MOLYBDENUM ALKYLIDENE COMPLEXES: SYNTHESES AND APPLICATIONS TO OLEFIN METATHESIS REACTIONS

by

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(2002)

Submitted to the Department of Chemistry
in Partial Fulfillment of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY
at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
June 2007

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To my Mom
Abstract

Chapter 1. Alkylimido Molybdenum Complexes: Synthesis, Characterization and Activity as Chiral Olefin Metathesis Catalysts.

Molybdenum olefin metathesis catalysts that contain previously unexplored aliphatic 1-phenylcyclohexylimido (PhCyN) and 2-phenyl-2-adamantylimido (PhAdN) groups were prepared and shown to be efficient and selective in a variety of olefin metathesis reactions. Five catalysts, Mo(NR)(CHCMe2Ph)[(S)-Biphen], Mo(NR)(CHCMe2Ph)[(R)-Trip](THF) (R = 1-adamantyl, PhCy, PhAd; Biphen = 3,3'-di-tert-butyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diolate; Trip = 3,3'-bis(2,4,6-triisopropylphenyl)-1,1'-binaphthyl-2,2'-dilolate) and Mo(NAd)(CHCMe2Ph)[(R)-Trip](THF) (Ad = 1-adamantyl), were synthesized. Their catalytic activity and enantioselectivity in desymmetrization reactions such as ring-closing metathesis of amines and lactams and ring-opening/cross metathesis of a substituted norborneol with styrene were compared to the results obtained with the only known alkylimido catalyst, Mo(NAd)(CHCMe2Ph)[(S)-Biphen]. The new catalysts prove to be similar to Mo(NAd)(CHCMe2Ph)[(S)-Biphen] in the majority of the studied reactions, and the examined catalysts show overall improvement in activity and enantioselectivity compared to the traditional arylimido catalysts.

Chapter 2. Synthesis of Molybdenum Imido Alkyl and Alkylidene Complexes from Molybdenum Imido Tetrachlorides.

Several new Mo(NR)Cl4(THF) species (R = C6F5, 3,5-(CF3)2C6H3, Ad, CPh3, and 2,6-i-Pr2C6H3) were prepared via the treatment of MoCl4(THF)2 with azides, and then alkylated with neopentyl reagents. Addition of Mo(NR)Cl4(THF) complexes in toluene to a cold solution of NpMgCl in ether gave Mo(NR)Np3Cl species (R = C6F5, 3,5-(CF3)2C6H3, Ad, CPh3, and 2,6-i-Pr2C6H3 (Ar); Np = CH2-t-Bu) in poor (35 %) to modest (51 %) yields. Heating Mo(NAr)Np3Cl in C6D6 to 50 °C results in α-hydrogen abstraction to give neopentane and a molecule whose
NMR spectra are consistent with it being Mo(NAr)(CH-t-Bu)NpCl; it decomposed bimolecularly upon attempted isolation. The other Mo(NR)Np3Cl species were found to be more stable than Mo(NAr)Np3Cl, but when they did decompose at elevated temperatures, no neopentylidene complex could be observed. Addition of neopentyllithium to Mo(NR)Np3Cl species (R = Ar, CPh3, or Ad) yielded Mo(NR)(CH-t-Bu)Np2 species, the adamantylimido version of which is unstable toward bimolecular decomposition. Addition of 1 equivalent of 2,6-diisopropylphenol, 2,6-dimethylphenol, or 3,5-(2,4,6-i-Pr3C6H2)2C6H3OH (HIPTOH) to Mo(NCPh3)(CH-t-Bu)Np2 led to formation of Mo(NCPh3)(CH-t-Bu)Np(OR) species, while treatment of Mo(NCPh3)(CH-t-Bu)Np2 with C6F5OH gave Mo(NCPh3)Np3(OC6F5). The three monophenoxide neopentylidene complexes showed metathesis activity for ring-closing a small selection of amines and an ether. X-ray studies were completed for Mo[N-3,5-(CF3)2C6H3]Cl4(THF), Mo[N-3,5-(CF3)2C6H3]Np3Cl, Mo(NCPh3)Np3Cl, and Mo(NCPh3)(CH-t-Bu)Np(OHIPT).

Chapter 3. Reactions of Mo Bispyrrolide Complexes with Enantiomerically Pure Diols: In Situ Catalyst Generation and Studies of Olefin Metathesis Reactions In the Fume Hood.

Reactions of bispyrrolide molybdenum complexes Mo(NAd)(CHCMe2Ph)(pyr)2 and Mo(N-2,6-i-Pr2C6H3)(CHCMe2Ph)(pyr)2 with (R)-BiphenH2, and (R)-Benz2BitetH2 were examined (pyr = C4H4N, Benz2BitetH2 = 3,3'-dibenzhydryl-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2,2'-diol). The resulting in situ generated catalysts were studied in three olefin metathesis reactions. These systems were found to be as active and enantioselective as the analogous isolated complexes. When the stock solutions of Mo(NAd)(CHCMe2Ph)(pyr)2, Mo(N-2,6-i-Pr2C6H3)(CHCMe2Ph)(pyr)2, (R)-BiphenH2, and (R)-Benz2BitetH2 were stored in the fume hood over a period of one month, the in situ prepared catalysts were determined to be nearly identical in terms of their catalytic properties to the catalysts generated in situ in the glovebox.
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<tr>
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<th>Full Form</th>
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<tbody>
<tr>
<td>Ad</td>
<td>1-adamantyl</td>
</tr>
<tr>
<td>Anal</td>
<td>Analysis</td>
</tr>
<tr>
<td>Ar</td>
<td>aryl</td>
</tr>
<tr>
<td>br</td>
<td>broad</td>
</tr>
<tr>
<td>Bn</td>
<td>benzyl, -CH$_2$(C$_6$H$_5$)</td>
</tr>
<tr>
<td>t-Bu</td>
<td>tert-butyl, -C(CH$_3$)$_3$</td>
</tr>
<tr>
<td>n-BuLi</td>
<td>n-butyllithium</td>
</tr>
<tr>
<td>Calcd</td>
<td>calculated</td>
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<tr>
<td>CBz</td>
<td>benzylcarboxylate, -CO$_2$CH$_2$Ph</td>
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<tr>
<td>Cy</td>
<td>cyclohexyl, -C$<em>6$H$</em>{11}$</td>
</tr>
<tr>
<td>d</td>
<td>doublet</td>
</tr>
<tr>
<td>deg, (°)</td>
<td>degree(s)</td>
</tr>
<tr>
<td>DEPT</td>
<td>Distortionless Enhancement by Polarization Transfer</td>
</tr>
<tr>
<td>DME</td>
<td>1,2-dimethoxyethane</td>
</tr>
<tr>
<td>dme</td>
<td>1,2-dimethoxyethane coordinated to a metal center</td>
</tr>
<tr>
<td>ee</td>
<td>enantiomeric excess</td>
</tr>
<tr>
<td>ESI</td>
<td>Electro-spray Ionization</td>
</tr>
<tr>
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<td>gram(s)</td>
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</tr>
<tr>
<td>J</td>
<td>coupling constant in Hertz</td>
</tr>
<tr>
<td>m</td>
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</table>
Me  methyl

min  minute(s)

NMR  Nuclear Magnetic Resonance

OTf  triflate, -OSO₂CF₃

Ph  phenyl, -C₆H₅

ppm  parts per million

i-Pr  isopropyl, -CH(CH₃)₂

py  pyrrolide, -NC₄H₄

pyr  pyridine

q  quartet

s  singlet

sep  septet

t  triplet

TFA  trifluoroacetic acid

THF  tetrahydrofuran

TMS  trimethylsilyl, -SiMe₃

TMSCl  trimethylsilyl chloride

trityl  -C(C₆H₅)₃

δ  chemical shift downfield from tetramethylsilane in ppm
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Chapter 1

Alkylimido Molybdenum Complexes: Synthesis, Characterization and Activity as Chiral Olefin Metathesis Catalysts.

A portion of this work has appeared in print:

1.1 Introduction.

In the last 10 years our laboratory in collaboration with the group led by Professor Amir Hoveyda at Boston College has been interested in design of catalysts for asymmetric olefin metathesis reactions. The research has been focused on development of Mo-based alkylidene complexes that would efficiently and enantioselectively catalyze reactions such as asymmetric ring-closing metathesis (ARCM), asymmetric ring-opening/ring-closing metathesis (AROM/RCM) and asymmetric ring-opening/cross metathesis (AROM/CM). As a result of this effort a large library of complexes has been synthesized over the last decade, and catalytic properties of these compounds have been studied extensively.\textsuperscript{1,2,3,4,5,6} The vast majority of the established catalysts are four- or five-coordinate species bearing an arylimido ligand along with a chiral diolate chelating the Mo center (Figure 1). The first catalyst that contained an alkylimido ligand, 1-adamantylimido, was synthesized in 1993,\textsuperscript{7} and various achiral versions of this catalyst have been used for olefin cross metathesis,\textsuperscript{8} ring-opening metathesis polymerization (ROMP)\textsuperscript{9} and living polymerization of substituted acetylenes.\textsuperscript{10}

In 2003 our group published a report on synthesis and catalytic studies of the first chiral alkylimido catalyst, Mo(NAd)(CHCMe\textsubscript{2}Ph)[(S)-Biphen] (Ad = 1-adamantyl; Biphen = 3,3\textsuperscript{'}-di-tert-butyl-5,5\textsuperscript{'}-6,6\textsuperscript{'}-tetramethyl-1,1\textsuperscript{'}-biphenyl-2,2\textsuperscript{'}-diolate) \textbf{1a} (Figure 1), which proved to be superior to the arylimido molybdenum complexes in terms of catalytic activity and selectivity, when applied to certain classes of substrates.\textsuperscript{11,15} Therefore we decided to take the next step in the expansion of the library of Mo-based olefin metathesis catalysts and synthesize a number of previously unexplored alkylimido Mo alkylidene complexes. The new compounds were to be studied as catalysts for olefin metathesis reaction with substrates that had been shown to be particularly challenging to metathesize employing traditional arylimido-containing catalysts.

The new imido groups to be introduced in the molybdenum complexes were designed to ensure relative stability and reactivity of the catalysts. We chose the two new imido groups, 1-phenylcyclohexylimido (PhCyN) and 2-phenyl-2-adamantylimido (AdPhN), believing that these
ligands would be bulky enough to prevent bimolecular decomposition of the complexes, yet they would leave open space in the coordination sphere of the catalysts for an olefinic substrate to be able to bind to the metal center. We also expected quaternary carbon atoms bound to the imido nitrogens to exclude the possibility of β-hydrogen activation. We proposed that the phenyl groups in the imido ligands would provide additional crystallinity to the catalysts and aid in the isolation and purification process.

We selected (S)-Biphen and (R)-Trip ligands from the pool of available chiral chelating diolates (Trip = 3,3'-bis(2,4,6-trisopropylphenyl)-2,2'-binaptholate) for the synthesis of the new alkylimido catalysts. Our choice was dictated by the results of earlier studies, which showed that when these ligands were introduced into the molybdenum imido alkylidene molecules, the resulting catalysts were particularly active and enantioselective in olefin metathesis.

![Chemical structures of Mo-based olefin metathesis catalysts](image)

**Figure 1.** Examples of Mo-based olefin metathesis catalysts bearing chiral diolate ligands.
1.2 Results and Discussion.

1.2.1 Synthesis and characterization of Mo-based alkylimido olefin metathesis catalysts.

1.2.1.a Synthesis and characterization of 1-phenylcyclohexylimido complexes.

The synthetic sequence leading to the Mo(RN)(CHCMe<sub>2</sub>Ph)(DIOLATE*) catalysts (R = PhCyN, PhAdN; DIOLATE* = (S)-Biphen, (R)-Trip) is similar to the established route towards structurally analogous arylimido compounds. 1-Phenylcyclohexylamine, easily prepared in two steps from 1-phenycyclohexanol, is converted into molybdenum diimido dichloride upon treatment with sodium molybdate, triethylamine and trimethysilyl chloride in DME (Scheme 1). At 90 °C the reaction takes 24 hours to complete, yielding the product in a form of 1,2-dimethoxyethane adduct.

![Scheme 1]

Alkylation of this complex in diethyl ether with two equivalents of neophyl Grignard reagent gives the corresponding dialkyl derivative (Scheme 2).

![Scheme 2]
The alkylidene fragment of the catalyst is generated in the next step, when Mo(PhCyN)₂(CH₂CMe₂Ph)₂ is treated with three equivalents of triflic acid in diethyl ether in the presence of ca. 5 vol. % of DME. This interaction results in complete protonation and loss of one of the imido groups followed by α-abstraction of one of the alkyl ligands (Scheme 3).

Scheme 3. Synthesis of Mo(PhCyN)(CH₂CMe₂Ph)(OTf)₂(dme).

The resulting bistriflate complex serves as a general precursor to the final catalysts of general formula Mo(RN)(CHCMe₂Ph)(DIOLATE*). Upon treatment with the enantiomerically pure lithium or potassium diolate, the bistriflate complex is converted into the desired catalyst (Scheme 4).

Scheme 4. Synthesis of Mo(PhCyN)(CHCMe₂Ph)((S)-Biphen] (5a) and Mo(PhCyN)(CHCMe₂Ph)((R)-Trip)(THF) (5b).
An alternative synthetic route to compounds 5a and 5b was attempted, but was found to be unsuccessful. The very first attempt to isolate Mo(PhCyN)(CH₂CMe₂Ph)(OTf)₂(dme) according to the reaction in Scheme 3 yielded a white crystalline compound, which was characterized by ¹H NMR and was believed to be the expected alkylidene bistriflate complex. The isolated compound decomposed quickly, and efforts to purify the product failed. We therefore decided to avoid isolation of Mo(PhCyN)(CH₂CMe₂Ph)(OTf)₂(dme) altogether, instead trapping it in situ with LiOCMe(CF₃)₂. The synthetic protocol for this reaction involved addition of an ethereal solution of LiOCMe(CF₃)₂ to the solution of Mo bisimido dialkyl complex, which had been stirred in the presence of triflic acid for 1 hour at -78 °C and then for 2 hours at room temperature. Mo(PhCyN)(CH₂CMe₂Ph)[OCMe(CF₃)₂]₂ was isolated and used as a precursor for 5a and 5b in salt metathesis reactions identical to the one shown in Scheme 4. Unfortunately, in situ formation of Mo(PhCyN)(CH₂CMe₂Ph)[OCMe(CF₃)₂]₂ turned out to be poorly reproducible, giving the product in very low yields (0 – 40 %). We decided to return to the original synthetic sequence involving isolation of Mo(PhCyN)(CH₂CMe₂Ph)(OTf)₂(dme). Optimization of the reaction time, temperature and the solvents allowed us to consistently obtain clean and thermally stable bistriflate precursor in 45 – 51 % yields.

Catalysts 5a and 5b are isolated as orange and yellow powders, respectively, which are extremely soluble in all common solvents and can be crystallized only from cold concentrated pentane solutions. The resonance of the alkylidene carbon in the ¹³C NMR spectrum of compound 5a appears at 274 ppm with JCH = 121 Hz, which is indicative of the syn conformation of the catalyst. In the ¹H NMR spectrum of compound 5a in C₆D₆ the most downfield resonance appears at 10.7 ppm and corresponds to the chemical shift of the alkylidene proton. Syn orientation of the alkylidene ligand with respect to the imido group positions the C-H bond of the alkylidene moiety trans to the imido group, which allows for α-agostic interaction between the C-H bond and the antibonding orbital of the molybdenum-nitrogen triple bond. This interaction results in a relative upfield shift of the alkylidene proton and carbon resonances and decreases the value of proton-carbon coupling constant in the NMR spectra of the complexes.
Heating a d₈-toluene sample of complex 5a to 100 °C or cooling it to -80 °C does not result in appearance of new peaks in the alkylidene area of the proton NMR spectrum, which makes us believe that the syn isomer is the dominating species in solution in this temperature interval.

Our assessment of the 5a alkylidene group conformation in solution as syn is in accord with the solid-state structure of the molecule, determined by X-ray crystallographic analysis. A thermal ellipsoid plot of the molecule is presented in Figure 2; selected bond lengths and angles are shown in Table 1; crystal data and structure refinement are shown in Table 2.

Figure 2. Thermal ellipsoid plot of complex 5a (50 % probability level, hydrogen atoms omitted for clarity). Crystals of compound 5a were grown form a concentrated pentane solution at -30 °C.
Table 1. Selected bond lengths (Å) and angles (°) of complex 5a.

<table>
<thead>
<tr>
<th>Bond Lengths/Angles</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Mo(1)-N(1)</td>
<td>1.7185(18)</td>
</tr>
<tr>
<td>Mo(1)-C(1)</td>
<td>1.889(2)</td>
</tr>
<tr>
<td>Mo-O(2)</td>
<td>2.0070(15)</td>
</tr>
<tr>
<td>Mo-O(1)</td>
<td>2.0140(16)</td>
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<tr>
<td>C(1)-C(2)</td>
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<td>O(1)-Mo(1)-O(2)</td>
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<tr>
<td>N(1)-Mo(1)-C(1)</td>
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</tr>
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</tr>
<tr>
<td>Mo(1)-O(2)-C(31)</td>
<td>94.26(11)</td>
</tr>
<tr>
<td>Mo(1)-N(1)-C(50)</td>
<td>167.18(15)</td>
</tr>
<tr>
<td>Mo(1)-C(1)-C(2)</td>
<td>144.51(16)</td>
</tr>
<tr>
<td>Mo(1)-(N1)-C(50)</td>
<td>167.18(15)</td>
</tr>
</tbody>
</table>

Structural parameters of the molecule 5a lie within the range of values observed for similar molybdenum complexes and are very close to the data obtained for complex 1a. The Mo-C(1) bond distance and Mo-C(1)-C(2) bond angle (1.889(2) Å and 144.51(16) deg) are comparable with the same bond distance and angle in 1a (1.867(4) Å and 149.3(3) deg). The Mo(1)-N(1) distance (1.7185(18) Å) is somewhat larger than in 1a (1.709(3) Å) and the Mo(1)-(N1)-C(50) angle (167.18(15) deg) is slightly smaller (172.8(3) deg in 1a), which points to lesser amount of electron-donation from the imido function to the metal center than in the 1-adamantylimido analog. Both imido groups exhibit greater electron-donating ability than previously studied similar arylimido systems, which manifests itself in shorter Mo-N bonds.

Complex 5b was synthesized in THF and isolated as a THF adduct. Due to the diastereotopic nature of the two CNO faces of the molecule, which are believed to be the THF binding sites, two isomers can be formed upon THF coordination. However, only one alkylidene resonance is observed in the 1H NMR spectrum of 5b at 14.0 ppm at room temperature in C6D6. The peak corresponding to the alkylidene carbon atom appears in the 13C NMR spectrum at 308 ppm with JCH = 145 Hz. Lower field chemical shift values in the proton and carbon NMR spectra as well as the large value of the coupling constant suggest that the alkylidene ligand in 5b is in anti configuration with respect to the imido group. Heating the toluene-d8 solution of complex
5b to 100 °C does not change the spectrum of the molecule. When the solution is cooled to -80 °C, one can observe resolution of the equilibrium alkylidene peak into two peaks corresponding to the different THF adducts (Figure 3). The alkylidene signal starts broadening at -30 °C, collapses into the baseline at -50 °C, and reemerges as two symmetrical peaks at -60 °C. Addition of 10 equivalents of THF to the sample provides the same variable temperature $^1$H NMR plot, which indicates that the process is not an equilibrium between a THF-free and a THF-bound species. We propose that the two peaks observed in the $^1$H NMR spectra at low temperatures correspond to the two diastereomeric THF adducts. Independence of the observed equilibrium from THF concentration suggests that the ligand exchange happens without THF dissociation, but as a result of a stepwise rearrangement of the ligands in the coordination sphere.

Figure 3. Variable temperature $^1$H NMR spectrum of d$_8$-toluene solution of complex 5b. The low temperature limit of the spectrum shows two peaks corresponding to the diastereomeric THF adducts.
1.2.1 b. Synthesis and characterization of 2-phenyl-2-adamantylimido complexes.

2-Phenyl-2-adamantylimido complexes 6a and 6b are synthesized through the same route as compounds 5a and 5b. The amine is prepared through a high-yielding three step sequence from 2-adamantanone.13 We were surprised to learn that when the reaction between 2-phenyl-2-adamantylamine and sodium molybdate is carried out in 1,2-dimethoxyethane, the resulting diimido dichloride complex does not contain coordinated solvent, unlike all the diimido dichloride compounds synthesized earlier in a similar manner. This reaction provides low yields of Mo(PhAdN)2Cl2 (20 – 40 %) and is not easily reproducible. We believe the inability of DME to coordinate to molybdenum to be due to the presence of two very large imido groups. If the same reaction is carried out in THF, a five-coordinate species with one molecule of the solvent in the coordination sphere is formed in 97 % yield (Scheme 5).

![Scheme 5. Synthesis of Mo(PhAdN)2Cl2 and Mo(PhAdN)2Cl2(THF) complexes.](image)

It is interesting to compare formation of Mo(PhAdN)2Cl2 with the similar synthesis of a Mo imido complex from a very sterically demanding 2,4,6-triphenylaniline. Nielson and coworkers reported in 1996 that the reaction between Na2MoO4 and 2,4,6-Ph3C6H2NH2 in DME under conditions, identical to the conditions employed in the synthesis of Mo(PhAdN)2Cl2, gives
six-coordinate monoimido monooxo Mo complex with one molecule of DME in the coordination sphere (Scheme 6). This result allows us to estimate the relative size of the 2-phenyl-2-adamantylimido group as “somewhere in between” the largest imido group that allows for formation of six-coordinate bisimido complex, such as Mo(2,6-i-Pr₂C₆H₃N)₂Cl₂(dme), and the 2,4,6-(triphenyl)phenylimido group, which is so sterically demanding that it cannot form a solvent-free four-coordinate bisimido complex, but instead yields a monooxo monoimido DME adduct.

\[
\text{Ph} \quad \text{Ph} \quad \text{Ph} \quad \text{NH}_2 \quad \text{Ph} \quad \text{Ph} \\
\text{Ph} \quad \text{Ph} \quad \text{Ph} \quad \text{Cl} \quad \text{O} \quad \text{Cl} \quad \text{O} \quad \text{Cl}
\]

Scheme 6. Synthesis of Mo(2,4,6-Ph₃C₆H₂N)Cl₂(O)(dme).

Alkylation of Mo(PhAdN)₂Cl₂ or Mo(PhAdN)₂Cl₂(THF) with 2.2 equivalents of neophyl Grignard reagent gives the corresponding diimido dialkyl complex. It can be converted into the bistriflate compound Mo(PhAdN)(CHCMe₂Ph)(OTf)₂(dme) upon treatment with three equivalents of triflic acid (the reaction is identical to the one shown in Scheme 3). Catalysts 6a and 6b are synthesized via reactions of Mo(PhAdN)(CHCMe₂Ph)(OTf)₂(dme) with (S)-BiphenK₂ and (R)-TripK₂, respectively. Compounds 6a and 6b as well as the NMR data for their alkylidene proton and carbon atoms are shown in Figure 4.
Values of the chemical shifts and coupling constants of the alkylidene CH fragment show that in solution complex 6a exists predominantly in syn conformation, while compound 6b adopts almost exclusively anti configuration. The $^1$H NMR spectrum of 6a does not change upon cooling the toluene-$_2$ solution of the complex to -80 °C or heating it to 100 °C.

6b presumably exists as a mixture of diastereomeric THF adducts in a way, similar to 5b. Only one alkylidene resonance can be observed by $^1$H NMR spectroscopy when the sample is cooled to -80 °C, suggesting that either the exchange equilibrium between the adducts is fast on NMR time scale, or only one diastereomer is present in toluene-$_2$ solution.

**Figure 4.** Catalysts 6a and 6b. Chemical shifts and coupling constants of the alkylidene proton and carbon atoms in $^1$H and $^{13}$C NMR spectra.
1.2.2 Asymmetric olefin metathesis reactions catalyzed by complexes 1a, 1b and 5a – 6b.

While 1a is the only known alkylimido molybdenum-based alkylidene complex that has been applied to asymmetric olefin metathesis, complex 1b (Figure 5) is the second previously reported chiral 1-adamantylimido compound.\textsuperscript{15} However, 1b has never been studied in olefin metathesis reactions. We decided to include 1b in the library of chiral alkylimido catalysts and screen 1b alongside with the four new catalysts 5a – 6b.

\begin{center}
\includegraphics[width=0.5\textwidth]{figure5.png}
\end{center}

\textbf{Figure 5.} Structure of Mo(AdN)(CHCMe2Ph)[(R)-Trip](THF) (1b).

For the sake of uniformity of the catalytic studies and in order to provide a basis for the catalyst comparison, we used similar reaction conditions (20 mL vials, 5 % catalyst loading, C\textsubscript{6}D\textsubscript{6} as solvent) for all the metathesis reactions discussed below.

1.2.2.a Asymmetric ring-opening metathesis/cross metathesis.

It has been shown that complex 1a exhibits a unique profile of reactivity and selectivity when applied to certain classes of olefin metathesis substrates.\textsuperscript{11} Research in our laboratories
indicates that one of the reactions, in which 1a is a significantly better catalyst than the arylimido catalysts, is a tandem asymmetric ring-opening metathesis/cross metathesis of norbornene derivatives with monosubstituted olefins. Therefore we chose to examine a previously studied AROM/CM reaction of syn-7-(benzyloxy)bicyclo[2.2.1]hept-2-ene (7) with styrene as a model process for the screening of the new catalysts 1b, 5a – 6b, and compare their performance with the results obtained for 1a.

Compound 7 was synthesized according to the sequence shown in Scheme 7. This synthesis differs from the originally reported procedure, but affords the product that is spectroscopically identical to the previously reported compound.

![Scheme 7](image)

**Scheme 7.** Synthesis of syn-7-norbornenyl ether 7.

Reaction between 7 and 1 equivalent of styrene and the results of the catalyst screenings are shown in Figure 6.
The AROM/CM reaction shown in Figure 6 gives rise to two major products. Compound 8 is the desired chiral product, and achiral compound 9 is formed when 8 undergoes cross-metathesis with one more equivalent of styrene. Data presented in Figure 6 show that catalysts 1a and 5a efficiently convert 7 into the AROM/CM products; however, the yields of the desired product 8 are quite low and significant amounts of compound 9 are isolated despite the fact that only one equivalent of styrene is introduced into the reaction mixture. This phenomenon can be explained by high activity of the catalysts, which impairs their selectivity in the reaction by allowing the catalysts to take part in an additional cross metathesis step instead of ring-opening a strained and reactive molecule of 7. AROM/CM reactions in entries 1 and 2 proceed with moderate enantioselectivities. Complexes 1b, 5b and 6b provide much better 8:9 product ratios and relatively high enantiomeric excesses for the desired product 8. It is important to note that catalysts 5b and 6b need to be thermally activated in order to reach indicated product yields. We propose that the thermal activation is necessary for the formation of coordination vacancy at the molybdenum center, which happens upon THF dissociation at higher temperatures. Catalyst 6a does not produce any of the AROM/CM products, but instead exclusively ring-opening
polymerizes substrate 7. At the moment we cannot explain such drastic difference in the reactivity pattern between 6a and the rest of the examined catalysts despite their structural similarities.

1.2.2.b Asymmetric ring-closing metathesis.

As part of our collaboration focused on development of new catalysts and their applications, Professor Amir Hoveyda and his colleagues at Boston College are interested in introduction of asymmetric olefin metathesis reactions into the syntheses of complex natural products. Among the targets that were recently approached by the Hoveyda group are secu’amamine A and (-)-quebrachamine. One of the sequences proposed for the synthesis of (-)-quebrachamine involved asymmetric ring-closing metathesis of a triolefinic amide precursor (Figure 7). Studies of model substrates for this transformation allowed the development of a protocol for enantioselective synthesis of cyclic amides and amines through Mo-catalyzed ring-closing metathesis. Some of the compounds studied in this project proved to be quite challenging for ARCM reactions using available arylimido catalysts and complex 1a. Results of the initial screening of ring-closing metathesis reaction with substrates 10 – 13 performed by Dr. Elizabeth Sattely are shown in Figure 7 (optimized conditions are shown in red). One can notice generally low conversions in ARCM reactions of 10 – 13, but it is important to note that substrates 10, 12, and 13 gave predominantly the expected ring-closed product, and the low conversions indicate large amounts of unreacted starting materials. Substrate 11, on the other hand, is entirely consumed in the presence of a variety of Mo-based catalysts, but the major product of these transformations is a dimer, formed as a result of cross-metathesis of two molecules of 11 through the 5-pentene olefinic arm on the lactam ring. The only catalyst that afforded product 15 in a significant yield was complex 4a, requiring unusually high 15 % catalyst loading.
Figure 7. (-)-Quebrachamine and secu’amamine A. ARCM of compounds 10 – 13 using arylimido-based catalysts 2a – 4a and 1a. Results of the optimized catalytic reactions are shown in red.
We decided to investigate ARCM of some of these substrates using compounds 1a, 1b, 5a – 6b as catalysts and determine relative activity and selectivity levels of the new complexes. All the metathesis reactions were carried out in 20 mL vials equipped with stir bars and teflon-lined caps. The ratio of the solution volume to the total volume of the reaction vessel was 1:10, and the solutions were vigorously stirred to ensure the escape of forming ethylene.

Data in Figure 8 show, that although lactams 10 and 11 are structurally similar compounds, they exhibit very different reactivity profiles under the conditions of ARCM reaction. Compound 10 can be efficiently metathesized at room temperature by the catalysts that contain (S)-Biphen diolate (1a, 5a and 6a). Complex 5a provides full conversion at room temperature in 20 hours, while reactions carried in the presence of 1a and 6a need longer times to give satisfactory conversions. The three catalysts yield product 14 with similar moderate enantioselectivities. Catalysts 5b and 6b give no conversion of the starting material 10 into ARCM products even if the reaction mixture is heated to 65 °C for 20 hours. The reaction carried
out in the presence of complex 1b upon heating to 65 °C for two days quantitatively affords product 14 in 97 % ee. This makes 1b the catalyst of choice for ARCM of substrate 10.

ARCM of compound 11, on the other hand, turns out to be a challenging task. Catalysts 1a and 5a are the only complexes that provide 15 in significant yields with excellent enantioselectivities. It is worth noting that catalyst 6a, being structurally similar to 1a and 5a, exhibits drastically diminished reactivity towards substrate 11. We presume that the reason for the decreased reactivity is the large size of the 2-phenyl-2-adamantylimido ligand, which sterically hinders the molybdenum atom and prevents an olefin from efficiently binding to the metal center and/or slows down the ligand rearrangement process that is necessary for the cycloreversion step of the catalytic cycle. The rest of the catalysts give moderate or low yields of the desired product, predominantly converting 11 into a dimer formed via cross metathesis of the 1-pentene fragment of the molecule. These results are not too surprising, since formation of the corresponding dimer instead of the bicyclic compound 15 has been observed in the initial screening of the ARMC of 11 employing arylimido complexes.\textsuperscript{18} We expected that higher temperatures might improve the yield of the desired product, since ring-closing metathesis reaction is entropically favored over cross metathesis. However, when reactions in entries 4 – 6 were conducted at room temperature and at 70 °C, similar conversions were observed. These experiments proved that the yield of 15 does not depend on the temperature of the reaction mixture.

The results of the last set of ARCM reactions catalyzed by 1a, 1b and 5a – 6b are shown in Figure 9. Amines 12 and 13 differ only in the nature of the protecting group on the nitrogen atom. It is worth noting that the corresponding unprotected amine is completely inert towards ARCM reactions.

In the case of substrate 12, the catalysts in entries 1 – 3 afford heterocycle 16 in high yields and excellent enantiomeric excesses. Similarly to the instances discussed above, 6a exhibits relatively low reactivity compared to analogous catalysts 1a and 5a. Complexes 1b and 5b require thermal activation to provide conversion of 12 into 16. However, even if heated to 70 °C for 48
hours, these catalysts give only moderate yields of the metathesis product. Catalyst 6b proves to be completely inactive towards ARCM of compound 12.

![Chemical Structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst a</th>
<th>Time, h</th>
<th>T, °C</th>
<th>Yield, % 16</th>
<th>ee, % 16</th>
<th>Yield, % 17</th>
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<td>48</td>
<td>70</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Entry a Catalyst loading 5 %, C6D6, b Yield determined by 1H NMR

**Figure 9.** ARCM of substrates 9 and 10 using catalysts 1a – 3b.

Heterocycle 17 can be synthesized more readily than compound 16 using catalysts 1a, 1b and 5a – 6b, as shown in Figure 9. Complexes 1a and 5a provide 17 in good yields and with high enantiomeric excesses. Catalysts 6a, 1b and 6b, even when heated, show lower conversions and only moderate enantioselectivities. When the reaction is carried out at 80 °C in the presence of catalyst 5b, 15% conversion can be achieved over the course of 36 hours. The rest of the starting material stays intact and can be recovered from the reaction mixture upon workup.

**1.3 Conclusions.**

Synthesis and structural investigations of four chiral molybdenum alkylimido alkylidene complexes are described above. Compounds 5a, 5b, 6a and 6b were prepared in four steps from the corresponding amines. Crystallographic determination of the solid state structure of 5a
showed that the bond lengths and bond angles in this molecule lie within the range previously observed for 1-adamantylimido alkylidene complex 1a and analogous arylimido species.

Complexes 1b and 5a – 6b were compared to the only previously known alkylimido catalyst 1a in ring-closing and ring-opening/cross metathesis reactions of a variety of amides and a protected norborneol 7. Complex 5a provides equal or superior to 1a reactivity and enantioselectivity in all the studied reactions. Catalysts containing binaphtholate-derived (R)-Trip ligand (1b, 5b and 6b) are generally less reactive, but upon heating afford products in varying yields and enantioselectivities. Complexes, bearing 2-phenyl-2-adamantylimido groups (6a and 6b), exhibit diminished reactivity most likely due to the large size of the imido substituent, which hinders the Mo center for olefin coordination.

1.4 Experimental Details.

General. All reactions were conducted in oven-dried (135 °C) and flame-dried glassware under an inert atmosphere of dry nitrogen employing standard Schlenk and glovebox techniques. Toluene, diethyl ether, and THF were degassed and then passed through a column of activated alumina. DME was distilled off sodium/benzophenone under nitrogen atmosphere. n-Pentane was washed with H2SO4 and water, dried over CaCl2, degassed, and then passed through a column of activated alumina. Deuturated benzene and toluene were dried over CaH2, degassed and filtered.

1-Phenylcyclohexylamine (PhCyNH2),12 2-phenyl-2-adamantylamine (PhAdNH2),13 catalysts 1a and 1b,15 substrates 7,17 10 – 1318 and diolates (S)-BiphenK219 and (R)-TripK220 were prepared according to literature procedures. Products of the olefin metathesis reactions 8, 9, 14 – 17 were isolated, purified and analyzed according to published procedures.16,18

1H and 13C NMR spectra were recorded on Varian spectrometers. Chemical shifts in 1H and 13C NMR spectra are reported in ppm from tetramethylsilane with the solvent as an internal standard. Elemental analyses were performed by H. Kolbe Microanalytisches Laboratorium, Mülheim an der Ruhr, Germany. Enantiomeric ratios were determined using chiral GC
Mo(PhCyN)\(_2\)Cl\(_2\)(dme). PhCyNH\(_2\) (20.0 g, 0.11 mol), Na\(_2\)MoO\(_4\) (11.3 g, 0.06 mol), Et\(_3\)N (38 mL, 0.27 mol), and trimethylsilyl chloride (76 mL, 0.6 mol) were dissolved in 300 mL of dry DME. Upon stirring at 90 °C for 18 hours the mixture became bright yellow. The solids were filtered off and the solvent was removed from the filtrate in vacuo to give a yellow powder. The powder was triturated with 100 mL of pentane, filtered off, and dried in vacuo. Yield 30.8 g (0.05 mol, 85 %): \(^1\)H NMR (C\(_6\)D\(_6\)): \(\delta\) 7.58 (d, \(J_{HH} = 7.5\) Hz, 4H), 7.28 (t, \(J_{HH} = 7.5\) Hz, 4H), 7.11 (t, \(J_{HH} = 7.5\) Hz, 2H), 3.34 (s, 6H), 3.19 (s, 4H), 2.21 (m, 4H), 2.07 (m, 4H), 1.85 (m, 4H), 1.58 (br s, 2H), 1.37 (m, 4H), 1.14 (m, 2H). Anal. Calcd. for C\(_{28}\)H\(_{40}\)MoO\(_2\)Cl\(_2\)N\(_2\): C, 55.73; H, 6.68; N, 4.64; Cl, 11.75. Found: C, 55.61; H, 6.64; N, 4.63; Cl, 11.80.

Mo(PhCyN)\(_2\)(CH\(_2\)CMe\(_2\)Ph). A suspension of Mo(PhCyN)\(_2\)Cl\(_2\)(dme) (9.5 g, 0.15 mol) in 100 mL of diethyl ether was cooled to -78 °C. A solution of (PhCMe\(_2\)CH\(_2\))MgCl (0.31 mol) in 50 mL of ether was added dropwise to the reaction mixture. The mixture was stirred at -78 °C for 3 hours, then allowed to warm up to room temperature and was stirred for 12 hours. The solvent was removed in vacuo and the solid residue was redissolved in 50 mL of toluene. After addition of 4 mL of 1,4-dioxane the mixture was stirred for 1 hour and the white precipitate was removed by filtration. The solvents were removed in vacuo and the solid was triturated with pentane overnight. The product was filtered off and the pentane washes were reduced to 10 mL and left at -35 °C for 12 hours. The crystallized material was collected and combined with the solid obtained from trituration to give 9.2 g of a bright yellow crystalline product (0.013 mol, 81 %). \(^1\)H NMR (C\(_6\)D\(_6\)): \(\delta\) 7.34-7.29 (m, 8H), 7.22-7.17 (m, 8H), 7.11-7.05 (m, 4H), 1.85 (m, 12H), 1.76 (s, 4H), 1.52 (m, 4H), 1.42 (s, 12H), 1.22 (m, 4H). Anal. Calcd. for C\(_{44}\)H\(_{56}\)MoN\(_2\): C, 74.55; H, 7.96; N, 3.95. Found: C, 74.46; H, 7.94; N, 3.87.
Mo(PhCyN)(CHCMe2Ph)(OTf)2(dme). Mo(NCyPh)2(CH2CMe2Ph)2 (5.2 g, 7.3 mmol) was dissolved in 200 mL of ether and 5 mL of DME was added. The mixture was cooled to -78 °C and a solution of TfOH (3.3 g, 21.9 mmol) in 15 mL of ether was added to it slowly. The mixture was stirred at -78 °C for 1 hour, then warmed to room temperature and stirred for 2 hours. Solvents were removed and the resulting brown oil was dissolved in 15 mL of toluene. Addition of 5 mL of pentane caused formation of precipitate. The precipitate was filtered off and the solvents were reduced to 1 mL in vacuo. 5 mL of ether was layered on top of the resulting solution and the mixture was left at -30 °C overnight. White crystalline material was filtered off. Two more crops were collected in a similar manner to give 2.9 g of white crystals (3.7 mmol, 51%). 1H NMR (C6D6): δ 13.96 (s, 1H), 7.57 (d, 2H, JHH = 8.5 Hz), 7.51 (d, 2H, JHH = 8.5 Hz), 7.28 – 7.00 (m, 6H), 3.32 (s, 4H), 2.68 (m, 2H), 2.46 (s, 6H), 2.12 (m, 2H), 1.84 (s, 6H), 1.59 – 1.14 (m, 6H). Anal. Calcd. for C28H37F6MoS2NO8: C, 42.59; H, 4.72; N, 1.77. Found: C, 42.68; H, 4.79; N, 1.77.

Mo(PhCyN)(CHCMe2Ph)[(S)-Biphen] 5a. (S)-BiphenH2 (99.3 mg, 0.28 mmol) was dissolved in 10 mL of THF and cooled to -35 °C. Benzyl potassium (74.2 mg, 0.57 mmol) was added to this solution and the resulting mixture was stirred for 1 hour. The mixture was added to a solution of Mo(PhCyN)(CHCMe2Ph)(OTf)2(dme) (240 mg, 0.28 mmol) in 20 mL of ether, precooled to -35 °C, and left to stir for 5 hours. The solvent was removed in vacuo and the resulting solid was extracted with 50 mL of pentane. The white precipitate was filtered off and the resulting yellow-orange solution was dried to give orange powder (180 mg, 0.22 mmol, 79%). 1H NMR (C6D6): δ 10.95 (s, 1H), 7.41 (m, 1H), 7.39 (m, 2H), 7.37 (m, 2H), 7.22-7.19 (m, 2H), 7.13 (br s, 1H), 7.08-7.04 (m, 1H), 7.00-6.95 (m, 3H), 2.27 (m, 1H), 2.18 (m, 1H), 2.09 (s, 3H), 2.07 (s, 3H), 1.75 (s, 3H), 1.71 (s, 3H), 1.68 (s, 3H), 1.62 (m, 2H), 1.59 (s, 9H), 1.55-1.49 (m, 4H), 1.45 (s, 9H), 1.16 (s, 3H), 1.03 (m, 2H). 13C NMR (C6D6): δ 273.6 (d, JCH = 119.8 Hz). Anal. Calcd. for C46H59MoNO2: C, 73.28; H, 7.89; N, 1.86. Found: C, 73.20; H, 8.05; N, 1.84.
**Mo(PhCyN)(CHCMe2Ph)(R-Trip)(THF) 5b.** (R)-TripK₂ (214 mg, 0.25 mmol) was dissolved in 10 mL of THF and cooled to -35 °C. The solution was added to a cold solution of Mo(PhCyN)(CHCMe2Ph)(OTf)₂(dme) (200 mg, 0.25 mmol) in 15 mL of THF and the resulting mixture was left to stir for 5 hours. The solvent was removed *in vacuo* and the solid was extracted with 50 mL of pentane. The white precipitate was filtered off and the resulting yellow solution was dried to give yellow powder (294 mg, 0.24 mmol, 99 %). \(^1\)H NMR (C₆D₆): δ 14.02 (s, 1H), 7.73 (s, 1H), 7.71-7.61 (m, 3H), 7.58 (s, 1H), 7.49 (m, 1H), 7.46 (s, 1H), 7.37 (m, 1H), 7.24-7.17 (m, 3H), 7.13 (br s, 1H), 7.12-6.58 (m, 13H), 3.53 (m, 2H), 3.25 (septet, J₃H₅ = 7 Hz, 1H), 3.07 (septet, J₃H₅ = 7 Hz, 1H), 2.95 (septet, J₃H₅ = 7 Hz, 1H), 2.78 (septet, J₃H₅ = 7 Hz, 1H), 2.56 (br d, J₃H₅ = 8 Hz, 1H), 2.32 (br d, J₃H₅ = 8 Hz), 2.14 (br s, 4H), 1.85 (d, J₃H₅ = 6.6 Hz, 6H), 1.77 (s, 3H), 1.64 (br s, 1H), 1.51 (d, J₃H₅ = 6.6 Hz, 6H), 1.42 (d, J₃H₅ = 6.9 Hz, 6H), 1.37 (d, J₃H₅ = 6.9 Hz, 12H), 1.34-1.20 (m, 3H), 1.24 (s, 3H), 1.17 (d, J₃H₅ = 6.9 Hz, 6H), 1.08-1.04 (m, 4H), 0.69 (br s, 4H). \(^1³\)C NMR (C₆D₆): δ 308.6 (d, J₃C₃ = 145 Hz). Anal. Calcd. for C₇₇H₉₃MoNO₃: C, 78.61; H, 7.97; N, 1.19. Found: C, 78.47; H, 8.09; N, 1.14.

**Mo(PhAdN)₂Cl₂.** PhAdNH₂ (5.0 g, 0.22 mol) was dissolved in 150 mL of DME and Na₂MoO₄ (2.3 g, 0.011 mol), Et₃N (6.1 mL, 0.044 mol) and TMSCl (13.9 mL, 0.11 mol) were added. The mixture was stirred at 60 °C for 18 hours, then the solids were filtered off and the solvent was removed to give yellow oil. Treatment of the oil with pentane gave white powder, which was filtered off and the resulting yellow solution was reduced to 20 mL and cooled to –30 °C. Yellow solid was filtered off 48 hours later (3.0 g, 0.05 mol, 44 %). \(^1\)H NMR (C₆D₆): δ 7.44 (d, 2H, J₃H₅ = 7.5 Hz), 7.25 (t, 2H, J₃H₅ = 8 Hz), 7.13 (t, 1H, J₃H₅ = 8 Hz), 2.66 (s, 2H), 2.61 (d, 2H, J₃H₅ = 13 Hz), 1.89 (s, 1H), 1.71 (d, 2H, J₃H₅ = 12.5 Hz), 1.63-1.54 (m, 7H). Anal. Calcd. for C₃₂H₃₈Cl₂MoN₂: C, 62.24; H, 6.20; N, 4.54. Found: C, 62.14; H, 6.16; N, 4.38.

**Mo(PhAdN)₂Cl₂(THF).** PhAdNH₂ (3.16 g, 0.14 mol) was dissolved in 100 mL of THF and Na₂MoO₄ (1.4 g, 0.07 mol), Et₃N (3.9 mL, 0.28 mol) and trimethylsilyl chloride (8.8 mL,
0.69 mol) were added. The mixture was stirred at 85 °C for 48 hours, then the solids were filtered off and the solvent was removed to give yellow solid. The solid was triturated with pentane to give pale yellow powder (4.6 g, 0.07 mmol, 97 %). $^1$H NMR (C$_6$D$_6$): $\delta$ 7.40 (br s, 4H), 7.30 (br s, 6H), 3.80 (s, 4H), 2.86 (s, 4H), 1.99 (s, 2H), 1.68-1.57 (m, 18H), 1.32 (s, 4H). Anal. Calcd. for C$_{36}$H$_{46}$Cl$_2$MoN$_2$O: C, 62.70; H, 6.72; N, 4.06; Cl, 10.28. Found: C, 62.86; H, 6.65; N, 4.14; Cl, 10.34.

Mo(PhAdN)$_2$(CH$_2$CMe$_2$Ph)$_2$.

A. Mo(PhAdN)$_2$Cl$_2$ (3.0 g, 4.8 mmol) was dissolved in 100 mL of ether and cooled to -78 °C. Solution of PhMe$_2$CCH$_2$MgCl in ether (10.2 mmol) was added dropwise to the reaction mixture. The mixture was stirred at -78 °C for 30 min, then warmed to room temperature and stirred overnight. The solution was diluted with 10 mL of 1,4-dioxane and stirred for 1 hour. The solids were filtered and the solvents were removed to give brown oil. It was dissolved in 10 mL of pentane, cooled to -30 °C and two crops of bright yellow crystals were collected (1.7 g, 2.0 mmol, 42%). $^1$H NMR (C$_6$D$_6$): $\delta$ 7.44 (d, $J_{HH} = 7.5$ Hz, 4H), 7.33 (t, $J_{HH} = 7.5$ Hz, 4H), 7.24 (m, 8H), 7.10 (m, 4H), 2.62 (s, 4H), 2.48 (d, 2H, $J_{HH} = 12$ Hz), 1.82 (d, 4H, $J_{HH} = 12$ Hz), 1.78 (s, 2H), 1.66-1.58 (m, 22H), 1.26 (s, 12H). Anal. Calcd for C$_{52}$H$_{64}$N$_2$Mo: C, 76.82; H, 7.93; N, 3.45. Found: C, 76.88; H, 8.02; N, 3.54.

B. Mo(PhAdN)$_2$Cl$_2$(THF) (4.4 g, 6.4 mmol) was dissolved in 50 mL of ether and cooled to -78 °C. Solution of PhMe$_2$CCH$_2$MgCl (11.8 mmol) in ether was added dropwise to the reaction mixture. The mixture was stirred at -78 °C for 30 min, then warmed to room temperature and stirred overnight. The solvents were removed in vacuo and the resulting solid was extracted with toluene. The white precipitate was filtered off and toluene was removed to give yellow solid. The solid was triturated with pentane, filtered and dried and the filtrate was reduced to 5 mL, cooled to -30 °C and left overnight. A crop of yellow solid was collected and combined with the triturated powder to give 2.7 g of the product (3.3 mmol, 52 %). The spectral data and
elemental analysis results of this material match the data obtained for the product synthesized via method A.

Mo(NPhAd)(CHCMe₂Ph)(OTf)₂(dme). Mo(PhAdN)₂(CH₂CMe₂Ph)₂ (1.0 g, 1.2 mmol) was dissolved in 50 mL of ether and 2 mL of DME was added. The mixture was cooled to -35 °C and a cold solution of freshly distilled TfOH (0.56 g, 3.7 mmol) in 10 mL of ether was added to it slowly. The mixture was stirred for 5 hours, then the solvents were removed and the resulting brown oil was extracted with toluene. The solids were filtered off and the toluene solution was reduced to 5 mL and cooled. White solid was filtered after 48 hours (461 mg, 0.55 mmol, 54 %).

1H NMR (C₆D₆): δ 15.65 (s, 0.6 H), 14.89 (s, 0.4H), 14.11 (s, 1H), 7.54 (d, 2H, J₉H = 7 Hz), 7.47-7.18 (m, 8H), 7.14-6.88 (m, 12H), 3.32 (s, 4H), 3.12 (s, 3.6H), 3.31-2.34 (m, 10H), 2.28 (s, 6H), 2.20-1.96 (m, 4H), 1.86 (s, 6H), 1.82-1.22 (m, 24H), 1.64 (s, 2.4 H). Anal. Calcd for C₃₂H₄₁F₆MoNO₈S₂: C, 45.66; H, 4.91; N, 1.66. Found: C, 45.32; H, 5.02; N, 1.78.

Mo(PhAdN)(CHCMe₂Ph)(S)-Biphen 6a. (S)-BiphenK₂ (136 mg, 0.31 mmol) was dissolved in 10 mL of ether and cooled to -35 °C. The solution was added to a solution of Mo(PhAdN)(CHCMe₂Ph)(OTf)₂(dme) (266 mg, 0.31 mmol) in 20 ml of ether, precooled to -35 °C, and left to stir for 10 hours. The solvent was removed in vacuo and the resulting solid was extracted with 50 ml of pentane. The white precipitate was filtered off and the resulting orange solution was dried to give orange powder (210 mg, 0.26 mmol, 84 %). 1H NMR (C₆D₆): δ 10.72 (s, 1H), 7.49 (d, J₉H = 7.2 Hz, 1H), 7.32 (d, J₉H = 7.2 Hz, 1H), 7.26 (s, 1H), 7.23-6.98 (m, 8H), 2.89 (br s, 1H), 2.54 (br s, 1H), 2.46 (br s, 1H), 2.22 (br s, 1H), 2.16 (s, 1H), 2.09 (s, 3H), 2.08 (s, 1H), 1.88 (br s, 1H), 1.85 (br s, 1H), 1.82 (br s, 1H), 1.79 (br s, 1H), 1.77 (s, 3H), 1.75 (s, 1H), 1.70 (s, 1H), 1.62 (s, 6H), 1.59 (s, 6H), 1.53 (s, 18H), 1.33 (s, 1H), 1.26 (s, 1H). 13C NMR (C₆D₆): δ 274.0 (d, J₉CH = 121.0 Hz). Anal. Calcd. for C₅₀H₆₃MoNO₂: C, 74.51; H, 7.88; N, 1.74. Found: C, 74.38; H, 8.08; N, 1.79.

Mo(PhAdN)(CHCMe₂Ph)(R)-Trip](THF) 6b. (R)-TripK₂ (181 mg, 0.23 mmol) was dissolved in 10 mL of THF and cooled to -35 °C. The solution was added to a solution of
Mo(PhAdN)(CHCMe2Ph)(OTf)2(dme) (198 mg, 0.23 mmol) in 10 ml of THF, pre-cooled to -35 °C, and left to stir for 10 hours. The solvent was removed in vacuo and the resulting solid was extracted with 50 ml of pentane. The white precipitate was filtered off and the resulting orange solution was dried to give orange powder (261 mg, 0.22 mmol, 98 %). $^1$H NMR (C$_6$D$_6$): $\delta$ 14.06 (s, 1H), 7.70 (s, 1H), 7.69-7.62 (m, 4H), 7.59 (s, 1H), 7.52-7.37(m, 5H), 7.34-7.18 (m, 7H), 7.15-6.76 (m, 6H), 5.34 (br s, 4H), 3.66 (septet, $J_{HH} = 7$ Hz, 1H), 3.52(septet, $J_{HH} = 7$ Hz, 1H), 3.07 (m, 2H), 2.84 (m, 2H), 2.60 (s, 1H), 2.33-2.16 (m, 2H), 2.03 (m, 1H), 1.79 (br m, 4H), 1.46 (m, 4H), 1.32-1.21 (m, 30H), 1.16 (d, $J_{HH} = 7$ Hz, 6H), 1.12 (d, $J_{HH} = 7$ Hz, 6H), 1.03 (m, 2H), 0.69 (br s, 4H). $^{13}$C NMR (C$_6$D$_6$): $\delta$ 310.4 (d, $J_{CH} = 145.0$ Hz). Anal. Calcd. for C$_{81}$H$_{97}$MoNO$_3$: C, 79.19; H, 7.96; N, 1.14. Found: C, 79.26; H, 8.09; N, 1.18.

**A representative procedure for AROM/CM.** Styrene (19.0 mg, 0.18 mmol) and compound 7 (36.6 mg, 0.18 mmol) were dissolved in 1 mL of C$_6$D$_6$ in a 20 mL vial and 0.36 mL of 0.026 M solution of catalyst 5a in C$_6$D$_6$ (7.2 mg, 9.5x10$^{-3}$ mmol) was added to the solution. The reaction mixture was stirred in a nitrogen filled glovebox at room temperature for 40 hours, then reduced to 0.5 ml and separated on a silica gel column using a mixture of hexanes and ether (10:1) as an eluent to give products 8 (20.6 mg, 0.068 mmol, 36 %) and 9 (14.7 mg, 0.038 mmol, 42 %) as colorless oils. The spectral data for the products match the published results.$^{16}$

**A representative procedure for ARCM.** In a nitrogen filled glovebox lactam 10 (67.3 mg, 0.26 mmol) was dissolved in 1 mL of C$_6$D$_6$ in a 20 mL vial and 0.74 mL of 0.017 M solution of catalyst 1b in C$_6$D$_6$ (14.8 mg, 12.9x10$^{-3}$ mmol) was added to the mixture. The vial was sealed and taken out of the glovebox. The mixture was stirred at 65 °C for 48 hours, and then the solution was reduced to 0.5 mL and separated on a silica gel column using ether as an eluent to give 52.0 mg of 14 as a colorless oil (0.25 mmol, 97 %). The spectral data for the product match the published results.$^{18}$
Table 2. Crystal data and structure refinement for complex 5a.

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1.5 References.


Chapter 2

Synthesis of Molybdenum Imido Alkyl and Alkylidene Complexes from Molybdenum Imido Tetrachlorides.

*A portion of this work has appeared in print:

2.1 Introduction.

Immobilization of homogeneous catalysts on solid supports facilitates catalyst separation from reaction mixtures and their recycling. In addition to this practical merit, some reports have demonstrated that immobilization of a catalyst can also affect aspects of the catalyst performance such as activity, stability, and selectivity.\textsuperscript{1,2,3,4,5} There are several examples of Ru- and Mo-based heterogeneous olefin metathesis catalysts grafted on polystyrene and polynorbornene supports in literature.\textsuperscript{6,7,8,9} We were interested in expanding the scope of solid-supported Mo-based olefin metathesis catalysts by immobilizing molybdenum alkylidene complexes on silica surfaces. It can potentially be accomplished in a way similar to the previously reported procedures for preparation of silica-supported Re alkylidene compounds. Drs. Christophe Copéret and Jean-Marie Basset at Laboratoire de Chimie Organométallique de Surface (Lyon School of Chemistry, Physics and Electronics) showed that a Re dialkyl alkylidene alkylidyne complex, Re(C-t-Bu)(CH-t-Bu)(CH2-t-Bu)\textsubscript{2}, can be immobilized on silica particles by substitution of one of the alkyl ligands with a siloxy group of the silica (Scheme 8). The resulting heterogeneous catalysts exhibited catalytic activity that surpasses the results obtained with both homogeneous Re alkylidene compounds and ill-defined heterogeneous Re-based olefin metathesis catalysts.\textsuperscript{10,11,12}

![Scheme 8. Immobilization of Re(C-t-Bu)(CH-t-Bu)(CH2-t-Bu)\textsubscript{2} on a partially dehydroxylated silica surface.](image)

Encouraged by these results, we decided to investigate a possibility of preparing Mo and W alkyl alkylidene complexes analogous to Re(C-t-Bu)(CH-t-Bu)(CH2-t-Bu)\textsubscript{2} and investigate...
their reactivity towards alcohols and, potentially, silica.

Dr. Amritanshu Sinha synthesized Mo(NAr)(CH-t-Bu)Np₂ (Np = CH₂-t-Bu) (18) by alkylation of the corresponding Mo imido alkylidene bistriflate complex, Mo(NAr)(CH-t-Bu)(OTf)₂(dme) (Ar = 2,6-i-Pr₂C₆H₃).₁³ Dr. Sinha also showed that upon exposure to relatively basic alcohols 18 undergoes a protonolysis reaction yielding Mo imido alkylidene alkyl alkoxide species 19 (Scheme 9). It is important to note that even in the presence of excess ROH 19 is formed exclusively. This result suggests that the second alkyl ligand in 19 is relatively inert towards protonolysis.

\[
\begin{align*}
\text{Scheme 9. Synthesis of compound 18. Protonolysis of 18 with a variety of alcohols produces Mo imido alkylidene alkyl alkoxide complexes 19 (Ad = 1-adamantyl).}
\end{align*}
\]

Complexes 19 were shown to be fast and efficient catalysts in ring-closing metathesis reactions (RCM) of several olefinic ethers and amines.₁⁴ This observation, together with the emerging applications of Mo(NAr)(CH-t-Bu)Np₂ to the synthesis of silica-supported catalysts, encouraged us to investigate alternative methods for preparation of the complexes of type 19.
The tungsten analog of 18, W(NAr)(CH-t-Bu)Np₂, can be prepared in a 4 step sequence from W(NAr)Cl₄(Et₂O). We proposed that a potentially more direct route to Mo(NR)(CH-t-Bu)Np₂ complexes would involve a synthesis patterned after that for the W analogs, i.e., addition of neopentyl groups to Mo(NR)Cl₄(THF) complexes. W(NAr)Cl₄(Et₂O), the starting material for the reported synthetic sequence, is formed upon treatment of W(O)Cl₄ with aryl isocyanate. This reaction is not viable for molybdenum compounds, since in the case of W(O)Cl₄ the transformation requires prolonged heating, while the corresponding starting material for the synthesis of Mo complexes, Mo(O)Cl₄, is thermally unstable.

The proposed new route to Mo(NR)Cl₄(THF) complexes involved 2-electron oxidation of MoCl₄(THF)₂ with organic azides. A reaction of metal complexes with azides is a well-established way to introduce imido ligands into inorganic compounds. Examples of imido complexes synthesized in this manner are known for Zr, V, Ta, W, Mn, Re, Fe, Co, Ni and U. Several Mo(NR)Cl₄(THF) complexes synthesized from arylazides have appeared in the literature. The first, Mo(N-p-tolyl)Cl₄(THF), was published in 1984 by Maatta. It was prepared in high yield by adding p-tolylazide to MoCl₄(THF)₂ and was crystallographically characterized. A dimeric version in which two imido nitrogens are linked with a p-phenylene group, (THF)Cl₄Mo=N-p-C₆H₄-N=MoCl₄(THF), was synthesized in an analogous manner. Mo(NCH₂CH=CH₂)Cl₄(THF) was prepared in situ from allylazide and MoCl₄(THF)₂; it was not isolated or characterized, but converted directly into a Mo(V) bisphosphine derivative. All published imido tetrachlorides are reduced readily by phosphines to yield Mo(V) species, e.g., Mo(NAllyl)Cl₃(PPh₃)₂.

The mechanism of the 2-electron oxidation reaction between metal complexes and azides was studied independently by Cummins and Bergman. Cummins and coworkers showed that the reaction between MesN₃ and V(I)(NRArF)₂ (Mes = 2,4,6-Me₃C₆H₂, R = C(CD₃)₂CH₃, ArF = 2,5-FMeC₆H₃) at -100 °C yields a “diazenylimido” species, V(N₃Mes)(I)(NRArF)₂. V(N₃Mes)(I)(NRArF)₂ decomposes bimolecularly upon mild heating to give N₂ and the expected imido complex V(NMes)(I)(NRArF)₂. This observation is in contrast to the report by Bergman.
and coworkers, who explored decomposition of a tantalum organoazido complex \( \text{Cp}_2\text{Ta}(\text{N}_3\text{Ph})(\text{CH}_3) \).\(^{19}\) \( \text{Cp}_2\text{Ta}(\text{N}_3\text{Ph})(\text{CH}_3) \) was shown to decompose unimolecularly to give the corresponding imido species. The likely mechanism of this reaction, involving a cyclic intermediate, was established through kinetic experiments and labeling studies (Scheme 10).

![Scheme 10](image)

**Scheme 10.** Mechanism of \( \text{Cp}_2\text{Ta}(\text{NPh})(\text{CH}_3) \) formation from \( \text{Cp}_2\text{Ta}(\text{N}_3\text{Ph})(\text{CH}_3) \).

We decided to further explore the reactivity of \( \text{MoCl}_4(\text{THF})_2 \) towards aromatic and aliphatic azides, and to approach the synthesis of \( \text{Mo(NR)(CH-t-Bu)(CH}_2\text{-t-Bu)}_2 \) complexes through alkylation of \( \text{Mo(NR)Cl}_4(\text{THF})_2 \) compounds.

### 2.2 Results and Discussion.

#### 2.2.1 Synthesis of Mo imido complexes with achiral imido groups.

##### 2.2.1.a Synthesis of Mo imido tetrachloride complexes.

We were interested in the possibility of preparing catalysts that contain an electron-withdrawing imido group, and therefore chose to attempt to prepare pentafluorophenylimido, 3,5-bis(trifluoromethyl)phenylimido and 2,4,6-tris(trifluoromethyl)phenylimido \( \text{Mo(NR)Cl}_4(\text{THF}) \) complexes. We also were interested in preparing alkylimido complexes, and for this reason chose 1-adamantylimido (AdN) and tritylimido (triphenylmethylimido). Finally,
we chose to prepare Mo(NAr)Cl₄(THF) (Ar = 2,6-i-Pr₂C₆H₃), since molybdenum alkylidene complexes that contain the NAr group are the most numerous and stable.¹³

Pentafluorophenyl azide, 3,5-bis(trifluoromethyl)phenyl azide, 2,4,6-tris(trifluoromethyl)phenyl azide, 1-adamantyl azide, triphenylmethyl azide, and 2,6-diisopropylphenyl azide were prepared according to Scheme 11.

\[
\begin{align*}
1. & \quad \text{HCl, NaNO}_2 \\
2. & \quad \text{NaN}_3 \\
& \quad \text{H}_2\text{O, 0 °C} \quad \text{ArN}_3 \\
\hline
\text{ArNH}_2 & \quad \text{Ar = C}_6\text{F}_5, 3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3, 2,6-\text{i-Pr}_2\text{C}_6\text{H}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{ROH} & \quad \text{CF}_3\text{COOH, NaN}_3 \\
& \quad \text{CHCl}_3, -5 \degree \text{C} \quad \text{RN}_3 \\
\hline
\text{R} & \quad 1-\text{Ad, Ph}_3\text{C} \\
\end{align*}
\]

Scheme 11. Synthesis of aromatic and aliphatic azides.

Pentafluorophenyl azide, 3,5-bis(trifluoromethyl)phenyl azide, 1-adamantyl azide, triphenylmethyl azide, and 2,6-diisopropylphenyl azide react with MoCl₄(THF)₂ to give complexes of the type Mo(NR)Cl₄(THF) in good (66 %) to excellent (96 %) yields (Scheme 12). The lowest yield was obtained for Mo(NAr)Cl₄(THF) in which the imido group is the most demanding sterically. Reactions carried in 1,2-dichloroethane were faster than the reactions in toluene, which is likely due to higher solubility of MoCl₄(THF)₂ in (CH₂Cl)₂. Slightly lower
yields of the product were obtained when 1,2-dichloroethane was used as a solvent (synthesis of Mo(NC₆F₅)Cl₄(THF): 8 hours, 50 °C, 73 % yield in (CH₂Cl)₂; 30 hours, 50 °C, 88 % yield in toluene).

\[
\text{MoCl}_4(\text{THF})_2 + \text{RN}_3 \rightarrow \text{MoN}_\text{RCl}_4(\text{THF})
\]


2,4,6-Tris(trifluoromethyl)phenyl azide failed to give the expected imido tetrachloride complex upon reaction with Mo(NR)Cl₄(THF) under various conditions.³⁹ The brick-red powder isolated from these reaction mixtures showed no resonances in the ¹⁹F NMR spectrum and broad signals in the ¹H NMR spectrum, indicating formation of a paramagnetic Mo complex. The nature of this product was not investigated further.

Single crystals of Mo[N-3,5-(CF₃)₂C₆H₃]Cl₄(THF) were grown from pentane and an X-ray determination was carried out (Tables 3 and 4, pages 58 and 91). The structure of [N-3,5-(CF₃)₂C₆H₃]Cl₄(THF) (Figure 10) is closely analogous to that of Mo(N-p-tolyl)Cl₄(THF).²⁹ The Mo-N(1) distance (1.715(3) Å) and Mo-N(1)-C(1) angle (171.2(3)°) are typical of imido complexes of Mo(VI). The chlorides are all bent away from the imido group as judged from the N(1)-Mo-Cl angles, which vary from ~92° to ~98°. The Mo-O(1) bond length (2.230(2) Å) is normal, even though it is trans to the pseudo triply-bound imido ligand.
2.2.1.b Synthesis of Mo imido trineopentyl complexes.

Osborn reported in 1987 that Mo(N-t-Bu)(O)Cl₂(MeCN)₃ could be alkylated with MgNp₂(Dioxane) in diethyl ether to yield Mo(N-t-Bu)Np₃Cl in 35% yield as a colorless crystalline solid. On the basis of proton NMR spectra he proposed that this compound has a trigonal bipyramidal structure with the neopentyl groups in equatorial positions. We have found that addition of Mo(NR)Cl₄(THF) complexes in toluene to a cold solution of NpMgCl in ether gave analogous Mo(NR)Np₃Cl species 20 - 24 (R = C₆F₅, 3,5-(CF₃)₂C₆H₃, Ad, Ph₃C, and 2,6-i-Pr₂C₆H₃) in poor (35 %) to modest (51 %) yields (Scheme 13). NMR data at room temperature are all in accord with three-fold symmetric species. Varying the order of addition, time, and
temperature (down to -78 °C) so far has not led to an increase in the yields. We suspect that a susceptibility of Mo to reduction is limiting the yields under the conditions and with the reagents employed so far. The trineopentyl species tend to be quite soluble and therefore relatively difficult to crystallize in good yield, especially in small quantities.

![Scheme 13](image)

**Scheme 13.** Synthesis of Mo imido trineopentyl chlorides 20 – 24.

X-ray structural determinations of 21 and 23 (Tables 3 and 4) confirmed that these molecules are approximately trigonal bipyramidal with neopentyl groups in equatorial positions (Figure 11). The neopentyl groups are all turned in one direction with their β carbon atoms approximately in the equatorial plane and with Mo-Cα-Cβ angles of ~121° and Mo-Cα bond distances of ~2.14 Å. These Mo-Cα-Cβ angles and Mo-Cα bond distances are typical for neopentyl ligands in Mo(VI) and W(VI) complexes. There is no evidence that the neopentyl ligands are distorted for steric reasons or that any α hydrogen is activated toward abstraction. The only notable feature of these structures are somewhat long Mo-Cl distances (2.3944(5) Å in 21 and 2.4286(7) Å in 23) that could be ascribed to the combined steric effect of the three equatorial neopentyl groups on the apical chloride ligand, plus the trans effect of the imido ligand.
Figure 11. Thermal ellipsoid plots of complexes 21 and 23 (50 % probability level, hydrogen atoms omitted for clarity).
Table 3. Selected bond lengths (Å) and angles (°) in Mo[N-3,5-(CF$_3$)$_2$C$_6$H$_3$]Cl$_4$(THF), Mo[N-3,5-(CF$_3$)$_2$C$_6$H$_3$]Np$_3$Cl (21), and Mo(NCPh$_3$)Np$_3$Cl (23).

<table>
<thead>
<tr>
<th></th>
<th>Mo[N-3,5-(CF$_3$)$_2$C$_6$H$_3$]Cl$_4$(THF)</th>
<th>Mo[N-3,5-(CF$_3$)$_2$C$_6$H$_3$]Np$_3$Cl</th>
<th>Mo(NCPh$_3$)Np$_3$Cl</th>
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<tr>
<td>Mo-N(1)</td>
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<td>1.7471(17)</td>
<td>1.7509(15)</td>
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<tr>
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<td>2.1473(19)</td>
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<td>2.1430(19)</td>
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<td>2.3311(11)</td>
<td>2.1281(19)</td>
<td>2.1475(18)</td>
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<tr>
<td>Mo-Cl(4)</td>
<td>2.3459(11)</td>
<td>2.3944(5)</td>
<td>2.4268(7)</td>
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<tr>
<td>Mo-O(1)</td>
<td>2.230(2)</td>
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<tr>
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<td></td>
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<td>Cl(3)-Mo-Cl(4)</td>
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</table>
2.2.1.c Synthesis of Mo imido neopentylidene complexes.

Heating 24 in C₆D₆ to 50 °C results in α-hydrogen abstraction to give neopentane and a molecule that we propose to be Mo(NAr)(CH-t-Bu)NpCl. The decomposition takes place in a unimolecular fashion in C₆D₆ with a rate constant of \( k_{50} = 9.0 \times 10^{-5} \) s⁻¹ at an initial concentration of 0.1 M, and \( k_{50} = 9.5 \times 10^{-5} \) s⁻¹ at an initial concentration of 0.2 M. At 60 °C \( k_{60} = 3.0 \times 10^{-4} \) s⁻¹. This rate constant should be compared with that found for decomposition of Mo(NAr)Np₃(OC₆F₅) to Mo(NAr)(CH-t-Bu)Np(OC₆F₅) in C₆D₆ at 60 °C (1.0 × 10⁻⁴ s⁻¹). A resonance for the alkylidene proton in Mo(NAr)(CH-t-Bu)NpCl is found at 11.70 ppm and for the alkylidene carbon atom at 283 ppm (\( J_{CH} = 109 \) Hz). Unfortunately this species is not stable toward bimolecular decomposition to yield di-t-butylethylene, and so far all attempts to isolate it have failed. The nature of the metal-containing decomposition product or products is (are) not known. The other Mo(NR)Np₃Cl species were found to be more stable than Mo(NAr)Np₃Cl, but when they did decompose (after several hours at 70 °C or higher temperatures), no neopentylidene complex could be observed. If neopentylidene complexes are formed, they presumably decompose too readily under these conditions to be observed.

Addition of neopentyllithium to 24 at -30 °C led to formation of Mo(NAr)(CH-t-Bu)Np₂ (18) in 90 % yield (\( \delta_{H\alpha} = 9.50 \) in C₆D₆, \( \delta_{C\alpha} = 255 \) ppm in C₆D₆, \( J_{CH} = 108 \) Hz). This compound is identical in all respects to the relatively stable crystalline solid prepared by alkylation of Mo(NAr)(CH-t-Bu)(OTf)₂(dme). The low Jₜₜ value is typical of imido alkylidenes that have a syn orientation with respect to the imido group.

Addition of neopentyllithium to Mo(NCPh₃)Np₃Cl led to formation of Mo(NCPh₃)(CH-t-Bu)Np₂ (25) as a pentane soluble ivory powder in 96 % yield (Scheme 14). The proton NMR spectrum of 25 in C₆D₆ shows the neopentylidene Hₐ resonance at 8.95 ppm and the Cₐ resonance at 250.1 ppm with \( J_{CH} = 109 \) Hz. It should be noted that although Mo(N-t-Bu)(CH-t-Bu)Np₂ could be prepared in 75 % yield, it could be isolated only as a brown oil (\( \delta_{H\alpha} = 9.22, \delta_{C\alpha} = 249.5 \) in C₆D₆). The purity of this compound was not confirmed.

Addition of neopentyllithium to Mo(NAd)Np₂Cl led to formation of what is believed to be Mo(NAd)(CH-t-Bu)Np₂ with δ Hₐ = 9.22 ppm in C₆D₆. This species is not stable in solution at 22 °C, judging from the appearance of olefinic resonances at 5.38 and 5.42 ppm, which are characteristic of cis and trans (t-Bu)CH=CH(t-Bu), the product of bimolecular coupling of neopentylenes. Mo(NAd)(CH-t-Bu)Np₂ prepared from Mo(NAd)(CH-t-Bu)(OTf)₂(dme)⁴² on a multigram scale also was found to be unstable at room temperature in solution and could be isolated only as a partially decomposed red oil. These results suggest that Mo(N-t-Bu)(CH-t-Bu)Np₂⁴⁰ also may not be completely stable with respect to decomposition to give di-t-butylethylene.

Addition of neopentyllithium to 20 and 21 led to complex product mixtures. The reaction between 20 and NpLi in pentane at -45 °C gave an intractable mixture of decomposition products. ¹H NMR spectrum of the reaction mixture containing 21 and 1 equivalent of neopentyllithium exhibited a characteristic sharp signal of an alkylidene proton at 8.99 ppm. The large number of side products in the reaction between 21 and NpLi made crystallization of the neopentylenic complex challenging. The presumed product, Mo[N-3,5-(CF₃)₂C₆H₃](CH-t-Bu)Np₂, could not be isolated from the mixture of products even when the reaction was carried on a 3 gram scale.
2.2.1.d Synthesis of Mo monoalkoxide complexes.

Addition of 1 equivalent of 2,6-dimethylphenol or 2,6-diisopropylphenol to 25 leads to formation of Mo(NCPh₃)(CH-t-Bu)Np(OAr) species 26 and 27, respectively, as a consequence of addition of the alcohol across a Mo–C single bond in a manner similar to the reactions reported for 18.¹⁴ The 2,6-dimethylphenoxide derivative is a colorless powder, while the extremely soluble 2,6-diisopropylphenoxide derivative could be obtained only as a brown oil. Reaction of one equivalent of 3,5-(2,4,6-i-Pr₃C₆H₂)₂C₆H₃OH (HIPTOH), which was prepared in 75 % yield from 3,5-(2,4,6-i-Pr₃C₆H₂)₂C₆H₃Br,⁴³,⁴⁴ with 25 gives Mo(NCPh₃)(CH-t-Bu)Np(OHIPT) (28) as a yellow-golden powder in 95 % yield.

The X-ray structure of 28 (Tables 4 and 5; Figure 12) shows it to be a monomeric species with a syn neopentylidene ligand. The two molecules in the unit cell are enantiomers in terms of the arrangement of the four ligands around the metal; only one of the two molecules (containing Mo(2); Table 5) is shown in Figure 12. The bond lengths and angles are typical of four-coordinate alkylidene imido compounds, although this is actually the first structural determination of a compound of this mononeopentyl monoalkoxide type.¹⁴ Several bond lengths and angles differ significantly in the two molecules, including (for example) the Mo-N-C angles (164.1(3)° in Mo(1) and 161.2(3)° in Mo(2)). Both are at the lower end of the range of angles typically found in "linear" imido alkylidene complexes. Since several other bond lengths and angles differ significantly from one another in the two molecules (Table 5), we believe that packing forces may play a significant role in determining the detailed structures of the two molecules of 28.
Figure 12. Thermal ellipsoid plot of 28 (50% probability level, hydrogen atoms omitted for clarity).
A reaction between 25 and C₆F₅OH gives Mo(NCPh₃)Np₃(OC₆F₅) (29) as an off-white powder in 93 % yield (Scheme 15). The difference in behavior between the phenols described above and pentafluorophenol in the manner in which they react with a dineopentyl neopentylidene complex is analogous to that reported for reactions of phenols and various other alcohols with 18,14 i.e., pentafluorophenol adds across the Mo=C bond instead of the Mo–C bond. Compound 30 does not undergo α-hydrogen abstraction upon heating in C₆D₆ to 60 °C for 2 days. In contrast, when d₆-benzene solutions of Mo(NAr)Np₃(OC₆F₅) are heated to 60 °C, neopentane evolves smoothly and Mo(NAr)(CH-t-Bu)Np(OC₆F₅) is formed in a monomolecular
manner with $k = 1.0 \times 10^{-4} \text{ s}^{-1}$. It is not clear whether the more rapid decomposition of Mo(NAr)Np$_3$(OC$_6$F$_5$) can be ascribed to steric or electronic differences between the imido groups, or both.

Scheme 15. Addition of pentafluorophenol across the Mo=−C bond of compound 25 to give complex 29.

The unsuccessful attempts to isolate alkylidene complexes via alkylation of compounds 20, 21 and 22 suggested that we looked for an alternative synthetic route to Mo(NR)(CH-t-Bu)Np(OR’)% complexes (R = C$_6$F$_5$, 3,5-(CF$_3$)$_2$C$_6$H$_3$ and 1-Ad). We hoped that the Mo(NR)(CH-t-Bu)Np(OR’) complexes prepared from 20, 21 and 22 would be more stable towards bimolecular decomposition than the Mo(NR)(CH-t-Bu)Np$_2$ compounds. The first step of the proposed synthetic scheme involved substitution of the chloride ligands in 20 – 22 by an alkoxide. The resulting products would be structurally similar to the known compound Mo(NAr)Np$_3$(OC$_6$F$_5$), which upon heating is smoothly converted into the alkylidene complex Mo(NAr)(CH-t-Bu)Np(OC$_6$F$_5$) via $\alpha$-H abstraction. We planned to employ a similar transformation to generate the desired alkylidene compounds (Scheme 16).
Scheme 16. The proposed synthetic sequence towards Mo(NR)(CH-t-Bu)Np(OR’) complexes.

Reactions between imido trineopentyl chloride complexes and lithium or potassium alkoxides under various conditions (Table 6) led to the formation of the desired Mo(NR)Np3(OR’) complexes along with small amounts of decomposition products, as judged by $^1$H NMR spectroscopy of the reaction mixtures. The spectra of these reaction mixtures invariably contained small amounts of di-tert-butylethylene, indicating that the expected trialkyl alkoxide products had undergone $\alpha$-H abstraction, followed by bimolecular decomposition. Due to the extremely high solubility of all the studied complexes even minor amounts of organic side products made isolation of the alkylidene complexes by crystallization virtually impossible. At this point we decided to limit our study of Mo(NR)(CH-t-Bu)Np(OR’) molecules to compounds 26, 27, and 28 and examine their catalytic properties in olefin metathesis reactions.
Table 6. Reaction conditions for the substitution of the chloride ligand in compounds 20, 21, and 22 with an alkoxide.

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<th>Mo complex</th>
<th>Alkoxide</th>
<th>Time, h</th>
<th>T, °C</th>
<th>Solvent</th>
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<td>24</td>
<td>25</td>
<td>C6D6</td>
</tr>
<tr>
<td>20</td>
<td>LiOCH(CF3)2</td>
<td>24</td>
<td>50</td>
<td>C6D6</td>
</tr>
<tr>
<td>20</td>
<td>LiOCH(CF3)2</td>
<td>48</td>
<td>50</td>
<td>THF</td>
</tr>
<tr>
<td>21</td>
<td>KOCH(CF3)2</td>
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<td>60</td>
<td>THF</td>
</tr>
<tr>
<td>21</td>
<td>KO-t-Bu</td>
<td>48</td>
<td>60</td>
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<td>24</td>
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<td>C6D6</td>
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</tbody>
</table>

2.2.2 Catalytic properties of compounds 26, 27, and 28.

The three monophenoxide neopentylidene complexes 26, 27, and 28 showed metathesis activity for ring-closing of a small selection of substrates shown in Figure 13.45 It is worth noting that in the case of complexes 26 and 27 the majority of the initial species can be observed throughout the reaction, i.e., no alkylidene resonance ascribed to an intermediate could be observed. Compound 28, on the other hand, was completely consumed in the initial reaction with an olefin. However, no intermediate alkylidene could be observed in this case either. No improvement in the metathesis conversions in the presence of 28 could be detected after the first hour of the experiment. Therefore we suspect that although the metal in 28 is sterically more accessible toward olefin substrates, for the same reason some intermediate alkylidenes, especially Mo(NCPh3)(CH2)Np(OHIPT), are unstable toward bimolecular decomposition, while in 26 and 27 the ortho methyl and isopropyl groups...
sterically prevent a reaction of the initial neopentylidene complex with olefin substrate. Therefore only a small fraction of any initial neopentylidene complex is consumed.

\[
\begin{array}{ccc}
\text{CPh}_3 & \text{N} & \text{Mo} \\
\text{O} & \text{N} & \text{Mo} \\
\text{CPh}_3 & \text{O} & \text{N} & \text{Mo} \\
\end{array}
\]

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<tr>
<th>Substrate</th>
<th>Product</th>
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$^a$ Catalyst loading $5\%$, $\text{C}_6\text{D}_6$, $25$ $\degree\text{C}$;

$^b$ The reaction mixture was stirred for $12$ h at $25$ $\degree\text{C}$, then for $18$ h at $65$ $\degree\text{C}$.

**Figure 13.** Catalytic studies with complexes $26$, $27$, and $28$. 
Data in Figure 13 show that complex 26 is the most active of the three studied catalysts, providing high conversions in the RCM of all three substrates within the first hour of the reaction. 26 is also a relatively stable catalyst, since the product conversions continue improving after the first hour. Compound 27 is significantly less active, likely due to the steric hindrance of the Mo atom provided by the bulky 2,6-diisopropylphenoxide ligand. This catalyst, however, can also provide nearly complete conversions in the examined ring-closing metathesis reactions, if longer reaction times and elevated temperatures are employed. 28 is also an active catalyst, giving relatively high conversions of the starting materials into the RCM products within the first hour of the reactions. However, the conversions do not improve over the next 23 hours, which indicates that the catalytically active species undergoes decomposition in solution during the first hour of the reaction.

2.2.3 Attempted synthesis of tritylimidonoephylidene bisalkoxide complexes.

We were interested in whether Mo(NCPh₃)(CH-t-Bu)(OR)₂ catalysts could be prepared via the "bistriflate" route, which currently is the only route to bisalkoxide complexes of this general type. That would require the synthesis of Mo(NCPh₃)₂Cl₂(dme) and Mo(NCPh₃)₂(CH₂CMe₂Ph)₂, and reaction of the latter with triflic acid to yield Mo(NCPh₃)(CHCMe₂Ph)(OTf)₂(dme). Mo(NCPh₃)₂Cl₂(dme) was prepared as shown in Scheme 17 as a yellow powder in 66 % yield. Alkylation of Mo(NCPh₃)₂Cl₂(dme) with 2 equivalents of PhMe₂CCH₂MgCl at -78 °C in ether gave Mo(NCPh₃)₂(CH₂CMe₂Ph)₂ in 60 % yield as yellow crystals. However, addition of 3 equivalents of triflic acid to Mo(NCPh₃)₂(CH₂CMe₂Ph)₂ yielded an orange oil whose ¹H NMR spectrum showed it to be a complex mixture of unidentifiable species, only a minor component of which could be the desired Mo(NCPh₃)(CHCMe₂Ph)(OTf)₂(dme). Varying the reaction conditions so far has not changed the outcome of this reaction. We suspect that the trityl group is cleaved from the imido nitrogen, although at this stage we have no proof. In any case, we must
turn to alternative methods of preparing what we believe should be relatively stable Mo(NCPh₃)(CHCMe₂Ph)(OR)₂ complexes.

**Scheme 17.** Synthesis of Mo(NCPh₃)₂Cl₂(dme).

### 2.2.3 Synthesis of Mo complexes with chiral imido groups.

Four-coordinate compounds of type Mo(NR)(CH-t-Bu)Np(OR’), such as 26, 27, and 28, are chiral due to the presence of four different substituents at the Mo center. In the absence of a chiral ligand in the coordination sphere these molecules are obtained as a racemic mixture. Therefore such catalysts cannot be used for asymmetric olefin metathesis applications. Dr. Monica Duval in our group attempted to synthesize Mo(NAr)(CH-t-Bu)Np(OR’) molecules in a diastereoselective fashion through introduction of an enantiomerically pure monodentate alcohol into the complexes. Dr. Duval showed that upon reaction of Mo(NAr)(CH-t-Bu)Np with a variety of enantiomerically pure alcohols R*OH the initial moderate excess of one of the diastereomers in the reaction mixture deteriorates over time to give a 1:1 mixture of diastereomers. It was determined that in the presence of catalytic amounts of alcohol the alkyl and alkoxide ligands in Mo(NAr)(CH-t-Bu)Np(OR*) rearrange, and the diastereomers equilibrate to give an equimolar mixture (**Scheme 18**). Based on these results, we proposed to introduce a sterically bulky chiral imido ligand in the precursor Mo(NR*)(CH-t-Bu)Np₂. We hoped that the catalyst will be synthesized diastereoselectively upon the reaction of an alcohol with the precursor that already bears a chiral element, and one of the alkyl substituents will be protected from protonation by the large asymmetric imido ligand. The resulting complex might
be sterically hindered enough to prevent excess of bulky alcohol from coordinating to the Mo center and assisting the ligand rearrangement.

![Scheme 18](image)

**Scheme 18.** Mechanism of the alcohol-catalyzed ligand rearrangement in Mo(NR)(CH-t-Bu)Np(OR’)

There are few examples of metal complexes bearing enantiomerically pure imido ligands in the literature ([Scheme 19](#)). Complexes shown in [Scheme 19](#) were prepared from the corresponding enantiomerically pure amines. We proposed to synthesize Mo(NR*)(CH-t-Bu)Np₂ complexes from the Mo imido tetrachloride molecules, which would be obtained through the reaction of MoCl₄(THF)₂ and the corresponding chiral azides. This route provides access to imido alkylidene complexes containing acid-sensitive imido substituents that cannot be synthesized via a traditional route employing triflic acid. The proposed synthetic sequence also does not involve a loss of one imido functionality, which in the case of expensive and sometimes synthetically challenging chiral amines might be undesirable. Chiral azides that we chose to pursue in this project were designed to a) have a quaternary carbon atom bound to the azide; b) be bulky in proximity to the Mo atom; c) be accessible from cheap chiral precursors. One class
of molecules that conform to all of these requirements consists of azides synthesized from camphor-derived alcohols.

\[
\begin{align*}
&M = \text{Mo, W} \\
&\text{Figure 14. Examples of metal complexes bearing enantiomerically pure imido ligands.}
\end{align*}
\]

\[
\begin{align*}
\text{Scheme 19. Synthesis of azide 30.}
\end{align*}
\]

Azide 30 was synthesized from (D)-camphor as shown in Scheme 19. The alcohol precursor was prepared as a single diastereomer according to the published procedure.49 Compound 30 was chromatographically isolated as a 2:3 mixture of diastereomers, and diastereomerically pure sample can be obtained after repeated crystallization from hexane.

Reaction of 30 with MoCl₄(THF)₂ (toluene, 70 °C, 12 h) followed by a standard workup procedure gave a brick-red solid that is soluble in toluene and benzene, but shows no signals in \(^1\text{H}\) NMR spectrum. The brick-red compound was proposed to be Mo(N)Cl₃, although this assignment was not confirmed by spectroscopic analysis.
Trying to explain our failure to obtain Mo(NCamPh)Cl₄(THF) complex (NCamPh = (1R,4R)-1,7,7-trimethyl-2-phenylbicyclo[2.2.1]heptan-2-imido) we thought of the possible mechanisms of Mo(IV) oxidation in the presence of organic azides that might yield a nitride species. Nitride complexes are commonly prepared upon treatment of metal complexes with trimethylsilyl azide, Me₃SiN₃.⁵⁰ Formation of a nitride ligand in this reaction is likely to proceed through the same cyclic intermediate that is proposed to form in the case of aryl and alkyl azides (Scheme 10, page 53). However, due to the lower Si-N bond energy (439 ± 38 kJ/mol) as compared to the C-N bond energy (770 ± 4 kJ/mol),⁵¹ the cycle rearranges to expel a molecule of N₂, a metal nitride and a cation (or radical) of SiMe₃, which abstracts an anion (or radical) from the metal complex to form Me₃SiX (Scheme 20). This reaction might occur through a concerted or a stepwise mechanism. In some cases the trimethylsilyl azide adduct can be observed by NMR spectroscopy at low temperatures, but it decomposes upon warming.⁵²

We propose that 30 resembles Me₃SiN₃ in terms of reactivity towards MoCl₄(THF)₂, due to a) the large size of the alkyl substituent in 30; possibly too bulky to form an imido species, and b) 30 can form a stabilized benzylic cation (or radical). In order to prove this theory we synthesized compounds bearing either smaller groups bound to α-carbon in the azide molecules.
(31), or substituents that would destabilize possible radical or cation species (32). Azides 31 and 32 were synthesized according to Scheme 21. Compound 31 is an oil obtained as a 1:1 mixture of diastereomers, while compound 32 is isolated as a solid and can be recrystallized from hexane to give a diastereomically pure sample.

Scheme 21. Synthesis of compounds 31 and 32.

Reactions of 31 and 32 with MoCl₄(THF)₂ under various conditions (solvents: toluene, THF; temperature: 25 °C, 70 °C) gave the same brick-red solid as was isolated in the reaction of MoCl₄(THF)₂ with 30. Reactions of 31 with MoCl₄(Et₂O)₂ and MoCl₄⁸ yielded the same product. Compounds 30, 31, and 32 were characterized by ¹H NMR and IR spectroscopies. All three compounds exhibited characteristic azide absorption at ca. 2100 cm⁻¹ in the IR spectra.

The last variation of the (D)-camphor-derived azides was prepared in a manner analogous to the syntheses of compounds 30, 31 and 32 (Scheme 22). Compound 34 was isolated as a single diastereomer as judged by ¹H NMR spectroscopy in 53 % yield.
Scheme 22. Synthesis of compound 34 via rearrangement and nucleophilic substitution of alcohol 33.

The $^1$H NMR spectrum of 34 suggested that the alcohol molecule rearranged upon nucleophilic substitution, since the signal of one of the methyl groups in the azide was split into a doublet. DEPT NMR showed that 34 contained 2 CH$_2$ groups and 4 CH groups, thus confirming the rearrangement of the carbon skeleton structure in 34. Several possible carbon frames of 34 were proposed, but the actual connectivity in the alkyl substituent was elucidated from the crystal structure of the product of the reaction in Scheme 23.


Pentane soluble complex 35 was isolated from the reaction mixture as a red powder. X-ray quality crystals were grown from a cold pentane solution. The solid state structure of 35 was determined by X-ray crystallography (Tables 7 and 8). The thermal ellipsoid plot of compound 35 is shown in Figure 15.
Figure 15. Thermal ellipsoid plot of 35 (50% probability level, hydrogen atoms omitted for clarity).
Table 7. Selected bond lengths (Å) and angles (°) in the molecule of 35.

<table>
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<th>Selected bond lengths (Å) and angles (°)</th>
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<td>Mo(1)-O(1)  2.272(5)</td>
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<tr>
<td>Mo(1)-Cl(2)  2.331(3)</td>
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<td>Mo(1)-Cl(1)  2.337(2)</td>
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<td>Mo(1)-Cl(3)  2.348(2)</td>
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<tr>
<td>N(1)-C(1)  1.468(11)</td>
</tr>
<tr>
<td>C(1)-N(1)-Mo(1)  171.8(7)</td>
</tr>
<tr>
<td>N(1)-C(1)-C(2)  105.5(8)</td>
</tr>
</tbody>
</table>

Structural parameters of 35 are similar to those of Mo [N-3, 5-(CF₃)₂C₆H₃]Cl₄(THF). The difference between an alkylimido and an arylimido group manifests itself in a shorter Mo-N bond than the one in Mo[N-3,5-(CF₃)₂C₆H₃]Cl₄(THF) (1.687(7) Å vs. 1.711(3) Å) and the longer Mo-O distance (2.272(5) Å vs. 2.230(2) Å in Mo[N-3,5-(CF₃)₂C₆H₃]Cl₄(THF)), which indicates greater degree of π-donation from the an electron rich alkylimido group.

The crystal structure of compound 35 was solved in the space group P1̅, with both enantiomers were present in the unit cell. When optical rotation of compounds 34 and 35 was measured, they were found to be optically active (specific optical rotation of compound 34: [α]²⁹⁸°D = +7.7 ± 0.7 deg cm² g⁻¹ (c = 0.01, pentane); specific optical rotation of compound 35: [α]²⁹⁸°D = -16.0 deg cm² g⁻¹ (c = 9*10⁻³, pentane). We explained the disagreement between the observed nonzero optical rotation and the racemic nature of the crystal structure of 35 by the presence of a minor amount of the opposite enantiomer of camphor in the commercial sample of
D-camphor used in the synthesis of 34. It is known that racemic crystals can precipitate from non-racemic solutions containing both enantiomers, since the properties of enantiomerically pure crystals (such as space group) are often significantly different from those of racemates.\textsuperscript{53} We proposed that the crystal picked for the structure determination of 35 happened to represent the minor fraction of racemic crystals in the bulk of enantiomerically enriched compound 35.

A sample of D-camphor (23.14 g), which was purchased from Alfa Aesar and used in the synthesis of 35, was recrystallized from ca. 50 mL of hot hexanes. Solid material was recovered (4.84 g), and specific optical rotations of the recrystallized and non-recrystallized samples of D-camphor were measured. The values were determined as follows: recrystallized material $[\alpha]^{298}_D = +58.10 \pm 0.01 \text{ deg cm}^2\text{g}^{-1}$ (c = 0.04, hexane); original D-camphor sample $[\alpha]^{298}_D = +58.56 \pm 0.01 \text{ deg cm}^2\text{g}^{-1}$ (c = 0.04, hexane). Pure D-camphor rotates polarized light at $[\alpha]^{298}_D = +59.0 \text{ deg cm}^2\text{g}^{-1}$ (hexane, c = 0.01).\textsuperscript{54} Comparison of these values shows that the original sample of camphor contains ca. 0.5 \% of the opposite enantiomer, while the recrystallized sample is enriched to ca. 1 \% of the opposite enantiomer. These observations support our hypothesis that both enantiomers of compound 35 found during the solid state structure determination are formed due to the contamination of the original D-camphor with the opposite enantiomer.

The 9-step mechanism for rearrangement of carbocations that are formed during the synthesis of 34 was proposed by Robert O’Brien (Hoveyda group, Boston College) and is shown in Scheme 24.
Enantiomer A is formed upon rearrangement of the alcohol 33 synthesized from D-camphor. The opposite enantiomer, B, shown in Scheme 23, is obtained from a small impurity of L-camphor.

Scheme 24. Proposed sequence of the non-classical carbocation rearrangements leading to the formation of 34.

In our effort to expand the pool of enantiomerically pure azides for the synthesis of chiral imido tetrachlorides we decided to explore other commercially available chiral ketones. L-Menthone and (-)-fenchone were converted into alcohols 36 and 37 according to the published procedures. Several attempts to synthesize the corresponding azides from 36 and 37 proved unsuccessful (Scheme 25).
The hydroxyl groups in compounds 36 and 37 are extremely sterically hindered and do not undergo nucleophilic substitution not only under mild conditions (Me$_3$SiN$_3$, BF$_3$•Et$_2$O), but also under harsh acidic conditions (trifluoroacetic acid, NaN$_3$). While the latter reaction protocol in the cases of compounds 31 – 34 gave exclusively the olefinic product of acid-assisted elimination, intact alcohols 36 and 37 were recovered from the reaction mixtures containing trifluoroacetic acid and NaN$_3$.

### 2.4 Conclusions.

Several new Mo(NR)Cl$_4$(THF) species (R = C$_6$F$_5$, 3,5-(CF$_3$)$_2$C$_6$H$_3$, Ad, CPh$_3$, and 2,6-i-Pr$_2$C$_6$H$_3$) were prepared via the treatment of MoCl$_4$(THF)$_2$ with azides, and then alkylated with neopentyl reagents. Addition of Mo(NR)Cl$_4$(THF) complexes in toluene to a cold solution of NpMgCl in ether gave Mo(NR)Np$_3$Cl species (R = C$_6$F$_5$, 3,5-(CF$_3$)$_2$C$_6$H$_3$, Ad, Ph$_3$C, and 2,6-i-Pr$_2$C$_6$H$_3$) in poor (35 %) to modest (51 %) yields. Heating Mo(NAr)Np$_3$Cl in C$_6$D$_6$ to 50 °C results in α-hydrogen abstraction to give neopentane and a molecule whose NMR spectra are consistent with it being Mo(NAr)(CH-t-Bu)NpCl; it decomposed bimolecularly upon attempted isolation. The other Mo(NR)Np$_3$Cl species were found to be more stable than Mo(NAr)Np$_3$Cl, but when they did decompose at elevated temperatures, no neopentylidene complex could be
observed. Addition of neopentyllithium to Mo(NR)Np₂Cl species (R = Ar, CPh₃, or Ad) yielded Mo(NR)(CH-t-Bu)Np₂ species, the adamantylimido version of which is unstable toward bimolecular decomposition. Addition of 1 equivalent of 2,6-diisopropylphenol, 2,6-dimethylphenol, or 3,5-(2,4,6-i-Pr₃C₆H₂)₂C₆H₃OH (HIPTOH) to Mo(NCPh₃)(CH-t-Bu)Np₂ led to formation of Mo(NCPh₃)(CH-t-Bu)Np(OR) species, while treatment of Mo(NCPh₃)(CH-t-Bu)Np₂ with C₆F₅OH gave Mo(NCPh₃)Np₃(OC₆F₅). The three monophenoxide neopentylidene complexes showed metathesis activity for ring-closing a small selection of amines and an ether. X-ray studies were completed for Mo[N-3,5-(CF₃)₂C₆H₃]Cl₄(THF), Mo[N-3,5-(CF₃)₂C₆H₃]Np₃Cl, Mo(NCPh₃)Np₃Cl, and Mo(NCPh₃)(CH-t-Bu)Np(OMe).

### 2.4 Experimental Details.

**General Details.** All reactions were conducted in oven-dried (135 °C) and flame-dried glassware under an inert atmosphere of dry nitrogen employing standard Schlenk and glovebox techniques. Toluene, diethyl ether, and THF were degassed and then passed through a column of activated alumina. DME was distilled from sodium/benzophenone under nitrogen atmosphere. n-Pentane was washed with H₂SO₄ and water, dried over CaCl₂, degassed, and then passed through a column of activated alumina. MoCl₄(THF)₂, C₆F₅N₃, 3,5-(CF₃)₂C₆H₃N₃, 1-AdN₃, Ph₃CN, and 3,5-(2,4,6-iPr₃C₆H₂)₂C₆H₃Br were prepared according to literature procedures.

¹H, ¹⁹F, and ¹³C NMR spectra were recorded on Varian spectrometers. Chemical shifts in ¹H and ¹³C NMR spectra are reported in ppm from tetramethylsilane with the solvent as an internal standard. ¹⁹F NMR spectra were referenced externally using C₆F₆ as a standard. Elemental analyses were performed by H. Kolbe Microanalytisches Laboratories, Mülheim an der Ruhr, Germany.

**2,6-i-Pr₂C₆H₃N₃.** 2,6-Diisopropyl aniline (8.81 g, 0.049 mol) was dissolved in a mixture of concentrated HCl and H₂O (10/30 mL) and 30 g of ice. The mixture was stirred
vigorously with a mechanical stirrer and a solution of NaNO₂ (3.80 g, 0.055 mol) in 20 mL of water was added slowly over a period of 5 minutes. The mixture was stirred for 20 min and then a saturated solution of NaHCO₃ (30 mL) was added. NaN₃ (3.71 g, 0.057 mol) in 30 mL of water was added. After 30 min the reaction mixture was warmed to room temperature and the organic layer was extracted with diethyl ether (3*50 mL). The ethereal fractions were combined and washed with a saturated solution of NaHCO₃ (50 mL) and water (2*50 mL) and dried over MgSO₄. The solvent was removed from the ether solution in vacuo and the oily residue was chromatographed on silica gel with hexane as an eluent to yield the product as a pale yellow, light-sensitive oil; yield 6.51 g (0.032 mol, 65 %): ¹H NMR (C₆D₆): δ 7.07-6.94 (m, 3H), 3.33 (septet, J HH = 6.9 Hz, 2H), 1.12 (d, J HH = 6.9 Hz, 12H); ¹³C NMR (C₆D₆): δ 143.31 (s, 2C), 135.52 (s, 1C), 127.02 (s, 1C), 124.14 (s, 1C), 29.01 (s, 1C), 23.73 (s, 2C); IR (neat, KBr, cm⁻¹) 2125 (azide). These NMR data match those for the published material.³⁷

**Mo(NC₆F₅)Cl₄(THF).** A 200 mL Schlenk vessel was loaded with MoCl₄(THF)₂ (5.48 g, 14.3 mmol), pentafluorophenyl azide (6.00 g, 28.7 mmol), and 50 mL of toluene. The reaction mixture was heated to 50 °C and stirred under a flow of dinitrogen for 30 h. The reaction mixture was filtered and the solvent was removed from the filtrate in vacuo to give a dark red solid. The solid was washed with cold pentane and dried to yield a red crystalline product; yield 6.16 g (12.0 mmol, 88 %): ¹H NMR (C₆D₆) δ 4.50 (m, 4H), 1.31 (m, 4H); ¹⁹F NMR (C₆D₆): δ -151.84 (m, 2F), -160.81 (m, 1F), -162.37 (m, 2F). Anal. Caled for C₁₀H₈NOCl₄F₅Mo: C, 24.47; H, 1.64; N, 2.85; Cl, 28.99. Found: C, 24.51; H, 1.58; N, 2.79; Cl, 28.70.

**Mo(N[3,5-(CF₃)₂C₆H₃])Cl₄(THF).** A 200 mL Schlenk vessel was loaded with MoCl₄(THF)₂ (4.68 g, 12.3 mmol), 3,5-bis(trifluoromethyl)phenyl azide (3.75 g, 14.7 mmol), and 30 mL of toluene. The reaction mixture was heated to 60 °C and stirred under a flow of dinitrogen for 10 h. The reaction mixture was filtered and the solvent was removed in vacuo to give a dark red solid. The solid was washed with cold pentane and dried to yield a red crystalline
product; yield 4.93 g (9.2 mmol, 75 %): \(^1\)H NMR (C\(\text{d}_6\)): \(\delta\) 7.77 (s, 2H), 7.10 (s, 1H), 4.49 (m, 4H), 1.32 (m, 4H); \(^{19}\)F NMR (C\(\text{d}_6\)): \(\delta\) -62.66 (s, 6F); \(^{13}\)C NMR (C\(\text{d}_6\)): \(\delta\) 152.8 (s), 132.8 (q, \(J_{\text{CF}} = 34.6\) Hz), 129.9 (s), 127.4 (s), 122.6 (q, \(J_{\text{CF}} = 274.1\) Hz), 74.7 (s), 25.9 (s). Anal. Calcd for C\(_{12}\)H\(_{11}\)NOCl\(_4\)F\(_6\)Mo: C, 26.84; H, 2.06; N, 2.61; Cl, 26.41. Found: C, 26.73; H, 2.11; N, 2.55; Cl, 26.58.

Single crystals for the X-ray study were grown from a pentane solution at -30 °C.

**Mo(NAd)Cl\(_4\)(THF).** A 300 mL Schlenk vessel was loaded with MoCl\(_4\)(THF)\(_2\) (7.52 g, 19.7 mmol), 1-adamantyl azide (3.49 g, 19.7 mmol) and 100 mL of toluene. The reaction mixture was heated to 55 °C and stirred under a flow of nitrogen for 17 h. The reaction mixture was filtered and the solvent was removed under vacuum to give a dark red solid. The solid was triturated with pentane for 10 h and the mixture was filtered and the red crystalline product thereby isolated; yield 8.34 g (18.3 mole, 93 %): \(^1\)H NMR (C\(\text{d}_6\)): \(\delta\) 4.55 (br s, 4H), 2.25 (d, \(J_{\text{HH}} = 3\) Hz, 6H), 1.74 (br s, 3H), 1.35 (br s, 4H), 1.14 (t, \(J_{\text{HH}} = 3\) Hz, 6H). Anal. Calcd for C\(_{14}\)H\(_{23}\)NOCl\(_4\)Mo: C, 36.63; H, 5.05; N, 3.05; Cl, 30.89. Found: C, 36.73; H, 5.12; N, 2.72; Cl, 30.75.

**Mo(NAr)Cl\(_4\)(THF).** ArN\(_3\) (3.35 g, 16.4 mmol) was added to a suspension of MoCl\(_4\)(THF)\(_2\) (6.28 g, 16.4 mmol) in 50 mL of toluene and the mixture was heated to 50 °C for 12 h under a flow of dinitrogen. The dark red reaction mixture was then cooled to room temperature and filtered, and the solvent was removed from the filtrate under vacuum to give dark red solid. The solid was stirred in pentane for 24 h and the mixture was filtered and the product dried to give red powder (5.30 g, 10.9 mmol, 66 %): \(^1\)H NMR (C\(\text{d}_6\)): \(\delta\) 6.91 (d, \(J_{\text{HH}} = 7.6\) Hz, 2H), 6.44 (t, \(J_{\text{HH}} = 7.6\) Hz, 1H), 5.08 (septet, \(J_{\text{HH}} = 6.4\) Hz, 2H), 4.53 (s, 4H), 1.23 (d, \(J_{\text{HH}} = 6.7\) Hz, 16H). Anal. Calcd for C\(_{16}\)H\(_{25}\)NOCl\(_4\)Mo: C, 39.61; H, 5.19; Cl, 29.23; N, 2.89. Found: C, 39.73; H, 5.25; Cl, 29.82; N, 2.84.
**Mo(NCPh₃)Cl₄(THF).** Ph₃CN₃ (7.12 g, 25 mmol) was added to a suspension of MoCl₄(THF)₂ (9.54 g, 25 mmol) in 100 mL of toluene and the mixture was stirred for 12 h at room temperature under a flow of N₂. The dark red reaction mixture was filtered and the solvent was removed *in vacuo*. The dark red solid residue was triturated with pentane for 24 h and the product was filtered off and dried *in vacuo*; yield 13.69 g (24 mmol, 96 %): ¹H NMR (C₆D₆): δ 7.75-7.72 (m, 6H), 7.17-7.00 (m, 9 H), 4.42 (s, 4H), 1.26 (s, 4H). Anal. Calcd for C₂₃H₂₃NOCl₄Mo: C, 48.70; H, 4.09; Cl, 25.00; N, 2.47. Found: C, 48.86; H, 4.03; Cl, 24.82; N, 2.39.

**(1S,4S)-5-(2-azidopropan-2-yl)-2,2,3-trimethylbicyclo[2.2.1]heptane (34).** Alcohol 33⁴⁹ (4.7 g, 23.9 mmol) was dissolved in 100 mL of CHCl₃ and cooled to -60 °C. TMSN₃ (4.75 mL, 35.9 mmol) was added to the reaction mixture, followed by BF₃·Et₂O (4.55 mL, 35.9 mmol), and the resulting yellow solution was allowed to warm to room temperature under stirring. The mixture was stirred for 18 hours, and then poured into 200 mL of water. The aqueous phase was extracted with chloroform (2*50 mL), and the chloroform fractions were combined and washed with saturated solution of NaHCO₃ (2*50 mL) and brine (50 mL). The solution was dried over MgSO₄ and the solvents were removed *in vacuo* to give pale yellow oil. Chromatographic separation (hexanes as an eluent) gave 2.8 g (12.6 mmol, 53 %) of colorless oil. ¹H NMR (C₆D₆): δ 1.81 (m, 1H), 1.64 (m, 1H), 1.55 (m, 1H), 1.37 (septet, 1H, J_HH = 7.2 Hz), 1.34 (m, 2H), 1.00 (m, 1H), 0.97 (s, 3H), 0.92 (s, 3H), 0.87 (s, 3H), 0.74 (d, 3H, J_HH = 12.5 Hz), 0.66 (s, 3H). ¹³C NMR (C₆D₆): δ 64.11, 49.49, 46.55, 46.27, 42.45, 37.04, 36.41, 32.22, 30.16, 24.99, 24.35, 21.61, 10.82. IR (KBr, neat) 3335 (w), 2966 (s), 2874 (s), 2490 (w), 2100 (s: azide), 2040 (m), 1466 (m), 1390 (m), 1368 (m), 1234 (m). HRMS (ESI) 194.1903 (Calcd for [M - N₂ + H]⁺ 194.1909). Anal. Calcd for C₁₃H₂₃N₃: C, 70.54; H, 10.47; N, 18.98. Found: C, 70.68; H, 10.38; N, 18.94. [α]²⁹⁸_D = +7.7 ± 0.7 deg cm² g⁻¹ (c = 0.1, pentane).
**Mo(NCamPr)Cl₄(THF)** (CamPr = (1S,4S)-5-(2-azidopropan-2-yl)-2,2,3-trimethylbicyclo[2.2.1]heptyl) (35). MoCl₄(THF)₂ (1.14g, 3.0 mmol) and 34 (660 mg, 3.0 mmol) were combined in a 500 mL Schlenk flask and 50 mL of toluene was added. The mixture was stirred under a flow of nitrogen at 70 °C overnight. The resulting red solution was reduced to 10 mL in vacuo, and then 200 mL of heptane were added to it. The resulting mixture was stirred for 30 min in a sealed 500 mL Schlenk vessel upon mild heating, then opened and filtered to give dark red solution and 160 mg of tan powder. The blood-red filtrate was reduced in vacuo to 1 mL, and 2 mL of pentane were added to it. It was left at -30 °C for 18 hours, at which point red-brown solid was collected by filtration (414 mg, 0.82 mmol, 43 %). ¹H NMR (C₆D₆): δ 4.49 (br s, 4H), 2.41 (m, 1H), 2.28 (m, 1H), 1.81 (m, 2H), 1.64 (m, 2H), 1.53 (s, 3H), 1.50 (s, 3H), 1.45 (m, 1H) 1.36 (br. s., 4H), 1.10 (m, 1H), 0.91 (d, 3H, J_HH = 7.3 Hz), 0.82 (s, 3H), 0.68 (s, 3H). Anal Calcd for C₁₇H₃₁NMoOCl₄: C, 40.58; H, 6.21; N, 2.78; Cl, 28.28. Found: C, 40.42; H, 6.30; N, 2.67; Cl, 28.39. [α]ᵢ₂⁹₈D = -16.0 deg cm² g⁻¹ (c = 0.01, pentane).

Single crystals for the X-ray study were grown from a pentane solution at -30 °C.

**Mo(NC₆F₅)Np₃Cl** (20). A solution of NpMgCl (25.0 mmol) in 20 mL of ether was cooled to -78 °C and a solution of Mo(NC₆F₅)Cl₄(THF) (4.09 g, 8.3 mmol) in 20 mL of toluene was added to it dropwise with stirring. The reaction mixture was stirred at -78 °C for 20 min then warmed to 20 °C and stirred for 2 h. The solvents were removed in vacuo, the solid residue was extracted with 70 mL of pentane, and the mixture was filtered. The pentane was removed in vacuo to give the pale yellow crystalline product; yield 1.84 g (3.7 mmol, 45 %). ¹H NMR (C₆D₆): δ 3.275 (s, 6H), 1.155 (s, 27H); ¹⁹F NMR (C₆D₆): δ -141.27 (d, J_FF = 22.2 Hz, 2F), -151.55 (m, F), -160.31 (m, 2F). Anal. Calcd for C₁₇H₃₁NMoOCl₄: C, 40.58; H, 6.21; N, 2.78; Cl, 28.28. Found: C, 47.81; H, 6.27; N, 2.66; Cl, 6.74. [α]ᵢ₂⁹₈D = -16.0 deg cm² g⁻¹ (c = 0.01, pentane).

**Mo(N[3,5-(CF₃)₂C₆H₃])Np₃Cl** (21). A solution of NpMgCl (37.4 mmol) in 25 mL of diethyl ether was cooled to -78 °C and a solution of Mo(3,5-(CF₃)₂C₆H₃N)Cl₄(THF) (7.13 g, 12.5
mmol) in 35 mL of ether was added to it dropwise while the mixture was stirred. The reaction mixture was stirred at -78 °C for 1 h, and then it was warmed to 20 °C and stirred for 2 h. Ether was removed in vacuo and the solid residue was extracted with 400 mL of pentane for 2 h. The mixture was filtered and pentane was removed from the filtrate in vacuo to give the yellow crystalline product; yield 2.52 g (4.4 mmol, 35 %): H NMR (C₆D₆): δ 8.16 (s, 2H), 7.52 (s, 1H), 3.09 (s, 6H), 1.05 (s, 27H); F NMR (C₆D₆): δ -62.49 (s, 6F); C NMR (C₆D₆) δ 154.3 (quintet, J_CF = 4 Hz), 133.3 (q, J_CF = 34.6 Hz), 129.0 (s), 126.6 (s), 122.6 (q, J_CF = 274.1 Hz), 86.7 (s), 36.1 (s), 33.7 (s). Anal. Calcd for C₂₃H₃₆NClF₆Mo: C, 48.30; H, 6.34; N, 2.45; Cl, 6.20. Found: C, 48.16; H, 6.29; N, 2.40; Cl, 6.30.

Single crystals for the X-ray study were grown from a pentane solution at -30 °C.

Mo(NAd)Np₃Cl (22). A solution of NpMgCl (4.00 mmol) in 15 mL of diethyl ether was cooled to -78 °C and a solution of Mo(NAd)Cl₄(THF) (608 mg, 1.33 mmol) in 15 mL of toluene was added to it dropwise with stirring. The reaction mixture was warmed to 20 °C and stirred for 2 h. The solvents were removed in vacuo and the solid residue was extracted with 100 mL of pentane. The mixture was filtered and the pentane was removed in vacuo to give a brown crystalline product; yield 193 mg (0.68 mmol, 51 %): H NMR (C₆D₆): δ 2.92 (s, 6H), 2.21 (d, J_HH = 2.8 Hz, 6H), 1.59 (s, 3H), 1.41 (br s, 6H), 1.24 (s, 27H). Anal. Calcd for C₂₅H₄₈NClMo: C, 60.78; H, 9.79; N, 2.84; Cl, 7.18. Found: C, 60.65; H, 9.85; N, 2.73; Cl, 7.14.

Mo(NAr)Np₃Cl (23). Mo(NAr)Cl₄(THF) (915 mg, 1.89 mmol) was dissolved in 10 mL of toluene. The solution was cooled to -30 °C and added dropwise to a cold solution of NpMgCl (5.66 mmol) in 5 mL of diethyl ether. The mixture was stirred at room temperature for 18 h. The solvents were removed in vacuo and the resulting brown residue was extracted with pentane. The mixture was filtered and the solvent was removed in vacuo to give yellow powder; yield 414 mg (0.80 mmol, 42 %): H NMR (C₆D₆): δ 6.97 (s, 3H), 4.07 (septet, J_HH = 6.6 Hz, 2H), 3.04 (s,
Mo(NCPh₃)Np₃Cl (24). Mo(NCPh₃)Cl₄(THF) (13.6 g, 24 mmol) was dissolved in 50 mL of toluene. The solution was cooled to -78 °C and added dropwise to a solution of NpMgCl (77 mmol) in 100 mL of diethyl ether. The mixture was stirred at room temperature for 3 h. The solvents were removed in vacuo and the resulting brown residue was extracted with 400 mL of pentane. The extract was filtered and the solution was reduced in volume in vacuo to 100 mL and left at -30 °C for 12 h. The first crop of off-white crystals was collected and the remaining solution was reduced in volume to 20 mL and left at -30 °C for 1 day. Three additional crops were collected over a period of three days; yield 6.28 g (10 mmol, 42 %): ¹H NMR (C₆D₆): δ 7.44-7.41 (m, 6H), 7.16-7.05 (m, 9H), 3.12 (s, 6H), 1.03 (s, 27H). Anal. Calcd for C₃₄H₄₈NClMo: C, 67.82; H, 8.03; Cl, 5.89; N, 2.33. Found: C, 68.48; H, 8.26; Cl, 5.69; N, 2.17.

Single crystals for the X-ray study were grown from a pentane solution at -30 °C.

Mo(NAr)(CH-t-Bu)Np₂ (18). 24 (465 mg, 0.89 mmol) and NpLi (69.4 mg, 0.89 mmol) were dissolved in 5 mL of pentane in separate vials and each solution was cooled to -30 °C. The solution of Mo(NAr)Np₃Cl was added to the solution of NpLi and the mixture was stirred at room temperature for 12 h. The LiCl was removed by filtration. The filtrate was stirred with dry activated charcoal, filtered and the solvent was removed to give brown powder; yield 389 mg (0.80 mmol, 90 %). The NMR spectral data for this compound match those reported.¹³

Mo(NCPh₃)(CH-t-Bu)Np₂ (25). 23 (600 mg, 0.95 mmol) was dissolved in 6 mL of toluene and the solution was cooled to -30 °C. Solid NpLi (81.7 mg, 1.05 mmol) was added to the solution and the reaction mixture was stirred for 24 h at room temperature. Activated charcoal was added to the reaction mixture and the mixture was stirred for 1 hr. Toluene was removed in vacuo. The mixture was redissolved in pentane and the solution was filtered. The
pentane was removed *in vacuo* to yield an ivory powder; yield 539 mg (0.91 mmol, 96 %): \( ^1\)H NMR (C\(_6\)D\(_6\)): \( \delta \) 8.95 (s, J\(_{CH} = 108.5 \) Hz, 1H), 7.61-7.58 (m, 6H), 7.15-7.02 (m, 9 H), 2.45 (d, J\(_{HH} = 11.7 \) Hz, 2H), 1.10 (s, 18H), 1.06 (s, 9H), 0.98 (d, J\(_{HH} = 11.7 \) Hz, 2H). Anal. Calcd for C\(_{34}\)H\(_{47}\)NMo: C, 72.19; H, 8.37; N, 2.48. Found: C, 72.28; H, 8.24; N, 2.39.

**Conversion of 24 to Mo(NAr)(CH-t-Bu)NpCl.**  24 (32.1 mg, 0.062 mmol) was dissolved in 0.6 mL of C\(_6\)D\(_6\) in a J. Young tube to give 0.1N solution and the solution was heated to 50 °C for 8 h. The \( ^1\)H NMR spectrum showed that Mo(NAr)Np\(_3\)Cl had been converted quantitatively to Mo(NAr)(CH-t-Bu)NpCl in a reaction that was unimolecular with \( k = 9.0 \times 10^{-5} \) s\(^{-1}\): \( ^1\)H NMR (C\(_6\)D\(_6\)): \( \delta \) 11.71 (s, J\(_{CH} = 109 \) Hz, 1H), 6.97 (s, 3H), 3.82 (septet, J\(_{HH} = 6.9 \) Hz, 2H), 2.63 (d, J\(_{HH} = 13.2 \) Hz, 1H), 1.91 (d, J\(_{HH} = 13.2 \) Hz, 1H), 1.22 (s, 3H), 1.20 (s, 3H), 1.19 (s, 3H), 1.17 (s, 3H), 1.14 (s, 9H), 1.01 (s, 9H).

A 0.2 N solution of Mo(NAr)Np\(_3\)Cl (72.8 mg, 0.14 mmol) in 0.7 mL of C\(_6\)D\(_6\) was heated to 50 °C for 8 h. The reaction was unimolecular with \( k = 9.5 \times 10^{-5} \) s\(^{-1}\). At an initial concentration of 0.1 M \( k_{50} = 9.0 \times 10^{-5} \) s\(^{-1}\).

A 0.1 N solution of Mo(NAr)Np\(_3\)Cl (35 mg, 0.07 mmol) in 0.7 mL of C\(_6\)D\(_6\) was heated to 60 °C for 4 h. The reaction was unimolecular with \( k = 3.0 \times 10^{-4} \) s\(^{-1}\).

**Mo(NCPh\(_3\))Np\(_3\)(OC\(_6\)F\(_5\)) (29).**  25 (244 mg, 0.41 mmol) was dissolved in 4 mL of benzene and solid C\(_6\)F\(_5\)OH (75.6 mg, 0.41 mmol) was added. The mixture was stirred for 24 h, then benzene was removed and solid residue was redissolved in 5 mL of pentane and stirred with dry activated charcoal for 1 hr. The solution was filtered and the solvent was removed from the filtrate to give off-white powder; yield 293 mg (0.38 mmol, 93 %): \( ^1\)H NMR (C\(_6\)D\(_6\)): \( \delta \) 7.50-7.47 (m, 6H), 7.17-7.06 (m, 9H), 2.76 (s, 6H), 0.93 (s, 27 H); \( ^{19}\)F NMR (C\(_6\)D\(_6\)): \( \delta \) -156. 08 (m, 2F), -165.46 (m, 2F), -175.42 (m, 1F). Anal. Calcd for C\(_{41}\)H\(_{56}\)NOF\(_5\)Mo: C, 63.97; H, 7.33; N, 1.82. Found: C, 64.14; H, 7.24; N, 1.76.
3,5-(2,4,6-i-Pr₃C₆H₂)₂C₆H₃OH (HIPTOH). n-BuLi (0.85 mmol) was added to a solution of 3,5-(2,4,6-i-Pr₃C₆H₂)₂C₆H₃Br (400 mg, 0.71 mmol) in 20 mL of dry THF, that had been cooled to –78 °C. In 15 min B(OMe)₃ (0.24 mL, 2.13 mmol) was added to the mixture. The mixture was allowed to warm to room temperature and was stirred for 2 h. Anhydrous N-methylmorpholine N-oxide (250 mg, 2.13 mmol) was added to the reaction mixture and the mixture was refluxed for 5 h. The mixture was diluted with 50 mL of diethyl ether and washed with water (5*50 mL). The aqueous washes were extracted with ether; the ethereal fractions were combined and dried with MgSO₄. The solvents were removed in vacuo; the oily residue was transferred to a silica gel column and eluted with hexanes, then 5:1 hexanes/ether mixture and then 1:1 hexanes/ether mixture. The second collected fraction upon solvent removal gave a white powder; yield 260 mg (0.52 mmol, 73 %): ¹H NMR (C₆D₆): δ 7.20 (s, 4H), 7.13 (s, 2H), 6.53 (s, 1H), 3.91 (s, 1H), 3.03 (septet, J₃H = 11.3 Hz, 4H), 2.87 (septet, J₃H = 11.1 Hz, 2H), 1.28 (d, J₃H = 11.3 Hz, 24H), 1.22 (septet, J₃H = 11.1 Hz, 12H).

Mo(NCPh₃)(CH-t-Bu)Np[O-(2,6-Me₂C₆H₃)] (26). 25 (486 mg, 0.76 mmol) was dissolved in 2 mL of pentane and 2,6-dimethyl phenol (92.5 mg, 0.82 mmol) was added. The solution was stirred for 24 h. Activated charcoal was added and the mixture was stirred for 1 hr. The solution was filtered and the solvent was removed in vacuo to give the product as a yellow powder; yield 434 mg (0.71 mmol, 93 %): ¹H NMR (C₆D₆): δ 11.69 (s, 1H), 7.54-7.16 (m, 6H), 7.10-6.93 (m, 9 H), 6.88-6.74 (m, 3H), 2.73 (d, J₃H = 12.4 Hz, 1H), 2.34 (d, J₃H = 12.4 Hz, 1H), 2.16 (s, 6H), 1.16 (s, 9H), 1.08 (s, 9H). ¹³C NMR (C₆D₆): δ 277.52 (d, J₃C = 109.4 Hz). Anal. Calcd for C₃₇H₄₅NOMo: C, 72.18; H, 7.37; N, 2.27. Found: C, 72.06; H, 7.41; N, 2.19.

Mo(NCPh₃)(CH-t-Bu)Np[O-(2,6-i-Pr₂C₆H₃)] (27). 25 (228 mg, 0.38 mmol) was dissolved in 2 mL of pentane and 2,6-diisopropyl phenol (68.5 mg, 0.38 mmol) was added. The solution was stirred for 24 h. Activated charcoal was added and the mixture was stirred for 1 hr. The solution was filtered and the solvent was removed to give brown oil; yield 235 mg (0.35
mmol, 92 %): $^1$H NMR (C$_6$D$_6$): $\delta$ 11.81 (s, 1H), 7.53-7.50 (m, 6H), 7.14-6.93 (m, 12 H), 3.44 (quintet, $J_{HH} = 6.9$ Hz, 2H), 2.82 (d, $J_{HH} = 12.5$ Hz, 1H), 2.29 (d, $J_{HH} = 12.5$ Hz, 1H), 1.19 (s, 9H), 1.19 (d, $J_{HH} = 6.6$ Hz, 12H), 1.10 (s, 9H); $^{13}$C NMR (C$_6$D$_6$): $\delta$ 278.38 (d, $J_{CH} = 111.7$ Hz).

Anal. Calcd for C$_{41}$H$_{53}$NOMo: C, 73.30; H, 7.95; N, 2.08. Found: C, 73.15; H, 7.90; N, 1.96.

**Mo(NCPh$_3$)(CH-t-Bu)Np(OHPT) (28).** 25 (159 mg, 0.32 mmol) was dissolved in 2 mL of pentane and 2 mL of ether and solid HIPTOH (189 mg, 0.32 mmol) was added. The solution was stirred for 24 h. Activated charcoal was added and the mixture was stirred for 1 hr. The solution was filtered and the solvent was removed to give the product as a golden yellow powder; yield 299 mg (0.30 mmol, 95 %): $^1$H NMR (C$_6$D$_6$): $\delta$ 11.45 (s, 1H), 7.57-7.42 (m, 8H), 7.32-6.90 (m, 13 H), 6.72 (s, 1H), 3.08 (septet, $J_{HH} = 11.3$ Hz, 4H), 2.88 (septet, $J_{HH} = 11.1$ Hz, 2H), 2.53 (d, $J_{HH} = 13$ Hz, 1H), 2.26 (d, $J_{HH} = 13$ Hz, 1H), 1.30 (d, $J_{HH} = 11.3$ Hz, 24H), 1.22 (s, 9H), 1.19 (d, $J_{HH} = 11.1$ Hz, 12H), 1.03 (s, 9H); $^{13}$C NMR (C$_6$D$_6$): $\delta$ 278.00 (d, $J_{CH} = 112.8$ Hz).

Anal. Calcd for C$_{65}$H$_{85}$NOMo: C, 78.67; H, 8.63; N, 1.41. Found: C, 78.58; H, 8.57; N, 1.37.

Single crystals for the X-ray study were grown from a pentane solution at -30°C.

**Mo(NCPh$_3$)$_2$Cl$_2$(dme).** Ph$_3$CNH$_2$ (11.53 g, 0.044 mol), Na$_2$MoO$_4$ (4.53 g, 0.022 mol), Et$_3$N (8.90 g, 12.3 mL, 0.088 mol), and trimethylsilyl chloride (23.9 g, 27.9 mL, 0.22 mol) were dissolved in 150 mL of dry DME. Upon stirring at 65 °C for 12 h the mixture became bright yellow. The solids were filtered off and the solvent was removed from the filtrate in vacuo to give a yellow powder. The yellow powder was triturbated with 100 mL of pentane, filtered off, and dried in vacuo. The pentane washes were reduced to 20 mL in volume in vacuo and an additional crop of the product was crystallized from this solution; yield 11.27 g (0.015 mol, 66 %): $^1$H NMR (C$_6$D$_6$): $\delta$ 7.57-7.53 (m, 12 H), 7.03-7.01 (m, 18 H), 3.05 (s, 4H), 3.01 (s, 6H).

Anal. Calcd for C$_{42}$H$_{40}$N$_2$O$_2$Cl$_2$Mo: C, 65.37; H, 5.23; N, 3.63; Cl, 9.19. Found: C, 65.47; H, 5.20; N, 3.51; Cl, 9.23.
Mo(NCPh₃)₂(CH₂CMe₂Ph)₂. A solution of Mo(Ph₃CN)₂Cl₂(dme) (2.06 g, 3.63 mmol) dissolved in 30 mL of toluene was cooled to -78 °C. A solution of (PhCMe₂CH₂)MgCl (7.25 mmol) in 15 mL of ether was added dropwise to the reaction mixture. The mixture was allowed to warm up to room temperature and was stirred for 12 h. The solvents were removed in vacuo and the solid residue was redissolved in 20 mL of toluene. After addition of 4 mL of 1,4-dioxane the mixture was stirred for 1 h and the white precipitate was removed by filtration. The solvents were removed in vacuo and the solid was triturated with pentane overnight. The product was filtered off and the pentane washes were reduced to 5 mL and left at -35 °C for 12 h. The material that crystallized from pentane was collected and combined with the solid obtained from trituration to give a tan powdery product; yield 1.84 g (2.1 mmol, 58 %): ¹H NMR (C₆D₆): δ 7.26-7.12 (m, 16 H), 7.10-7.01 (m, 24 H), 2.13 (s, 4H), 1.34 (s, 12H). Anal. Calcd for C₅₈H₅₆N₂Mo: C, 79.43; H, 6.44; N, 3.19. Found: C, 79.57; H, 6.41; N, 3.11.

Representative olefin metathesis with Mo(NCPh₃)(CH-t-Bu)Np(OR) complexes. Diallyl ether (10.6 mg, 0.108 mmol) was dissolved in 1 mL of C₆D₆ in a 20 mL vial and 28 (5.4 mg, 5.5x10⁻³ mmol) was added. The reaction mixture was stirred for 1 hr and then transferred to a J. Young tube. Conversion of the ring-closing metathesis reaction with time was judged by analysis of the ¹H NMR spectrum. The amine substrates shown in Figure 14 were prepared as described in the literature.⁵⁶
Table 4. Crystal data and structure refinement for Mo[N-3,5-(CF3)2C6H3]Cl4(THF), Mo[N-3,5-(CF3)2C6H3]Np3Cl (21), Mo[NC(C6H5)3]Np3Cl (23), and Mo(NCPh3)(CH-t-Bu)Np(OHIPT) (28).a

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<td>9.8338(7)</td>
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<td>32.380(2)</td>
<td>17.416(4)</td>
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<td>90</td>
<td>90</td>
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<td>103.7330(10)</td>
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<td>3171.7(11)</td>
<td>5642(6)</td>
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<td>4</td>
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<td>54550</td>
<td>125702</td>
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<td>R(int)</td>
<td>R(int)</td>
<td>R(int)</td>
<td>R(int)</td>
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<td>--------------------------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
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</tr>
<tr>
<td>Indep. reflections</td>
<td>3233 [0.0233]</td>
<td>6297 [0.0153]</td>
<td>6532 [0.0300]</td>
<td>27827 [0.07980]</td>
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<td>99.8 % (26.44°)</td>
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<td>1.114</td>
<td>1.097</td>
<td>1.091</td>
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<td>R1 = 0.0309</td>
<td>R1 = 0.0265</td>
<td>R1 = 0.0685</td>
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<td>wR2 = 0.0883</td>
<td>wR2 = 0.0755</td>
<td>wR2 = 0.0669</td>
<td>wR2 = 0.1461</td>
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<td>wR2 = 0.0929</td>
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<td>1.268 and -1.101</td>
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* In each case the wavelength was 0.71073 Å, the refinement method a full-matrix least-squares on F^2, and the absorption correction was semi-empirical.
Table 8. Crystal data and structure refinement for complex 35.

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<td>Formula weight</td>
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<td>Temperature</td>
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<td>Wavelength</td>
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<td>Crystal system</td>
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<td>Space group</td>
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<td>Unit cell dimensions</td>
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<tr>
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<td>Density (calculated)</td>
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<td>Reflections collected</td>
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<td>Independent reflections</td>
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<td>Absorption correction</td>
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<td>Largest diff. peak and hole</td>
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</table>
2.5 References.


39 (CH₂Cl)₂, 70 °C, 18h; toluene, 50 °C, 12h; THF, room temperature, 9 days.


Chapter 3

Reactions of Mo Bispyrrolide Complexes with Enantiomerically Pure Diols: In Situ Catalyst Generation and Studies of Olefin Metathesis Reactions In the Fume Hood.

\[
\text{In Situ}
\]

\[
\text{N}_{2} \quad \xleftarrow{\text{PhN}} \quad \text{PhN} \quad \xrightarrow{2 \, h, \, 25 \, ^{\circ}\text{C}} \quad \text{PhN} \\
\text{In Situ}
\]

\[
\text{N}_{2} \quad \xleftarrow{\text{PhN}} \quad \text{PhN} \quad \xrightarrow{2 \, h, \, 25 \, ^{\circ}\text{C}} \quad \text{PhN} \\
\text{In Situ}
\]

\[
\text{N}_{2} \quad \xleftarrow{\text{PhN}} \quad \text{PhN} \quad \xrightarrow{2 \, h, \, 25 \, ^{\circ}\text{C}} \quad \text{PhN} \\
\text{In Situ}
\]

\[
\text{N}_{2} \quad \xleftarrow{\text{PhN}} \quad \text{PhN} \quad \xrightarrow{2 \, h, \, 25 \, ^{\circ}\text{C}} \quad \text{PhN} \\
\text{In Situ}
\]

\[
\text{N}_{2} \quad \xleftarrow{\text{PhN}} \quad \text{PhN} \quad \xrightarrow{2 \, h, \, 25 \, ^{\circ}\text{C}} \quad \text{PhN} \\
\text{In Situ}
\]
3.1 Introduction.

Over the last ten years our group has developed a large library of asymmetric olefin metathesis catalysts that vary in their activity and selectivity towards different classes of organic substrates.\(^1\) Presently ten to twenty catalysts are routinely screened in our laboratory and in the Hoveyda group at Boston College when the metathesis reactions of new organic compounds are investigated. The isolation of individual catalysts and setting up the catalytic reactions is time- and labor-consuming, therefore we started to look for a universal protocol for in situ generation of Mo-based catalysts several years ago.

Generation of catalysts in situ is a technique widely applied to the discovery and applications of organic reactions. The individual catalysts are not isolated and can be prepared from a common precatalyst, therefore allowing for screening of large libraries of catalysts in short periods of time or simultaneously, employing high-throughput screening procedures.\(^2,3,4,5,6,7,8,9\) Chemists may also use stable precatalysts in order to generate much more sensitive catalytic species without isolation. This approach allows one to avoid the cumbersome process of preparation and purification of highly reactive compounds.\(^10\) The organometallic precursors for in situ catalysts are generally designed to meet several necessary criteria: a) they should yield the catalytic species via a clean and rapid reaction; b) the side products of this conversion should not interfere with the catalytic reaction; and c) the precatalysts should be minimally reactive towards the substrates.

Several examples of the in situ prepared 2\(^{\text{nd}}\) generation Grubbs catalysts applied to ring-opening metathesis polymerization, cross metathesis, and ring-closing metathesis reactions have been published.\(^9,11,12,13\) Our group also reported the in situ synthesis of an asymmetric olefin metathesis catalyst from a Mo imido alkylidene bistriflate complex and an enantiomerically pure lithium diolate. The catalysts gave levels of activity and selectivity identical to the ones obtained with the analogous isolated catalyst.\(^14\) However, this approach to catalyst preparation in some
cases yields undesired side products and therefore cannot be used as a universal method to synthesize Mo-based catalysts in situ.

Certain amido complexes of Mo are known to react with alcohols giving molybdenum alkoxide complexes.\textsuperscript{15,16,17} Dr. Amritanshu Sinha showed that this transformation can be employed in the synthesis of catalytically active Mo(NAr)(CHCMe\textsubscript{2}Ph)(OR)\textsubscript{2} species from bisamido complexes Mo(NAr)(CHCMe\textsubscript{2}Ph)(NR’’R’’)\textsubscript{2} (Ar = 2,6-i-Pr\textsubscript{2}C\textsubscript{6}H\textsubscript{3}, 2,6-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{3}; NR’’ = NPh\textsubscript{2}, N(t-Bu)(3,5-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{3}), N(i-Pr)(3,5-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{3})) upon treatment with 2 equivalents of alcohol ROH.\textsuperscript{18} The bisamido complexes slowly reacted with monobasic alcohols and enantiomerically pure binaphthols, but failed to give appreciable conversions to the desired bisalkoxide upon exposure to a bulky biphenol, (S)-BiphenH\textsubscript{2} (BiphenH\textsubscript{2} = 3,3’-di-tert-butyl-5,5’,6,6’-tetramethyl-1,1’-biphenyl-2,2’-diol).\textsuperscript{19} Slow alcoholysis rates and the difficulties in isolation of the complexes of type Mo(NAr)(CHCMe\textsubscript{2}Ph)(NR’’R’’)\textsubscript{2} suggested that these species are not ideal precursors to the in situ Mo(NAr)(CHCMe\textsubscript{2}Ph)(OR)\textsubscript{2} catalysts. The focus of the project shifted towards investigation of a different type of amido ligands, and Dr. Adam Hock discovered that molybdenum bispyrrolide complexes, Mo(NR)(CH-t-Bu)(pyr)\textsubscript{2} (pyr = NC\textsubscript{4}H\textsubscript{4}), can serve as convenient precursors to Mo(NR)(CH-t-Bu)(OR’)\textsubscript{2} catalysts.\textsuperscript{20} Mo(NR)(CH-t-Bu)(pyr)\textsubscript{2} are synthesized via a reaction of the corresponding bistriolate complexes, Mo(NR)(CH-t-Bu)(OTf)\textsubscript{2}(dme), with lithium pyrrolide, and can be rapidly and cleanly converted into Mo(NR)(CH-t-Bu)(OR’)\textsubscript{2} complexes upon treatment with alcohols (including bulky biphenols). Mo(NAr)(CH-t-Bu)(pyr)\textsubscript{2} (Ar = 2,6-i-Pr\textsubscript{2}C\textsubscript{6}H\textsubscript{3}) was shown to be almost unreactive towards olefins, producing one equivalent of PhMe\textsubscript{2}CHC=CH\textsubscript{2} in neat isobutylene over two days and failing to yield any ring-closing metathesis product in the presence of 10 equivalents of diallyl ether.\textsuperscript{21} Based on these observations it was concluded that the complexes of the type Mo(NR)(CH-t-Bu)(pyr)\textsubscript{2} are promising candidates for a new method to generate olefin metathesis catalysts in situ. Therefore we decided to study the catalytic properties of enantiomerically pure
complexes synthesized in situ from Mo bispyrrolide precursors and chiral diols, and compare the results to those obtained with the corresponding isolated catalysts. We were also interested in establishing a protocol that would allow synthetic organic chemists to take advantage of this new convenient way of catalysts generation, and show that Mo-catalyzed metathesis reactions can be carried in the fume hood using standard precautions applied to air-sensitive compound.

3.2 Results and Discussion.

3.2.1 Reactions of Mo bispyrrolide complexes with alcohols.

Some of the Mo-based olefin metathesis catalysts synthesized in our group are isolated as THF adducts (Figure 16). It is known that the reactivity and selectivity of these species towards certain substrates is altered when excess THF is introduced into the reaction mixture. Coordinating solvent therefore plays an important role in the catalytic properties of such complexes. We were interested in preparing some of these complexes from bispyrrolide precursors and investigating whether pyrrole liberated in the course of the reaction binds to the formed products. In order to determine if C_4H_4NH binds to the bisalkoxide complexes, the reactions involving bispyrrolide complexes were compared to the reactions involving bulkier bis(2,5-dimethylpyrrolide) species. We chose to study the reactions of complexes 40 and 41 with (R)-TripH \_2 \ (TripH \_2 = 3,3'\text{-bis}(2,4,6\text{-triisopropylphenyl})\text{-}1,1'\text{-binaphthyl}-2,2'\text{-diol}) as well as the reactions of compounds 42 and 43 (Figure 17) with (R)-Benz_2BitetH \_2 \ (Benz_2BitetH \_2 = 3,3'\text{-dibenzydryl}-5,5',6,6',7,7',8,8'-octahydro-1,1'\text{-binaphthyl}-2,2'\text{-diol}).

Pyrrole is an aromatic compound with resonance stabilization energy 21.6 KJ/mol. The lone pair on the pyrrole nitrogen is perpendicular to the plane of the molecule and contributes to the aromatic π-system. Therefore pyrrole is a poor donor and does not efficiently coordinate to metal complexes through the nitrogen atom; no example of a structurally characterized pyrrole complex of this type is known.
Figure 16. Examples of enantiomerically pure Mo-based olefin metathesis catalysts isolated as THF adducts.

Figure 17. Molybdenum imido alkylidene bispyrrolide complexes 40 – 43.
In solution pyrrole exists as an equilibrium of three tautomeric forms (Scheme 26). Tautomers of unsubstituted pyrrole B and C are non-aromatic compounds and therefore are higher in energy than structure A; these molecules have never been experimentally observed in the absence of external stabilization such as formation of Lewis acid adducts. Different calculations place tautomer B, known as 2H-pyrrole or pyrrolenine, at 10.30 kcal/mol, 12.0 kcal/mol, 14.0 kcal/mol, 13.8 kcal/mol, and 16.0 kcal/mol higher than pyrrole A. The same calculations show that tautomer C, known as 3H-pyrrole, is approximately 2 kcal/mol higher in energy than compound B. The transition state in the $A \rightarrow B$ transformation was calculated to be at 43 – 48 kcal/mol, which means that at room temperature this reaction is relatively slow. Nitrogen is not the most basic site of the molecule; protonation of pyrrole occurs at $\beta$-carbon atom, and its conjugate acid has a pKa of -3.8.

Reaction of pyrrole with B(C$_6$F$_5$)$_3$ leads to formation of a pyrrolenine adduct. This adduct can also be isolated upon treatment of Li pyrrolide with B(C$_6$F$_5$)$_3$, followed by addition of HCl. Therefore it is not surprising that coordinated pyrrolide anions and $\eta^2$-coordinated pyrroles tend to undergo rearrangement upon protonation to form pyrrolenine. Examples of the rearrangements of this type are known for complexes of Os, Re, and W. In some cases pyrrolenine was observed to form $\sigma$-bonds with the metal center through the nitrogen or $\beta$-carbon atoms. Pyrrolenine ligand can also be $\eta^2$-coordinated through C=C or C=N bond.

Coordinated pyrrolenines exhibit a characteristic chemical shift of the imine carbon in the $^{13}$C NMR spectra at 170-185 ppm. These values lie within the typical range of $^{13}$C

Scheme 26. Three tautomeric forms of pyrrole.
chemical shifts of non-aromatic imines, while the chemical shift of β-carbons in pyrrole is 117.3 ppm, and the imine carbons in pyrazole and imidazole resonate at 136.3 ppm and 134.6 ppm, respectively. We were planning to use these data to assess the structure and binding mode of pyrrole in the possible adducts formed upon reactions of 40, 41, 42, and 43 with diols.

3.2.1.a Reactions of 40 and 41 with (R)-TripH₂.

\(^1\)H NMR spectra of the reaction between 40 and (R)-TripH₂ are shown in Figure 18. After the reaction mixture is stirred for 20 minutes, several new peaks can be observed in the alkylidene region of the spectrum. The major signal at 11.62 ppm (\(J_{CH} = 115\) Hz) is assigned to the syn isomer of the product. After 18 hours one of the initially minor peaks at 13.56 ppm (anti isomer, \(J_{CH} = 145\) Hz) becomes the major one (ca. 75 %), while the signal at 11.62 ppm remains relatively strong (ca. 25 %).

Close examination of the \(^1\)H and \(^{13}\)C NMR spectra of the 40 + (R)-TripH₂ reaction mixture reveals that the anti isomer formed in this reaction (alkylidene proton chemical shift at 13.56 ppm) is most likely a pyrrolenine adduct. In the olefinic region of the \(^1\)H NMR spectrum of this mixture two doublets are observed at 6.27 ppm and 5.76 ppm (\(J_{HH} = 5.3\) Hz). These peaks can be assigned to the \(\text{N}=\text{CH}-\text{CH}_{2}-\text{CH}=\text{CH}\) protons. Two signals of the AB system corresponding to the allylic hydrogens (\(\text{N}=\text{CH}-\text{CH}_{2}-\text{CH}=\text{CH}\)) are found at 3.62 ppm and 2.83 ppm (\(J_{HH} = 25.5\) Hz). These values are in agreement with the \(^1\)H NMR data reported for the complex of pyrrolenine and B\((\text{C}_6\text{F}_5)_3\). Large values for the spin-spin coupling constants of allylic protons were reported for a pyrrolenine molecule \(\eta^2\)-coordinated to a Re atom (\(J_{HH} = 19.6\) Hz), but in this case the chemical shifts of these protons were observed at 5.02 ppm and 4.91 ppm. The \(^{13}\)C NMR spectrum of the reaction mixture 40 + (R)-TripH₂ contains a peak at 172.25 ppm (doublet, \(J_{CH} = 189\) Hz) and a signal at 78.03 ppm. The resonance at 172.25 ppm is assigned to an imine carbon (the large coupling constant supports this assignment) and the peak at 78.03 ppm corresponds to an allylic
carbon.$^{33,31,37,38}$ These signals are not present in the spectrum of the analogous THF adduct, 38, and point at the formation of a pyrrolenine adduct. The resonance at 78.03 indicates the presence of pyrrolenine, and not 3H-pyrrole, since allylic protons in 3H-pyrroles usually resonate more upfield.$^{39,34}$

We believe that the signal at 11.63 ppm belongs to a solvent-free syn species, since there is only one set of pyrrolenine signals in the $^{13}$C and $^1$H NMR spectra of the product mixture. We attribute these signals to the molecule of pyrrolenine bound to the anti isomer. The resonance at 11.63 ppm is also observed in the reaction mixture of Mo bis(2,5-dimethylpyrrolide) complex 41 and (R)-TripH$_2$ (see below). We do not expect the alkylidene protons in the syn adducts of pyrrolenine (formed from 40) and 2,5-dimethylpyrrolenine (formed from 41) to have the same chemical shift, therefore this finding supports the proposed solvent-free structure of this syn species.

Our assignment of the signal at 13.56 ppm to the pyrrolenine-bound anti isomer is supported by the results that were observed when a mixture of 40 and (R)-TripH$_2$ was exposed to 10 equivalents of THF (Figure 19). While THF seems to bind instantaneously to the syn complexes, the proposed pyrrolenine-bound anti isomer is still the major species in solution 20 minutes after THF addition. After 20 hours in the presence of excess THF some amount of the pyrrolenine adduct can still be observed (13.54 ppm). Therefore we are quite confident that the complex formed in the reaction between 40 and (R)-TripH$_2$ contains coordinated pyrrolenine and is similar in this respect to the analogous isolated catalyst 38, which contains a coordinated THF.$^{40}$
Figure 18. $^1$H NMR spectra of the reaction between 40 and (R)-Triph$_2$ (25 °C, C$_6$D$_6$).
Figure 19. $^1$H NMR spectra of the reaction between 40 and (R)-TripH$_2$ in the presence of 10 equivalents of THF (25 °C, C$_6$D$_6$).
The observations discussed above are reminiscent of the results obtained in our laboratory by Dr. Stefan Arndt. Dr. Arndt showed that compound $W(2,6$-Cl$_2$C$_6$H$_3$N)(CH-t-Bu)(2,5-Me$_2$C$_4$H$_2$N)$_2$ upon treatment with 1 equivalent of [HNMe$_2$Ph][B(ArF)$_4$] undergoes protonation. The resulting cationic complex contains a 2,5-dimethylpyrrolenine molecule, coordinated to the W atom through a W-N σ-bond. When the 2,5-dimethylpyrrolenine complex is treated with various amounts of THF (1 – 10 equivalents), partial substitution of 2,5-dimethylpyrrolenine by THF occurs. Complete displacement of pyrrolenine happens only when the complex is dissolved in THF-$d_8$; 2,5-dimethylpyrrole can then be observed in solution by $^1$H NMR.

$^1$H NMR spectra of the reaction between 41 and (R)-TripH$_2$ are shown in Figure 20. At room temperature 41 does not react with (R)-TripH$_2$ in C$_6$D$_6$. When the reaction mixture is heated to 75 °C for 20 h, a new resonance appears in the alkylidene region of the $^1$H NMR spectrum at 11.63 ppm. If the mixture is heated for another 20 h, the ratio of the peaks representing the starting material (at 12.94 ppm) and the product (at 11.63 ppm) becomes 1 to 2.6. The $^1$H NMR spectrum does not change if the reaction mixture is left for five days at room temperature. The alkylidene proton resonance at 11.63 ppm can be assigned to the syn solvent-free bisalkoxide product based on the $J_{CH} = 119$ Hz and the fact that this species is also observed in the reaction between 40 and (R)-TripH$_2$. The minor signal at 13.60 ppm is currently believed to represent the anti 2,5-dimethylpyrrolenine adduct.

When the reaction between 41 and (R)-TripH$_2$ in C$_6$D$_6$ is conducted in the presence of 7 equivalents of pyrrole, a different substitution process happens over time (Figure 21). After 3 hours at room temperature only a minor new signal at 13.02 ppm can be observed in the $^1$H NMR spectrum of the reaction mixture. Twenty-three hours later this resonance becomes the major signal in the $^1$H NMR spectrum of the reaction mixture. The signal corresponding to the starting material (41, 12.94 ppm) is still present in the spectrum, and several new signals appear at 13.60 ppm (tentatively assigned to the anti isomer, 2,5-dimethylpyrrolenine adduct), 13.56 ppm (assigned to the anti isomer, pyrrolenine adduct), and 11.63 ppm (assigned to the syn isomer, pyrrole-free complex). After five days at room temperature the $^1$H NMR spectrum of the reaction
mixture does not contain resonances of the starting material at 12.94 ppm or the signal at 13.02 ppm; only four peaks are observed in the alkylidene region of the spectrum (tentative assignment): a major resonance at 13.56 ppm (anti isomer, pyrrolenine adduct), a small signal at 13.60 ppm (anti isomer, 2,5-dimethylpyrrolenine adduct), and two small peaks at 11.93 ppm (syn isomer, an adduct) and at 11.63 ppm (syn isomer, pyrrole-free complex). The nature of the pyrrole molecule bound to the complex with an alkylidene peak at 11.93 ppm is not clear at the moment.

These observations indicate that pyrrole is involved in the substitution process, by presumably first binding to 41 and protonating one of the 2,5-dimethylpyrrolide ligands. The resulting complex 44, with an alkylidene proton appearing at 13.02 ppm in the \(^1\)H NMR spectrum, is less sterically hindered and is capable of reacting with (R)-TripH\(_2\) at room temperature (Scheme 27). It is proposed that the initially formed syn isomer over time binds pyrrole, and the bisalkoxide complex exists in solution predominantly as an anti pyrrolenine adduct.

![Scheme 27](image)

**Scheme 27.** Proposed mechanism of the reaction between 41 and (R)-TripH\(_2\) in the presence of pyrrole.
Figure 20. \(^1\)H NMR spectra of the reaction between 41 and (R)-TripH\(_2\).
Figure 21. $^1$H NMR spectra of the reaction between 41 and (R)-TripH$_2$ in the presence of 7 equivalents of pyrrole (25°C, C$_6$D$_6$).
Our conclusion about the structure of the catalyst formed in situ from 40 and (R)-TripH$_2$ is supported by the results obtained in asymmetric ring-closing metathesis reactions (ARCM) catalyzed by this system. Activities and enantioselectivities of the in situ generated catalyst toward substrates 10 and 13 are essentially identical to the results obtained with the isolated THF-containing catalyst 38 (Schemes 28 and 29). Catalytic reactions with the in situ generated catalyst (ISGC) were carried according to the following procedure: in the nitrogen-filled glovebox a 20 mL vial was charged with an aliquot of 40 (stock solution, C$_6$D$_6$, 10 mg/mL) and (R)-TripH$_2$ (one equivalent, stock solution, C$_6$D$_6$, 10 mg/mL). The mixture was stirred for 15 minutes, at which time the substrate was added (20 equivalents, stock solution, C$_6$D$_6$, 20 mg/mL). The reactions were monitored by $^1$H NMR and TLC; the products were isolated using column chromatography.

![Chemical structure](image)

<table>
<thead>
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<td>92</td>
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$^a$ (R)-TripH$_2$ and 40 were stirred for 18 h at 25 °C prior to the addition of 10.

**Scheme 28.** Asymmetric ring-closing metathesis reaction of 10 using isolated catalyst 38 and ISGC derived from 40 and (R)-TripH$_2$. 
<table>
<thead>
<tr>
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<th>Yield, %</th>
<th>ee, %</th>
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<td>ISGC</td>
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<td>25</td>
<td>67</td>
<td>71</td>
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</table>

Scheme 29. Asymmetric ring-closing metathesis reaction of 13 using isolated catalyst 38 and ISGC derived from 40 and (R)-TripH₂.

The small disparities between results obtained with isolated catalyst 38 and the ISGC can be attributed to the differing reaction conditions shown in Schemes 28 and 29. A comprehensive comparison study employing identical optimized conditions for the reactions with isolated catalysts and ISGCs is discussed below. These preliminary results, however, showed that the ISGC performed at least as well as 38 in terms of both conversions and enantioselectivities in ARCM of compounds 10 and 13. It is worth noting that even though the major species present in solution 20 minutes after complex 40 is mixed with the alcohol are not the same as 18 hours after mixing, as judged by $^1$H NMR spectroscopy (Figure 19), the results of the catalytic studies obtained with the freshly prepared ISGC and the ISGC, that was stirred for 18 hours prior to the substrate addition, were identical (Scheme 28). Note that functionalities in the substrate can bind to Mo and promote loss of pyrroline and its rearrangement to pyrrole.

3.2.1.b Reactions of 42 and 43 with (R)-Benz₂BitetH₂.

Complex 4a, isolated as a THF adduct, is an efficient catalyst for asymmetric olefin metathesis transformations. We were interested in preparing the ISGC from 41 and (R)-
Benz₂BitetH₂ and screen it in olefin metathesis reactions, and therefore needed to know whether the complex formed in the absence of THF from a bispyrrolide precursor would coordinate pyrrole.

¹H NMR spectra of the reactions between the bis(2,5-dimethylpyrrolide) complex 43 with (R)-Benz₂BitetH₂, as well as the reaction of 42 with (R)-Benz₂BitetH₂, are shown in Figure 22. The spectra in Figure 22, A and Figure 22, C indicate that 42 and 43 gave the same product upon treatment with one equivalent of (R)-Benz₂BitetH₂, proving that pyrrole does not bind to the ISGC. The spectra did not change in the next 24 hours, indicating that the reaction is done within the first hour for both Mo complexes. When 25 equivalents of THF were added to both reaction mixtures, identical mixtures of syn and anti THF adducts were formed, as judged by ¹H NMR spectroscopy (Figure 22, B and D). We propose that the resonances at ca. 12.0 ppm (Figure 22, B and D) correspond to the syn THF adduct. The original synthesis of complex 4a reports two alkylidene resonances at 14.07 ppm and 11.16 ppm. The signal at 11.16 ppm represents the syn solvent-free species. The described procedure for the isolation of 4a involved extensive drying and lyophilization of the product with benzene, which was sufficient to remove weakly coordinated THF from the syn, but not from the anti isomer. Overall these findings show that the complex derived from 42 and (R)-Benz₂BitetH₂ is a solvent-free species, and therefore differs structurally from the corresponding isolated complex 4a.
Figure 22. $^1$H NMR spectra of the reactions between 42 and (R)-Benz$_2$BitetH$_2$ (A and B) and 43 and (R)-Benz$_2$BitetH$_2$ (C and D) in the absence and presence of THF (25 equivalents).

3.2.2 Asymmetric olefin metathesis reactions with ISGCs and corresponding isolated catalysts performed in a glovebox.

Initial studies showed that in situ generated catalysts are a valid alternative to the isolated catalysts for the small subset of substrates and catalysts shown in Schemes 28 and 29. Therefore we decided to examine a broader scope of catalytic reactions. Three olefin metathesis reactions shown in Scheme 30 were chosen for the new study, providing a diversity of the substrates
(amine, ethers) and the metathesis transformations: asymmetric ring-closing (ARCM), asymmetric ring-opening/cross metathesis (AROM/CM), and asymmetric ring-opening/ring-closing metathesis (AROM/RCM).

Scheme 30. Asymmetric ring-closing metathesis, asymmetric ring-opening/cross metathesis, and asymmetric ring-opening/ring-closing metathesis reactions chosen for the screening of the ISGCs and analogous isolated catalysts.

Olefin metathesis reactions of 45, 47, and 7 were examined in the presence of three catalytic systems prepared in situ: a) 40 and (R)-BiphenH2 (ISGC 1); 2) 42 and (R)-BiphenH2
These combinations of Mo complexes and chiral diols were chosen because the analogous isolated catalysts (1a, 2a, and 4a, Scheme 31) generally provide efficient and enantioselective metathesis transformations when screened with structurally diverse substrates.

Scheme 31. Catalysts 1a, 2a, and 4a; in situ generated catalysts ISGC 1, ISGC 2, and ISGC 3.

Substrate 45 was synthesized according to the previously published procedure. The synthesis of compound 7 is described in Chapter 1 (Scheme 7, page 31). Substrate 47, on the other hand, was less straightforward to prepare. The original publication discussing this substrate does
not provide the synthetic path to the molecule, and no experimental details are mentioned. The sequence that was employed in the synthesis of compound 47 in this project is shown in Scheme 32.

Scheme 32. Synthesis of compound 47.\textsuperscript{45,46}

Our initial goal was to confirm that catalysts generated in situ provide the same levels of activity and enantioselectivity as the isolated analogs in the reactions carried under standard conditions in the glovebox. These experiments would also allow us to establish a baseline for the future screenings performed in the fume hood. The results of the catalyst screenings are presented in Schemes 33 and 34.
**Scheme 33.** ARCM of compound 45 using ISGCs and catalysts 1a, 2a, and 4a. Results obtained with isolated catalysts 2a and 4a are reported from an earlier publication.\(^{47}\)

<table>
<thead>
<tr>
<th>Mo Precursor</th>
<th>Diol</th>
<th>Time, h</th>
<th>Conv., %</th>
<th>Yield, %</th>
<th>ee, %</th>
<th>Isolated catalyst</th>
<th>Time, h</th>
<th>Conv., %</th>
<th>Yield, %</th>
<th>ee, %</th>
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<tbody>
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<td>90</td>
<td>97</td>
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<td>3</td>
<td>98</td>
<td>80</td>
<td>98</td>
</tr>
<tr>
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<td>(R)-BiphenH₂</td>
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<td>98</td>
<td>86</td>
<td>97</td>
<td>2a</td>
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<td>60</td>
<td>4a</td>
<td>1</td>
<td>95</td>
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<td>61</td>
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</table>

Catalysts loading 5 %, C₆D₆, 25 °C

**Scheme 34.** AROM/CM of compound 7 using ISGCs and catalysts 1a, 2a, and 4a. Results obtained with isolated catalysts 1a and 2a are reported from earlier publications.\(^{47,48}\)

<table>
<thead>
<tr>
<th>Mo Precursor</th>
<th>Diol</th>
<th>Time, h</th>
<th>Conv., %</th>
<th>ee, %</th>
<th>Isolated catalyst</th>
<th>Time, h</th>
<th>Conv., %</th>
<th>ee, %</th>
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<td>53</td>
<td>4a</td>
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<td>98</td>
<td>93</td>
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</tbody>
</table>

Catalysts loading 5 %, C₆D₆, 25 °C
Data presented in Scheme 33 show nearly perfect agreement between the conversion and ee’s obtained with ISGCs and the isolated catalysts.

The results of AROM/CM of compound 7 catalyzed by ISGC 1 and ISGC 2 are very similar to those obtained with the isolated complexes 1a and 2a (Scheme 34, lines 1 and 2). However, the conversion and enantioselectivity delivered by ISGC 3 are drastically different from those obtained with the isolated complex 4a. It was discussed earlier that the species that are formed upon reaction of 42 with (R)-Benz₂BietetH₂ is solvent-free, while 4a is isolated as a THF adduct. We suspected that the observed disparity in the catalytic properties of ISGC 3 and 4a are due to the presence of THF in the coordination sphere of 4a. Therefore it was decided to examine the AROM/CM reaction of 7 with ISGC 3 synthesized in the presence of a large excess of THF (the reaction was carried in a mixture of 1.5 mL of C₆D₆ and 0.5 mL of THF). The results of this study are shown in Scheme 35.

![Scheme 35](image)

<table>
<thead>
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<td>44</td>
</tr>
<tr>
<td>ISGC 3 + THF</td>
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<td>88</td>
</tr>
<tr>
<td>4a</td>
<td>2</td>
<td>72</td>
<td>91</td>
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</table>

Scheme 35. AROM/CM reaction of compound 7 with one equivalent of styrene in the presence of 4a and ISGC 3 (with and without THF).

The data in Scheme 35 confirmed that the solvent-free ISGC 3 is inferior to the ISGC 3 synthesized in the presence of a large excess of THF. We propose that the catalytically active
species derived in situ from 42, (R)-Benz₂BitetH₂, and THF are identical to 4a, and therefore provide significantly improved levels of selectivity compared to the solvent-free analog.

The results in Schemes 33 – 35 demonstrated that the ISGCs derived from Mo imido alkylidene bispyrrolide complexes and enantiomerically pure diols are as efficient and selective in catalyzing olefin metathesis reactions as the corresponding isolated catalysts. It was also shown that the ARCM of 45 and the AROM/CM of 7 are excellent model reactions for the development of a general protocol for applications of in situ generated catalysts outside the glovebox. For the next stage of this project we decided to study these transformations as well as the AROM/RCM reactions of substrate 47 in Schlenk flasks under N₂ in the fume hood, and determine the rate and pattern of deterioration of the stock solutions of 40 and 42 over time.

3.2.3 Asymmetric olefin metathesis reactions with ISGCs and the corresponding isolated catalysts performed in the fume hood.

3.2.3.a Experimental setup of olefin metathesis reactions performed in the fume hood using stock solutions of 40, 42, (R)-BiphenH₂, (R)-Benz₂BitetH₂, and substrates 45, 47, and 7.

Stock solutions of (R)-BiphenH₂, (R)-Benz₂BitetH₂, 40, and 42 in C₆D₆ were prepared in a nitrogen-filled glovebox. The diols were purified by column chromatography and dried over 4Å molecular sieves prior to use; freshly synthesized 40 and 42²⁰ were used to prepare the stock solutions. All experiments described below involved 10 mg/mL solutions of 40 (0.019 M), 42 (0.018 M), (R)-BiphenH₂ (0.028 M), and (R)-Benz₂BitetH₂ (0.016 M). Substrates 45, 47, and 7 were dried over 4Å molecular sieves and used as 20 mg/mL solutions in C₆D₆. Styrene was purchased from Aldrich and distilled from CaH₂ under vacuum. Styrene (stock solution, C₆D₆, 0.5 M) was stored frozen at -30 °C in the glovebox freezer and thawed prior to use. Deuturated benzene used in preparation of the stock solutions was purchased from Cambridge Isotope Laboratories, dried over CaH₂, and degassed via three freeze-pump-thaw cycles.
The stock solutions were loaded in 25 mL or 50 mL Schlenk flasks equipped with flow control adapters (Figure 23) in the glovebox. All flasks and adapters were used with glass stopcocks and were greased with Krytox®. The solutions were removed from the glovebox and stored in the fume hood to prepare ISGCs and reaction mixtures.

Figure 23. Schlenk flask with a flow control adapter used to store stock solutions of Mo bispyrrolide complexes, chiral diols, and substrates.

The procedure for performing an olefin metathesis reaction in the fume hood is schematically shown in Figure 24. All glassware and 6 inch stainless steel needles employed in this setup were dried in the oven at 135 °C prior to use. The needles were assembled with plastic syringes (1 mL or 2 mL) and cooled in a flow of nitrogen on a Schlenk line. Schlenk reaction vessels (25 mL or 50 mL flasks equipped with stir bars) were taken out of the oven and evacuated on the high vacuum line until they reached room temperature. The flasks were filled with nitrogen using a hose attached through a flow control adapter. Each time a new solution was introduced into the reaction mixture the following procedure was performed:

1. The hose attached to the flow control adapter was evacuated on the high vacuum line and refilled with nitrogen.
2. The stopcock in the flow control adapter was opened to the flask and the reaction mixture was exposed to nitrogen.
3. The stopcock in the side arm of the reaction vessel was opened, and nitrogen was allowed to flow through the reaction vessel.
4. Stock solutions of the reagents were introduced into the reaction vessels via a syringe through the stopcock in the side arm of the reaction flask under nitrogen flow.
Aliquots of the stock solutions were drawn from the storage flasks via the same sequence of steps.

**Figure 24.** Example of reaction setup in the fume hood: ARCM of substrate 45 with ISGC 1.
3.2.3.b Asymmetric olefin metathesis reactions of the substrates 45, 47, and 7 with ISGCs in the fume hood.

Olefin metathesis reactions of compounds 45, 47, and compound 7 with styrene were examined in the presence of ISGC 1, ISGC 2, and ISGC 3 in the fume hood. The stock solutions of 40 and 42 were stored in the fume hood for ca. 30 days and were screened three times during this time. Solutions of the diols and substrates 45 and 47 were also stored in the fume hood. However, these stock solutions ran out several times during the screening process and were replaced with the fresh samples removed from the glovebox. Stock solutions of compound 7 and styrene were stored in the glovebox freezer at -30 °C. These solutions were thawed prior to each reaction and mixed in a 20 mL vial fitted with a rubber septum in the glovebox. The vial was taken out of the glovebox and the mixture of substrates was drawn from the vial via a syringe and introduced into the reaction mixture.

The results of the periodical screenings of the ARCM of 45 by ISGCs are shown in Figure 25. The in situ catalysts were synthesized from the stock solutions of 40 and 42 after three, ten, and thirty-one days in the fume hood. The data in Figure 25 show that ISGC 1, ISGC 2, and ISGC 3 are as active and enantioselective after one month in the fume hood as they are in the glovebox. ISGC 1 was additionally screened after 41 days of storage outside the glovebox, and moderate deterioration of the conversion was observed, while the enantioselectivity was retained.
Catalyst loading 5 mol %, C₆D₆, 25 °C

**Catalyst: ISGC 1**

<table>
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<td>Fume hood, 31 days</td>
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<tr>
<td>Fume hood, 41 days</td>
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**Catalyst: ISGC 2**

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<tr>
<td>Fume hood, 3 days</td>
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<td>98</td>
<td>95</td>
</tr>
<tr>
<td>Fume hood, 10 days</td>
<td>2</td>
<td>98</td>
<td>93</td>
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<tr>
<td>Fume hood, 31 days</td>
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**Catalyst: ISGC 3**

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<td>Fume hood, 31 days</td>
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**Figure 25.** ARCM of 45 with ISGC 1, ISGC 2, and ISGC 3 in the fume hood and in the glovebox.
Catalyst: ISGC 1

<table>
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Catalyst: ISGC 2

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Catalyst: ISGC 3

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<td>43</td>
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</table>

**Figure 26.** AROM/RCM of 47 with ISGC 1, ISGC 2, and ISGC 3.
The AROM/RCM reactions of 47 with ISGC 1, ISGC 2, and ISGC 3 are shown in Figure 26. Enantioselectivities of the AROM/RCM of 47 carried in the glovebox at 25 °C were very low. The original report on AROM/RCM of 47 mentions that the enantiomeric ratios of product 48 increased when the catalytic reactions were conducted at a higher temperature. Therefore we decided to perform these transformations in the fume hood with 3 day old stock solutions at 70 °C. However, formation of 48 in the presence of ISGC 1, ISGC 2 and ISGC 3 at 70 °C proceeded with the same low enantioselectivities. Additionally, conversions provided by ISGC 2 and ISGC 3 at 70 °C were lower than those obtained at room temperature. Based on these observations future screenings with substrate 47 were conducted at 25 °C.

The results of AROM/CM of 47 obtained with ISGC 1 in the fume hood at 10 and 31 days are almost identical to those obtained in the glovebox. ISGC 2 and ISGC 3, on the other hand, give slightly lower conversions after 32 days in the fume hood. We believe that the solution of 42 deteriorates somewhat faster than the solution of 40, which explains the better performance of ISGC 1 as compared to ISGC 2 and ISGC 3 after one month. Crystal structure determination of 42 showed that this complex is a dimer in the solid state. The Mo atoms in this dimer are bound by one bridging pyrrolide ligand, providing 18 and 16 electrons for the two Mo centers. We propose that some of the dimeric structure is retained in solution, stabilizing 42 towards decomposition. Compound 40 is likely to exist in solution in the form of a similar dimer. Due to the smaller size of the imido group in 40 as compared to 42, the dimer/monomer equilibrium in the solution of 40 should be shifted more towards the dimer than the equilibrium in solution of 42. Therefore 40 is proposed to decompose at a slower rate than 42, which is supported by the results discussed above.

Asymmetric ring-opening metathesis/cross metathesis of 7 with one equivalent of styrene was performed in the presence of ISGC 1, ISGC 2, and ISGC 3 (Figure 27). ISGC 1 efficiently catalyzes this transformation with excellent enantioselectivity in the glovebox as well as in the fume hood after 4, 10, and 30 days. Conversions to 8 increases at 30 days.
Figure 27. AROM/CM of 7 with one equivalent of styrene in the presence of ISGC 1, ISGC 2, and ISGC 3.
In the case of ISGC 3 this improvement is even more dramatic: not only the conversion to 8 increases from 54 % to 71 %, but also the enantiomeric excess rises from 44 % to 94 % over one month! These puzzling results prompted us to investigate the observed phenomenon. We knew from the studies discussed above that enantioselectivity of the conversion of 7 into 8 with ISGC 3 improves significantly in the presence of THF (Scheme 34). It was suggested that the observed increase in the ee of 8 in the reaction catalyzed by ISGC 3 is due to the partial decomposition of 42 in solution. We proposed that the decomposition products play the same role in this reaction as THF did in the reactions shown in Scheme 34. In order to check this hypothesis fresh solutions of 42 (solution #2) and (R)-Benz2BitetH2 were prepared and screened in the glovebox and in the fume hood. We were surprised to find out that ISGC 3 prepared from the solution #2 produced the same results, whether the reaction was conducted in the glovebox or in the fume hood. These data were identical to those obtained with the original stock solutions after ten to thirty days in the fume hood. When ISGC 3 was used in the fume hood immediately after the new solutions were taken out of the glovebox, 55 % conversion and 88 % ee were determined; ISGC 3 made with the new solutions in the glovebox afforded 56 % conversion and 89 % ee.

At this point we decided to perform a new study with two fresh solutions of 42 in the fume hood (solutions #3 and #4) and compare the obtained results with the data shown in Figure 27. ISGC 3 made with the two new solutions of 42 afforded high enantioselectivities in the synthesis of 8 in the fume hood (Figure 28). It is clear from the data in Figure 28 that the catalytic reaction with ISGC 3 made with the new solutions of 42 is different from the reaction with ISGC 3 obtained with the original solution of 42 and used in the system shown in Figure 27. The solid bispyrrolide complex 42 that was used to prepare solutions #3 and #4 came from the same batch of the Mo complex as the material employed in the preparation of the original stock solution and solution #2. No decomposition of the solid 42 (stored in the glovebox freezer) was determined by 1H NMR spectroscopy. At this point the only components that remained constant throughout the screenings were the stock solutions of substrate 7 and styrene. We do not observe decomposition products in the 1H NMR spectrum of the stock solution of 7, but we believe that a small amount
of these products is present in the solution. These oxygen-containing compounds might be capable of binding to the Mo atom in ISGC 3 and producing the same beneficial effect on enantioselectivity of the AROM/CM of 7, as THF does in the study shown in Scheme 34.

\[
\begin{array}{c}
\text{Catalyst loading 5 mol %, } \text{C}_6\text{D}_6, 25 ^\circ\text{C} \\
7 \quad \text{+} \quad \text{AROM/CM} \quad \rightarrow \quad 8
\end{array}
\]

**Solution of 42 #3**

<table>
<thead>
<tr>
<th>Time, h</th>
<th>Conv., %</th>
<th>Yield, %</th>
<th>ee, %</th>
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<tbody>
<tr>
<td>Fume hood, 6 days</td>
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<td>48</td>
<td>40</td>
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<tr>
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<tr>
<td>Fume hood, 32 days</td>
<td>2</td>
<td>56</td>
<td>51</td>
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**Solution of 42 #4**

<table>
<thead>
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<th>Yield, %</th>
<th>ee, %</th>
</tr>
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<tbody>
<tr>
<td>Fume hood, 1 day</td>
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<td>45</td>
</tr>
<tr>
<td>Fume hood, 9 days</td>
<td>2</td>
<td>60</td>
<td>57</td>
</tr>
<tr>
<td>Fume hood, 29 days</td>
<td>2</td>
<td>68</td>
<td>66</td>
</tr>
</tbody>
</table>

**Figure 28.** AROM/CM of 7 with styrene in the presence of ISGC 3 made with the two new stock solutions of 42.
3.2.3.c ARCM of 45 using ISGC 1 and ISGC 2 synthesized with the stock solutions of 40 and 42 that were prepared in the fume hood from solid Mo bispyrrolide complexes.

Solid Mo complexes 40 and 42 can be used to prepare stock solutions of the complexes in the fume hood. Complexes 40 and 42 (ca. 100 mg) were each placed in a 5 mL vial fitted with teflon-lined cap. The vial was removed from the glovebox and emptied into a Schlenk flask filled with N2. The flask was fitted with a flow control adapter and evacuated on a high vacuum line, and then refilled with nitrogen. This cycle was repeated three times, at which point the flask was weighed and the amount of the transferred solid Mo bispyrrolide complex was determined by difference. The volume of dry toluene was introduced into the flask via a syringe to produce a stock solution of the desired concentration (10 mg/mL). In the case of complex 42, the resulting solution was degassed by three freeze-pump-thaw cycles.

The stock solutions of 40 and 42 were used to prepare ISGC 1 and ISGC 2. These catalysts were screened in ARCM reactions of 45 (Figure 29). Deterioration of the conversion obtained with ISGC 1 over one month indicates that freeze-pump-thawing of the stock solution is essential for the stability of the complex. Nonetheless, both ISGC 1 and ISGC 2 produce 46 in yields and enantioselectivities comparable to those obtained in the similar reaction in the glovebox.

3.2.3.d ARCM of 45 catalyzed by ISGC 2, which was synthesized from Mo(NAr)(CHCMe2Ph)(OTf)2(dme) via sequential addition of lithium pyrrolide and (R)-BiphenH2.

ARCM of 45 can be catalyzed by ISGC 2 synthesized in the fume hood from a stock solution of Mo(NAr)(CHCMe2Ph)(OTf)2(dme) in toluene (10 mg/mL). Sequential addition of aliquots of the lithium pyrrolide solution in THF (2 mg/mL) and the stock solution of (R)-BiphenH2 to Mo(NAr)(CHCMe2Ph)(OTf)2(dme) was employed. The solutions of the Mo bistriflate complex and lithium pyrrolide were prepared in the glovebox, stored in the fume hood, and used in the same manner as the stock solutions of 40 and 42. There was no difference in the
results obtained with ISGC 2 derived from the solution of Mo(NAr)(CHCMe₂Ph)(OTf)₂(dme) (Figure 30) and those observed with ISGC 2 synthesized from the stock solution of 42 (Figure 25). In a typical procedure, an aliquot of the toluene solution of Mo(NAr)(CHCMe₂Ph)(OTf)₂(dme) was introduced into a Schlenk flask equipped with a stir bar, and cooled to 0 °C. Two equivalents of lithium pyrrolide in THF were added, and the resulting bright yellow reaction mixture was stirred at room temperature for 45 min. At this point 1.5 equivalents of (R)-BiphenH₂ were added and the reaction mixture was stirred for 15 min prior to the addition of the substrate.

![Reaction Scheme](image)

**Catalyst: ISGC 1**

<table>
<thead>
<tr>
<th>Time, h</th>
<th>Conv., %</th>
<th>Yield, %</th>
<th>ee, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fume hood, 1 day</td>
<td>3</td>
<td>&gt;98</td>
<td>95</td>
</tr>
<tr>
<td>Fume hood, 9 days</td>
<td>3</td>
<td>90</td>
<td>83</td>
</tr>
<tr>
<td>Fume hood, 29 days</td>
<td>3</td>
<td>61</td>
<td>60</td>
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</tbody>
</table>

**Catalyst: ISGC 2**

<table>
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<th>Conv., %</th>
<th>Yield, %</th>
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<td>89</td>
</tr>
<tr>
<td>Fume hood, 12 days</td>
<td>2</td>
<td>95</td>
<td>90</td>
</tr>
<tr>
<td>Fume hood, 32 days</td>
<td>2</td>
<td>&gt;98</td>
<td>89</td>
</tr>
</tbody>
</table>

**Figure 29.** ARCM of 45 with ISGC 1 and ISGC 2. The catalysts were synthesized from the stock solutions of 40 and 42 that were prepared in the fume hood from solid Mo bispyrrole complexes.
Catalyst loading 5 mol %, C₆D₆, 25 °C

**Catalyst: ISGC 2**

<table>
<thead>
<tr>
<th>Time, h</th>
<th>Conv., %</th>
<th>Yield, %</th>
<th>ee, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fume hood, 1 day</td>
<td>&gt;98</td>
<td>88</td>
<td>96</td>
</tr>
<tr>
<td>Fume hood, 9 days</td>
<td>&gt;98</td>
<td>98</td>
<td>96</td>
</tr>
<tr>
<td>Fume hood, 29 days</td>
<td>&gt;98</td>
<td>95</td>
<td>97</td>
</tr>
</tbody>
</table>

**Figure 30.** ARCM of 45 catalyzed by ISGC 2, which was synthesized from Mo(NAr)(CHCMe₂Ph)(OTf)₂(dme) via sequential addition of lithium pyrrolide and (R)-BiphenH₂.

The stock solutions of Mo(NAr)(CHCMe₂Ph)(OTf)₂(dme) and lithium pyrrolide do not undergo any significant decomposition in the fume hood over one month, as judged by the results presented in **Figure 30.** These data are particularly valuable since Mo(NAr)(CHCMe₂Ph)(OTf)₂(dme) is commercially available from Strem, while lithium pyrrolide can be readily synthesized from pyrrole and n-BuLi employing standard Schlenk technique.
3.2.3.e ARCM of 45 using ISGC 2 synthesized in the presence of different amounts of (R)-BiphenH₂.

Compounds 40 and 42 decompose to some extent over time when they are stored as C₆D₆ or toluene stock solutions in the fume hood. The actual concentration of these solutions decreases over time. Therefore when aged solutions of 40 or 42 are used to prepare catalysts in situ, the amount of the diol added to the Mo bispyrrolide complex may be greater than one equivalent. Therefore we wanted to study the effect of excess diol on the performance of ISGC 2 in the ARCM of 45. In the nitrogen-filled glovebox, complex 42 was treated with three equivalents of (R)-BiphenH₂ in C₆D₆, and 15 min later 20 equivalents of 45 were added to the reaction mixture. The product of ARCM reaction was isolated 2 hours later in 96 % yield, 97 % ee. This observation indicates that excess (R)-BiphenH₂ does not interfere with the ARCM catalyzed by ISGC 2. It is important to note that (R)-BiphenH₂ is a very bulky diol and is most likely not capable of coordinating to the sterically saturated species ISGC 2. The results obtained with excess (R)-BiphenH₂ cannot, therefore, be extrapolated for smaller alcohols. Less bulky alcohols could still bind to the Mo center in ISGC 2 and potentially inhibit the catalytic properties of this system.

An independent set of experiments was carried out in order to investigate whether it is necessary to prepare ISGCs prior to the substrate addition. We were also interested in determining whether a system containing excess of 42 with respect to the amount of (R)-BiphenH₂ produces the same results as a 1:1 mixture of 42 and the diol. Data in Figure 31 show that when complex 42 was mixed with 20 equivalents of substrate 45, followed by addition of 1 or 0.5 equivalents of (R)-BiphenH₂, the observed conversions of the ARCM reaction were identical to those obtained with ISGC 2 that were synthesized in the manner discussed above. The enantioselectivities determined in these systems are somewhat lower than the ee obtained with ISGC 2, but the simplified reaction procedure might be worth the minor decrease in enantioselectivity. These results give evidence that in situ catalysts can be prepared from Mo bispyrrolide complexes premixed with the substrates without significant loss of activity and
selectivity in the catalytic reaction. Varying the amounts of (R)-BiphenH$_2$ employed in the ISGC synthesis does not alter the outcome of the reaction.

![Chemical structure of 45 and 46](image.png)

<table>
<thead>
<tr>
<th>Time, h</th>
<th>Conv., %</th>
<th>Yield, %</th>
<th>ee, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISGC 2</td>
<td>2</td>
<td>&gt;98</td>
<td>86</td>
</tr>
<tr>
<td>42 + 1 (R)-Biphen H$_2$</td>
<td>2</td>
<td>&gt;98</td>
<td>92</td>
</tr>
<tr>
<td>42 + 0.5 (R)-Biphen H$_2$</td>
<td>2</td>
<td>&gt;98</td>
<td>98</td>
</tr>
</tbody>
</table>

$^a$ 42 was wixed with with 20 equivalents of 45, then (R)-BiphenH$_2$ was added.

**Figure 31.** ARCM of 45 catalyzed by ISGC 2 and the mixtures of 42 with different amounts of (R)-BiphenH$_2$.

### 3.2.3.f Comparison of the rates of ARCM of 45 with ISGC 1 synthesized in the glovebox and in the fume hood after 36 days.

In order to determine the degree of decomposition of 40 in the solution that was stored in the fume hood for 36 days, the following set of experiments was performed: ARCM of 45 was performed in the glovebox and in the fume hood simultaneously (2.5 mol % catalyst loading). The conversions of 45 into 46 in both reaction mixtures were monitored by $^1$H NMR. The results of these experiments are shown in **Figure 32**.
2.5 mol % ISGC 1, C₆D₆, 25 °C

**Figure 32.** ARCM of 45 monitored for 20 h with ISGC 1. The reactions were conducted in the glovebox and in the fume hood with the 36 day old stock solution of 40.

Data in Figure 32 show that IGSC 1 synthesized in the glovebox is approximately twice as active in ARCM of 45 as IGSC 1 prepared in the fume hood from the 36 day old solution of 40. One can conclude that ca. 50 % of 40 in the stock solution kept in the fume hood have decomposed over 36 days. ISGC 1 studied in the fume hood decomposes within the first hour of the catalytic reaction, while ISGC 1 in the glovebox is active for at least three hours. The low conversions obtained in the glovebox experiment also show that 2.5 mol % loading of ISGC 1 is too low to obtain a complete conversion of 45 into 46. This finding validates a relatively high 5 mol % loading of ISGC 1 that was employed in the screening experiments discussed in this chapter.
3.3 Conclusions.

Reactions of bispyrrolide molybdenum complexes \textbf{40}, \textbf{41}, \textbf{42}, and \textbf{43} with enantiomerically pure diols were studied. It was determined that the in situ catalyst generated from \textbf{40} and (R)-TripH\textsubscript{2} predominantly exists in solution as an \textit{anti} pyrrolenine adduct. The complex synthesized from \textbf{42} and (R)-Benz\textsubscript{2}BitetH\textsubscript{2} is a solvent-free species, differing in this respect from the analogous isolated complex \textbf{4a}.

\textbf{ISGC 1}, \textbf{ISGC 2}, and \textbf{ISGC 3} were screened in the catalytic transformations of substrates \textbf{45} and \textbf{7} in the glovebox. These systems were found to be as active and enantioselective as the analogous isolated complexes. \textbf{ISGC 3} was shown to be less enantioselective in the AROM/CM of \textbf{7} with styrene, than the isolated analog \textbf{4a}. The enantioselectivity of this system was restored when \textbf{ISGC 3} was prepared in the presence of THF.

\textbf{ISGC 1}, \textbf{ISGC 2}, and \textbf{ISGC 3} were synthesized from the stock solutions of \textbf{40}, \textbf{42}, (R)-BiphenH\textsubscript{2}, and (R)-Benz\textsubscript{2}BitetH\textsubscript{2} in the fume hood over one month. Studies of these catalytic systems in the metathesis reactions of \textbf{45}, \textbf{47}, and \textbf{7} showed that \textbf{ISGC 1}, \textbf{ISGC 2}, and \textbf{ISGC 3} prepared in the fume hood are nearly identical in terms of their catalytic properties to the \textbf{ISGCs} prepared in the glovebox. The stock solutions of \textbf{40} and \textbf{42} deteriorate slowly in the fume hood over time, with ca. 50 \% of \textbf{40} remaining in solution after 36 days.

\textbf{Mo(NAr)(CHCMe\textsubscript{2}Ph)(OTf)\textsubscript{2}(dme)} was used as a precursor for the in situ synthesis of an active and enantioselective olefin metathesis catalyst via addition of lithium pyrrolide, followed by addition of (R)-BiphenH\textsubscript{2}. This system retains its activity and enantioselectivity even when the stock solutions of \textbf{Mo(NAr)(CHCMe\textsubscript{2}Ph)(OTf)\textsubscript{2}(dme)} and lithium pyrrolide are stored in the fume hood for one month.

3.4 Experimental Details.

\textbf{General Details.} All reactions were conducted in oven-dried (135 °C) glassware under an inert atmosphere of dry nitrogen employing standard Schlenk and glovebox techniques. Toluene, diethyl ether, and THF were degassed and then passed through a column of activated alumina. Compounds \textbf{7}, \textbf{41}, \textbf{42}, \textbf{43}, \textbf{45}, \textbf{47} and \textbf{Mo(NAr)(CHCMe\textsubscript{2}Ph)(OTf)\textsubscript{2}(dme)} were prepared
according to literature procedures. The synthesis of compound 40 was modified from the published procedure and is reported below. Products of olefin metathesis reactions 46, 48, and 8 were isolated and analyzed according to published procedures.

$^1$H and $^{19}$F NMR spectra were recorded on Varian spectrometers. Enantiomeric ratios were determined using chiral HPLC analyses (Chiralcel OD and Chiralcel OJ columns) in comparison with authentic racemic materials.

Mo(NAd)(CHCMe$_2$Ph)(pyr)$_2$ 40. Mo(NAd)(CHCMe$_2$Ph)(OTf)$_2$(dme) (2.0 g, 2.61 mmol) was suspended in 30 mL of diethyl ether and cooled to -30 °C. Solid lithium pyrrolide (381 mg, 5.22 mmol) was added to the cold white suspension, and the mixture became clear and yellow. The reaction mixture was stirred at room temperature for 10 min, at which time yellow precipitate started forming. The reaction mixture was allowed to stir for additional 30 min, and then the yellow precipitate was isolated by filtration, washed with diethyl ether, and dried in vacuo. The isolated product exhibited no signal in the $^{19}$F NMR spectrum (1.0 g, 1.96 mmol, 75 %). The spectral data for this compound matched the reported data.

A representative procedure for an olefin metathesis reaction catalyzed by an ISGC in the glovebox. In a nitrogen-filled glovebox 40 (0.22 mL, 10 mg/mL stock solution in C$_6$D$_6$, 2.2 mg, 4.4*10$^{-3}$ mmol) was loaded into a 20 mL vial equipped with a stir bar and a teflon-lined cap. (R)-BiphenH$_2$ (0.16 mL, 10 mg/mL solution in C$_6$D$_6$, 1.6 mg, 4.4*10$^{-3}$ mmol) was added to the solution of 40, and the resulting yellow mixture was stirred for 15 min. Compound 47 (1 mL, 20 mg/mL stock solution in C$_6$D$_6$, 20 mg, 87.6*10$^{-3}$ mmol) was added to the catalyst solution, which immediately turned brown. After 3 hours the reaction mixture was taken out of the glovebox and quenched with wet diethyl ether. The solvents were removed in vacuo and the resulting yellow oil was purified by chromatography to give 15.2 mg of colorless oil (66.6*10$^{-3}$ mmol, 76 %). The spectral data for this compound matched the reported data.
A representative procedure for an olefin metathesis reaction catalyzed by an ISGC in the fume hood. A 50 mL Schlenk flask equipped with a flow control adapter and a stir bar was taken out of the oven and cooled under high vacuum. The flask was refilled with nitrogen and loaded via syringes with 40 (0.25 mL, 30 day old 10 mg/mL stock solution in C\textsubscript{6}D\textsubscript{6}, 2.5 mg, 5*10\textsuperscript{-3} mmol) and (R)-BiphenH\textsubscript{2} (0.18 mL, 10 mg/mL solution in C\textsubscript{6}D\textsubscript{6}, 1.8 mg, 5*10\textsuperscript{-3} mmol). The resulting yellow mixture was stirred for 15 min. In a nitrogen-filled glovebox compound 7 (1 mL, 20 mg/mL stock solution in C\textsubscript{6}D\textsubscript{6}, 20 mg, 100*10\textsuperscript{-3} mmol) and styrene (0.2 mL, 52 mg/mL stock solution in C\textsubscript{6}D\textsubscript{6}, 10.4 mg, 100*10\textsuperscript{-3} mmol) were mixed in a 20 mL vial fitted with a rubber septum. The vial was taken out of the glovebox and the mixture was drawn from the vial using a syringe. The substrate mixture was added to the catalyst solution, which immediately turned brown. After 2 hours the reaction mixture was quenched by exposure to air. The volatile components were removed in vacuo and the resulting yellow oil was purified by chromatography to give 27.8 mg of colorless oil (91.3*10\textsuperscript{-3} mmol, 91 %). The spectral data for this compound matched the reported data.\textsuperscript{44}

A representative procedure for an olefin metathesis reaction catalyzed by an ISGC derived from Mo(NAr)(CHCM\textsubscript{2}Ph)(OTf)\textsubscript{2}(dme) in the fume hood. A 50 mL Schlenk flask equipped with a flow control adapter and a stir bar was taken out of the oven and cooled under high vacuum. The flask was refilled with nitrogen and charged with Mo(NAr)(CHCM\textsubscript{2}Ph)(OTf)\textsubscript{2}(dme) (0.31 mL, 9 day old 10 mg/mL stock solution in toluene, 3.1 mg, 3.9*10\textsuperscript{-3} mmol) via a syringe, then cooled to 0 °C. Lithium pyrrolide (0.29 mL, 9 day old 2 mg/mL stock solution in THF, 0.57 mg, 7.8*10\textsuperscript{-3} mmol) was added to the solution of Mo bistri triflate, causing the mixture to turn bright yellow. The mixture was stirred for 45 min at room temperature, and (R)-BiphenH\textsubscript{2} (0.27 mL, 10 mg/mL solution in C\textsubscript{6}D\textsubscript{6}, 2.7 mg, 7.5*10\textsuperscript{-3} mmol) was added to reaction. The resulting yellow mixture was stirred for 15 min. Compound 45 (1 mL, 20 mg/mL stock solution in C\textsubscript{6}D\textsubscript{6}, 20 mg, 78.3*10\textsuperscript{-3} mmol) was added to the catalyst solution. After 3 hours the reaction mixture was quenched by exposure to air. The volatile components were removed in vacuo and the resulting yellow oil was purified by chromatography to give 17.5 mg of white needles (77.0*10\textsuperscript{-3} mmol, 98 %). The spectral data for this compound matched the reported data.\textsuperscript{47}
3.5 References.


Acknowledgements

First of all, I want to thank my advisor Professor Richard R. Schrock for being an exceptional mentor during my five years at MIT. He was supportive of my interest in organic synthesis, allowing me to stray away from the traditional organometallic ways of this group. He was interested in my ideas and let me pursue them. RRS was always there to answer questions and provide guidance, which I am very thankful for.

My research in the Schrock group focused on catalyst development for olefin metathesis, which is conducted in collaboration with Professor Amir H. Hoveyda’s group at Boston College. I want to thank Professor Hoveyda for always being available for advice, providing constructive critique, and make 6-hour long joint MIT/BC meetings enjoyable. I also want to thank him for welcoming me into his group, which I will join in Fall 2008 as a postdoctoral researcher. I am extremely excited about this opportunity and looking forward to the “organic adventure” that I am about to embark on.

Professors Christopher C. Cummins and Joseph P. Sadighi have been very helpful during my time at MIT. I want to thank them for taking time to discuss my research projects and career choices.

I would not be here now if it wasn’t for my high school chemistry teacher and first research advisor Professor Anna A. Kartsova. She showed me how much fun chemistry research is, and I have not thought about a different career ever since. I also want to thank my undergraduate research advisor Professor Sergey P. Tunik, who first introduced me to synthetic organometallic chemistry, and supported me in my decision to apply to graduate school in the United States.

I found a lot of friends while working in the Schrock group. Andrea Gabert is an amazing friend, who supports me in difficult times and is always ready to share the fun. She is a great person and I am very happy to have met her.
Sarah Dolman was my labmate for the first two years at MIT, and I will never forget her patience during my first several months in the lab. We developed a close friendship, and I wish she didn’t move so far away. Thank God they have phones in Canada!

Zach Tonzetich is a good friend and a great chemist. I hope we can continue our friendship, since he is staying at MIT and I will be in Boston again starting Fall 2008.

Constatin Czekelius was a postdoc in our lab for two years, and I learned a great deal of organic chemistry from him. He is a good friend who was always available for discussions of chemistry and life in general.

I shared a glovebox for two years with Jia Min Chin, and I appreciate her being able to put up with me and calmly discuss any problems that arose while sharing the box. She is a great officemate and labmate, and I will miss her a lot.

Rojendra Singh, Brian Hanna, Keith Wampler, Monica Duval, Stefan Arndt, and many others made this lab a great place to come to every day.

Alex Cortez is one of the members of the Hoveyda group at Boston College. We spent a lot of time figuring out the tricks of metathesis together and ended up being close friends.

I want to thank Nadya Nilina, David Laitar, Venda Porter, Mary Rozenman, Danil and Yana Kirsanov, and Christopher Clough for being great friends. These people helped me to stay sane during these five years. They were always willing to listen to me and supported me during the rough times, and shared my joy and during happy times.

Gretchen Guidess is the reason the Schrock group can focus on our research without worrying about keeping the lab running smoothly. I appreciate all her help, her amazing sense of humor, and wisdom. I turned to her a lot for advice and support during all these years.

I want to thank Ed Mitchell, the Schrock group glassblower. I appreciate that he never made fun of me for producing so much work for him on a weekly basis. He is a great listener, and I want to thank him for always being genuinely interested in my life and available for a chat.
My Mom is my best friend and my inspiration in life. Her unconditional love and daily support kept me going every day of these five years. I am extremely grateful to her for who she is and everything she does for me.

MIT is the place where I met my fiancé Matt Headrick, and it’s impossible to describe how happy I am to be with him. He is an amazing person, and I want to thank him for always helping me to see the bright side of things and supporting me through the stressful years of graduate school. These years together showed me that there is no other man I want to spend the rest of my life with.
Curriculum Vitae

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2002-2007
Massachusetts Institute of Technology, Cambridge, MA.
Doctor of Philosophy

1997-2002
St. Petersburg State University, St. Petersburg, Russia.
Department of Chemistry.
Graduated with degree of Specialist in chemistry first in class.

Research experience

Massachusetts Institute of Technology, Department of Chemistry

Developed new alkylimido Mo-containing asymmetric olefin metathesis catalysts to compare their catalytic activity with the known arylimido Mo complexes. Established superior activity and enantioselectivity of the new catalysts in asymmetric ring-closing metathesis and ring-opening/cross metathesis with a variety of olefin-containing amines, ethers and amides.
Designed new synthetic routes for previously unknown molybdenum imido complexes employing organic azides. Studied structurally differing metathesis catalysts originating from the prepared imido complexes.
Established a protocol for in situ olefin metathesis catalyst generation from Mo bispyrrolide complexes and chiral diols.

**St. Petersburg State University, Department of Chemistry**

**1999-2002** Research assistant in the Laboratory of platinum group metals, group of cluster compounds under guidance of Prof. S. P. Tunik. Investigated synthesis and structural properties of Rh and Ru carbonyl clusters with phosphine ligands.

**1997-1999** Research assistant in the Laboratory of mass-spectrometry under guidance of Prof. S. I. Lopatin. Worked on determination of thermodynamic parameters in vapors of inorganic salts mixtures by mass-spectrometry.

**1996-1997** Research assistant in the Laboratory of gas chromatography under guidance of Prof. A. A. Kartsova. Participated in development of new chromatographic methods for detection of formaldehyde.

**Teaching Experience**

**January 2006 – May 2006**
Teaching assistant for the “Intermediate Chemical Experimentation” course, Massachusetts Institute of Technology.

**January 2003 – May 2003**
Teaching assistant for the “Principles of Inorganic Chemistry I” course, Massachusetts Institute of Technology.

**September 2002 – December 2002**
Teaching assistant for the “Principles of Chemical Science” course, Massachusetts Institute of Technology.
September 2001 – December 2001
Teaching assistant for the “General and Inorganic Chemistry” course, St. Petersburg State University, St. Petersburg, Russia.

Awards

2006 Travel grant provided by the Morse Family Foundation.

2005 Travel grant provided by the Cambridge Science Foundation, Inc.

2000 Scholarship from JSC “Ekros” (leading supplier of chemicals and chemical laboratory equipment in the north-western region of Russia).

2000 Scholarship provided by the Ministry of Education of Russia and the Russian Academy of Sciences.

2000 Soros Student scholarship (selected and named by the International Soros Science Education Program).

1999 Soros Student scholarship (selected and named by the International Soros Science Education Program).

1999 2nd prize for a talk “Thermochemical studies of gaseous cesium tungstate and germanium molybdate” given at the 10th Mendeleyev Chemistry Students Conferences organized by the Association for the Advancement of Chemical Education. 11-12 December 1999. Moscow, Russia.

1998 2nd prize for a talk “Thermochemical studies of gaseous alkaline-earth metal tantalates” given at the 9th Mendeleyev Chemistry Students Conference organized by the Association for the Advancement of Chemical Education. 12-13 December 1998. Moscow, Russia.
1997 1st prize for a talk “New GC method for detection of formaldehyde in air and paper samples in a form of hexamethylenetetramine” given at the 8th Mendeleyev Chemistry Students Conference organized by the Association for the Advancement of Chemical Education. 12-14 December 1997. Moscow, Russia.


Publications


2. Gracheva, E. V.; Krupenya, D. V.; Pilyugina, T. S.; Tunik, S. P.; Pursiainen, J.; Haukka, M. Reactions of carbonyl clusters with heterobidentate ligands. Synthesis and structural characterization of $\text{H}_4\text{Ru}_4(\text{CO})_{10}[k^2(\text{P},\text{S})-\text{Ph}_2\text{P}(2-\text{CH}_3\text{SC}_6\text{H}_4)]$ and $\text{Rh}_6(\text{CO})_{14}[k^2(\text{P},\text{S})-\text{Ph}_2\text{P}(2-\text{CH}_3\text{SC}_6\text{H}_4)]$ clusters. *Rus. J. Gen. Chem.* 2006, 76(5), 682-686.


Presentations
