Synthesis and Reactivity of Molybdenum Organometallic Complexes Supported by Amide Ligands

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Our eyesight is a test to see if we can see beyond it.

Matter is here as a test for our curiosity.

Examine the nature of everything you observe.

-Waking Life

For my amazing family.

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Thesis Supervisor: Richard R. Schrock

Title: Frederick G. Keyes Professor of Chemistry

Abstracts

Chapter 1. Synthesis and Reactivity of Molybdenum Alkyl Complexes Supported by a Diamidoamine Ligand

The synthesis of a new diamidoamine ligand, $CH_3N[CH_2CH_2NH(3\text{-}(CF_3)C_6H_4)]_2$ (H_2**L**) is reported. Molybdenum complexes of the type X[**L**$MoCl_3$] (X = Et_3NH, Bu_4N) are readily synthesized as purple air and moisture sensitive crystalline solids. They may be alkylated by Grignard reagents to yield the monoalkyl complex **L**Mo(Cl)(CH_2CMe_3), the alkylidyne complex **L**Mo($CCMe_3$)(CH_2CMe_3) *via* α,α – elimination of dihydrogen, and the stable complex **L**Mo(CH_2TMS)$_2$ (TMS = $SiMe_3$). **L**Mo(CH_2TMS)$_2$ is readily oxidized by cyclohexene sulfide and hexachloroethane to yield, initially, molybdenum alkylidenes that readily undergo decomposition reactions to the bridging sulfide complex {**L**MoS}$_2$ and [**L**Mo(CTMS)Cl]$_2$, respectively. However, the alkylidene complex **L**Mo(CHTMS)(η^2 – MeCCMe) may be isolated if **L**Mo(CH_2TMS)$_2$ is heated in the presence of five equivalents of 2-butyne. It is a rare example of an alkylidene and alkyne in the coordination sphere of a group six metal. The relationship between oxidation and alkyne binding is discussed.

Chapter 2. Early Transition Metal Pyrrolyl Complexes: Structure, Spectroscopy, Hapticity, and Fluxional Processes.

A review of group 4, 5,and 6 transition metal pyrrolyl complexes is presented. The focus is on the unique bonding and dynamic processes that the pyrrolyl (and related ligands) can undergo. It is concluded that η^1 bound pyrrolyl ligands are poor π donors.

Chapter 3. Synthesis and Characterization of Molybdenum Imido Alkylidene Bis(amide) Complexes

The synthesis of bis(amide) complexes $Mo(NR)(CHR')(X)_2$ (R = Ar, Ad, 2,6-Br_2-4-MeC_6H_2; X = N(*t*-Bu)Ar', NC_4H_4) from the bis(triflate) complexes $Mo(NR)(CHR')(OTf)_2(DME)$ (OTf = trifluoromethanesulfonate, DME = 1,2-dimethoxyethane) is reported. These complexes are of interest as potential precursors for the *in situ* generation of active and enantioselective metathesis catalysts. The *tert*-butyl anilide complexes are found to be unreactive towards enantiopure diols. The bis(pyrrolyl) complexes exist in rapid equilibrium between a dimeric form $[Mo(NR)(CHR')(NC_4H_4)_2]_2$ and one in which all pyrrolyl resonances are equilibrating rapidly. The nature of the bis(pyrrolyl) complexes was interrogated by variable temperature ^1H and ^{13}C NMR for R = Ar and Ad. The dimeric form was confirmed through an x-ray structural study of $\{Mo(NAr)(syn\text{-}CHCMe_2Ph)(\eta^5\text{-}NC_4H_4)(\eta^1\text{-}NC_4H_4)\}\{Mo(NAr)(syn\text{-}CHCMe_2Ph)(\eta^1\text{-}NC_4H_4)_2\}$.

Chapter 4. Reactivity of Molybdenum Imido Alkylidene Bis(pyrrolyl) Complexes

The Lewis amphoteric nature of the bis(pyrrolyl) complexes reported in chapter 3 is examined by demonstrating that these complexes react with both trimethylphosphine (at the molybdenum center) and $B(C_6F_5)_3$ (at a η^5 pyrrolyl nitrogen). A structure of a trimethylphosphine adduct is reported. The bis(pyrrolyl) complexes are found to serve as excellent precursors for the *in situ* generation of olefin metathesis catalysts at room temperature and millimolar concentration. Furthermore, catalysts not accessible *via* traditional routes may now be accessed from bis(pyrrolyl) precursors. The bis(pyrrolyl) complexes also react with simple olefins such as ethylene and isobutylene to yield what are proposed to be a bimetallic dimer $[Mo(NAr)(NC_4H_4)_2]_2$ and a 2-propylidene complex *via* olefin metathesis. The impact of *in situ* synthesis on *syn* and *anti* isomer ratios is discussed as is reactivity with protic reagents other than alcohols.

Biographical Note

Adam Scott Hock was born in the mid-morning on February 24th, 1979 in Bloomsburg, Pennsylvania. Scott and Suzanne Hock brought Adam home several days later. He grew up in the rural area outside of the town of Bloomsburg, where he made acquaintance with the beauty of nature. Once enrolled in the Central Columbia school district and a proud Blue Jay, he commenced in his education. Generally a good student, Adam was always interested in the details that seemed to be left out of his science classes. His parents rapidly realized that they should invest in a library card and teach him to always search out his own answers. This eventually led to a stimulating academic life outside of the classroom, occasionally involving household chemicals during his early years.

It was not until high school chemistry, under the guidance of Mr. Brett Criswell, where Adam truly began to understand the vast scope of "aesthetically pleasing" chemical transformations the world had to offer. As a member of the Chemistry for Kids Club, he was able to share some of the joy that such a knowledge can offer (with proper safety equipment present, of course). He still hopes that those demonstrations helped to motivate another generation of future chemists.

In the fall of 1997, Adam moved from Blue Jay to Blue Hen, beginning studies as an undergraduate chemistry major at the University of Delaware. In the winter of his freshman year, under the guidance of Professor Arnold Rheingold, he was exposed to the beauty lying in the depths of the main group of the periodic table. That exploration was continued over the next four years. He also found the time to teach himself guitar, become completely addicted to coffee and conversation, and to learn a few things about cooking on a budget.

There was no question in his mind that Adam wanted to continue his pursuit of chemical knowledge, and he was very pleased to begin pursuing his doctoral degree in inorganic chemistry at the Massachusetts Institute of Technology in fall of 2001. Adam was fortunate to be accepted into Professor Richard R. Schrock's group, where he was given the chance to explore fundamental reactivity as well as solve practical problems in organometallic synthesis.

Adam has many interests and some of his favorites include conversation, chemistry, music, cooking, art, and catching an occasional football, baseball, or soccer game.

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List of Abbreviations Used in Text

Ad = 1-Adamantyl

Anal. = combustion analysis

anti = alkylidene species with an alkyl group facing away from an imido ligand

Ar = 2,6-di*iso*propylphenyl (2,6-*i*-$Pr_2C_6H_3$)

Ar' = 2,6-dimethylphenyl (2,6-$Me_2C_6H_3$)

Ar'' = 3,5-dimethylphenyl (3,5-$Me_2C_6H_3$)

Ar^{CF3} = 3-trifluromethylphenyl (3-$(CF_3)C_6H_4$)

Ar^{Cl2} = 2,6-dichlorophenyl (2,6-$Cl_2C_6H_3$)

Å = Angstrom (10^{-10} m)

a = unit cell axis a

atm = atmosphere

a.u. = atomic units

α = position one-atom away, unit cell angle α

Bu = butyl ($CH_2CH_2CH_2CH_3$)

b = broad, unit cell axis b

β = position two atoms away, unit cell angle β

Cp = cyclopentadienide anion ($C_5H_5^-$)

c = unit cell axis c

cal = calories

calcd = calculated

cb = carbazole anion (9-azafluorene)

cm^{-1} = wavenumber

°C = degrees Celsious

D = density

DFT = Density Functional Theory

DME = 1,2-dimethoxyethane

DMP = 2,5-dimethylpyrrolide

d = doublet, days, deuterated

d^n = electron count n of a transition metal in the d-orbitals

dia = diamagnetic

Δ = difference

δ = delta (Nuclear Magnetic Resonance chemical shift)

E = energy

Et = ethyl (CH_2CH_3)

e = electron

ee = enantiomeric excess

equiv = equivalents

eqn. = equation

eV = electron volts (23.060 kcal/mol)

F = crystallographic structure factor

F(000) = number of electrons in the unit cell

fw = formula weight

GoF = Goodness of Fit (also abbreviated S)

g = grams

γ = unit cell angle γ

H = enthalpy

HOMO = Highest Occupied Molecular Orbital

Hz = Herz (cycles per second, S^{-1})

h = hours

i-Pr = isopropyl ($CH(CH_3)_2$)

J = Joules

^nJ = n^{th} bond NMR coupling constant

K = degrees Kelvin

k = kilo (10^3)

L = liters

LUMO = Lowest Unoccupied Molecular Orbital

M = transition metal (defined when applicable), molar (moles/L)

Me = methyl (CH_3)

Mes = mesityl, 2,4,6-trimethylphenyl (2,4,6-$Me_3C_6H_2$)

MO = Molecular Orbital

m = multiplet, meters, milli (10^{-3})

m = *meta* position of a phenyl group (3-substitution)

min = minutes

mol = moles

μ = x-ray absorption coefficient (crystallography)

NMR = Nuclear Magnetic Resonance

Np = Neopentyl ($CH_2C(CH_3)_3$)

n = nano (10^{-9})

OTf = trifluoromethanesulfonate ($[OSO_2CF_3]^-$); see also "triflate"

o = *ortho* position of a phenyl group (2-substitution)

Ph = phenyl (C_6H_5)

Pr = propyl ($CH_2CH_2CH_3$)

Py = pyridine (NC_5H_5)

p = *para* position of a phenyl group (4-substitution)

ppm = parts per million

para = paramagnetic

q = quartet

rt = room temperature (typically ~23 °C)

R = residual value (crystallography)

S = singlet electronic state

S = entropy, total sum of electronic spin quantum numbers

SOMO = Singly Occupied Molecular Orbital

s = single peak (singlet)

sec = seconds

syn = alkylidene species with an alkyl group facing towards an imido ligand

σ = sigma, NMR shielding tensor

Σ = sum

T = temperature, triplet electronic state

THF = tetrahydrofuran

TMP = 2,3,4,5-tetramethypyrroliide

tmeda = tetramethylethylenediamine (N,N,N′,N′-tetramethyl-1,2-diaminoethane)

tol = toluene (methylbenzene, C_7H_8)

triflate = trifluoromethanesulfonate ($[OSO_2CF_3]^-$); see also "OTf"

TS = transition state

t-Bu = *tertiary*-butyl (*tert*, $C(CH_3)_3$)

V = volume

VT = variable temperature

w = weighted

Z = number of molecules in the unit cell

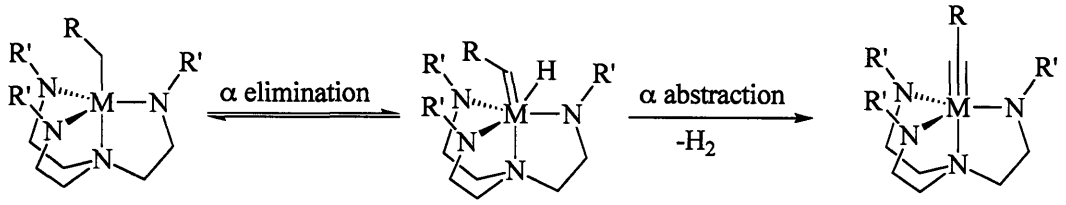
Chapter 1

Synthesis and Reactivity of Molybdenum Alkyl Complexes Supported by a Diamidoamine Ligand

A portion of this work has appeared in print:
Cochran, F. V., Hock, A. S., and Schrock, R. R.
Organometallics **2004**, *23*, 665.

Introduction

Utilization of methods involving redox processes to create[1,2,3,4] or induce[5,6] formation of metal-carbon multiple bonds has experienced a large expansion. One example is the intramolecular oxidation in which two α hydrogen atoms are expelled as dihydrogen with concomitant formation of a metal-carbon triple bond.[2] This reaction has only been documented in two systems, the triamidoamine system $[(RNCH_2CH_2)_3N]^{3-}$ (R = TMS,[2a] C_6F_5,[2b] 2,2',4,4',6,6'-hexa*iso*propyl-3,5-terphenyl[2d]) and the diamidoamine system $[(RNCH_2CH_2)_2NMe]^{2-}$ (R = C_6F_5,[4a] 3,4,5-$C_6F_3H_2$,[4b] 3,5-$Cl_2C_6H_3$[4c]). The molybdenum triamidoamine platform has provided a unique ability to reduce dinitrogen to ammonia using protons and electrons at ambient temperature and pressure.[17] This is due to the ability of the triamidoamine(molybdenum) fragment to stabilize a wide variety of molybdenum nitrogen bonds ranging from triple to dative to Dewar-Chatt-Duncanson donor-acceptor type.[7] It is not surprising that group 6 triamidoamine complexes also have a rich organometallic chemistry. In 1994 it was first reported[8] that the tungsten complex $[N3N]WCH_3$ ($[N3N] = [(TMSNCH_2CH_2)_3N]^{3-}$) spontaneously evolved molecular hydrogen to form the alkylidyne complex [N3N]WCH. This previously unprecedented transformation is believed to occur *via* an intermediate alkylidene hydride on the basis of isolation and structural characterization of $[N3N]W(=CC_4H_8)(H)$.[9] The proposed mechanism of α, α –elimination is shown in eqn 1.1. Through detailed labeling studies it was established that in species containing β protons, the α-elimination process occurs approximately a million times more rapidly that the more documented and studied β elimination process.[2a,9]



(1.1)

M = Mo, W
R= *t*-Bu, $SiMe_3$
R' = $SiMe_3$, C_6F_5

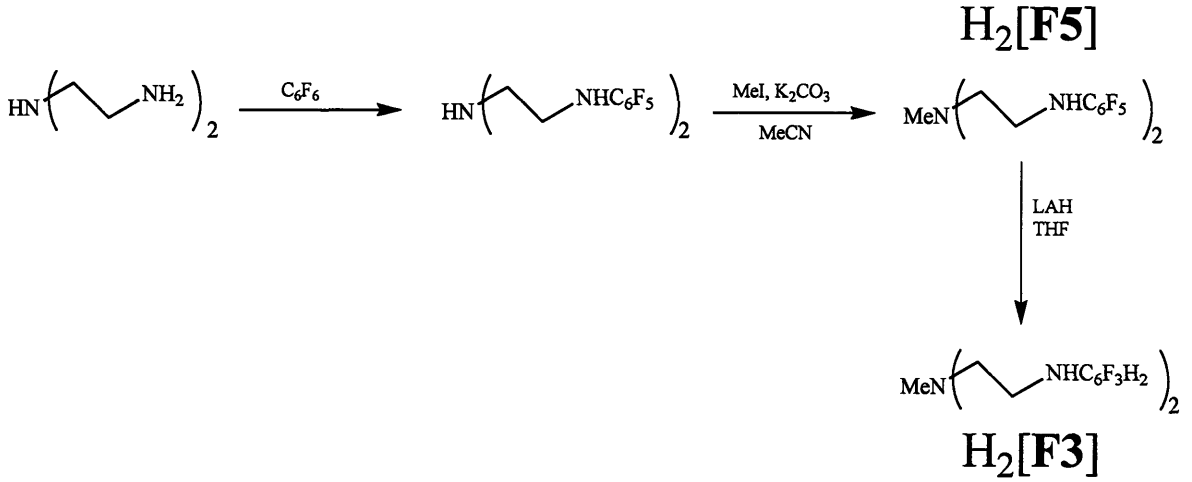
During early studies of dinitrogen functionalization in the triamidoamine platform, several metal complexes were isolated in which various ligand activation reactions had produced a diamidoamine ligand.[10,11,12,13] Triamidoamine ligand degradation in tantalum chemistry was found to result in triamido ligands via C-N cleavage at the amine donor.[14]

At the time these results and other reports of diamido-donor supported dinitrogen chemistry[15,16] motivated rational design and synthesis of diamidoamine systems. Since that time, dinitrogen reduction has been realized[17] and continues to be explored[18] in the above mentioned triamidoamine system. Attempts to functionalize dinitrogen in a group 6 diamidoamine platform have been abandoned due to the success of the triamidoamine system. However the organometallic chemistry of these systems has proven very interesting. Work in group 6 diamido-donor complexes has previously involved the perfluorophenyl ligand $[(C_6F_5NCH_2CH_2)_2NMe]^{2-}$ (**[F5]**) and the related ligand $[(3,4,5\text{-}F_3C_6H_2NCH_2CH_2)_2NMe]^{2-}$, (**[F3]**).[4a-c] Tantalum and molybdenum complexes supported by the ligand $[(3,5\text{-}Cl_2C_6H_3NCH_2CH_2)NMe]^{2-}$ ($\mathbf{Ar_{Cl}}$)[4d] were also surveyed, and the reactivity examined proved similar to the $[(3,4,5\text{-}F_3C_6H_2NCH_2CH_2)_2NMe]^{2-}$ ligand. Electron-withdrawing aryl groups were found to be critical to the high-yield synthesis of group 6 metal starting materials, the "-ate" complexes $\{Et_3NH\}\{$**[F5]**$MCl_3\}$ and $\{Et_3NH\}\{$**[F3]**$MCl_3\}$. The **[F3]** complexes were smoothly alkylated by neopentylmagnesium chloride and rapidly yielded the alkylidyne/alkyl species **[F3]**$M(CCMe_3)(CH_2CMe_3)$. The fact that the molybdenum dineopentyl species was not stable at room temperature showed that the diamidoamine system is much more reactive than the corresponding triamidoamine system, which required extended heating to produce the molybdenum neopentylidyne. The smaller trimethylsilylmethyl alkyl also evolved dihydrogen at room temperature to yield an alkylidyne/alkyl species in the tungsten system. However, the **[F3]**$Mo(CH_2SiMe_3)_2$ complex was stable in the molybdenum system. This was not surprising, given the smaller steric size of the alkyl.[19] Upon thermolysis of solutions of **[F3]**$Mo(CH_2TMS)_2$ evolution of tetramethylsilane rather than dihydrogen was observed, and the bridging alkylidyne complex $\{$**[F3]**$Mo(CTMS)\}_2$ was isolated.[4b] The divergent reactivity was a surprise, and was confirmed by the spectroscopic characterization

of the trapped alkylidene **[F3]**Mo(MeCCMe)(CHTMS). In order to probe the source of the divergent reactivity and to further the understanding of reduced molybdenum alkyls in general, further study of diamidoamine molybdenum alkyls was carried out.

1.1 Ligand Synthesis

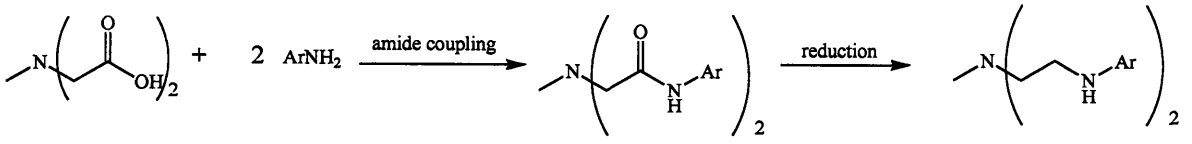
The diamidoamine ligands H_2**[F5]** and H_2**[F3]** are synthesized as shown in scheme 1.1 below. The main drawback in the synthesis and study of complexes containing the ligands $[\mathbf{F5}]^{2-}$ and $[\mathbf{F3}]^{2-}$ is that the ligand syntheses are not readily scaled up.



Scheme 1.1. Synthesis of H_2**[F5]** and H_2**[F3]**.

The methylation of the central nitrogen amine donor proceeds poorly on large scales.[20] Therefore, a new route to the known ligands or a new ligand was sought.

In order to obviate the need for the methylation step, routes employing the readily available[21] acid, $MeN(CH_2COOH)_2$, were explored. Prior to adoption of palladium-catalyzed C-N bond formation for the synthesis of aryl [N3N] complexes,[11] amide



Scheme 1.2. Modified synthetic strategy for synthesis of diamidoamine ligands.

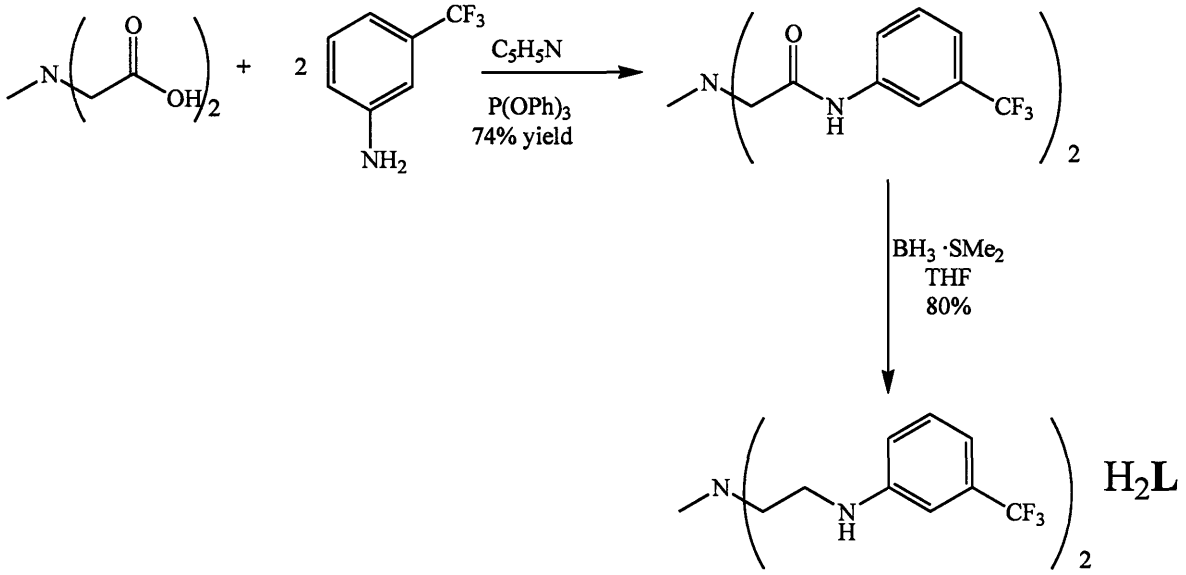
coupling followed by reduction of the carbonyl was employed and the diamidoamine variation is shown in scheme 1.2. This route suffered from low yields and was abandoned in favor of palladium coupling.[11] Triphenylphosphite-mediated amide coupling[22] has been shown to readily produce high yields in cases where the conventional reagents dicyclohexylcarbodiimide[23] (DCC) and acid-chloride amide couplings fail. Reduction of the amide is readily accomplished using typical reagents such as lithium aluminum hydride or borane reagents.[23] Verkade has applied this approach to the synthesis of enantiopure amino-acid derivatives of triamidoamine ligands.[24]

Perfluoroaniline did not undergo amide coupling in these conditions and only unreacted aniline was observed in ^{19}F NMR of reaction mixtures. Presumably, pentafluoroaniline is too poor a nucleophile to react with the activated phosphorous ester produced in the reaction conditions. Dr. Pia Lopez also found that 2,6-dichloroaniline did not undergo coupling using these conditions.[25] Since 3,4,5-trifluoroaniline is not readily available, a new ligand was designed that might be amenable to this synthetic route.

The following observations guided the search for a modified ligand: 1) syntheses of metal complexes are greatly facilitated by first making an adduct of the free amine ligand and metal starting material *in situ*, followed by addition of base,[11] and 2) an electron-poor amine adduct may be deprotonated by a relatively weak base that is convenient to handle, such as triethylamine.[4,26] This is important to prevent reduction of the metal center during installation of the ligand, a frequent problem in transition metal chemistry in relatively redox-active oxidation states.[27,28] Fluorinated ligands satisfy these criteria and also provide the powerful diagnostic handle of ^{19}F NMR. Use of ^{19}F NMR allows monitoring of paramagnetic products *via* ^{19}F NMR and may be performed on reaction mixtures without deuterated solvent. 3-Trifluoromethyl substitution was targeted as a potentially useful target and the new ligand $CH_3N[CH_2CH_2NH(3\text{-}(CF_3)C_6H_4)]_2$ (H_2**L**) was synthesized. The CF_3 group is a sharp singlet in ^{19}F NMR spectra due to its large distance from the paramagnetic metal center.

The aniline $3\text{-}CF_3C_6H_4NH_2$ is readily available and inexpensive. 3-Trifluoromethylanilline readily undergoes amide coupling with methylimidodiacetic acid to produce the corresponding amide in good yield on a half mole scale (Scheme 1.3). Reduction with lithium aluminum hydride (LAH) has been reported to attack the benzylic

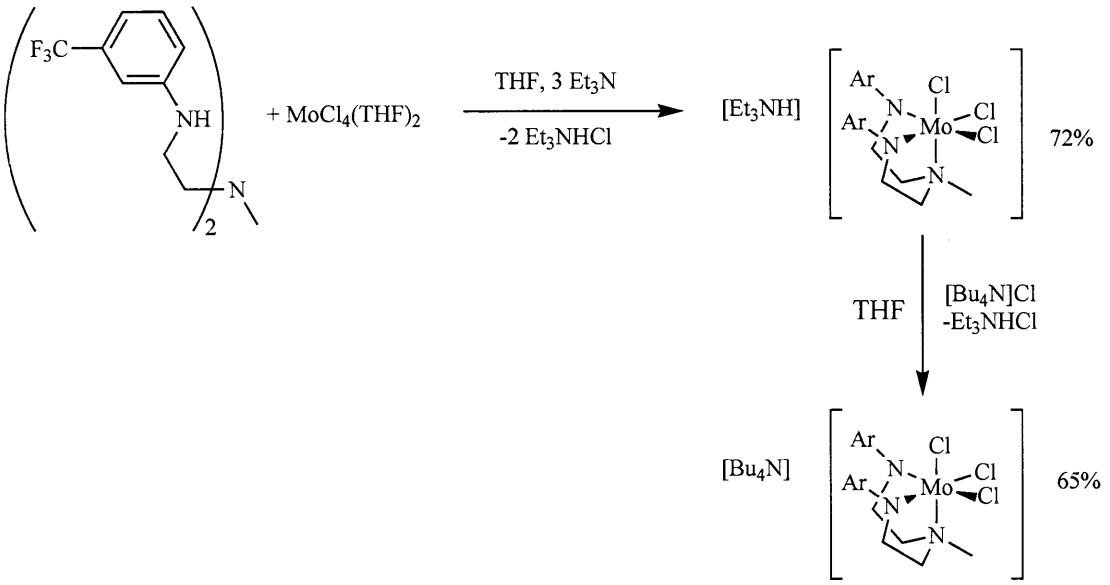
fluorides,[29] thus borane-dimethyl sulfide[30] was chosen as a reductant. H_2**L** is isolated as a colorless oil in high yield from the reaction.



Scheme 1.3. Synthesis of $CH_3N[CH_2CH_2NH(3\text{-}(CF_3)C_6H_4)]_2$ (H_2**L**).

1.2 Synthesis of Metal Precursors.

Addition of solid $MoCl_4(THF)_2$[31] to a THF solution of H_2**L** produces a red solution, believed to contain an adduct of the free amine ligand and $MoCl_4$.[4,10] Addition of triethylamine immediately produces a precipitate and a purple solution of $[Et_3NH][$**L**$MoCl_3]$. Synthesis of $[Et_3NH][$**L**$MoCl_3]$ and $[Bu_4N][$**L**$MoCl_3]$ is summarized Scheme 1.4. After filtration through Celite, $[Et_3NH][$**L**$MoCl_3]$ may be crystallized from THF/pentane. The tetrabutylammonium salt may be synthesized *via* salt exchange with tetrabutylammonium chloride in THF. Alternatively, a crude solution of $[Et_3NH][$**L**$MoCl_3]$ may be filtered and the filtrate treated with excess tetrabutylammonium chloride to give $[Bu_4N][$**L**$MoCl_3]$. Both ammonum salts are dark purple, air and moisture-sensitive, paramagnetic solids. They are stable indefinitely in an inert atmosphere and remain unchanged in C_6D_6 at 80 °C for days when monitored by ^{19}F and ^1H NMR.



Scheme 1.4. Synthesis of $[Et_3NH][\mathbf{L}MoCl_3]$ and $[Bu_4N][\mathbf{L}MoCl_3]$.

A structural determination was pursued to see if the solid state structure of $[Bu_4N][\mathbf{L}MoCl_3]$ differed from the previously characterized triethylammonium salts and to ensure that the ligand had been installed intact. Activation of carbon – fluorine bonds by molybdenum has previously been observed in the diamidoamine system. An attempt to prepare $[\mathbf{F5}]Mo(NMe_2)_2$ from $H_2[\mathbf{F5}]$ and $Mo(NMe_2)_4$ resulted in $[(C_6F_4(NMe_2)NCH_2CH_2)_2NMe]MoF_2$, in which the dimethylamido ligands have inserted into the *ortho* carbon – fluorine bond.[4a] Activation of 3-trifluromethyl groups during ligation to molybdenum has also been observed in the reaction of $LiN(t\text{-}Bu)(3\text{-}(CF_3)C_6H_4)$ with *mer*-$MoCl_3(THF)$.[32] In this case, the molybdenum(V) complex $Mo[N(t\text{-}Bu)(3\text{-}(CF_3)C_6H_4)]_3(F)_2$ was isolated in low yield. The only source of fluoride is the trifluoromethyl group. $Mo[N(t\text{-}Bu)(3\text{-}(CF_3)C_6H_4)]_3(F)_2$ was not fully characterized

An ellipsoid plot of $[Bu_4N][\mathbf{L}MoCl_3]$ is shown in Figure 1.1 below. The bond lengths and angles are almost identical to the previously reported[4] $[Et_3NH][\mathbf{F5}MoCl_3]$ and $[Et_3NH][\mathbf{F5}WCl_3]$ complexes, with the diamidoamine ligand oriented in a *fac* geometry about the pseudo octahedron. Apparently there is not much perturbation of this structure upon altering the ligand from $[\mathbf{F5}]^{2-}$ to the trifluoromethyl substituted $\mathbf{L}^{2-}$ ligand.

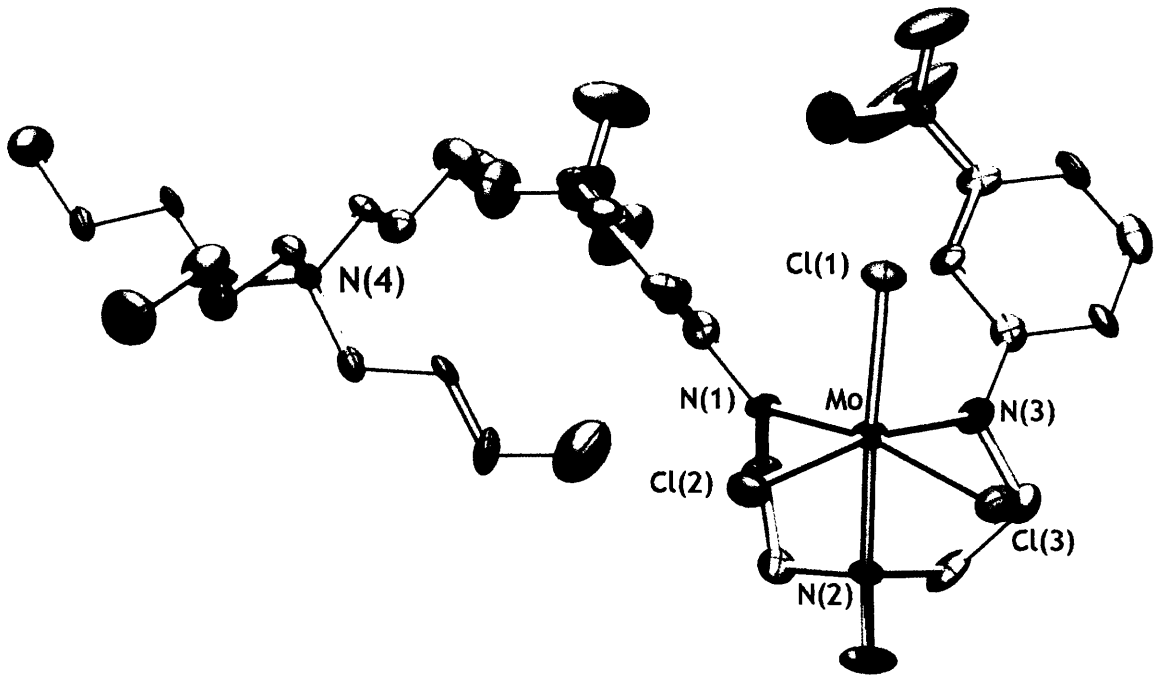


Figure 1.1 Solid-state structure of $[Bu_4N][LMoCl_3]$. Thermal ellipsoids are at 50% and hydrogen atoms have been omitted for clarity.

Table1.1. Selected bond lengths [Å] and angles [°] for $[Bu_4N][LMoCl_3]$.

Mo – N(1) 2.003(8)	Mo – Cl(1) 2.377(3)
Mo – N(2) 2.250(8)	Mo – Cl(2) 2.446(3)
Mo – N(3) 1.995(9)	Mo – Cl(3) 2.496(3)
N(1) – Mo – N(2) 81.0(3)	N(2) – Mo – Cl(1) 172.9(3)
N(1) – Mo – N(3) 96.2(3)	N(2) – Mo – Cl(2) 93.2(3)

Numerous attempts to obtain the salt-free "**L**$MoCl_2$" or solvated species failed. $[Bu_4N][$**L**$MoCl_3]$ does not react with PMe_3 (~10 eq., C_6D_6, 80 °C, 3d) and is recovered unchanged from neat PMe_3 after addition of several volumes of pentane, filtration, and removal of the phosphine and solvent. $[Bu_4N][$**L**$MoCl_3]$ and $[Et_3NH][$**L**$MoCl_3]$ also do not react with 2-butyne (~5 eq., C_6D_6, 80 °C, 8hr) and addition of butyl lithium to a solution of $[Et_3NH][$**L**$MoCl_3]$ in the presence of 5 equivalents of 2-butyne resulted in decomposition. (η^2-PhC≡CPh)$MoCl_4 \cdot Et_2O$[33] and H_2**L** were combined followed by addition of 2.1 equivalents of triethylamine, however, this resulted in formation of $[Et_3NH][$**L**$MoCl_3]$ and free diphenylacetylene. Nevertheless, we have found that $[Et_3NH][$**L**$MoCl_3]$ and $[Bu_4N][$**L**$MoCl_3]$ are excellent starting materials for the formation of bis(alkyl) molybdenum complexes.

1.3 Synthesis of Molybdenum Alkyl Complexes.

Treatment of $[Et_3NH][$**L**$MoCl_3]$ with two equivalent of neopentylmagnesium chloride in cold THF results in a lightening of the solution from purple to green. **L**$Mo(Cl)(CH_2CMe_3)$ may be isolated in good yield as a paramagnetic, air and moisture-sensitive crystalline solid. The ^{19}F resonance is found at -59.8 ppm. **L**$Mo(Cl)(CH_2CMe_3)$ does not evolve dihydrogen to yield an alkylidyne of the type **L**$Mo(CCMe_3)(Cl)$ at room temperature, though a related alkylidyne dimer $[$**L**$Mo(CTMS)Cl]_2$ has been prepared independently (*vide infra*). Thermolysis of a C_6D_6 solution at 80 °C for 36 hours yielded only a 75% conversion to unidentified decomposition products and no dihydrogen was observed. The crystal structures of [**F3**]$Mo(Cl)(CH_2CMe_3)$[4] and **L**$Mo(Cl)9CH_2SiMe_2Ph)$ *(vide infra)* show the alkyl group in the equatorial position of the pseudo trigonal bipyramid. If this is the solution phase geometry, it appears that this complex must first rearrange to give an axially-coordinated alkyl group in order to undergo α, α elimination to produce the alkylidyne. Regardless, other ill-defined pathways are the mode of reactivty of **L**$Mo(Cl)(CH_2CMe_3)$.

During attempts to purify the product of the reaction of three equivalents of $ClMgCH_2SiMe_2Ph$ with $[Et_3NH][$**L**$MoCl_3]$ in THF (an attempt to synthesize **L**$Mo(CH_2SiMe_2Ph)_2$) a very small quantity of purple crystals was obtained. Numerous

crystals were examined, but only one that diffracted well was found. This compound was found to be the monoalkyl complex **L**Mo(Cl)(CH_2SiMe_2Ph), which crystallized in the monoclinic space group *C2/c*. A reliable synthesis of this complex has not been developed, but the results of the diffraction study are reported and discussed here. A thermal ellipsoid plot (Figure 1.2) and selected structural parameters (Table 1.2) are listed below.

Figure 1.2. Structure of **L**Mo(Cl)(CH_2SiMe_2Ph), ellipsoids at 50% Hydrogen atoms have been omitted for clarity.

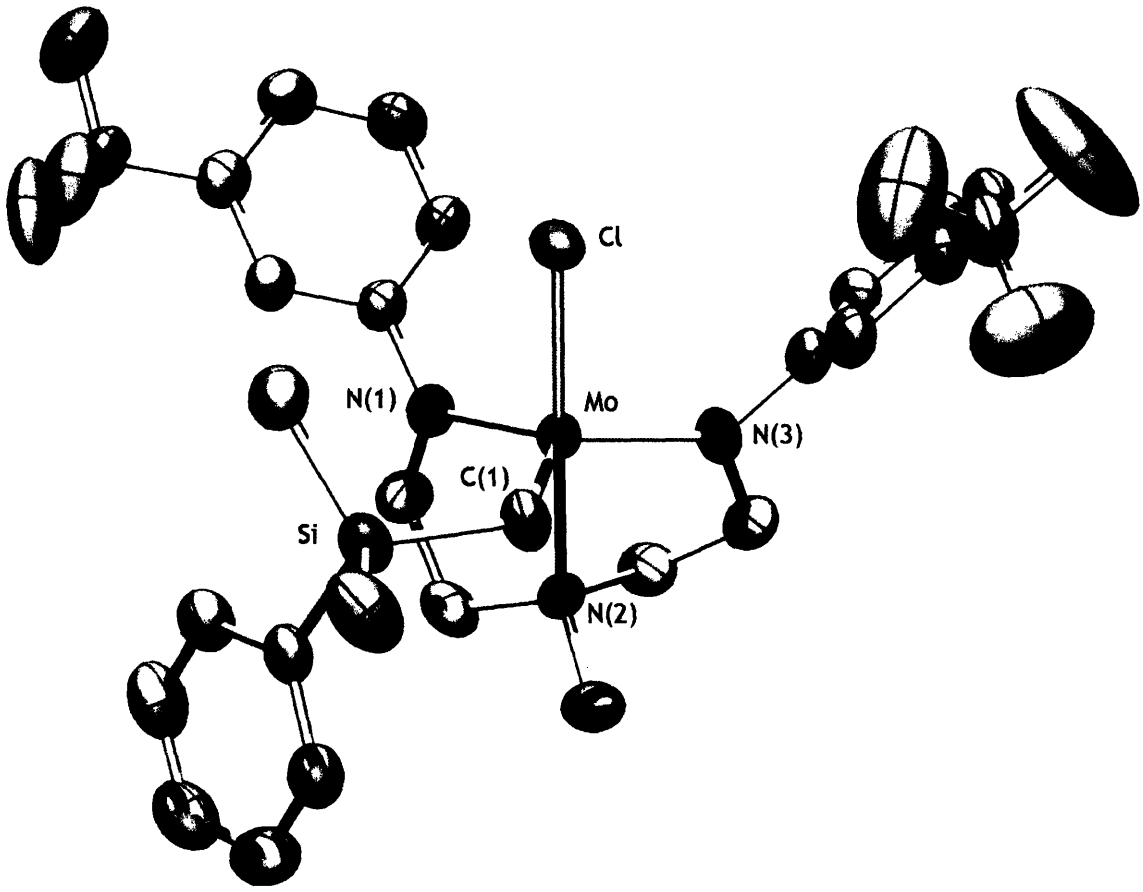


Table 1.2. Selected Bond lengths [Å] and angles [°] for **L**Mo(Cl)(CH_2SiMe_2Ph)

Mo – C(1)	2.136(5)	Mo – C(1) – Si	120.5(3)
Mo – Cl(1)	2.3934(13)	N(2) – Mo – Cl(1)	173.84(11)
Mo – N(1)	1.968(4)	N(1) – Mo – N(2)	79.45(16)
Mo – N(2)	2.220(4)	N(2) – Mo – N(3)	80.06(16)
Mo – N(3)	1.969(4)	N(1) – Mo – N(3)	123.33(18)

The Mo – Cl distance of 2.3934(13) Å is comparable but slightly longer than the axial Mo – Cl distance in [Bu_4N][**L**$MoCl_3$], **[F5]**Mo(Cl)(CH_2CMe_3), and **[Ar$_{Cl}$]**Mo(Cl)(CH_2CMe_3) (2.377(3), 2.3847(14), and 2.3881(8) Å, respectively[4]). The Mo – C(1) distance of 2.136(5) is statistically identical to that of **[Ar$_{Cl}$]**Mo(Cl)CH_2CMe_3,[4d] the equatorial methyl in **[F5]**$MoMe_2$, and **[F5]**Mo(Cl)(CH_2CMe_3) (2.137(3), 2.134(6), and 2.141(6) Å, respectively[4]). The amide-molybdenum bonds also show similar lengths. A more telling structural parameter is the N_{donor} — Mo — Cl angle, which deviates only 6.1° from linear, compared to 13.3° and 12.2° for **[F5]**Mo(Cl)(CH_2CMe_3) and **[Ar$_{Cl}$]**Mo(Cl)CH_2CMe_3 (For comparison, this angle is 7° in **[F3]**Mo($CCMe_3$)(CH_2CMe_3), where the alkylidyne carbon is smaller than a chloride ligand and allows its bulky *tert*-butyl group to point away from the other alkyl.). The change in the N_{donor} — Mo — Cl angle illustrates the well-known steric bulk of the neopentyl ligand compared to the longer carbon-silicon bond of neosilyl ligands.[19] Compared to a typical N_{donor} — Mo — Cl angle in TREN compounds (e.g. **[N3N]**$MoCl^2$) which is linear within 1-3°, it is evident that **[N2N]** compounds alleviate steric pressure by rotating the **[N2N]** ligand back from the bulky alkyl ligand, pushing the chloride ligand away from linear and into the space between the aryl groups. These structures show that two neopentyl ligands would provide a very congested coordination sphere about molybdenum. In the [N3N]WCH_2R system, bulkier R groups were correlated with faster rates of α, α – elimination.[2a]

If [Et_3NH][**L**$MoCl_3$] is treated with three equivalents of neopentylmagnesium chloride in THF the solution lightens to pale amber, and **L**Mo($CCMe_3$)(CH_2CMe_3) may be isolated in good yield as a yellow solid. The alkylidyne carbon resonates at 307.7 ppm in

benzene-d_6. This species is analogous to the previously reported **[F3]**Mo($CCMe_3$)(CH_2CMe_3),[4c] however it is important to establish that the new ligand system still supports α,α – elimination reactivity analogous to the previously isolated complexes.

Also analogous to the H_2**[F3]**,[4c] system, the paramagnetic dialkyl complex **L**Mo(CH_2SiMe_3)$_2$ can be prepared in 60% yield through addition of 3.1 equiv of (trimethylsilylmethyl)magnesium chloride to [Et_3NH][**L**$MoCl_3$] in THF at -78 °C. The ^{19}F resonance is observed at -55.8 ppm in benzene-d_6. Compound **L**Mo(CH_2SiMe_3)$_2$ is dark red, paramagnetic, and very air and moisture sensitive, properties that are very similar to those of **[F3]**Mo(CH_2SiMe_3)$_2$.

A "direct" route to **L**Mo(CH_2SiMe_3)$_2$ is also possible. It was noted that the formation of both [Et_3NH][**L**$MoCl_3$] and **L**Mo(CH_2SiMe_3)$_2$ is very clean, if the starting materials from which they are prepared are pure. Thus, addition of 4.1 equivalents of trimethylsilylmethyl magnesium chloride (or other alkylmagnesium reagent) to the crude mixture of [Et_3NH][**L**$MoCl_3$] and (Et_3NH)Cl proceeds smoothly to the desired bis(alkyl)molybdenum compound, as shown in eqn 1.2.

$$\mathbf{H_2L} + MoCl_4(THF)_2 \xrightarrow[2)\ 4.1\ RMgCl,\ -40^{o}C\ to\ RT]{1)\ 2.1\ Et_3N,\ THF,\ 30\ min} \mathbf{L}MoR_2 \qquad (1.2)$$

This method has also been successfully applied to the synthesis of **L**Mo(Cl)(CH_2CMe_3), **L**Mo($CCMe_3$)(CH_2CMe_3), and **L**Mo(CH_2SiMe_3)$_2$. This direct method to the dialkyl complexes is preferable for the saving of time and solvent, but does require that the starting materials be very clean in order to succeed in good yield.

Crystals of **L**Mo(CH_2SiMe_3)$_2$ were grown from a saturated pentane solution over the course of several months. An ellipsoid plot is shown in Figure 1.3. The molybdenum carbon bond lengths are almost identical to previously characterized **[F5]**$MoMe_2$[4]. The Mo – N(2) distance is comparable to **L**Mo(Cl)(CH_2SiMe_2Ph) and **[F5]**$MoMe_2$.[4a] The molybdenum – carbon bond lengths are comparable to **[F5]**$MoMe_2$, with the axial bond

Figure 1.3. Structure of **L**Mo(CH_2SiMe_3)$_2$, ellipsoids at 50% Hydrogen atoms have been omitted for clarity.

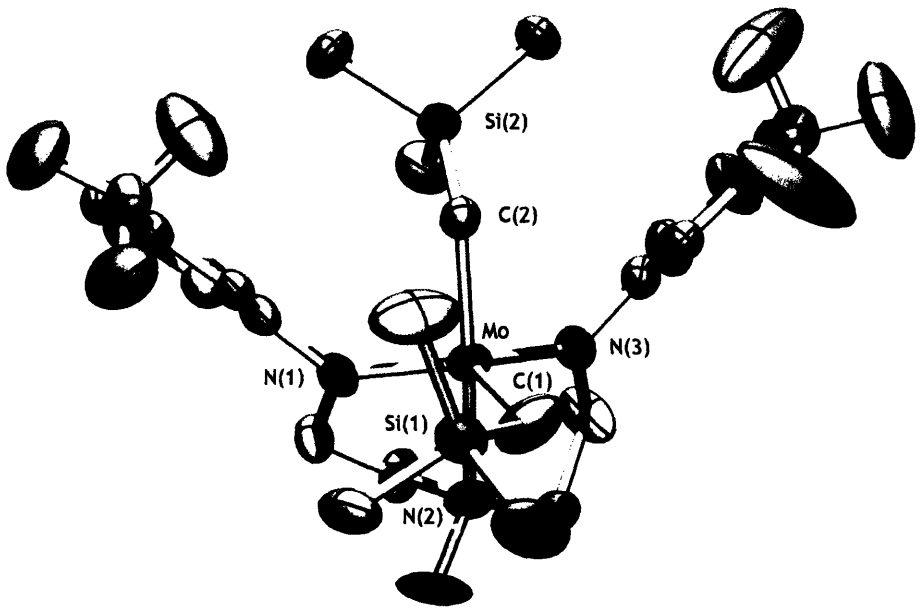


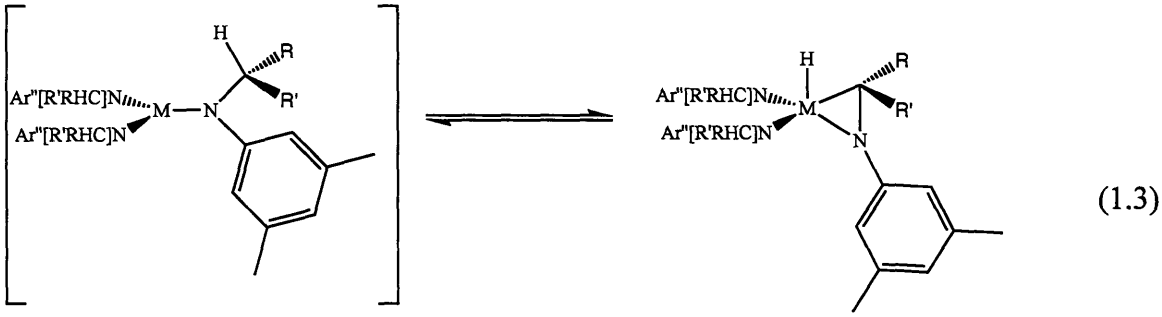
Table 1.3. Selected Bond lengths [Å] and angles [°] for **L**Mo(CH_2SiMe_3)$_2$.

Mo – N(1)	1.989(3)	N(2) – Mo – C(2)	170.20(9)
Mo – N(2)	2.320(2)	N(1) – Mo – N(2)	78.24(10)
Mo – N(3)	1.986(2)	N(2) – Mo – N(3)	77.94(9)
Mo – C(1)	2.226(8)	N(1) – Mo – N(3)	128.08(11)
Mo – C(2)	2.177(3)	N(1) – Mo – C(1)	125.9(2)

being slightly longer in both complexes. The N(2) – Mo – C(2) angle deviates from linearby 9.8°, intermediate between the angles of 6.1° in **L**Mo(Cl)(CH_2SiMe_2Ph) (vide supra) and 13.3° for **[F]**Mo(Cl)(CH_2CMe_3).[4a] With **L**Mo(CH_2SiMe_3)$_2$ in hand, reactivity studies were initiated to explore the fundamental chemistry of this relatively rare molybdenum(IV) dialkyl.

1.4 Reactivity of $LMo(CH_2SiMe_3)_2$

No products could be isolated upon thermolysis of $LMo(CH_2SiMe_3)_2$ in various solvents (benzene, acetonitrile, toluene, 60 °C to 100 °C, monitoring *via* ^1H and ^{19}F NMR). Apparently the mode of reactivity is complex as numerous ^{19}F peaks were always visible. However, varying amounts of tetramethylsilane observed in crude mixtures, not dihydrogen. Several attempts were made to address the possibility of an equilibrium between the proposed intermediate "$LMo(H)(CHSiMe_3)(CH_2SiMe_3)$" complex (which would eliminate tetramethylsilane rather than dihydrogen) and $LMo(CH_2SiMe_3)_2$. The $\alpha,\alpha-$ elimination reaction is believed to proceed through an alkylidene-hydride intermediate, only one example of which has been structurally characterized.[2] Reversible intramolecular oxidative addition of C-H bonds (eqn 1.3) has also been observed for



(1.3)

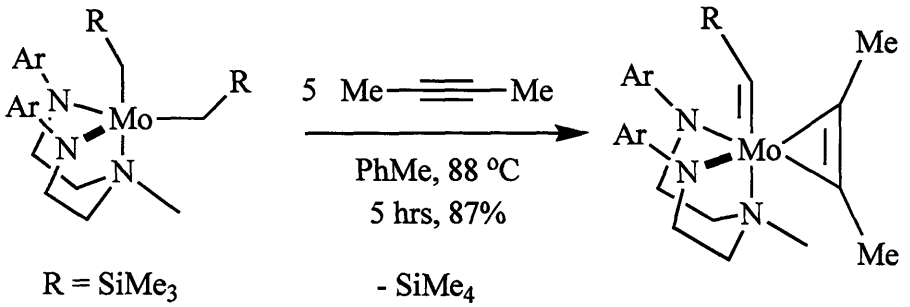
M = Mo; R = R' = Me
M = Nb; R = H, R' = *t*-Bu

β-hydride containing complexes $Mo(\eta^2\text{-}NCMe_2Ar")(N[i\text{-}Pr](Ar")_2$[34] and $Nb(\eta^2\text{-}NCHCMe_3Ar")(N[Np](Ar")_2$.[28a] However, the molybdenum complexes behave as a "$Mo(NRAr)_3$" source, binding substrates to the molybdenum center that may potentially insert into theMo-H bond in either an η^1 or η^2 manner. The mechanism has been shown to be coordination-induced reductive elimination in at least one case.[32] In contrast, examples of both reversible reductive elimination as well as insertion chemistry have been observed in the Nb system.[28a]

Efforts to trap the proposed alkylidene hydride species formed upon thermolysis of $LMo(CH_2TMS)_2$ were not successful. The complex does not react at room temperature with neat benzonitrile or acetonitrile, or excess benzophenone in benzene solution. Heating

solutions of nitrile or ketone with **L**Mo(CH_2TMS)$_2$ in benzene-d_6 results in intractable mixtures. With benzophenone, C-F activation is observed, recognizable by the appearance of doublets and triplets in the ^{19}F NMR from CF_2H and CFH_2 groups, respectively. Presumably the highly stable benzophenone radical,[35] produced via reduction by the molybdenum center, activates the benzylic fluoride, resulting in the observed ligand degradation. It was hoped that either a trapped nitrile product would be obtained, or perhaps nitrile insertion into a molybdenum hydride would be observed and shed light into the mechanism of tetramethylsilane elimination.

To explore further reactivity of **L**Mo(CH_2SiMe_3)$_2$, C_6D_6 solutions of **L**Mo(CH_2SiMe_3)$_2$ were heated and monitored *via* ^{19}F and ^1H NMR (60 to 80 °C, monitored hourly). Direct thermolysis resulted in complex mixtures of products and no product analogous to {**[F3]**MoCTMS}$_2$[4] has been isolated. Thermolysis of **L**Mo(CH_2SiMe_3)$_2$ in the presence of 5 equivalents of 2-butyne produces tetramethylsilane (*via* ^1H NMR) and a diamagnetic product whose NMR resonances are consistent with a diamagnetic alkylidene/alkyne adduct, **L**Mo(CHSiMe$_3$)(η^2-MeC≡CMe) as shown in eqn 1.4. The backbone ^1H resonances are typical of C_S symmetric diamido/amine complexes. The alkyne carbons resonate



(1.4)

at 195.3 ppm and the alkylidene resonates at 305.0 ppm in the ^{13}C NMR with a J_{CH} of 131 Hz. The alkylidene proton resonates at 15.12 ppm in the ^1H NMR. The deshielded ^{13}C alkyne resonance is typical of an alkyne behaving as a 4 electron donor.[36] The proton-carbon coupling constant is consistent with a bent alkylidene (M-C_α-H angle ~ 120°).[19] These observations in solution agree with the solid state structure, shown below in Figure 1.4.

Figure 1.4. Structure of **L**Mo(CHSiMe$_3$)(η^2-MeC≡CMe), ellipsoids at 50% and hydrogen atoms have been omitted for clarity.

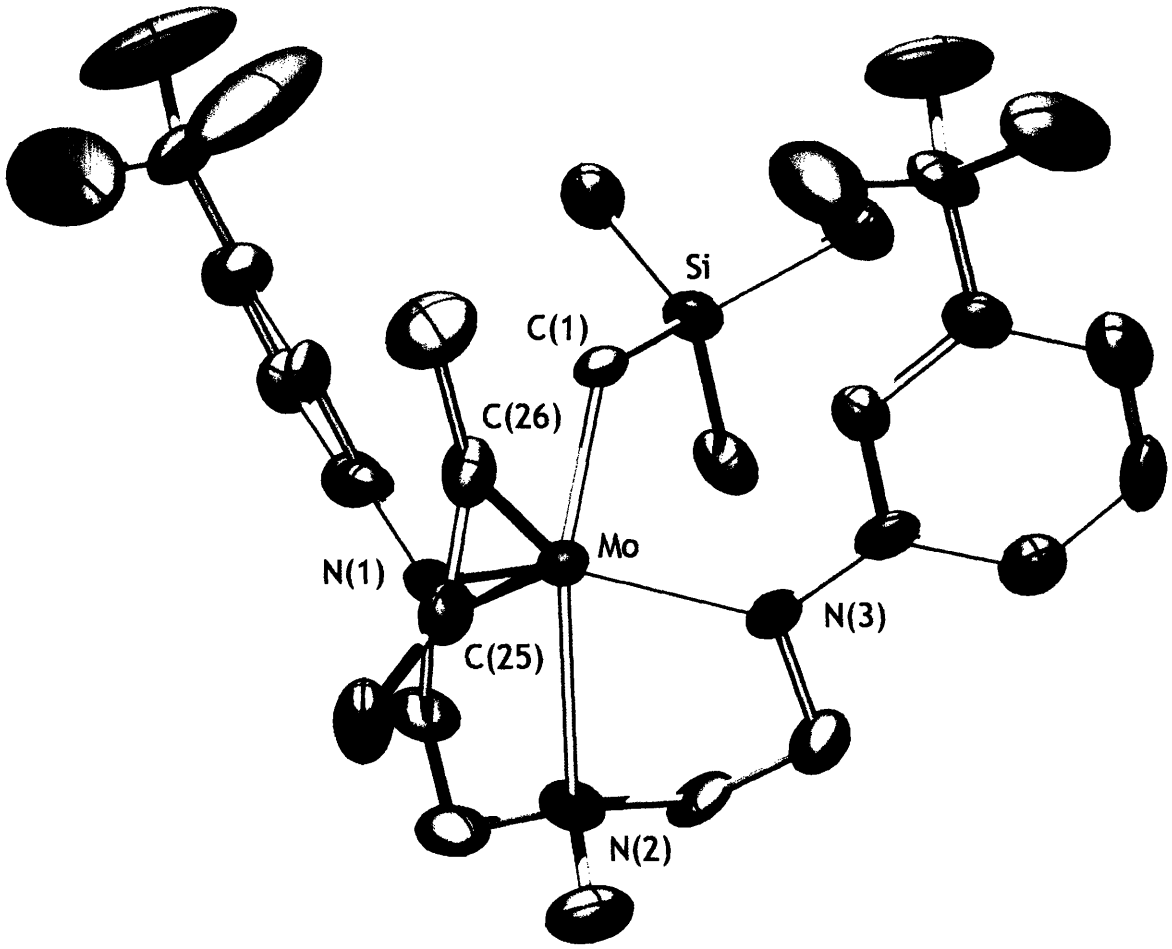
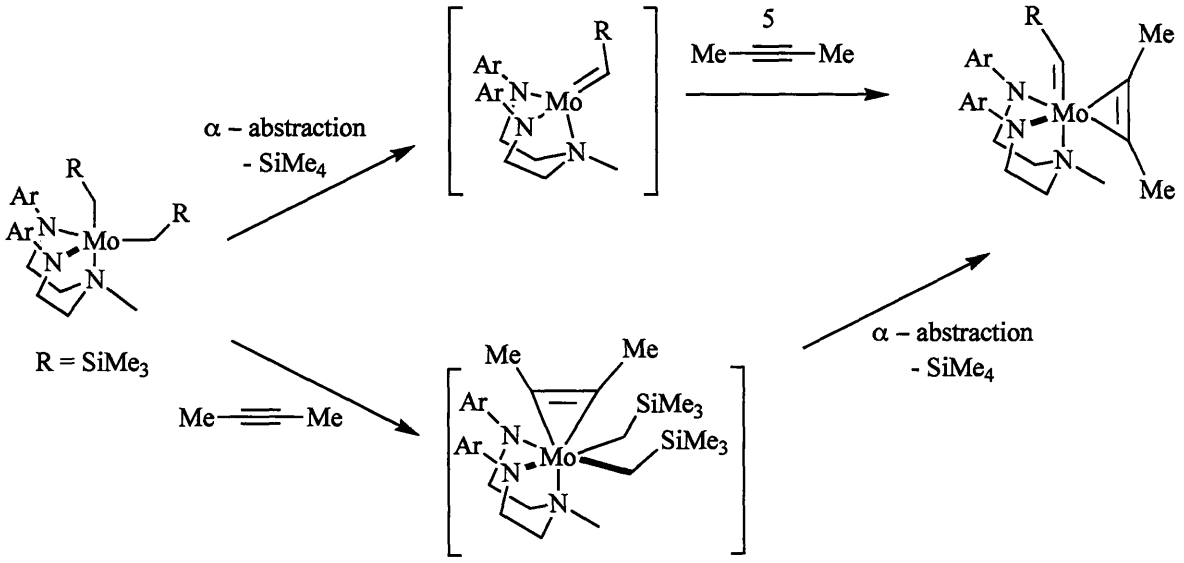


Table 1.4. Selected Bond lengths [Å] and angles [°] for LMo(CHSiMe$_3$)(η^2-MeC≡CMe).

Mo – C(1)	1.959(8)	Si – C(1) – Mo	123.0(4)
C(25) – C(26)	1.303(11)	C(1) – Mo – N(2)	152.7(3)
Mo – C(26)	2.031(8)	N(3) – Mo – N(1)	130.0(3)
Mo – C(25)	2.052(8)	N(3) – Mo – N(2)	76.6(2)
Mo – N(1)	2.057(6)	N(2) – Mo – N(1)	75.5(2)
Mo – N(2)	2.375(6)	C(1) – Mo – N(2)	93.2(3)
Mo – N(3)	2.035(6)	C(26) – Mo – N(1)	117.1(3)
		C(26) • • • C(1)	2.59

LMo(CHSiMe$_3$)(η^2-MeC≡CMe) crystallized from a concentrated toluene solution over several days in the orthorhombic space group *P*bca. The molybdenum – alkyne carbon distances of 2.031(8) and 2.052(8) Å and lengthened C(25) – C(26) distance of 1.303(11) Å correspond with the empirical spectroscopic assignment of the alkyne as a 4 electron donor metallocyclopropene. An alkyne bound in such a manner is isolobal with the commonly employed imido group.[37] However, this species is noteworthy due to the fact that transition-metal carbon carbene complexes often polymerize alkynes rapidly, even when the transition metal is not in the highest oxidation state.[38] The Mo – $C_{alkylidene}$ – Si angle is 123°, in marginal agreement with observed coupling constant. The orientation of the alkylidene with respect to the imido ligand may be predicted on the basis of the alkylidene proton – carbon coupling constant in imido systems.[38,39] In LMo(CHSiMe$_3$)(η^2-MeC≡CMe), the alkylidene ligand pointing away (*anti*) from the 2-butyne ligand and parallel to the alkyne vector. The distance between the alkyne carbon and alkylidene carbon of 2.59 Å is well outside bonding distance. In the related, structurally characterized, complex W(CHPh)(η^2 - PhC≡CPh)(Cl)$_2$(PMe$_3$)$_2$ the alkylidene is oriented *syn* to the alkyne ligand and the alkylidene proton – carbon coupling constant is 128.5 Hz. In these two examples it appears that the J_{CH} is not a useful indicator of alkylidene orientation, contrary to the large consistency in the Mo(NR)(CHR')(X)$_2$ complexes and related base adducts.[19,38]

The The overall structure of **L**Mo(CHSiMe$_3$)(η^2-MeC≡CMe) may be best described as a square pyramid with the alkyne occupying the axial site. The molybdenum atom sits out of the basal plane somewhat, with a N(2) – Mo – $C_{alkylidene}$ angle of 152.7(3)° and a somewhat more acute N(1) – Mo – N(3) angle of 130.0(3)°, presumably to maximize overlap between the amide π orbitals and the molybdenum. Considering the alkyne as a four electron donor, this species is isoelectronic with a base adduct of an *anti* alkylidene complex, of which numerous structures have appeared.[38,39] This complex is the first structurally characterized example of both an alkylidene and alkyne in the coordination sphere of molybdenum, though two tungsten examples exist in the literature.[40,41]



Scheme 1.5 Possible mechanisms for the formation of **L**Mo(CHSiMe$_3$)(η^2-MeC≡CMe).

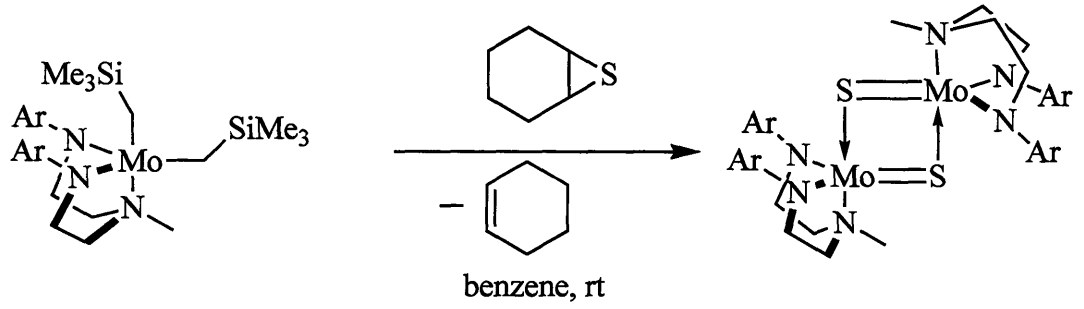
Two likely routes to **L**Mo(CHSiMe$_3$)(η^2-MeC≡CMe) exist (Scheme 1.5). One possibility is that **L**Mo(CH$_2$SiMe$_3$)$_2$ undergoes α abstraction to generate a free, four-coordinate molybdenum(IV) alkylidene in solution which is sequestered by alkyne. Another possibility is that the alkyne coordinates to the molybdenum center in **L**Mo(CH$_2$SiMe$_3$)$_2$, oxidizing it to molybdenum(VI) and this pseudo octahedral (assuming the amine donor remains bound during the course of the reaction) species undergoes α - abstraction to yield the observed product. The second mechanism is favored for several reasons. First, a related alkyne dialkyl compound, W[(OC$_6$H$_3$R')$_2$O](η^2-PhC≡CPh)(R)$_2$ (R

= CH_2TMS, R' = *t*-Bu) has been reported that generates an observable alkylidene species upon heating.[42] Attempts to perform kinetic studies upon the formation of **L**Mo(CHSiMe$_3$)(η^2 – MeC≡CMe) were not reproducible due to alkyne polymerization by an unknown mechanism. Circumstantial evidence for an alkyne binding mechanism consists of the fact that the reaction of **L**Mo(CH_2SiMe_3)$_2$ with 1-phenyl-1-propyne is considerably slower than the reaction to produce **L**Mo(CHSiMe$_3$)(η^2 – MeC≡CMe) with 2-butyne ($t_{1/2}$ ca. 7 vs. 3 hours, respectively.) and the reaction between diphenylacetylene and **L**Mo(CH_2SiMe_3)$_2$ does not form any tractable product. The alkylidene resonates at 15.2 ppm in the 1-phenyl-1-propyne reaction, though the product could not be isolated.

1.5 Oxidation of LMo(CH_2SiMe_3)$_2$.

In order to more fully understand the potential relationship between oxidation of the molybdenum center and multiple bond formation, inner-sphere oxidation[43] reagents were explored. Oxidation of **L**Mo(CH_2SiMe_3)$_2$ by the common atom transfer[43] reagent pyridine-*N*-oxide proceeds rapidly in thawing benzene or cold (-40°C) ether solution to yield an unstable blue product. Evidence for oxygen atom transfer followed by α – abstraction consists of the observation of tetramethylsilane in crude product mixtures. However, the nature of the final metal-containing product cannot be commented on with certainty.

One equivalent of cyclohexene sulfide reacts at room temperature with **L**Mo(CH_2SiMe_3)$_2$ to produce a diamagnetic material, the dimeric molybdenum (IV) sulfido complex {**L**MoS}$_2$, in good yield (eqn 1.5). Elemental sulfur does not react with **L**Mo(CH_2SiMe_3)$_2$, nor does trimethylphosphinesulfide. The complex is almost entirely



(1.5)

insoluble in common solvents and precipitates during the course of the reaction. However, diffraction-grade crystals were obtained by addition of cyclohexene sulfide to a solution of $\mathbf{L}Mo(CH_2SiMe_3)_2$ followed by storage of the mixture shielded from any mechanical agitation for 15 hours.

$\{\mathbf{L}MoS\}_2$ crystallized as long, black, needle-like crystals in the space group $P2_1/c$. A thermal ellipsoid plot and table of selected bonds and angles are listed below in Figure and Table 1.5, respectively.

Figure 1.5. Structure of $\{\mathbf{L}MoS\}_2$, ellipsoids at 50%. Only the *ipso*-carbons of the aryl rings are shown and hydrogen atoms are omitted for clarity.

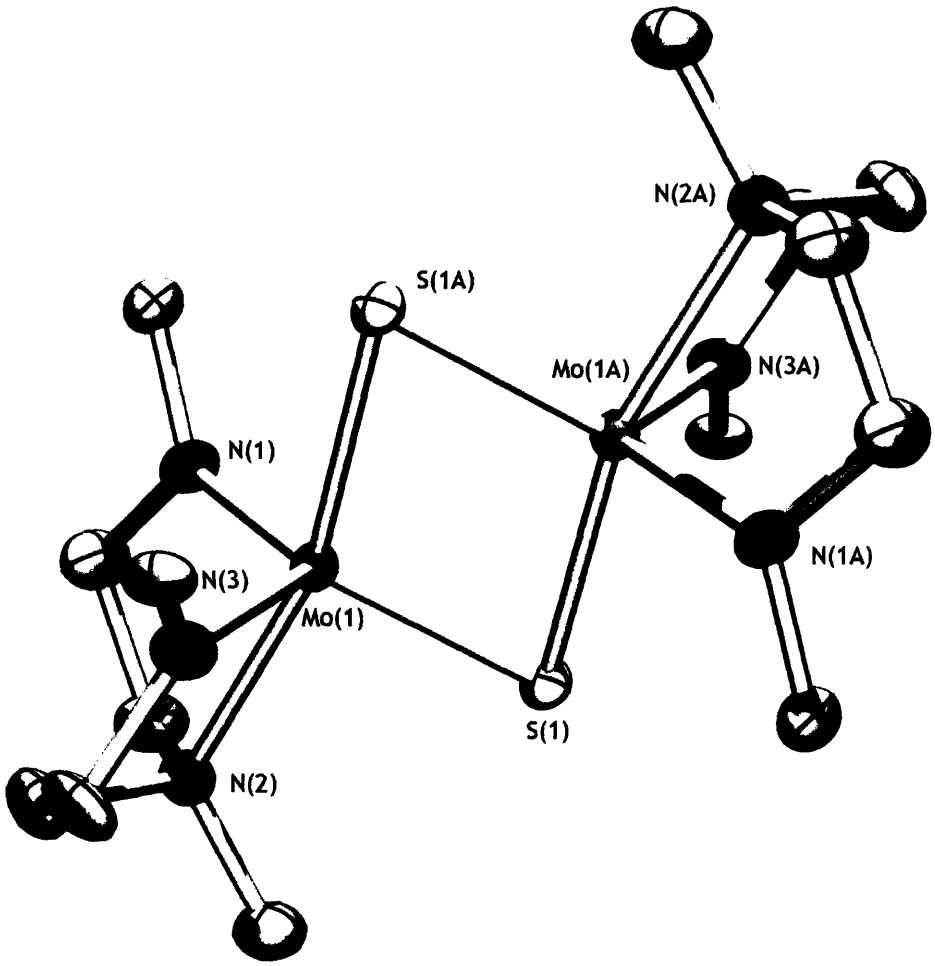


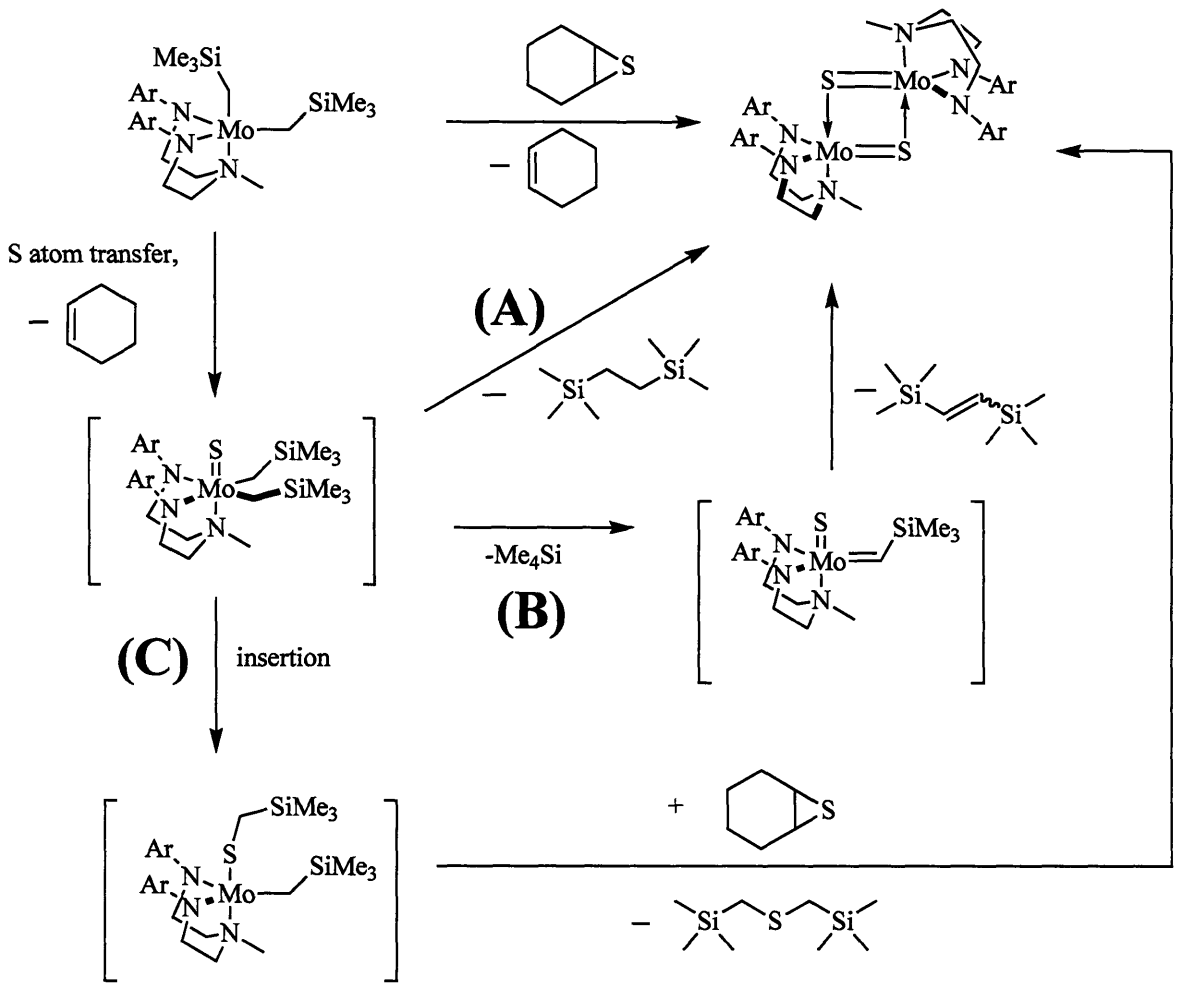
Table 1.5. Selected Bond lengths [Å] and angles [°] for $\{\mathbf{L}MoS\}_2$.*

Mo(1) – S(1)	2.2531(12)	N(2) – Mo(1) – S(1)	87.80(11)
Mo(1) – S(1A)	2.3393(12)	N(2) – Mo(1) – S(1A)	164.33(11)
Mo(1) – N(1)	1.972(4)	N(1) – Mo(1) – N(2)	78.19(15)
Mo(1) – N(2)	2.2531(12)	N(1) – Mo(1) – N(3)	115.75(17)
Mo(1) – N(3)	1.984(4)	N(2) – Mo(1) – N(3)	79.48(15)
Mo(1) – Mo(1A)	2.7077(8)	N(1) – Mo(1) – S(1)	118.08(12)
S(1) – Mo(1) – S(1A)	107.77(4)	N(3) – Mo – S(1)	120.27(12)

*The atoms labeled with the "A" designation are generated by crystallographic symmetry.

The Mo – S_{eq} bond length of 2.2616(13) Å is considerably shorter than the Mo – S_{ax} distance of 2.3482(13) Å, consistent with the a Mo – S double bond in the equatorial site and a Mo – S single dative bond in the axial site, as shown in equation 1.5. This description of the bonding does not contain a molybdenum – molybdenum bond and the long Mo – Mo distance of 2.7178(8) Å supports this notion. The nitrogen – molybdenum bonds and angles are typical for a trigonal bipyramid **[N2N]** molybdenum complexes.

The proposed mechanism for this transformation is shown in Scheme 1.6 below. Unfortunately, the low solubility of the product $\{\mathbf{L}MoS\}_2$ precluded kinetic measurements by NMR spectroscopy. Given the appearance of cyclohexene in ^{1}H NMR spectra of reaction mixtures (>90% of theory), the first step of the reaction is believed to be S-atom transfer[43] to form a dialkyl molybdenum sulfide. Paths A and C, direct reductive elimination of bis(trimethylsilyl)ethane and sulfide insertion into the alkyl ligands, may be ruled out by examination of the byproducts *via* ^{1}H NMR. Tetramethylsilane and the olefinic product *trans*-1,2-bis(trimethylsilyl) ethene[44] are observed in a 1:1 ratio (80% of theory) when benzene-d_6 solutions of reaction mixtures are examined *via* ^{1}H NMR.



Scheme 1.6. Proposed Mechanism for the Formation of {**L**MoS}$_2$.

Path B is the proposed mechanism. Though a putative "**L**Mo(S)(CHSiMe$_3$)" species is isoelectronic with the isolated **L**Mo(CHTMS)(η^2 – MeC≡CMe) species (and a base adduct of an imido alkyidene species), the "**L**Mo(S)(CHSiMe$_3$)" species is unstable with respect to bimolecular coupling of alkylidene ligands, a common mode of decomposition for sterically unprotected alkylidene ligands.[19,45] It is also worthwhile to mention that the α-abstraction step to form "**L**Mo(S)(CHSiMe$_3$)" may be bimolecular, with the terminal sulfido ligand of **L**Mo(S)(CH$_2$SiMe$_3$)$_2$ acting as a Lewis base, inducing α-abstraction.

Treatment of a solution of **L**Mo(CH$_2$SiMe$_3$)$_2$ with 1.1 equivalents of the oxidizing agent C_2Cl_6 results in formation of tetramethylsilane and HCl (which is sequestered in the form of protonated free ligand), and the formation of the molybdenum alkylidyne chloride complex, [**L**Mo(Cl)(CSiMe$_3$)]$_2$ in moderate yield. The external base triethylamine may

alternatively be used and the yield of $[\mathbf{L}Mo(Cl)(CSiMe_3)]_2$ is close to 100% when monitored by ^1H NMR. Red crystals of the sparingly soluble complex were obtained and examined by X-ray diffraction. The complex crystallizes in the monoclinic space group $P2_1/c$ and is shown below in Figure 1.6. $[\mathbf{L}Mo(Cl)(CSiMe_3)]_2$ crystallizes as an edge-sharing octahedron with fairly symmetric Mo – Cl distances. The short Mo – C(1) distance of 1.762(4) Å is typical for a molybdenum-carbon triple bond[38b,47] and forms a well-defined series with the Mo – carbon bond lengths of 1.959(8) Å in the molybdenum alkylidene $\mathbf{L}Mo(CHTMS)(\eta^2\text{-MeCCMe})$, and 2.226(8) Å in the axial alkyl ligand in $\mathbf{L}Mo(CH_2SiMe_3)$. The C(1) – Mo – N(2) angle deviates from linearity by 12.3° as a result of steric pressure between the amine methyl group and the *tert*-butyl group on the other half of the dimer. This results in a slight distortion from octahedral geometry.

Figure 1.6. Structure of $[\mathbf{L}Mo(Cl)(CSiMe_3)]_2$, ellipsoids at 50%. Only the *ipso*-carbon atoms of the aryl rings are shown and hydrogen atoms have been omitted for clarity.

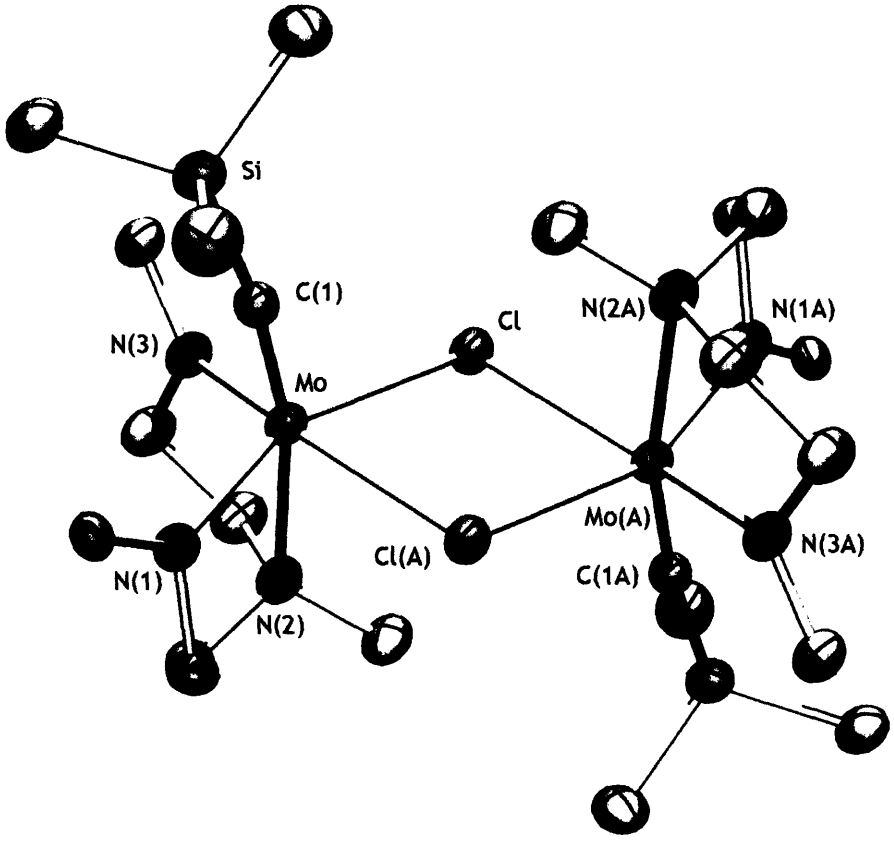


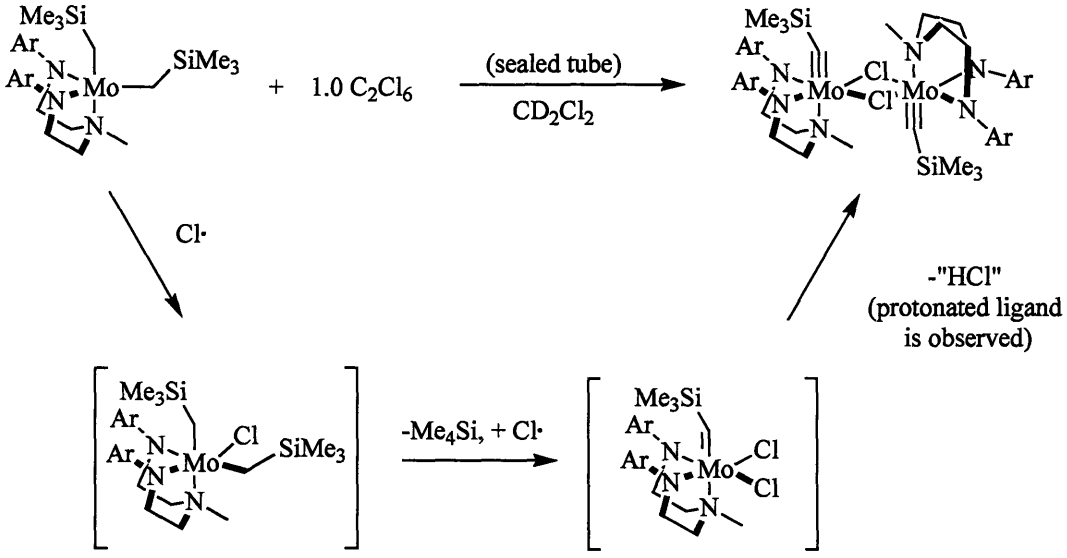
Table 1.6. Selected Bond lengths [Å] and angles [°] for [LMo(Cl)($CSiMe_3$)]$_2$.*

Mo – C(1)	1.762(4)	C(1) – Mo – Si	172.27(19)
Mo – Cl	2.5695(10)	C(1) – Mo – N(2)	167.73(14)
Mo – Cl(A)	2.5975(10)	N(1) – Mo – N(2)	76.68(12)
Mo – N(1)	1.985(3)	N(1) – Mo – N(3)	104.41(13)
Mo – N(2)	2.455(3)	N(2) – Mo – N(3)	77.28(11)
Mo – N(3)	1.998(3)	Cl – Mo – N(2)	88.33(8)
Mo – Mo(A)	4.100(n/a)[a]	Cl(A) – Mo – N(2)	87.26(8)

*The atoms labeled with the "A" designation are generated by crystallographic symmetry.

[a]Not a refined parameter.

Complex [LMo(Cl)($CSiMe_3$)]$_2$ is proposed to be formed via the mechanism shown in Scheme 1.7. It is proposed that inner-sphere atom transfer[43] of Cl· from C_2Cl_6 is followed by α - abstraction to generate a Mo(VI) alkylidene dichloride. [LMo(Cl)($CSiMe_3$)]$_2$ is generated upon losing one equivalent of HCl from the resulting alkylidene dichloride complex. Deprotonation of alkylidene ligands to yield alkylidyne



Scheme 1.7. Proposed Mechanism for the Formation of [LMo(Cl)$CSiMe_3$]$_2$.

complexes has been used in the past as a synthetic method.[46,47] Triethylamine may be used as an external base and the yield is ~100%. Direct chlorination of one of the alkyl ligands does not occur, as no $ClCH_2SiMe_3$ is observed. Redox-induced α abstraction[48] is a relatively new tool for the synthesis of multiple metal-ligand bonds, however it has already proven useful to synthesize species which are not available by traditional routes.[5] In this case, an oxidant is used to remove two electrons and render the metal center more electrophilic, inducing abstraction, often when a base coordinates.[5]

In contrast to the above examples of oxidants that react quickly and relatively cleanly with **L**Mo$(CH_2SiMe_3)_2$, reactions with σ Lewis bases are not nearly as facile, as might be expected due to the likely crowded coordination sphere at molybdenum and the singly occupied molecular orbitals (~ the d_{xz} and d_{yz}, which are A' and A" in C_S symmetry) that would be repulsive towards incoming σ donors. For example, **L**Mo$(CH_2SiMe_3)_2$ does not react cleanly with trimethylphosphine either in solution or in neat PMe_3. Extended heating is required and numerous species may be observed by ^{19}F and ^{31}P NMR. As mentioned earlier, nitriles also do not react at room temperature with **L**Mo$(CH_2SiMe_3)_2$.

1.5 Conclusions

The new ligand $CH_3N[CH_2CH_2NH(3\text{-}(CF_3)C_6H_4)]_2$ was found to support the synthesis of molybdenum alkyls similar to the those previously supported by the **[F3]** ligand and succeeded in simplifying the synthetic route. Molybdenum alkyl complexes were able to be synthesized in quantity and the molybdenum dialkyl **L**Mo$(CH_2TMS)_2$ readily undergoes oxidation. Upon oxidation with inner-sphere electron transfer reagents, α-abstraction to yield an alkylidene of the general type **L**Mo(CHTMS)(L) is generated. However, the small steric size of the diamidoamine ligand set leaves the resulting product susceptible to bimolecular reactivity. In one case, an example of the coexistence of an alkylidene and alkyne ligand in the coordination sphere of a transition metal was documented in species **L**Mo(CHTMS)(η^2 - MeC≡CMe), which was structurally characterized. With the oxidants cyclohexene sulfide and hexachloroethane, no alkylidene species could be isolated and the products were result of alkylidene coupling in the case of

$\{$**L**MoS$\}_2$ and deprotonation in the case of [**L**Mo(CTMS)Cl]$_2$. It is suggested that investigation of bulkier ligand systems may prevent dimerization, potentially allowing isolation of a currently unknown sulfido alkylidene species. One such way to achieve this is to use a larger substituent on the N_{donor} atom. This may render the donor a poorer Lewis base, but it is not know what, if any, role is played by the donor atom in these systems. The investigation of variants would prove facile utilizing syntheses beginning with varying $RN(CH_2COOH)_2$ species. Another avenue of interest are the hybrid diamido/di(donor) systems developed by Dr. Nathan Smythe in this lab.[49] Such a ligand could provide a more saturated environment (if the donor remains bound) and potentially protect against bimolecular reactivity pathways.

Experimental

General

All reactions were performed with standard Schlenk techniques or in a Vacuum Atmospheres glove box under an atmosphere of dry dinitrogen, unless otherwise noted. Pentane, diethyl ether, and benzene were sparged with dinitrogen then passed through a column of activated alumina. THF and was predried over potassium hydroxide, sparged with N_2, then passed through 2 columns of activated alumina. All solvents were stored over 4Å sieves in a dinitrogen filled glove box. NMR spectra were recorded on a Varian Mercury 300, Unity 300, or INOVA 500 and referenced to the residual protio resonances (^{1}H) or to external C_6F_6 at –163.0 ppm (^{19}F). $MoCl_4(THF)_2$,[31] $MoCl_4(Et_2O)_2$[31] and methyliminodiacetic acid,[50] were prepared as previously reported. 3-Aminobenzotrifluoride and triethylamine were dried over molecular sieves and calcium hydride, respectively. Tetrabutylammonium chloride was purchased from Alfa Aesar, recrystallized from acetone/ether, washed with ether, and dried at 75°C under full vacuum for 18 hours. Pyridine-*N*-oxide (Alfa Aesar) was sublimed under dynamic vacuum onto a 0 °C probe prior to use. Neopentylmagnesium chloride[51] and trimethylsilylmethylmagnesium chloride[52] were prepared by literature methods. All organolithium and Grignard reagents were titrated prior to use. All other reagents were obtained from commercial suppliers and used as received unless otherwise noted. The temperature of reactions was controlled by a Digitrol II (Glas-COL) instrument using a H-type thermocouple. Typical variation was < ± 2 °C. Celite and 4Å sieves were dried in full vacuum at a temperature greater than 180 °C for at least 18 hours.

$CH_3N[CH_2CONH(3\text{-}CF_3C_6H_4)]_2$

To a 2L round bottom flask equipped with a gas adapter, addition funnel, stir bar, and reflux condenser was added 74 g (0.5 mol) of methyliminodiacetic acid. 150 ml of pyridine was added via cannula. To the resulting suspension was added 162.67 ml (1 mol) of 3-aminobenzotrifluoride via cannula. The resulting suspension was heated to 50°C, upon which 390 ml (1.06 mol) of triphenylphosphite in 60 ml of pyridine was

added dropwise. The mixture was heated to 100°C for 16 hours, upon which the reaction becomes homogenous and bright yellow in color. The reaction is allowed to cool to room temperature, then the pyridine is removed at reduced pressure. The resulting thick yellow oil is stirred with 500 ml of 5 N HCl for 1 hour to hydrolyze the phosphorous containing byproducts. Then the entire mixture is made alkaline with sodium hydroxide pellets (ca. pH 13, litmus paper) and extracted with 3x1 L of CH_2Cl_2. The extracts were combined, dried over $MgSO_4$ and the solvent is removed at reduced pressure. Crude $CH_3N\{CH_2CONH(3\text{-}CF_3C_6H_4)\}_2$ is obtained as an off white solid. The product is recrystallized from THF/hexanes to give a white solid; yield 159.3g (74%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.55 (s 3H C*H*$_3$N), 3.40 (s, 4H, NC*H*$_2$CONH), 7.35-7.44 (m, 4H, Ar-*H),* 7.85 (d, 2H, Ar-*H),* 9.22 (s, 2H, Ar-*H*); ^{19}F NMR ($CDCl_3$) δ -63.87, s. HRMS (ESI) Calcd for $C_{19}H_{17}N_3F_6$: 434.1298. Found: 434.1304.

$CH_3N[CH_2CH_2NH(3\text{-}CF_3C_6H_4)]_2$, H_2**L**

To 65.2 g of $CH_3N[CH_2CONH(3\text{-}CF_3C_6H_4)]_2$ (0.15 mol) in 230 ml of THF was added 62 ml (0.62 mol) of BH_3SMe_2 dropwise. The mixture was then refluxed for 6 hours and allowed to cool. The reaction was quenched with 325 ml of 5 N HCl, made alkaline with 76.76 g of NaOH pellets and extracted (3x350 ml) with methylene chloride. The extracts were combined, dried with $MgSO_4$ and the solvent removed at reduced pressure. The resulting thick oil was taken up in pentane and 9.8g of unreacted amide was recovered via filtration. The amide residue was washed with pentane and the pentane was removed *in vacuo* to yield H_2**L** as a colorless oil; yield 41.7 g (80 %): ^{1}H NMR (C_6D_6, 300 MHz) δ 1.77 (s, 3H, C*H*$_3$N), 1.99 (t, 4H, NC*H*$_2$CH$_2$N), 2.53 (q, NCH$_2$C*H*$_2$N), 3.73 (s, 2H, N*H*), 6.3 (m, 2H, Ar-*H*), 6.66 (s, 2H, Ar-*H*), 6.90 (d, 2H, Ar-*H*), 7.13 (s, 2H Ar-*H*); ^{19}F NMR (C_6D_6, 283 MHz) δ -63.2, s; ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.99 (CH_2), 41.91 (CH_2), 55.95 (NCH_3), 108.85, 113.77, 116.074, 124.61 (q, J_{CF} = 272.38 Hz, *C*$F_3C_6H_4$), 129.81, 131.62 (q, J_{CF} = 31.6 Hz, C_6H_4), 148.61; ^{19}F NMR (283 MHz, $CDCl_3$) δ -63.2 (s); HRMS (ESI) Calcd for $C_{19}H_{21}F_6N_3$ 406.1712 [M + H+], found 406.1715 [M + H+].

Synthesis of $[Et_3NH][\mathbf{L}MoCl_3]$

$MoCl_4(THF)_2$ (2.79 g, 0.78 mmol) was added in several portions to a stirred solution of $H_2\mathbf{L}$ (3.14 g, 0.78 mmol) in 50 mL of THF. The solution was stirred for 30 min at room temperature, upon which the solution turned red. Et_3N (2.28 mL, 1.63 mmol) in 5 mL of THF was then added dropwise via pipet, and the solution was stirred for 2 h at room temperature. The volatile components were removed *in vacuo*, and the residue was extracted with 100 mL of THF, the extract was filtered through Celite, and the Celite was washed with 3 x 50 mL of THF. The product is crystallized by adding 2 volumes of pentane to a concentrated THF solution and storing at -40 °C overnight. The deep purple solid was collected on a frit, washed with 50 mL of pentane, and dried *in vacuo*; yield 4.57 g (83%): ^{1}H NMR (C_6D_6, 300 MHz) δ 19.4 (s, 3, NMe), 6.21, 1.54, 1.16, 0.97, -24.9, -30.8, -97.7, -103.7; ^{19}F NMR (C_6D_6) δ -54.5 (s).

Synthesis of $[Bu_4N][\mathbf{L}MoCl_3]$

Procedure 1: To 0.4581g of $[Et_3NH][\mathbf{L}MoCl_3]$ in 10 ml of THF was added 0.2014g of tetrabutylammonium chloride. The mixture was stirred for 3.5 hours, upon which the solvent was removed at reduced pressure. During removal of solvent, bumping is an extreme problem. The residue was extracted with 20 ml of benzene, filtered through celite and the cake was washed with additional benzene until the washings were clear (ca. 40 ml). The benzene was removed *in vacuo* to afford 321 mg of purple powder. ^{1}H NMR showed no residual Et_3NH^+. Yield: 62% NMR: ^{19}F: -54.2 ppm.

Procedure 2. A 2.63 g amount of $H_2\mathbf{L}$ (6.5 mmol) and 2.49 g of $MoCl_4(Et_2O)_2$ (6.5 mmol) were combined in 80 mL of THF and stirred for 30 min. A 2.0 mL portion of triethylamine (14.3 mmol) in 4 mL of THF was added dropwise via pipet and the mixture stirred for 1 h. The purple solution was filtered through Celite and washed with 2 x 40 mL of THF. A 1.98 g amount of tetrabutylammonium chloride (7.1 mmol) was added as a solid to the solution, and the mixture was stirred vigorously for 15 h. The solution was then stripped to a dark purple solid and extracted with 200 mL of toluene, and the extract was filtered through Celite, which was washed with 3 x 40 mL of additional toluene. $[Bu4N][\mathbf{L}MoCl_3]$ was isolated as a purple powder by concentration of the solution and addition of pentane followed by storage at -40 °C. The purple solid was dried thoroughly

in vacuo; yield 4.18 g (76%): ^{1}H NMR (C_6D_6, 500 MHz) δ 28.16, 25.95, 19.37 (s, 3, NMe), 6.29, 4.67, 1.1 (NBu), 1.0 (NBu), 0.87 (NBu), 0.78(NBu), -2.33, -30.9, -99.4, -105.4; ^{19}F NMR (C_6D_6) δ -54.8. Anal. Calcd for $C_{35}H_{55}N_4F_6Cl_3Mo$: C, 49.57; H, 6.54; N, 6.61; Cl, 12.54. Found: C, 49.66; H, 6.51; N, 6.48; Cl, 12.61.

LMo(CH_2TMS)$_2$

Procedure 1. A 3.036 g sample (4.3mmol) of [Et_3NH][**L**MoCl_3] was dissolved in 25 mL of THF and chilled to -78 °C. To the purple solution was added a solution of ((trimethylsilyl)methyl)magnesium chloride (16.7 mL, 0.8 M in Et2O, 13.3 mmol, 3.1 equiv) with stirring. The solution turned dark green over 4 h, and the color darkened to deep red as the reaction mixture was naturally warmed to room temperature. After 15 h all volatile components were removed, and the residue was extracted into pentane, the extract was filtered through Celite, and the Celite was washed with pentane until the washings were colorless. The solution was concentrated to ca. 30 mL and filtered through Celite a second time. The solution was concentrated to 15 mL and stored at -40 °C for 2 days, affording dark blocks of crystalline **L**Mo(CH_2SiMe_3)$_2$, which were dried *in vacuo.* yield 1.6 g (55%). A second crop yielded an additional 180 mg of product, for a total yield of 62%. The complex has also been synthesized in the same fashion and in similar yield from [Bu4N][**L**MoCl_3] and 2.1 equiv of alkylmagnesium reagent: ^{1}H NMR (C_6D_6, 500 MHz) δ 15.8, 13.25 (s, 3, N*Me*), 11.68, 10.9, 5.43, 3.8, 3.5 (br s,9, $SiMe_3$), 1.3, 1.2 (br s, 9, $SiMe_3$), -46.3, -60.1; ^{19}F NMR (C_6D_6, 283 MHz) δ -55.8. Anal. Calcd for $C_{27}H_{41}N_3F_6Si_2Mo$: C, 48.13; H, 6.13; N, 6.24. Found: C, 47.88; H, 6.06; N 6.14.

Procedure 2. To 2.389g of H_2**L** (7.12 mmol) in 40 ml THF was added 2.72 g of $MoCl_4(THF)_2$ in small portions over several minutes with vigorous stirring. The resulting red solution was stirred for 15 minutes and 2.1 ml (15 mmol) of triethylamine was added dropwise. The resulting solution was stirred for 30 minutes then cooled to -78 °C, upon which 24.3 ml (29.2 mmol) of trimethylsilylmethyl magnesium chloride in diethyl ether was added dropwise. The solution was allowed to stir and warm naturally to room temperature over ca. 15 hours. All volatile components were removed *in vacuo*, the resulting solid was treated with 100 ml of toluene and 2.6 ml (27 mmol) of 1, 4 dioxane was added. The resulting suspension was stirred vigorously for 30 minutes, allowed to

settle, filtered through Celite, and the Celite was washed with ca. 150 ml additional toluene (3 x 50 ml). The deep red solution was concentrated *in vacuo* to ca 10 ml and stored at -40 °C to yield the compound as a dark purple-red solid, which was washed with cold pentane and dried *in vacuo* to yield 3.5 g (61%) of material was spectroscopically identical to that prepared using procedure 1.

LMo(Cl)(CH_2CMe_3)

0.1400 g of [Et_3NH][**L**$MoCl_3$] was dissolved in 12 ml THF and chilled to -30°C. To the purple, cold solution was added 2.2 equivalents of neopentyl magnesium chloride (2.10M in Et_2O) with stirring. The reaction was stirred for 30 minutes, then all volatiles were removed. The residue was taken up in a minimum of diethyl ether and filtered through celite. The filtrate was concentrated and pentane was added. After storing the solution for 18 hours at -30°C, dark green crystals were isolated, rinsed with a minimum of pentane, and dried *in vacuo*. The compound exhibits poor solubility in arene solvents and reacts with dichloromethane but is moderately soluble in ether and soluble in THF; yield 98 mg (89%): ^{1}H NMR (C_6D_6, 300 MHz) δ 15.67, 13.5 (br s, 3H, NMe), 4.33 (2H, s) 3.93 (br s, 9, CH_2CMe_3), -51 (br s, 2), -88 (br s, 2); ^{19}F NMR (C_6D_6, 283 MHz) δ -59.8. Anal. Calcd for $C_{24}H_{30}N_3F_6ClMo$: C, 47.58; H, 4.99; N,6.94. Found: C, 47.64; H, 5.11; N, 6.58.

LMo($CCMe_3$)(CH_2CMe_3)

312 mg of [Et_3NH][**L**$MoCl_3$] was dissolved in 25 ml THF and chilled to -30°C. To the purple, cold solution was added 3.3 equivalents of neopentyl magnesium chloride (2.47M in Et_2O) with stirring. The solution turned dark green over 30 minutes and the color lightened to dark yellow. After 2 hours all volatiles were removed and the residue was extracted into toluene, filtered through celite and the celite was washed with toluene until the washings were clear (ca. 25 ml). The toluene was removed to leave a brown solid. The brown solid was taken up in a minimum of ether and pentane was added. Storage of the solution at -30°C for three days afforded yellow crystalline **L**Mo($CCMe_3$)CH_2CMe_3,. yield; 126 mg (63%): ^{1}H NMR (C_6D_6) δ 7.47 (s, 2, C_6H_4), 7.14 (d, 2, C_6H_4), 7.02-6.94 (m, 4, C_6H_4), 3.34 (m, 2, CH_2), 3.25 (m, 2, CH_2), 2.27 (m, 2,

CH_2), 2.04 (m, 2, CH_2), 2.03 (s, 3, NMe), 1.64 (s, 2, CH_2CMe_3), 1.47, (s, 9, $CCMe_3$), 0.52 (s, 9, $CCMe_3$); ^{13}C (tol-d_8) δ 307.7 (Mo*C*CMe_3), 165.3, 137.7, 130.8 (J_{CF} = 31.6 Hz), 125.58, 125.1 (J_{CF} = 272.6 Hz), 121.5, 119.95, 69.90, 59.38, 55.13, 49.95, 43.45, 37.17, 34.98, 29.20; ^{19}F NMR (C_6D_6) δ -61.7 ppm.

LMo($CHSiMe_3$)(η^2-MeC≡CMe)

135.5 mg (0.20 mmol) of **L**Mo(CH_2SiMe_3)$_2$ was dissolved in 1 ml of toluene in glass bomb equipped with a Teflon sealed joint. 80 μl of 2-butyne (1 mmol, 5 eq.) was dissolved in 1 ml of toluene and added to the bomb and it was sealed. The reaction was heated to 88°C for 5 hours. The reaction was then filtered through celite and washed with ~3 ml of additional toluene. The volatiles were removed *in vacuo* and the residue recrystallized from pentane at -40°C to give **L**Mo($CHSiMe_3$)(η^2-MeC≡CMe) as yellow blocks, yield 110 mg (86%): ^1H NMR (C_6D_6, 500 MHz) δ 15.12 (s, H, C*H*$SiMe_3$), 7.00 (m, 2H, *Ar*), 6.91-6.86 (m, 4H, *Ar*), 6.27 (s, 2H, *Ar*), 3.60 (m, 2H, backbone), 3.02-2.9 (m, 4H, backbone; overlaps with MeC≡CMe), 2.98 (s, 6H, *Me*C≡C*Me*; overlaps with backbone), 2.49 (s, 3H, N*Me*), 2.32 (m, 2H, backbone), -0.50 (s, 9H, Si*Me*$_3$); ^{13}C NMR (C_6D_6) δ 305.04 (J_{CH} 131 Hz, Mo*C*HR), 195.34 (Me*CC*Me), 160.65, 149.31, (CF_3 group obs by solvent), 127.74, 120.27, 119.15, 116.11, 55.69, 53.44, 48.72, 16.49, 2.42 (MoCHSi*Me*$_3$); ^{19}F (C_6D_6) δ -62.6 (s). Anal. Calcd for $C_{27}H_{35}N_3F_6MoSi$: C, 50.70; H, 5.52; N, 6.57. Found: C, 50.75; H, 5.75; N, 6.31.

[**L**MoS]$_2$

To 76 mg of **L**Mo(CH_2SiMe_3)$_2$ in 1 ml of benzene was added 50 mg of cyclohexene sulfide. The resulting solution was placed away from mechanical agitation and allowed to sit for 15 hours. Large, black needles of [**L**MoS]$_2$ precipitated and were washed with pentane and dried *in vacuo* to give [**L**MoS]$_2$; yield 42 mg (70%): ^1H NMR (1:1 CD_2Cl_2: diethyl ether, 500 MHz) δ 3.4 (m, 2, backbone), 3.66 (m, 2, backbone), 3.77 (m, 2, backbone), 3.9 (m, 2, backbone, overlaps with N*Me*), 4.0 (s, 3, N*Me*), 6.18 (s, 2, Ar-H), 7.01 (d, 2, Ar-H), 7.12 (t, 2, Ar-H); ^{19}F NMR (C_6D_6, 283 MHz) δ -62.1. Anal. Calcd for $C_{38}H_{38}N_6F_{12}Mo_2S_2$: C, 42.95; H, 3.60; N, 7.91. Found: C, 43.11; H, 3.75 ; N, 7.76.

[**L**Mo(Cl)($CSiMe_3$)]$_2$

To a solution of **L**Mo(CH_2SiMe_3)$_2$ 118.5 mg (0.18 mmol) in 3 ml pentane was added 1.1 equivalents (45.8 mg, 0.19 mmol) of C_2Cl_6. 5 drops of benzene were added and the mixture was shaken gently to dissolve all components. The solution was allowed to stand at room temperature for 12 hours and all volatile components were removed *in vacuo*. The resulting red solid was washed with 3 ml of pentane and dried *in vacuo* to give [**L**Mo(Cl)($CSiMe_3$)]$_2$; yield 67 mg (61%). The complex is sparingly soluble in common organic solvents: ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 7.54 (m, 2H, Ar), 7.42 (m, 4H, Ar), 7.33 (m, 2H, Ar), 4.1 (m, 2, backbone), 3.9 (m, 2H, backbone), 3.0 (m, 2H, backbone), 2.81 (m, 2H, backbone), 2.6 (s, 3, N*Me*), -0.63 (s, 9H, Si*Me*$_3$). Analyses have consistently been low in carbon. For example: Anal. Calcd for $C_{46}H_{56}Cl_2F_{12}Mo_2N_6Si_2$: C, 44.56; H, 4.55; N, 6.78. Found: C, 41.76; H, 4.93; N, 6.30.

Sealed tube formation of [**L**Mo(Cl)($CSiMe_3$)]$_2$

A 5 mm NMR tube sealed to a 14/20 ground glass joint was flamed out under dynamic vacuum and charged with solid **L**Mo(CH_2SiMe_3)$_2$ (17.0 mg, 25.2 μ mol) and solid C_2Cl_6 (6.5 mg, 27.7 μ mol). CD_2Cl_2 (~0.5 ml, dried over CaH_2 and degassed) was added *via* vacuum transfer at -196 °C and the tube was sealed with a torch. The solution was allowed to thaw and the contents were shaken gently to mix and allowed to stand at room temperature for 1 hour. ^{1}H NMR (500 MHz) showed the presence of [**L**Mo(Cl)$CSiMe_3$]$_2$ and protonated H_2**L** as well as Me_4Si at 0.00 ppm. No $ClCH_2SiMe_3$ was observed.

Table 1.7. Crystal data and structure refinement for **L**Mo(Cl)(CH_2SiMe_2Ph).

Identification code	03312	
Empirical formula	$C_{28}H_{32}ClF_6MoN_3Si$	
Formula weight	684.05	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 44.1044(19) Å	α= 90°
	b = 8.6831(4) Å	β= 107.9310(10) °
	c = 16.7644(7) Å	γ = 90°
Volume	6108.3(5) $Å^3$	
Z	8	
Density (calculated)	1.488 Mg/m^3	
Absorption coefficient	0.615 mm^{-1}	
F(000)	2784	
Theta range for data collection	1.94 to 22.50°.	
Index ranges	$-47 \le h \le 47$, $-7 \le k \le 9$, $-16 \le l \le 18$	
Reflections collected	10570	
Independent reflections	3734 [R(int) = 0.0209]	
Completeness to theta = 22.50°	93.5 %	
Absorption correction	Empirical	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3734 / 0 / 361	
Goodness-of-fit on F^2	1.151	
Final R indices [I>2sigma(I)]	R1 = 0.0479, wR2 = 0.1574	
R indices (all data)	R1 = 0.0551, wR2 = 0.1830	
Largest diff. peak and hole	0.620 and -0.633 e/$Å^3$	

Table 1.8. Crystal data and structure refinement for **L**Mo(CH_2SiMe_3)$_2$.

Identification code	04062	
Empirical formula	$C_{27}H_{41}F_6MoN_3Si_2$	
Formula weight	673.75	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 9.2737(13) Å	α= 90°
	b = 27.439(4) Å	β= 99.761(4)°
	c = 12.6102(17) Å	γ = 90°
Volume	3162.4(8) Å^3	
Z	4	
Density (calculated)	1.415 Mg/m^3	
Absorption coefficient	0.547 mm^{-1}	
F(000)	1392	
Crystal Size	0.20 x 0.15 x 0.10 mm^3	
Theta range for data collection	1.48 to 26.49°	
Index ranges	$-11 \le h \le 11$, $0 \le k \le 34$, $0 \le l \le 15$	
Reflections collected	18206	
Independent reflections	6532 [R(int) = 0.0265]	
Completeness to theta = 22.50°	99.7 %	
Absorption correction	Empirical	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6532 / 89 / 500	
Goodness of fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0400, wR2 = 0.0873	
R indices (all data)	R1 = 0.0519, wR2 = 0.0936	
Largest diff. peak and hole	0.822 and -0.792 e/Å^3	

Table 1.9. Crystal data and structure refinement for **L**Mo(CHSiMe$_3$)(η^2 - MeC≡CMe).

Identification code	03119	
Empirical formula	$C_{27}H_{35}F_6MoN_3Si$	
Formula weight	639.61	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	*P*bca	
Unit cell dimensions	a = 19.5713(18) Å	α= 90°
	b = 14.2824(14) Å	β= 90°
	c = 21.163(2) Å	γ = 90°
Volume	5915.5(10) Å^3	
Z	8	
Density (calculated)	1.436 Mg/m^3	
Absorption coefficient	0.542 mm^{-1}	
F(000)	2624	
Theta range for data collection	1.92 to 22.50°	
Index ranges	$-17 \leq h \leq 21$, $-12 \leq k \leq 15$, $-21 \leq l \leq 22$	
Reflections collected	21274	
Independent reflections	3858 [R(int) = 0.0892]	
Completeness to theta = 22.50°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3858 / 0 / 349	
Goodness of fit on F^2	1.134	
Final R indices [I>2sigma(I)]	R1 = 0.0776, wR2 = 0.1415	
R indices (all data)	R1 = 0.1098, wR2 = 0.1530	
Largest diff. peak and hole	0.675 and -1.133 e/Å^3	

Table 1.10. Crystal data and structure refinement for $[\mathbf{L}MoS]_2$.

Identification code	03234	
Empirical formula	$C_{38}H_{38}F_{12}Mo_2N_6S_2$	
Formula weight	1062.74	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 11.0776(9) Å	$\alpha = 90°$
	b = 10.7527(9) Å	$\beta = 93.570(2)°$
	c = 17.1936(15) Å	$\gamma = 90°$
Volume	2044.0(3) $Å^3$	
Z	2	
Density (calculated)	1.727 Mg/m^3	
Absorption coefficient	0.808 mm^{-1}	
F(000)	1064	
Crystal size	0.20 x 0.20 x 0.26 mm^3	
Theta range for data collection	2.24 to 26.49°	
Index ranges	$-13 \leq h \leq 13, 0 \leq k \leq 13, 0 \leq l \leq 21$	
Reflections collected	11410	
Independent reflections	4210 [R(int) = 0.0348]	
Completeness to theta = 26.49°	99.3 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9235 and 0.8551	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4210 / 60 / 328	
Goodness-of-fit on F^2	1.266	
Final R indices [I>2sigma(I)]	R1 = 0.0575, wR2 = 0.1033	
R indices (all data)	R1 = 0.0671, wR2 = 0.1062	
Largest diff. peak and hole	1.241 and -1.479 $e/Å^3$	

Table 1.12. Crystal data and structure refinement for [**L**Mo(Cl)($CSiMe_3$)]$_2$.

Identification code	03215	
Empirical formula	$C_{46}H_{56}Cl_2F_{12}Mo_2N_6Si_2$	
Formula weight	1239.93	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 12.4041(8) Å	α= 90°
	b = 16.8435(10) Å	β= 113.2950(10)°
	c = 13.8243(8) Å	γ = 90°
Volume	2652.8(3) Å^3	
Z	2	
Density (calculated)	1.552 Mg/m^3	
Absorption coefficient	0.699 mm^{-1}	
F(000)	1256	
Crystal size	0.48 x 0.30 x 0.23 mm^3	
Theta range for data collection	1.79 to 25.00°	
Index ranges	$-14 \le h \le 14$, $-20 \le k \le 19$, $-16 \le l \le 8$	
Reflections collected	14117	
Independent reflections	4677 [R(int) = 0.0349]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Empirical	
Max. and min. transmission	0.8557 and 0.7301	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4677 / 0 / 317	
Goodness of fit on F^2	1.055	
Final R indices [I>2sigma(I)]	R1 = 0.0356, wR2 = 0.0920	
R indices (all data)	R1 = 0.0420, wR2 = 0.0947	
Largest diff. peak and hole	1.065 and -0.719 e/Å^3	

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Chapter 2

Early Transition Metal Pyrrolyl Complexes: Structure, Spectroscopy, Hapticity, and Fluxional Processes.

Introduction

Pyrrolyl complexes of late transition metals have received a fair amount of attention, mostly as azacyclopentadienyl complexes in the η^5 bonding mode.[1,2,3] There has been a growing interest in utilizing pyrrolide anion (called pyrrolyl when bound to a transition metal in analogy with the cyclopentadienyl ligand) as a ligand for early transition metal complexes.[4] This is in part due to the unique electronic properties of the pyrrolide anion with respect to traditional amides. No review focusing on the early (groups 4, 5, and 6) transition metal pyrrolyl complexes has yet appeared, with the exception of a review on group 3 heterocyclopentadienide complexes.[5] Collected here are the structurally characterized group 4, 5, and 6 pyrrolyl complexes and some spectroscopically characterized species as well. A focus of this review is the unique electronic and dynamic properties of the pyrrolyl ligand. Some related ligands such as indolyl and dipyrrolylmethanes have been included when germane to the discussion.

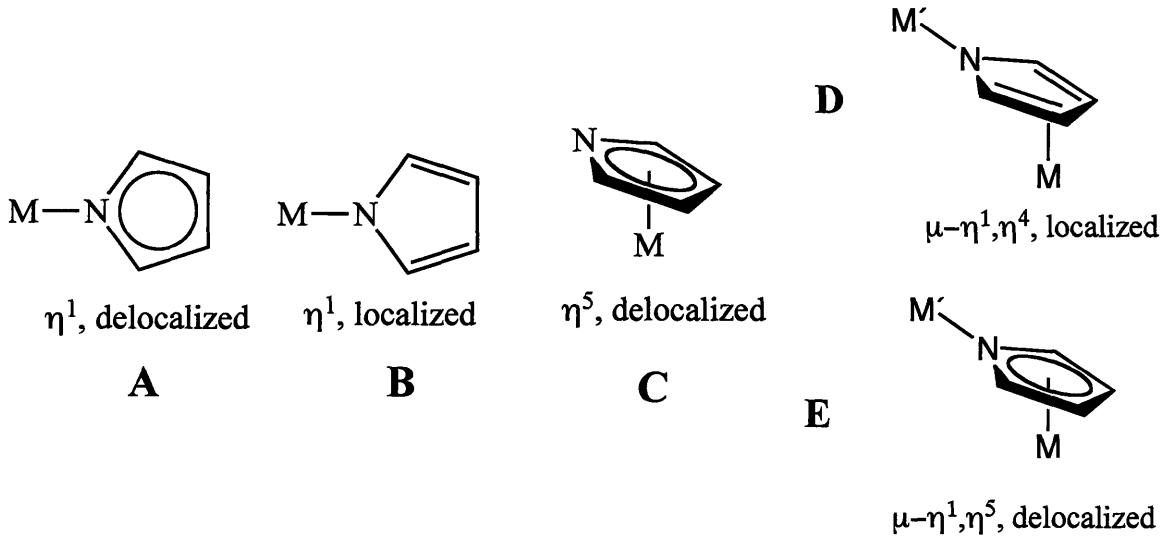
2.1 Properties and characteristics of pyrrole and pyrrolide anion.

Pyrrole and its anion conform to the Hückel 4n+2 π electron rule[6] and are aromatic.[7] The stabilization energy has been calculated to be 22 kcal/mol for pyrrole.[8] This is somewhat less than the estimated 27 kcal/mol[9] of the corresponding anion cyclopentadienide. The decreased stabilization is due to the introduction of the electronegative nitrogen atom. In the calculated free pyrrolide anion, the nitrogen atom has a substantial negative charge. The HOMO of the pyrrole anion is largely a nitrogen lone pair, capable of σ bonding. However, the HOMO -1 and LUMO largely resemble the cyclopentadienyl anion,[10] capable of similar bonding interactions with transition metals. Thus, one would expect that the η^5 coordination would be prevalent in electron-rich species capable of significant backbonding or in electrophilic, sterically open systems in which the donation of more than two electrons is desired. This is indeed the case. However, the availability of the nitrogen lone pair electron density leads to a substantial amount of μ-η^5,η^1 bonding modes for pyrrolyl ligands when coordinated to electrophilic metal centers.[3] It seems reasonable that the paucity of early transition

metal-pyrrolyl chemistry is a direct result of the need for other supporting ligands capable of preventing oligomerization of metal complexes by bridging pyrrolyl ligands and formation of intractable materials.

Much of late metal pyrrolyl chemistry is dominated by η^5 coordination and cyclopentadienide-like behavior; (for example electrophilic aromatic substitution[2]) it is tempting to presume that early metal chemistry of η^5 pyrrolide also will demonstrate cyclopentadienide-like behavior. However, the hard nitrogen donor and the fact that there it is not necessary to break the aromaticity of the pyrrolide anion to engage in η^1 or η^5 coordination yields a unique ligand with the ability to accommodate a variety of electron counts and substitution patterns.

Pyrrole is a relatively simple organic molecule with a very rich and sometimes unpredictable chemistry. In stark contrast to the isoelectronic, all-carbon cyclopentadienide anion, pyrrolide shows a marked propensity to engage in multiple bonding modes, donating 2, 4, or 6 electrons to the metal as shown in Scheme 2.1. The focus of this review is to examine the structurally characterized examples of pyrrolyl complexes of the early transition metals (groups 4, 5, and 6). When data are available, analysis of fluxional behavior and relevant spectroscopy will be included.



Scheme 2.1 Common pyrrolyl bonding modes.

Table 2.1. Selected Data for Pyrrolyl (and Related) Complexes. NMR data are listed for ring ^{13}C and ^{1}H resonances.

Complex	M-N distance (Å)	^{13}C NMR (ppm)	^{1}H NMR (ppm)	Ref
$Zr(\eta^1\text{-}2,5\text{-}Me_2NC_4H_2)_4$	2.090(3), 2.069(3), 2.080(3), 2.076(3)	nr	nr	12
$[Na(THF)_6]_2Zr(\eta^1\text{-}NC_4H_4)_6$	2.198(6)	nr	nr	11
$Ti(Cp)_2(\eta^1\text{-}NC_4H_4)_2$	2.070(5), 2.100(4)	nr	nr	11
$Zr(Cp)_2(\eta^1\text{-}NC_4H_4)_2$	2.171(2), 2.167(2)	nr	nr	11
$Zr(Cp)_2(\eta^1\text{-}2,5\text{-}Me_2NC_4H_4)_2$	2.22(2), 2.25(2)	nr	nr	12
$Ti(\eta^5\text{-}2,5\text{-}t\text{-}Bu_2NC_4H_2)Cl_3$	2.249(11)	172.41, 123.90	6.52	14
$Ti(\eta^5\text{-}2,5\text{-}t\text{-}Bu_2\text{-}3\text{-}Me_3SiNC_4H)Cl_3$	nr	176.16, 174.94, 141.87, 132.51	7.30	14
$Zr(\eta^5\text{-}2,5\text{-}t\text{-}Bu_2NC_4H_2)Cl_3$	nr	165.57, 121.30	6.39	14
$Zr(\eta^5\text{-}2,5\text{-}t\text{-}Bu_2\text{-}3\text{-}Me_3SiNC_4H)Cl_3$	nr	170.30, 167.76, 136.11, 127.52	7.16	14
$Hf(\eta^5\text{-}2,5\text{-}t\text{-}Bu_2NC_4H_2)Cl_3$	nr	163.90, 119.50	6.53	14
$Hf(\eta^5\text{-}2,5\text{-}t\text{-}Bu_2\text{-}3\text{-}Me_3SiNC_4H)Cl_3$	nr	168.87, 165.01, 133.52, 125.86	7.00	14
$Zr(\eta^5\text{-}2,5\text{-}Ph_2NC_4H_2)(NMe_2)_3$	2.481(3)	143.6, 111.4	6.77	17
$Zr(\eta^1\text{-}2,5\text{-}Ph_2NC_4H_2)(NMe_2)_3(Me_2NH)$	2.256(3)	143.5, 111.5	6.77	17

$Ti(\eta^1\text{-}2,5\text{-}Ph_2NC_4H_2)(NMe_2)_3$	2.052(4)	143.3, 112.1	6.77	17
$Zr(\eta^1\text{-}2,5\text{-}Xyl_2NC_4H_2)(NMe_2)_3$ (Xyl = 2,4-$Me_2C_6H_3$)	2.220(3)	140.0, 113.2	6.73	17
$Zr(\eta^5\text{-}2,5\text{-}Ph_2NC_4H_2)_2I_2$	2.426(10), 2.490(10),	144.2, 114.4	7.14	17
$Zr(\eta^5\text{-}2,5\text{-}Ph_2NC_4H_2)_2Cl_2$	2.4270(15), 2.5103(15)	146.9, 122.3	6.75	17
$Zr(\eta^5\text{-}2,5\text{-}Xyl_2NC_4H_2)_2Cl_2$	2.426(4), 2.467(3)	148.9, 121.7	nr	17
$Zr(\eta^5\text{-}2,5\text{-}Ar_2NC_4H_2)(NMe_2)I_2$ (Ar = Ph, Xyl)	Ph = 2.433(7) Ar = Xyl; 2.413(5)	Ar = Ph; 146.8, 116.8 Ar = Xyl; 145.0, 116.7	Ar = Ph; 7.01 Ar = Xyl; 6.84	17
$Ti(\eta^5, \eta^1$ - dppm)$(NMe_2)_2$ (dppm = 5,5'-dipropylpyrrolmethane)	η^1: 2.046 η^5: 2.275	161.5, 126.1, 111.9, 109.6	6.28, 6.32, 6.95	20b
$[Me_2Si(C_5Me_4)_2]Ti(\eta^1\text{-}NC_4H_4)Cl$	2.090(3)	109.4, 111.0, 121.9	5.73, 6.66, 7.05	18
$[Me_2Si(C_5Me_4)_2]Ti(\eta^1\text{-}NC_4H_4)Me$	2.090(7)	109.4, 123.3	5.94, 6.61	18
$[Me_2Si(C_5Me_4)_2]Ti(\eta^1\text{-}NC_4H_4)_2$	2.086(3)	108.4, 128.4	6.57, 6.74	18
$[Me_2Si(C_5Me_4)_2]Ti(\eta^1\text{-}NC_4H_4)H$	2.058(2)	108.7, 118.5	6.09, 6.66	18
$[Me_2Si(C_5Me_4)(C_5Me_3CH_2)]Ti(\eta^1\text{-}NC_4H_4)$	2.072(4)	106.5, 121.1	5.65, 6.46	18
$Ti(\eta^5\text{-TMP})MeCl_2$	2.1882(2)	147.40, 136.44	n/a	16a
$M(\eta^5\text{-TMP})(CH_2Ph)_3$ M = (Ti, Zr, Hf)	nr nr nr	M = Ti; 144.45, 130.29 M= Zr, 143.09, 137.80 M = Hf; 144.38, 139.32	n/a	16a
$Ti(\eta^5\text{-}2,5\text{-}Me_2NC_4H_2)(NMe_2)_2Cl$	2.283(3)	138.0, 112.9	5.93	15

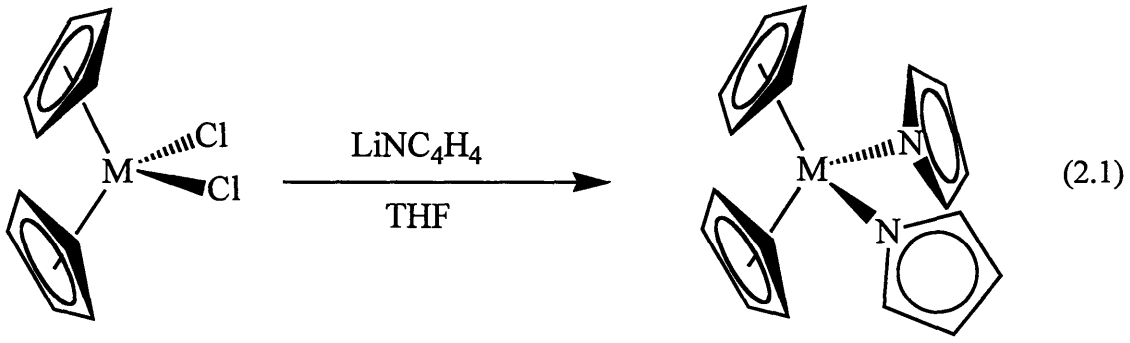
$Ti(\eta^5\text{-TMP})Cl_3$	2.181(6)	141.95, 153.65	n/a	16b
$Ti(\eta^5\text{-TMP})_2Cl_2$	nr	113.48, 119.86, 140.09, 147.71	n/a	16b
$Ti(\eta^5\text{-TMP})(SPh)_3$	2.168(10)	142.31, 148.28	n/a	16b
$Ti(\eta^5\text{-TMP})(SPh)Cl_2$	nr	143.25, 150.77	n/a	16b
$Ti(Cp)(\eta^5\text{-TMP})Cl_2$	2.254(9)	nr	n/a	16b
$[K([15]crown\text{-}5)_2]Ti(\eta^5\text{-}NC_4H_4)(CO)_3$	nr	114, 99 (0 °C)	5.40, 6.16 (0 °C)	22

$Ta(\eta^5\text{-TMP})Me_2Cl_2$ (TMP = 2,3,4,5-Me_4NC_4)	2.253(14)[η^5]	nr	n/a	30
$Ta(\eta^5\text{-TMP})Me_3Cl$	nr	137.3, 132.9	n/a	30
$Ta(\eta^5\text{-TMP})Me_3(\eta^1\text{-}NC_8H_6)$	2.238(11)[η^5] 2.070(11)[η^1]	145.2, 133.0 (TMP) (indolide unassigned)	n/a	30
$Ta(\eta^5\text{-TMP})Me_4$	nr	134.9, 132.2	n/a	30
$Ta(\eta^5\text{-TMP})Me_3(\eta^1\text{-}NC_4H_4)$	nr	135.0, 130.6 (TMP) 127.3, 111.6 (pyrr)	n/a	30
$V(\eta^1\text{-}2,5\text{-}Me_2C_4H_4)_2Py_3$	2.169(4), 2.141(2)	nr	nr	24
$V(NMe_2)_2(cb)_2$ (cb = carbazole anion)	1.930(10), 1.917(7)	nr	nr	25
$[Nb(\eta^1\text{-}2,5\text{-}Me_2C_4H_4)_2\text{-}\mu\text{-}N\text{-}\mu\text{-}2,4\text{-hexene-}\eta^1\text{-}2,5\text{-}Me_2C_4H_4\text{-}\eta^5\text{-}2,5\text{-}Me_2C_4H_4Nb][LiNb_2Cl_5(tmeda)_3]$	η^5 = 2.483(4) η^1 = 2.154(3), 2.166(3)	135.3, 132.3, 107.6, 107.0	nr	26

$Nb(\eta^1\text{-}2,5\text{-}Me_2C_4H_4)(Me_2NCH_2CH_2NMe)(\eta^5\text{-}\mu\text{-}\eta^1\text{-}2,5\text{-}Me_2C_4H_4)(\mu\text{-}CH_2)Nb(H)(\eta^5\text{-}2,5\text{-}Me_2C_4H_4)$	η^5 = 2.341(3) η^1 = 2.004(3)	nr	nr	26
$Cr(\eta^1\text{-}NC_4H_4)_2(py)_3 \cdot tol$ (py = NC_5H_5)	2.061(4), 2.174(4)	nr	nr	32
$Cr(\eta^1\text{-}2,5\text{-}Me_2NC_4H_2)_2(py)_2$	2.145(2), 2.036(1)	nr	nr	32
$[\{Na(THF)_2\}_2Cr(\eta^1\text{-}2,5\text{-}Me_2NC_4H_2)_4(Et_2O)_2]_n$	2.074(5), 2.086(4)	nr	nr	32
$[Cr(7\text{-azaindolyl})_2(DMF)_2]_2$	2.062(6), 2.084(2)	nr	nr	32
$Mo\{HB(3,5\text{-}Me_2C_3N_2H)\}(NO)(\eta^1\text{-}NC_4H_4)_2$	2.045, 1.982	nr	nr	34
$W(TMP)_2Cl_2$	nr	120.0, 118.0	n/a	38
$W(TMP)_2Me_2$	nr	114.6, 106.0	n/a	38

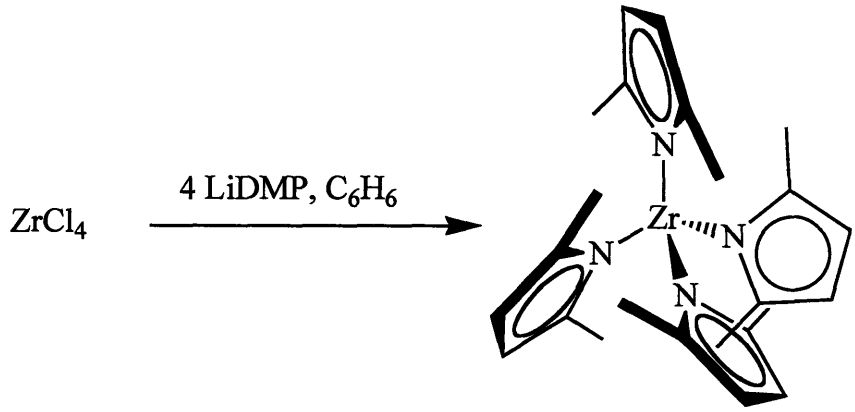
2.2 Group 4 Pyrrolyls

In 1980 Atwood and coworkers published the first structural study of group 4 pyrrolyl complexes.[11] Treatment of MCp_2Cl_2 (M = Ti, Zr) with two equivalents of $NaNC_4H_4$ in THF resulted in the formation of the corresponding $M(\eta^5\text{-}Cp)_2(\eta^1\text{-}NC_4H_4)_2$ complexes in high yield. The complexes contain planar pyrrolyl rings with ring bond distances consistent with the pyrrolyl ligands retaining a significant amount of delocalized character. The NMR spectra are not reported. The average M to η^1–NC_4H_4



(2.1)

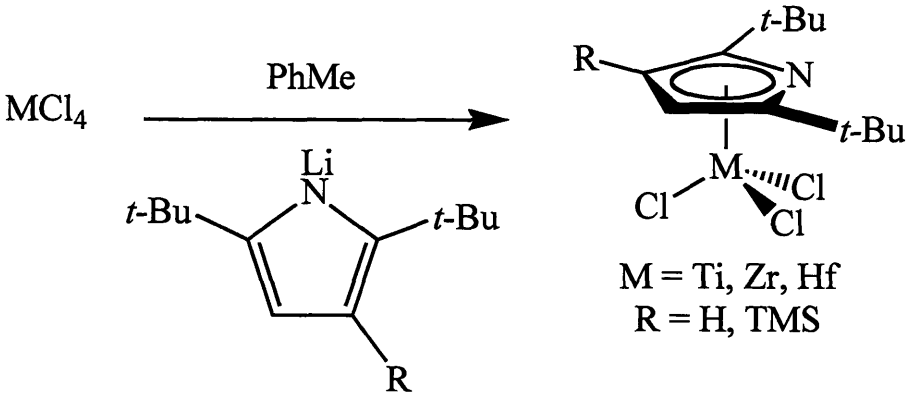
distances are 2.085 (Ti) and 2.17 Å (Zr), respectively. One other feature of note was the reported air-stability of the titanium complex. Atwood and coworkers also reported the 2,5-dimethylpyrrolyl complexes, $Zr(Cp)_2(DMP)_2$, which show a longer average zirconium - $N_{pyrrolyl}$ distance of 2.224 Å. Treatment of $ZrCp_2Cl_2$ with two equivalents of $NaNC_4H_4$ in THF under reflux conditions lead to the formation of $[Na(THF)_6]_2[Zr(\eta^1\text{-}NC_4H_4)_6]$[11] in low yield. The complex was reported to readily lose THF and was not analyzed by methods other than X-ray diffraction. The analogous, octahedral 2,5-dimethylpyrroly complex is unknown. However the homoleptic four-coordinate $Zr(\eta^1\text{-}DMP)_4$ complex was prepared from the reaction of NaDMP with $ZrCl_4$ in benzene.[12] The electron count at the metal center is 8 electrons, not counting any potential pyrrolyl Zr – $N_{pyrrolyl}$ π overlap. However, some interaction is likely, as the Zr-$N_{pyrrolyl}$ distance



(2.2)

is quite short, averaging 2.078(4) Å. By comparison, the terminal Zr – NMe_2 bonds are 2.050(5) and 2.104(5) Å in the dimer $[Zr(NMe_2)_4]_2$.[13] Furthermore, the carbon-carbon bond distances in the pyrrolyl rings show some bond alternation, indicative of bonding type **B** interaction, as shown above.

Later work has provided examples of simple group 4 η^5-pyrrolyl trichlorides (eqn 2.3).[14] This was achieved by utilizing a large amount of steric bulk in the 2 and 5 positions of the pyrrolyl ring, blocking η^1 – coordination. It is worthwhile to note that in examples that have pyrrolyl hydrogens, the proton NMR resonance is shielded relative to the free pyrrole. For example, the values are 6.52, 6.39, and 6.53 ppm for the 3 and 4 hydrogen atoms in $M(\eta^5\text{-}2,5\text{-}t\text{-}Bu_2C_4H_2N)(Cl)_3$ (M = Ti, Zr, Hf respectively). The complex $Ti(\eta^5\text{-}Me_2C_4H_2N)(NMe_2)_2Cl$ also shows an upfield proton shift of 5.93 ppm.[15] A number of η^5 - 2,3,4,5-tetramethylpyrrolyl (TMP) complexes have also been characterized.[16]



(2.3)

Parkin and Tanski conducted a study of 2,5-diaryl substituted pyrrolyl complexes of zirconium.[17] A number of complexes were observed to adopt η^5 or η^1 geometries in what appears to be a delicate balance involving the bulk of the 2,5-aryl substitutents. If the aryl rings could become coplanar with the η^5 pyrrolyl ring, then η^5 coordination was observed. The xylyl substitution blocked this orientation and these complexes were observed to favor η^1 coordination. The calculated barriers for η^5/η^1 interconversion ranged from 3 to 10 kcal/mol and agreed with the steric arguments presented above. Also, more electrophilic complexes were found to favor η^5 coordination. In another study of monopyrrolyl complexes of *ansa* metallocenes of the type $[Me_2Si(C_4Me_4)_2]Ti(\eta^1\text{-}NC_4H_4)X$[18] it was concluded that the pyrrolyl ligand was a poor π donor relative to traditional amides. Reversible activation of the cyclopentadienyl ligand was observed in the conversion of "tucked" $[Me_2Si(C_5Me_4)(C_5Me_3CH_2)]Ti(\eta^1\text{-}NC_4H_4)$ to $[Me_2Si(C_5Me_4)_2]Ti(\eta^1\text{-}NC_4H_4)H$ by addition of H_2 to the tucked complex.

Protonolysis of group 4 amide and alkyl complexes has been used to synthesize many species, including those containing multidentate ligands. This route has been used to synthesize a number of mixed pyrrolyl-amide and alkyl as well as dipyrrolylmethane complexes.[19,20] The related tribenzyl complexes $M(\eta^5\text{-}NC_4Me_4)(CH_2Ph)_3$ were synthesized from the common tetrabenzyl precursors *via* protonation with tetramethylpyrrole. The resulting complexes were postulated to contain α-agostic benzyl groups on the basis of pyrrolyl ring ^{13}C NMR resonances and comparison with the structurally characterized $Ti(Cp)(CH_2Ph)_3$. However, the proton-carbon coupling constants of ca. 124 Hz are not consistent with this assertion, unfortunately no structural study has appeared to date.[16a]

Ellis' longstanding interest in low-valent transition metals[21] includes the report of the formally zerovalent $\{K[15]crown\text{-}5\}[Ti(\eta^5\text{-}C_4H_4N)(CO)_3]$,[22] prepared by salt metathesis at low temperature. The complex is apparently thermally stable once isolated. A structural study apparently was conducted as the bis(triphenylphosphane)iminium salt. However, the structure has not yet been reported. Once again, the pyrrolyl ring proton resonances are significantly deshielded (compared to free pyrrole) at 6.16 and 5.40 ppm in the $\{K[15]crown\text{-}5\}^+$ salt.

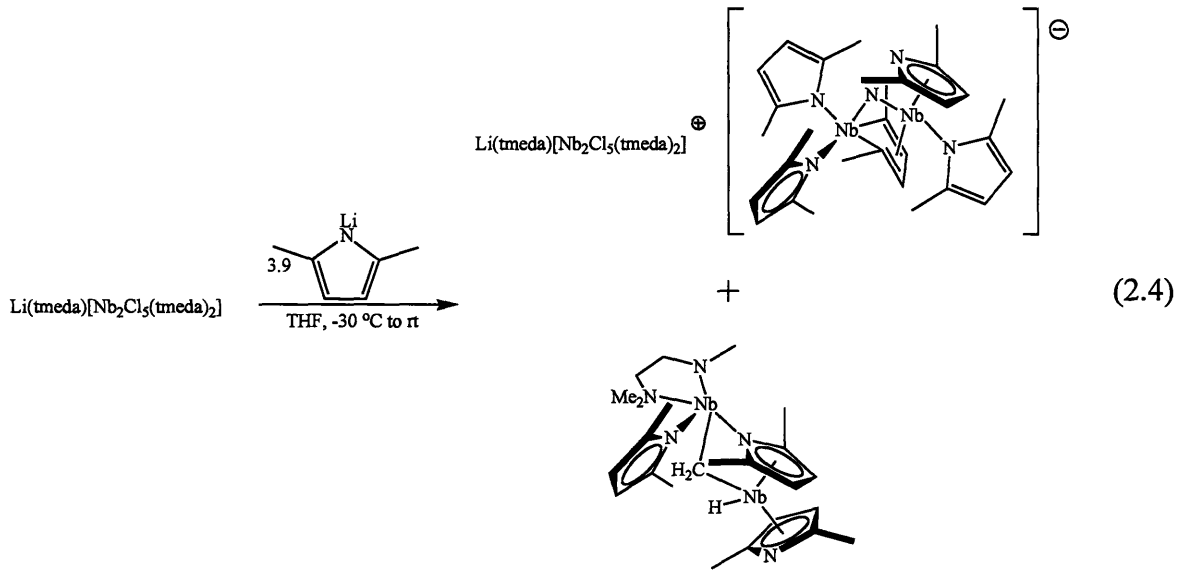
Two dynamic studies have appeared in the literature. One was the interconversion barrier of the η^5 and η^1 rings of $Ti(NMe_2)_2$(5,5'-dimethyldipyrrolylmethane), which was

measured to be 10.2 kcal/mol in dichloromethane-d_2.[20b] It should be noted that these and related complexes are excellent catalyst[5] for many hydroamination[20b] and other[4] reactions. In another study, the interconversion of the *meso* and *rac* forms of Zr(2,4-dimethyl-3-ethylpyrrolyl)$_2$Cl$_2$, the barrier for which was measured to be 7.2 kcal/mol.[23] This study also included calculations that were in agreement with the experimentally measured barrier.

2.3 Group 5 Pyrrolyls

There are few structurally characterized pyrrolyls of group 5 metals. The simple vanadium(II) species V(η^1-DMP)$_2$(Py)$_3$[24] was prepared from *trans*-(tmeda)VCl$_2$ and sodium pyrrolide in THF followed by addition of pyridine. The structure was determined to be a distorted square pyramid with the pyrrolyl ligands oriented *trans* to one another in the basal plane. The pseudo tetrahedral vanadium(IV) complex V(NMe$_2$)$_2$(cb)$_2$ (cb = carbazole anion) was synthesized by addition of cbH to V(NMe$_2$)$_4$.[25] The V – N_{amide} bonds are 1.811(10) and 1.816(10) Å, significantly shorter than the V – N_{cb} bonds at 1.930(10) and 1.917(7) Å. This species is an active catalyst for the hydroamination of 1-hexyne with aniline.

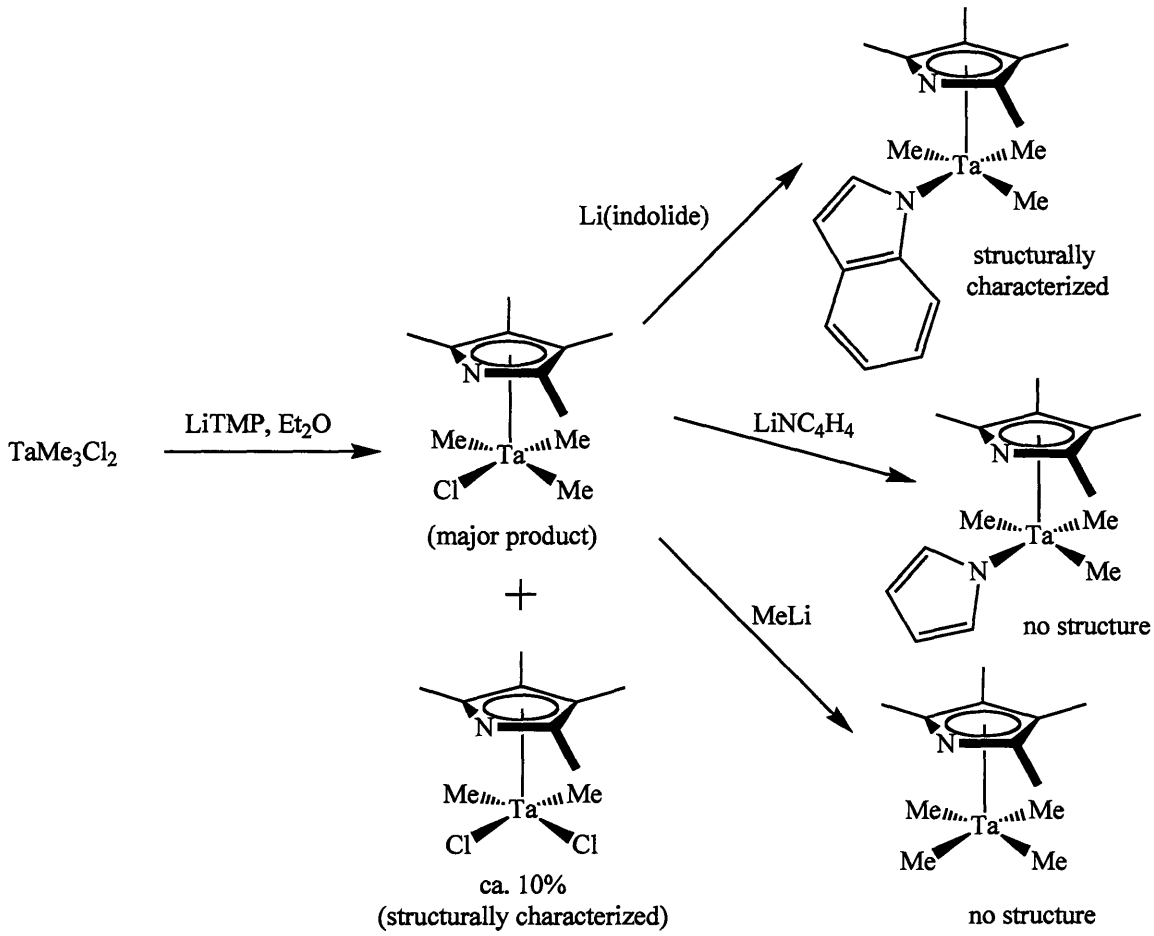
Gambarotta and coworkers examined[26] the reaction of alkali pyrrolyls with Li(tmeda)[Nb$_2$Cl$_5$(tmeda)$_2$]. Two products were isolated in low yields. The first was the salt of Li(tmeda)[Nb$_2$Cl$_5$(tmeda)$_2$] cation shown below in eqn 2.4. In a spectacular example



(2.4)

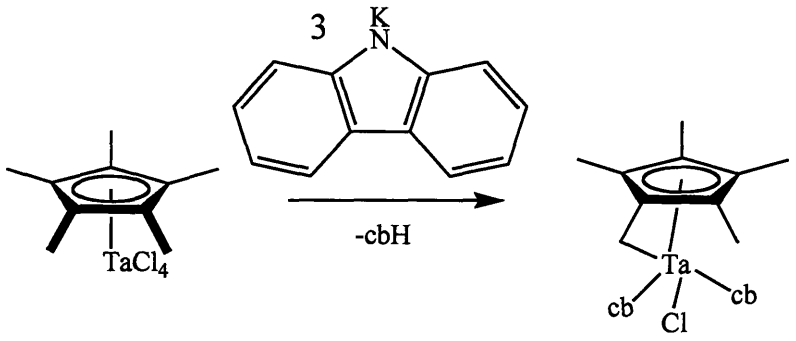
of C-N activation, the pyrrole nitrogen is extricated from the ring and incorporated as a bridging nitride! This complex is supported by a mixture of η^1 and η^5 pyrrolyl ligands which shows the plastic capability of pyrrolide anion to supply electron density to the metal. The neutral complex is the result of C-N activation of the tmeda methyl group followed by a C - H α – elimination,[27] resulting in an asymmetrically bridging alkylidene and a hydride ligand. The η^5, η^5 Nb - $C_{alkylidene}$ distance of 2.098(4) Å is typical for a non-agostic alkylidene ligand, and the other Nb - C distance is quite long at 2.272(4) Å. In fact, the μ-η^5, η^1 pyrrolyl η^1 distance is shorter at 2.201(3) Å. Other than the molybdenum dimer {Mo(NAr)(*syn*-CHCMe$_2$Ph)(η^5-NC$_4$H$_4$)(η^1-NC$_4$H$_4$)}{Mo(NAr)(*syn*-CHCMe$_2$Ph)(η^1-NC$_4$H$_4$)$_2$},[28] and the recently determined structure of W(NAr)(CHCMe$_3$)(η^5-Me$_2$C$_4$H$_2$N)(η^1-Me$_2$C$_4$H$_2$N)[29] this is the only structurally characterized alkylidene complex containing an η^5 pyrrolyl ligand.

DuBois and coworkers explored the chemistry of a series of tantalum η^5 – tetramethylpyrrolyls[30] as shown in Scheme 2.2. Treatment of TaMe$_3$Cl$_2$ with one equivalent of LiTMP (TMP = NC$_4$Me$_4^-$) yielded a mixture of Ta(η^x-TMP)(Me)$_3$Cl and Ta(η^5-TMP)(Me)$_2$Cl$_2$. The minor product Ta(η^5-TMP)(Me)$_2$Cl$_2$ was shown to contain an η^5-pyrrolide ligand in the solid state. It is reasonable to believe that the pyrrolyl is coordinated in an η^5 fashion in Ta(η^x-TMP)(Me)$_3$Cl, given that the derivative Ta(η^5-TMP)Me$_3$(η^1-NC$_8$H$_6$) was shown to contain an η^5 TMP ligand by a structural study. Several other derivatives were also prepared, although structural studies were not performed. It is interesting to note that variable temperature studies were consistent with the equilibration of methyl groups in the indolyl complex Ta(η^5-TMP)Me$_3$(η^1-NC$_8$H$_6$) and pyrrolide complex Ta(η^5-TMP)Me$_3$(η^1-NC$_4$H$_4$), but there was no reported signs of isomerizing to Ta(η^1-TMP)Me$_3$(η^5-NC$_8$H$_6$) or Ta(η^1-TMP)Me$_3$(η^5-NC$_4$H$_4$).



Scheme 2.2. Reactivity of Ta(η^5 – TMP)$(Me)_3Cl$.

Rothwell and coworkers explored the chemistry of the carbazole (cbH) ligand in some detail.[31] Only η^1 binding modes were observed. However, several interesting observations were made. First, upon attempted synthesis of the Cp* derivative shown below, a carbazole ligand acts as an internal base to remove a proton and facilitate C-H activation.[31d] In the same paper they note that the Ta-N distances are 0.2 Å longer than the corresponding Ta – NMe_2 distances. They ascribe this to the poor π donor capabilities of the carbazole moiety.

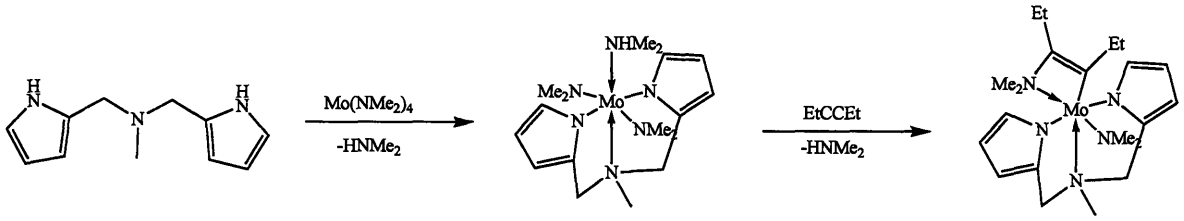


(2.5)

2.4 Group 6 Pyrrolyls.

Several low-valent group 6 pyrrolyl complexes have been examined. Gambarotta and coworkers reported several chromium(II) derivatives of pyrrolide, 2,5-dimethylpyrrolide and 7-azaindolide.[32] All complexes show η^1 binding modes and their paramagnetism prevents NMR spectroscopic study. One unusual species is the square-pyramidal chromium complex $Cr(\eta^1\text{-}NC_4H_4)_2Py_3$, which is isostructural with the vanadium complex mentioned before. The homoleptic complex $[\{Na(THF)_2\}_2Cr(\eta^1\text{-}2,5\text{-}Me_2C_4H_2N)_4(Et_2O)]_n$ crystallizes as an infinite chain bridged by sodium cations intercalated in the π clouds of the 2,5-dimethylpyrrolyl ligands of $[Cr(\eta^1\text{-}DMP)_4]^{2-}$ species. This behavior has not been reported often in mononuclear pyrrolyl systems. However, the low isolated yields of many complexes hints that products that retain alkali cations in polymeric form may be present in many cases and not tractable.

Odom has reported the unusual insertion of 3-hexyne into a molybdenum amide bond in a complex supported by a chelating bis(pyrrolyl)amine ligand[33] as shown in Scheme 2.3. The molybdenum(IV) species shown below was readily synthesized through protonolysis. Unfortunately no further studies have appeared of the resulting highly reactive species.



Scheme 2.3. Formation and reactivity of a molybdenum bis(pyrrolyl)amine complex.

$Mo\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(NO)(\eta^1\text{-}NC_4H_4)_2$ was reported in 1984 by Jones and coworkers.[34,35] The complex contains one very short Mo-$N_{pyrrolyl}$ distance of 1.982 Å; to the best of our knowledge, this is one of the shortest transition metal-$N_{pyrrolyl}$ distance reported in the Cambridge Structural Database. The reason for the very short Mo - $N_{pyrrolyl}$ distance is not entirely clear. Later, an electrochemical study[35] with chloride, thiolate, phenoxide and several amide complexes placed the π donation ability of pyrrolyl between that of chloride and thiolate for this system.

The only d^0 group 6 pyrrolyl complexes that have been structurally characterized are $\{Mo(NAr)(syn\text{-}CHCMe_2Ph)(\eta^5\text{-}NC_4H_4)(\eta^1\text{-}NC_4H_4)\}\{Mo(NAr)(syn\text{-}CHCMe_2Ph)(\eta^1\text{-}NC_4H_4)_2\}$ and $Mo(NAd)(CHCMe_2Ph)(\eta^1\text{-}NC_4H_4)_2(PMe_3)$, which are detailed in chapters 3 and 4 of this work, respectively. The molybdenum-nitrogen distances are typical of pyrrolyl complexes at an average of 2.10 Å. It is instructive to compare these with the metal - amide distances in the related diphenyl amide complex $Mo(NAr)(CHCMe_2Ph)(NPh_2)_2$ (2.007(3) and 2.009(3) Å).[36]

Dias and coworkers have reported the TMP complexes analogous to the bent metallocene complexes WCp_2X_2.[37] Treatment of WCl_4(DME) with two equivalents of LiTMP produced diamagnetic $W(\eta^5 - NC_4Me_4)_2Cl_2$ in low yield.[38] Alkylation with MeLi produced a diamagnetic dimethyl complex $W(\eta^5 - NC_4Me_4)_2Me_2$, which was also isolated in low yield. The mass spectrum showed both parent ions, and a series of calculations were performed to examine the η^5 / η^1 interconversion as closed-shell species. The calculations did not include open shell species. It is also worthy of note that the related, potentially isoelectronic (depending on pyrrolyl binding mode) species of the type "$WCpMe_2X$" (X = Cl, Me) are known to bind dinitrogen in a bridging fashion between two tungsten centers.[39] The dinitrogen activation chemistry of these systems has been examined in detail.[40]

2.5 Conclusions and outlook.

In the cases where direct comparison of bond lengths is possible, transition metal M - $N_{pyrrolyl}$ bonds tend to be 0.1 to 0.2 Å longer than amide analogues. The empirical evidence suggests that the π donating ability of a η^1 pyrrolyl ligand is slightly more than that of a halide. Fluxional η^5/η^1 interconversion is observed in complexes where there is 1) enough space around the metal to accommodate the pyrrolyl ring and 2) the metal is electron deficient enough to accommodate the electron density. Still, few variable temperature studies of pyrrolyl complexes which appear to be η^1 at room temperature have been reported. There is emerging evidence that η^5/η^1 interconversion can play a key role in stabilizing reactive species. The low observed barriers to η^5/η^1 interconversion (<11 kcal/mol in all early metal cases reported thus far), indicate that far more metal complexes may be undergoing similar fluxional processes than the room temperature ^{1}H NMR spectra may indicate.

With this knowledge in hand, further tuning of reactive transition metal centers may be possible by incorporating the pyrrolyl η^5 / η^1 interconversion as another tool to protect unsaturated transition metal species.

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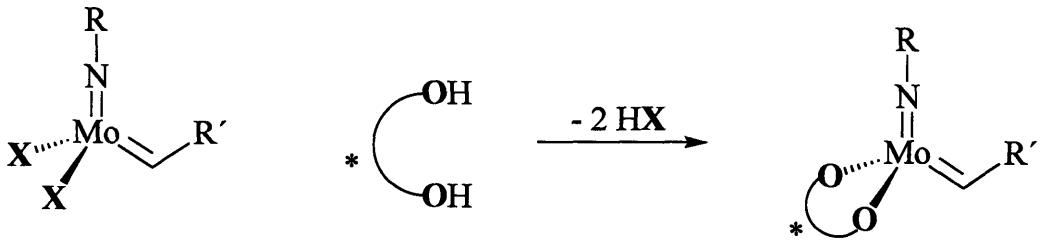
Chapter 3

Synthesis and Characterization of Molybdenum Imido Alkylidene Bis(amide) Complexes

A portion of this work has appeared in print:
A. S. Hock, R. R. Schrock, and A. H. Hovyeda
"Dipyrrolyl Precursors to Molybdenum Olefin Metathesis Catalysts"
J. Am. Chem. Soc., **2006**, *128*, 16373

Introduction

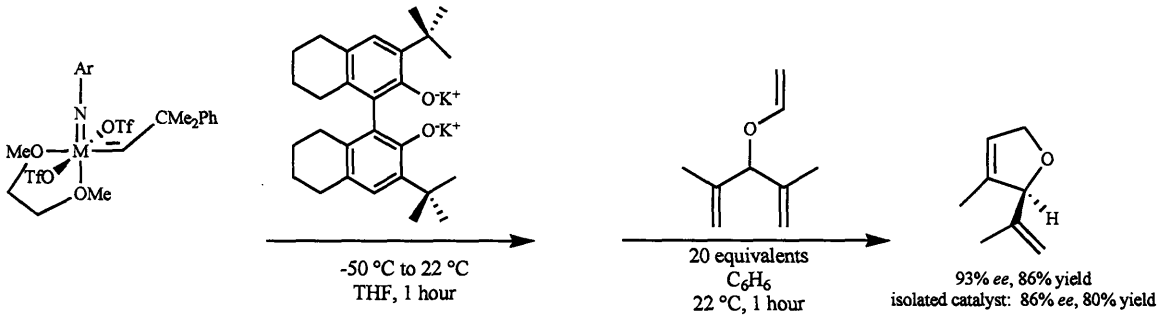
The rational development of active[1] and enantioselective molybdenum metathesis catalysts[2] has produced a large library of catalysts. It has been observed that the enantioselectivity of a given reaction varies depending on the substrate of interest combined with the choice of supporting imido and diolate ligands, as well as other influences such as the presence of Lewis bases such as THF.[12] It has become evident that there is no "magic bullet" catalyst which is effective for all applications. Thus, development of new catalyst variations in imido[2,3] and alkoxide ligands continues to be a fruitful area of research. With every new catalyst variation synthesized, the daunting challenge of storage and handling of catalysts (>100 possibilities to date)[2] grows. Clearly it would be desirable to generate many possible catalysts *in situ* from a common precursor. Ideally this method could be extended to catalyst derivatives which are not isolable due to bimolecular decomposition[21,22] or other, unknown, pathways.[41] The readily available starting material $Mo(NR)(CHR')(OTf)_2(DME)$[4,5] provides a convenient entry point by which complexes of the type $Mo(NR)(CHR')(\mathbf{X})_2$ might be synthesized. Given the wide use of protonation[6] to establish early transition metal-oxygen bonds, the X ligands could potentially be replaced by protonation with an alcohol, phenol, or enantiopure diol to yield the desired catalyst (Scheme 3.1).



Scheme 3.1 Strategy for *in situ* asymmetric metathesis catalyst synthesis.

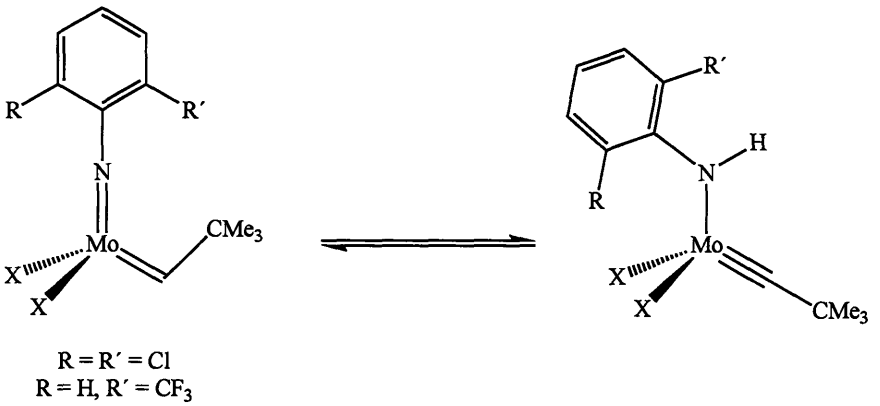
There are several requirements for the choice of the **X** ligand. First, in order to react with the very bulky substituted biphenol-based diols, the ligand must be sterically accessible. Concomitant with this requirement is that the small conjugate acid, HX, be a poor Lewis base to avoid producing a base adduct of the catalyst which would be inactive

for olefin metathesis.[7] Several ill-defined systems have appeared in the literature[1b,8] for the *in situ* generation of ROMP systems with little progress in enantioselective reactivity including RCM and variants thereof.



Scheme 3.2 Synthesis of catalysts *in situ* from bis(triflate) complexes.

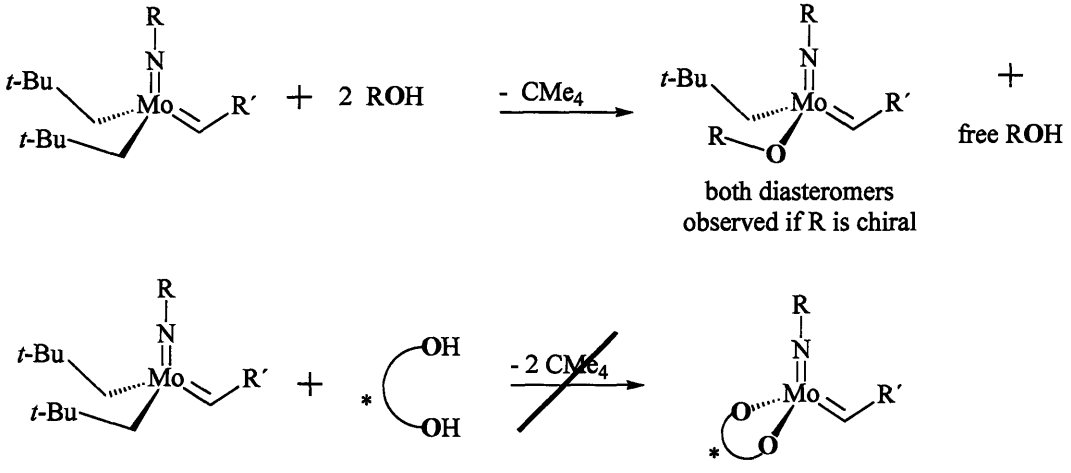
The first report from the Schrock group of the *in-situ* generation of a metathesis catalyst was the simple salt-metathesis of K_2(diolate) with the standard "universal precursor" alkylidene complex Mo(NAr)(CHR)$(OTf)_2$DME (R = CMe_2Ph) in THF,[9] as shown in Scheme 3.2. This route works well for the synthesis of the reported catalysts, but it has several drawbacks. First, the method is not applicable to the 2-trifluoromethylphenyl and 2,6-dichlorophenyl imido groups due to the competing ^1H tautomerization (Scheme 3.3).[10,11,41]



Scheme 3.3 Tautomerization of an alkylidene ligand.

The tautomerization reaction has not been elucidated fully, but the mechanism appears to be base-catalyzed.[11] The second potential drawback is that the THF solvent from the salt metathesis is present (varying amounts of THF have been shown to have a profound effect on enantioselectivity[12]). Furthermore, some species containing very electron poor diolates show no metathesis activity in the presence of any excess Lewis base, rendering this route useless for the synthesis of these species.[14,13] Third, clean deprotonation of electron-poor diols is sometimes problematic.[14]

The second class of compounds examined were the $M(NR)(CHR')(R'')_2$ complexes (M = Mo,[15,16,17] W;[17,18] R'' = CH_2CMe_3 or CH_2CMe_2Ph). The rationale was that alcoholysis would release neopentane (or *tert*-butyl benzene), producing the desired complexes and an innocent byproduct. This was found not to be the case. Monodentate alcohols react by either O – H addition across the M-C double bond, alcoholysis of only

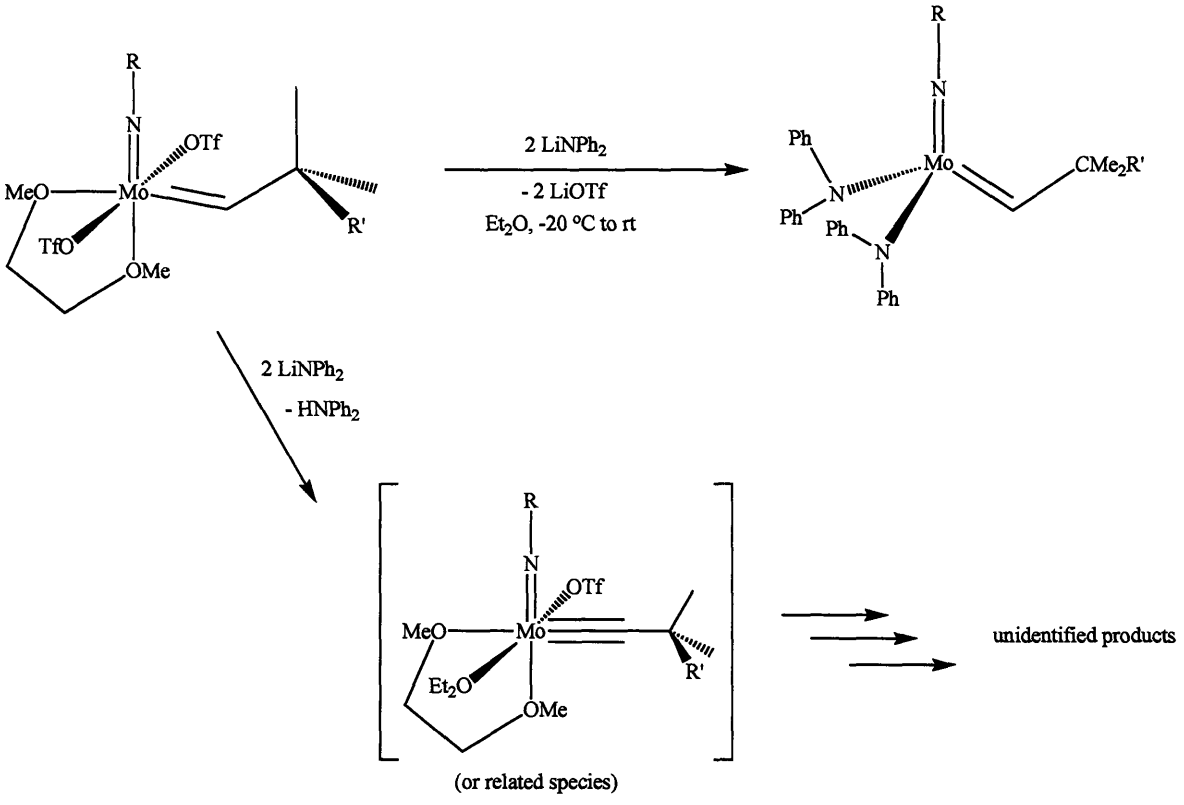


Scheme 3.4 Alcoholysis of $Mo(NR)(CHR')(CH_2CMe_3)_2$ complexes.

one alkyl ligand, or both, as shown in Scheme 3.4. The resulting mono-alkyl/alkoxide complexes proved to be catalysts for ring-closing metathesis in some cases[17] and contain the intriguing property of being chiral at the metal center, the effects of which are poorly understood at this time.[19] Diastereomerically pure catalysts of this type have yet to be synthesized.[20] Monoalkoxide alkylidene complexes also decompose in some cases to yield

dimers of the type $\{M(NR)(X)_2\}_2$ (R = Ad, Ar, Ar′; X = neopentyl, various alkoxides).[21,22] Due to the results obtained with mondentate alcohols, it was anticipated that diols might present a problem. The reaction of these species with chiral diols leads to intractable materials.[23] Preparation of a "Universal Precursor" to the desired class of biphenolate and binaptholate catalysts was again unsuccessful.

The next group of potential precursors examined were bis(amide) complexes.[24] Amritanshu Sinha prepared a number of bis(diphenylamide) and bis(anilide) species from the bis(triflate) complexes in low yield by direct salt metathesis with the typical $Mo(NR)(CHR')(OTf)_2(DME)$ precursor.[24] The low yield is presumed to be a result of competing deprotonation of the alkylidene ligand (Scheme 3.5). Eventually this problem



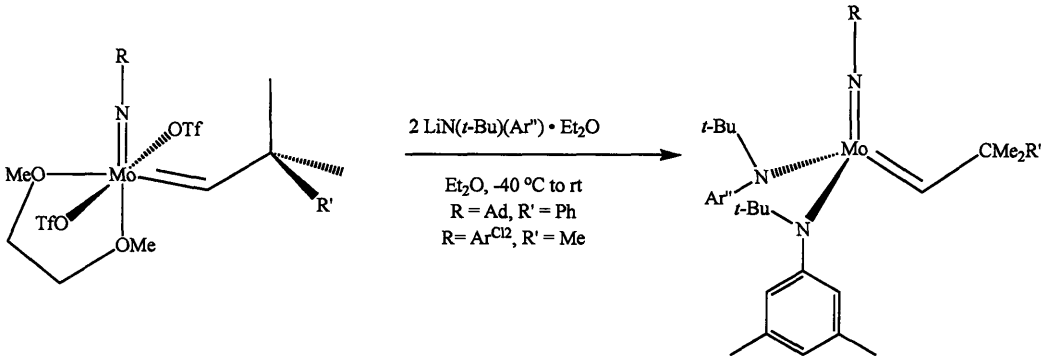
Scheme 3.5. Competing salt metathesis and alkylidene deprotonation.

was overcome by using the hexafluoro-*tert*-butoxide complexes $Mo(NAr)(CHR)[OC(CF_3)_2Me]_2$ as starting material. The bis(diphenylamide) complexes do serve, in some cases, as precursors for *in situ* generation of metathesis catalysts. Furthermore, enantioselectivities are similar to that of isolated catalysts. However, substitution is not complete in many cases, and the reaction does not proceed at all (even with extended heating) with what we believe to be the most sterically demanding case, i.e., the reaction of molybdenum species containing the 2,6-di*iso*propylphenylimido group and 5,5',6,6'-tetramethyl-3,3'-di*tert*butyl-1,1'-biphenyl-2,2'-diol (H_2[biphen]). Despite this caveat, bis(diphenylamide) precursors proved to be a substantial advance in the rational *in situ* synthesis of molybdenum olefin metathesis catalysts. It was concluded that further examination of amido ligands might provide the right combination of synthetic utility and reactivity to be a useful system for *in situ* catalyst generation.

Results and Discussion

3.1 Synthesis of *tert*-butylanilide Complexes.

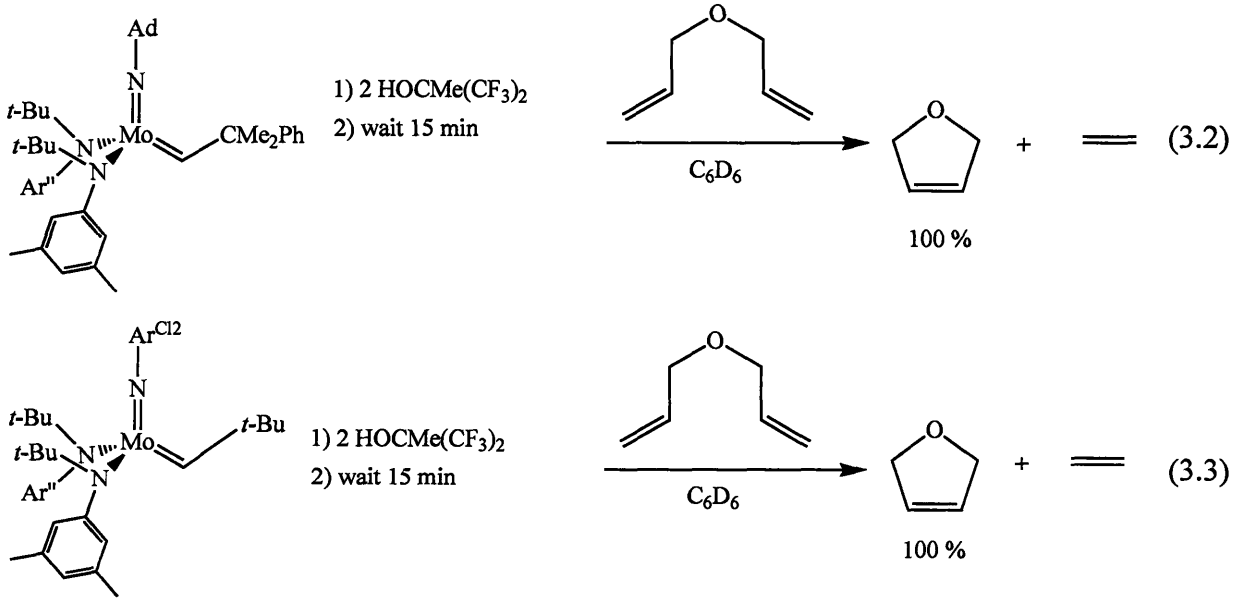
Prior to the belief that deprotonation of the molybdenum alkylidene was the main source of free amine during the synthesis of complexes of the type $Mo(NR)(CHCMe_2R')(NPh_2)_2$,[32] a more crystalline amide complex was sought. The readily available[25] $\{Li(Et_2O)N(t\text{-}Bu)(3,5\text{-}Me_2C_6H_3)\}_2$ is known to produce highly soluble and stable complexes.[26] Furthermore, alkylidyne complexes of the type $Mo(CR)[N(t\text{-}Bu)Ar'']_3$[27,28,] and the related *iso*propylanilide[29] complexes may be protonated to yield alkyne metathesis catalysts. Treatment of a suspension of $Mo(NAr)(CHCMe_2Ph)(OTf)_2DME$, $Mo(N\text{-}2,6\text{-}Cl_2C_6H_3)(CHCMe_3)(OTf)_2DME$ or



(3.1)

Mo(NAd)(CHCMe$_2$Ph)(OTf)$_2$DME at -35 °C with two equivalents of LiN(*t*-Bu)Ar" results in the formation of the corresponding bis(anilide) complexes in good yield (eqn 3.1). The crystalline nature of the complexes allows the residual aniline to be washed away by cold pentane. Mo(NAd)(CHCMe$_2$Ph)(N(*t*-Bu)Ar")$_2$ is golden yellow, Mo(NAr^{Cl2})(CHCMe$_3$)(N(*t*-Bu)Ar")$_2$ is dark red in color. The alkylidene protons resonate at 10.4 and 10.6 ppm, respectively. Dr. Amritanshu Sinha has reported several related species Mo(NR)(CHCMe$_3$)[N(*i*-Pr)Ar"]$_2$ (R = 2,6-*i*-Pr$_2$C$_6$H$_3$, 2,6-Me$_2$C$_6$H$_3$) and Mo(NAr)(CHCMe$_2$Ph)[N(*t*-Bu)Ar"]$_2$[24,23] in which the alkylidene protons resonate at 11.1 and 10.7 ppm, respectively. Neither species was found to react with chiral diols.

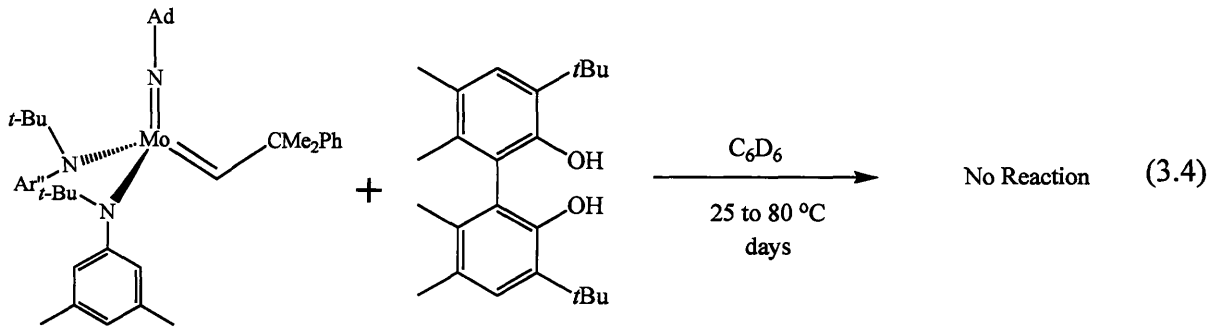
Mo(NAd)(CHCMe$_2$Ph)[N(*t*-Bu)Ar"]$_2$ and Mo(NAr^{Cl2})(CHCMe$_3$)[N(*t*-Bu)Ar"]$_2$ react rapidly with hexafluoro-*tert*-butanol to produce the known adamantyl derivative[30] and



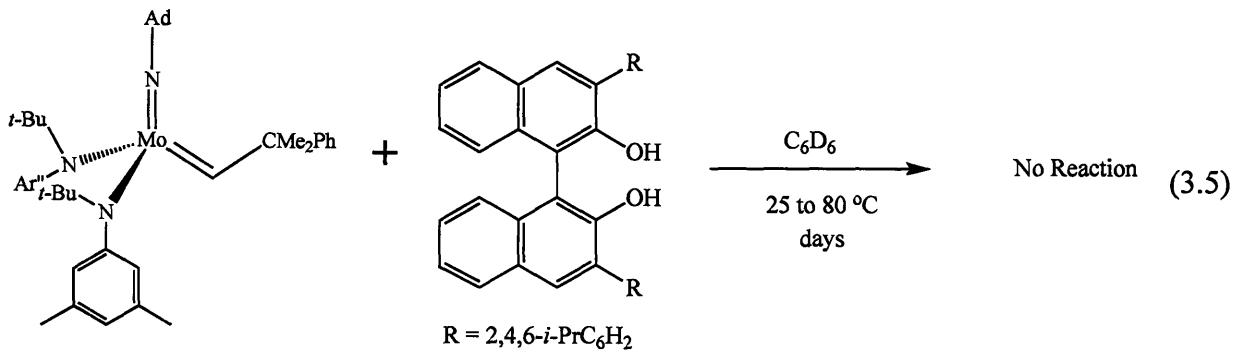
previously unreported 2,6-dichlorophenylimido catalysts *in situ* (equations 3.2, 3.3). Ring closing of 20 equivalents of the common substrate diallyl ether to dihydrofuran rapidly at room temperature demonstrated that the residual aniline was not a hindrance to catalytic activity. One other feature of note is that no signs of production of an alkylidyne/amide complex via tautomerization of the alkylidene proton during either the synthesis of the bis(anilide) complexes nor the alcoholysis were observed for either imido group.

In an attempt to determine the source of the free aniline during the synthesis of $Mo(NAr)(CHCMe_2Ph)[N(t\text{-}Bu)Ar'']_2$,[24] isolated bis(amide) was treated with several bases. $Mo(NAr)(CHCMe_2Ph)[N(t\text{-}Bu)Ar'']_2$ does not react with n-butyl lithium in the presence of THF, 1 equivalent of $LiN(t\text{-}Bu)(Ar'')$ etherate in benzene, nor the ylide Ph_3PCH_2. The closely related complexes $Mo(NAr)(CHR)[OC(CF_3)_2Me]_2$ (R = CMe_2Ph and CMe_3) were shown to produce anionic alkylidyne complexes when treated with phosphorane bases.[31] Treatment of the bis(triflate) molybdenum precursor with only one equivalent of $LiN(t\text{-}Bu)Ar''$ in diethyl either at -40 °C results in $Mo(NAr)(CHCMe_2Ph)[N(t\text{-}Bu)Ar'']_2$ and starting bis(triflate) in an approximately 50/50 ratio. No free aniline is observed. These results are consistent with the free amine in salt metathesis reactions arising from the mechanism shown in Scheme 3.5. The amine is formed by competitive deprotonation of the relatively acidic alkylidene proton in the bis(triflate) complex,[38c] rather than by deprotonation of the product by $LiN(t\text{-}Bu)Ar''$.

Around the same time that difficulties were encountered with alcoholysis of the diphenyl amide ligands[32] and the related *iso*-propylanilide ligands[23,32] in combination with the bulky imido groups 2,6-$i\text{-}Pr_2C_6H_3N$ and 2,6-$Me_2C_6H_3N$, alcoholysis with commonly used chiral diols was attempted with bis(anilide) complexes containing what we consider to be the *least* sterically hindered imido group, 1-adamantyl (eqn 3.4, 3.5).



(3.4)



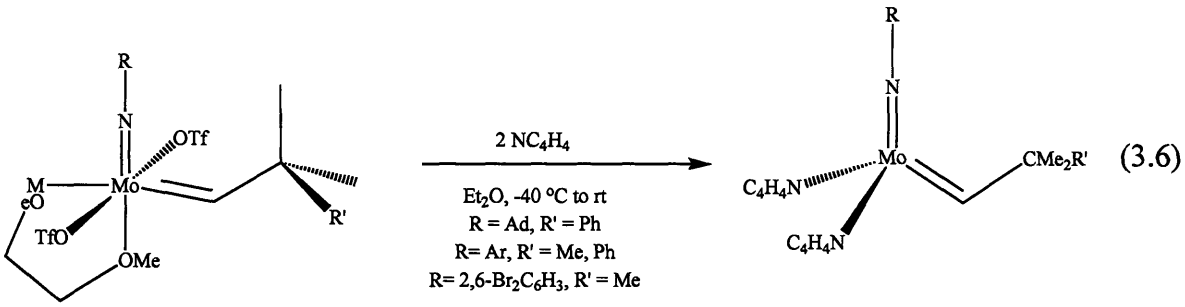
(3.5)

No reaction was observed with either H_2[biphen] (eqn 3.4) or what we consider to be the least sterically hindered diol system, the 3,3′-disubstituted napthols (eqn 3.5). It was concluded that the bis(anilide) and bis(diphenylamide) complexes were too sterically crowed to react with bulky diols readily.

These results demanded that a new system be designed. A number of criteria were determined to be desirable for the new system. First, in order to react with the very bulky substituted biphenol-based diols, the ligand must be sterically small. Concomitant with this requirement is that the smaller, nitrogen containing, conjugate acid HX be a poor Lewis base to avoid producing a base adduct of the catalyst which would be inactive for olefin metathesis. Secondary amines R_2NH are rarely compatible with known asymmetric metathesis catalyst stystems.[1,33] For synthetic utility it is desirable to avoid the competitive deprotonation of the alkylidene described above, thus a ligand with a lower pKa than an amide was sought. The conjugate base of the ubiquitous pyrrole molecule, pyrrolide, $C_4H_4N^-$, was chosen as an excellent fit to the above criteria.

3.2 Synthesis and Characterization of Molybdenum Imido Alkylidene Bis(pyrrolyl) Complexes

Addition of two equivalents of lithium pyrrolide[34] to a stirring diethyl ether suspension of Mo(NR)CHR')(OTf)$_2$DME (OTf = OSO_2CF_3; R=2,6-*i*-$Pr_2C_6H_3$, 1-adamantyl) or dichloromethane/ether solution (R=2,6-Br_2-4-MeC_6H_2) rapidly produces the Mo(NR)(CHR')$(NC_4H_4)_2$ complexes in high yield on multigram scales (eqn 3.6). No



(3.6)

signs of competitive deprotonation of the alkylidene have been observed in any cases. The compounds are air and moisture sensitive, crystalline materials and are readily recrystallized from toluene or mixtures of pentane and ether. Mo(NAd)(CHR')$(NC_4H_4)_2$ is pale yellow, Mo(N-2,6-*i*-$Pr_2C_6H_3$)(CHR')$(NC_4H_4)_2$ is orange-yellow and Mo(N-2,6-Br_2-4-MeC_6H_2)(CHR')$(NC_4H_4)_2$ is red-yellow. These complexes are relatively thermally stable. Solutions of these species at millimolar concentration in benzene-d_6 maintained at elevated temperature (80 °C) darken slightly but show no significant decomposition for at least 1 day.

All of the complexes thus far characterized are fluxional in solution at room temperature. The complexes contain no ^{19}F resonance; thus they are not "ate" complexes due to retention of triflate anion. They are not weak solvent adducts. No solvent is observed in the ^1H NMR upon addition of trimethylphosphine, which yields base adducts of the type Mo(NR)(CHR')$(NC_4H_4)_2(PMe_3)$ (see next chapter).

The fluxional behavior of Mo(NAr)$(CHCMe_2Ph)(NC_4H_4)_2$ was examined *via* variable-temperature ^1H NMR as shown in Figure 3.1. The high-temperature limit is consistent with the formulation of a C_s symmetric Mo(NAr)$(CHCMe_2Ph)(\eta^1\text{-}NC_4H_4)_2$ isomer with fast rotation about the Mo-$N_{pyrrolyl}$ bonds. The alkylidene resonance is clearly visible at 13.4 ppm. This spectrum is consistent with the assertion that the pyrrolyl ligands do not contribute much π-bonding to the metal center, rendering the metal center relatively electrophilic. For example, in the 4-coordinate series of Mo(NAr)$(CHCMe_2Ph)(OR)_2$ complexes, the alkylidene proton resonates at 11.34, 11.68, 12.12 and 12.87 ppm for the series R = *t*-Bu, CMe_2CF_3, $CMe(CF_3)_2$, and $C(CF_3)_3$.[5] Some perturbation is expected from the shift from oxygen to nitrogen ligands, however this trend seems to hold, as the *t*-butyl anilide complexes resonance at 10.4 and 10.6 ppm for the

1-adamantylimido and 2,6-dichlorophenylimido derivatives prepared earlier in this chapter, which would be expected to be far more saturated species. The low temperature behavior may be ascribed to the result of such electrophilicity.

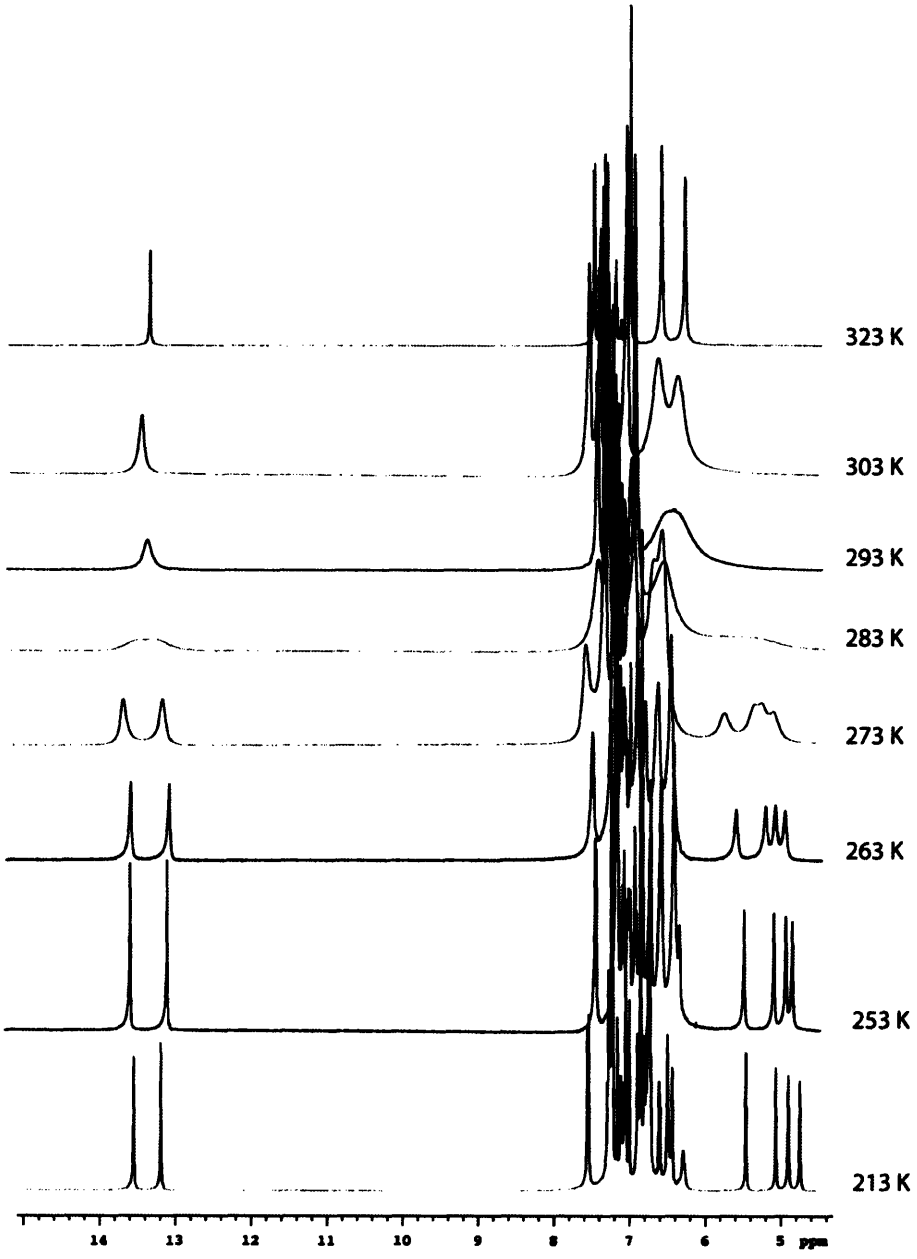


Figure 3.1. Variable Temperature proton NMR spectrum of $Mo(NAr)(CHCMe_2Ph)(NC_4H_4)_2$ in toluene-d_8.

At the low-temperature limit in toluene-d_8 (Figure 3.1), there are two alkylidene resonances at 13.2 and 13.6 ppm. Examination of the remainder of the spectrum shows that there are indeed two unique sets of resonances in solution. One species has no symmetry. The other is C_s symmetric on the NMR time scale. We assigned the C_s symmetric species to be a *syn* isomer in which both the pyrrolyl ligands are associated in an η^1 fashion. The complex with no symmetry can be assigned to the isomer in which one pyrrolyl ligand is η^1 and the other pyrrolyl ligand is associated with the metal an η^5 manner. The fact that this complex has no symmetry is consistent with a chiral, *pseudo* tetrahedral molybdenum center (accounting the η^5 pyrrolyl ligand as occupying a single coordination site). The ^{13}C NMR spectrum at -50 °C in dichloromethane-d_2 shows two doublets for the alkylidene carbons that resonate at 313.9 ppm (J_{CH} = 122.8 Hz) and 293.9 ppm (J_{CH} = 121.3 Hz). Both coupling constants are consistent with the formulation of *syn* alkylidenes.[30]

It was determined that "Mo(NAr)CHCMe$_2$Ph)(NC$_4$H$_4$)$_2$" is a dimer, i.e. {Mo(NAr)(*syn*-CHCMe$_2$Ph)(η^5-NC$_4$H$_4$)(η^1-NC$_4$H$_4$)}{Mo(NAr)(*syn*-CHCMe$_2$Ph)(η^1-NC$_4$H$_4$)$_2$} as shown in Figure 3.2. This is one of only three known crystal structures of molybdenum-bound pyrrolyl complexes. The others are Mo(Tp*)(NO)(η^1-NC$_4$H$_4$)$_2$[35] and Mo(NAd)(CHCMe$_2$Ph)(η^1-NC$_4$H$_4$)$_2$(PMe$_3$) (see chapter 4). Several dimolybdenum pyrrolylmethanes have also been structurally characterized.[36] The unique feature of {Mo(NAr)(*syn*-CHCMe$_2$Ph)(η^5-NC$_4$H$_4$)(η^1-NC$_4$H$_4$)}{Mo(NAr)(*syn*-CHCMe$_2$Ph)(η^1-NC$_4$H$_4$)$_2$} is the η^5 pyrrolyl ligand, which is the only structurally characterized example for molybdenum. The related tungsten complex W(NAr)(CHCMe$_2$Ph)(η^5 – DMP)(η^1 – DMP) (DMP = 2,5-Me$_2$C$_4$H$_2$N) has recently been structurally characterized.[37] The pyrrolyl methyl groups provide enough steric encumberment around the η^5 pyrrolyl group to prevent the dimerization observed in {Mo(NAr)(CHCMe$_2$Ph)(NC$_4$H$_4$)}$_2$. In {Mo(NAr)(CHCMe$_2$Ph)(NC$_4$H$_4$)}$_2$, counting the η^5 pyrrolyl ligand as a 6-electron donor, the electron count at the metal is 18 at the η^1, η^5 half and 16 in the η^1, η^1 half. The overall geometry of the η^1, η^5 half of {Mo(NAr)(*syn*-CHCMe$_2$Ph)(η^5-NC$_4$H$_4$)(η^1-NC$_4$H$_4$)}{Mo(NAr)(*syn*-CHCMe$_2$Ph)(η^1-NC$_4$H$_4$)$_2$} is similar to that of W(NAr)(CHCMe$_2$Ph)(η^5 – DMP)(η^1 – DMP).

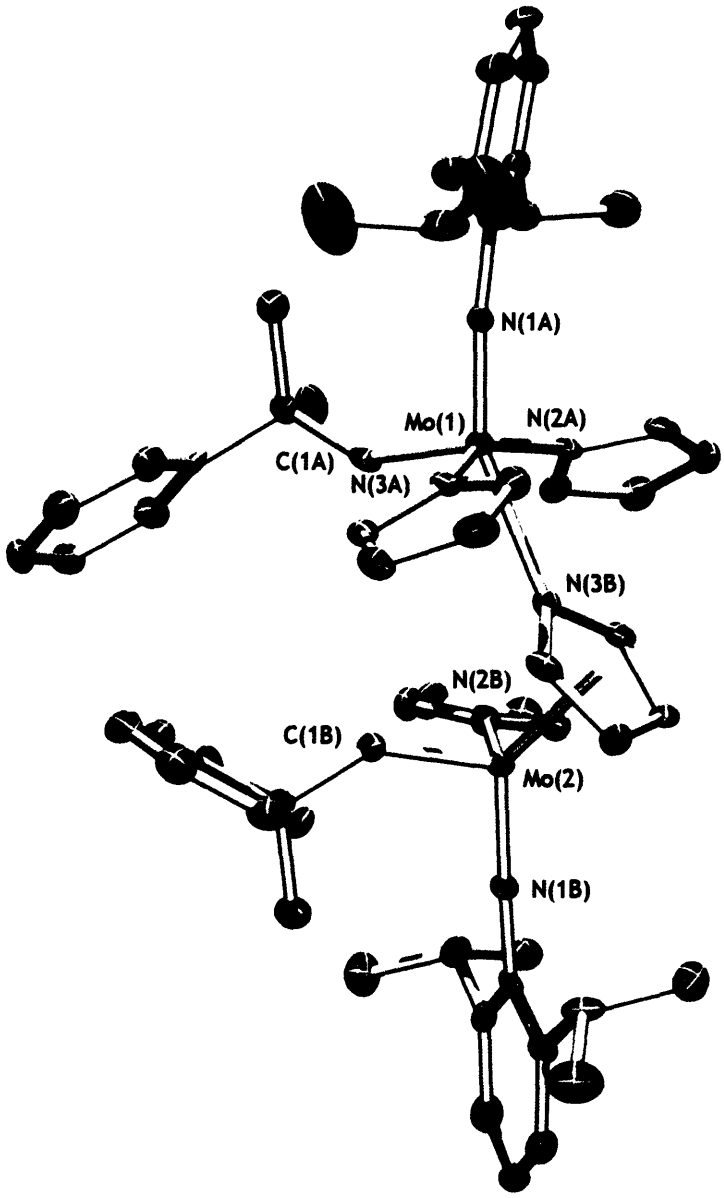


Figure 3.2. Solid State Structure of {Mo(NAr)(*syn*-CHCMe$_2$Ph)(η^5-NC$_4$H$_4$)(η^1-NC$_4$H$_4$)}{Mo(NAr)(*syn*-CHCMe$_2$Ph)(η^1-NC$_4$H$_4$)$_2$}. Thermal ellipsoids are at 50%. Hydrogen atoms and cocrystallized toluene molecules have been omitted for clarity.

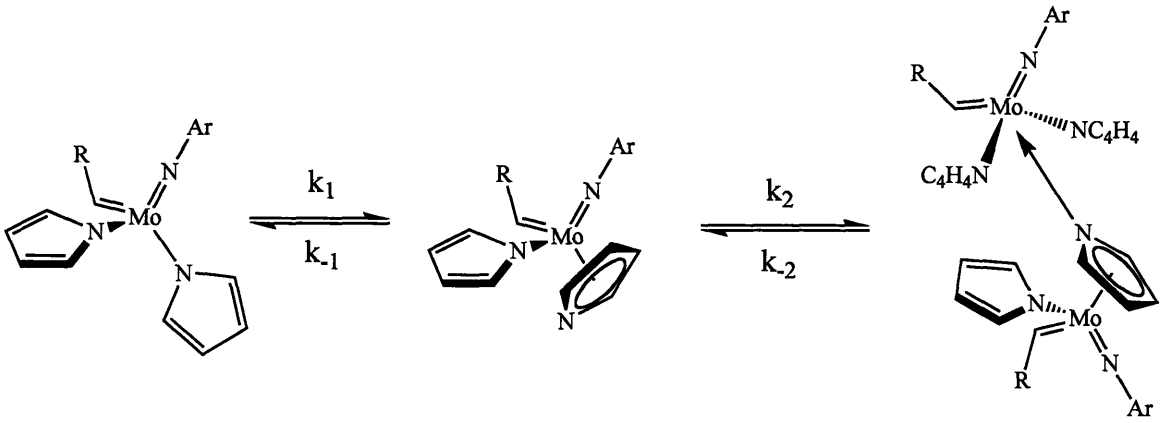
Table 3.1. Selected bond lengths (Å) and angles (°) of {Mo(NAr)(*syn*-CHCMe$_2$Ph)(η^5-NC$_4$H$_4$)(η^1-NC$_4$H$_4$)}{Mo(NAr)(*syn*-CHCMe$_2$Ph)(η^1-NC$_4$H$_4$)$_2$}.

Mo(1) – C(1A) 1.859(5)	Mo(2) – C(1B) 1.912(5)
Mo(1) – N(1A) 1.725(4)	Mo(2) – N(1B) 1.730(4)
Mo(1) – N(2A) 2.082(4)	Mo(2) – N(2B) 2.060(4)
Mo(1) – N(3A) 2.097(4)	Mo(2) – N(3B) 2.479(4)
N(1A) – Mo(1) – C(1A) 99.5(2)	N(1B) – Mo(2) – C(1B) 100.5(2)
N(1A) – Mo(1) – N(3B) 155.16(16)	N(1B) – Mo(2) – cent* 157.3
N(2A) – Mo(1) – N(3A) 150.98(16)	N(1B) – Mo(2) – N(2B) 101.80(17)
*cent = centroid of η^5 pyrrolyl ring	Mo(1) – Mo(2) 4.53

The Mo-N$_{pyrrolyl}$ distances average 2.090(4) Å in the η^1, η^1 half of the molecule and the η^1 distance is 2.060(4) Å in the η^1, η^5 half. The η^5 Mo-N distance is 2.479(4) Å, typical for an η^5 pyrrolyl ligand bound to a second-row metal. Interestingly, the dative distance for the pyrrolyl ligand is only 2.395(4) Å, fairly similar to the donor distance of 2.325 Å in the isoelectronic complex **L**Mo(η^2-MeCCMe)(CHTMS) (**L** = CH$_3$N[CH$_2$CH$_2$N((3-CF$_3$)C$_6$H$_4$)]$_2$). Also of note is the fact that the η^5 pyrrolyl donor interaction is *trans* to the imido group at the η^1, η^1 molybdenum center with the overall geometry being approximately square pyramidal. Typically, Lewis bases coordinate on the C$_{alkylidene}$-N$_{imido}$-O face[7] (or C$_{alkylidene}$-N$_{imido}$-N$_{pyrrolyl}$, see chapter 4). The aforementioned **L**Mo(η^2-MeCCMe)(CHTMS) complex has a tethered donor, possibly accounting for the different coordination geometry, however this cannot be asserted with certainty. One distinct possibility is that the steric bulk of the "(η^5-NC$_4$H$_4$)Mo(NAr)(CHCMe$_2$Ph)(η^1-NC$_4$H$_4$)" fragment renders approach on the more traditionally observed face of the pseudo tetrahedron impossible. The molybdenum-molybdenum distance is 4.53 Å. This long distance is fortunate, given the high propensity for sterically unprotected alkylidene species to dimerize via coupling of alkylidene ligands and expulsion of olefin.[21-23,38]

The $\Delta G^{\ddagger}_{(283)}$ value for this fluxional process is 13(1) kcal/mol according to the variable temperature ^{1}H NMR. This barrier is considerably higher than those observed for η^5 / η^1 fluxional processes in the literature, which reach a maximum of 11 kcal/mol in a

titanium dipyrrolylmethane system.[39] Therefore it seems unlikely that the observed barrier is due to the η^5 / η^1 interconversion. Since {Mo(NAr)(*syn*-CHCMe$_2$Ph)(η^5-NC$_4$H$_4$)(η^1-NC$_4$H$_4$)}{Mo(NAr)(*syn*-CHCMe$_2$Ph)(η^1-NC$_4$H$_4$)$_2$} is a dimer



Scheme 3.6. Equilibria involved in η^5 / η^1 interconversion from the dimer {Mo(NAr)(CHR)(NC$_4$H$_4$)$_2$}$_2$.

(vide supra), the barrier may be ascribed to unimolecular dissociation of the η^5 pyrrolyl donor (k_{-2}) from the η^1 / η^1 molybdenum center as shown in Scheme 3.6. The observed barrier is within the range typically observed for coordination of a bulky base to a molybdenum imido/alkylidene species.[7] Variable temperature spectra of {Mo(NAr)(CHR)(NC$_4$H$_4$)$_2$}$_2$ are identical at different concentrations, consistent with k_{-2} being the rate-limiting step of the interconversion. However, the asymmetry at the η^5 molybdenum center is apparently not enough to induce observable splitting of the resonances at the other molybdenum under the conditions employed.

The alkylimido complex {Mo(NAd)(CHCMe$_2$Ph)(NC$_4$H$_4$)$_2$}$_2$ was also examined by VT NMR. The alkylidene region of the low-temperature limit proton-coupled ^{13}C and ^{1}H NMR spectra are shown in Figure 3. The coalescence was not as clearly assignable in the adamantyl region as with the resonances in 2,6-di*iso*propyl phenyl imido derivative were, however at the low temperature limit, two *syn* alkylidene carbon resonances may be

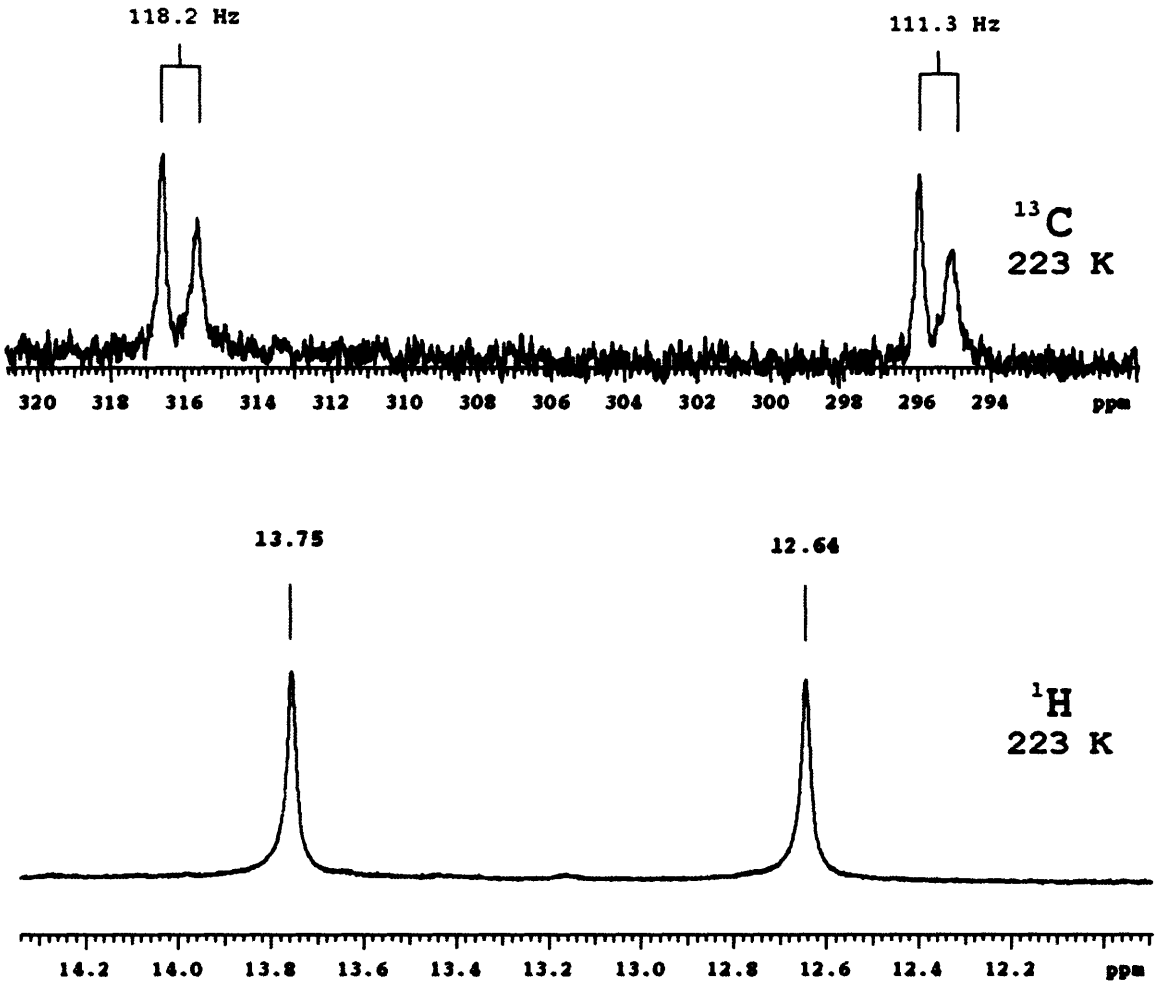


Figure 3.3. Low temperature NMR of {Mo(NAd)(CH_2CMe_2Ph)(NC_4H_4)$_2$ in methlyene chloride-d_2.

observed at 223K in methylene chloride-d_2 at 316.1 (J_{CH} = 118.2 Hz) and 295.48 ppm (J_{CH} = 111.3 Hz) in the proton-coupled ^{13}C NMR. The alkylidene protons resonate at 13.75 and 12.64 ppm. The adamantyl resonances overlap significantly. The pyrrolyl resonances show a similar pattern of 4 singlets ascribable to an η^5 pyrrolyl ring. There is no reason to believe that the adamantylimido derivative is not also a *syn, syn* dimer at low temperature. A measurement of the barrier to interconversion using the alkylidene resonances coalescence gave a $\Delta G^{\ddagger}_{(293)}$ of 13(1) kcal/mol, similar to the 2,6-di*iso*propylphenylimido complex discussed above. No other resonances could be assigned with enough certainty to

compare the calculated $\Delta G^{\ddagger}$ with the barrier obtained by measuring the alkylidene resonances.

The variable temperature NMR of the bis(pyrrolyl) [Mo(2,6-Br_2-4-Me-C_6H_2)(CHCMe$_3$)(NC_4H_4)$_2$]$_2$ was not examined. The alkylidene resonates at 13.4 ppm in benzene-d_6 and the resonances at room temperature are broad. There is no reason to believe that this complex is not also a rapidly dissociating dimer similar to the other complexes discussed in this chapter.

Conclusions

The bis(anilide) complexes Mo(NR)(CHR)(N(*t*-Bu)Ar")$_2$ are reactive toward acidic alcohols such as hexafluoro-*tert*-butanol to produce active metathesis catalysts *in situ*. However, they are unreactive towards sterically encumbered diols which are known to promote enantioselective metathesis. Furthermore, free aniline is observed during their synthesis which complicates isolation. This is believed to arise from the deprotonation of the alkylidene ligand in competition with salt metathesis.

The electronically very different amide, pyrrolide anion, was used to prepare several complexes of the type "Mo(NR)(CHR')(NC_4H_4)$_2$". Variable temperature NMR of two of these species showed that at the slow exchange limit two *syn* alkylidene species are present. A crystal structure of the 2,6-di*iso*propylphenyl imido derivative showed the structure to be a dimer in which one pyrrolyl ligand is engaged in a μ–η^5, η^1 binding mode between the two metal centers. This unique structure suggests that the η^5 / η^1 interconversion is able to provide electronic stabilization to an otherwise electronically and sterically unsaturated metal center. The reactivity of these species is the subject of the next chapter of this thesis.

Experimental

All complexes were handled using standard Schlenk techniques or in a Vacuum Atmospheres glove box under an argon or dinitrogen atmosphere. All solvents were dried, degassed, and stored over activated molecular sieves in a dinitrogen-filled glovebox. Pyrrole was distilled from CaH_2 in an inert atmosphere and lithium pyrrolide was prepared using published procedures.[40] Mo(N-2,6-*i*-$Pr_2C_6H_3$)(CHCMe$_2$Ph)(OTf)$_2$DME,[5] Mo(NAd)(CHR)(OTf)$_2$DME,[5] and Mo(N-2,6-Br_2-4-MeC_6H_2)(CHCMe$_3$)(OTf)$_2$DME[41] were synthesized by published procedures. Elemental analyses were performed by Desert Analytics, Tucson, Arizona.

Mo(NAd)(CHCMe$_2$Ph)(N[*t*-Bu]Ar'')$_2$. To a -40° C suspension of 1.248 g (1.65 mmol) of Mo(NAd)(CHCMe$_2$Ph)(OTf$_2$) · DME in 25 ml Et_2O was added 0.849 g of LiN(*t*-Bu)Ar" · Et_2O (3.30 mmol) as a solid. The solids go into solution as the reaction progresses and the solution turns brown. Solvent was removed, the residue extracted with a minimum of dichloromethane, and filtered through celite. The dichloromethane was removed and the brownish residue was dissolved in ca 0.8 ml of pentane. Storage of this solution at -40° C for 2 days yielded yellow crystals of the title compound. They were washed with very cold pentane and dried *in vacuo*; yield 0.80 g (65%). Attempts to use toluene as the reaction solvent resulted in very oily product which could not be isolated as crystalline material: ^{1}H NMR (C_6D_6, 300 MHz) δ 10.4 (s, 1H, MoC*H*CMe$_2$Ph), 7.35 (d, 2H, MoCHCMe$_2$*Ph*), 7.24 (d, 2H, MoCHCMe$_2$*Ph*), 6.98 (t, 1H, MoCHCMe$_2$*Ph*), 6.83 (s, 4H, N[*t*-Bu]*Ar*), 6.68 (2, 2H, N[*t*-Bu]*Ar*), 2.2 (s, 12H, N[*t*-Bu]Ar'-*Me$_2$*), 2.1 (br s, 6H, *Ad*-N) 1.96 (br s, 3H, *Ad*-N), 1.6-1.4 (overlapping s, 12H, *Ad*-N + MoCHC*Me$_2$*Ph), 1.20 (s, 18H, N[*t-Bu*]Ar).

Mo(N2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(N[t-Bu]Ar'')$_2$. To a -40° C suspension of 0.1754 g (0.246 mmol) of Mo(N2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(OTf$_2$) · DME in 4 ml Et_2O was added 0.1264 g of LiN(t-Bu)Ar" · Et_2O (0.491 mmol) as a solid. The solids go into solution as the reaction progresses and the solution turns brown. Solvent was removed, the residue extracted with a minimum of pentane, and filtered through celite. The pentane was removed and the

brownish, foamy residue was dissolved in a minimum pentane. Storage of this solution at -40° C for 3 days yielded reddish crystals of the title compound. They were washed with very cold pentane and dried *in vacuo*; yield, 0.066 g (40%). Attempts to use toluene as the reaction solvent resulted in very oily product which could not be isolated as crystalline material: ^{1}H NMR (C_6D_6, 300 MHz) δ 10.6 (s, 1H, MoC*H*CMe$_{23}$), 7.2 (s, 4H, N[t-Bu]*Ar*), 7.05 (d, 2H, Ar$_{Cl2}$), 6.67 (s, 2H, N[t-Bu]*Ar*), 6.29 (t, 1H, Ar$_{Cl2}$), 2.2 (s, 12H, N[t-Bu]Ar'-*Me$_2$*), 1.37 (s, 18H, N[*t-Bu*]Ar), 1.05 (s, 9H, MoCHC*Me$_3$*).

Mo(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHCMe$_3$)(NC$_4$H$_4$)$_2$. To a -35 °C solution of 0.193 g (0. 27 mmol) Mo(NAr)(CHCMe$_3$)(OTf)$_2$(DME) in 4 mL diethyl ether was added 38.6 mg (0.53 mmol) of LiNC$_4$H$_4$ as a solid in one portion. The mixture was stirred at room temperature for 1 hour, then all volatiles were removed *in vacuo*. The resulting brown powder was extracted with 5 mL of toluene and the solution was filtered through celite. The celite was washed with toluene (1 mL) and the resulting solution was taken to dryness *in vacuo*. The product may be recrystallized from mixtures of pentane/toluene or pure toluene at-35 °C as a toluene solvate; yield 110 mg (74%): ^{1}H NMR (300 MHz, 293K, toluene-*d$_8$*) δ 13.5 (br s, 1H, MoC*H*R), 7-6.2 (v br s, overlapping, 11 H, Ar- *H* and NC$_4$*H$_4$*), 3.8-2.9 (br s, 2H, *i*-Pr), 1.3 (br s, 9H, C*Me$_3$*), 1.1 (br s, 12H, *i*-Pr).

Mo(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(NC$_4$H$_4$)$_2$. LiNC$_4$H$_4$ (410 mg, 5.62 mmol) was added as a solid in several small portions a -40 °C solution of 2.223 g (2.81 mmol) Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(DME) in 60 mL of diethyl ether. The mixture was stirred at room temperature for 1 hour. All volatiles were removed *in vacuo* and the resulting powder was extracted with 65 mL of a 1:1 mixture of toluene and pentane and the solution was filtered through celite. The celite was washed with toluene (3x15 mL) and the resulting solution was reduced to dryness *in vacuo*. The solid was recrystallized from pentane -35 °C; yield 1.2 g (80%): ^{1}H NMR (toluene-d$_8$, 500 MHz) (223 K) δ 13.55 (s, 1H, MoC*H*R),

13.16 (s, 1H, MoC*H*R), 7.4-6.7 (m, Ar-H, NC_4H_4), 5.85 (s, 1H, NC_4H_4), 5.10 (s, 1H, NC_4H_4), 4.91 (s, 1H, NC_4H_4), 4.83 (s, 1H, NC_4H_4), 3.85 (sept, 2H, *i*-Pr methine), 2.85 (sept, 2H, *i*-Pr methine), 1.75 (s, 6H, MoCHC*Me*$_2$Ph), 1.71 (s, 3H, MoCHC*Me*$_2$Ph), 1.68 (s, 3H, MoCHC*Me*$_2$Ph), 1.19 (br d, 12H, Ar-*i*-Pr), 1.12 (d, 3H, Ar-*i*-Pr), 1.03 (overlapping d, 6H, Ar-*i*-Pr), 0.55 (d, 3H, Ar-*i*-Pr). ^{1}H NMR (toluene-d_8, 500 MHz) (323 K) δ 13.18 (s, 1H, MoC*H*R), 7.33 (d, 2H, MoCHCMe$_2$*Ar*), 7.18 (t, 2H, MoCHCMe$_2$*Ar*), 7.05 (t, 1H, MoCHCMe$_2$*Ar*), 6.86 (m, 3H, MoN*Ar*), 6.44 (s, 4H, NC_4H_4), 6.14, (s, 4H, NC_4H_4), 3.22 (sept, 2H, *i*-Pr methine), 1.56 (s, 6H, MoCHC*Me*$_2$Ar), 0.96 (d, 12H, *i*-Pr methyl). ^{13}C NMR (CD_2Cl_2, 126 MHz, 223 K): 313.9 (J_{CH} 122.8 Hz), 293.9 (J_{CH} 121.3 Hz). Anal. Calcd for $C_{30}H_{37}MoN_3$: C, 67.28; H 6.96; N 7.85. Found: C, 67.38; H, 7.20; N, 7.70.

Mo(NAd)(CHCMe$_2$Ph)(NC$_4$H$_4$)$_2$. $LiNC_4H_4$ (169 mg, 2.32 mmol) was added as a solid in small portions to a -35 °C solution of 0.890 g (1.16 mmol) Mo(NAd)(CHCMe$_2$Ph)(OTf)$_2$(DME) in 50 mL of diethyl ether. The mixture was stirred at room temperature for 1.5 h, then all volatiles were removed *in vacuo*. The resulting brown powder was extracted with toluene and the solution was filtered through celite. The celite was washed with toluene and the combined filtrates were taken to dryness *in vacuo*. The off-white solid may be recrystallized from toluene at -35 °C; yield 420 mg (2 crops, 71%): ^{1}H NMR (C_6D_6, 500 MHz, 293 K) δ 13.6 (br s, 1H, MoC*H*R), 12.8 (br s, 1H, MoC*H*R), 7.5, (br s, 4 H, MoCHCMe$_2$*Ph*), 7.0-4.7 (2 overlapping br s, MoCHCMe$_2$*Ph* and NC_4H_4), 1.8-1.6 (br multiplet, 15H, MoN*Ad*), 1.3 (br s, 6H, MoCHC*Me*$_2$Ph); ^{13}C NMR (CD_2Cl_2 126 MHz, 223K) δ 316.1 (J_{CH} 118.2 Hz), 295.5 (J_{CH} 111.3 Hz). Anal. Calcd for $C_{28}H_{35}MoN_3$: C, 66.00; H, 6.92; N 8.25. Found: C, 65.10; H, 6.60; N, 7.04.

Mo(N-2,6-Br$_2$-4-MeC$_6$H$_2$)(CHCMe$_3$)(NC$_4$H$_4$)$_2$. $LiNC_4H_4$ (35.4 mg, 0.485 mmol) in diethyl ether (~2 mL) was added to a -40 °C solution of 0.198 g (0.243 mmol) Mo(NAr)(CHCMe$_3$)(OTf)$_2$(DME) in 3 mL of dichloromethane. The mixture was stirred at

room temperature for 1 hour and all volatiles were removed *in vacuo*. The resulting red-brown powder was extracted with benzene and the solution was filtered through celite. The celite was washed with benzene and the combined filtrates were taken to dryness *in vacuo*. The product was recrystallized from pentane containing a few drops of benzene at -35 °C; yield 94 mg (62%): ^{1}H NMR (300 MHz, C_6D_6,, 293 K) δ 13.4 (br s, 1H MoC*H*R), 6.8-6.4 (br overlapping s, 10H, MoN*Ar* and NC_4H_4), 3.1 (s, 3H, MoNAr methyl), 1.4 (br s, 9H, MoCHCMe_3). Anal. Calcd for $C_{20}H_{23}MoBr_2N_3$: C, 42.81; H 4.13; N 7.49. Found: C, 42.52; H, 4.12; N, 6.83.

Representative procedure for the *in situ* catalyst generation. The molybdenum precursor (ca. 0.02 mmol) is dissolved in 0.2 mL of C_6D_6. An equimolar amount of diol or two equivalents of alcohol is dissolved in 0.3 mL of C_6D_6 and the solutions are combined in a Teflon-sealed NMR tube. The ^{1}H NMR spectrum was recorded within 15 minutes.

Variable Temperature NMR Studies.

Samples of the complex of interest were dissolved in deuterated solvent, placed in Teflon-sealed NMR tubes, and spectra were recorded on a Varian Inova 500 every 10 °C, allowing at least 10 minutes for temperature equilibration. The activation barriers were calculated using the following formula:[42]

$$\Delta G^{\ddagger} = 19.13 \cdot T_{coal}(9.97 + \log(T_{coal} / \delta\nu) \ \ [J/mol]$$

where T_{coal} is the temperature of coalescence in K and δν is the peak separation at the slow exchange limit in Hz. For $\{Mo(NAr)(CHCMe_2Ph)(NC_4H_4)_2\}_2$, the barriers were calculated using the alkylidene peaks as well as the *iso*-propyl methine peaks for the η^5 / η^1 isomer. The barriers calculated for both were 13(1) kcal/mol. The same barrier was determined by VT NMR of $\{Mo(NAr)(CHCMe_2Ph)(NC_4H_4)_2\}_2$ performed on solutions of 15.8 and 50 mg of material in the same volume of

toluene-d_8. The low-temperature proton-coupled ^{13}C NMR of $\{Mo(NAr)(CHCMe_2Ph)(NC_4H_4)_2\}_2$ was determined upon 144 mg of material in ca. 0.5 ml methylene chloride-d_2 and the barrier to exchange of ^1H alkylidene resonances was measured to be 12(1) kcal/mol in methylene chloride-d_2. For $\{Mo(NAd)(CHCMe_2Ph)(NC_4H_4)_2\}_2$, only the ^1H resonances of the alkylidene peaks were used to calculate $\Delta G^{\ddagger}$ and the barrier was found to be 13(1) kcal/mol in methylene chloride-d_2. Low-temperature proton-coupled ^{13}C measurements were performed upon ca. 200 mg of material in ca. 0.5 ml of methylene chloride-d_2.

X-Ray Structural Studies

Low temperature diffraction data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS SMART Apex CCD detector with graphite-monochromated MoKα radiation (λ = 0.71073 Å), performing φ and ω-scans. The structures were solved by direct methods using SHELXS[43] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[44] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). Crystal and structural refinement data for the structure is listed below. The full labeling scheme may be seen on http://reciprocal.lms.mit.edu/recipnet/index.jsp by searching the code 06172.

Crystals of $\{Mo(NAr)(syn\text{-}CHCMe_2Ph)(\eta^5\text{-}NC_4H_4)(\eta^1\text{-}NC_4H_4)\}\{Mo(NAr)(syn\text{-}CHCMe_2Ph)(\eta^1\text{-}NC_4H_4)_2\}$ (**06172**) grown at -40 °C from a mixture of pentane and toluene were coated with Paratone-N oil (an Exxon-Mobile (TM) product) in a dinitrogen-filled glovebox and examined under a microscope. A suitable crystal measuring 0.10 x 0.08 x 0.03 mm^3 was selected and mounted in a nylon loop. Initial examination of the data indicated that the space group was P2(1)/c. However, no reasonable solution could be

obtained *via* direct methods or from the Patterson map. The program CELL_NOW[45] was used to re-determine the unit cell from 999 reflections sampled from several regions in the hemisphere of data. The resulting, slightly different, unit cell was used to integrate the data in the SAINT software package in the triclinic setting. A solution in the space group P_1 (#1) was refined isotropically and the routines ADDSYM and NEWSYM in Platon[46] were used to confirm that the correct space group was indeed P2(1)/c. Re-integration in the primitive, monoclinic setting followed by absorption correction with the SADABS[47] package yielded the data set from which the correct initial solution was obtained. Confirmation of the space group/setting was substantiated by the successful refinement of the structure and use of the ADDSYM and NEWSYM functions in the Platon software package.

Table 3.2. Crystal data and structure refinement for $\{Mo(NAr)(CHR)(NC_4H_4)_2\}_2$.

Identification code	06172	
Empirical formula	$C_{67}H_{82}Mo_2N_6$	
Formula weight	1163.27	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 24.903(12) Å	α= 90°
	b = 12.723(5) Å	β= 106.001(12)°
	c = 19.434(9) Å	γ = 90°
Volume	5919(4) Å^3	
Z	4	
Density (calculated)	1.305 Mg/m^3	
Absorption coefficient	0.469 mm^{-1}	
F(000)	2440	
Crystal size	0.10 x 0.08 x 0.03 mm^3	
Theta range for data collection	1.70 to 21.97°	
Index ranges	$-26 \le h \le 25$, $0 \le k \le 13$, $0 \le l \le 20$	
Reflections collected	7216	
Independent reflections	7216 [R(int) = 0.1879]	
Completeness to theta = 21.97°	99.6 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9861 and 0.9546	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7216 / 0 / 670	
Goodness-of-fit on F^2	1.013	
Final R indices [I>2sigma(I)]	R1 = 0.0412, wR2 = 0.0775	
R indices (all data)	R1 = 0.0753, wR2 = 0.0901	
Largest diff. peak and hole	0.590 and -0.534 e/Å^3	

References

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Chapter 4

Reactivity of Molybdenum Imido Alkylidene Bis(pyrrolyl) Complexes

A portion of this work has appeared in print:
A. S. Hock, R. R. Schrock, and A. H. Hoveyda
"Dipyrrolyl Precursors to Molybdenum Olefin Metathesis Catalysts"
J. Am. Chem. Soc., **2006**, *128*, 16373.

Introduction

Systematic variation of amido ligands provides numerous platforms for the support of reactive functionalities.[1,2,3,4,5] However, it has been observed that group 6 species containing alkylidene ligands supported by amides are typically unreactive.[6,7] This is likely due to the combination of two factors. Amides are considered strong π donors,[8] which tends to produce more electronically saturated metal centers. In combination with this fact is the inherent steric properties of disubstituted amides, which in combination with the other supporting ligands common to alkylidene complex precursors, creates a sterically encumbered species. Low-coordinate group 4[10] and 5[9] alkylidene ligands supported by amide ligands tend also to react in unusual ways,[10] including C-H activation across the alkylidene bond. These complexes rarely display long-lived olefin metathesis behavior. Typical Wittig-like reactivity has been observed in several cases.[9]

Boncella and coworkers have reported a number of studies of a tungsten alkylidene complex incorporating the *ortho*-substituted chelating amido ligand $[1,2\text{-}N(TMS)C_6H_4]^{2-}$ with a phenylimido substituent.[7] The alkylidene species may be generated *in situ* by thermolysis of a dialkyl precursor or isolated as the trimethyphosphine adduct. These species readily polymerize norbornene but no RCM or enantioselective ligand variations have been reported to date.

Several molybdenum imido alkylidene species containing N,N'-disubstituted-2,2'-bisamido-1,1'-binaphthyl ligands were prepared recently in this lab and are unreactive towards all substrates examined, including benzaldehyde and even ethylene.[6] No exploration of reactivity with protic reagents was attempted. However, it seems likely that these species would not react with alcohols, either. Recent work with bis(diphenylamide)[11] complexes has shown that protonation with chiral diols is possible and *in situ* synthesis of active metathesis catalysts is readily achievable if the protonation reaction is facile. It is not in the more sterically challenging cases. The bis(diphenylamide) precursors are not

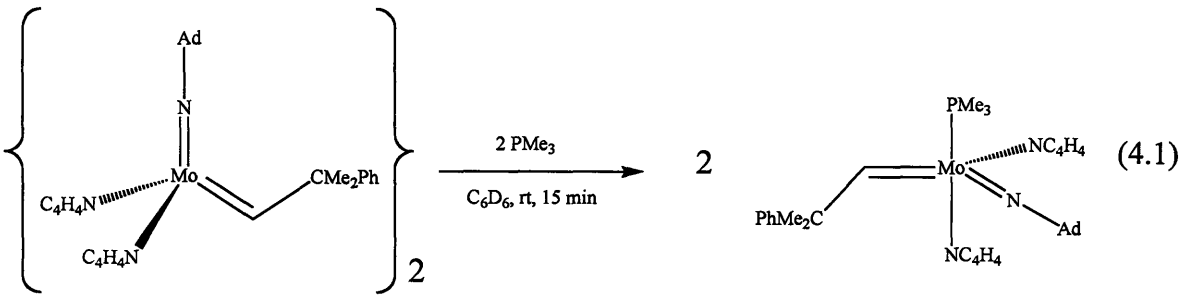
reactive towards olefins or aldehydes (neither are the related bis(*tert*-butylanilide) species, as detailed in the previous chapter). It is desirable to retain the relative lack of reactivity of the alkylidene ligand towards common substrates, most specifically to prevent O-H addition across the molybdenum alkylidene double bond,[35] and alkylidene proton migration,[12] from the previously reported amide complexes while enhancing the reactivity of the leaving groups towards alcoholysis.

The bis(pyrrolyl) species detailed in the proceeding chapter show a much higher degree of reactivity with protic reagents to generate active metathesis catalysts. However, the poorer π donation ability of the pyrrolyl ligand renders these species much more reactive than their more traditional amide counterparts. This reactivity was explored in some detail. In addition to alcoholysis studies relating to the *in situ* synthesis of active and enantioselective metathesis catalysts, the reactivity of these species with substrates other than alcohols is detailed, and comments on applications are made.

Results and Discussion

4.1 Reactivity with Lewis acids and bases.

The initial spectroscopic studies of the bis(pyrrolyl) complexes "Mo(NR)(CHR')(NC_4H_4)$_2$" indicated that these complexes were relatively electrophilic and would likely prove much more reactive than the related bis(alkyl) and bis(aryl) amide complexes. The first experiments performed were simple base-binding studies. Weak Lewis bases such as THF do not bind stoichiometrically, but in the presence of 50 to 100 equivalents of THF, significant sharpening of the pyrrolyl complex resonances may be observed in the ^{1}H NMR, indicative of fast exchange on the NMR time scale. Several equivalents of trimethylphosphine react rapidly with a solution of {Mo(NAd)($CHCMe_2Ph$)(NC_4H_4)$_2$}$_2$ in benzene to yield the base adduct Mo(NAd)($CHCMe_2Ph$)(η^1-NC_4H_4)$_2$(PMe_3). The alkylidene proton resonates at 12.5 ppm ($J_{H\text{-}P}$ 5 Hz) and the NMR is consistent with a C_s structure at room temperature



(4.1)

in solution. The alkylidene carbon is visible as a doublet at 301.7 ppm ($^2J_{C\text{-}P}$ 19.5 Hz). The sharp resonances and observable proton – phosphorus coupling indicate that the trimethylphosphine ligand is bound to the metal on the NMR time scale. The pyrrolyl resonances are consistent with η^1/η^1 binding and fast rotation about the Mo-$N_{pyrrolyl}$ bond. However, the C_s spectrum is not consistent with the solid state structure (vide infra). It is likely that the molecule, like many other 5-coordinate species,[8] is undergoing rapid rearrangement on the NMR time scale. It is noteworthy that this behavior is not observed in alkoxide complexes,[13] nor in 2,6-di*iso*propylphenylimido species $Mo(NAr)(CHCMe_2Ph)(NC_4H_4)_2(PMe_3)$. $Mo(NAr)(CHCMe_2Ph)(NC_4H_4)_2(PMe_3)$ was spectroscop characterized and the alkylidene resonates at 11.9 ppm with a J_{CH} of 116.0 Hz and J_{CP} of 4.3 Hz in benzene-d_6. This constitutes > 95% of the alkylidene species. A minor isomer is visible at 14.15 ppm with a J_{CP} of 7.3 Hz. These coupling constants are consistent with the major isomer being a *syn* alkylidene phosphine adduct with a small amount of *anti* base adduct also present. This is the first time evidence for population of any *anti* species of a bis(pyrrolyl) alkylidene complex has been observed. The trimethylphosphine ligands do not exchange with free trimethylphosphine at room temperature with either imido complex.

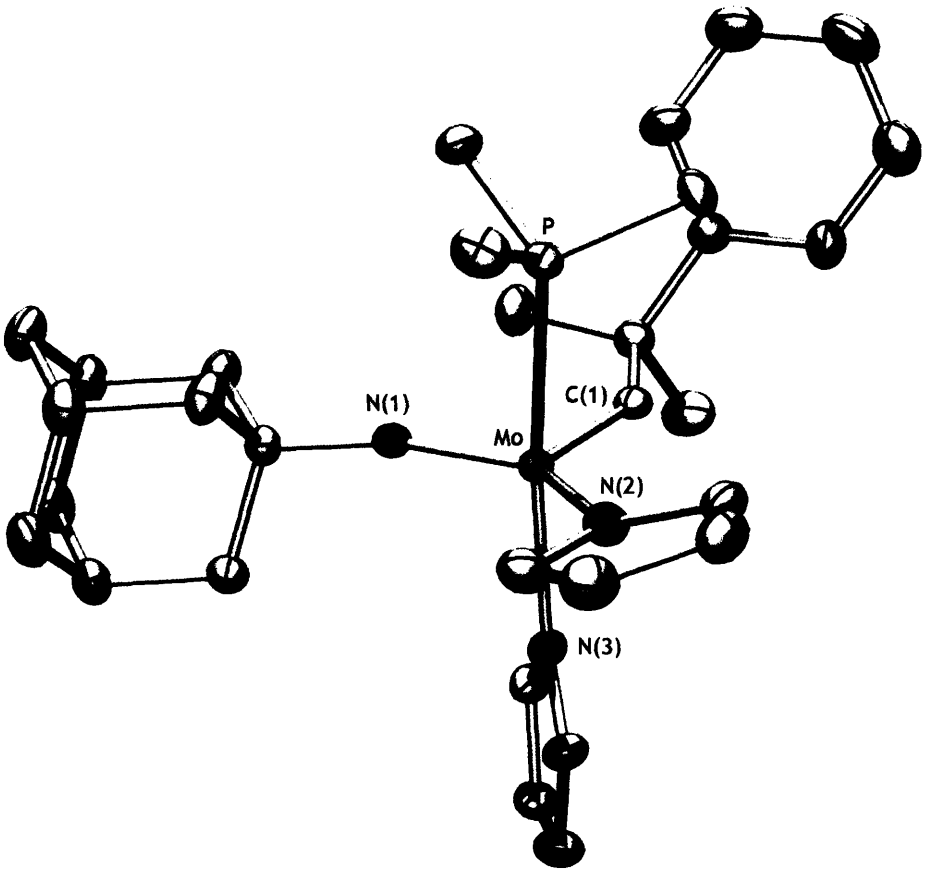


Figure 4.1. Structure of $Mo(NAd)(CHCMe_2Ph)(NC_4H_4)_2(PMe_3)$. Hydrogen atoms and cocrystallized solvent molecules have been removed for clarity and only one of two independent molecules shown. Thermal ellipsoids at 50%.

Table 4.1. Selected bond lengths [Å] and angles [°] for the two independent molecules of $Mo(NAd)(CHCMe_2Ph)(\eta^1\text{-}NC_4H_4)_2(PMe_3)$.*

	Mo(1)	Mo(2)
Mo - PMe_3	2.5269(6)	2.5254(6)
Mo - $C_{alkylidene}$	1.885(2)	1.890(2)
Mo - N_{imido}	1.7254(16)	1.704(6)
Mo - $N_{pyrrolyl}$	2.1183(17), 2.1375(17)	2.1147(17), 2.1376(17)
Mo - N_{imido} - $C_{adamantyl}$	158.78(14)	153.6(6)
Mo - $C_{alkylidene}$ - CMe_2Ph	146.52(15)	146.87(19)

*For Mo(2) the bonds and angles listed are for the major component.

The structure of $Mo(NAd)(CHCMe_2Ph)(NC_4H_4)_2(PMe_3)$ (as the toluene solvate) was determined *via* X-Ray diffraction (Figure 4.1). Selected bond lengths and angles are collected in Table 4.1 and refinement parameters in Table 4.3 in the experimental section. The trimethylphosphine binds on the C -N_{imido} – $N_{pyrrolyl}$ face. The observed geometry is virtually identical to many of the structurally characterized base adducts of molybdenum[14,15,16] and tungsten[17] complexes. The Mo-N_{imido} and Mo-$C_{alkylidene}$ bond lengths and angles are typical of a *syn* base adduct in $Mo(NR)(CHR)(X)_2$ complexes.
The Mo-$N_{pyrrolyl}$ bond distances are similar to the η^1 pyrrolyl bond distances in $\{Mo(NAr)(CHCMe_2Ph)(NC_4H_4)_2\}_2$ detailed in chapter 3. They are ca. 0.1 Å longer than the Mo-N_{amide} distances in the analogous $Mo(NAr)(CHCMe_3)(NPh_2)_2$ complex. However, the pyrrolide ligands *are* oriented at 90° to one another, so some degree of π-donation cannot be ruled out. The ring bond lengths in the pyrrolide ligands are consistent with some degree of delocalization in the ligand. To the best of our knowledge, only one other molybdenum pyrrolyl complex, $Mo(Tp^*)(NO)(NC_4H_4)_2$ ($Tp^* = HB(3,5\text{-}Me_2C_3N_2H)_3^-$), has been structurally characterized.[18] The average Mo-$N_{pyrrolyl}$ distance in $Mo(Tp^*)(NO)(NC_4H_4)_2$ of 2.01 Å is somewhat shorter than the distance of 2.13 Å in $Mo(NAd)(CHCMe_2Ph)(NC_4H_4)_2(PMe_3)$. The reason for this is not clear. To the best of our knowledge, the shorter of the two Mo-$N_{pyrrolyl}$ distances in the Tp* complex of 1.982 Å is one of the shortest M-$N_{pyrrolyl}$ distance reported for second and third-row transition metals of groups 4, 5 and 6.

In contrast to the above base-adduct, $Mo(N\text{-}2,6\text{-}Me_2C_6H_3)(CHMe_3)(NPh_2)_2$[11] does not react with excess trimethylphosphine at room temperature in benzene. The lack of reactivity confirms that the metal center in molybdenum bis(pyrrolyl) complexes retains significant electrophilic character *versus* the bis(amide)complexes and that the metal is more sterically accessible. Comparison of the ^1H alkylidene resonances also is consistent with this assertion. The alkylidene protons of the bis(amide) complexes resonate at 10.8 to 11.6 ppm *versus* 13.2 to 13.6 ppm for the bis(pyrrolide) complexes. Indeed, on the basis of the downfield resonance of the alkylidene proton, it is reasonable to postulate that $Mo(NR)(CHR')(NC_4H_4)_2$ complexes might react with olefins. They do in some cases (vide infra). The electrophilic molybdenum center and the reduced steric size (at least in the η^1

coordination mode) of the pyrrolyl ligand indicate that these are in fact good candidates for *in situ* generation of metathesis catalysts.

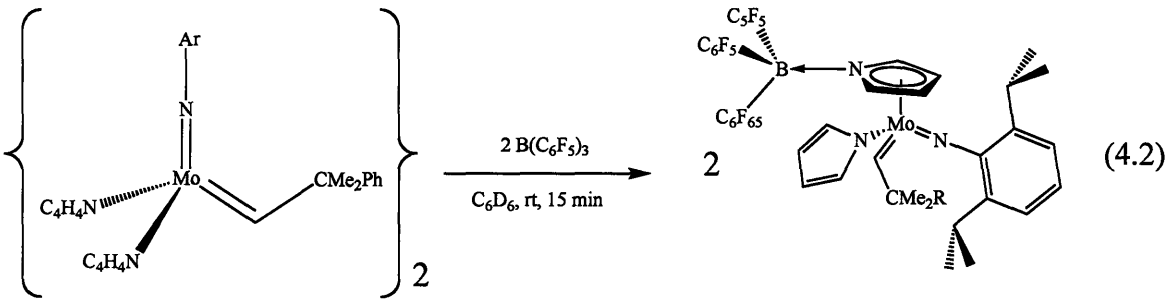
4.2 Bonding in bis(pyrrolyl) η^5/η^1 versus η^1/η^1 isomers.

The η^5/η^1 isomer may be considered to be isolobal with the traditional bent-metallocene[19] structure viewing the imido group and an η^5 pyrrolyl ligand both as triply bound. That is, three wedge orbitals are available for binding the η^1 pyrrolyl ligand and forming the $\sigma + \pi$ bonds of the alkylidene ligand. However, given the coupling constants for the *syn* alkylidene ligands are typical of related species,[20] this picture would be inadequate and the actual molecular orbital contains some mixing of the pyrrolyl π system overlap with molybdenum and an agostic interaction with the alkylidene proton must be occurring to account for the lowered $J_{C\text{-}H}$ which is not consistent with only three available wedge orbitals. Regardless, the formal electron count for the species is 18, with some combination of electron density coming from the η^5-pyrrolyl π system and some from an agostic alkylidene interaction. The spectroscopy of this molecule compares well with the related tungsten species $CpW(NCMe_3)(CHAd)Cl$.[21] The reactivity of this isomer indicates that the HOMO is largely a lone pair on the η^5 pyrrolyl nitrogen. Detailed calculations on this species (and the interconversion to the η^1/η^1 isomer) are highly desirable in order to investigate systematically the energetics of this unique system.

The η^1/η^1 isomer should be compared with the calculations of the prototypical system $Mo(NH)(CH_2)(OH)_2$, performed by several groups.[22,23] In this scheme, it would appear that the poor π donor pyrrolyl ligands contribute less electron density than electron-rich alkoxides such as *tert*-butoxide and are more similar in properties to the commonly used hexafluoro-*tert*-butoxide ligand. The LUMO remains largely molybdenum-centered and forms donor complexes like the trimethylphosphine adduct discussed above. As detailed in chapter 2, the η^1 pyrrolyl ligand appears to donate qualitatively slightly more π electron density than a chloride ligand. There is no evidence of population of η^1/η^1 *anti* isomers (< 2%) at low temperature, where the coupling constants may be measured.

4.3 Reactivity with Lewis acids.

It is likely that the fluxional nature of these complexes render them Lewis amphoteric. The dissociation of the crystallographically characterized dimer as well as the rate of interconversion between η^5/η^1 and η^1/η^1 isomers is evidently fast given the above observation of rapid (<15 minutes) PMe_3 binding at molybdenum and the rate of reactivity with the potent Lewis acid $B(C_6F_5)_3$ (also < 15 minutes) at the η^5 pyrrolyl nitrogen. Adding an equimolar amount of borane (per molybdenum) to $[Mo(NAr)(CHCMe_2Ph)(NC_4H_4)_2]_2$ produces, after 15 minutes, a solution of that contains two species in ~80/20 ratio



(4.2)

They are proposed to be the *syn* and *anti* isomers of the borane η^5 NC_4H_4 complex. The alkylidene protons resonate at 13.08 and 13.89 for the major and minor isomers, respectively. Four broad resonances are clearly visible at 7.7, 7.2, 5.7, and 5.4 ppm for the η^5-$H_4C_4N{\rightarrow}B(C_6F_5)_3$ ligand protons in the ^1H NMR spectrum. The species decomposes at room temperature over time, possibly by dissociation of the $[H_4C_4N{\rightarrow}B(C_6F_5)_3]^-$ ion. The anion $[H_4C_4N{\rightarrow}B(C_6F_5)_3]^-$ has been independently synthesized as the lithium salt and crystallographically characterized.[24] In the solid state, the lithium ion is coordinated to the pyrrole ring in a distorted η^5 geometry. The proton NMR spectrum in benzene-d_6 shows resonances at 6.72 and 5.84 for the α and β hydrogen atoms, respectively, which agrees well with the molybdenum complex. The only observed transition metal complex thought to coordinate this anion was recently reported, and resonances occur at 7.21, 7.18, 5.83, and 5.25 ppm in benzene-d_6 for the pyrrolyl protons.[25]

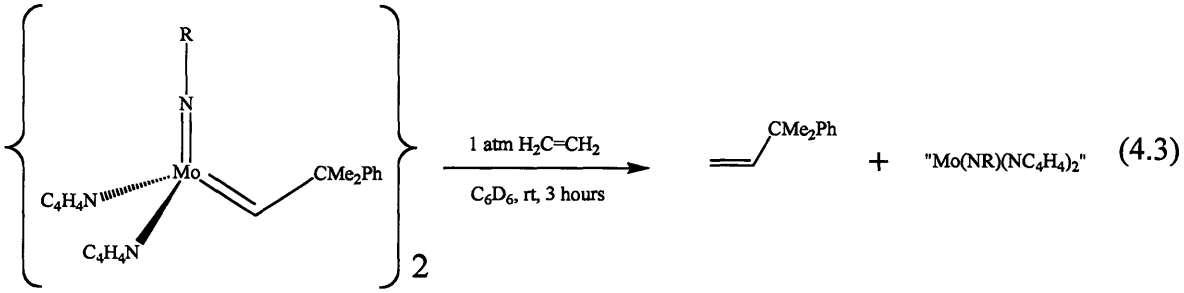
An attempt to displace the $[H_4C_4N{\rightarrow}B(C_6F_5)_3]^-$ ion by treating a benzene-d_6 solution of $Mo(NAr)(CHCMe_2Ph)(\eta^1\text{-}NC_4H_4)[\eta^5\text{-}C_4H_4NB(C_6F_5)_3]$ with ca. 20 equivalents of THF was not successful. $Mo(NAr)(CHCMe_2Ph)(\eta^1\text{-}NC_4H_4)[\eta^5\text{-}C_4H_4NB(C_6F_5)_3]$ slowly

decomposed without signs of forming a discrete ionic species. Annie Jiang has recently shown that the related complex $[Mo(NAr)(CHR)(NC_4H_4)(THF)_3][B(Ar_F)_4]$ (Ar_F = 3,5-$(CF_3)C_6H_3$) may be prepared by the protonation of one pyrrolyl ligand with $[Me_2PhNH][B(Ar_F)_4]$.[26] Use of a different borane may provide access to monopyrrolyl cations in one step. Stronger Lewis bases such as trimethylphosphine may also displace the borate anion, though the retention of the phosphine ligands may not be desirable.

4.4 Reactions with olefins

Since the bis(pyrrolyl) complexes detailed in this chapter are designed to serve as *in situ* precursors of metathesis catalysts, it is important to gauge their reactivity towards olefins, in the event that some unreacted precursor remains in solution.

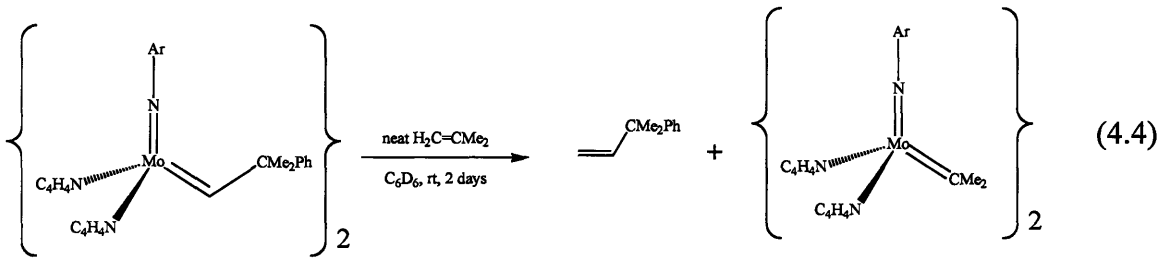
The common ring-closing metathesis substrate diallyl ether is not ring-closed by $\{Mo(NAr)(CHCMe_2Ph)(NC_4H_4)_2\}_2$ (10 mol % loading) in benzene-d_6 in two hours at room temperature and examination of the reaction mixture by ^1H NMR shows slightly sharpened resonances for the bis(pyrrolyl) complex and no signs of the first metathesis product are observed, consistent with the binding of the diallyl ether oxygen atom. Exposure of ethylene (1 atm) to a benzene-d_6 solution of $\{Mo(NR)(CHCMe_2Ph)(NC_4H_4)_2\}_2$ results in the production of the first metathesis product and a complex of the apparent composition "$Mo(NR)(NC_4H_4)_2$" (eqn 4.3). This material was not isolated analytically pure in either the 1-adamantylimido or 2,6-di*iso*propylphenylimido case, but it is believed that it



(4.3)

is a bimetallic dimer similar to the tungsten complex $[W(N\text{-}2,6\text{-}Cl_2C_6H_3)(NC_4H_4)_2]_2$, which has been structurally characterized by Dr. Stefan Arndt.[27] This reaction is believed to occur through the bimolecular coupling of alkylidene ligands[28] and be catalytic in ethylene.

It was found that neat isobutylene reacts with bis(pyrrolyl) complexes to yield what appears to be the dimer $[Mo(NAr)(CMe_2)(NC_4H_4)_2]_2$ over approximately 1-2 days (eqn 4.4)



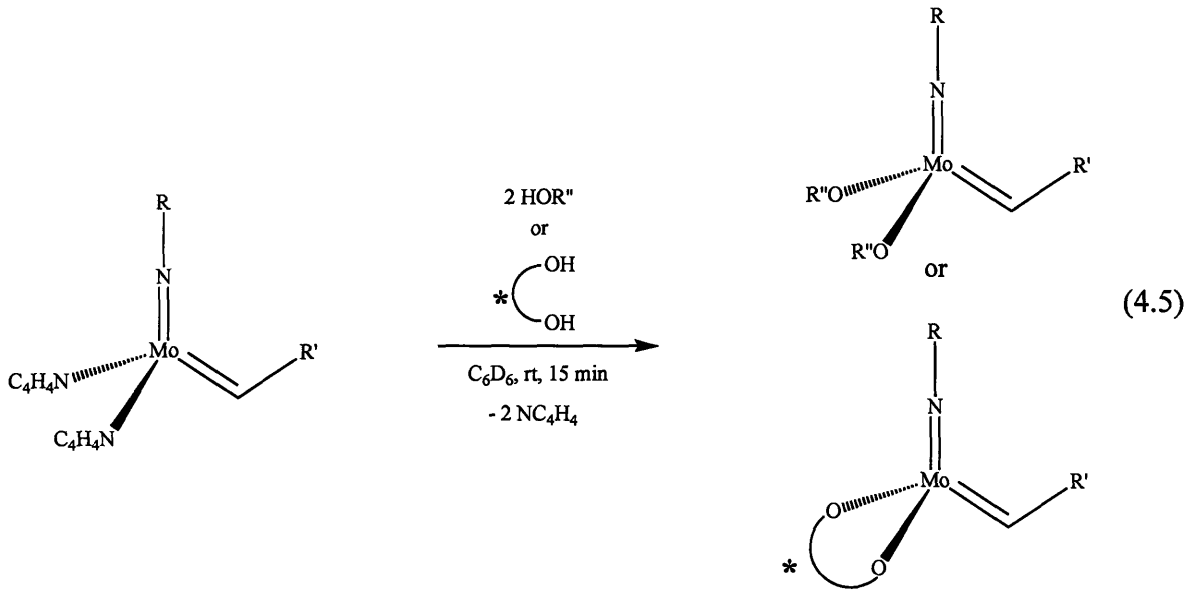
(4.4)

The room-temperature ^1H NMR features of the complex appear similar to the low temperature limit of the corresponding neophylidene complex. Two species may be observed, one of which has no symmetry. However, the material could not be isolated analytically pure, so further discussion will not be made about the detailed nature of the substance. It is possible that the larger steric protection provided by dimethylpyrrolyl ligands might allow isolation of smaller alkylidene species. If these species may be readily synthesized, it would allow access to a wide variety of precursors with differing initiation properties for polymerization reactions. Such initiation effects have been found to be important in the synthesis of polyacetylenes.[29,30]

4.5 Reactivity with Alcohols

All pyrrolyl complexes (presumed to exist in monomer/dimer equilbria) of the type $Mo(NR)(CHR')(NC_4H_4)_2$ react rapidly with all alcohols and diols screened thus far (eqn 4.5). Typically, a millimolar solution of precursor complex is combined with solution of an

equimolar amount of alcohol in a hydrocarbon solvent such as benzene, toluene, or pentane. All reactions screened thus far are complete in ca. 15 minutes at room temperature. Donor solvents such as diethyl ether and THF significantly retard the rate

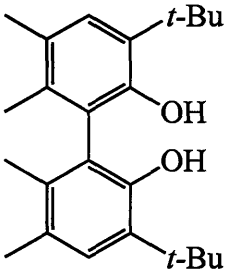
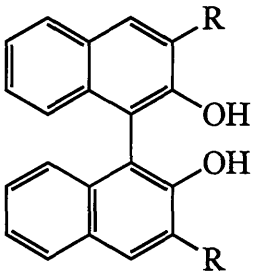
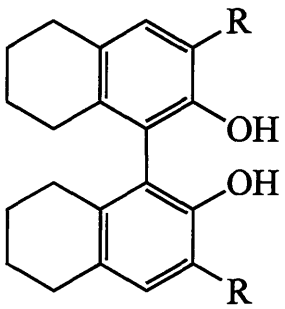


(4.5)

of reaction and were not investigated. On the basis of this observation, the mechanism of protonation is believed to be initial coordination of the oxygen atom followed by proton transfer. Another possible mechanism is direct protonation of the nitrogen atom in the η^5/η^1 form, in analogy with the $B(C_6F_5)_3$ complex reported above. Protonation at the 2 and 3 carbons of a η^1 pyrrole ligand, followed by dissociation of the resulting imine and proton rearrangement is also possible. However, given the pKa of the 2-H and 3-H tautomers of pyrrole (-3.8 and -4.4 for α and β, respectively versus 17.5 for the pyrrole N-H),[31] this is highly unlikely.

Alcoholysis reactions were aimed at screening the most challenging and commonly used combinations of imido groups and diols. All reactions were performed at millimolar concentrations typical for catalyst loading conditions in RCM reactions and at ambient temperature. The products were verified by comparison of spectroscopic features with the

Table 4.2. Alcohols and diols screened with bis(pyrroly) precursors.[a]

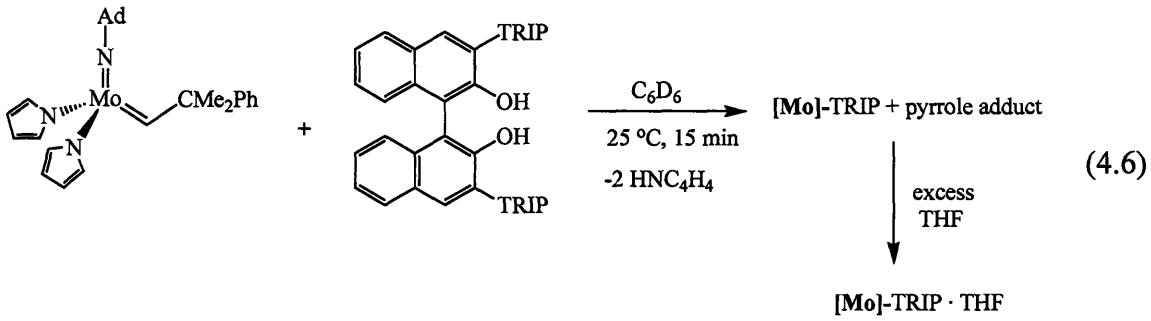
Alcohol or Diol	**Mo(NR)(CHR')(NC4H4)2**
$HOCMe_3$	R = Ar, Ad
$HOC(CF_3)_2Me$	R = Ar, Ad, 2,6-Br_2-4-MeC_6H_2
$HOC(CF_3)_2Ph$	R = Ar
	R = Ar, Ad, 2,6-Br_2-4-MeC_6H_2
 R = 2,4,6-*i*-$Pr_3C_6H_2$, 2,4,6-$Me_3C_6H_2$,	R = Ar, Ad
 R = $CHPh_2$, *t*-Bu	R = Ar, Ad, 2,6-Br_2-4-MeC_6H_2

a. Conditions: Solutions in C_6D_6 at millimolar concentration were combined at ambient temperature. Reaction mixtures were examined after 15 minutes by ^1H NMR.

known catalysts, when available. The most challenging combination on the basis of steric arguments is the 2,6-di*iso*propylphenylimido precursor and H_2[biphen]. The reaction between these two at millimolar concentrations in benzene-d_6 proceeds smoothly in 15 minutes and Mo(NAr)(CHR)[biphen] is observed by comparison of the NMR resonances

with the previously reported,[32] isolated catalyst. Furthermore, a slight (~5%) excess of diol does not appear to react with the *in situ* produced catalyst over 3 hours at room temperature.

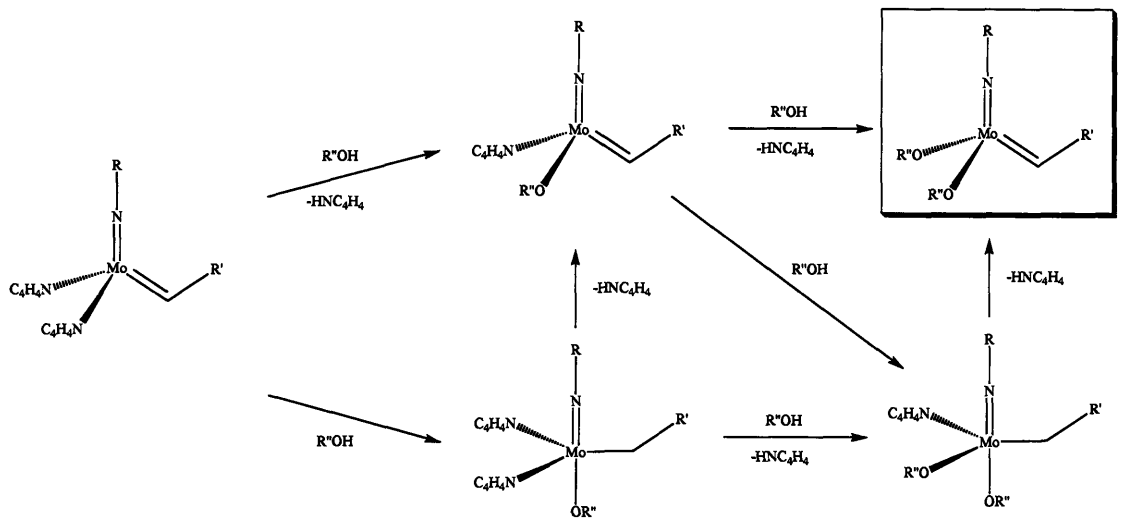
Catalysts prepared in this fashion that contain the less sterically encumbering 3,3'-binaptholate ligands are believed to coordinate pyrrole in the form of base adducts. Several small resonances are visible in the ^{1}H NMR spectrum in the alkylidene region which may be ascribed to the numerous diasteromeric base adducts which are possible. Addition of excess THF (>50 equivalents) converts the complexes to the known THF adducts, which may be isolated in high yields. The example of the reaction of 3,3'-(2,4,6-*i*-$Pr_3C_6H_2$)-1,1'-binapthol and adamantylimido molybdenum precursor is shown in equation 4.6.



(4.6)

This catalyst has been found to be very useful for many enantioselective RCM applications and generally shows a very different reaction profile from the arylimido catalysts.[33]

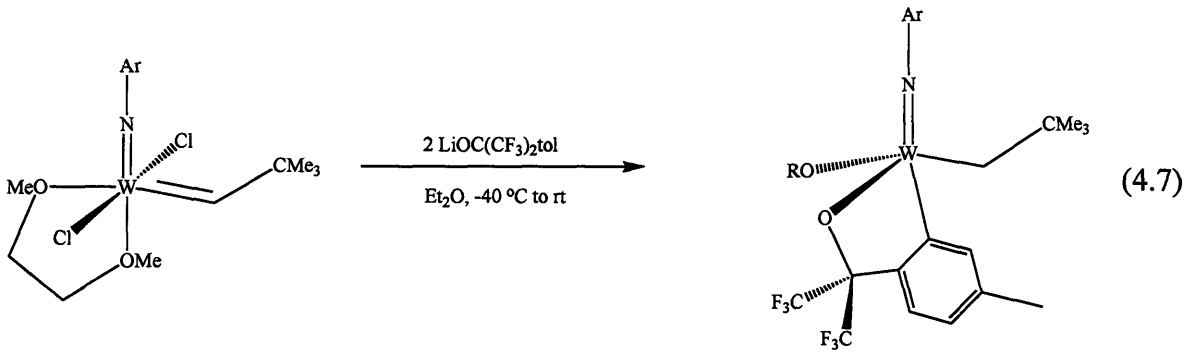
Experiments allowing sub-stoichiometric amounts of *tert*-butanol and H_2[biphen] to react with the 2,6-di*iso*propylphenylimido precursor show mixtures of the bis(alkoxide) or diolate complex and starting material; that is, it does not appear to be possible to replace only one pyrrolyl ligand under these conditions. This is unfortunate, as a hypothetical Mo(NR)(CHR')(OR'')(NC_4H_4) species would be chiral at the metal center and potentially amenable to synthesizing a single diasteromer using an addition of a second, monodentate, enantiopure alcohol. This system remains elusive for alcohols.[34] However, Keith Wapler has successfully isolated the monosiloxide complex Mo(NAr)($CHCMe_2Ph$)(NC_4H_4)(silox) (silox = *t*-Bu_3O^-) and explored the protonation of the remaining pyrrolyl ligand in some detail.[42]



Scheme 4.1. Potential mechanisms for alcohol addition to catalyst precursors.

No definitive signs of O-H addition across the alkylidene to produce an intermediate alkyl complex $Mo(NR)(CH_2R')(NC_4H_4)_2(OR'')$ were observed (Scheme 4.2), though evidence has been observed for alkylidene protonation with a stoichiometric amount of $HOC(CF_3)_2Ph$ (vide infra). Intermediates in which the alcohol O – H has added across the alkylidene linkage have been seen upon addition of alcohols to the 2,6-dichlorophenylimido tungsten system by Dr. Stefan Arndt,[27] and are observed upon addition of some alcohols to complexes of the type $M(NR)(CHR')(CH_2CMe_3)_3$ (M = Mo, W).[35] The possibility of pyrrolyl ligands removing an α proton is intriguing, as α-abstraction by ligands other than alkyls is extremely rare.[28c] No detailed labeling studies of the protonation reaction have yet been attempted. In the system $Mo(NR)(CHR')(R'')_2$, where the addition of alcohol halts at one equivalent, both mechanisms are apparently in competition, dependent on the nature of the alcohol.[35] Similar results were obtained with related tritylimido complex.[36] No signs of competitive protonation of the *imido* Mo-N bond to yield a hypothetical complex of the type $Mo(NHR)(CHR)(OR)_2(NC_4H_4)$ or related species were observed.

A relative of the commonly used $HOC(CF_3)_2Me$, $HOC(CF_3)_2Ph$, was shown to react smoothly with the 2,6-di*iso*propylphenylimido derivative to yield the corresponding, previously unreported, catalyst $Mo(NAr)(CHCMe_2Ph)(OC(CF_3)_2Ph)_2$. The alkylidene proton resonates at 12.5 ppm in benzene-d_6. A report of an attempt to synthesize the tungsten congener by salt metathesis resulted in the C-H activated species (eqn 7), in which

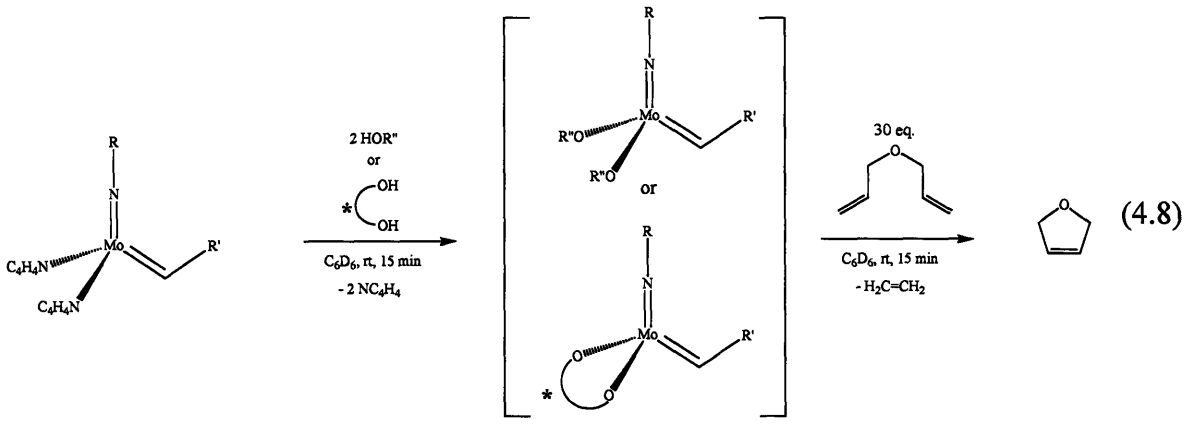


(4.7)

the an aromatic C-H bond has added across the alkylidene ligand. It is unknown if synthesis of the molybdenum species also proceeds with this reactivity by salt metathesis. It is of note that a small (<5%) impurity is visible in the ^{1}H NMR spectrum after 15 minutes which has characteristic resonances consisting of two doublets at 4.4 and 2.06 ppm with a $J_{C\text{-}H}$ of 9.7 Hz. This may be assigned to the species $Mo(NAr)(CH_2CMe_2Ph)(L)_3$ in which L is some combination of pyrrolyl and alkoxide ligands. The formation of an alkyl complex would occur *via* addition of the alcohol O-H across the alkylidene linkage. Further investigation into the nature of alkyl species though the screening of a wide variety of alcohols will be a valuable goal in the context of potentially utilizing pyrrolyl ligands as internal bases for the removal of an α proton to generate an alkylidene.

4.6 Evaluation of catalytic reactivity.

The catalytic ability of *in situ* generated catalysts was examined by ring-closing the common substrate diallyl ether at room temperature. All complexes that were screened



(4.8)

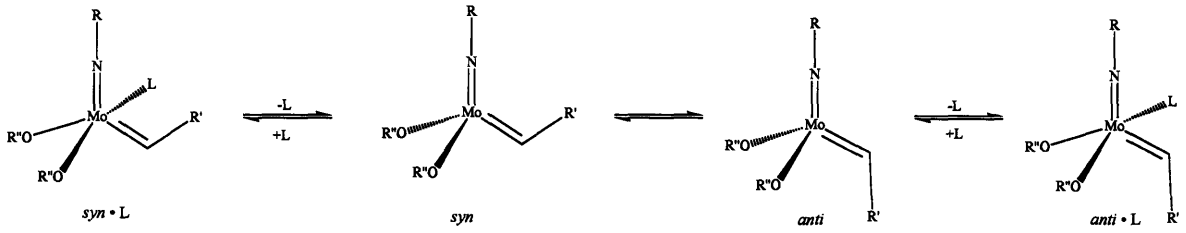
performed the reaction well (see Table 4.2), including the previously unknown Mo(N-2,6-Br_2-4-MeC_6H_2)($CHCMe_3$)[biphen] complex. This species was observed *in situ* to have an alkylidene resonance at 11.3 ppm with a J_{C-H} of 132.6 Hz. This is typical for base-free [biphen] species.[15c] Like the other *in situ* prepared species, this complex is also a catalyst for the ring closing metathesis of diallyl ether at room temperature.

Tatiana Pilyugina has examined the ring-closing of several substrates using *in situ* prepared catalysts.[37] In all cases examined, the enantioselectivity was close to that of isolated catalysts. Small deviations were observed and potential causes are discussed below. A detailed study of the capabilities of the pyrrolyl system for *in situ* synthesis of catalysts is currently underway.[37]

4.7 Comments on alkylidene isomers and the protonation reaction: potential effect on enantiomeric excess and polymerization stereocontrol.

It is well-documented that the *syn* and *anti* isomers of the alkylidene ligand may have drastically different reactivity rates in solution.[14,40] No signs of the *anti* isomer have yet been observed in solution for any bis(pyrrolyl) precursor and protonation reactions seem

to provide the *syn* isomer as the kinetic product in reactions I and others[37,38] have performed. If the solution is allowed to stand (and the *anti* species is more stable), interconversion may be observed. The overall effect of the competing equilibria is that the protonation reaction may produce an initial alkylidene that is *syn* and the kinetic



Scheme 4.2. Equilibria between alkylidene isomers and base adducts thereof.

product, whereas the thermodynamic catalyst may be *anti*. This can be further complicated by the binding of pyrrole, as several catalysts have been isolated as *anti* base adducts and some of these bind pyrrole weakly. For example, Mo(NAd)(CHR)(binap)(THF). In the *in situ* synthesis, there appears to be the *syn*-base free species and various diastereotopic pyrrole adducts, believed to be *syn* alkylidenes. If the solution is allowed to stand at room temperature for 24 hours, a more stable *anti* pyrrole adduct becomes the major product. Tatiana Pilyugina has shown that the *ee* of ring-closing metathesis using both solutions is similar.[37] This may be understood in that after one turnover, a methylene unit is the common intermediate and also explains small deviations in *ee* from isolated catalysts given that the effect may be negligible and is only relevant for one turnover in the absence of further Lewis base effects. The presence of Lewis bases is known to *positively* affect *ee* in some cases as well; the two equivalents of pyrrole in solution do not bind as strongly as THF, but are another factor which must be considered when comparing *in situ* and isolated catalysts. It may be suggested that with substrates similar to those shown to have enantioselectivity enhancement by added THF,[39] that it is added to the *in situ* system, as well.

In ROMP and acetylene polymerizations, where initiation rates and chain-end control are often important factors,[30,40] significantly different results might be found with "aged" solutions containing thermodynamic isomers *versus* freshly prepared catalysts.

Control experiments varying aging time of *in situ* generated catalysts are recommended for future work in these areas.

4.8 Other variations of Mo(NR)(CHR)$(X)_2$ system.

Dimethylpyrrolyl complexes have been prepared by Rojendra Singh. These complexes appear to be monomers in solution with η^5 / η^1 pyrrolyl ligand isomerization exchanging pyrrolyl ligand environments at room temperature. These complexes function as precursors for catalysts containing the 3,3'-binaphtholate ligands, but do not react with H_2[biphen]. However, they may be prepared in high yield and work as the parent derivatives for the combinations of ligands mentioned above. Comparison of these complexes as precursors with the parent pyrrolyl complexes would be interesting, as 2,5-dimethylpyrrole does not appear to bind, even to very electrophilic catalyst centers. One practical consideration is that the product 2,5-dimethylpyrrole is far less volatile than pyrrole (bp 165 and 129-131 °C, respectively) thus, in cases were isolation of the catalyst is desired, use of the parent pyrrolyl complexes is preferable if the desired complex cannot be readily crystallized, though this has not been an obstacle to date.

The free pyrrole (or 2,5-dimethylpyrrole) generated in this reaction may prove problematic with some substrates. Should pyrrole react with the substrate or product molecules; a corresponding indole or substituted carbazole precursor may be more desirable. I have attempted the synthesis of the adamantylimido bis(indolyl); an oily product was obtained, however the crude material had ^{1}H NMR consistent with the formation of Mo(NAd)(CHR)$(indolyl)_2$. The alkylidene resonates at 12.18 ppm and is slightly broadened. Extensive characterization has not been pursued at this point. Of course, any increase in size of the pyrrolyl-derived ligand precursor will likely show a corresponding decrease in reactivity for the alcoholysis reaction. These alternatives were not pursued.

4.9 Reactivity with other protic reagents.

The complex Mo(NAr)(CHR)$(O_2CPh_3)_2$ may be synthesized from the bis(pyrrolyl) complex and two equivalents of triphenylacetic acid in benzene. Given that this is the

most challenging imido substituent, it is to be expected that synthesis of other imido variants is possible. $Mo(NAr)(CHR)(O_2CPh_3)_2$ has been independently synthesized and characterized by Dr. Florian Schattenmann.[41]

Keith Wampler has demonstrated that the 1-adamantylimido and 2,6-di*iso*propylphenylimido complexes, react rapidly with silanols such as triphenylsilanol, tri*iso*propylsilanol and tri-*tert*-butylsilanol (siloxH).[42] The silanols examined react rapidly to form complexes of the type $Mo(NR)(CHR')(OSiR_3)_2$, with the exception of siloxH. This reaction requires extended heating at temperatures in excess of 90 °C to proceed to completion. It is important to note that the reaction with two equivalents of siloxH is the only case observed to date in which reactivity with a second equivalent of an acidic proton source proceeds slowly enough to isolate the first protonation product. Work with the complex $Mo(NAr)(CHR)(silox)(NC_4H_4)$ is continuing.[42]

In collaboration with Prof. Christophe Copéret,[43] $Mo(NAr)(CHCMe_2Ph)(NC_4H_4)_2$ has been immobilized on a partially dehydroxylated silica surface. The solid state ^1H NMR resembles that of the monosilanol complexes described above. The surface bound $Mo(NAr)(CHCMe_2Ph)(NC_4H_4)(O_{surface})$ is a poor catalyst for the metathesis of functionalized olefins.

4.10 Conclusions and future work.

The pyrrolyl complexes of the type $Mo(NR)(CHR')(NC_4H_4)_2$ are far more reactive than traditional bis(amide) complexes. The unique electronic features of the pyrrolyl ligand support complexes displaying Lewis amphoteric reactivity, depending on the hapticity of the pyrrolyl ligands. In the η^1/η^1 form they are Lewis acidic, binding Lewis bases to form adducts, one of which was crystallographically characterized and found to be similar to the many bis(alkoxide) derivatives which have been previously characterized. In the η^5/η^1 isomer they are Lewis basic at the pyrrolyl nitrogen and may be trapped by electrophilic boranes. It is likely that the η^5 to η^1 interconversion has a relatively low barrier in these species given the rapid rates of reactions with Lewis acids and bases.

The bis(pyrrolyl) complexes react slowly with olefins to produce new alkylidene species which appear to decompose to dimeric molybdenum products in the case of

ethylene and to form a new, disubstituted 2-propylidene complex with isobutylene. Heteroatom-containing substrates seem to bind strongly enough to significantly slow any potential metathesis reactivity. As a result, unreacted bis(pyrrolyl) precursor complex is not expected to be detrimental to enantioselectivity due to competitive metathesis of substrate in enantiopure reactions. Future work into synthesizing smaller alkylidene bis(pyrrolyl) complexes by reaction with olefins might produce precursors which resemble growing polymer chains, providing the opportunity to synthesize well behaved, living polymerization catalysts *in situ.*

It was found that chiral diols react rapidly and quantitatively with $\{Mo(NR)(CHR')(NC_4H_4)_2\}_2$ complexes to yield previously prepared catalysts *in situ.* Furthermore, the byproduct pyrrole was not found to be detrimental to catalytic activity in the few cases that have been tested thus far. Future work examining the impact of the kinetically determined ratios of *syn* and *anti* isomers on metathesis reactions, most specifically polymerization reactions, is definitely needed to see if this trend remains true. In the case of the reaction of $HOC(CF_3)_2Ph$ with $\{Mo(NAr)(CHCMe_2Ph)(NC_4H_4)_2\}_2$, some evidence for a competing or parallel pathway involving O-H addition across the alkylidene double bond was found. Further work aimed at examining the scope of this protonolysis reaction is certainly needed. One area which has yet to be addressed is the *in situ* synthesis of combinations of small imido and small diolate ligands for the metathesis of crowded, challenging substrates. The Hoveyda group, in collaboration with this group, has often found that enantioselective RCM of elaborate organic molecules for total synthesis proceeds sluggishly.[44] For example, many successful RCM reactions use the smaller 2,6-dimethylphenylimido catalyst rather than the more common 2,6-di*iso*propylphenylimido system. Expansion of the precursor system to the smaller imido substituents such as[45] 2,6-diethylphenyl, 2-*iso*propylphenyl, and even 3,5-dimethylphenyl would provide a tremendously less crowded environment for the metathesis of difficult substrates. The purpose is to allow the use of diols which have previously been shown to promote enantioselective reactivity, possibly by steric induction, with imido groups which are not large enough to readily support isolation of such catalysts. .

A study examining the longevity and practicality of storage of stock solutions of catalyst precursor is currently underway by Tatiana Pilyugina. The results of this study will

illuminate the degree to which these complexes make enantioselective molybdenum olefin metathesis even more "user friendly". The bis(pyrrolyl) precursors should be studied in the context of high throughput screening methods and are readily immobilized on partially dehydroxylated silica surfaces for heterogeneous catalysis.

There are further avenues for research and developent of *in situ* metathesis catalyst precursors. For example, the design of a truly Universal Precursor; a complex which reacts with alkylating reagent, nitrene source such as an amine or aniline, and an alcohol or diol (not necessarily added in that order) in a well-defined manner to yield group 6 metathesis catalysts of the type M(NR)(CHR')(diolate). The fact that pyrrolyl[27] (and pyrrolyl-like[46]) ligands show the ability to participate in α-abstraction and related C-H activations to form alkylidene ligands show tantalizing evidence that this may indeed be possible in certain cases.

Experimental

General. Precursor complexes were synthesized and handled as detailed in the previous chapter. Diallyl ether was distilled prior to use. All liquid reagents were degassed, dried over activated molecular sieves, and stored over activated molecular sieves in a drybox. Solid protic reagents were dissolved in ether or benzene and stored over activated molecular sieves for several days followed filtration through celite to remove sieves and removal of the solvent. Gasses (ethylene, 2-methylpropene) were used as received. Trimethylphosphine was purchased from Strem Chemicals and stored over activated molecular sieves. Mo(N-2,6-$Me_2C_6H_3$)($CHMe_3$)(NPh_2)$_2$ was a generous gift from Dr. Amritanshu Sinha.

Mo(NAd)($CHCMe_2Ph$)(NC_4H_4)$_2$(PMe_3). Excess trimethylphosphine (50 μl) was added to 150 mg (0.25 mmol) of Mo(NAd)($CHCMe_2Ph$)(NC_4H_4)$_2$ · tol in diethyl ether. The mixture was stirred at room temperature for 30 minutes and the solvent was removed *in vacuo*. Mo(NAd)($CHCMe_2Ph$)(NC_4H_4)$_2$(PMe_3) may be crystallized from pentane as orange blocks, yield 100 mg (69%): ^{1}H NMR (300 MHz, C_6D_6) δ 12.49 (d, 1H, J_{H-P} 4.8Hz C*H*CMe_2Ph), 7.16-6.98 (m, 5H, $CHCMe_2$*Ph*), 6.97 (s, 4H, NC_4*H*$_4$), 6.40 (s, 4H, NC_4H_4), 1.99 (s, 3H, N*Ad*), 1.9-1.79 (m, 6H, N*Ad*), 1.68 (s, 6H, MoCHC*Me*$_2$Ph), 1.35 (s, 6H, N*Ad*), 0.45 (d, 9H, P*Me*$_3$); ^{13}C NMR (C_6D_6) δ 301.73 (d, $^2J_{C-P}$ 19.5 Hz, Mo*C*HCMe_2Ph,), 148, 132.19, 129.13, 126.37, 125.96, 109.16, 108.62, 42.22, 36.21, 30.03, 16.50 (d, P*Me*$_3$, J_{C-P} 25 Hz). Anal. Calcd for $C_{31}H_{44}MoN_3P$: C, 63.58; H, 7.57; N, 7.17. Found: C, 63.37; H, 7.45; N, 6.04.

Observation of Mo(NAr)($CHCMe_2Ph$)(NC_4H_4)$_2$(PMe_3). Trimethylphosphine (2.3 μl, 0.03 mmol) was added to 15 mg (0.03 mmol) of (Mo(NAr)($CHCMe_2Ph$)(NC_4H_4)$_2$}$_2$ in ca. 0.5 ml of benzene-d_6. The solution turns dark orange rapidly and the spectrum was acquired within 30 minutes: ^{1}H NMR (500 MHz, C_6D_6) δ 14.15 (minor isomer, d, 1H, J_{CP} 7.3 Hz), 11.90 (major isomer, d, 1H, J_{CH} 116.0 Hz, J_{H-P} 4.3Hz C*H*CMe_2Ph), 7.24 (s, 2H, NC_4*H*$_4$), 7.20 (s, 2H, NC_4*H*$_4$), 7.17-7.13 (m; overlaps with C_6D_5H, 2H, $CHCMe_2$*Ph*), 7.02 (m, 1H, $CHCMe_2$*Ph*), 6.96 (m, 3H, MoN*Ar*), 6.93 (m, 2H, $CHCMe_2$*Ph*), 6.79 (s, 2H, NC_4*H*$_4$), 6.66 (s, 2H, NC_4*H*$_4$), 3.87 (sept, 2H, *i*-Pr methine), 1.67 (s, 3H, CHC*Me*$_2$Ph), 1.64

(s, 3H, CHC*Me*$_2$Ph), 1.20 (d, 6H, *i*-Pr methyl), 1.13 (d, 6H, *i*-Pr methyl), 0.55 (d, 9H, P*Me*$_3$). The resonances are unchanged in the presence of an additional 4 equivalents of trimethylphosphine.

Observation of Mo(N-2,6-Me$_2$C$_6$H$_3$)(CHMe$_3$)(NPh$_2$)$_2$ and excess trimethylphosphine. Mo(N-2,6-Me$_2$C$_6$H$_3$)(CHMe$_3$)(NPh$_2$)$_2$ (23 mg, 0.037 mmol) dissolved in 0.6 ml of C_6D_6 was treated with trimethylphosphine (7 eq, 19.7 mg, 0.26 mmol). The observed resonances were identical to the literature[11] values.

"Mo(NAd)(NC$_4$H$_4$)$_2$". {Mo(NAd)(CHCMe$_2$Ph)(NC$_4$H$_4$)$_2$}$_2$ was dissolved in benzene and freeze-pump-thaw degassed three times. Ethylene (1 atm) was admitted and the solution stirred for several hours. The ethylene and solvent were removed in vacuo and ^{1}H NMR recorded (C_6D_6, 300 MHz): 6.72 (br s, 6H), 6.36 (br s, 2H), 1.81 (s, 6H, Ad) 1.69 (s, 3H, Ad), 1.07 (s, 6H, Ad). The first metathesis product is also visible if the reaction is performed in C_6D_6.

{Mo(NAr)(CMe$_2$)(NC$_4$H$_4$)$_2$}$_2$. Solid {Mo(NAr)(CHCMe$_2$Ph)(NC$_4$H$_4$)$_2$}$_2$ (400 mg) was placed in a Teflon-sealed bomb (50 ml) with a stir bar. Isobutylene (ca. 3 mL) was carefully condensed in at 77 K. A blast shield was erected and the contents were allowed to warm to room temperature and stir for 2 days. All volatiles were removed *in vacuo* and the solid material was examined by ^{1}H NMR (500 MHz, C_6D_6): δ 7.3-7.0 (m, 6H, Ar), 6.5 (m, 8H, NC$_4$*H*$_4$), 6.3 (d, 2H, NC$_4$*H*$_4$), 5.4 (s, 1H, NC$_4$*H*$_4$), 5.3 (s, 1H, NC$_4$*H*$_4$), 5.25 (s, 1H, NC$_4$*H*$_4$), 5.0 (s, 1H, NC$_4$*H*$_4$), 3.4 (sept, 2H, *i*-Pr methine), 3.35 (sept, 1H, *i*-Pr methine), 2.23 (sept, 1H, *i*-Pr methine), 1.6 (s, 6H, MoC*Me*$_2$), 1.5-1.3 (2 x overlapping br s, 6H, MoC*Me*$_2$), 1.2 (d, 6H, *i*-Pr methyl), 1.15 (2 x overlapping d, 6H, *i*-Pr methyl), 1.04 (d, 6H, *i*-Pr methyl), 0.8 (d, 3H, *i*-Pr methyl), 0.71 (d, 3H, *i*-Pr methyl).

Representative procedure for the *in situ* catalyst generation. The molybdenum precursor (ca. 0.02 mmol) is dissolved in 0.2 mL of C_6D_6. An equimolar amount of diol or two equivalents of alcohol is dissolved in 0.3 mL of C_6D_6 and the solutions are combined in a Teflon-sealed NMR tube. The ^{1}H NMR spectrum was recorded within 15 minutes. Stock solutions of catalyst precursor may also be prepared from ca. 0.2 mmol of compound in 2 ml of C_6D_6. All stock solutions were stored at -35 °C in the glovebox freezer and allowed to thaw prior to use.

***In situ* observation of Mo(N-Ar)(CHCMe$_2$Ph)(OC(CF$_3$)$_2$Ph)$_2$.** ^{1}H NMR (300 MHz, C_6D_6): 12.50 (s, 1H, MoC*H*R major isomer ~90%), 12.4 (s, 1H, MoC*H*R minor isomer ~10%), 7.6 (d, 2H, Ar) 7.2 (d, 2H, Ar), 7.1 (t, 1H, Ar) 7.08-6.95 (m, 13H, Ar), 3.68 (sept, 2H, *i*-Pr methine), 1.61 (s, 3H, MoCHC*Me*$_2$Ph), 1.51 (s, 3H, MoCHC*Me*$_2$Ph), 1.18 (d, 6H, *i*-Pr methyl), 1.14 (d, 6H, *i*-Pr methyl).

***In situ* observation of Mo(N-2,6-Br$_2$-4-MeC$_6$H$_2$)(CHCMe$_3$)(rac-biphen).** A stock solution was prepared by using Mo(N-2,6-Br$_2$-4-MeC$_6$H$_2$)(CHCMe$_3$)(NC$_4$H$_4$)$_2$ (87.7 mg, 0.16 mmol) dissolved in 1.5 ml of C_6D_6. *rac*-biphen (55.4 mg, 0.16 mmol) was added as a solid. After 10 minutes ^{1}H NMR was recorded of ca. 0.5 ml of the solution. ^{1}H (300 MHz, C_6D_6): 11.3 (s, 1H, MoC*H*R, $J_{C\text{-}H}$ 132.6 Hz).

Observation of Mo(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(η^1-NC$_4$H$_4$)(η^5-C$_4$H$_4$NB(C$_6$F$_5$)$_3$. To 23.0 mg (0.021 mmol) of {Mo(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(NC$_4$H$_4$)$_2$}$_2$ in ~0.25 mL of C_6D_6 was added B(C$_6$F$_5$)$_3$ (22 mg, 0.043 mmol) in ca. 0.25 mL C_6D_6. The solution was transferred to a Teflon-sealed NMR tube and the ^{1}H NMR spectrum was recorded (500 MHz, 293 K) δ 13.89 (s, 1H, MoC*H*R minor isomer), 13.08 (s, 1H, MoC*H*R major isomer), 7.72 (br s, 1H, η^5-C$_4$*H*$_4$NB(C$_6$F$_5$)$_3$), 7.28 (br s, 1H, η^5-C$_4$*H*$_4$NB(C$_6$F$_5$)$_3$), 7.08 (m, 4H, MoCHCMe$_2$*Ph*), 7.02 (d, J_{HH}7.6 Hz, 2H, η^1-NC$_4$*H*$_4$), 6.87 (m, 1H, MoCHCMe$_2$*Ph*), 6.78 (d, J_{HH}7.6 Hz, 2H, η^1-NC$_4$*H*$_4$), 5.78 (br s, 1H, η^5-C$_4$*H*$_4$NB(C$_6$F$_5$)$_3$), 5.41, (br s, 1H, η^5-

$C_4H_4NB(C_6F_5)_3$), 2.82 (br s, 2H, *i*-Pr methine), 1.51 (s, 3H, MoCHCMe_2Ph), 1.25 (s, 3H, MoCHCMe_2Ph), 0.92 (br mult, 12H, *i*-Pr methyls).

X-Ray Structural Studies

Low temperature diffraction data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS SMART Apex CCD detector with graphite-monochromated MoKα radiation (λ = 0.71073 Å), performing φ and ω-scans. The structures were solved by direct methods using SHELXS[47] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[48] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl groups). One adamantyl group was found to be disordered in the structure and was refined with similarity restraints on 1,2 and 1,3 bonds and angles as well as restraints on thermal parameters. Crystal and structural refinement data for the structure are listed below.

Table 4.3. Crystal data and structure refinement for $Mo(NAd)(CHCMe_2Ph)(NC_4H_4)_2PMe_3 \cdot C_7H_8$.

Identification code	06080	
Empirical formula	$C_{38}H_{52}MoN_3P$	
Formula weight	677.74	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 11.3552(4) Å	α= 91.9910(10)°
	b = 11.7692(3) Å	β= 100.0450(10)°
	c = 26.8328(9) Å	γ = 94.9460(10)°
Volume	3513.33(19) $Å^3$	
Z	4	
Density (calculated)	1.281 Mg/m^3	
Absorption coefficient	0.448 mm^{-1}	
F(000)	1432	
Crystal size	0.15 x 0.15 x 0.09 mm^3	
Theta range for data collection	0.77 to 26.40°	
Index ranges	$-14 \le h \le 13$, $-14 \le k \le 14$, $0 \le l \le 33$	
Reflections collected	64064	
Independent reflections	14387 [R(int) = 0.0452]	
Completeness to theta = 26.40°	99.8 %	
Max. and min. transmission	0.9608 and 0.9358	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14387 / 1054 / 1002	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0323, wR2 = 0.0724	
R indices (all data)	R1 = 0.0466, wR2 = 0.0787	
Largest diff. peak and hole	0.529 and -0.263 $e/Å^3$	

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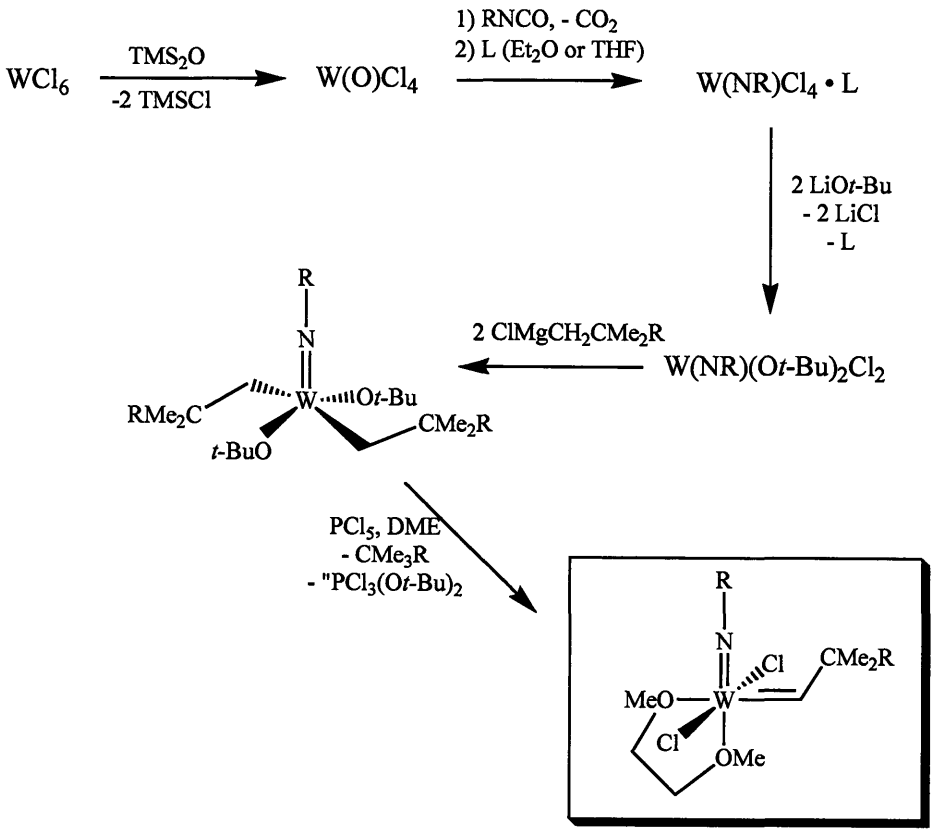
Appendix A

Synthesis of Tungsten Imido Tetra(pyrrolyl) Complexes and Preliminary Reactivity.

Introduction

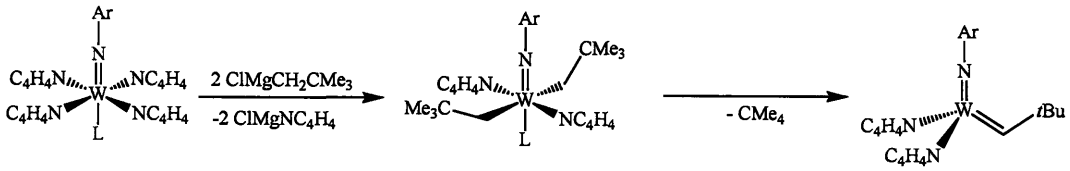
One ongoing project in the Schrock group has been the pursuit of new routes to metathesis catalysts. The "universal precursor" $M(NR)(CHR)X_2(DME)$[1] (X = OTf, Cl) complexes are excellent starting materials for the synthesis of many catalysts and the pyrrolyl derivatives detailed in this thesis. However, their synthesis requires the successful protonolysis of an imido ligand with the somewhat dangerous reagent triflic acid[2] and some imido species do not survive the reaction conditions.[1a,3-4] In addition to these caveats, impure triflic acid may lead to low or zero yield, especially for the more sensitive imido ligands such as 2,6-$Cl_2C_6H_3N$.[5] Prior to the discovery of this synthetic pathway, it was



Scheme A.1. Synthesis of $W(NR)(CHCMe_2R)Cl_2DME$ Precursors.

found that tungsten metathesis catalysts could be synthesized via a separate pathway not involving triflic acid from an imido/alkylidene dichloro species synthesized as shown in Scheme A.1.[1b]

These complexes were synthesized for R = Ad, Ar, and Ar′. They react readily with lithium alkoxides and dipotassium diolates to produce active metathesis catalysts. Although the corresponding route fails for molybdenum due to the ready reduction of $MoOCl_4$,[1b,6] a related route involving oxidation of molybdenum(IV) with organic azides to produce analogous $Mo(NR)Cl_4 \bullet L$ complexes has been detailed.[14] Tungsten was chosen for the initial investigations due to the higher electrophilicity of the metal and ready availability of the commonly used Ar and Ar′ imido substituents (synthesis electron-rich, hindered aryl azides proceeds in low yields,[14] hindering preliminary investigations). The purpose of this investigation was to see if a synthesis involving pyrrolyl ligands in place of *tert*-butoxide ligands could be realized. The synthesis was targeted such that a complex of the type $\{W(NR)(CHCMe_2R)(NC_4H_4)_2\}_x$ would be the product of alkylation (eqn A.1). It was hoped that the poorly π-donating pyrrolyl ligands would have an enough ionic character in the tungsten-nitrogen bond to be susceptible to alkylation. This would produce



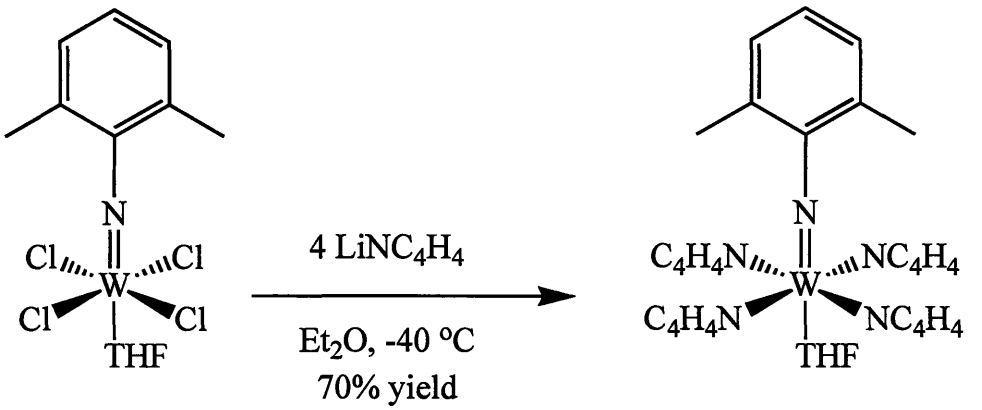
(A.1)

an electrophilic tungsten center that could undergo α-abstraction to produce the desired precursor in three steps. Dr. Stefan Arndt has recently shown that $W(N\text{-}2,6\text{-}Cl_2C_6H_3)(CHCMe_3)(NC_4H_4)_2(DME)$ may be synthesized[7] from $W(N\text{-}2,6\text{-}Cl_2C_6H_3)(CHCMe_3)(OTf)_2DME$ and two equivalents of lithium pyrrolide. It is a stable molecule and it is reasonable to believe that other pyrrolyl derivatives are as well. It is also of note that the synthesis of $WOCl_4$[8] (also commercially available from Strem Chemicals) and $W(NR)Cl_4 \bullet L$ proceed in high yield on very large scales, giving this route, if successful, the potential to compete with the traditional synthesis in expediency as well as avoiding the oft-maligned reagent triflic acid.

Results and Discussion

A1. Synthesis and Attempted Alkylation of W(NAr′)(NC_4H_4)$_4$(THF)

W(NAr′)Cl_4(THF) (Ar′ = 2,6-$Me_2C_6H_3$) reacts with 4 equivalents of lithium pyrrolide in ether to produce W(NAr′)(NC_4H_4)$_4$(THF) in good yield (eqn A.2)



(A.2)

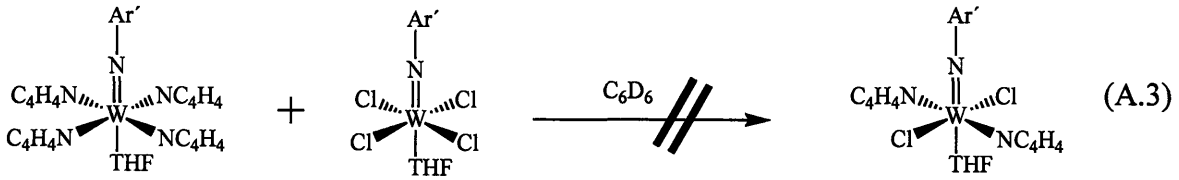
as a very dark red crystalline powder. The THF is retained from the starting material, despite diethyl ether being the reaction solvent, and is not removed at room temperature *in vacuo*, nor does it exchange with free THF on the NMR time scale. The complex has C_{4v} symmetry on the ^{1}H NMR time scale at room temperature with slightly broad pyrrolyl ligand resonances. The ^{13}C spectrum shows broad resonances at 113.94 and 133.46 for the α and β carbons of the pyrrolyl ligands. The resonances for the rest of the molecule are sharp. The fluxional process is believed to be hindered rotation about the W-$N_{pyrrolyl}$ bonds on the NMR time scale and not involve any dissociation of the THF ligand because the resonances for the coordinated THF are sharp in the ^{13}C NMR. The tight binding of THF also demonstrates the electrophilicity of the metal center. In the related complexes,[9] W(NPh)(NMe_2)$_4$ and W(O)(NMe_2)$_4$, THF is not retained although the nuclearity of W(O)(NMe_2)$_4$ was not determined.

Preliminary reactivity with alkylating reagents has shown that addition of 1 or 2 equivalents of neopentylmagnesium chloride and neopentyl lithium result in a multitude of unidentified products. Some tentative signs of W(NAr′)(CHR)(η^x-NC_4H_4)$_2$ were observed in small amounts as a broad singlet around 11 ppm. The products were not separated and the peak diminishes over an hour or two. W(NAr′)(NC_4H_4)$_4$(THF) does not react with

dineopentyl zinc at room temperature and heating produced rapid decomposition. It seems that despite their poor π-donating ability, the pyrrolyl ligands are not readily removed by alkylation. Two reasons are likely for this result. First, as THF does not exchange on the NMR time scale, alkylation of a fairly crowded six-coordinate species is not favorable. Second, while pyrrole itself is not readily susceptible to nucleophilic attack, any π-overlap with a transition metal (in a η^1 coordination geometry) lowers the aromaticity, rendering the species more reactive towards nucleophiles. The use of η^5 pyrrole coordination to induce nucleophilic substitution behavior has recently been reviewed.[10]

A2. Preliminary Investigations of Alternate Synthetic Routes.

Following the discovery that W(NAr′)$(NC_4H_4)_4$(THF) does not react cleanly with alkylating reagents, some attempts to synthesize complexes that contain better leaving groups were performed. One frequently used methodology in early transition metal chemistry is conproportionation of an amide complex and a halide species.[11] This methodology has also been used in a redox fashion with group 6 species.[12] An attempt to conproportionate equimolar amounts of W(NAr′)Cl_4(THF) with W(NAr′)$(NC_4H_4)_4$(THF) in benzene (eqn 3) resulted in no reaction at room temperature and rapid decomposition at elevated temperature (65 °C, 5 minutes).



(A.3)

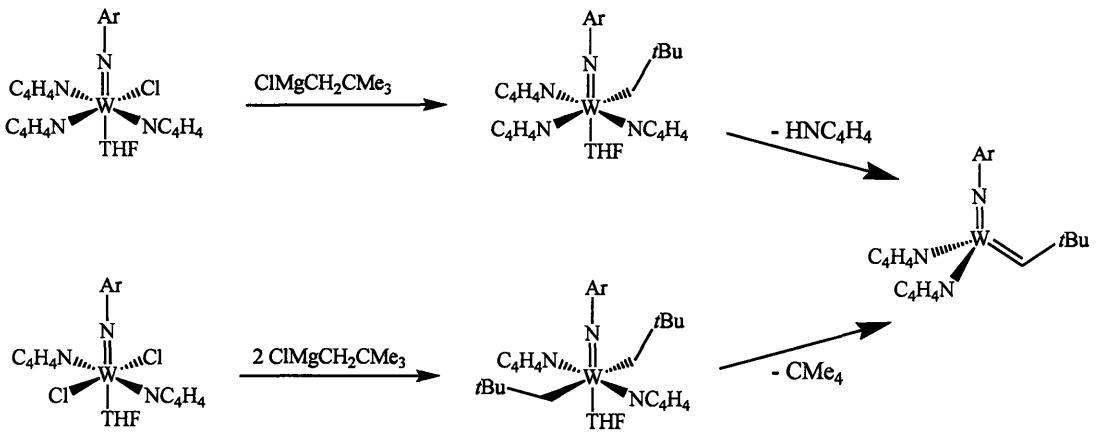
W(NAr′)$(NC_4H_4)_4$(THF) does react rapidly with alcohols. Treatment of W(NAr′)$(NC_4H_4)_4$(THF) in benzene with one equivalent of HODIP (DIP = 2,6-*i*-PrC_6H_3) rapidly produces spectroscopically characterized W(NAr′)(ODIP)$(NC_4H_4)_3$. This complex shows inequivalent pyrrolyl ligands and the exact nature has not yet been unequivocally established. It is important to note that this species does not retain THF, and a 5-coordinate species should react more cleanly with alkylating reagents. Furthermore, it has been shown that the ODIP ligand can be removed cleanly by alkylation in some cases.[13] This possibility

has not yet been examined in detail. Two equivalents of *sec*-butanol in benzene produced two products in a 1:1 ratio, believed to be the racemic and meso species of $W(NAr')(NC_4H_4)_2(OCH(Me)(Et))_2$. It is not known if THF coordinates to the species and it was not able to be isolated analytically pure. Attempts to alklylate this species generated *in situ* did not produce tractable material.

A3. Conclusions and Future Work.

In at least one case, $W(NAr')(NC_4H_4)_4(THF)$, tungsten imido tetrapyrrolyl complexes may be readily synthesized in high yield. However, these complexes do not react with common alkylating reagents to yield the desired metathesis catalyst precursors. $W(NAr')(NC_4H_4)_4(THF)$ does react with alcohols to yield mixed alkoxide and aryloxide pyrrolyls. Further exploration of their chemistry, most especially attempts to alkylate these complexes are needed to see if an *in situ* alcoholysis followed by alkylation is a viable route to metathesis precursors.

Alternatively, replacement of the pyrrolyl ligands with more ionic species is likely to produce complexes amenable to alkylation. Two highly desirable target compounds are $W(NR)(NC_4H_4)_3Cl$ and $W(NR)(NC_4H_4)_2Cl_2$. Addition of only two or three equivalents of lithium pyrrolide under a variety of conditions produced a number of species, with the tetrasubstituted complex always visible in some proportion. The small size of η^1-pyrrolyl ligands is believed to be the cause of this problem. However, these species should be accessible from $W(NR)(NC_4H_4)_4$ complexes *via* protonolysis with HCl in ether. Synthesis of other leaving groups may be possibly by use of other electrophiles such as MeOTf, TMSOTf and Tf_2O. Better leaving groups should allow for the synthesis of mixed alkyl/pyrrolyl species which may undergo α-abstraction, producing the desired $W(NAr)(CHR)(NC_4H_4)_2$ precursor, as shown below.



Scheme A.2. Potential synthetic route to tungsten bis(pyrrolyl) metathesis catalyst precursors.

Given the ease of synthesis of the tungsten(imido)tetrapyrrolyls, this route would be expedient way of accessing metathesis catalyst precursors despite being one step longer. Furthermore, given the report[14] of using azides to synthesize molybdenum(imido)tetrachlorides, it may also be possible to synthesize molybdenum precursors in this fashion. A particularly intriguing example is the readily available azide 2,6-$Cl_2C_6H_3N_3$. Clearly more study of the fundamental reaction chemistry of poly(pyrrolyl) complexes is needed.

Experimental

W(N-2,6-$Me_2C_6H_3$)(NC_4H_4)$_4$(THF). To 1.86 g (3.5 mmol) of W(N-2,6-$Me_2C_6H_3$)Cl_4(THF) suspended in 50 ml of -35 °C diethyl ether was added a -35 °C solution of $LiNC_4H_4$ (1.05 g, 14.4 mmol) in ca. 15 ml of THF. The mixture was stirred at ambient temperature for 45 minutes and the solvent was removed from the resulting dark red solution. The solid was extracted with 80 ml of toluene and filtered through celite. The celite was washed with 3x50 ml of toluene. The filtrate containing very dark red-brown W(N-2,6-$Me_2C_6H_3$)(NC_4H_4)$_4$(THF) was dried thoroughly; yield 1.62 g (70 %): ^{1}H NMR (C_6D_6, 300 MHz) δ 6.83, (br s, 8H, pyrrole); 6.69, (d, 2H, *Ar*N); 6.43, (t, 1H, *Ar*N); 6.29, (br s, 8H, pyrrole); 3.49, (br s, 4H, THF); 2.32, (s, 6H, Ar-*Me*$_2$N); 0.93, (br s, 4H, THF); ^{13}C NMR (C_6D_6) δ 149.6, 144.09, 133.46 (br, N*C*$_4H_4$), 132.19, 127.91, 113.94 (br, N*C*$_4H_4$), 72.39, 25.89, 16.81. Two attempts at analysis both resulted in unacceptable results. Typical result: Anal. Calcd for $C_{28}H_{33}N_5OW$: C, 52.59; H, 5.20; N, 10.95. Found: C, 50.75; H, 5.55; N, 6.31.

Attempts to synthesize W(N-2,6-$Me_2C_6H_3$)(NC_4H_4)$_2Cl_2$(THF). Addition of only 2 equivalents of LiC_4H_4 to an ether suspension of W(N-2,6-$Me_2C_6H_3$)Cl_4(THF) resulted in a mixture of compounds, including known W(N-2,6-$Me_2C_6H_3$)(NC_4H_4)$_4$(THF). An attempt to conproportionate W(N-2,6-$Me_2C_6H_3$)Cl_4(THF) with an equimolar amount of W(N-2,6-$Me_2C_6H_3$)(NC_4H_4)$_4$(THF) in C_6D_6 (~0.1 mmol of both complexes in 0.5 mL C_6D_6) resulted in no reaction at room temperature. Heating to 60 °C for 5 minutes produced copious precipitate and intractable material.

Alcoholysis of W(N-2,6-$Me_2C_6H_3$)(NC_4H_4)$_4$(THF). To a solution of W(N-2,6-$Me_2C_6H_3$)(NC_4H_4)$_4$(THF) in benzene was added one equivalent of 2,6-*i*-PrC_6H_3OH dropwise. The solution was stirred for an hour then all volatiles were removed *in vacuo*. The resulting reddish solid was then examined by ^{1}H NMR (300 mHz, C_6D_6) δ 7.28 (m, 3H, NC_4H_4), 7.11 (m, 3H, NC_4H_4), 6.98 (t, 1H, *Ar)*, 6.77 (d, 2H, *Ar*), 6.7 (d, 1H, *Ar),* 6.51 (t, 1H, *Ar*), 6.45 (d, 1H, *Ar),* 6.29 (m, 3H, NC_4H_4), 6.19 (m, 3H NC_4H_4), 3.50 (sept, 2H, C*H*Me_2), 2.20 (s, 6H, Ar*Me*$_2$), 1.13 (d, 12H, CH*Me*$_2$)

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Education

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  Thesis: "Synthesis and Reactivity of Molybdenum Oraganometallic Complexes Supported by Amide Ligands"
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Training

- Experienced in the synthesis, manipulation, and characterization of air and moisture-sensitive, paramagnetic and diamagnetic metal complexes.
- Developed a system for the *in situ* synthesis of olefin metathesis catalysts of the type Mo(NR)(CHR′)(OR″)$_2$ and Mo(NR)(CHR)(diolate).
- Extended the system to the *in situ* synthesis of previously unknown metathesis catalysts, including those inaccessible by traditional methods.
- Experienced in X-ray crystallography, including refinements involving disorder, twinning, and other "problem structures".
- Mentored an undergraduate student.

Awards and Honors

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Patents and Presentations

- **Hock, A. S.** and Schrock, R. R. "Dipyrrolyl Precursors to Molybdenum Olefin Metathesis Catalysts" *patent application filed*
- **Hock, A. S.** and Schrock, R. R. "Structure and Reactivity of Molybdenum(IV) Bis(alkyl) Complexes Supported by a Diamidoamine Ligand" American Chemical Society National Meeting, March 2005, San Diego, CA.

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