹H NMR spectrum that the students obtained of Mo(N[R]ArMe)₃ appeared to have a greater portion of (µ-N₂)[Mo(N[R]ArMe)₃]₂ than Mo(N[R]ArMe)₃. Theo Agapie repeated the scaled-up ligand synthesis procedure and obtained essentially the same results. The
yield he obtained was 63 \% instead of 64\%.

A.3 Conclusions

In this experiment, the students were first able to optimize a procedure for the synthesis of HN[R]Ar_{Me} that has since been employed in the research laboratory. This experiment therefore demonstrates a potential symbiotic relationship between the research laboratory and the undergraduate laboratory.

A.4 Experimental Procedures

A.4.1 Synthesis of 2,4,6 trimethyl pyrylium tetrafluroborate

A 2 L, 2 necked flask was charged with a stir bar and acetic anhydride (1 kg, 9.8 mol, 10 equiv). 4-hydroxy-4-methyl-2 pentanone (122 mL, 0.98 mol, 1 equiv) was added over 5 min and allowed to stir 10 min. HBF_{4} (127 mL, 48 \% solution in water, 0.97 mol, 1 equiv) was then added via dropping addition funnel over a period of 75 min. This addition rate maintained the internal temperature at about 80 °C. After addition was complete, the solution was heated to 80 °C for an additional 1 hr and then allowed to cool. It was diluted with diethyl ether (200 mL), and the solid was collected by vacuum filtration, washed with diethyl ether (800 mL) and dried under vacuum to give the pyrylium salt (120 g, 0.57 mol, 59 \%) as an off-white solid. \textsuperscript{1}H NMR (CD\textsubscript{3}CN) δ 2.68, 2.80, 7.72

A.4.2 Synthesis of HN[R]Ar_{Me}

A 4 L flask was charged with stir bar, tert-butyl amine (360 mL, 3.42 mol, 6 equiv), and acetonitrile (200 mL). The flask was purged with argon. Meanwhile, the pyrylium salt (120 g, 0.57 mol, 1 equiv) was dissolved in acetonitrile (1.8 L). The solution was added dropwise over 10 hr. The reaction was concentrated, and the residue was partitioned between water (400 mL) and petroleum ether (800 mL). The organic layer was concentrated and distilled under vacuum (80 °C) to give N-tert-butyl-3,5-dimethylaniline (65 g, 0.37 mol, 64 \%) as a light yellow oil with a \textsuperscript{1}H NMR spectrum
that matches the literature.

A.5 Acknowledgements

This appendix deserves a special set of acknowledgments. This work would not have been possible without many people. Most of all, Dr. Mircea Gheorghiu developed the plans to implement the Mo(N[R]ArMe)₃ synthesis and worked on the pyrylium salt route to HN[R]ArMe before the students even came into the lab. Daniel Kramer TA'd the lab with me the first year, and spent countless hours helping the students with the different ligand synthesis procedures. Fran Stephens was the other TA the second year, and also spent many hours making sure that the experiment worked. Finally, all of the 5.33 students in both classes showed much enthusiasm for experiments and much patience while we worked out the kinks.
Appendix B

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