MOLYBDENUM ALKYLIDENE COMPLEXES: SYNTHESES AND APPLICATIONS TO OLEFIN METATHESIS REACTIONS

by

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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, $Mo(NR)(CHCMe_2Ph)$[(S)-Biphen], $Mo(NR)(CHCMe_2Ph)$[(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'-diolate) and $Mo(NAd)(CHCMe_2Ph)$[(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, $Mo(NAd)(CHCMe_2Ph)$[(S)-Biphen]. The new catalysts prove to be similar to $Mo(NAd)(CHCMe_2Ph)$[(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 $Mo(NR)Cl_4(THF)$ species (R = C_6F_5, 3,5-$(CF_3)_2C_6H_3$, Ad, CPh_3, and 2,6-i-$Pr_2C_6H_3$) 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 $Mo(NR)Np_3Cl$ species (R = C_6F_5, 3,5-$(CF_3)_2C_6H_3$, Ad, Ph_3C, and 2,6-i-$Pr_2C_6H_3$ (Ar); Np = CH_2-t-Bu) in poor (35 %) to modest (51 %) yields. Heating $Mo(NAr)Np_3Cl$ in C_6D_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_3Cl species were found to be more stable than Mo(NAr)Np_3Cl, but when they did decompose at elevated temperatures, no neopentylidene complex could be observed. Addition of neopentyllithium to Mo(NR)Np_3Cl species (R = Ar, CPh_3, or Ad) yielded Mo(NR)(CH-t-Bu)Np_2 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-$Pr_3C_6H_2)_2C_6H_3$OH (HIPTOH) to Mo($NCPh_3$)(CH-t-Bu)Np_2 led to formation of Mo($NCPh_3$)(CH-t-Bu)Np(OR) species, while treatment of Mo($NCPh_3$)(CH-t-Bu)Np_2 with C_6F_5OH gave Mo($NCPh_3$)Np_3(OC_6F_5). 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-$(CF_3)_2C_6H_3$]Cl_4(THF), Mo[N-3,5-$(CF_3)_2C_6H_3$]Np_3Cl, Mo($NCPh_3$)Np_3Cl, and Mo($NCPh_3$)(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)($CHCMe_2Ph$)$(pyr)_2$ and Mo(N-2-6-i-$Pr_2C_6H_3$)($CHCMe_2Ph$)$(pyr)_2$ with (R)-BiphenH_2, and (R)-$Benz_2$BitetH_2 were examined (pyr = C_4H_4N, $Benz_2$BitetH_2 = 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)($CHCMe_2Ph$)$(pyr)_2$, Mo(N-2,6-i-$Pr_2C_6H_3$)($CHCMe_2Ph$)$(pyr)_2$, (R)-BiphenH_2, and (R)-$Benz_2$BitetH_2 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.

Table of Contents

List of Abbreviations

Ad	1-adamantyl
Anal	Analysis
Ar	aryl
br	broad
Bn	benzyl, $-CH_2(C_6H_5)$
t-Bu	tert-butyl, $-C(CH_3)_3$
n-BuLi	n-butyllithium
Calcd	calculated
CBz	benzylcarboxylate, $-CO_2CH_2Ph$
conv.	conversion
Cy	cyclohexyl, $-C_6H_{11}$
d	doublet
deg, (°)	degree(s)
DEPT	Distortionless Enhancement by Polarization Transfer
DME	1,2-dimethoxyethane
dme	1,2-dimethoxyethane coordinated to a metal center
ee	enantiomeric excess
ESI	Electro-spray Ionization
g	gram(s)
GC	Gas Chromatography
h	hour(s)
HPLC	High Performance Liquid Chromatography
HRMS	High Resolution Mass Spectrometry
J	coupling constant in Hertz
m	multiplet

Me	methyl
min	minute(s)
NMR	Nuclear Magnetic Resonance
OTf	triflate, $-OSO_2CF_3$
Ph	phenyl, $-C_6H_5$
ppm	parts per million
i-Pr	isopropyl, $-CH(CH_3)_2$
py	pyrrolide, $-NC_4H_4$
pyr	pyridine
q	quartet
s	singlet
sep	septet
t	triplet
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TMS	trimethylsilyl, $-SiMe_3$
TMSCl	trimethylsilyl chloride
trityl	$-C(C_6H_5)_3$
δ	chemical shift downfield from tetramethylsilane in ppm

List of Figures

Chapter 1

Chapter 2

Chapter 3

List of Schemes

Chapter 1

Chapter 2

Chapter 3

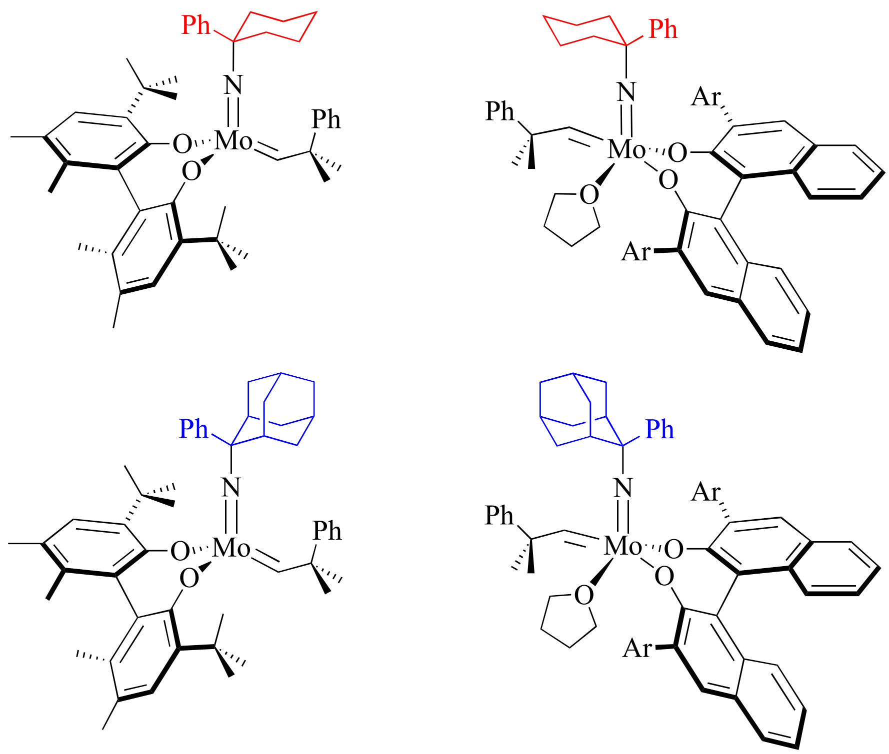
List of Tables

Chapter 1

Chapter 2

Chapter 1

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



A portion of this work has appeared in print:

Pilyugina, T. S.; Schrock, R. R.; Mueller, P.; Hoveyda, A. H. New enantiomerically pure alkylimido Mo-based complexes. Synthesis, characterization and activity as chiral olefin metathesis catalysts. *Organometallics* **2007** *26*, 831-837.

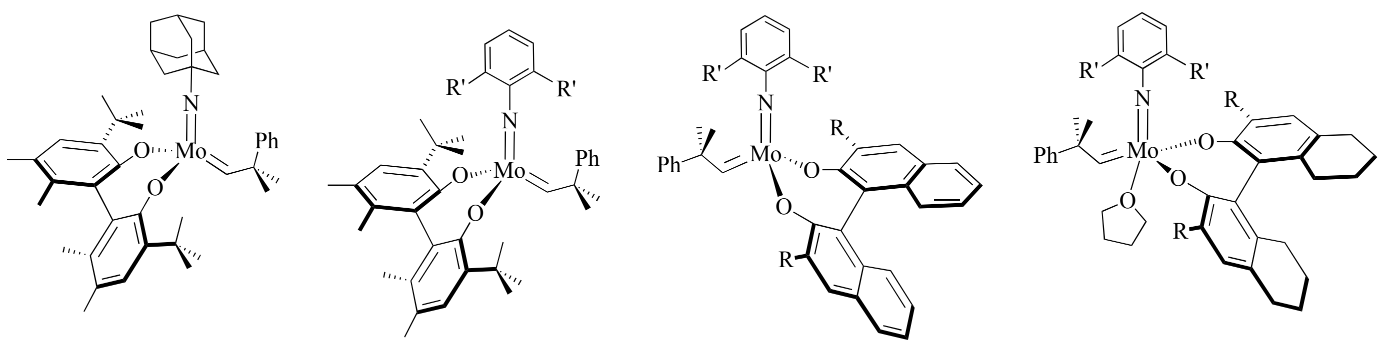
1.1 Introduction.

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.[1,2,3,4,5,6] The vast majority of the established catalysts are four- or five-coordinate species bearing an *aryl*imido ligand along with a chiral diolate chelating the Mo center (**Figure 1**). The first catalyst that contained an *alkyl*imido ligand, 1-adamantylimido, was synthesized in 1993,[7] and various achiral versions of this catalyst have been used for olefin cross metathesis,[8] ring-opening metathesis polymerization (ROMP)[9] and living polymerization of substituted acetylenes.[10]

In 2003 our group published a report on synthesis and catalytic studies of the first chiral alkylimido catalyst, Mo(NAd)($CHCMe_2Ph$)[(S)-Biphen] (Ad = 1-adamantyl; Biphen = 3,3'-di-tert-butyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diolate) **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.[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-triisopropylphenyl)-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.



R = Ph, 2,4,6-i-$Pr_2C_6H_3$

R = t-Bu, 2,4,6-$Me_2C_6H_3$, $CHPh_2$

1a

2a R' = i-Pr
2b R' = Me
2c R' = Cl

3a R' = i-Pr; R = 2,4,6-i-$Pr_3C_6H_2$

4a R' = i-Pr; R = $CHPh_2$

Figure 1. Examples of Mo-based olefin metathesis catalysts bearing chiral diolate ligands.

1.2 Results and Discussion.

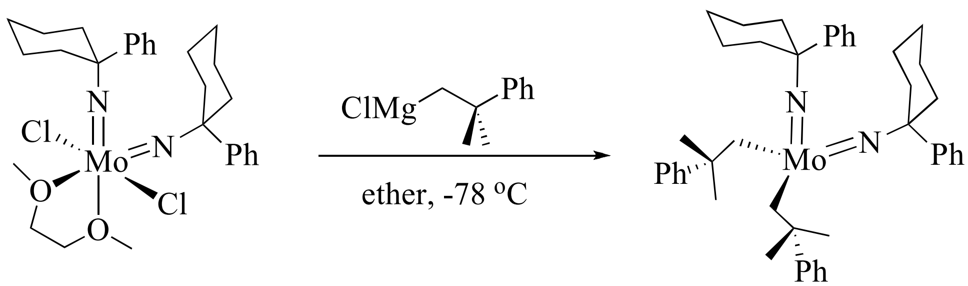
1.2.1 Synthesis and characterization of Mo-based alkylimido olefin metathesis catalysts.

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

The synthetic sequence leading to the Mo(RN)(CHCMe$_2$Ph)(DIOLATE*) catalysts (R = PhCyN, PhAdN; DIOLATE* = (S)-Biphen, (R)-Trip) is similar to the established route towards structurally analogous arylimido compounds.[7] 1-Phenylcyclohexylamine, easily prepared in two steps from 1-phenycyclohexanol,[12] is converted into molybdenum diimido dichloride upon treatment with sodium molybdate, triethylamine and trimethysilyl chloride in DME (**Scheme 1**). At 90 ^{o}C the reaction takes 24 hours to complete, yielding the product in a form of 1,2-dimethoxyethane adduct.

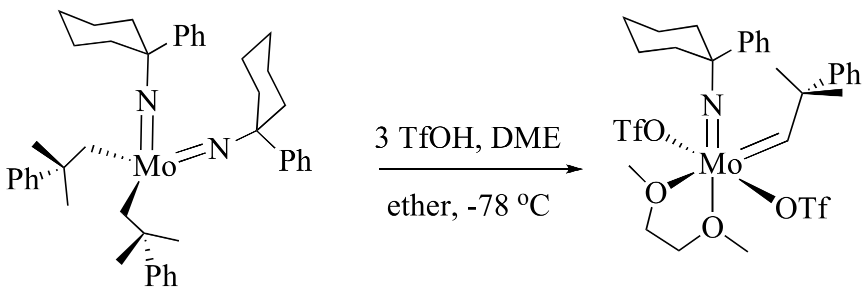
Scheme 1. Synthesis of Mo(PhCyN)Cl$_2$(dme).

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



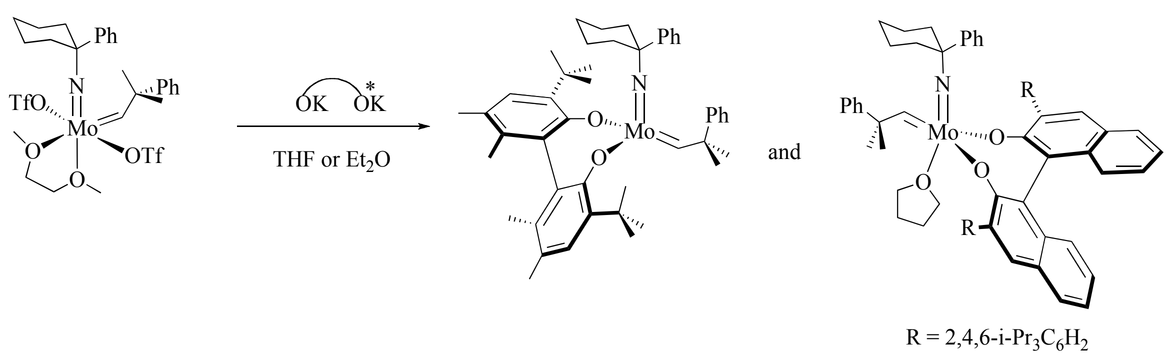
Scheme 2. Synthesis of Mo(PhCyN)$_2$(CH$_2$CMe$_2$Ph)$_2$.

The alkylidene fragment of the catalyst is generated in the next step, when $Mo(PhCyN)_2(CH_2CMe_2Ph)_2$ 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 $Mo(PhCyN)(CH_2CMe_2Ph)(OTf)_2(dme)$.

The resulting bistriflate complex serves as a general precursor to the final catalysts of general formula $Mo(RN)(CHCMe_2Ph)(DIOLATE^*)$. Upon treatment with the enantiomerically pure lithium or potassium diolate, the bistriflate complex is converted into the desired catalyst (**Scheme 4**).



5a **5b**

Scheme 4. Synthesis of $Mo(PhCyN)(CHCMe_2Ph)$[(S)-Biphen] (**5a)** and $Mo(PhCyN)(CHCMe_2Ph)$[(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)(CH_2CMe_2Ph)$(OTf)_2$(dme) according to the reaction in **Scheme 3** yielded a white crystalline compound, which was characterized by ^{1}H 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)(CH_2CMe_2Ph)$(OTf)_2$(dme) altogether, instead trapping it in situ with LiOCMe$(CF_3)_2$. The synthetic protocol for this reaction involved addition of an ethereal solution of LiOCMe$(CF_3)_2$ to the solution of Mo bisimido dialkyl complex, which had been stirred in the presence of triflic acid for 1 hour at -78 ^{o}C and then for 2 hours at room temperature. Mo(PhCyN)(CH_2CMe_2Ph)[OCMe$(CF_3)_2$]$_2$ 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)(CH_2CMe_2Ph)[OCMe$(CF_3)_2$]$_2$ 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)(CH_2CMe_2Ph)$(OTf)_2$(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 ^{13}C NMR spectrum of compound **5a** appears at 274 ppm with J_{CH} = 121 Hz, which is indicative of the *syn* conformation of the catalyst. In the ^{1}H NMR spectrum of compound **5a** in C_6D_6 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 d_8-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**.

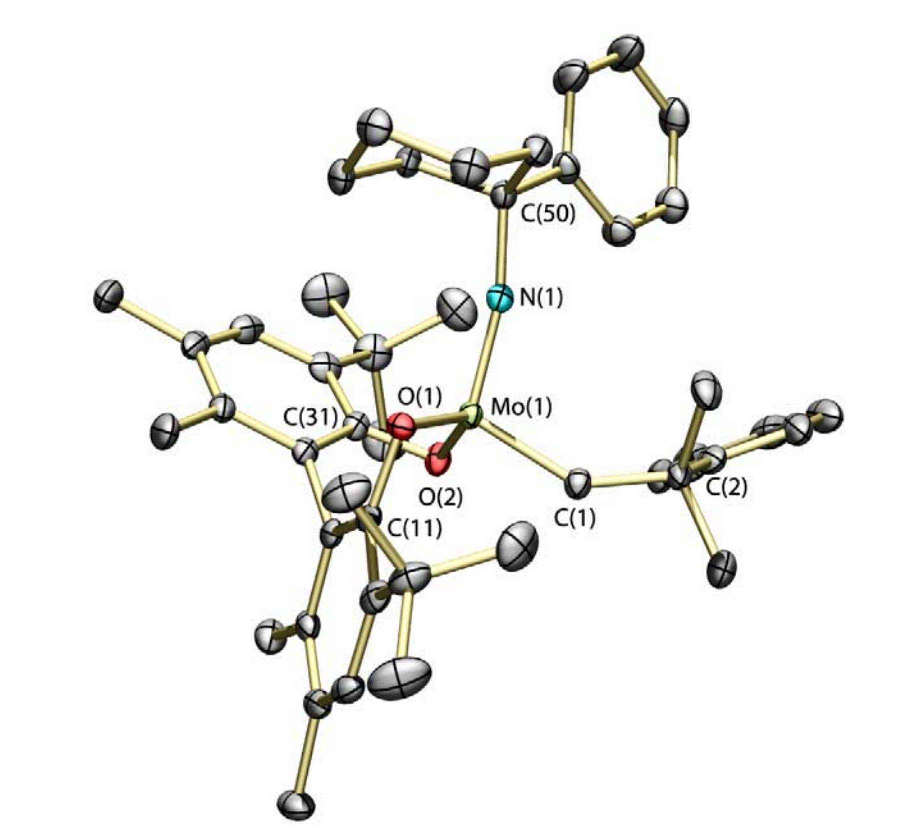


Figure 2. Thermal ellipsoid plot of complex **5a** (50 % probability level, hydrogen atoms omitted for clarity). Crystals of compound **5a** were grown form a concentrated pentane solution at -30 °C.

Table 1. Selected bond lengths (Å) and angles (°) of complex **5a**.

Selected bond lengths (Å) and angles (°)			
Mo(1)-N(1)	1.7185(18)	O(1)-Mo(1)-O(2)	129.45(6)
Mo(1)-C(1)	1.889(2)	N(1)-Mo(1)-C(1)	105.97(9)
Mo-O(2)	2.0070(15)	Mo(1)-O(1)-C(11)	96.30(11)
Mo-O(1)	2.0140(16)	Mo(1)-O(2)-C(31)	94.26(11)
C(1)-C(2)	1.518(3)	Mo(1)-C(1)-C(2)	144.51(16)
N(1)-C(50)	1.458(3)	Mo(1)-(N1)-C(50)	167.18(15)
O(1)-C(11)	1.362(2)		
O(2)-C(31)	1.367(2)		

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**.[11] 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 ^{1}H NMR spectrum of **5b** at 14.0 ppm at room temperature in C_6D_6. The peak corresponding to the alkylidene carbon atom appears in the ^{13}C NMR spectrum at 308 ppm with J_{CH} = 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-d_8 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.

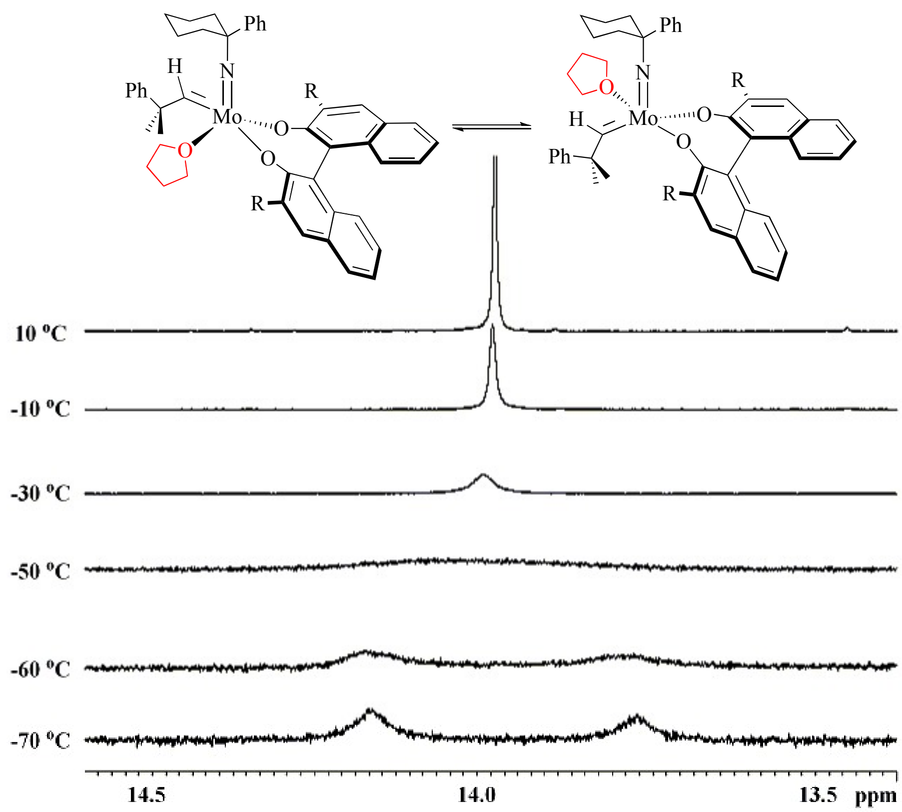
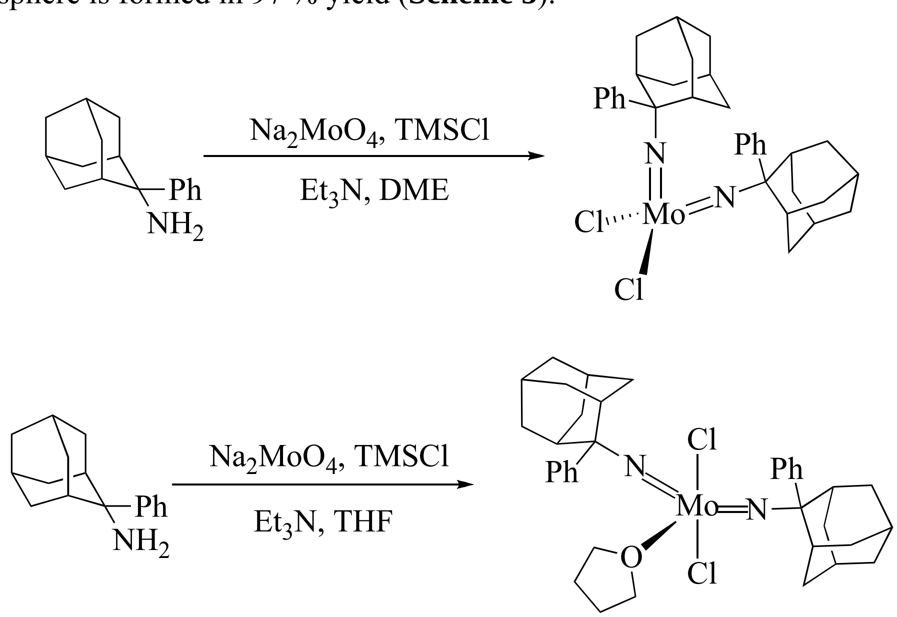


Figure 3. Variable temperature ^{1}H NMR spectrum of d_8-toluene solution of complex **5b.** The low temperature limit of the spectrum shows two peaks corresponding to the diastereomeric THF adducts.

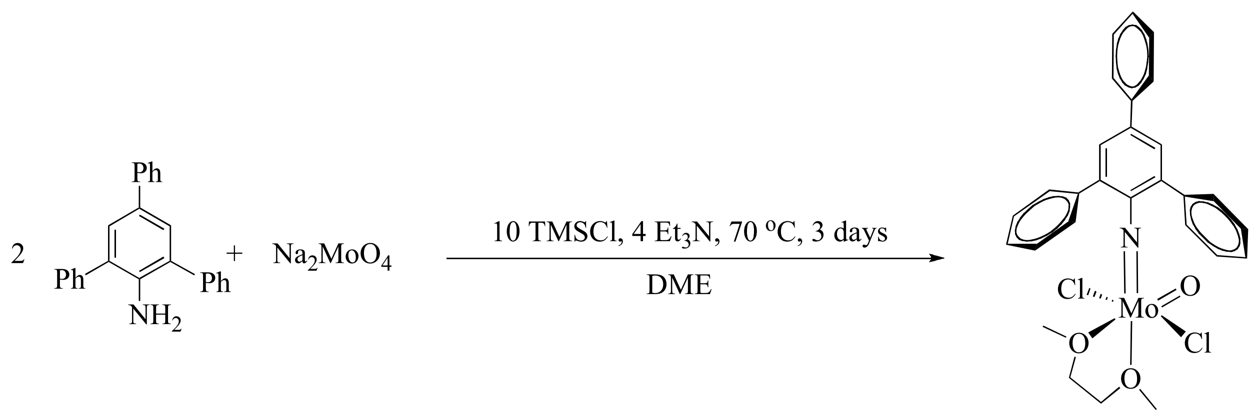
1.2.1 b. Synthesis and characterization of 2-phenyl-2-adamantylimido complexes.

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 $Mo(PhAdN)_2Cl_2$ (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**).



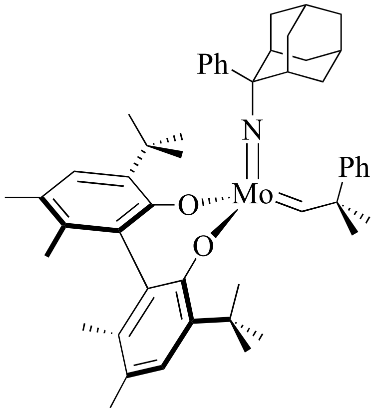
Scheme 5. Synthesis of $Mo(PhAdN)_2Cl_2$ and $Mo(PhAdN)_2Cl_2(THF)$ complexes.

It is interesting to compare formation of $Mo(PhAdN)_2Cl_2$ 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 Na_2MoO_4 and 2,4,6-$Ph_3C_6H_2NH_2$ in DME under conditions, identical to the conditions employed in the synthesis of $Mo(PhAdN)_2Cl_2$, gives six-coordinate monoimido monooxo Mo complex with one molecule of DME in the coordination sphere (**Scheme 6**).[14] 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-$Pr_2C_6H_3N)_2Cl_2$(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.

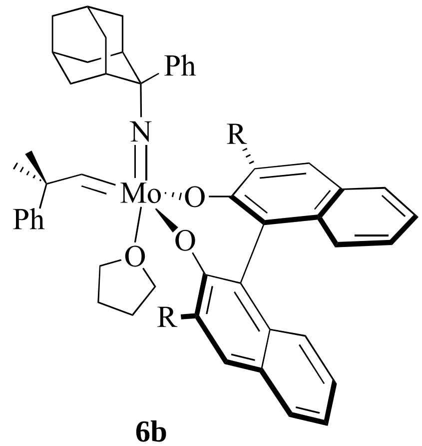


Scheme 6. Synthesis of Mo(2,4,6-$Ph_3C_6H_2N)Cl_2$(O)(dme).

Alkylation of Mo(PhAdN)$_2$Cl$_2$ or Mo(PhAdN)$_2$Cl$_2$(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)(CHCMe$_2$Ph)(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)(CHCMe$_2$Ph)(OTf)$_2$(dme) with (S)-BiphenK$_2$ and (R)-TripK$_2$, respectively. Compounds **6a** and **6b** as well as the NMR data for their alkylidene proton and carbon atoms are shown in **Figure 4**.



6a



6b

^{1}H NMR (C_6D_6): δ 10.7

^{13}C NMR (C_6D_6): δ 274, J_{CH} = 121 Hz

^{1}H NMR (C_6D_6): δ 14.0

^{13}C NMR (C_6D_6): δ 310, J_{CH} = 145 Hz

R = 2,4,6-i-$Pr_3C_6H_2$

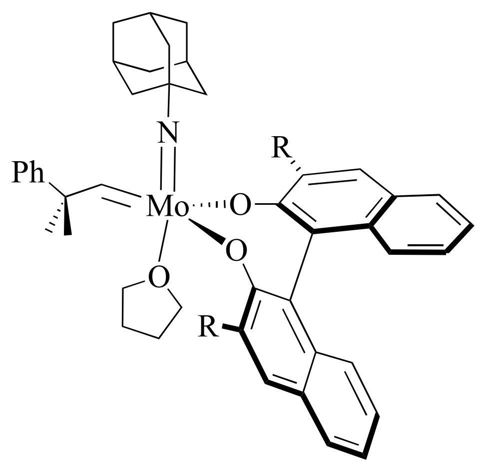
Figure 4. Catalysts **6a** and **6b**. Chemical shifts and coupling constants of the alkylidene proton and carbon atoms in ^{1}H and ^{13}C NMR spectra.

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-d_8 solution of the complex to -80 ^{o}C or heating it to 100 ^{o}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 ^{o}C, suggesting that either the exchange equilibrium between the adducts is fast on NMR time scale, or only one diastereomer is present in toluene-d_8 solution.

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.[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**.



1b

R = 2,4,6-i-$Pr_3C_6H_2$

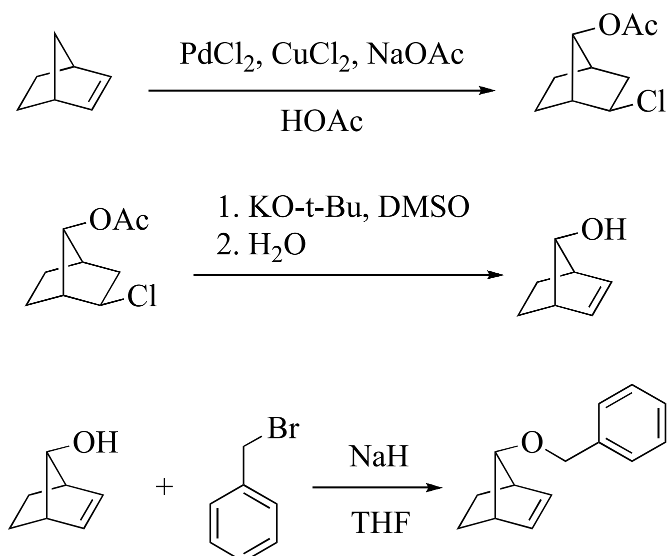
Figure 5. Structure of Mo(AdN)($CHCMe_2Ph$)[(R)-Trip](THF) (**1b**).

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_6D_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.[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.[15] 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**.[16]

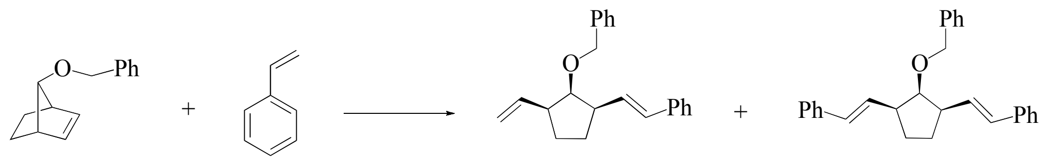
Compound **7** was synthesized according to the sequence shown in **Scheme 7**.[17] This synthesis differs from the originally reported procedure, but affords the product that is spectroscopically identical to the previously reported compound.[16]



7

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**.



7 8 9

Entry	Catalyst [a]	Time, h	T, °C	Yield, % 8	Yield, % 9	ee, % 8
1	**1a**	40	25	56	36	91
2	**5a**	40	25	36	42	80
3	**6a**	40	25	0 [b]	0	-
4	**1b**	40	25	64	24	96
5	**5b**	40	75	61	14	98
6	**6b**	40	75	57	14	98

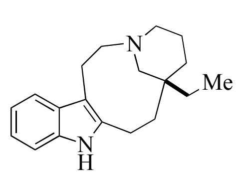
[a] Catalyst loading 5 %, C_6D_6; [b] ROMP of **7** is observed

Figure 6. AROM/CM catalyzed by complexes **1a, 1b, 5a – 6b**.

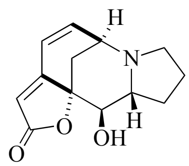
The AROM/CM reaction shown in **Figure 6** gives rise to two major products. Compound **8** is the desired chiral product, and achiral compound **9** is formed when **8** undergoes cross-metathesis with one more equivalent of styrene. Data presented in **Figure 6** show that catalysts **1a** and **5a** 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.

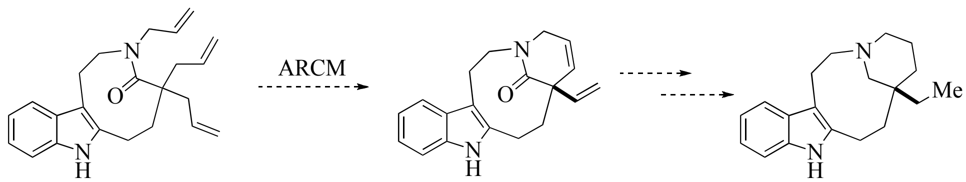
As part of our collaboration focused on development of new catalysts and their applications, Professor Amir Hoveyda and his colleagues at Boston College are interested in introduction of asymmetric olefin metathesis reactions into the syntheses of complex natural products. Among the targets that were 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.[18] 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.

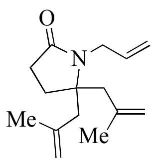


(-)-quebrachamine



secu'amamine A



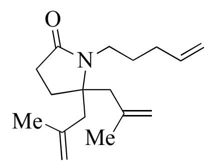


10

5 mol % catalyst
84 h, 22 °C, C_6H_6

Catalyst	Conversion, %	ee, %
2a	>98	93
2b	23	-
2c	17	-
3a	63	>98
4a	69	94

2a, 10% loading, 90% yield, 98% ee

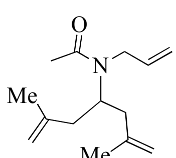


11

10 mol % catalyst
48 h, 22 °C, C_6H_6

Catalyst	Conversion, %	ee, %
4a	20	90

4a, 15% loading, 94% yield, 90% ee

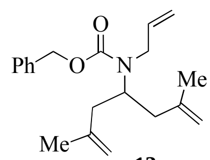


12

5 mol % catalyst
24 h, 22 °C, C_6H_6

Catalyst	Conversion, %	ee, %
1a	>98	96
2a	>98	93
2b	42	90
3a	90	93
4a	13	77

1a, 5% loading, 90% yield, 96% ee



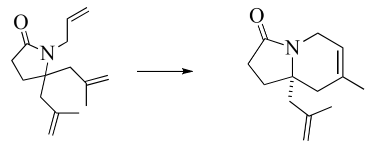
13

5 mol % catalyst
24 h, 22 °C, C_6H_6

Catalyst	Conversion, %	ee, %
1a	>98	96
2b	>98	80
3a	50	-
4a	53	-

1a, 5% loading, 98% yield, 95% ee

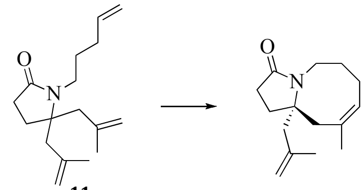
Figure 7. (-)-Quebrachamine and secu'amamine A. ARCM of compounds **10** – **13** using arylimido-based catalysts **2a** – **4a** and **1a**. Results of the optimized catalytic reactions are shown in red.



10 → 14

Entry	Catalyst [a]	Time, h	T, °C	Yield, % **14**	ee, % **14**
1	**1a**	60	25	84	83
2	**5a**	20	25	96	82
3	**6a**	60	25	86	79
4	**1b**	48	65	97	97
5	**5b**	20	65	0	-
6	**6b**	20	65	0	-

[a] Catalyst loading 5 %, C_6D_6



11 → 15

Entry	Catalyst [a]	Time, h	T, °C	Yield, % **15**	ee, % **15**
1	**1a**	44	25	62	>98
2	**5a**	44	25	69	>98
3	**6a**	20	25	23 [b]	-
4	**1b**	48	70	37 [b]	-
5	**5b**	48	70	<5 [b]	-
6	**6b**	48	70	20 [b]	-

[a] Catalyst loading 5 %, C_6D_6; [b] Yield determined by ^1H NMR

Figure 8. ARCM of substrates **10** and **11** using catalysts **1a, 1b, 5a** – **6b**.

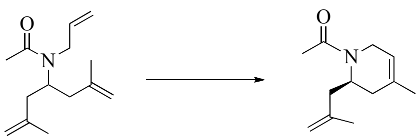
We decided to investigate ARCM of some of these substrates using compounds **1a, 1b, 5a** – **6b** as catalysts and determine relative activity and selectivity levels of the new complexes. All the metathesis reactions were carried out in 20 mL vials equipped with stir bars and teflon-lined caps. The 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 ^{o}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.[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 ^{o}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.

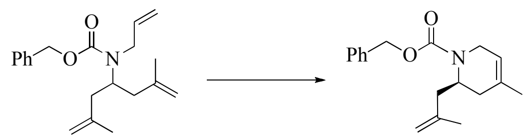
In the case of substrate **12**, the catalysts in entries 1 – 3 afford heterocycle **16** in high yields and excellent enantiomeric excesses. Similarly to the instances discussed above, **6a** exhibits relatively low reactivity compared to analogous catalysts **1a** and **5a**. Complexes **1b** and **5b** require thermal activation to provide conversion of **12** into **16**. However, even if heated to 70 ^{o}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**.



12 **16**

Entry	Catalyst [a]	Time, h	T, ºC	Yield, % **16**	ee, % **16**
1	**1a**	24	25	84	96
2	**5a**	24	25	84	96
3	**6a**	24	25	69	94
4	**1b**	48	70	33 [b]	-
5	**5b**	48	70	34 [b]	-
6	**6b**	48	70	0 [b]	-

[a] Catalyst loading 5 %, C_6D_6; [b] Yield determined by ^1H NMR



13 **17**

Entry	Catalyst [a]	Time, h	T, ºC	Yield, % **17**	ee, % **17**
1	**1a**	48	25	90	96
2	**5a**	48	25	86	94
3	**6a**	48	25	81	83
4	**1b**	36	80	66	81
5	**5b**	36	80	15 [b]	-
6	**6b**	36	80	42	90

[a] Catalyst loading 5 %, C_6D_6; [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 ^oC 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 ^{o}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 H_2SO_4 and water, dried over $CaCl_2$, degassed, and then passed through a column of activated alumina. Deuturated benzene and toluene were dried over CaH_2, degassed and filtered.

1-Phenylcyclohexylamine ($PhCyNH_2$),[12] 2-phenyl-2-adamantylamine ($PhAdNH_2$),[13] catalysts **1a** and **1b**,[15] substrates **7**,[17] **10 – 13**[18] and diolates (S)-BiphenK_2[19] and (R)-TripK_2[20] 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]

^{1}H and ^{13}C NMR spectra were recorded on Varian spectrometers. Chemical shifts in ^{1}H and ^{13}C 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

(Chiraldex CD-GTA column) or chiral HPLC (Chiralcel OD column) analyses in comparison with authentic racemic materials.

Mo(PhCyN)$_2$Cl$_2$(dme). PhCyNH$_2$ (20.0 g, 0.11 mol), Na_2MoO_4 (11.3 g, 0.06 mol), Et_3N (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 ^oC 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 %): ^1H NMR (C_6D_6): δ 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 $C_{28}H_{40}MoO_2Cl_2N_2$: 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)$_2$. 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 ^oC. 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 ^oC 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 %). ^1H NMR (C_6D_6): δ 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)(CHCMe$_2$Ph)(OTf)$_2$(dme). Mo(NCyPh)$_2$(CH$_2$CMe$_2$Ph)$_2$ (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 ^{o}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 ^{o}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 ^{o}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 %). ^{1}H NMR (C$_6$D$_6$): δ 13.96 (s, 1H), 7.57 (d, 2H, J_{HH} = 8.5 Hz), 7.51 (d, 2H, J_{HH} = 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 $C_{28}H_{37}F_6MoS_2NO_8$: C, 42.59; H, 4.72; N, 1.77. Found: C, 42.68; H, 4.79; N, 1.77.

Mo(PhCyN)(CHCMe$_2$Ph)[(S)-Biphen] 5a. (S)-BiphenH$_2$ (99.3 mg, 0.28 mmol) was dissolved in 10 mL of THF and cooled to -35 ^{o}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)(CHCMe$_2$Ph)(OTf)$_2$(dme) (240 mg, 0.28 mmol) in 20 mL of ether, precooled to -35 ^{o}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 %). ^{1}H NMR (C$_6$D$_6$): 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). ^{13}C NMR (C$_6$D$_6$): δ 273.6 (d, J_{CH} = 119.8 Hz). Anal. Calcd. for $C_{46}H_{59}MoNO_2$: C, 73.28; H, 7.89; N, 1.86. Found: C, 73.20; H, 8.05; N, 1.84.

Mo(PhCyN)(CHCMe$_2$Ph)[(R)-Trip](THF) 5b. (R)-TripK$_2$ (214 mg, 0.25 mmol) was dissolved in 10 mL of THF and cooled to -35 ^{o}C. The solution was added to a cold solution of Mo(PhCyN)(CHCMe$_2$Ph)(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 (C_6D_6): 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, J_{HH} = 7 Hz, 1H), 3.07 (septet, J_{HH} = 7 Hz, 1H), 2.95 (septet, J_{HH} = 7 Hz, 1H), 2.78 (septet, J_{HH} = 7 Hz, 1H), 2.56 (br d, J_{HH} = 8 Hz, 1H), 2.32 (br d, J_{HH} = 8 Hz), 2.14 (br s, 4H), 1.85 (d, J_{HH} = 6.6 Hz, 6H), 1.77 (s, 3H), 1.64 (br s, 1H), 1.51 (d, J_{HH} = 6.6 Hz, 6H), 1.42 (d, J_{HH} = 6.9 Hz, 6H), 1.37 (d, J_{HH} = 6.9 Hz, 12H), 1.34-1.20 (m, 3H), 1.24 (s, 3H), 1.17 (d, J_{HH} = 6.9 Hz, 6H), 1.08-1.04 (m, 4H), 0.69 (br s, 4H). ^{13}C NMR (C_6D_6): δ 308.6 (d, J_{CH} = 145 Hz). Anal. Calcd. for $C_{77}H_{93}MoNO_3$: C, 78.61; H, 7.97; N, 1.19. Found: C, 78.47; H, 8.09; N, 1.14.

Mo(PhAdN)$_2$Cl$_2$. PhAdNH$_2$ (5.0 g, 0.22 mol) was dissolved in 150 mL of DME and Na_2MoO_4 (2.3 g, 0.011 mol), Et_3N (6.1 mL, 0.044 mol) and TMSCl (13.9 mL, 0.11 mol) were added. The mixture was stirred at 60 ^{o}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 ^{o}C. Yellow solid was filtered off 48 hours later (3.0 g, 0.05 mol, 44 %). ^{1}H NMR (C_6D_6): δ 7.44 (d, 2H, J_{HH} = 7.5 Hz), 7.25 (t, 2H, J_{HH} = 8 Hz), 7.13 (t, 1H, J_{HH} = 8 Hz), 2.66 (s, 2H), 2.61 (d, 2H, J_{HH} = 13 Hz), 1.89 (s, 1H), 1.71 (d, 2H, J_{HH} = 12.5 Hz), 1.63-1.54 (m, 7H). Anal. Calcd. for $C_{32}H_{38}Cl_2MoN_2$: C, 62.24; H, 6.20; N, 4.54. Found: C, 62.14; H, 6.16; N, 4.38.

Mo(PhAdN)$_2$Cl$_2$(THF). PhAdNH$_2$ (3.16 g, 0.14 mol) was dissolved in 100 mL of THF and Na_2MoO_4 (1.4 g, 0.07 mol), Et_3N (3.9 mL, 0.28 mol) and trimethylsilyl chloride (8.8 mL, 0.69 mol) were added. The mixture was stirred at 85 ^{o}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_6D_6): δ 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 $C_{36}H_{46}Cl_2MoN_2O$: 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 ^{o}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 ^{o}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 ^{o}C and two crops of bright yellow crystals were collected (1.7 g, 2.0 mmol, 42%). ^{1}H NMR (C_6D_6): δ 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 $C_{52}H_{64}N_2Mo$: 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 ^{o}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 ^{o}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 ^{o}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)(CHCMe$_2$Ph)(OTf)$_2$(dme). Mo(PhAdN)$_2$(CH$_2$CMe$_2$Ph)$_2$ (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 ^{o}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 %). ^{1}H NMR (C_6D_6): δ 15.65 (s, 0.6 H), 14.89 (s, 0.4H), 14.11 (s, 1H), 7.54 (d, 2H, J_{HH} = 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 $C_{32}H_{41}F_6MoNO_8S_2$: C, 45.66; H, 4.91; N, 1.66. Found: C, 45.32; H, 5.02; N, 1.78.

Mo(PhAdN)(CHCMe$_2$Ph)[(S)-Biphen] 6a. (S)-BiphenK$_2$ (136 mg, 0.31 mmol) was dissolved in 10 mL of ether and cooled to -35 ^{o}C. The solution was added to a solution of Mo(PhAdN)(CHCMe$_2$Ph)(OTf)$_2$(dme) (266 mg, 0.31 mmol) in 20 ml of ether, precooled to -35 ^{o}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 %). ^{1}H NMR (C_6D_6): δ 10.72 (s, 1H), 7.49 (d, J_{HH} = 7.2 Hz, 1H), 7.32 (d, J_{HH} = 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). ^{13}C NMR (C_6D_6): δ 274.0 (d, J_{CH} = 121.0 Hz). Anal. Calcd. for $C_{50}H_{63}MoNO_2$: C, 74.51; H, 7.88; N, 1.74. Found: C, 74.38; H, 8.08; N, 1.79.

Mo(PhAdN)(CHCMe$_2$Ph)[(R)-Trip](THF) 6b. (R)-TripK$_2$ (181 mg, 0.23 mmol) was dissolved in 10 mL of THF and cooled to -35 ^{o}C. The solution was added to a solution of

Mo(PhAdN)($CHCMe_2Ph$)$(OTf)_2$(dme) (198 mg, 0.23 mmol) in 10 ml of THF, precooled to -35 ^oC, 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 %). ^1H NMR (C_6D_6): δ 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_6D_6): δ 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_6D_6 in a 20 mL vial and 0.36 mL of 0.026 M solution of catalyst **5a** in C_6D_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_6D_6 in a 20 mL vial and 0.74 mL of 0.017 M solution of catalyst **1b** in C_6D_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 ^oC 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**.

Empirical formula	$C_{46}H_{59}MoNO_2$	
Formula weight	753.88	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 12.9341(10) Å	α= 90°
	b = 16.5919(16) Å	β= 90°
	c = 19.2463(18) Å	γ = 90°
Volume	4130.3(6) $Å^3$	
Z	4	
Density (calculated)	1.212 Mg/m^3	
Absorption coefficient	0.354 mm^{-1}	
F(000)	1600	
Crystal size	0.15 x 0.05 x 0.04 mm^3	
Theta range for data collection	1.90 to 29.57°.	
Index ranges	-17<=h<=17, 0<=k<=23, 0<=l<=26	
Reflections collected	93372	
Independent reflections	11592 [R(int) = 0.0647]	
Completeness to theta = 29.57°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9860 and 0.9489	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11592 / 0 / 463	
Goodness-of-fit on F^2	1.095	
Final R indices [I>2sigma(I)]	R1 = 0.0365, wR2 = 0.0828	
R indices (all data)	R1 = 0.0416, wR2 = 0.0856	
Absolute structure parameter	-0.01(2)	
Largest diff. peak and hole	1.443 and -0.315 e.$Å^{-3}$	

1.5 References.

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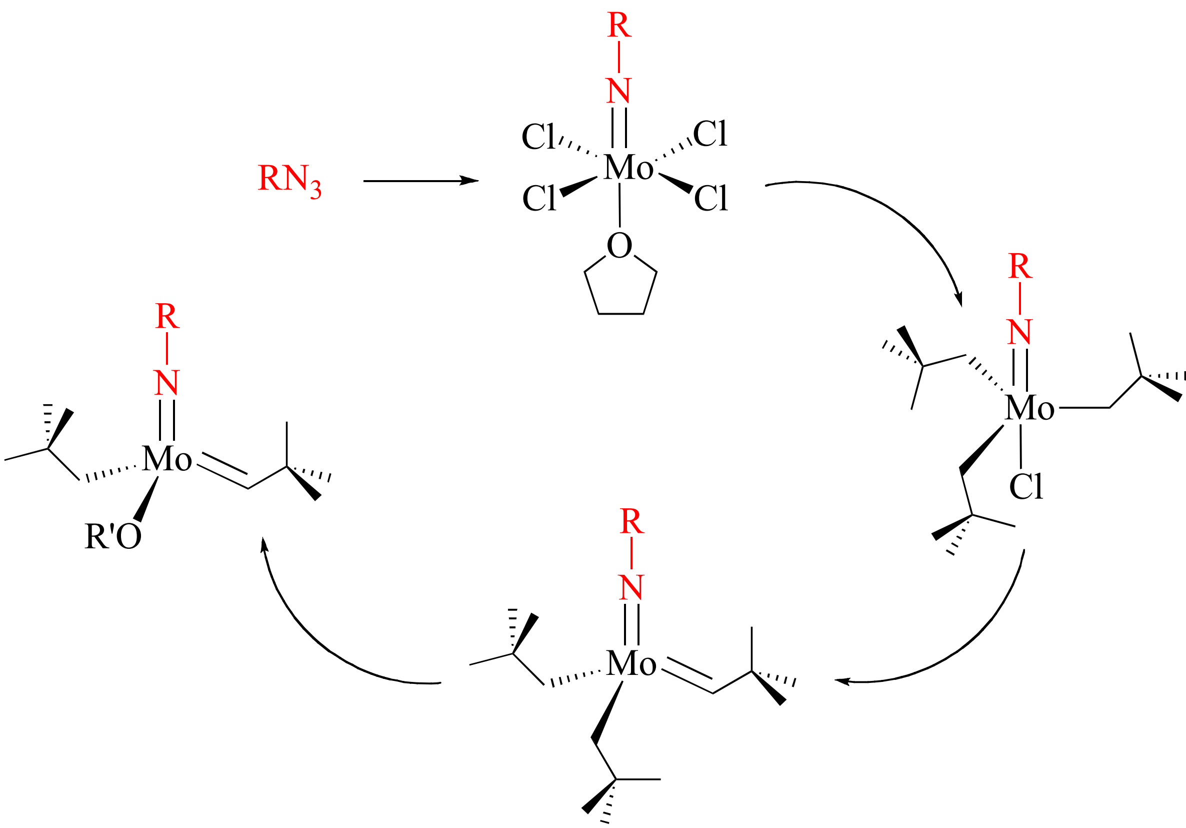
Chapter 2

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

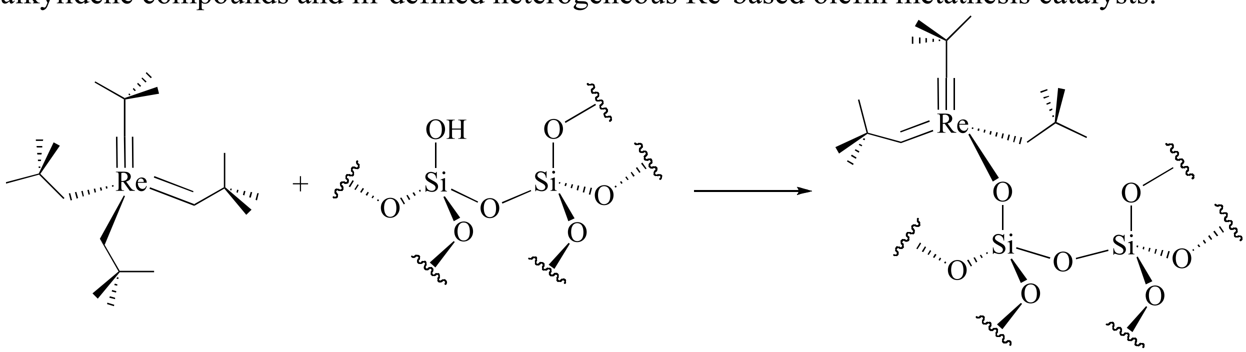


A portion of this work has appeared in print:

Pilyugina, T. S.; Schrock, R. R.; Hock, A. S.; Mueller, P. Synthesis of Molybdenum(VI) Monoimido Alkyl and Alkylidene Complexes. *Organometallics* **2005**, *24*, 1929-1937.

2.1 Introduction.

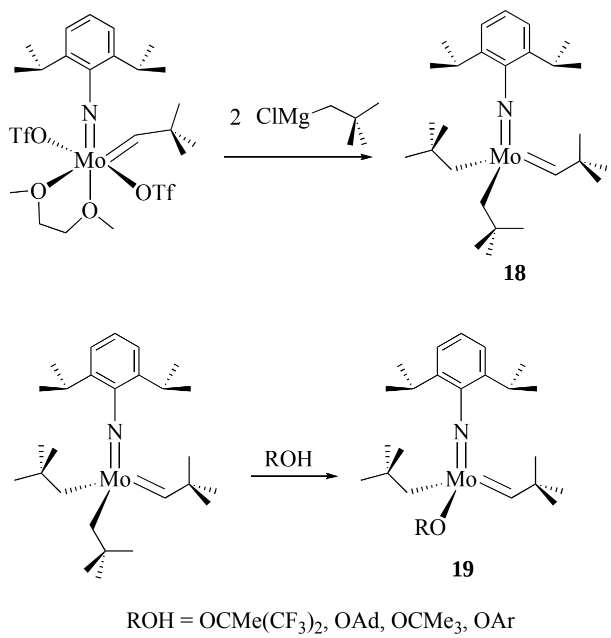
Immobilization of homogeneous catalysts on solid supports facilitates catalyst separation from reaction mixtures and their recycling. In addition to this practical merit, some reports have demonstrated that immobilization of a catalyst can also affect aspects of the catalyst performance such as activity, stability, and selectivity.[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.[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)(CH_2-t-Bu)$_2$, 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.[10,11,12]



Scheme 8. Immobilization of Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)$_2$ on a partially dehydroxylated silica surface.

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)(CH_2-t-Bu)$_2$ and investigate their reactivity towards alcohols and, potentially, silica.

Dr. Amritanshu Sinha synthesized Mo(NAr)(CH-t-Bu)Np_2 (Np = CH_2-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-$Pr_2C_6H_3$).[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.



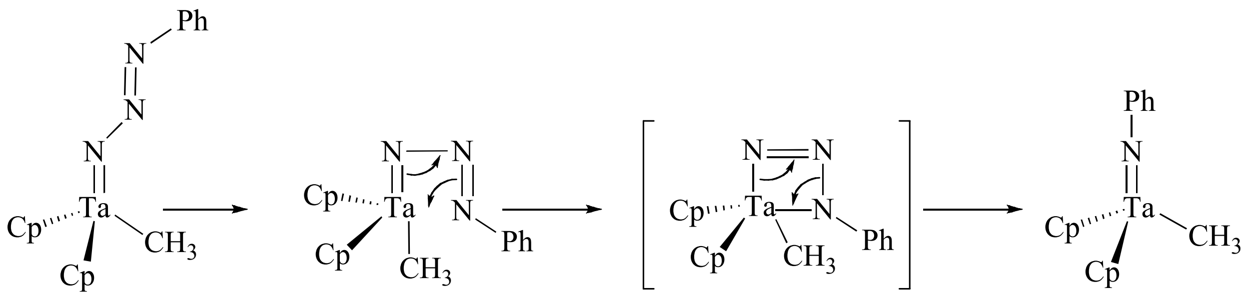
Scheme 9. Synthesis of compound **18**. Protonolysis of **18** with a variety of alcohols produces Mo imido alkylidene alkyl alkoxide complexes **19** (Ad = 1-adamantyl).

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)Np_2 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)Np_2, can be prepared in a 4 step sequence from W(NAr)Cl_4(Et_2O).[15] We proposed that a potentially more direct route to Mo(NR)(CH-t-Bu)Np_2 complexes would involve a synthesis patterned after that for the W analogs, i.e., addition of neopentyl groups to Mo(NR)Cl_4(THF) complexes. W(NAr)Cl_4(Et_2O), the starting material for the reported synthetic sequence, is formed upon treatment of W(O)Cl_4 with aryl isocyanate. This reaction is not viable for molybdenum compounds, since in the case of W(O)Cl_4 the transformation requires prolonged heating, while the corresponding starting material for the synthesis of Mo complexes, Mo(O)Cl_4, is thermally unstable.

The proposed new route to Mo(NR)Cl_4(THF) complexes involved 2-electron oxidation of $MoCl_4(THF)_2$ 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,[16] V,[17] Ta,[18,19] W,[20] Mn,[21] Re,[22] Fe,[23] Co,[24,25,26] Ni [27] and U.[28] Several Mo(NR)Cl_4(THF) complexes synthesized from arylazides have appeared in the literature. The first, Mo(N-p-tolyl)Cl_4(THF), was published in 1984 by Maatta.[29] It was prepared in high yield by adding p-tolylazide to $MoCl_4(THF)_2$ and was crystallographically characterized. A dimeric version in which two imido nitrogens are linked with a p-phenylene group, (THF)Cl_4Mo=N-p-C_6H_4-N=MoCl_4(THF), was synthesized in an analogous manner.[30] Mo($NCH_2CH=CH_2$)Cl_4(THF) was prepared in situ from allylazide and $MoCl_4(THF)_2$; it was not isolated or characterized, but converted directly into a Mo(V) bisphosphine derivative.[31] All published imido tetrachlorides are reduced readily by phosphines to yield Mo(V) species, e.g., Mo(NAllyl)$Cl_3(PPh_3)_2$.

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 $MesN_3$ and V(I)$(NRAr_F)_2$ (Mes = 2,4,6-$Me_3C_6H_2$, R = $C(CD_3)_2CH_3$, Ar_F = 2,5-$FMeC_6H_3$) at -100 ^oC yields a "diazenylimido" species, V(N_3Mes)(I)$(NRAr_F)_2$.[17] V(N_3Mes)(I)$(NRAr_F)_2$ decomposes bimolecularly upon mild heating to give N_2 and the expected imido complex V(NMes)(I)$(NRAr_F)_2$. This observation is in contrast to the report by Bergman and coworkers, who explored decomposition of a tantalum organoazido complex $Cp_2Ta(N_3Ph)(CH_3)$.[19] $Cp_2Ta(N_3Ph)(CH_3)$ 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. Mechanism of $Cp_2Ta(NPh)(CH_3)$ formation from $Cp_2Ta(N_3Ph)(CH_3)$.

We decided to further explore the reactivity of $MoCl_4(THF)_2$ towards aromatic and aliphatic azides, and to approach the synthesis of Mo(NR)(CH-t-Bu)(CH_2-t-Bu)$_2$ complexes through alkylation of Mo(NR)$Cl_4(THF)_2$ compounds.

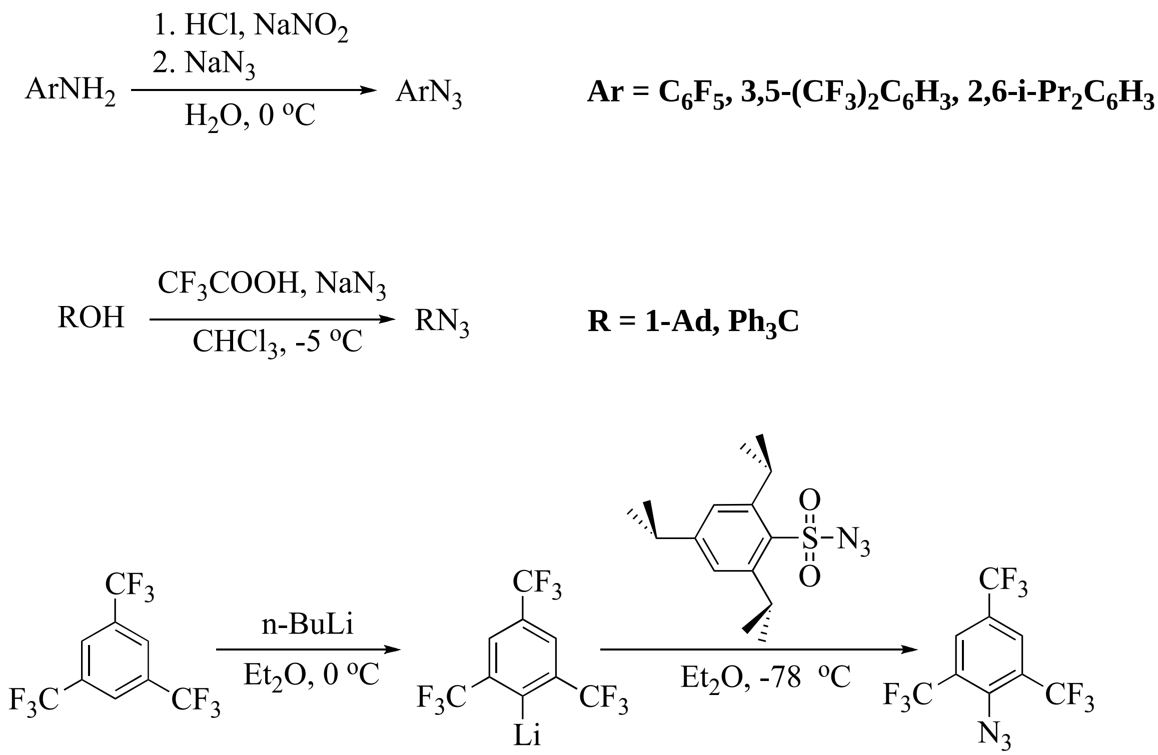
2.2 Results and Discussion.

2.2.1 Synthesis of Mo imido complexes with achiral imido groups.

2.2.1.a Synthesis of Mo imido tetrachloride complexes.

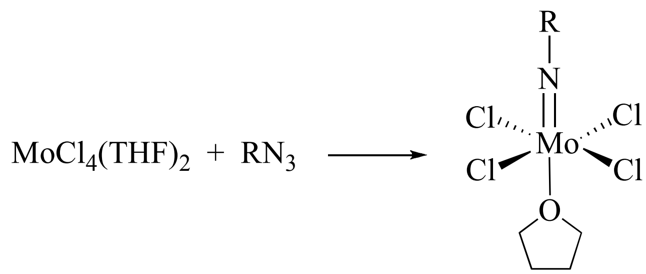
We were interested in the possibility of preparing catalysts that contain an electron-withdrawing imido group, and therefore chose to attempt to prepare pentafluorophenylimido, 3,5-bis(trifluoromethyl)phenylimido and 2,4,6-tris(trifluoromethyl)phenylimido Mo(NR)Cl_4(THF) complexes. We also were interested in preparing alkylimido complexes, and for this reason chose 1-adamantylimido (AdN) and tritylimido (triphenylmethylimido). Finally, we chose to prepare $Mo(NAr)Cl_4(THF)$ (Ar = 2,6-i-$Pr_2C_6H_3$), since molybdenum alkylidene complexes that contain the NAr group are the most numerous and stable.[13]

Pentafluorophenyl azide,[32] 3,5-bis(trifluoromethyl)phenyl azide,[33] 2,4,6-tris(trifluoromethyl)phenyl azide,[34] 1-adamantyl azide,[35] triphenylmethyl azide,[36] and 2,6-diisopropylphenyl azide [37] were prepared according to **Scheme 11**.



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 $MoCl_4(THF)_2$[38] to give complexes of the type $Mo(NR)Cl_4(THF)$ in good (66 %) to excellent (96 %) yields (**Scheme 12**). The lowest yield was obtained for $Mo(NAr)Cl_4(THF)$ 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 $MoCl_4(THF)_2$ in $(CH_2Cl)_2$. Slightly lower yields of the product were obtained when 1,2-dichloroethane was used as a solvent (synthesis of $Mo(NC_6F_5)Cl_4(THF)$: 8 hours, 50 °C, 73 % yield in $(CH_2Cl)_2$; 30 hours, 50 °C, 88 % yield in toluene).



Scheme 12. Synthesis of $Mo(NR)Cl_4(THF)$ complexes.

2,4,6-Tris(trifluoromethyl)phenyl azide failed to give the expected imido tetrachloride complex upon reaction with $Mo(NR)Cl_4(THF)$ under various condition.[39] The brick-red powder isolated from these reaction mixtures showed no resonances in the ^{19}F NMR spectrum and broad signals in the ^{1}H NMR spectrum, indicating formation of a paramagnetic Mo complex. The nature of this product was not investigated further.

Single crystals of $Mo[N\text{-}3,5\text{-}(CF_3)_2C_6H_3]Cl_4(THF)$ were grown from pentane and an X-ray determination was carried out (**Tables 3** and **4,** pages 58 and 91). The structure of $[N\text{-}3,5\text{-}(CF_3)_2C_6H_3]Cl_4(THF)$ (**Figure 10**) is closely analogous to that of $Mo(N\text{-}p\text{-}tolyl)Cl_4(THF)$.[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.

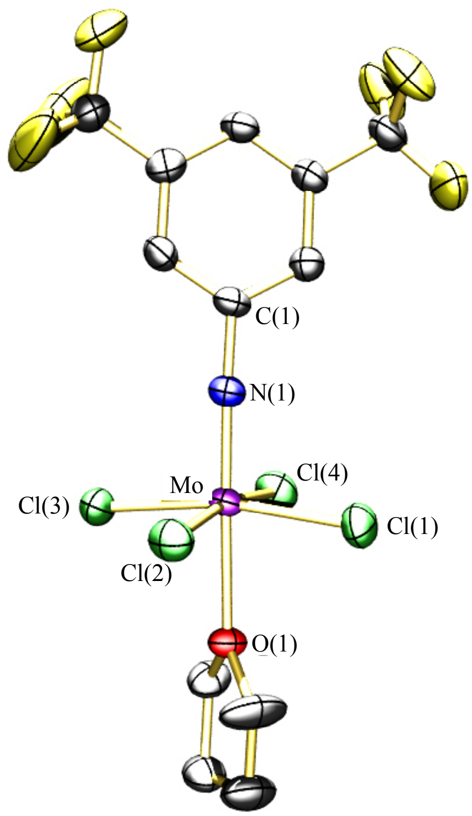
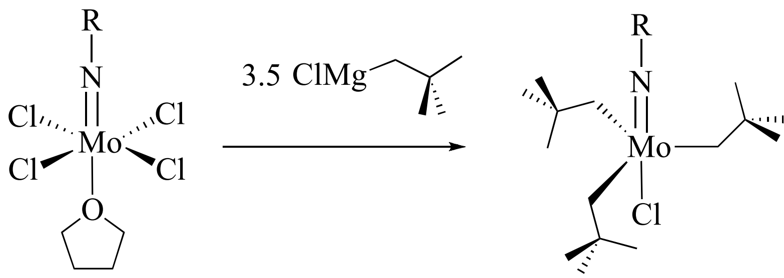


Figure 10. Thermal ellipsoid plot of complex $Mo[N\text{-}3,5\text{-}(CF_3)_2C_6H_3]Cl_4(THF)$ (50 % probability level, hydrogen atoms omitted for clarity).

2.2.1.b Synthesis of Mo imido trineopentyl complexes.

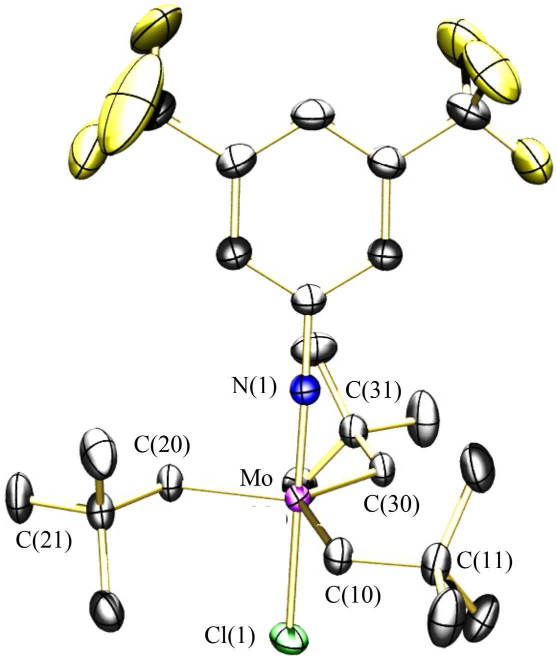
Osborn reported in 1987 that $Mo(N\text{-}t\text{-}Bu)(O)Cl_2(MeCN)_3$ could be alkylated with $MgNp_2$(Dioxane) in diethyl ether to yield $Mo(N\text{-}t\text{-}Bu)Np_3Cl$ in 35% yield as a colorless crystalline solid.[40] On the basis of proton NMR spectra he proposed that this compound has a trigonal bipyramidal structure with the neopentyl groups in equatorial positions. We have found that addition of $Mo(NR)Cl_4(THF)$ complexes in toluene to a cold solution of NpMgCl in ether gave analogous $Mo(NR)Np_3Cl$ species **20** - **24** (R = C_6F_5, $3,5\text{-}(CF_3)_2C_6H_3$, Ad, Ph_3C, and $2,6\text{-}i\text{-}Pr_2C_6H_3$) 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.



R = C_6F_5	**20**
R = 3,5-$(CF_3)_2C_6H_3$	**21**
R = 1-Ad	**22**
R = Ph_3C	**23**
R = 2,6-i-$Pr_2C_6H_3$	**24**

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-C_α-C_β angles of ~121° and Mo-C_α bond distances of ~2.14 Å. These Mo-C_α-C_β angles and Mo-C_α 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.



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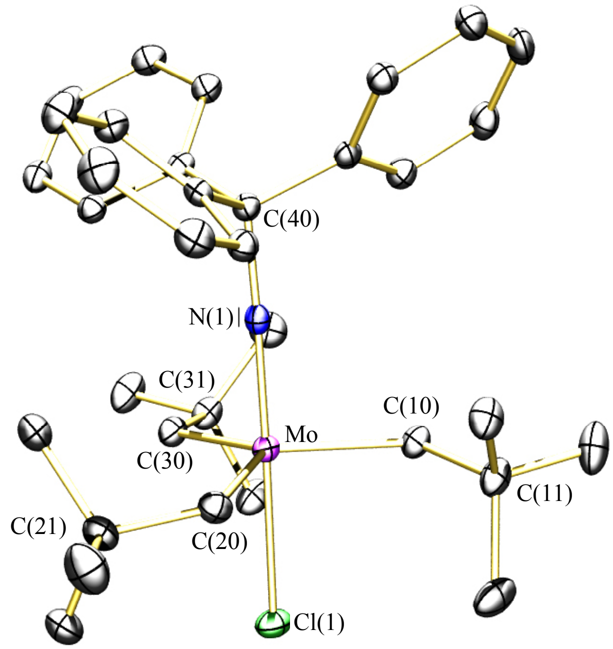


23

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-$(CF_3)_2C_6H_3$]Cl_4(THF), Mo[N-3,5-$(CF_3)_2C_6H_3$]Np_3Cl (**21**), and Mo($NCPh_3$)Np_3Cl (**23**).

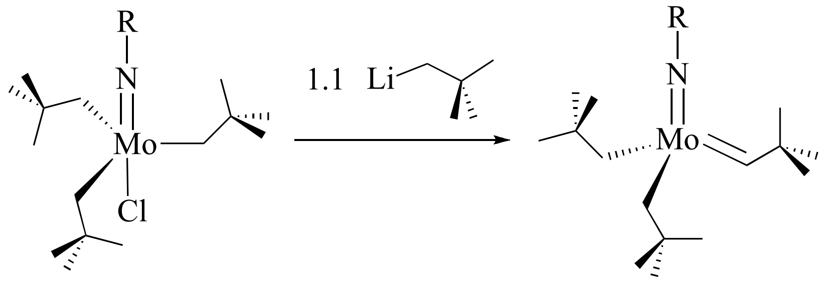
Mo[N-3,5-$(CF_3)_2C_6H_3$]Cl_4(THF)		Mo[N-3,5-$(CF_3)_2C_6H_3$]Np_3Cl		Mo($NCPh_3$)Np_3Cl	
Mo-N(1)	1.711(3)	Mo-N(1)	1.7471(17)	Mo-N(1)	1.7509(15)
Mo-Cl(1)	2.3271(12)	Mo-C(10)	2.1473(19)	Mo-C(10)	2.1507(18)
Mo-Cl(2)	2.3137(11)	Mo-C(20)	2.151(2)	Mo-C(20)	2.1430(19)
Mo-Cl(3)	2.3311(11)	Mo-C(30)	2.1281(19)	Mo-C(30)	2.1475(18)
Mo-Cl(4)	2.3459(11)	Mo-Cl(1)	2.3944(5)	Mo-Cl(1)	2.4268(7)
Mo-O(1)	2.230(2)	N(1)-Mo-C(10)	90.24(8)	N(1)-Mo-C(10)	93.83(7)
N(1)-Mo-Cl(1)	95.39(12)	N(1)-Mo-C(20)	91.69(8)	N(1)-Mo-C(20)	94.03(7)
N(1)-Mo-Cl(2)	98.03(12)	N(1)-Mo-C(30)	93.06(8)	N(1)-Mo-C(30)	93.03(7)
N(1)-Mo-Cl(3)	95.69(12)	C(10)-Mo-C(20)	120.17(8)	C(10)-Mo-C(20)	117.89(7)
N(1)-Mo-Cl(4)	92.20(12)	C(10)-Mo-C(30)	120.34(7)	C(10)-Mo-C(30)	121.13(7)
N(1)-Mo-O(1)	176.09(13)	C(20)-Mo-C(30)	119.23(8)	C(20)-Mo-C(30)	119.80(7)
C(1)-N(1)-Mo	171.4(3)	N(1)-Mo-Cl(1)	177.39(6)	N(1)-Mo-Cl(1)	178.25(5)
O(1)-Mo-Cl(1)	84.51(7)	C(1)-N(1)-Mo	174.94(15)	C(40)-N(1)-Mo	178.16(12)
O(1)-Mo-Cl(2)	85.88(7)	C(10)-Mo-Cl(1)	87.55(6)	C(10)-Mo-Cl(1)	86.77(5)
O(1)-Mo-Cl(3)	84.39(7)	C(20)-Mo-Cl(1)	88.24(6)	C(20)-Mo-Cl(1)	87.14(5)
O(1)-Mo-Cl(4)	83.89(7)	C(30)-Mo-Cl(1)	89.24(6)	C(30)-Mo-Cl(1)	85.26(5)
Cl(2)-Mo-Cl(1)	89.42(4)	C(11)-C(10)-Mo	120.42(13)	C(11)-C(10)-Mo	123.86(12)
Cl(2)-Mo-Cl(3)	89.73(4)	C(21)-C(20)-Mo	121.25(14)	C(21)-C(20)-Mo	121.10(12)
Cl(2)-Mo-Cl(4)	169.77(4)	C(31)-C(30)-Mo	121.71(13)	C(31)-C(30)-Mo	122.69(12)
Cl(1)-Mo-Cl(3)	168.89(4)				
Cl(1)-Mo-Cl(4)	89.61(5)				
Cl(3)-Mo-Cl(4)	89.26(4)				

2.2.1.c Synthesis of Mo imido neopentylidene complexes.

Heating **24** in C_6D_6 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 C_6D_6 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 $Mo(NAr)Np_3(OC_6F_5)$ to $Mo(NAr)(CH\text{-}t\text{-}Bu)Np(OC_6F_5)$ in C_6D_6 at 60 °C ($1.0 \times 10^{-4}\ s^{-1}$).[14] 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 $Mo(NR)Np_3Cl$ species were found to be more stable than $Mo(NAr)Np_3Cl$, 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 $Mo(NAr)(CH\text{-}t\text{-}Bu)Np_2$ (**18**) in 90 % yield (δ H_α = 9.50 in C_6D_6, δ C_α = 255 ppm in C_6D_6, J_{CH} = 108 Hz). This compound is identical in all respects to the relatively stable crystalline solid prepared by alkylation of $Mo(NAr)(CH\text{-}t\text{-}Bu)(OTf)_2(dme)$.[13] The low J_{CH} value is typical of imido alkylidenes that have a *syn* orientation with respect to the imido group.[41]

Addition of neopentyllithium to $Mo(NCPh_3)Np_3Cl$ led to formation of $Mo(NCPh_3)(CH\text{-}t\text{-}Bu)Np_2$ (**25**) as a pentane soluble ivory powder in 96 % yield (**Scheme 14**). The proton NMR spectrum of **25** in C_6D_6 shows the neopentylidene H_α resonance at 8.95 ppm and the C_α resonance at 250.1 ppm with J_{CH} = 109 Hz. It should be noted that although $Mo(N\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)Np_2$ could be prepared in 75 % yield, it could be isolated only as a brown oil (δ H_α = 9.22, δ C_α = 249.5 in C_6D_6).[40] The purity of this compound was not confirmed.



R = 2,6-i-PrC_6H_3 **18**
R = CPh_3 **25**

Scheme 14. Synthesis of the Mo imido dialkyl alkylidene complexes **18** and **25**.

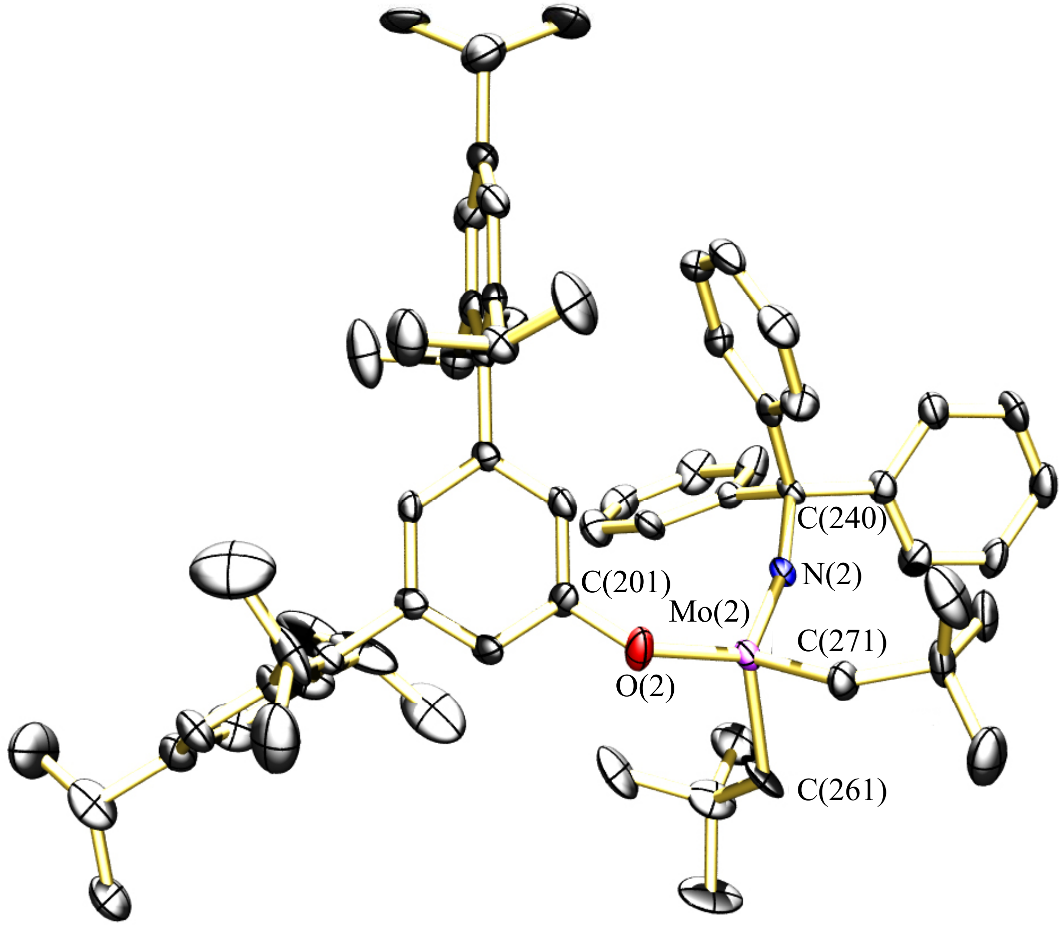
Addition of neopentyllithium to Mo(NAd)Np_3Cl led to formation of what is believed to be Mo(NAd)(CH-t-Bu)Np_2 with δ H_α = 9.22 ppm in C_6D_6. This species is not stable in solution at 22 °C, judging from the appearance of olefinic resonances at 5.38 and 5.42 ppm, which are characteristic of *cis* and *trans* (t-Bu)CH=CH(t-Bu), the product of bimolecular coupling of neopentylidenes. Mo(NAd)(CH-t-Bu)Np_2 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)Np_2[40] 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. ^{1}H 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 neopentylidene complex challenging. The presumed product, Mo[N-3,5-$(CF_3)_2C_6H_3$](CH-t-Bu)Np_2, 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($NCPh_3$)(CH-t-Bu)Np(OAryl) 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-$Pr_3C_6H_2)_2C_6H_3OH$ (HIPTOH), which was prepared in 75 % yield from 3,5-(2,4,6-i-$Pr_3C_6H_2)_2C_6H_3Br$,[43,44] with **25** gives Mo($NCPh_3$)(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**.



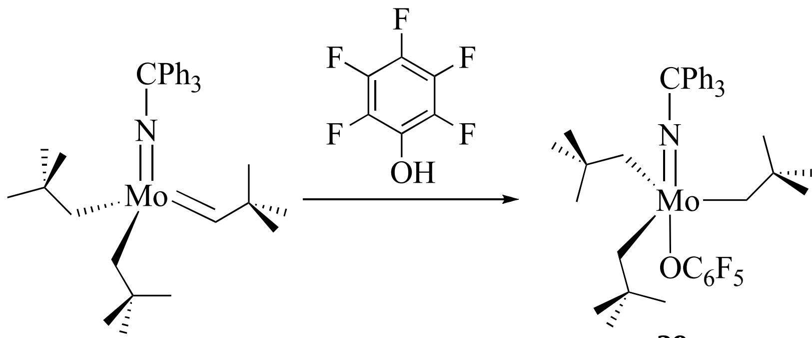
28

Figure 12. Thermal ellipsoid plot of **28** (50 % probability level, hydrogen atoms omitted for clarity).

Table 5. Selected bond lengths (Å) and angles (°) in the two molecules of **28**.

Selected bond lengths (Å) and angles (°)					
Mo(1)-N(1)	1.725(4)	Mo(2)-N(2)	1.725(4)	Mo(1)-C(171)	1.886(5)
Mo(2)-C(271)	1.855(5)	Mo(1)-O(1)	1.928(4)	Mo(2)-O(2)	1.926(4)
Mo(1)-C(161)	2.154(5)	Mo(2)-C(261)	2.107(6)		
N(1)-Mo(1)-C(171)	105.4(2)	N(2)-Mo(2)-C(271)	106.7(2)		
N(1)-Mo(1)-O(1)	123.97(15)	N(2)-Mo(2)-O(2)	125.29(16)		
C(171)-Mo(1)-O(1)	111.0(2)	C(271)-Mo(2)-O(2)	109.7(2)		
N(1)-Mo(1)-C(161)	105.0(2)	N(2)-Mo(2)-C(261)	107.7(2)		
C(171)-Mo(1)-C(161)	92.9(2)	C(271)-Mo(2)-C(261)	106.5(3)		
O(1)-Mo(1)-C(161)	113.9(2)	O(2)-Mo(2)-C(261)	99.4(2)		
C(162)-C(161)-Mo(1)	122.3(4)	C(262)-C(261)-Mo(2)	131.9(4)		
C(172)-C(171)-Mo(1)	146.9(4)	C(272)-C(271)-Mo(2)	148.5(4)		
C(101)-O(1)-Mo(1)	133.4(3)	C(201)-O(2)-Mo(2)	126.0(4)		
C(140)-N(1)-Mo(1)	164.1(3)	C(240)-N(2)-Mo(2)	161.2(3)		

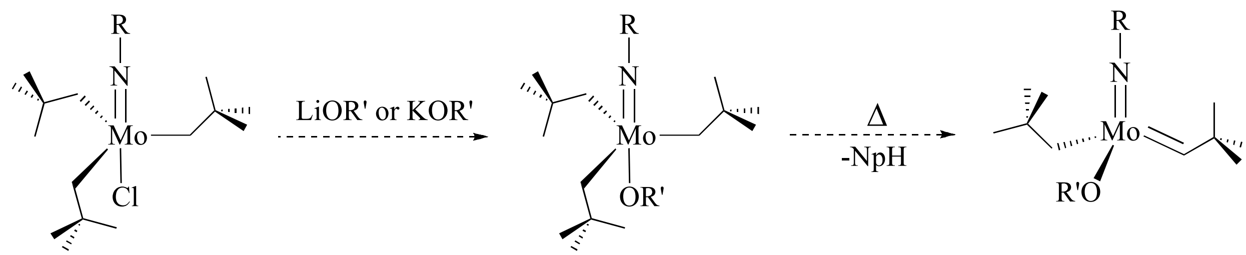
A reaction between **25** and C_6F_5OH gives $Mo(NCPh_3)Np_3(OC_6F_5)$ (**29**) as an off-white powder in 93 % yield (**Scheme 15**). The difference in behavior between the phenols described above and pentafluorophenol in the manner in which they react with a dineopentyl neopentylidene complex is analogous 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 C_6D_6 to 60 ^oC for 2 days. In contrast, when d_6-benzene solutions of $Mo(NAr)Np_3(OC_6F_5)$ are heated to 60 °C, neopentane evolves smoothly and $Mo(NAr)(CH\text{-}t\text{-}Bu)Np(OC_6F_5)$ is formed in a monomolecular manner with k = 1.0 x 10^{-4} s^{-1}.[14] It is not clear whether the more rapid decomposition of $Mo(NAr)Np_3(OC_6F_5)$ can be ascribed to steric or electronic differences between the imido groups, or both.



29

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_6F_5, 3,5-$(CF_3)_2C_6H_3$ 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 $Mo(NR)(CH\text{-}t\text{-}Bu)Np_2$ 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 $Mo(NAr)Np_3(OC_6F_5)$, which upon heating is smoothly converted into the alkylidene complex Mo(NAr)(CH-t-Bu)$Np(OC_6F_5)$ via α-H abstraction. We planned to employ a similar transformation to generate the desired alkylidene compounds (**Scheme 16**).



20, **21** and **22**

Scheme 16. The proposed synthetic sequence towards Mo(NR)(CH-t-Bu)Np(OR’) complexes.

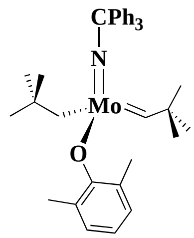
Reactions between imido trineopentyl chloride complexes and lithium or potassium alkoxides under various conditions (**Table 6**) led to the formation of the desired Mo(NR)Np_3(OR’) complexes along with small amounts of decomposition products, as judged by ^{1}H NMR spectroscopy of the reaction mixtures. The spectra of these reaction mixtures invariably contained small amounts of di-tert-butylethylene, indicating that the expected trialkyl alkoxide products had undergone α-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.

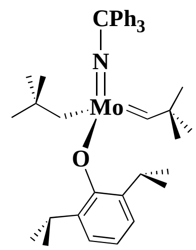
Mo complex	Alkoxide	Time, h	T, °C	Solvent
20	$LiOCMe(CF_3)_2$	24	25	C_6D_6
20	$LiOCMe(CF_3)_2$	24	50	C_6D_6
20	$LiOCMe(CF_3)_2$	48	50	THF
21	$KOCH(CF_3)_2$	12	60	THF
21	KO-t-Bu	48	60	C_6H_6
21	KO-t-Bu	24	25	THF
21	KO-t-Bu	24	60	THF
22	KO-t-Bu	24	25	C_6D_6
22	KO-t-Bu	24	70	C_6D_6

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

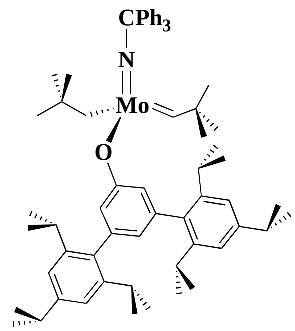
The three monophenoxide neopentylidene complexes **26**, **27** and **28** showed metathesis activity for ring-closing of a small selection of substrates shown in **Figure 13**.[45] It is worth noting that in the case of complexes **26** and **27** the majority of the initial species can be observed 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 $Mo(NCPh_3)(CH_2)Np(OHIPT)$, 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.



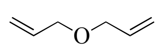
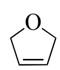
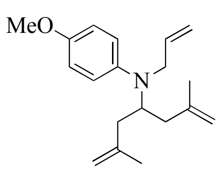
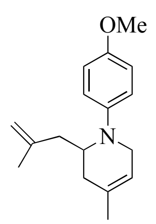
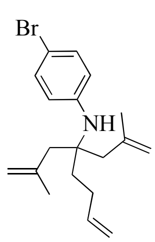
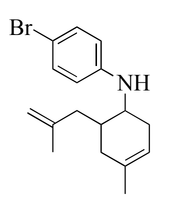
26



27



28

Substrate	Product	Catalyst	Time, h	Conversion, % [a]
		**26**	1	85
			12	100
		27	0.3	4
			12	100
		28	1	40
			24	40
		**26**	1	89
		27	12	54
			30	78[b]
		28	1	30
			24	36
		**26**	1	40
			24	89
		27	12	54
			30	75[b]
		28	1	34
			24	34

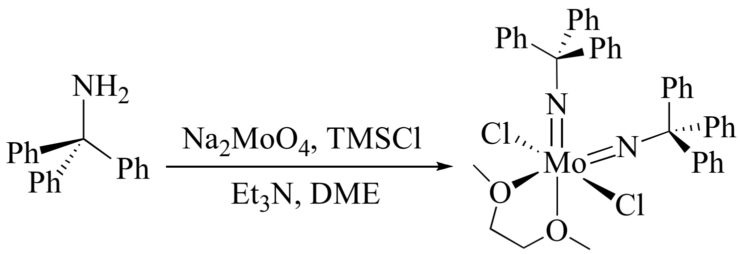
[a] Catalyst loading 5 %, C_6D_6, 25 °C;
[b] The reaction mixture was stirred for 12 h at 25 °C, then for 18 h at 65 °C.

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 tritylimido neophylidene bisalkoxide complexes.

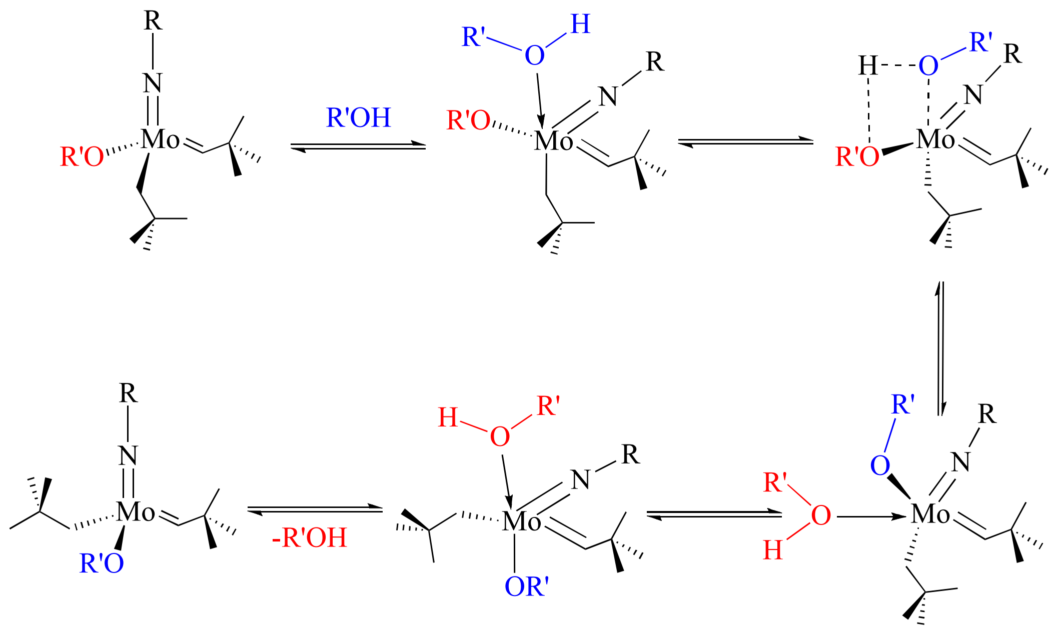
We were interested in whether $Mo(NCPh_3)(CH\text{-}t\text{-}Bu)(OR)_2$ catalysts could be prepared via the "bistriflate" route,[46] which currently is the only route to bisalkoxide complexes of this general type. That would require the synthesis of $Mo(NCPh_3)_2Cl_2(dme)$ and $Mo(NCPh_3)_2(CH_2CMe_2Ph)_2$, and reaction of the latter with triflic acid to yield $Mo(NCPh_3)(CHCMe_2Ph)(OTf)_2(dme)$. $Mo(NCPh_3)_2Cl_2(dme)$ was prepared as shown in **Scheme 17** as a yellow powder in 66 % yield. Alkylation of $Mo(NCPh_3)_2Cl_2(dme)$ with 2 equivalents of $PhMe_2CCH_2MgCl$ at –78 ^oC in ether gave $Mo(NCPh_3)_2(CH_2CMe_2Ph)_2$ in 60 % yield as yellow crystals. However, addition of 3 equivalents of triflic acid to $Mo(NCPh_3)_2(CH_2CMe_2Ph)_2$ 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 $Mo(NCPh_3)(CHCMe_2Ph)(OTf)_2(dme)$. 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 $Mo(NCPh_3)(CHCMe_2Ph)(OR)_2$ complexes.



Scheme 17. Synthesis of $Mo(NCPh_3)_2Cl_2(dme)$.

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 $Mo(NAr)(CH\text{-}t\text{-}Bu)Np_2$ 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 $Mo(NR^*)(CH\text{-}t\text{-}Bu)Np_2$. 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. Mechanism of the alcohol-catalyzed ligand rearrangement in Mo(NR)(CH-t-Bu)Np(OR') complexes.

There are few examples of metal complexes bearing enantiomerically pure imido ligands in the literature (**Scheme 19**).[47,48] Complexes shown in **Scheme 19** were prepared from the corresponding enantiomerically pure amines. We proposed to synthesize Mo(NR*)(CH-t-Bu)Np_2 complexes from the Mo imido tetrachloride molecules, which would be obtained through the reaction of $MoCl_4(THF)_2$ 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.

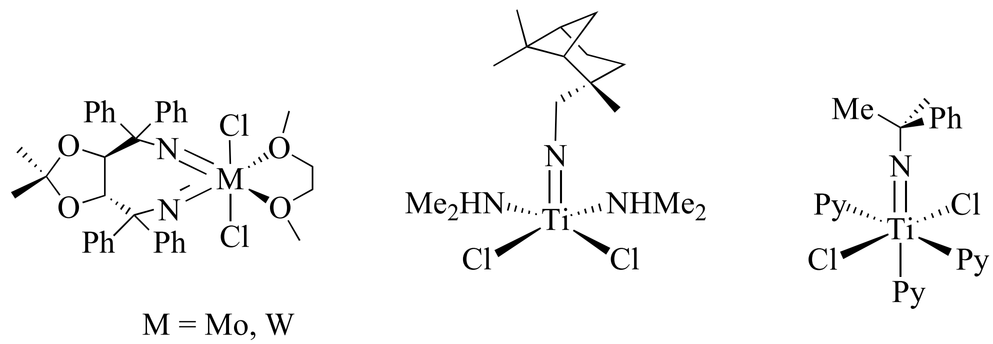
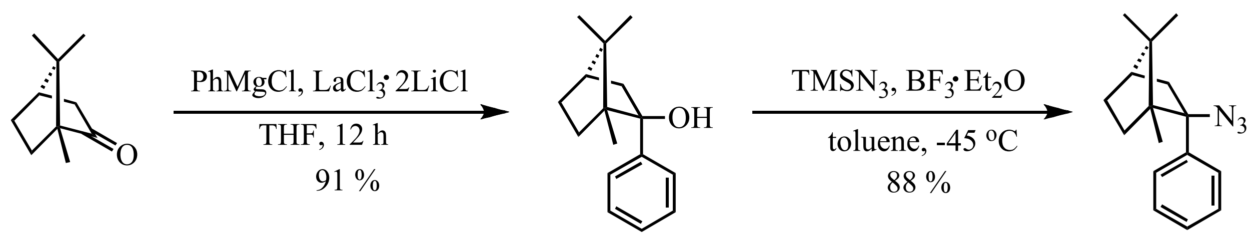


Figure 14. Examples of metal complexes bearing enantiomerically pure imido ligands.



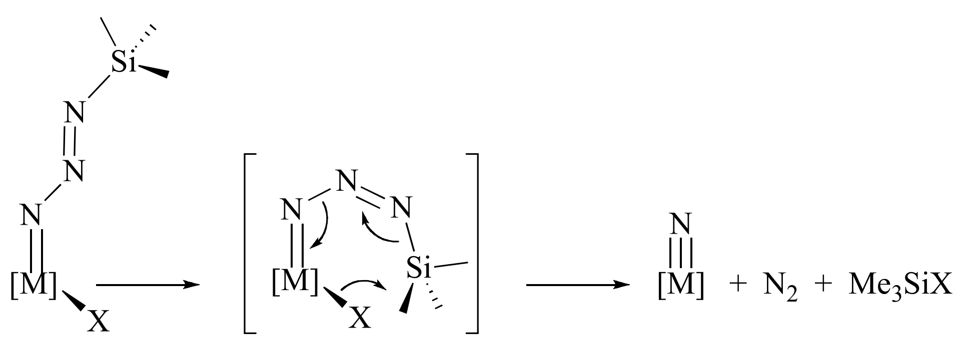
30

Scheme 19. Synthesis of azide **30**.

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 $MoCl_4(THF)_2$ (toluene, 70 ^oC, 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 ^1H NMR spectrum. The brick-red compound was proposed to be $Mo(N)Cl_3$, although this assignment was not confirmed by spectroscopic analysis.

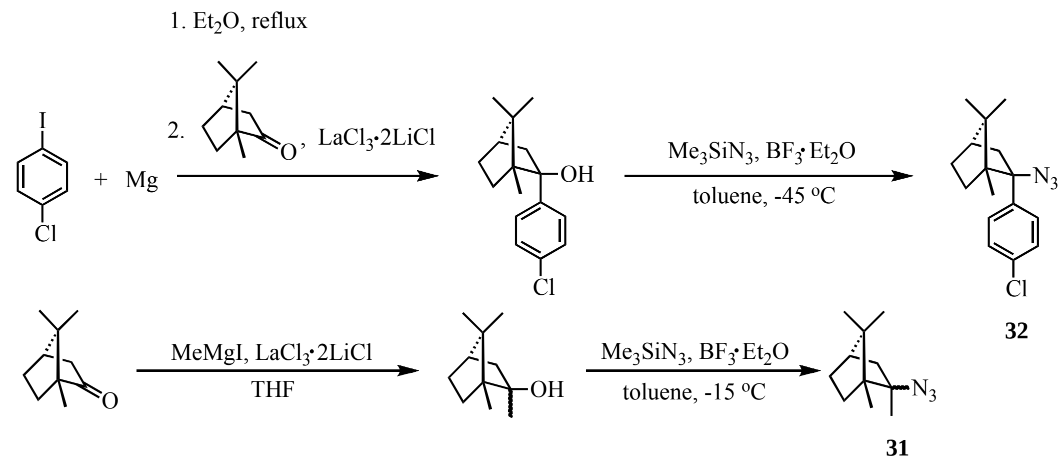
Trying to explain our failure to obtain Mo(NCamPh)Cl_4(THF) complex (NCamPh = (1R,4R)-1,7,7-trimethyl-2-phenylbicyclo[2.2.1]heptan-2-imido) we thought of the possible mechanisms of Mo(IV) oxidation in the presence of organic azides that might yield a nitride species. Nitride complexes are commonly prepared upon treatment of metal complexes with trimethylsilyl azide, Me_3SiN_3.[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 N_2, a metal nitride and a cation (or radical) of $SiMe_3$, which abstracts an anion (or radical) from the metal complex to form Me_3SiX (**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]



Scheme 20. Proposed mechanism of nitride formation in the reaction of a metal complex [M]X with Me_3SiN_3.

We propose that **30** resembles Me_3SiN_3 in terms of reactivity towards $MoCl_4(THF)_2$, 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

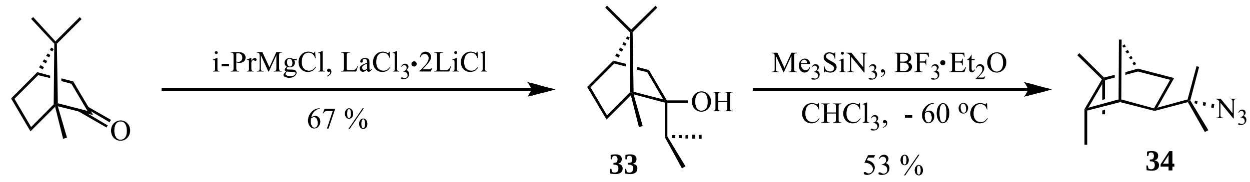
(**31**), or substituents that would destabilize possible radical or cation species (**32**). Azides **31** and **32** were synthesized according to **Scheme 21**. Compound **31** is an oil obtained as a 1:1 mixture of diastereomers, while compound **32** is isolated as a solid and can be recrystallized from hexane to give a diastereomerically pure sample.



Scheme 21. Synthesis of compounds **31** and **32**.

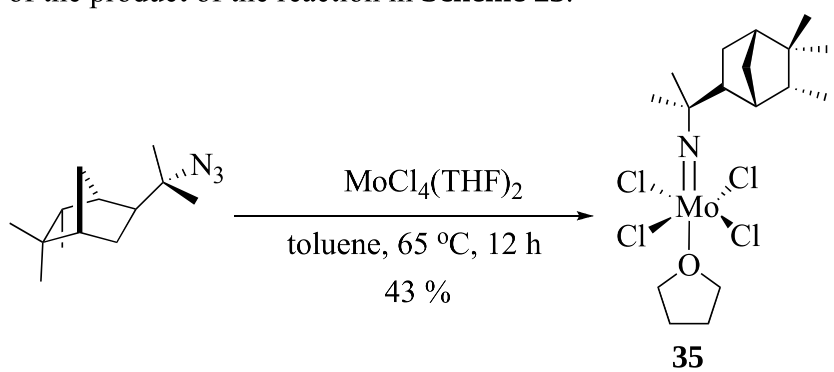
Reactions of **31** and **32** with $MoCl_4(THF)_2$ under various conditions (solvents: toluene, THF; temperature: 25 °C, 70 °C) gave the same brick-red solid as was isolated in the reaction of $MoCl_4(THF)_2$ with **30**. Reactions of **31** with $MoCl_4(Et_2O)_2$ and $MoCl_4$[38] yielded the same product. Compounds **30**, **31**, and **32** were characterized by ^{1}H 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 ^{1}H 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**.



Scheme 23. Synthesis of imido tetrachloride complex **35**.

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**.

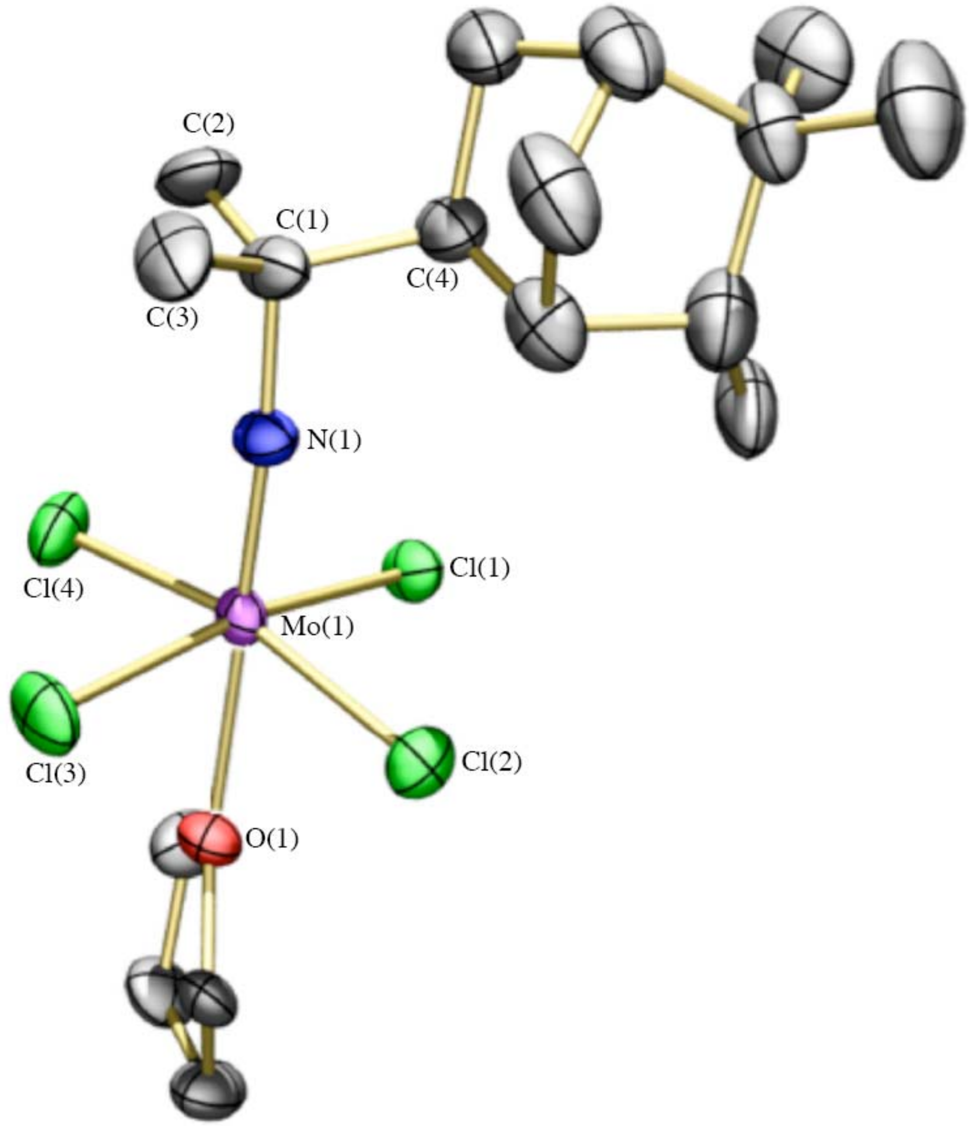


Figure 15. Thermal ellipsoid plot of **35** (50% probability level, hydrogen atoms omitted for clarity).

Table 7. Selected bond lengths (Å) and angles (°) in the molecule of **35**.

Selected bond lengths (Å) and angles (°)			
Mo(1)-N(1)	1.678(7)	N(1)-Mo(1)-O(1)	176.3(3)
Mo(1)-O(1)	2.272(5)	N(1)-Mo(1)-Cl(2)	97.9(3)
Mo(1)-Cl(2)	2.331(3)	O(1)-Mo(1)-Cl(2)	84.75(16)
Mo(1)-Cl(1)	2.337(2)	N(1)-Mo(1)-Cl(1)	93.9(2)
Mo(1)-Cl(4)	2.347(3)	O(1)-Mo(1)-Cl(1)	83.36(15)
Mo(1)-Cl(3)	2.348(2)	Cl(2)-Mo(1)-Cl(1)	90.79(9)
N(1)-C(1)	1.468(11)	Cl(2)-Mo(1)-Cl(4)	167.96(9)
		N(1)-C(1)-C(3)	104.0(7)
C(1)-N(1)-Mo(1)	171.8(7)	C(2)-C(1)-C(3)	111.2(8)
N(1)-C(1)-C(2)	105.5(8)	N(1)-C(1)-C(4)	104.8(7)

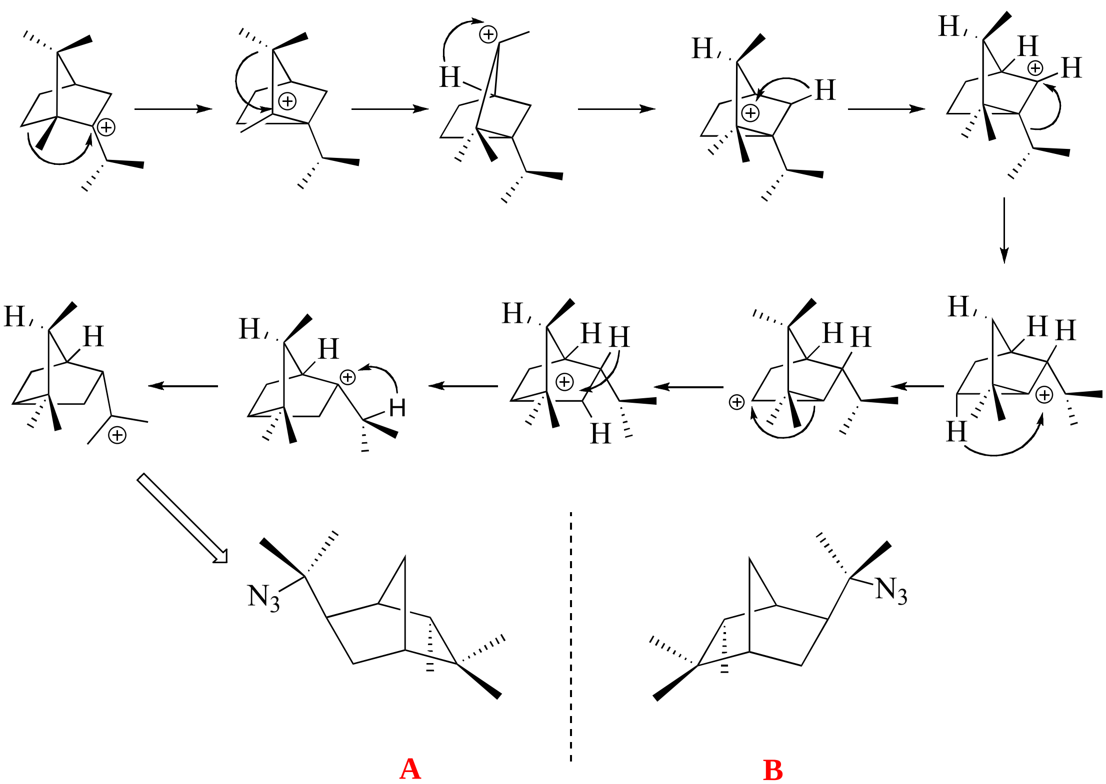
Structural parameters of **35** are similar to those of Mo [N-3, 5-$(CF_3)_2C_6H_3$]Cl_4(THF). The difference between an alkylimido and an arylimido group manifests itself in a shorter Mo-N bond than the one in Mo[N-3,5-$(CF_3)_2C_6H_3$]Cl_4(THF) (1.687(7) Å vs. 1.711(3) Å) and the longer Mo-O distance (2.272(5) Å vs. 2.230(2) Å in Mo[N-3,5-$(CF_3)_2C_6H_3$]Cl_4(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 $P\bar{1}$, 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** $[\alpha]^{298}_D = +7.7 \pm 0.7$ deg·cm^2·g^{-1} (c = 0.01, pentane); specific optical rotation of compound **35**: $[\alpha]^{298}_D = -16.0$ deg·cm^2·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.[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 ± 0.01 $deg\cdot cm^{2}\cdot g^{-1}$ (c = 0.04, hexane); original D-camphor sample $[\alpha]^{298}_{D}$ = +58.56 ± 0.01 $deg\cdot cm^{2}\cdot g^{-1}$ (c = 0.04, hexane). Pure D-camphor rotates polarized light at $[\alpha]^{298}_{D}$ = +59.0 $deg\cdot cm^{2}\cdot g^{-1}$ (hexane, c = 0.01).[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.

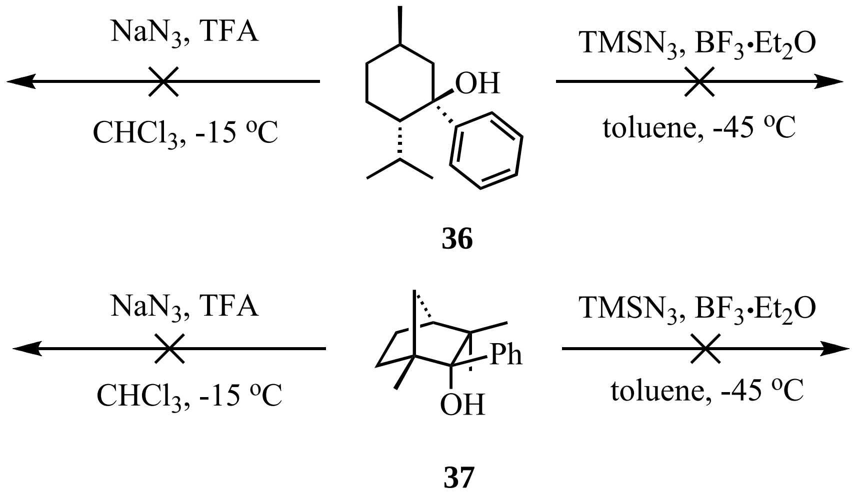
The 9-step mechanism for rearrangement of carbocations that are formed during the synthesis of **34** was proposed by Robert O’Brien (Hoveyda group, Boston College) and is shown in **Scheme 24**.



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.[55] Several attempts to synthesize the corresponding azides from **36** and **37** proved unsuccessful (**Scheme 25**).



Scheme 25. Attempts to convert alcohols **36** and **37** into the corresponding azides.

The hydroxyl groups in compounds **36** and **37** are extremely sterically hindered and do not undergo nucleophilic substitution not only under mild conditions (Me_3SiN_3, BF_3•Et_2O), 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_6F_5, 3,5-$(CF_3)_2C_6H_3$, Ad, CPh_3, and 2,6-i-$Pr_2C_6H_3$) 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 $Mo(NR)Np_3Cl$ species (R = C_6F_5, 3,5-$(CF_3)_2C_6H_3$, Ad, Ph_3C, and 2,6-i-$Pr_2C_6H_3$) in poor (35 %) to modest (51 %) yields. Heating $Mo(NAr)Np_3Cl$ in C_6D_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 $Mo(NR)Np_3Cl$ species were found to be more stable than $Mo(NAr)Np_3Cl$, but when they did decompose at elevated temperatures, no neopentylidene complex could be observed. Addition of neopentyllithium to Mo(NR)Np_3Cl species (R = Ar, CPh_3, or Ad) yielded Mo(NR)(CH-t-Bu)Np_2 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-$Pr_3C_6H_2)_2C_6H_3OH$ (HIPTOH) to Mo($NCPh_3$)(CH-t-Bu)Np_2 led to formation of Mo($NCPh_3$)(CH-t-Bu)Np(OR) species, while treatment of Mo($NCPh_3$)(CH-t-Bu)Np_2 with C_6F_5OH gave Mo($NCPh_3$)Np_3(OC_6F_5). 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-$(CF_3)_2C_6H_3$]Cl_4(THF), Mo[N-3,5-$(CF_3)_2C_6H_3$]Np_3Cl, Mo($NCPh_3$)Np_3Cl, and Mo($NCPh_3$)(CH-t-Bu)Np(OHIPT).

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 H_2SO_4 and water, dried over $CaCl_2$, degassed, and then passed through a column of activated alumina. $MoCl_4(THF)_2$,[38] $C_6F_5N_3$,[32] 3,5-$(CF_3)_2C_6H_3N_3$,[33] 1-AdN_3,[35] Ph_3CN_3,[36] and 3,5-(2,4,6,-i$Pr_3C_6H_2)_2C_6H_3Br$[44] were prepared according to literature procedures.

^1H, ^{19}F, and ^{13}C NMR spectra were recorded on Varian spectrometers. Chemical shifts in ^1H and ^{13}C NMR spectra are reported in ppm from tetramethylsilane with the solvent as an internal standard. ^{19}F NMR spectra were referenced externally using C_6F_6 as a standard. Elemental analyses were performed by H. Kolbe Microanalytisches Laboratories, Mülheim an der Ruhr, Germany.

2,6-i-$Pr_2C_6H_3N_3$.[37] 2,6-Diisopropyl aniline (8.81 g, 0.049 mol) was dissolved in a mixture of concentrated HCl and H_2O (10/30 mL) and 30 g of ice. The mixture was stirred vigorously with a mechanical stirrer and a solution of $NaNO_2$ (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 $NaHCO_3$ (30 mL) was added. NaN_3 (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 $NaHCO_3$ (50 mL) and water (2*50 mL) and dried over $MgSO_4$. 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 (C_6D_6): 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); ^{13}C NMR (C_6D_6): 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]

$Mo(NC_6F_5)Cl_4(THF)$. A 200 mL Schlenk vessel was loaded with $MoCl_4(THF)_2$ (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 (C_6D_6) δ 4.50 (m, 4H), 1.31 (m, 4H); ^{19}F NMR (C_6D_6): δ -151.84 (m, 2F), -160.81 (m, 1F), -162.37 (m, 2F). Anal. Calcd for $C_{10}H_8NOCl_4F_5Mo$: 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.

$Mo(N[3,5-(CF_3)_2C_6H_3])Cl_4(THF)$. A 200 mL Schlenk vessel was loaded with $MoCl_4(THF)_2$ (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_6D_6): δ 7.77 (s, 2H), 7.10 (s, 1H), 4.49 (m, 4H), 1.32 (m, 4H); ^{19}F NMR (C_6D_6): δ -62.66 (s, 6F); ^{13}C NMR (C_6D_6): δ 152.8 (s), 132.8 (q, J_{CF} = 34.6 Hz), 129.9 (s), 127.4 (s), 122.6 (q, J_{CF} = 274.1 Hz), 74.7 (s), 25.9 (s). Anal. Calcd for $C_{12}H_{11}NOCl_4F_6Mo$: 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_6D_6): δ 4.55 (br s, 4H), 2.25 (d, J_{HH} = 3 Hz, 6H), 1.74 (br s, 3H), 1.35 (br s, 4H), 1.14 (t, J_{HH} = 3 Hz**,** 6H). Anal. Calcd for $C_{14}H_{23}NOCl_4Mo$: C, 36.63; H, 5.05; N, 3.05; Cl, 30.89. Found: C, 36.54; 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_6D_6): δ 6.91 (d, J_{HH} = 7.6 Hz, 2H), 6.44 (t, J_{HH} = 7.6 Hz, 1H), 5.08 (septet, J_{HH} = 6.4 Hz, 2H), 4.53 (s, 4H), 1.23 (d, J_{HH} = 6.7 Hz, 16H). Anal. Calcd for $C_{16}H_{25}NOCl_4Mo$: 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(NCPh$_3$)Cl$_4$(THF). Ph_3CN_3 (7.12 g, 25 mmol) was added to a suspension of $MoCl_4(THF)_2$ (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 N_2. 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 %): ^{1}H NMR (C_6D_6): 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 $C_{23}H_{23}NOCl_4Mo$: 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 **33**[49] (4.7 g, 23.9 mmol) was dissolved in 100 mL of $CHCl_3$ and cooled to -60 ^oC. $TMSN_3$ (4.75 mL, 35.9 mmol) was added to the reaction mixture, followed by $BF_3 \cdot Et_2O$ (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 $NaHCO_3$ (2*50 mL) and brine (50 mL). The solution was dried over $MgSO_4$ 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. ^{1}H NMR (C_6D_6): 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). ^{13}C NMR (C_6D_6): 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 $[M - N_2 + H]^+$ 194.1909). Anal. Calcd for $C_{13}H_{23}N_3$: C, 70.54; H, 10.47; N, 18.98. Found: C, 70.68; H, 10.38; N, 18.94. $[\alpha]^{298}_D = +7.7 \pm 0.7$ deg·cm^2·g^{-1} (c = 0.1, pentane).

Mo(NCamPr)Cl_4(THF) (CamPr = (1S,4S)-5-(2-azidopropan-2-yl)-2,2,3-trimethylbicyclo[2.2.1]heptyl) (**35**). $MoCl_4(THF)_2$ (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 ^{o}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 ^{o}C for 18 hours, at which point red-brown solid was collected by filtration (414 mg, 0.82 mmol, 43 %). ^{1}H NMR (C_6D_6): 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 $C_{17}H_{31}NMoOCl_4$: 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. $[\alpha]^{298}_{D}$ = -16.0 deg·cm^{2}·g^{-1} (c = 0.01, pentane).

Single crystals for the X-ray study were grown from a pentane solution at -30 ^{o}C.

Mo(NC_6F_5)Np_3Cl (**20**). A solution of NpMgCl (25.0 mmol) in 20 mL of ether was cooled to -78 ^{o}C and a solution of Mo(NC_6F_5)Cl_4(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 ^{o}C for 20 min then warmed to 20 ^{o}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 %). ^{1}H NMR (C_6D_6): δ 3.275 (s, 6H), 1.155 (s, 27H); ^{19}F NMR (C_6D_6): δ -141.27 (d, J_{FF} = 22.2 Hz, 2F), -151.55 (m, F), -160.31 (m, 2F). Anal. Calcd for $C_{21}H_{33}NClF_5Mo$: C, 47.96; H, 6.33; N, 2.66; Cl, 6.74. Found: C, 47.81; H, 6.27; N, 2.56; Cl, 6.63.

Mo(N[3,5-$(CF_3)_2C_6H_3$])Np_3Cl (**21**). A solution of NpMgCl (37.4 mmol) in 25 mL of diethyl ether was cooled to -78 ^{o}C and a solution of Mo(3,5-$(CF_3)_2C_6H_3$N)Cl_4(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 %): ^{1}H NMR (C_6D_6): δ 8.16 (s, 2H), 7.52 (s, 1H), 3.09 (s, 6H), 1.05 (s, 27H); ^{19}F NMR (C_6D_6): δ -62.49 (s, 6F); ^{13}C NMR (C_6D_6) 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 $C_{23}H_{36}NClF_6Mo$: 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)Np$_3$Cl (**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)Cl_4(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 %): ^{1}H NMR (C_6D_6): 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 $C_{25}H_{48}NClMo$: 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)Np$_3$Cl (**23**). Mo(NAr)Cl_4(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 %): ^{1}H NMR (C_6D_6): δ 6.97 (s, 3H), 4.07 (septet, J_{HH} = 6.6 Hz, 2H), 3.04 (s, 6H), 1.25 (s, 27 H), 1.22 (d, J_{HH} = 6.6 Hz, 12H). Anal. Calcd for $C_{27}H_{50}NClMo$: C, 62.35; H, 9.69; Cl, 6.82; N, 2.69. Found: C, 62.31; H, 9.56; Cl, 6.74; N, 2.71.

Mo(NCPh$_3$)Np$_3$Cl (**24**). Mo(NCPh$_3$)Cl$_4$(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 %): ^{1}H NMR (C_6D_6): δ 7.44-7.41 (m, 6H), 7.16-7.05 (m, 9 H), 3.12 (s, 6H), 1.03 (s, 27H). Anal. Calcd for $C_{34}H_{48}NClMo$: 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 ^{o}C.

Mo(NAr)(CH-t-Bu)Np$_2$ (**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)Np$_3$Cl 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(NCPh$_3$)(CH-t-Bu)Np$_2$ (**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_6D_6): δ 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_6D_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_3Cl had been converted quantitatively to Mo(NAr)(CH-t-Bu)NpCl in a reaction that was unimolecular with k = 9.0x10^{-5} s^{1}: ^{1}H NMR (C_6D_6): δ 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_3Cl (72.8 mg, 0.14 mmol) in 0.7 mL of C_6D_6 was heated to 50 °C for 8 h. The reaction was unimolecular with k = 9.5x10^{-5} s^{-1}. At an initial concentration of 0.1 M k_{50} = 9.0 x 10^{-5} s^{-1}.

A 0.1 N solution of Mo(NAr)Np_3Cl (35 mg, 0.07 mmol) in 0.7 mL of C_6D_6 was heated to 60 °C for 4 h. The reaction was unimolecular with k = 3.0x10^{-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_6F_5OH (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_6D_6): δ 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_6D_6): δ -156. 08 (m, 2F), -165.46 (m, 2F), -175.42 (m, 1F). Anal. Calcd for $C_{41}H_{56}NOF_5Mo$: 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-$Pr_3C_6H_2)_2C_6H_3OH$ (HIPTOH).[43] n-BuLi (0.85 mmol) was added to a solution of 3,5-(2,4,6-i-$Pr_3C_6H_2)_2C_6H_3Br$ (400 mg, 0.71 mmol) in 20 mL of dry THF, that had been cooled to –78 ^oC. 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 $MgSO_4$. 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 (C_6D_6): δ 7.20 (s, 4H), 7.13 (s, 2H), 6.53 (s, 1H), 3.91 (s, 1H), 3.03 (septet, J_{HH} = 11.3 Hz, 4H), 2.87 (septet, J_{HH} = 11.1 Hz, 2H), 1.28 (d, J_{HH} = 11.3 Hz, 24H), 1.22 (septet, J_{HH} = 11.1 Hz, 12H).

Mo($NCPh_3$)(CH-t-Bu)Np[O-(2,6-$Me_2C_6H_3$)] (**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 (C_6D_6): 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, J_{HH} = 12.4 Hz, 1H), 2.34 (d, J_{HH} = 12.4 Hz, 1H), 2.16 (s, 6H), 1.16 (s, 9H), 1.08 (s, 9H). ^{13}C NMR (C_6D_6): δ 277.52 (d, J_{CH} = 109.4 Hz). Anal. Calcd for $C_{37}H_{45}NOMo$: C, 72.18; H, 7.37; N, 2.27. Found: C, 72.06; H, 7.41; N, 2.19.

Mo($NCPh_3$)(CH-t-Bu)Np[O-(2,6-i-$Pr_2C_6H_3$)] (**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_6D_6): δ 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_6D_6): δ 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(OHIPT) (**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_6D_6): δ 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_6D_6): δ 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 ^{o}C.

Mo(NCPh$_3$)$_2$Cl$_2$(dme). Ph_3CNH_2 (11.53 g, 0.044 mol), Na_2MoO_4 (4.53 g, 0.022 mol), Et_3N (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 ^{o}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 triturated 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_6D_6): δ 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 $C_{42}H_{40}N_2O_2Cl_2Mo$: 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.

$Mo(NCPh_3)_2(CH_2CMe_2Ph)_2$. A solution of $Mo(Ph_3CN)_2Cl_2(dme)$ (2.06 g, 3.63 mmol) dissolved in 30 mL of toluene was cooled to -78 ^oC. A solution of $(PhCMe_2CH_2)MgCl$ (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 (C_6D_6): 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 $C_{58}H_{56}N_2Mo$: C, 79.43; H, 6.44; N, 3.19. Found: C, 79.57; H, 6.41; N, 3.11.

Representative olefin metathesis with $Mo(NCPh_3)(CH\text{-}t\text{-}Bu)Np(OR)$ complexes. Diallyl ether (10.6 mg, 0.108 mmol) was dissolved in 1 mL of C_6D_6 in a 20 mL vial and **28** (5.4 mg, 5.5×10^{-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-$(CF_3)_2C_6H_3$]Cl_4(THF), Mo[N-3,5-$(CF_3)_2C_6H_3$]Np_3Cl (**21**), Mo[NC$(C_6H_5)_3$]Np_3Cl (**23**), and Mo(NCPh_3)(CH-t-Bu)Np(OHIPT) (**28**).[a]

Empirical formula	$C_{12}H_{11}Cl_4F_6MoNO$	$C_{23}H_{36}ClF_6MoN$	$C_{34}H_{48}ClMoN$	$C_{65}H_{85}MoNO$
Formula weight	536.96	571.92	602.12	992.28
T (K)	193(2)	193(2)	193(2)	100(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	C2/c	P2(1)/n	P2(1)
Unit cell dimensions (Å, °)	a = 9.0151(8)	17.3743(13)	10.153(2)	10.212(6)
	b = 10.3616(9)	9.8338(7)	18.451(4)	40.85(3)
	c = 11.0455(10)	32.380(2)	17.416(4)	13.861(9)
	α = 63.349(2)	90	90	90
	β = 86.872(2)	103.7330(10)	103.55(3)	102.618(12)
	γ = 88.901(2)	90	90	90
Volume ($Å^3$)	920.76(14)	5374.2(7)	3171.7(11)	5642(6)
Z	2	8	4	4
Density (calcd; Mg/m^3)	1.937	1.414	1.261	1.168
Absorp coeff (mm^{-1})	1.351	0.639	0.519	0.273
F(000)	524	2352	1272	2128
Crystal size (mm)	0.3 x 0.16 x 0.09	0.38 x 0.28 x 0.20	0.25 x 0.20 x 0.20	0.25 x 0.08 x 0.08
Theta range (°)	2.07 to 24.99	1.29 to 28.30	1.63 to 26.44	1.00 to 28.28
Index ranges	-10<=h<=9	-22<=h<=23	-12<=h<=12	-13<=h<=13
	-7<=k<=12	-8<=k<=13	-23<=k<=23	-54<=k<=54
	-13<=l<=12	-32<=l<=42	-21<=l<=21	0<=l<=18
Reflections collected	5000	16562	54550	125702

Indep. reflections [R(int)]	3233 [0.0233]	6297 [0.0153]	6532 [0.0300]	27827 [0.07980]
Completeness (to theta =)	99.6 % (24.99°)	94.1 % (28.30°)	99.8 % (26.44°)	99.7 % (28.28°)
Data / restraints / parameters	3233 / 0 / 227	6297 / 0 / 290	6532/0/334	27827 / 1374 / 1247
Goodness-of-fit on F^2	1.076	1.114	1.097	1.091
Final R indices [I > 2s(I)]	R1 = 0.0360	R1 = 0.0309	R1 = 0.0265	R1 = 0.0685
	wR2 = 0.0883	wR2 = 0.0755	wR2 = 0.0669	wR2 = 0.1461
R indices (all data)	R1 = 0.0524	R1 = 0.0321	R1 = 0.0313	R1 = 0.0875
	wR2 = 0.0929	wR2 = 0.0762	wR2 = 0.0706	wR2 = 0.1562
Largest diff. peak and hole (e.Å^{-3})	0.518 and -0.486	0.800 and -0.608	0.816 and -0.257	1.268 and -1.101

[a] 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**.

Empirical formula	$C_{17}H_{31}Cl_4MoNO$	
Formula weight	503.17	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\overline{1}$	
Unit cell dimensions	a = 7.620(3) Å	α= 96.414(8)°
	b = 7.852(3) Å	β= 92.691(8)°
	c = 18.095(7) Å	γ = 94.613(7)°
Volume	1070.7(7) $Å^3$	
Z	2	
Density (calculated)	1.561 Mg/m^3	
Absorption coefficient	1.117 mm^{-1}	
F(000)	516	
Crystal size	0.07 x 0.05 x 0.02 mm^3	
Theta range for data collection	2.27 to 22.72°.	
Index ranges	-8<=h<=8, -8<=k<=8, 0<=l<=19	
Reflections collected	3283	
Independent reflections	3283 non-merohedral twin	
Completeness to theta = 22.72°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9889 and 0.9259	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3284 / 329 / 255	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2s(I)]	R1 = 0.0675, wR2 = 0.1448	
R indices (all data)	R1 = 0.1058, wR2 = 0.1591	
Largest diff. peak and hole	1.858 and -0.672 e.$Å^{-3}$	

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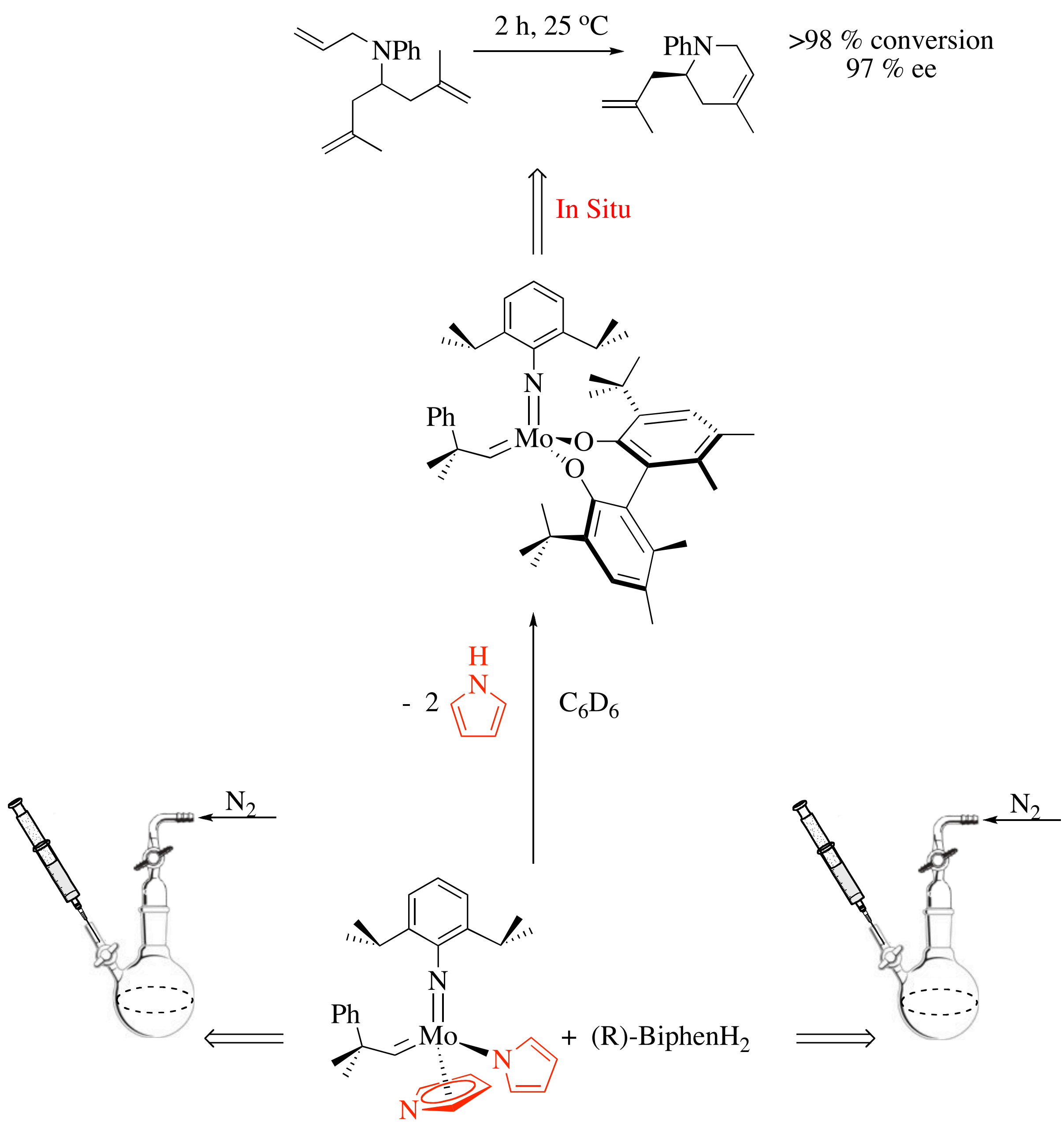
Chapter 3

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



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 2nd 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.

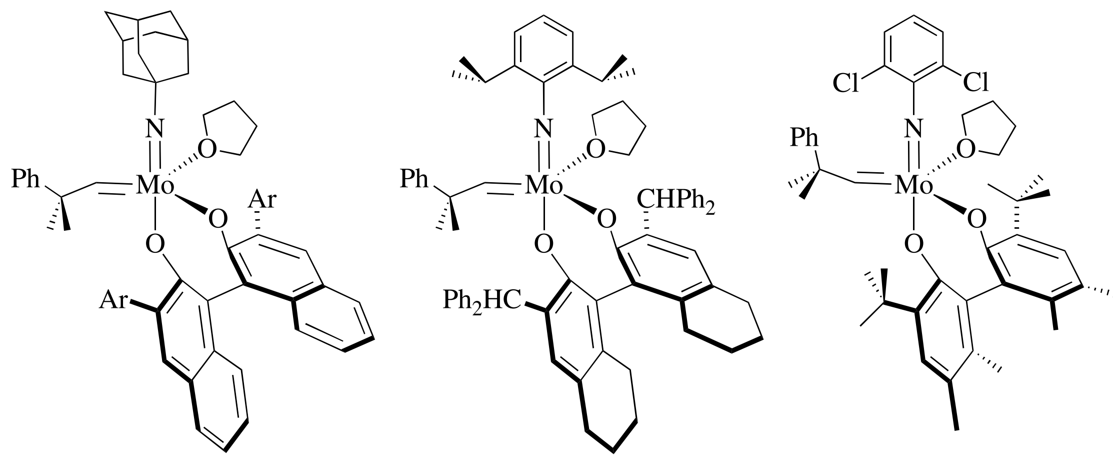
Certain amido complexes of Mo are known to react with alcohols giving molybdenum alkoxide complexes.[15,16,17] Dr. Amritanshu Sinha showed that this transformation can be employed in the synthesis of catalytically active $Mo(NAr)(CHCMe_2Ph)(OR)_2$ species from bisamido complexes $Mo(NAr)(CHCMe_2Ph)(NR'R'')_2$ (Ar = 2,6-i-$Pr_2C_6H_3$, 2,6-$Me_2C_6H_3$; NR'R'' = NPh_2, N(t-Bu)(3,5-$Me_2C_6H_3$), N(i-Pr)(3,5-$Me_2C_6H_3$)) upon treatment with 2 equivalents of alcohol ROH.[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)-$BiphenH_2$ ($BiphenH_2$ = 3,3'-di-tert-butyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diol).[19] Slow alcoholysis rates and the difficulties in isolation of the complexes of type $Mo(NAr)(CHCMe_2Ph)(NR'R'')_2$ suggested that these species are not ideal precursors to the in situ $Mo(NAr)(CHCMe_2Ph)(OR)_2$ 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, $Mo(NR)(CH\text{-}t\text{-}Bu)(pyr)_2$ (pyr = NC_4H_4), can serve as convenient precursors to $Mo(NR)(CH\text{-}t\text{-}Bu)(OR')_2$ catalysts.[20] $Mo(NR)(CH\text{-}t\text{-}Bu)(pyr)_2$ are synthesized via a reaction of the corresponding bistriflate complexes, $Mo(NR)(CH\text{-}t\text{-}Bu)(OTf)_2(dme)$, with lithium pyrrolide, and can be rapidly and cleanly converted into $Mo(NR)(CH\text{-}t\text{-}Bu)(OR')_2$ complexes upon treatment with alcohols (including bulky biphenols). $Mo(NAr)(CH\text{-}t\text{-}Bu)(pyr)_2$ (Ar = 2,6-i-$Pr_2C_6H_3$) was shown to be almost unreactive towards olefins, producing one equivalent of $PhMe_2CHC{=}CH_2$ in neat isobutylene over two days and failing to yield any ring-closing metathesis product in the presence of 10 equivalents of diallyl ether.[21] Based on these observations it was concluded that the complexes of the type $Mo(NR)(CH\text{-}t\text{-}Bu)(pyr)_2$ 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.[22] 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.[23] We chose to study the reactions of complexes **40** and **41** with (R)-TripH_2 (TripH_2 = 3,3'-bis(2,4,6-triisopropylphenyl)-1,1'-binaphthyl-2,2'-diol) as well as the reactions of compounds **42** and **43** (**Figure 17**) with (R)-Benz$_2$BitetH_2 (Benz$_2$BitetH_2 = 3,3'-dibenzhydryl-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2,2'-diol).

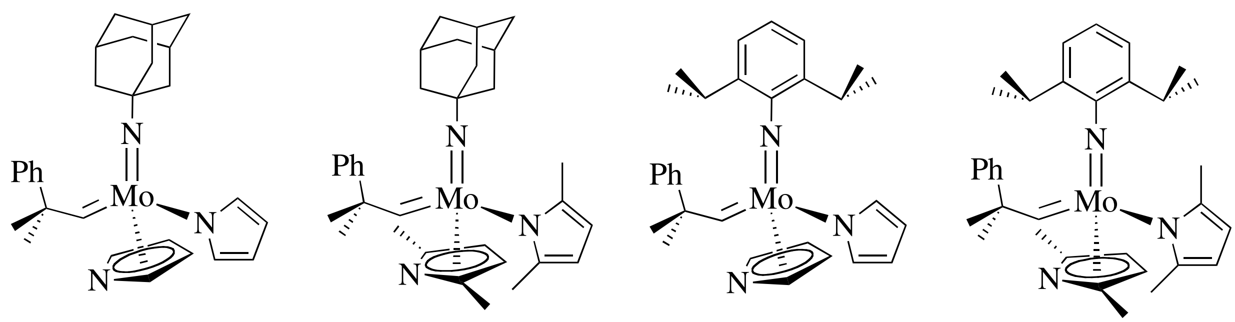
Pyrrole is an aromatic compound with resonance stabilization energy 21.6 KJ/mol.[24] The lone pair on the pyrrole nitrogen is perpendicular to the plane of the molecule and contributes to the aromatic π-system. Therefore pyrrole is a poor donor and does not efficiently coordinate to metal complexes through the nitrogen atom; no example of a structurally characterized pyrrole complex of this type is known.



$Ar = 2,6\text{-}i\text{-}Pr_2C_6H_3$

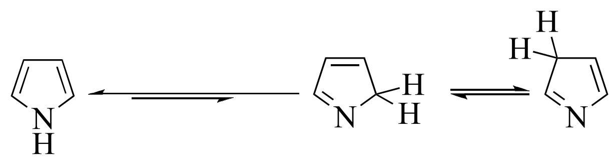
38 **4a** **39**

Figure 16. Examples of enantiomerically pure Mo-based olefin metathesis catalysts isolated as THF adducts.



40 **41** **42** **43**

Figure 17. Molybdenum imido alkylidene bispyrrolide complexes **40 – 43**.



Scheme 26. Three tautomeric forms of pyrrole.

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.[25,26] Different calculations place tautomer **B**, known as 2H-pyrrole or pyrrolenine, at 10.30 kcal/mol,[26] 12.0 kcal/mol, 14.0 kcal/mol,[27] 13.8 kcal/mol, and 16.0 kcal/mol higher than pyrrole **A**.[28] 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.[26,27,28] Nitrogen is not the most basic site of the molecule; protonation of pyrrole occurs at ß-carbon atom, and its conjugate acid has a p*K*a of - 3.8.[29]

Reaction of pyrrole with $B(C_6F_5)_3$ leads to formation of a pyrrolenine adduct.[30] This adduct can also be isolated upon treatment of Li pyrrolide with $B(C_6F_5)_3$, followed by addition of HCl.[30,31] Therefore it is not surprising that coordinated pyrrolide anions and η^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,[32,33] Re,[34,35,36] and W.[36] In some cases pyrrolenine was observed to form σ-bonds with the metal center through the nitrogen or β-carbon atoms.[34,35,37] Pyrrolenine ligand can also be η^2-coordinated through C=C or C=N bond.[32,33,36]

Coordinated pyrrolenines exhibit a characteristic chemical shift of the imine carbon in the ^{13}C NMR spectra at 170-185 ppm.[33,31,37,34] These values lie within the typical range of ^{13}C

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.[38] 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)-TripH$_2$.

^{1}H NMR spectra of the reaction between **40** and (R)-TripH$_2$ 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)-TripH$_2$ 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 N=CH-CH$_2$-C**H**=C**H** protons. Two signals of the AB system corresponding to the allylic hydrogens (N=CH-C**H**$_2$-CH=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 $B(C_6F_5)_3$.[31] Large values for the spin-spin coupling constants of allylic protons were reported for a pyrrolenine molecule η^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.[36] The ^{13}C NMR spectrum of the reaction mixture **40** + (R)-TripH$_2$ 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.[33,31,37,34,38] 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]

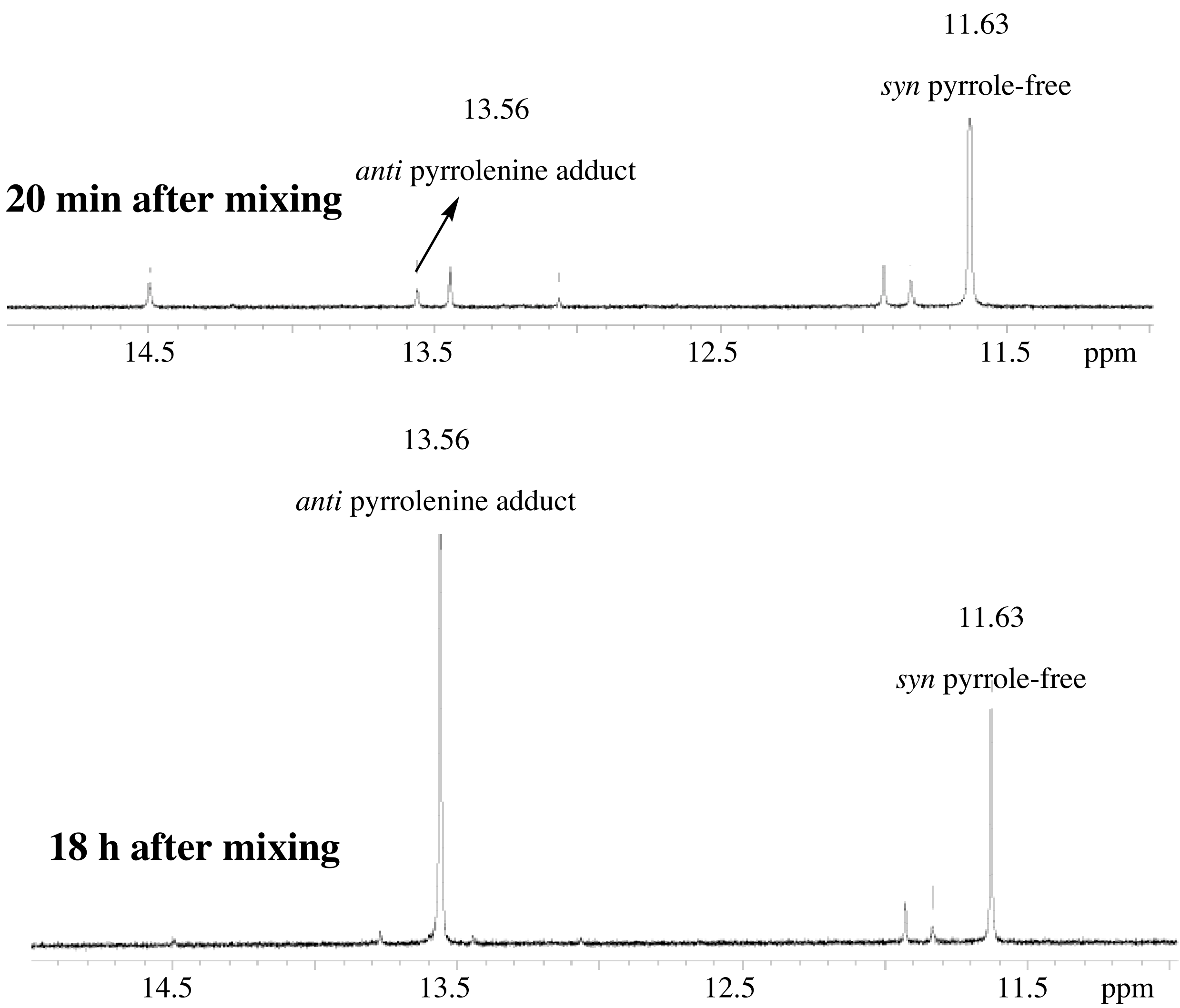


Figure 18. ^{1}H NMR spectra of the reaction between **40** and (R)-TripH_2 (25 ^{o}C, C_6D_6).

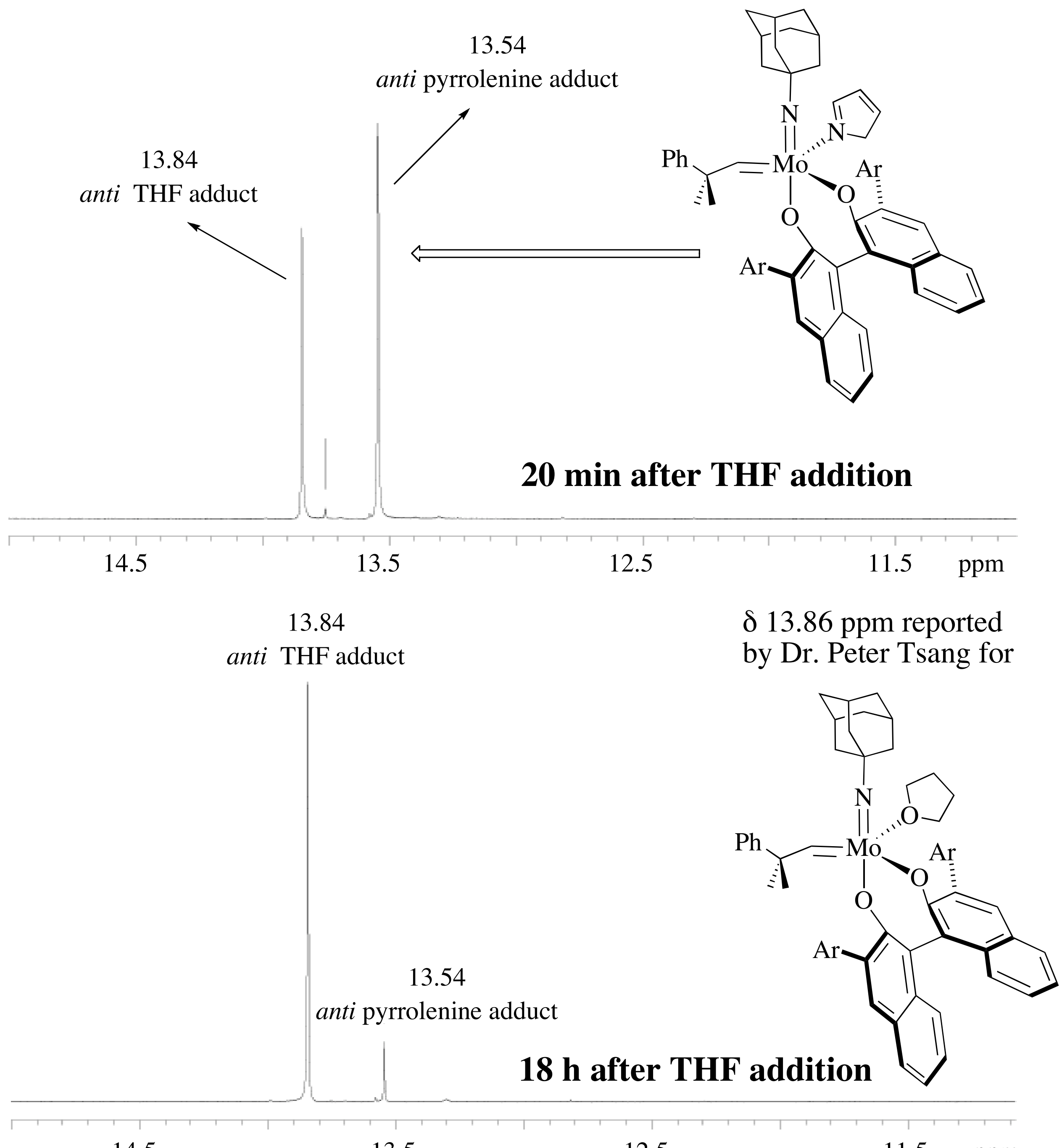


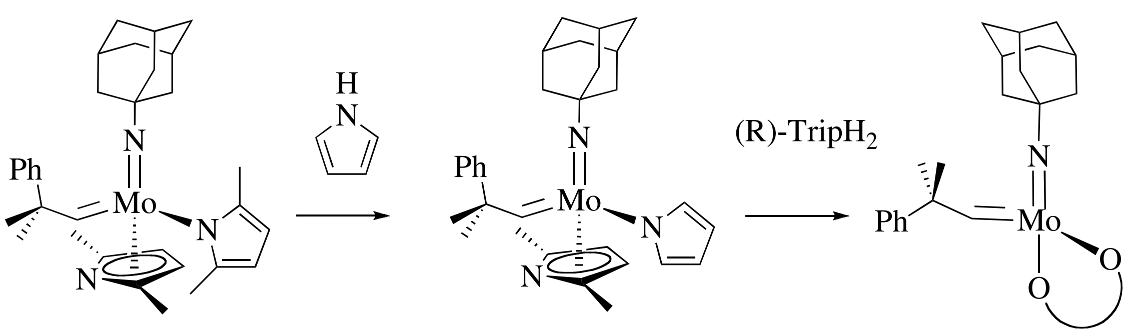
Figure 19. ^{1}H NMR spectra of the reaction between **40** and (R)-TripH_2 in the presence of 10 equivalents of THF (25 ^{o}C, C_6D_6).

The observations discussed above are reminiscent of the results obtained in our laboratory by Dr. Stefan Arndt.[41] Dr. Arndt showed that compound $W(2,6\text{-}Cl_2C_6H_3N)(CH\text{-}t\text{-}Bu)(2,5\text{-}Me_2C_4H_2N)_2$ upon treatment with 1 equivalent of $[HNMe_2Ph][B(Ar_F)_4]$ 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 ^1H NMR.

^1H 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_6D_6. When the reaction mixture is heated to 75 ^oC for 20 h, a new resonance appears in the alkylidene region of the ^1H 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 ^1H 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_6D_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 ^1H NMR spectrum of the reaction mixture. Twenty-three hours later this resonance becomes the major signal in the ^1H 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 ^1H 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.



44

Scheme 27. Proposed mechanism of the reaction between **41** and (R)-TripH_2 in the presence of pyrrole.

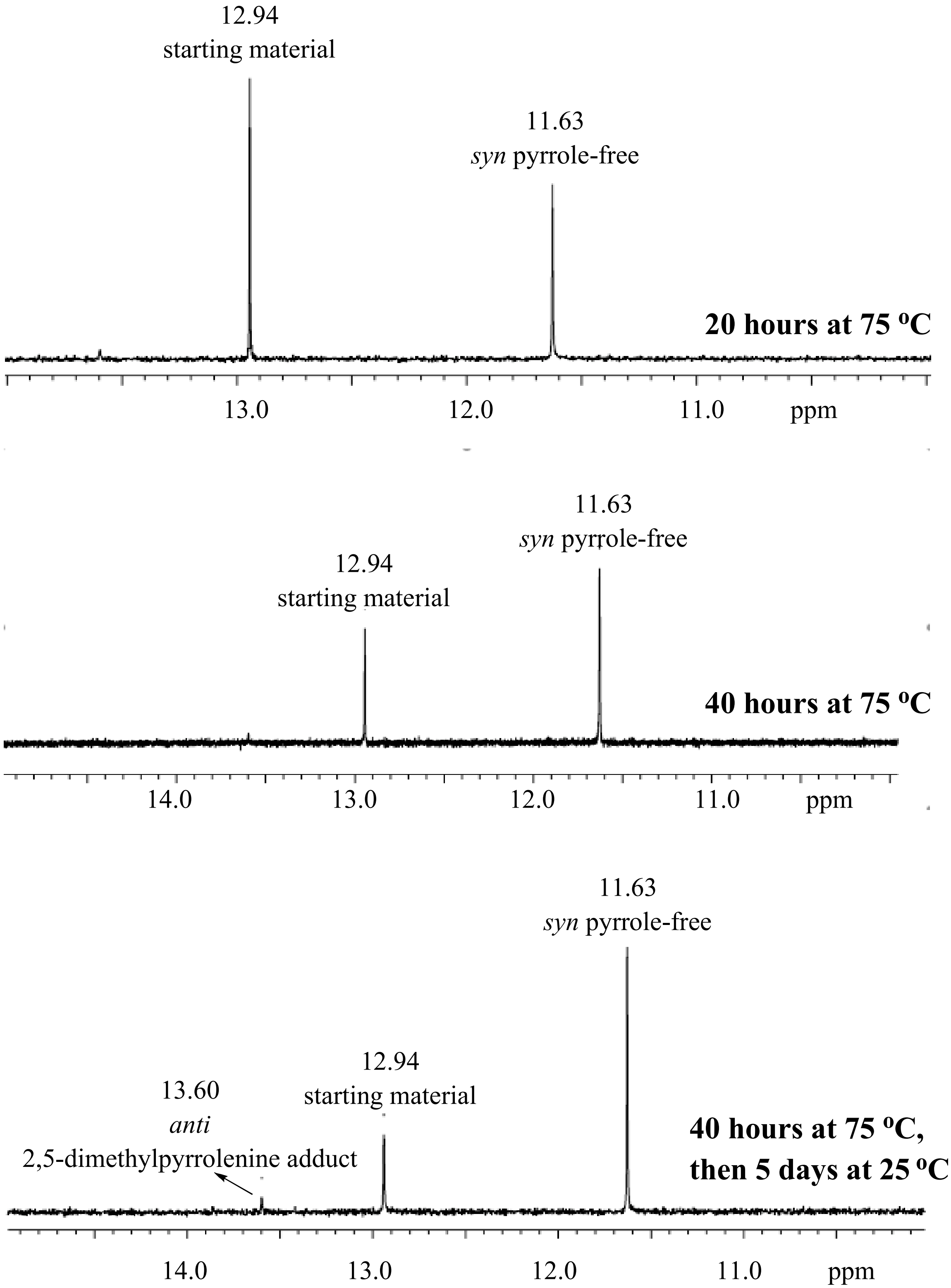


Figure 20. ^{1}H NMR spectra of the reaction between **41** and (R)-TripH_2.

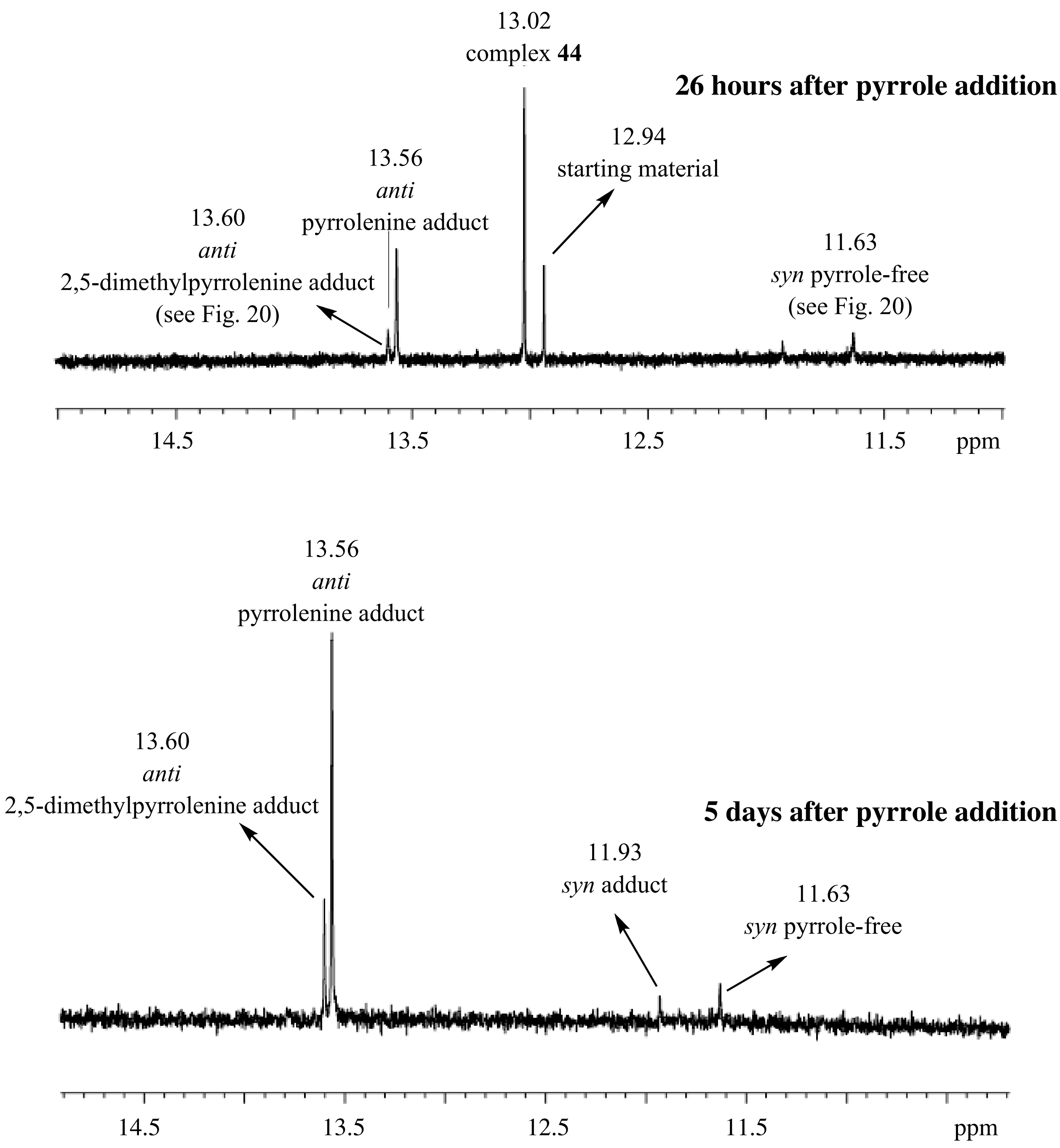
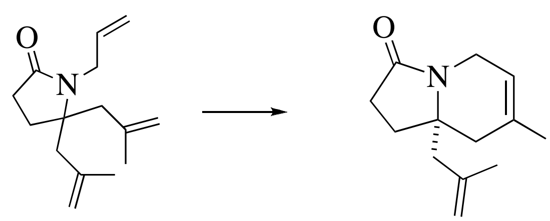


Figure 21. ^{1}H NMR spectra of the reaction between **41** and (R)-TripH_2 in the presence of 7 equivalents of pyrrole (25 ^{o}C, C_6D_6).

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_6D_6, 10 mg/mL) and (R)-TripH_2 (one equivalent, stock solution, C_6D_6, 10 mg/mL). The mixture was stirred for 15 minutes, at which time the substrate was added (20 equivalents, stock solution, C_6D_6, 20 mg/mL). The reactions were monitored by ^{1}H NMR and TLC; the products were isolated using column chromatography.

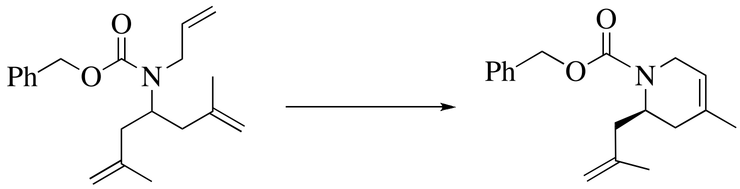


10 **14**

Entry	Catalyst	Time, h	T, °C	Conv., %	Yield, %	ee, %
1	**38**	48	65	>98	97	97
2	**ISGC**	50	70	94	61	93
3 [a]	**ISGC**	24	70	95	78	92

[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.



Entry	Catalyst	Time, h	T, ºC	Yield, %	ee, %
1	**38**	36	80	66	80
2	**ISGC**	50	25	67	71

Scheme 29. Asymmetric ring-closing metathesis reaction of **13** using isolated catalyst **38** and **ISGC** derived from **40** and (R)-TripH_2.

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 **ISGC**s 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 pyrrolenine and its rearrangement to pyrrole.

3.2.1.b Reactions of 42 and 43 with (R)-Benz$_2$BitetH$_2$.

Complex **4a**, isolated as a THF adduct, is an efficient catalyst for asymmetric olefin metathesis transformations.[42] We were interested in preparing the **ISGC** from **41** and (R)-

$Benz_2BitetH_2$ 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.

^{1}H NMR spectra of the reactions between the bis(2,5-dimethylpyrrolide) complex **43** with (R)-$Benz_2BitetH_2$, as well as the reaction of **42** with (R)-$Benz_2BitetH_2$, 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)-$Benz_2BitetH_2$, 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 ^{1}H 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)-$Benz_2BitetH_2$ is a solvent-free species, and therefore differs structurally from the corresponding isolated complex **4a**.

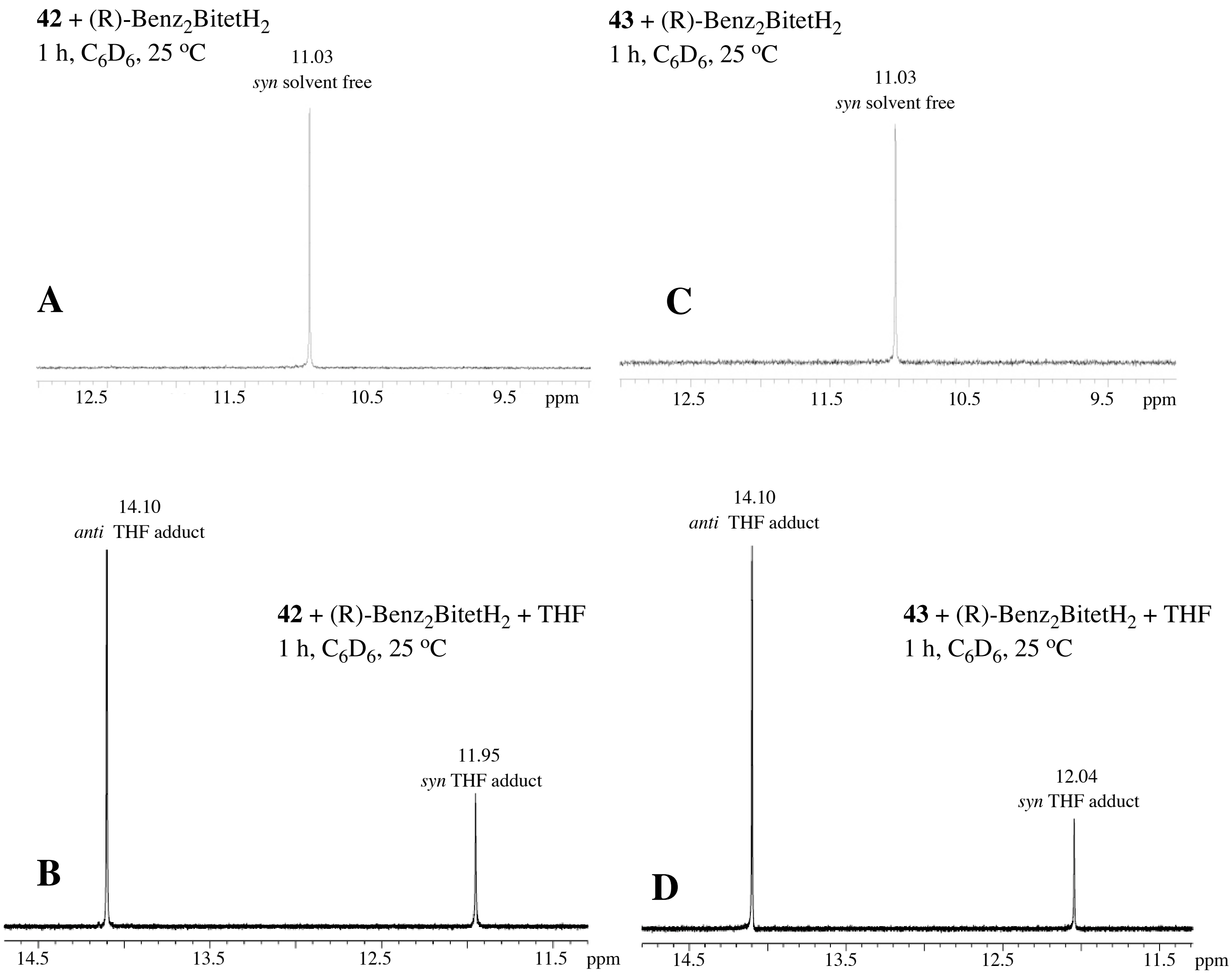
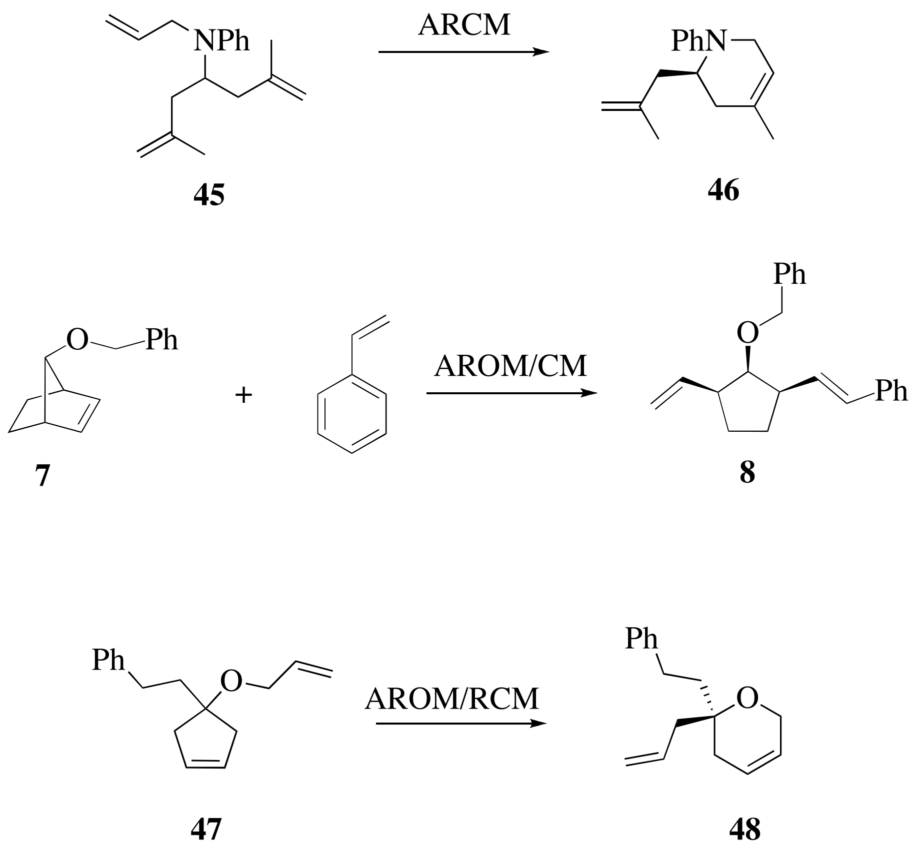


Figure 22. ^{1}H NMR spectra of the reactions between **42** and (R)-Benz$_2$BitetH$_2$ (**A** and **B**) and **43** and (R)-Benz$_2$BitetH$_2$ (**C** and **D**) in the absence and presence of THF (25 equivalents).

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

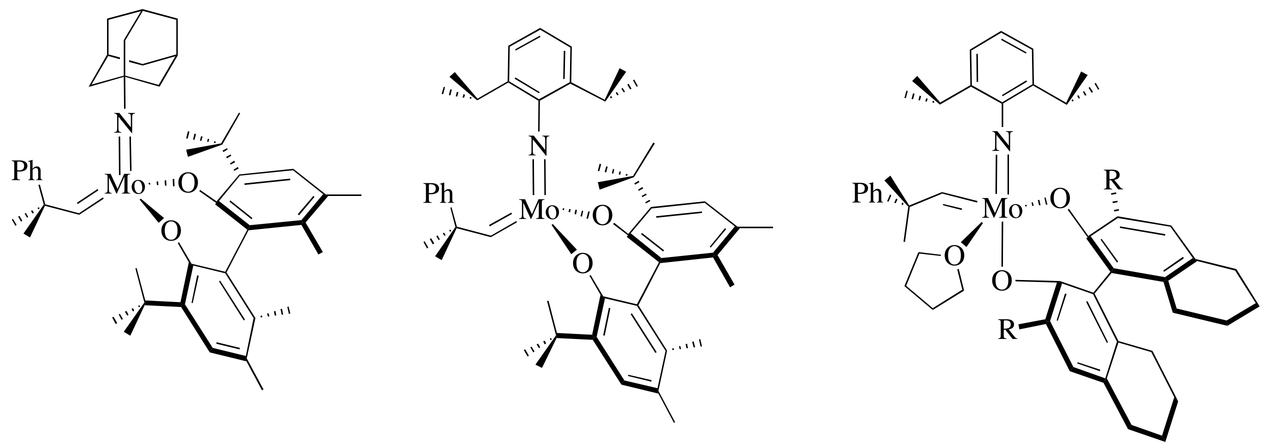
Initial studies showed that in situ generated catalysts are a valid alternative to the isolated catalysts for the small subset of substrates and catalysts shown in **Schemes 28** and **29**. Therefore we decided to examine a broader scope of catalytic reactions. Three olefin metathesis reactions shown 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).



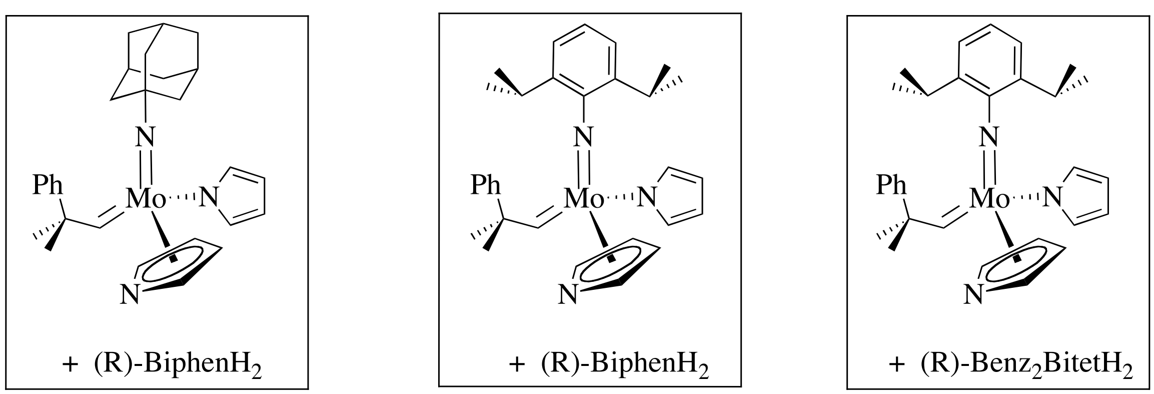
Scheme 30. Asymmetric ring-closing metathesis, asymmetric ring-opening/cross metathesis, and asymmetric ring-opening/ring-closing metathesis reactions chosen for the screening of the **ISGC**s and analogous isolated catalysts.

Olefin metathesis reactions of **45**, **47**, and **7** were examined in the presence of three catalytic systems prepared in situ: a) **40** and (R)-BiphenH_2 (**ISGC 1**); 2) **42** and (R)-BiphenH_2

(**ISGC 2**); and 3) **42** and (R)-Benz$_2$BitetH$_2$ (**ISGC 3**). 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.



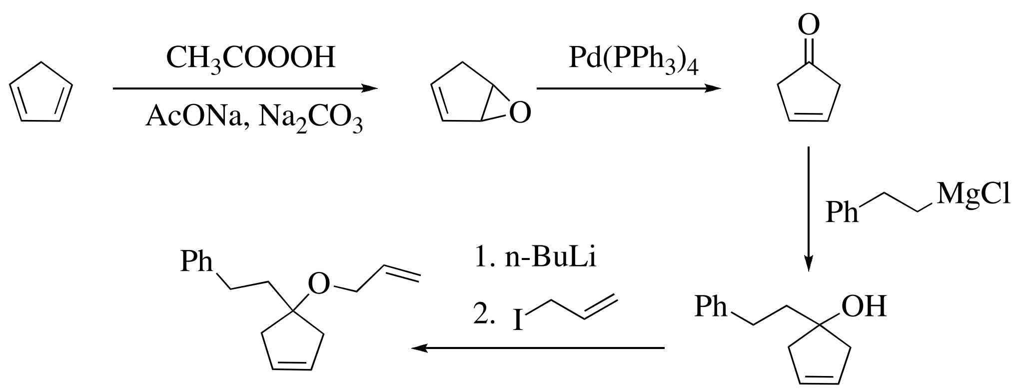
1a **2a** **4a** R = CHPh$_2$



ISGC 1 **ISGC 2** **ISGC 3**

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.[43] 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.[44] The sequence that was employed in the synthesis of compound **47** in this project is shown in **Scheme 32**.



47

Scheme 32. Synthesis of compound **47**.[45,46]

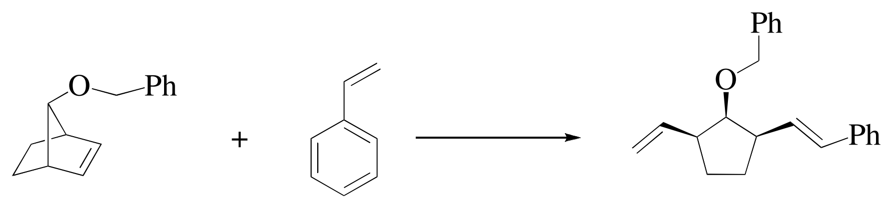
Our initial goal was to confirm that catalysts generated in situ provide the same levels of activity and enantioselectivity as the isolated analogs in the reactions carried under standard conditions in the glovebox. These experiments would also allow us to establish a baseline for the future screenings performed in the fume hood. The results of the catalyst screenings are presented in Schemes **33** and **34**.

45 46

Mo Precursor	Diol	Time, h	Conv., %	Yield, %	ee, %	Isolated catalyst	Time, h	Conv., %	Yield, %	ee, %
40	(R)-BiphenH_2	3	95	90	97	**1a**	3	98	80	98
42	(R)-BiphenH_2	2	98	86	97	**2a**	0.3	95	78	98
42	(R)-$Benz_2BitetH_2$	2	98	77	60	**4a**	1	95	-	61

Catalysts loading 5 %, C_6D_6, 25 ºC

Scheme 33. ARCM of compound **45** using **ISGC**s and catalysts **1a**, **2a**, and **4a**. Results obtained with isolated catalysts **2a** and **4a** are reported from an earlier publication.[47]



7 8

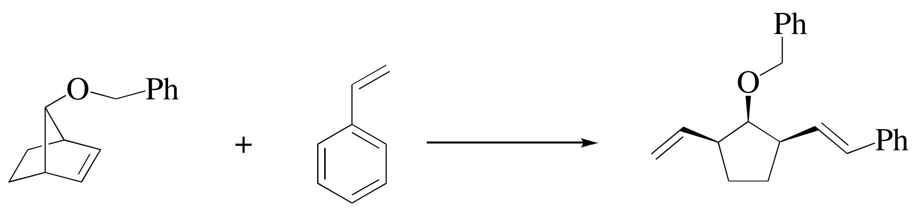
Mo Precursor	Diol	Time, h	Conv., %	ee, %	Isolated catalyst	Time, h	Conv., %	ee, %
40	(R)-BiphenH_2	2	79	98	**1a**	2	76	97
42	(R)-BiphenH_2	2	80	98	**2a**	0.5	95	98
42	(R)-$Benz_2BitetH_2$	2	51	53	**4a**	2	98	93

Catalysts loading 5 %, C_6D_6, 25 ºC

Scheme 34. AROM/CM of compound **7** using **ISGC**s and catalysts **1a**, **2a**, and **4a**. Results obtained with isolated catalysts **1a** and **2a** are reported from earlier publications.[47,48]

Data presented in **Scheme 33** show nearly perfect agreement between the conversion and ee's obtained with **ISGC**s 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)-$Benz_2BietetH_2$ 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 C_6D_6 and 0.5 mL of THF). The results of this study are shown in **Scheme 35**.



7 **8**

Catalyst	Time, h	Conv., %	ee, %
ISGC 3	2	54	44
ISGC 3 + THF	2	67	88
4a	2	72	91

Catalysts loading 5 mol %, C_6D_6, 25 °C

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)-Benz$_2$BitetH$_2$, 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 **ISGC**s 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 N_2 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)-BiphenH$_2$, (R)-Benz$_2$BitetH$_2$, and substrates 45, 47, and 7.

Stock solutions of (R)-BiphenH$_2$, (R)-Benz$_2$BitetH$_2$, **40**, and **42** in C_6D_6 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 **42**[20] 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)-BiphenH$_2$ (0.028 M), and (R)-Benz$_2$BitetH$_2$ (0.016 M). Substrates **45**, **47**, and **7** were dried over 4Å molecular sieves and used as 20 mg/mL solutions in C_6D_6. Styrene was purchased from Aldrich and distilled from CaH_2 under vacuum. Styrene (stock solution, C_6D_6, 0.5 M) was stored frozen at -30 ^oC 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 CaH_2, 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 **ISGC**s 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 ^{o}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.

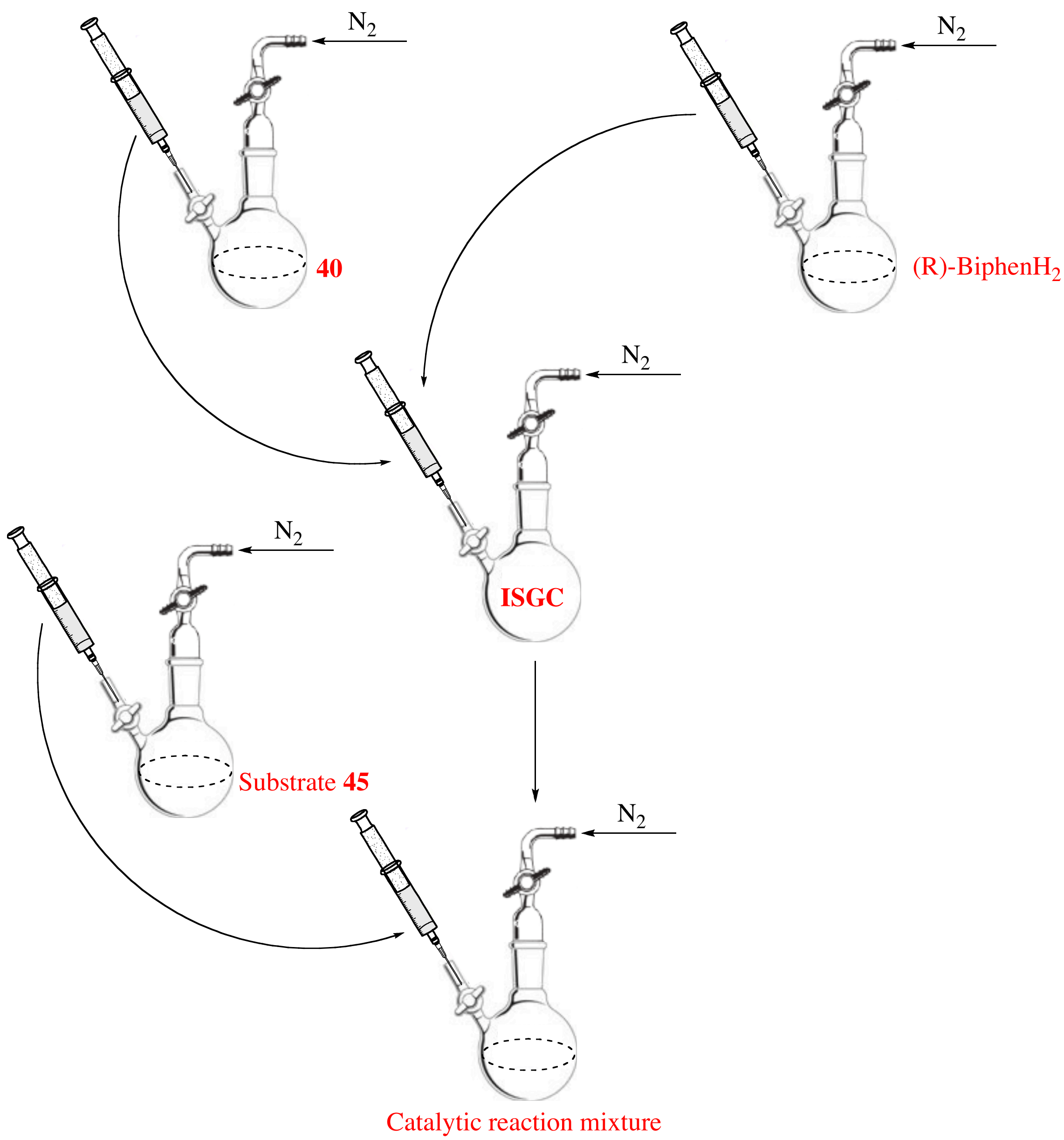
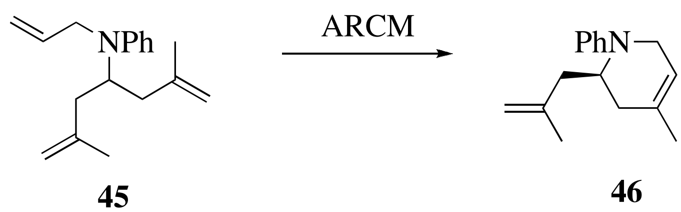


Figure 24. Example of reaction setup in the fume hood: ARCM of substrate **45** with **ISGC 1**.

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 ^{o}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 **ISGC**s 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 %, C_6D_6, 25 °C

Catalyst: ISGC 1

	Time, h	Conv., %	Yield, %	ee, %
Glovebox	3	91	90	98
Fume hood, 3 days	3	96	94	96
Fume hood, 10 days	2	77	74	96
Fume hood, 31 days	3	96	87	97
Fume hood, 41 days	3	68	65	97

Catalyst: ISGC 2

	Time, h	Conv., %	Yield, %	ee, %
Glovebox	2	98	86	97
Fume hood, 3 days	2	98	95	97
Fume hood, 10 days	2	98	93	97
Fume hood, 31 days	2	98	98	95

Catalyst: ISGC 3

	Time, h	Conv., %	Yield, %	ee, %
Glovebox	2	98	77	60
Fume hood, 3 days	2	98	93	61
Fume hood, 10 days	2	98	91	62
Fume hood, 31 days	2	98	90	62

Figure 25. ARCM of **45** with **ISGC 1**, **ISGC 2**, and **ISGC 3** in the fume hood and in the glovebox.

47 **48**

Catalyst loading 5 mol %, C_6D_6

Catalyst: ISGC 1

	T, °C	Time, h	Conv., %	Yield, %	ee, %
Glovebox	25	3	90	76	-12
Fume hood, 3 days	70	3	93	77	-17
Fume hood, 10 days	25	3	91	68	-15
Fume hood, 31 days	25	3	90	86	-17

Catalyst: ISGC 2

	T, °C	Time, h	Conv., %	Yield, %	ee, %
Glovebox	25	3	84	58	28
Fume hood, 3 days	70	3	71	46	21
Fume hood, 10 days	25	3	81	53	24
Fume hood, 32 days	25	3	73	60	15

Catalyst: ISGC 3

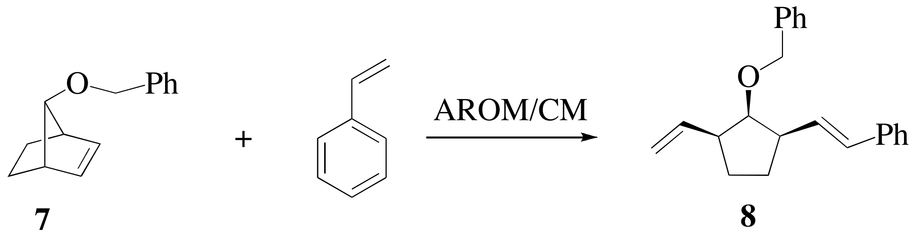
	T, °C	Time, h	Conv., %	Yield, %	ee, %
Glovebox	25	3	79	64	0
Fume hood, 3 days	70	3	51	40	0
Fume hood, 10 days	25	3	85	56	0
Fume hood, 32 days	25	3	71	43	1

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 ^{o}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.[44] Therefore we decided to perform these transformations in the fume hood with 3 day old stock solutions at 70 ^{o}C. However, formation of **48** in the presence of **ISGC 1**, **ISGC 2** and **ISGC 3** at 70 ^{o}C proceeded with the same low enantioselectivities. Additionally, conversions provided by **ISGC 2** and **ISGC 3** at 70 ^{o}C were lower than those obtained at room temperature. Based on these observations future screenings with substrate **47** were conducted at 25 ^{o}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.[21] 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.



Catalyst loading 5 mol %, C_6D_6, 25 °C

Catalyst: ISGC 1

	Time, h	Conv., %	Yield, %	ee, %
Glovebox	2	79	-	98
Fume hood, 4 days	2	92	80	>98
Fume hood, 10 days	2	91	89	>98
Fume hood, 30 days	2	98	91	>98

Catalyst: ISGC 2

	Time, h	Conv., %	Yield, %	ee, %
Glovebox	2	80	-	98
Fume hood, 4 days	2	68	60	98
Fume hood, 10 days	2	72	63	>98
Fume hood, 32 days	2	85	80	93

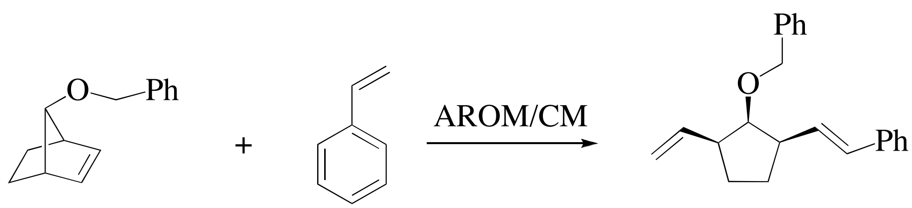
Catalyst: ISGC 3

	Time, h	Conv., %	Yield, %	ee, %
Glovebox	2	54	39	44
Fume hood, 4 days	2	50	28	73
Fume hood, 10 days	2	57	37	88
Fume hood, 30 days	2	71	66	94

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)-$Benz_2BitetH_2$ 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 ^{1}H 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 ^{1}H 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**.



7 **8**

Catalyst loading 5 mol %, C_6D_6, 25 °C

Solution of **42** #3

	Time, h	Conv., %	Yield, %	ee, %
Fume hood, 6 days	2	48	40	80
Fume hood, 12 days	2	62	58	93
Fume hood, 32 days	2	56	51	87

Solution of **42** #4

	Time, h	Conv., %	Yield, %	ee, %
Fume hood, 1 day	2	55	45	88
Fume hood, 9 days	2	60	57	91
Fume hood, 29 days	2	68	66	95

Figure 28. AROM/CM of **7** with styrene in the presence of **ISGC 3** made with the two new stock solutions of **42**.

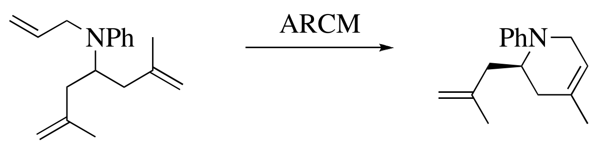
3.2.3.c ARCM of 45 using ISGC 1 and ISGC 2 synthesized with the stock solutions of 40 and 42 that were prepared in the fume hood from solid Mo bispyrrolide complexes.

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 N_2. 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)(CHCMe$_2$Ph)(OTf)$_2$(dme) via sequential addition of lithium pyrrolide and (R)-BiphenH$_2$.

ARCM of **45** can be catalyzed by **ISGC 2** synthesized in the fume hood from a stock solution of Mo(NAr)(CHCMe$_2$Ph)(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)-BiphenH$_2$ to Mo(NAr)(CHCMe$_2$Ph)(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 $Mo(NAr)(CHCMe_2Ph)(OTf)_2(dme)$ (**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 $Mo(NAr)(CHCMe_2Ph)(OTf)_2(dme)$ was introduced into a Schlenk flask equipped with a stir bar, and cooled to 0 ^{o}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)-BiphenH_2 were added and the reaction mixture was stirred for 15 min prior to the addition of the substrate.



45 **46**

Catalyst loading 5 mol %, C_6D_6, 25 ^{o}C

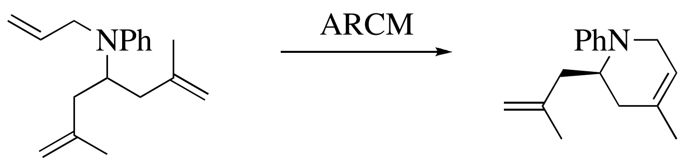
Catalyst: ISGC 1

	Time, h	Conv., %	Yield, %	ee, %
Fume hood, 1 day	3	>98	95	97
Fume hood, 9 days	3	90	83	97
Fume hood, 29 days	3	61	60	97

Catalyst: ISGC 2

	Time, h	Conv., %	Yield, %	ee, %
Fume hood, 1 day	2	>98	89	96
Fume hood, 12 days	2	95	90	97
Fume hood, 32 days	2	>98	89	96

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 bispyrrolide complexes.



45 **46**

Catalyst loading 5 mol %, C_6D_6, 25 °C

Catalyst: ISGC 2

	Time, h	Conv., %	Yield, %	ee, %
Fume hood, 1 day	2	>98	88	96
Fume hood, 9 days	2	>98	98	96
Fume hood, 29 days	2	>98	95	97

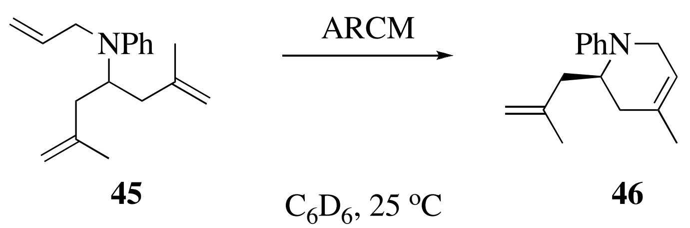
Figure 30. ARCM of **45** catalyzed by **ISGC 2**, which was synthesized from $Mo(NAr)(CHCMe_2Ph)(OTf)_2(dme)$ via sequential addition of lithium pyrrolide and (R)-$BiphenH_2$.

The stock solutions of $Mo(NAr)(CHCMe_2Ph)(OTf)_2(dme)$ 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 $Mo(NAr)(CHCMe_2Ph)(OTf)_2(dme)$ 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)-BiphenH_2.

Compounds **40** and **42** decompose to some extent over time when they are stored as C_6D_6 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)-BiphenH_2 in C_6D_6, 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)-BiphenH_2 does not interfere with the ARCM catalyzed by **ISGC 2**. It is important to note that (R)-BiphenH_2 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)-BiphenH_2 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 **ISGC**s 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)-BiphenH_2 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)-BiphenH_2, 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.



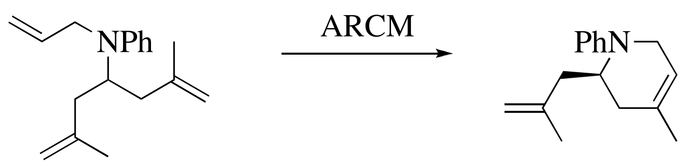
	Time, h	Conv., %	Yield, %	ee, %
ISGC 2	2	>98	86	97
42 + 1 (R)-Biphen H_2[a]	2	>98	92	94
42 + 0.5 (R)-Biphen H_2[a]	2	>98	98	93

[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**.



45 **46**

2.5 mol % **ISGC 1**, C_6D_6, 25 °C

Glovebox		Fume hood (36 days)	
Time, h	Conv., %	Time, h	Conv., %
1	42	1	23
2	52	2	24
3	55	3	24
20	54	20	24

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 **40**, **41**, **42**, and **43** with enantiomerically pure diols were studied. It was determined that the in situ catalyst generated from **40** and (R)-TripH_2 predominantly exists in solution as an *anti* pyrrolenine adduct. The complex synthesized from **42** and (R)-$Benz_2BitetH_2$ is a solvent-free species, differing in this respect from the analogous isolated complex **4a**.

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

ISGC 1, **ISGC 2**, and **ISGC 3** were synthesized from the stock solutions of **40**, **42**, (R)-BiphenH_2, and (R)-$Benz_2BitetH_2$ in the fume hood over one month. Studies of these catalytic systems in the metathesis reactions of **45**, **47**, and **7** showed that **ISGC 1**, **ISGC 2**, and **ISGC 3** prepared in the fume hood are nearly identical in terms of their catalytic properties to the **ISGC**s prepared in the glovebox. The stock solutions of **40** and **42** deteriorate slowly in the fume hood over time, with ca. 50 % of **40** remaining in solution after 36 days.

Mo(NAr)($CHCMe_2Ph$)$(OTf)_2$(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_2. This system retains its activity and enantioselectivity even when the stock solutions of Mo(NAr)($CHCMe_2Ph$)$(OTf)_2$(dme) and lithium pyrrolide are stored in the fume hood for one month.

3.4 Experimental Details.

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 **7**, **41**, **42**, **43**, **45**, **47** and Mo(NAr)($CHCMe_2Ph$)$(OTf)_2$(dme) were prepared according to literature procedures.[20,23,26,28,29,49,50,51] The synthesis of compound **40** was modified from the published procedure[20] and is reported below. Products of olefin metathesis reactions **46**, **48**, and **8** were isolated and analyzed according to published procedures.[43,44,50]

^{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 ^{o}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.[20]

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_6D_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_6D_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_6D_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.[44]

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_6D_6, 2.5 mg, $5*10^{-3}$ mmol) and (R)-BiphenH_2 (0.18 mL, 10 mg/mL solution in C_6D_6, 1.8 mg, $5*10^{-3}$ 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_6D_6, 20 mg, $100*10^{-3}$ mmol) and styrene (0.2 mL, 52 mg/mL stock solution in C_6D_6, 10.4 mg, $100*10^{-3}$ 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 ($91.3*10^{-3}$ mmol, 91 %). The spectral data for this compound matched the reported data.[44]

A representative procedure for an olefin metathesis reaction catalyzed by an ISGC derived from Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(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)(CHCMe$_2$Ph)(OTf)$_2$(dme) (0.31 mL, 9 day old 10 mg/mL stock solution in toluene, 3.1 mg, $3.9*10^{-3}$ mmol) via a syringe, then cooled to 0 ^{o}C. Lithium pyrrolide (0.29 mL, 9 day old 2 mg/mL stock solution in THF, 0.57 mg, $7.8*10^{-3}$ mmol) was added to the solution of Mo bistriflate, causing the mixture to turn bright yellow. The mixture was stirred for 45 min at room temperature, and (R)-BiphenH_2 (0.27 mL, 10 mg/mL solution in C_6D_6, 2.7 mg, $7.5*10^{-3}$ 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_6D_6, 20 mg, $78.3*10^{-3}$ 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 ($77.0*10^{-3}$ mmol, 98 %). The spectral data for this compound matched the reported data.[47]

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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.

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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.

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

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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.

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 6th Russian Scientific and Practical Conference of Outstanding Students organized by the Ministry of Education of Russia. 26 January – 03 February 1997. Moscow, Russia.

Publications

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Presentations

1. Pilyugina, T. S.; Schrock, R. R. Asymmetric olefin metathesis catalyzed by alkylimido alkylidene molybdenum complexes. The abstract is published in *Abstracts of Papers, 232nd ACS National Meeting, San Francisco, CA, United States, Sept. 10-14, 2006* **2006**, INOR-553.

2. Pilyugina, T. S.; Schrock, R. R.; Hock, A. S. Molybdenum Alkylimido Complexes as Catalysts for Enantioselective Olefin Metathesis. The abstract is published in *Abstracts of Papers, International Symposium "Advances in Science for Drug Discovery", Moscow, July 11-16, 2005* **2005**, C-23.

3. Pilyugina, T. S.; Schrock, R. R.; Hock, A. S. Synthesis and properties of $Mo(NR)Cl_4(THF)$, $Mo(NR)(CH_2\text{-t-Bu})_3Cl$ and $Mo(NR)(CH\text{-t-Bu})(CH_2\text{-t-Bu})_2$. The abstract is published in *Abstracts of Papers, 229th ACS National Meeting, San Diego, CA, United States, March 13-17, 2005* **2005**, INOR-198.