Z-Selective Olefin Metathesis Processes and Cis/Syndioselective ROMP with High Oxidation State Molybdenum Alkylidenes

by

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B.S. (magna cum laude) in Chemistry
Tufts University, Medford, MA

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Abstract

Chapter 1
Reaction of W(CCMe₃)Cl₃(dme) with one equivalent of (3,5-Me₂C₆H₃NCH₂CH₂)₃NLi₃ affords yellow, crystalline W(CCMe₃)(N₃N) in good yield. The reactivity of this new alkylidyne complex towards terminal alkynes was investigated. Two other new tungsten alkylidenes, W(CCMe₃)(pyr)₃ (pyr = 2,5-dimethylpyrrolide) and W(CCMe₃)(Ph₂N)₃ were prepared by the addition of three equivalents of lithium dimethylpyrrolide or lithium diphenylamide, respectively, to W(CCMe₃)Cl₃(dme). The reactivity of these new alkylidenes with various alcohols is reported. The reactivity of several tungsten alkylidyne compounds towards ligand displacement by surface silanols is reported, resulting in the synthesis of several new silica-supported tungsten alkylidenes. The alkyne metathesis activity of all new homogeneous and heterogeneous alkylidyne complexes is reported.

Chapter 2
Addition of one equivalent of 2,4,6,2’,4’,6’-hexaisopropylterphenol to Mo(NAd)(CHCM₆Ph)(pyr)₂ results in the formation of Mo(NAd)(CHCM₆Ph)(pyr)(HIPTO) (HIPTO = hexaisopropylterphenoxide). This new alkylidene compound was found to catalyze the metathesis of 1-hexene in 20% yield to 95% cis 5-decene, which represents the first report of highly Z-selective metathesis homocoupling of a terminal olefin. The decomposition of the catalyst in the presence of ethylene is explored. The syntheses of several new bulky achiral phenoxide ligands are presented, along with the syntheses of the corresponding MAP (monoalkoxide monopyrrolide) molybdenum imido alkylidene compounds. The reactivity of new MAP compounds containing bulky phenoxide ligands towards the Z-selective metathesis of terminal and internal olefins is presented. The cis-selectivity of this system is proposed to arise from the combination of a relatively small imido ligand in conjunction with a very bulky alkoxide forcing the substituents of the substrate to point in this same direction with each insertion. Photolysis of MAP compounds with 366 nm radiation was found to produce significant amounts of anti alkylidenes, and the kinetics of decay of unstable anti alkylidenes are investigated.
Chapter 3

The reaction of 2,3-dicarbomethoxynorbornadiene (DCMNBD) with Mo(NAd)(CHCM<sub>2</sub>Ph)(pyr)(HIPTO) (Ad = 1-adamantyl, HIPTO = hexaisopropylterphenoxide) affords >98% cis, >98% tactic polyDCMNBD. The tacticity of this polymer is proved to be syndiotactic through polymerization of DCMenthNBD (2,3-dicarbomenthoxynorbornadiene) and <sup>1</sup>H-H COSY. A variety of related MAP alkylidene compounds are also investigated towards the ROMP of DCMNBD and found to produce polyDCMNBD in a range of tacticities and cis contents. Highly *cis* polyNBDF<sub>6</sub> (poly-bis(CF<sub>3</sub>)-norbomadiene) was also prepared using molybdenum MAP compounds, and the resulting polymer was found to be essentially insoluble in common organic solvents. Solid state CPMAS <sup>13</sup>C NMR spectroscopy revealed insoluble polyNBDF<sub>6</sub> to be highly tactic, and the tacticity is proposed to be syndiotactic. *Cis*, tactic polymer was prepared through the addition of 3,3-methylphenylcyclopropene (MPCP) to molybdenum MAP compounds. Attempts towards determination of the tacticity of *cis*-polyMPCP are presented, including the synthesis of three 3,3-disubstituted cyclopropene monomers containing chiral tags. The *cis*-selective ROMP of cyclooctene and 1,5-cyclooctadiene are reported. The syndioselectivity of the catalysts is proposed to be controlled by the configuration of the 4-coordinate metal center, which alternates with each insertion of monomer.

Chapter 4

Racemic 2,3-dicarbomethoxynorbornene (rac-DCMNBE) is polymerized by Mo(NAd)(CHCM<sub>2</sub>Ph)(pyr)(HMTO) (Ad = 1-adamantyl, pyr = pyrrolide, HMTO = hexamethylterphenoxide) to afford an all-cis polymer that is syndiotactic and composed of alternating enantiomers. The *cis*, syndiotactic ROMP of several other racemic chiral monomers are reported, also affording structures containing a high degree of enantiomer alteration. Attempts towards the alternating copolymerization of two different monomers are reported. The ROMP of enantiomerically pure (+)-dicarbomethoxynorbornene with Mo(NAd)(CHCM<sub>2</sub>Ph)(pyr)(HIPTO) leads to the production of 92% *trans*-isotactic polyDCMNBE. The structure of *trans*-isotactic polyDCMNBD is proved through hydrogenation and comparison of its <sup>13</sup>C NMR spectrum with that of known *cis*-isotactic polyDCMNBE. Both cis/syndiotactic/alternating poly-rac-DCMNBE and *trans*/isotactic poly-(+)-DCMNBE are polymer structures that have not been previously reported. The thermal properties of all new polymers and their hydrogenated counterparts are reported and are found to correlate closely with polymer structure.

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<td>Ad</td>
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<tr>
<td>Anal. Calcd</td>
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<td>anti</td>
<td>orientation in which the substituents of alkylidene ligand or of a substrate point away from the imido group</td>
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<td>Ar'</td>
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</tr>
</tbody>
</table>
h  hour
HIPTOH  hexaisopropylterphenol, (2,6-bis(2,4,6-triisopropylphenyl)phenol)
HMTOH  hexamethylterphenol, (2,6-bis(2,4,6-trimethylphenyl)phenol)
HORF6  hexafluoro-t-butanol
iPr  isopropyl
$^{n}J_{AB}$  NMR coupling constant between atoms A and B, through n number of bonds
k  rate constant
$k_i$  rate of initiation
$k_p$  rate of propagation
$m$  meta-substituted
M  molar
MAP  Mono-Alkoxide, mono-Pyrrolide
me  methyl
Me$_2$Pyr  2,5-dimethylpyrroline
Mes  1,3,5-trimethylphenyl
min  minutes
mM  millimolar
mmol  millimoles
mol  moles
MOM  methoxymethyl
MPCP  3,3-methylphenylcyclopropene
NMR  nuclear magnetic resonance
o  ortho-substituted
OTf  triflate, trifluoromethanesulfonate
$p$  para-substituted
PDI  polydispersity index
Ph  phenyl
pyr  pyrrole, pyrrolyl
rac  racemic
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>RCM</td>
<td>ring-closing metathesis</td>
</tr>
<tr>
<td>ROCM</td>
<td>ring-opening/cross metathesis</td>
</tr>
<tr>
<td>ROMP</td>
<td>ring-opening metathesis polymerization</td>
</tr>
<tr>
<td>rt</td>
<td>room temperature</td>
</tr>
<tr>
<td>syn</td>
<td>orientation in which the substituents of alkylidene ligand or of a substrate point towards the imido group</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TMS</td>
<td>trimethylsilyl</td>
</tr>
<tr>
<td>TRIP</td>
<td>2,4,6-triisopropylphenyl</td>
</tr>
<tr>
<td>tol</td>
<td>toluene</td>
</tr>
<tr>
<td>Ts</td>
<td>tosyl, para-toluene sulfonyl</td>
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General Introduction
The development of the olefin metathesis reaction in the past few decades has led to huge advances in organic synthesis, polymer chemistry, and organometallic chemistry. Olefin metathesis refers to the pair-wise exchange of substituents of two olefins; a general example of which is described in Scheme 1. Originally reported by Banks and Bailey at Phillips Petroleum, the metathesis of propene to a mixture of butenes and ethylene was found to occur in the presence of molybdenum catalyst at high temperatures. While a number of possible mechanisms were proposed in the years following this discovery, none of the early proposals fit with the experimental evidence. Chauvin first correctly proposed the mechanism and described the active species in olefin metathesis.

Chauvin’s mechanism invoked the presence of a catalyst containing a metal-carbon double bond (metal alkylidene) which reacts with olefins to form a metallacyclobutane species. This metallacycle breaks up to form a new alkylidene species and a new olefin, as shown in Scheme 2. The new metal alkylidene species can then act as a metathesis catalyst, reacting with another equivalent of either the starting or product olefin and forming a new alkylidene and new olefin.

A few years after Chauvin’s proposal for the existence of alkylidene species, Schrock reported the first stable transition metal alkylidene compound, Ta(CH₂CMe₃)₃(CHCMMe₂). While this tantalum neopentylidene compound did not react with olefins in a metathetical
manner, further investigation led to the development of Ta(CHCMe 3 )(PMe 3 )Cl(OtBu) 2 , which catalyzed the metathesis of 2-pentene, thus confirming Chauvin’s proposal that metal alkylidenes were the active species in olefin metathesis. Soon after, a class of related molybdenum and tungsten compounds that could metathesize olefins efficiently was reported. This new class of olefin metathesis catalyst contains a metal-carbon double bond (alkylidene), and is supported by a bulky, dianionic aryl- or alkylimido ligand and two alkoxide ligands.

![Figure 1: Schrock olefin metathesis catalyst](image)

One advantage of the Schrock olefin metathesis catalyst described in Figure 1 is its modularity: the substituents on both the imido and the alkoxide ligands easily can be varied to tune the nature of the catalytic site. The catalyst can be made even more active through the introduction of electron-withdrawing fluorinated alkoxide ligands, presumably due to the increased electron-deficiency of the metal center allowing it to react more readily with olefins.

Molybdenum imido alkylidene bisalkoxide compounds can be prepared in 4 steps from commercially available ammonium molybdate. The synthesis (described in Scheme 3) begins with the installation of the imido ligand – the molybdenum starting material is exposed to 4 equivalents (2 per molybdenum) of the desired amine in the presence of excess triethylamine, trimethylsilylchloride, and dimethoxyethane. The second step is alkylation of the diimido-dichloride complex with two equivalents of the desired Grignard reagent, generally either 2,2-dimethylpropylmagnesium chloride (neopentyl Grignard) or (2-methyl-2-phenylpropyl)magnesium chloride (neophyl Grignard), both commercially available or easily prepared. In the third step of the synthesis of molybdenum imido alkylidene catalysts, the diimido-dichloride complex is treated with three equivalents triflic acid to both displace one of the imido ligands, and force an alkyl ligand to undergo alpha-abstraction, releasing one equivalent of RCH 3 and generating a metal-carbon double bond. The final step is straightforward salt metathesis to replace the triflate ligands with alkoxides, generating active
olefin metathesis catalysts. The synthesis described here has been applied towards the preparation of a number of R, R', and R'' substituents, and has been adapted for the synthesis of related tungsten alkylidene compounds.12,14,15

After the initial development of high-oxidation state transition metal alkylidene complexes as olefin metathesis catalysts by Schrock, a ruthenium carbene complex was developed by Grubbs that can also metathesize olefins.16,17 The Grubbs catalyst (Figure 2), while not as active as the Schrock catalyst, was found to be significantly more stable towards water and oxygen. The two catalysts have complementary functional group tolerance – the ruthenium complex is more stable towards protic substrates, while the molybdenum and tungsten catalysts are more tolerant towards sulfur, nitrogen, and phospine-based functionalities.7

The reaction described in the general mechanism displayed in Scheme 1 is not especially synthetically useful, as it is reversible and will produce a mixture of the three possible olefins, R1C=CR1, R1C=CR2, and R2C=CR2, which are not necessarily easily separated from each other. By tweaking the nature of the starting olefin to provide a driving force for the desired reaction, the olefin metathesis reactions described in Scheme 4 allow for the synthesis of a single, isolable
In Ring Opening Metathesis Polymerization (ROMP), a strained cyclic olefin is metathesized to form an olefin-containing polymer; the strain of the initial substrate prevents the backwards reaction from occurring. In terminal Olefin Cross Metathesis (CM) and Ring Closing Metathesis (RCM), the escape of ethylene from the reaction mixture provides this force.

One major advance in the field of olefin metathesis was the development of catalysts that are able to catalyze enantioselective metathesis reactions. The first of such catalysts, developed by Schrock in collaboration with Hoveyda, contained an enantiomerically pure chelating biphenoxy ligand such as the one shown in Scheme 5. One of the first reported examples to show the utility of chiral molybdenum catalysts is also shown in Scheme 5: the kinetic resolution of an acyclic diene to the enantioenriched cyclic olefin product. In this reaction, an acyclic diene substrate undergoes ring-closing metathesis to form a single enantiomer of the cyclopentene product, leaving behind >99% enantiopure starting material.
Extensive development of chiral molybdenum and tungsten olefin metathesis catalysts has been carried out since the initial report described in Scheme 5, and enantioselective olefin metathesis with Group VI alkylidene compounds has been extended to a wide range of asymmetric metathesis processes.\textsuperscript{21-25} Molybdenum and tungsten catalysts containing chelating chiral diolate ligands have also been shown to afford all-\textit{cis}, isotactic polymers in the ROMP of substituted cyclic norbornenes and norbornadienes through enantiomorphic site control.\textsuperscript{26,27} Further details concerning the development of catalysts for stereoselective ROMP are available in Chapter 3.

With a growing library of molybdenum and tungsten imido alkylidene catalysts available, interest in the beginning of the 21\textsuperscript{st} century moved towards the development of well-defined single site heterogeneous olefin metathesis catalysts.\textsuperscript{28,29} Early goals in this area were to develop a suitable alkylidene catalyst precursor that could be grafting to a solid silica support by protonation and displacement by surface silanols. Amides and alkyls were originally chosen for this purpose, and active mono-amide, mono-siloxide surface-supported catalysts could be prepared upon the addition of M(NR)(CHCR')(NR''\textsubscript{2})\textsubscript{2} to partially dehydroxylated silica. Bispyrrolide complexes of the type M(NR)(CHCR')(pyr)\textsubscript{2} (pyr = pyrrolide or 2,5-dimethylpyrrolide), which can be synthesized cleanly from the addition of two equivalents of Li(pyr) to M(NR)(CHCR')(OTf)\textsubscript{2}(dme), were developed next. It was found that the pyrrolide ligand could be cleanly displaced by a surface silanol ligand to produce a silica supported active olefin metathesis catalyst, as displayed in Scheme 6.\textsuperscript{29,30}
While bispyrrolide imido alkylidene complexes are relatively unreactive olefin metathesis catalysts on their own, they can be used as in situ precursors to a wide variety of bisalkoxide or diolate-based alkylidene compounds, including compounds that could not be made through traditional routes. Neither pyrrole nor 2,5-dimethylpyrrole was found to interact...
significantly with the metal center, meaning that they did not need to be removed from the reaction mixture before addition of substrate in a metathesis reaction. Pyrrolides were found to be displaced more easily than amides, making bispyrrolide complexes better catalyst precursors than bisamide complexes.

When only one equivalent of an alcohol is added to a bispyrrolide complex (Scheme 7), a MonoAlkoxide-monoPyrrolide (MAP) of the type M(NR)(CHR')(pyr)(OR'') can be isolated. It was at first expected that these mixed alkoxide-pyrrolide alkylidene complexes would behave as olefin metathesis catalysts with reactivity that was intermediate between that of the bispyrrolide and bisalkoxide compounds. Surprisingly, however, it was found that MAP alkylidene complexes exhibited high reactivity, and in some cases outperforming their bisalkoxide counterparts. An initial example of the unique activity of MAP catalysts is the metathesis of an enyne substrate (Scheme 8), a reaction that previously could not be carried out with Group VI imido alkylidene compounds.31

![Scheme 8: Enyne metathesis with Ru and Mo catalysts](image)

The enyne metathesis product in the reaction described in Scheme 8 produced by Mo(NAr)(CHCMe2Ph)(Me2Pyr)(OAr) was primarily the product derived from β-addition of the substrate, which is in contrast to the product isolated using ruthenium catalysts. This reaction represents the first example of the utility of MAP catalysts to extend the scope of molybdenum imido alkylidene catalysts towards metathesis of a variety of substrates.
MAP alkylidenes contain four different substituents around the metal center and are therefore chiral at the metal and exist as a mixture of two enantiomers.

When an enantiomerically pure chiral alkoxide ligand is incorporated, the MAP complex exists as a mixture of two diastereomers. One such class of compounds has been prepared using an enantiomerically pure monoprotected diolate ligand, as shown in Figure 3.33

The introduction of enantiopure ligands into the MAP framework allows for asymmetric olefin metathesis, and it was found that compounds of the class shown in Figure 3 were able to catalyze asymmetric olefin metathesis reactions with good yield and enantioselectivity. One notable result using MAP catalysts is described in Scheme 9. The reaction described in Scheme 9 is an important ring closing metathesis step in the synthesis of the natural product (-)-quebrachamine that could not be performed in good yield with existing chiral catalysts.32,33

Scheme 9: RCM using MAP catalyst of an intermediate in the synthesis of quebrachamine. Ar = 2,6-diisopropylphenyl
The high activity and selectivity of MAP catalysts in the reactions described above prompted significant further investigation of catalyst variations utilizing the MAP framework in the years since their discovery. Theoretical studies have reported that complexes of the type \( \text{M(NR)(CHR')(X)(Y)} \) \((X \neq Y)\) should be especially active olefin metathesis catalysts,\(^{34}\) which is what has been observed experimentally, as described above.

Three of the chapters of this report will concern the development of MAP catalysts for use as catalysts in a variety of olefin metathesis reactions. Chapter 2 will discuss the synthesis of MAP alkylidene compounds containing bulky alkoxide, siloxide, and phenoxide ligands and their use in \(Z\)-selective metathesis processes. Chapters 3 and 4 involve the application of the compounds reported in Chapter 2 towards ring opening metathesis polymerization (ROMP). Specifically, Chapter 3 will report the ROMP of achiral cyclic olefin substrates to produce selectively \(cis\)-syndiotactic polymers, and Chapter 4 will discuss a variety of selective ROMP processes with MAP catalysts and chiral olefinic substrates. All three chapters highlight the unique reactivity and selectivity of molybdenum MAP catalysts in olefin metathesis reactions.

The remaining chapter of this report concerns developments in alkyne metathesis. Alkyne metathesis has not achieved the same level of attention as olefin metathesis, although the two processes were discovered concurrently and involve many of the same principles. Catalysts for alkyne metathesis a metal-carbon triple bond (alkylidyne ligand); the most active well-defined alkyne metathesis catalysts are supported by alkoxide ligands, such as in the compound displayed in Figure 4.

![Figure 4: Alkyne metathesis catalyst](image)

The mechanism of alkyne metathesis is analogous to that of olefin metathesis (Scheme 2), and involves the \([2+2]\) cycloaddition of an alkyne to the alkylidyne catalyst to form a metallacyclobutadiene intermediate. This intermediate can break up to form a new alkyne and a new alkylidyne complex, which can perform further metathesis reactions. Chapter 1 of this
report will describe the synthesis of several new well-defined homogeneous and heterogeneous alkyne metathesis catalysts. While Chapters 2-4 of this report will discuss the synthesis of alkylidene compounds containing mixed pyrrolide and alkoxide ligands, Chapter 1 will discuss the application of this idea to alkyne metathesis, and will describe the synthesis of Group VI alkylidyne compounds containing mixed pyrrolide, alkoxide, and amide ligands. Chapter 1 will address some of the problems inherent to alkyne metathesis and describe attempts to bring alkyne metathesis to the same level of success that olefin metathesis has seen over the past few decades.
REFERENCES


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Chapter 1

Alkyne Metathesis with Molybdenum and Tungsten Alkylidyne Complexes
INTRODUCTION

Alkyne metathesis has the potential to be a powerful tool in organic synthesis; however it has yet to achieve the same level of widespread use as olefin metathesis. Transition metal catalysts for alkyne metathesis have been well-studied; the active catalyst contains a metal-carbon triple bond (alkylidyne), as shown in Scheme 1.1. The mechanism of alkyne metathesis is understood to proceed through a metallacyclobutadiene intermediate, analogous to the metallacyclobutane intermediates in the metathesis of olefins with metal alkylidene catalysts. Applications of alkyne metathesis are complementary to olefin metathesis, and include Ring-Closing Alkyne Metathesis (RCAM), and Acyclic Diyne Metathesis Polymerization (ADIMET). Until the highly Z-selective metathesis of terminal olefins was reported by our group in 2009, RCAM followed by Lindlar reduction was the only relatively synthetically practical option for the synthesis of exclusively cis olefins.

Although active, stable alkyne metathesis catalysts have been studied for years, the metathesis of terminal alkynes (R₂=H in Scheme 1.1) has consistently posed obstacles that have yet to be entirely overcome. One such obstacle is that an expected metathesis product of a terminal alkyne is acetylene, the most reactive of alkynes, making the undesired backward metathesis reaction, or side reactions, potentially faster than the desired reaction. Also, a necessary intermediate in the metathesis of terminal alkynes is a metallacyclobutadiene intermediate containing at least one proton substituent. The metallacycle intermediate of one active alkyne metathesis catalyst, W(CMe₃)(O-t-Bu)₃, can be deprotonated by an alkoxide ligand, giving an inactive species and one equivalent of alcohol (Scheme 1.2). Also, an intermediate in the metathesis of terminal alkynes is a tungsten methylidyne compound, which may decompose bimolecularly to the bridged complex shown in equation (2) of Scheme 1.2.

![Scheme 1.1](image_url)

Scheme 1.1: Alkyne metathesis with trialkoxy tungsten alkylidyne
In an effort to overcome the problems inherent to the metathesis of terminal alkynes, we turned to tungsten alkylidyne complexes containing a chelating triamidoamine (tren) ligand. Tren alkylidyne complexes of tungsten have been reported, but their activity as alkyne metathesis catalysts has not yet been fully explored. One advantage of a tren-based catalyst is that the chelating ligand would not be able to undergo the type of decomposition reaction shown in reaction (1) of Scheme 1.2. Bulky substituents on the tren ligand create a sterically protected metal center, discouraging the bimolecular decomposition shown in reaction (2) of Scheme 1.2. Both the degree of steric protection provided by the ligand and the electronic nature of the metal center could potentially be tuned by changing the nature of the substituents on the tren backbone.

Scheme 1.2: Processes that interfere with alkyne metathesis with Group VI alkylidyne trisalkoxide complexes
RESULTS AND DISCUSSION

I. Tren-based tungsten alkylidyne complexes

A series of trimethylsilyl-substituted tren tungsten alkylidyynes, reported by Joel Freundlich\(^9\), were found to react stoichiometrically with terminal alkynes, although slowly, and significant amounts of polymer were formed as a side product of the reaction. These results suggest that the tren backbone might be a good starting point in the development of new terminal alkyne metathesis catalysts. Due to its relatively facile synthesis, the tren-based ligand employed in this project was chosen to be the trisubstituted 3,5-dimethylphenyl tren (Scheme 1.3).

I. A. Synthesis of a tungsten alkylidyne with a triamidoamine ligand

Group VI metal-alkyl complexes employing tren-based ligands have been shown to spontaneously undergo \(\alpha\)-hydrogen abstraction to form an alkylidyne and one equivalent of hydrogen.\(^2\) These results pointed to a logical synthetic route to the desired tungsten tren complex: alkylation of a tungsten (IV) monochloride tren complex, which would hopefully undergo spontaneous hydrogen abstraction to yield the desired alkylidyne. The synthesis of \([\text{N}_3\text{N}]\text{WC}1\) (\(\text{N}_3\text{N} = (3,5-\text{Me}_2\text{C}_6\text{H}_3\text{NCH}_2\text{CH}_2)_3\text{N}\)) has been reported previously through the reaction of the ligand with \(\text{WCl}_4\)(dme), followed by deprotonation by \(\text{MeMgCl}\)\(^10\). However, attempts to repeat these results afforded a product mixture containing the expected paramagnetic \(^1\text{H}\) NMR resonances, in addition to multiple unidentifiable resonances. The desired product could not be isolated cleanly through multiple recrystallizations, so variations on the procedure were employed in an attempt to obtain the desired monochloride product in adequate purity, as described in Scheme 1.3. None of the above synthetic routes afforded the desired product in usable purity, so a different approach ultimately was taken for this synthesis. In the synthesis of tungsten alkylidyne complexes of the TMS-substituted tren ligand reported by Freundlich, it was
found that a more viable synthetic route is the reaction of the trilithium salt of the ligand with W(C(C Me3)3)Cl3(dme). Following the general procedure outlined by Freundlich, W(C(CMe3)3)Cl3(dme) reacts with Li3[N3N] at -25°C in toluene to give yellow, crystalline [N3N]W(C(CMe3)3) (1) in 49% yield (Scheme 1.4). The spectroscopic features of 1 reveal a C3v symmetric structure, with 1H NMR resonances correlating well to those observed in similar tren alkylidyne complexes. One notable feature is the presence of the expected alkylidyne carbon resonance in the 13C NMR spectrum at 297.99 ppm, with a Jcw of 255 Hz, falling within the expected range for coupling of the 13C nucleus to tungsten.
I. B. Reaction of [N\textsubscript{3}N]W(C\textsubscript{3}Me\textsubscript{3}) with Terminal Alkynes

To determine if 1 was a suitable alkyne metathesis catalyst, the reactivity of 1 towards terminal alkynes was investigated. When 5 eq phenylacetylene were added to a C\textsubscript{6}D\textsubscript{6} solution of 1 as described in Scheme 1.5, the reaction mixture immediately became red, and within one hour the \textsuperscript{1}H NMR spectrum of the reaction mixture showed the appearance of a resonance corresponding to a small amount of a new alkylidyne (10% of total resonances).

The \textsuperscript{1}H NMR resonances monitored to determine the existence of a new alkylidyne or disappearance of the starting alkylidyne were two aromatic resonances of integration 1:2, corresponding to the ortho- and para- protons of the 3,5-dimethylphenyl substituents. The appearance of the new alkylidyne resonances was monitored by \textsuperscript{1}H NMR over 6 days, after which time approximately equal amounts of the original alkylidyne and a new alkylidyne were present in the mixture, suggesting that this complex reacts only very slowly with the alkyne. In addition to the expected resonances corresponding to a new alkylidyne, a number of very broad resonances in the aliphatic region appeared over the course of the reaction, suggesting polymerization or oligomerization of the alkyne. Similar results were obtained in the reaction of 1 with two additional terminal alkynes: 1-pentyne and 1-hexyne – slow conversion of the original alkylidyne accompanied by significant amounts of polymer formation. These results are similar to the results obtained in the TMS-substituted system; 1 does react with terminal alkynes, but only slowly and alongside a significant competing polymerization reaction\textsuperscript{5}.

The results obtained in this project suggest that tren-based tungsten alkylidyne compounds are not an ideal framework for the development of new terminal alkyne metathesis catalysts. Most likely, the nitrogen-donor tren ligand does not provide an adequately electron-
deficient tungsten center to react rapidly enough with alkynes. The tren ligand might be tuned in order to obtain a balance between a sufficiently reactive complex, and one that does not readily decompose or undergo competing reactions to any significant degree. For example, the replacement of the 3,5-dimethylphenyl groups of the ligand for a more electron-withdrawing substituent such as 3,5-di(trifluoromethyl)phenyl or pentafluorophenyl might render the tungsten center sufficiently electron deficient to undergo fast electrophilic attack on the alkyne substrate. Optimizing the metathesis reaction conditions could also improve the catalytic activity of tren-based tungsten alkylidyne complexes.

While it is possible that the triamidoamine framework could be further tuned to produce a tungsten alkylidyne compound that is an active terminal alkyne metathesis catalyst, efforts moved away from this ligand system for this purpose and towards a new strategy for overcoming the issues in terminal alkyne metathesis, namely the development of silica-supported transition metal alkylidyne complexes.

II. Surface-supported molybdenum and tungsten alkylidyne complexes

Recently, a number of surface-supported tungsten and molybdenum olefin and alkyne metathesis catalysts have emerged, and proved to be highly stable, active, and reusable. The synthesis of these silica-supported olefin metathesis catalysts indicates that a silica-supported tungsten alkylidyne compound might be a good candidate for improving the existing alkyne metathesis systems. One potential advantage of a supported catalyst is that immobilization of the organometallic compound on the surface essentially eliminates any possible bimolecular decomposition pathways such as the one described in reaction (2) of Scheme 1.2. Also, isolation of the desired organic product should be more straightforward than in homogeneous systems, and if the system is sufficiently stable, the used catalyst potentially could be recycled.
One particularly active catalyst system has been recently reported by Moore and coworkers, employing a tris-anilide molybdenum alkylidyne compound reported by Cummins.\cite{12,13} This precursor, once grafted onto the silica surface, affords a highly active internal alkyne metathesis catalyst, capable of performing previously unknown alkyne metathesis reactions. The high activity of the bis-anilide supported compound prompted the idea that a similar tungsten alkylidyne supported compound could potentially have similar activity and robustness. A potential precursor for a supported tungsten species would ideally be of the form W(CCMe₃)L₃, where L is a ligand such as an anilide or a pyrrolide, that is easily displaced by a surface silanol, as described in Scheme 1.6.

Inspired by the recent success in our group with the use of the pyrrolyl ligands in olefin metathesis catalyst precursors,\cite{14} a tris-pyrrolyl tungsten alkylidyne complex was the first candidate for use in this system.

II. A. New homogeneous Group VI alkylidyynes as precursors for supported catalysts and reactions with alcohols

Previous attempts in our group to synthesize a tris-pyrrolyl tungsten alkylidyne species through the salt metathesis of lithium pyrrolide with W(CCMe₃)Cl₃(dme) did not lead to the isolation of a tungsten alkylidyne pyrrolide compound.\cite{15} The use of substituted 2,5-dimethyl pyrrolyl ligand afforded a more sterically protected complex. W(CCMe₃)(2,5-Me₂C₄H₂N)₃ (2) was prepared by the addition of 3 equivalents of lithium dimethylpyrrolide to W(CCMe₃)Cl₃(dme), and the resulting orange compound was isolated in 47% yield from the reaction mixture after recrystallization from pentane (Scheme 1.7).
The $^1$H NMR spectrum of the crude reaction mixture shows that the desired product is present in high purity, suggesting that the limiting factor in improving the yield of this reaction is the recovery of the relatively soluble product from the pentane mother liquor. The $^{13}$C NMR spectrum displays a resonance at 327.02 ppm, with a $J_{CW}$ of 254 Hz, in the expected range of an alkylidyne carbon. Only one sharp $^1$H NMR resonance each was observed for the pyrrolyl methyl and backbone protons, suggesting that the compound is $C_{3v}$ symmetric, with the pyrrolide ligands rotating rapidly on the NMR time scale.

The $^1$H NMR spectrum of 2 shows no change when recorded at various temperatures between room temperature and -90°C, suggesting that all three of the pyrrolide ligands are bound $\eta^1$, as drawn in Scheme 1.7. If one or more pyrrolide ligands were bound in an $\eta^5$ fashion to tungsten, the NMR spectrum at low temperatures would be expected to show a splitting of the backbone or methyl pyrrolide protons. The apparent inability of 2 to form an $\eta^5,\eta^1,\eta^1$ structure might be due to the steric bulk of the pyrrolyl methyl groups preventing any of the ligands converting to the $\eta^5$ configuration. The $^1$H NMR resonances due to the methyl groups and the backbone protons of the pyrrolide ligands do not broaden upon cooling to -90°C in CD$_2$Cl$_2$, suggesting that the ligands are rotating rapidly on the NMR time scale along the W-N axis, and are either all bound $\eta^1$ to tungsten or rapidly equilibrating between $\eta^1$ and $\eta^5$ binding modes.

In addition to the trisdimehtylpyrrolyl 2, the high activity and selectivity of the Moore system prompted the further investigation of tris-amido tungsten alkylidyne as precursors for a supported alkyn metathesis catalyst and as homogeneous catalysts. WCCMe$_3$(NMe$_2$)$_3$ (8) is a known compound, although it does not metathesize 3-heptyne to the expected products at room temperature. A tungsten alkylidyne employing the more poorly electron donating diphenylamido
ligand would be expected to be a more active alkyne metathesis catalyst or supported catalyst precursor.

\[ W(CCMe_3)(NPh_2)_3 \] (3) was synthesized in 67% yield by treatment of a THF solution of \( W(CCMe_3)Cl_3(dme) \) with three equivalents lithium diphenylamide (Scheme 1.8). As determined by \(^1\)H NMR spectroscopy, 3 has the structure depicted in Scheme 1.8, with all three amide ligands equivalent on the NMR time scale.

To determine if 2 and 3 are viable precursors for surface-supported alkylidyne complexes, the ability of the pyrrolide ligands to be displaced by a tert-butoxide ligand was investigated, in analogy to their potential displacement by a surface siloxy ligand. The addition of 1 eq tert-butanol to a \( C_6D_6 \) solution of 2 at room temperature contains (by \(^1\)H NMR spectroscopy) a mixture of 2, along with \( W(CCMe_3)(2,5-Me_2C_4H_2N)_2(O-t-Bu) \) (4) and \( W(CCMe_3)(2,5-Me_2C_4H_2N)(O-t-Bu)_2 \) (5). Addition of 2 equivalents tert-butanol affords 5 and \( W(CCMe_3)(O-t-Bu)_3 \) (6), and finally, addition of 3 equivalents of the alcohol yields only \( W(CCMe_3)(O-t-Bu)_3 \) (Scheme 1.9).

The results displayed in Scheme 1.9 suggest that the 2,5-dimethylpyrrolide ligand can be displaced by tert-butanol at room temperature, however, more than one type of alkylidyne product is formed with each addition of alcohol. To isolate 4 or 5 cleanly, the reaction would most likely need to be performed at lower temperature or lower concentrations, to ensure that tert-butanol reacts slowly enough to afford only one product. However, since the possibility of two surface siloxy groups reacting with one alkylidyne molecule is very low, the successful alcoholysis of the pyrrolyl ligands by tert-butanol shows that 2 might nevertheless be a good choice for a surface-supported catalyst precursor.
Scheme 1.9: Reactions of 2 with tert-butanol. pyr = dimethylpyrrolide, OR = O-\(\text{t-Bu}\).

\[
\begin{align*}
\text{pyr} & \quad \begin{array}{c}
\text{W} \text{pyr} \text{pyr} \\
\text{pyr} \text{pyr} \text{pyr} \\
\text{pyr} \text{pyr} \text{pyr}
\end{array}
\quad \overset{1 \text{ t-BuOH}}{\rightarrow}
\begin{array}{c}
\text{pyr} \\
\text{pyr} \\
\text{pyr}
\end{array}
\text{W} \text{pyr} \text{pyr} \\
\text{pyr} \text{pyr} \text{pyr}
\end{align*}
\]

\[
\begin{align*}
\text{pyr} & \quad \begin{array}{c}
\text{W} \text{pyr} \text{pyr} \\
\text{pyr} \text{pyr} \text{pyr} \\
\text{pyr} \text{pyr} \text{pyr}
\end{array}
\quad \overset{2 \text{ t-BuOH}}{\rightarrow}
\begin{array}{c}
\text{pyr} \\
\text{pyr} \\
\text{pyr}
\end{array}
\text{W} \text{pyr} \text{pyr} \\
\text{pyr} \text{pyr} \text{pyr}
\end{align*}
\]

Scheme 1.10: Synthesis of 7

W(CCM\text{Me}_3)(2,5-Me_2\text{Pyr})_2(\text{OAd}) (7) (Ad = 1-adamantoxide) was synthesized in poor (10 \%) yield from the reaction of 2 with one equivalent 1-adamantanol at -78°C (Scheme 1.10). The \(^1\text{H NMR spectrum of 7 shows broad resonances corresponding to the pyrrolyl-methyl and backbone protons, suggesting that these ligands are either rotating slowly on the NMR time scale along the W-N axis, or are in equilibrium between an \(\eta-1\) and \(\eta-5\) configuration. Although 7 can be recrystallized from pentane at -25°C, resonances corresponding to small amounts of both the starting material 2 and what can be attributed to W(CCM\text{Me}_3)(\text{OAd})_2(\text{pyr}), are visible in the \(^1\text{H NMR spectrum of 7}.\) Due to the high solubility and low yield of 7, a second recrystallization for further purification was not practical.
In addition to the pursuit of new $C_3$-symmetric tungsten alkylidyne, the recent development of mono-alkoxide-mono-pyrrolide molybdenum alkylidenes such as Mo(NAr)(CHCMe₂Ph)(2,5-Me₂Pyr)[OCMe(CF₃)₂] in our group prompted the pursuit of monoalkoxide-bispyrrolide or bisalkoxide-monopyrrolide tungsten alkylidyne. Attempts at the synthesis of other various tungsten alkylidyne containing mixed $\text{N}$ and $\text{O}$ donor ligands were unsuccessful. The high solubility and low crystallinity of tungsten neopentylidyne complexes makes isolation and purification through recrystallization difficult. Attempts towards synthesis of tungsten alkylidyne containing mixed $\text{N}$- and $\text{O}$-donor ligands are displayed in Scheme 1.11.

Many of the expected products of the reactions outlined in Scheme 1.11 were observable by $^1\text{H}$ NMR spectroscopy, but could not be isolated from the reaction mixture. Similar attempts to isolate mixed amide/alkoxide alkylidyne through alcoholysis of the amide ligands of 3 or salt metathesis of alkoxide ligands afforded intractable product mixtures. Difficulties in synthesizing the alkylidyne starting material W(CCMe₃)Cl₃(dme) on a large scale prohibited the large scale preparation of compounds described in Scheme 1.11. Mixed alkoxide/ pyrrolide or alkoxide/amide alkylidyne would be ideal homogeneous analogues to supported tungsten alkylidyne.

The results of reactions of 50 equivalents 3-heptyne with compounds 2, 3, and 7 are outlined in Table 1.1, alongside the analogous reaction with known compounds W(CCMe₃)(NMe₂)₃ (3) and W(CCMe₃)(O-t-Bu)₃ (6).
In the case of C₃-symmetric compounds 2, 3, 6, and 8, the activity of the catalyst towards alkyne metathesis is roughly inversely related to the π-donating ability of the ligand, with 6 at the most reactive end of the spectrum, and 8 at the least reactive end. The intermediate reactivity of the pyrrolyl and diphenylamido alkylidynes 2 and 3 fits with this model, as the trend in increasing electron donating ability of the ligands follows: alkoxides < pyrrolides < phenyl amides < alkyl amides. This suggests that the rate determining step in alkyne metathesis is

![Diagram of alkyne metathesis](image)

**Table 1.1: Metathesis of 3-heptyne by tungsten alkylidyynes.** % complete calculated as 100 x ([hexyne]+[octyne])/[heptyne] where 100% conversion corresponds to 1:2:1 mixture of hexyne:heptyne:octyne as determined by integration of GC peaks. Pyr = 2,5-dimethylpyrrolide, OAd = 1-adamantoxide, OtBu = tert-butoxide

<table>
<thead>
<tr>
<th>Compound number</th>
<th>L₁ =</th>
<th>L₂ =</th>
<th>L₃ =</th>
<th>% Complete</th>
<th>Time</th>
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<tr>
<td>2</td>
<td>Pyr</td>
<td>Pyr</td>
<td></td>
<td>100</td>
<td>15 min</td>
</tr>
<tr>
<td>3</td>
<td>NPh₂</td>
<td>NPh₂</td>
<td></td>
<td>100</td>
<td>2 weeks</td>
</tr>
<tr>
<td>6</td>
<td>O-t-Bu</td>
<td>O-t-Bu</td>
<td></td>
<td>100</td>
<td>&lt; 3 min</td>
</tr>
<tr>
<td>7</td>
<td>OAd</td>
<td>Pyr</td>
<td></td>
<td>100</td>
<td>&lt; 3 min</td>
</tr>
<tr>
<td>8</td>
<td>NMe₂</td>
<td>NMe₂</td>
<td></td>
<td>0¹⁷</td>
<td>---</td>
</tr>
</tbody>
</table>

approach of the alkyne to the metal center, and the more electrophilic tungsten centers of compounds 6 and 2 are better able to attract the incoming alkyne.¹⁷

It was suggested by the authors of a recent report that a tungsten alkylidyne with both relatively electron donating and electron withdrawing ligands would have increased reactivity compared to similar C₃ symmetric alkylidyynes due to the lower activation energy in formation of metallacyclobutadienes.¹⁸ Compound 7 reacts faster with 3-heptyne than 2, but shows no improvement in reactivity as compared to W(CCMe₃)(O-t-Bu₃) (6). Any increase in activity due to the asymmetry of 7 is overshadowed by the more electrophilic metal center of 6.

**II. B. Surface-supported alkylidyne compounds**

Supported tungsten alkylidyenes were synthesized by adding a pentane solution of the alkylidyne precursors 2-10 (Figure 1.1) to a stirring pentane suspension of silica (~10 eq
supported silanol vs. W) as described in Table 1.2. The silica used in these experiments was obtained commercially from Grace Divisions, and was pretreated to 700°C by the manufacturer to remove the bulk of surface silanols. According to the supplier, the surface contains 0.75 mmol of free silanols per gram of silica, and can be treated like a very bulky siloxy substituent. The silanol groups on silica treated in this manner are reported to be sufficiently far from neighboring groups so that attack of more than one silanol on the catalyst precursor is unlikely, and it can be assumed that only one siloxy group will ever be present on each tungsten center. 19

Figure 1.1: Tungsten alkylidyne precursors to silica supported species
The silica used by Moore, however, was pretreated at a lower temperature, so silanol groups are likely to be sufficiently close to one another to bind to the same metal center. Therefore, it is not clear if the active catalyst species of this surface-supported complex contains one or two siloxy ligands. Any supported species grafted onto the silica used in this project, however, could be assumed to only contain one siloxy substituent that can bind to a metal, if the distribution of silanol groups on the surface is uniform.

The color of the catalyst precursor solution immediately transferred to the silica, leaving the pentane supernatant completely colorless. The colored solid was isolated by filtration. In the case of 8, the grafting procedure was performed in a sealed J-young type NMR tube to prohibit the escape of the liberated dimethylamine gas from the system.

<table>
<thead>
<tr>
<th>Precursor compound #</th>
<th>L₁=</th>
<th>L₂=</th>
<th>L₃=</th>
<th>Species released in grafting</th>
<th>Yield (molar equiv. based on W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>pyr</td>
<td>pyr</td>
<td>pyr</td>
<td>pyrrole</td>
<td>1.1</td>
</tr>
<tr>
<td>3</td>
<td>NPh₂</td>
<td>NPh₂</td>
<td>NPh₂</td>
<td>HNPh₂</td>
<td>1.0</td>
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<tr>
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<td>t-butoxide</td>
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<td>t-butoxide</td>
<td>t-butanol</td>
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<tr>
<td>7</td>
<td>pyr</td>
<td>pyr</td>
<td>OAd</td>
<td>pyrrole</td>
<td>1.6</td>
</tr>
<tr>
<td>8</td>
<td>NMe₂</td>
<td>NMe₂</td>
<td>NMe₂</td>
<td>NMe₂</td>
<td>0.9</td>
</tr>
<tr>
<td>9</td>
<td>OAr</td>
<td>OAr</td>
<td>CH₂CMe₃</td>
<td>HOAr</td>
<td>1.1</td>
</tr>
<tr>
<td>10a</td>
<td>ORF₆</td>
<td>ORF₆</td>
<td>ORF₆</td>
<td>HORF₆, dme</td>
<td>1.8</td>
</tr>
<tr>
<td>10b</td>
<td>ORF₆</td>
<td>ORF₆</td>
<td>ORF₆</td>
<td>HORF₆</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Table 1.2: Grafting of tungsten alkylidyne compounds onto silica. Yield determined by ¹H NMR, relative to number of moles precursor employed, measured against ferrocene or hexamethylbenzene internal standard. Pyr = 2,5-dimethylpyrrole or 2,5-dimethylpyrrolyl, ORF₆ = hexafluoro-t-butoxide, HORF₆ = hexafluoro-t-butoanol, OAd = adamantoxide, Ar = 2,6-i-Pr₂Ph
To quantify the amount of ligand released in grafting, this procedure was repeated for each case on a smaller scale in \( \text{C}_6\text{H}_6 \) or \( \text{CD}_2\text{Cl}_2 \), and the supernatant was analyzed by \(^1\text{H}\) NMR after the addition of an internal standard (ferrocene or hexamethylbenzene). In no case were the alkylidyynes 2-10 observed by NMR in the washings, suggesting that the reaction with surface silanols proceeded as expected (described in Table 1.2), and the change in color was not simply due to physical adsorption onto the silica surface. These results are reported in Table 1.2.

The grafting procedure proceeded as expected in the case of most precursors, releasing approximately one equivalent of ligand per mole precursor employed. In the case of 7, only 2,5-dimethylpyrrole was observed by NMR, and no adamantanol was detected in the washings. The failure to observe free adamantanol does not necessarily suggest that the pyrrolyl ligand undergoes protonation faster than the alkoxide ligand, forming exclusively \( \text{W(CCMMe}_3\text{(pyr)}\text{(OAd)}\text{(OSi}}_\text{surr}) \). Although exclusive protonation of the pyrrolyl ligand is possible, the observation of one equivalent of pyrrole could also be explained by alcoholysis of either the pyrrolyl or alkoxide ligand, followed by further alcoholysis of a remaining pyrrolyl ligand by free adamantanol in solution. The first scenario would lead to the formation of exclusively \( \text{W(CCMMe}_3\text{(pyr)}\text{(OAd)}\text{(OSi}}_\text{surr}) \). However, the latter scenario could produce a mixture of \( \text{W(CCMMe}_3\text{(pyr)}\text{(OAd)}\text{(OSi}}_\text{surr}) \), \( \text{W(CCMMe}_3\text{(pyr)}_2\text{(OSi}}_\text{surr}) \), and \( \text{W(CCMMe}_3\text{(OAd)}_2\text{(OSi}}_\text{surr}) \). Both scenarios would result in the ultimate formation of only 1 equivalent 2,5-dimethylpyrrole per tungsten, and are indistinguishable. It is difficult to make definitive statements about the reactivity of supported catalysts without further characterization of the active species. However, the issues described in the grafting of 7 onto silica do not apply to the \( \text{C}_3\)-symmetric compounds, and the release of approximately the expected amount of ligand upon protonolysis of 2, 3, 6, 8, 9, and 10b suggests that the structures of the corresponding silica-supported species.

Once grafted onto silica, the amount of catalyst present per gram of compound was calculated as:

\[
\frac{\text{mol W}}{\text{g silica} + \text{g alkylidyne}} \quad (1)
\]
Equation (1) was used to determine the mole ratio of catalyst used in the reactivity studies reported below. At this time, no further characterization of supported compounds is planned, so the structure of these supported catalysts will be assumed to be as drawn in Table 1.2.

Two types of silica were employed in this study, type 1 was obtained commercially from Grace Davison (Columbia, MD), and type 2 was obtained commercially from Degussa (now Evonik) and calcined by the Copéret group at the University of Lyon (see Table 1.3 for comparison). Both types of silica were calcined at 700°C, therefore, as described in the literature, consist of exclusively isolated silanol groups. For the purposes of the studies presented here, the silica surface is thought of as an extremely bulky mono-silanol, which is only able to attack once on each metal center. The major difference between the two types of silica is the surface morphology: type 1 is listed by the manufacturer as containing pores of 1.5 mL/g volume, while type 2 is advertised as “non-porous.” The implications of these differences in terms of the relative reactivity of the two types of supported catalysts will be discussed in a later section. No difference in grafting results were observed between the two types of silica.

The ability of supported alkylidyne $2_{\text{Si}} - 10_{\text{Si}}$ (The subscript “Si” denotes the silica-supported compound) to catalyze the metathesis of 3-heptyne was investigated. As expected, a number of the supported tungsten alkylidyne were able to catalyze the reaction described in Table 1.4. However, the relationship between proposed structure and relative activity of compounds $2_{\text{Si}} - 10_{\text{Si}}$ was not as clear as the one described in Table 1.1 using homogeneous alkyne metathesis catalysts 2-10.

Among the species most active in the metathesis of 3-heptyne was $6_{\text{Si}}$, which was able to equilibrate 50 equivalents of 3-heptyne to 100% of the expected metathesis products within three minutes. This result is in line with the high activity of the unsupported alkoxide-based...
alkylidyne 6. However, replacing the t-butoxide ligands of 6 with the more electron-withdrawing hexafluoro-t-butoxide, compound 10a, does not, as expected due to increased electron-deficiency at the metal create a more active alkyne metathesis catalyst. Instead, 10a is almost completely inactive towards metathesis. To eliminate the possibility that some of the bound dme from the precursor 10a still remains bound in the supported species, thereby slowing metathesis, known compound 10b was synthesized and subject to the same grafting procedure to produce 10b. The metallacycle compound 10b can be isolated free of dme, and therefore the possibility of dme bound to the supported species is eliminated. However, the metathesis activity of 10b was found to be as low as 10a, suggesting that bound dme was not the reason for low activity of 10a. Without information about the structure of surface species, it is difficult to speculate on the reason for the low activity of 10a in metathesis of 3-heptyne.

![Chemical structure](attachment:image.png)

<table>
<thead>
<tr>
<th>Compound number</th>
<th>L=</th>
<th>Type 1 silica (Grace)</th>
<th>Type 2 silica (Degussa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% complete</td>
<td>time</td>
<td>% complete</td>
</tr>
<tr>
<td>2s1</td>
<td>Pyr</td>
<td>100</td>
<td>2 h</td>
</tr>
<tr>
<td>3s1</td>
<td>NPh2</td>
<td>100</td>
<td>&lt;3 min</td>
</tr>
<tr>
<td>6s1</td>
<td>O-t-Bu</td>
<td>100</td>
<td>&lt;3 min</td>
</tr>
<tr>
<td>7s1</td>
<td>(OAd),(Pyr)</td>
<td>100</td>
<td>&lt;3 min</td>
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<td>NMe2</td>
<td>100</td>
<td>2 h</td>
</tr>
<tr>
<td>9s1</td>
<td>(OAr),(CH2CMe3)</td>
<td>&lt;2</td>
<td>-</td>
</tr>
<tr>
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<td>ORF6</td>
<td>&lt;2</td>
<td>-</td>
</tr>
<tr>
<td>10bs1</td>
<td>ORF6 (metallacycle)</td>
<td>&lt;2</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 1.4: Reaction of supported tungsten alkylidyne compounds 2s1 – 10as1 with 3-heptyne. % complete calc’d as 100*(hexyne+[octyne])/[heptyne] as det’d by integration of relevant GC peaks, where 100% complete is a 1:2:1 mixture of hexyne:heptyne:octyne. Pyr = 2,5-dimethylpyrrole. ORF6 = OCM(CF3)2, Ar = 2,6-diisopropylphenyl.
Another unexpected result in the studies of 3-heptyne metathesis with supported tungsten alkylidyynes was the low metathesis activity of compound $9_{\text{si}}$. An alkoxide derivative to the precursor $9$ ($W(\text{CCMe}_3)(\text{CH}_2\text{CMe}_3)(\text{OAd})_2$) is known to catalyze this reaction efficiently,$^{22}$ so it would follow logically that the surface-siloxide based $9_{\text{si}}$ would also be an effective catalyst. The low activity of the alkoxide and phenoxide based supported alkylidyynes $9_{\text{si}}, 10_{\text{as}},$ and $10_{\text{bsi}}$ suggest a few possibilities: 1) the structures of supported compounds are not as straightforward as depicted in Table 1.4, 2) the supported catalyst decomposes via unknown routes during or before metathesis, or 3) side reactions such as polymerization compete with productive metathesis. Scenarios 1 and 2 are difficult to detect without further characterization of the active species, but there is evidence for polymerization of alkynes.

Close examination of the GC traces of aliquots of the reaction mixture between $2_{\text{si}}$ and 3-heptyne (Figure 1.2) gives evidence for the competing polymerization of alkynes alongside metathesis.

<table>
<thead>
<tr>
<th>Reaction time: 10 minutes</th>
</tr>
</thead>
</table>

![Diagram](image)

2% $2_{\text{si}}$
RT, pentane

![Graph](image)
After the formation of the expected equilibrium mixture of 1:2:1 hexyne:heptyne:octyne in this reaction mixture, when the mixture was allowed to continue to stir, the GC peaks corresponding to these three alkynes decrease over time (relative to an internal standard of 5-
decene). The smaller alkyne 3-hexyne disappears the fastest, followed by the two larger alkynes. However, the two small peaks in the GC trace corresponding to the expected “first-turnover” products t-butyl-propylacetylene and t-butyl-ethylacetylene (identified by GC-MS) do not disappear from the reaction mixture over time. If the branched alkynes disappeared at the same rate as the linear alkynes, then their consumption could be attributed to simple evaporation. The fact that only linear alkynes are consumed after three days is consistent with alkyne polymerization - the small and unbranched alkynes 3-heptyne, 3-hexyne, and 4-octyne are readily polymerized by $2_{\text{Si}}$, while the branched alkynes are not. The GC chromatograms of aliquots of the reaction mixture of the reaction between 50 equivalents 3-heptyne and $2_{\text{Si}}$ are displayed in Figure 1.2. The formation of polymer on a supported catalyst has the potential to be more detrimental to the metathesis activity than polymer formation from a homogeneous catalyst, as a polymer coating on the surface can physically block any further substrate from reaching the active sites, leaving the catalyst inactive.

Unfortunately, after metathesis of 3-heptyne using $2_{\text{Si}}$-$10_{\text{Si}}$, followed by isolation and washing of the solid catalyst, none of the metathesis activity of the supported catalysts remained after an addition of a second aliquot of alkyne. Another drawback of supported catalysts $2_{\text{Si}}$-$10_{\text{Si}}$ is that they lose alkyne metathesis activity over time, but the decomposition cannot be simply detected or analyzed by routine NMR techniques. For example, a sample of compound $2_{\text{Si}}$ left in a nitrogen atmosphere at -25°C for one month was no longer able to metathesize 3-heptyne. The highly hygroscopic nature of silica could make silica-supported catalysts especially sensitive to trace amounts of water in the atmosphere, even in a glove box.

The reactivity of compounds $2_{\text{Si}}$-$10_{\text{Si}}$ towards metathesis of the terminal alkyne 1-pentyne was explored (Table 1.5). In an effort to remove acetylene, the reaction mixture was exposed to a slight dynamic vacuum (~1 Torr) while the reaction proceeded. None of the compounds described in Table 1.5 was able to catalyze the formation of 4-octyne. In accordance with the polymerization theory of the previous section, a less hindered monosubstituted alkyne will be polymerized even more readily than an internal alkyne, leaving the surface of the catalyst coated with polymer and therefore likely to be inactive.
To compare with tungsten alkylidyne complexes and potentially develop a more active alkyne metathesis catalyst, molybdenum alkylidyne complexes were investigated. Homogeneous molybdenum alkyne metathesis catalysts are generally less active than their tungsten analogues \(^2\); this reduction in activity possibly could be exploited to develop a catalyst that is selective for metathesis over polymerization. A molybdenum analogue of 2 would be especially useful for this comparison. However, the attempted synthesis of 11 (Scheme 1.12) was unsuccessful. While resonances corresponding to 11 were observed by \(^{1}\text{H} \text{NMR}, the compound could not be isolated.

A major difficulty in the study of new molybdenum alkylidyne is the absence of a versatile starting material that can be synthesized in adequate yield to develop and study new compounds. Although Mo(C2Me3)Cl3(dme) is a known compound, the current published synthesis employs Mo(C2Me3)(CH2CMe3)3, which has not been prepared on a large scale, and has a low and irreproducible yield compared to W(C2Me3)(CH2CMe3)3. Recently, the synthesis of Mo(CCEt)(NtBuAr)3 (Ar = 3,5-dimethylphenyl), a more readily accessible molybdenum alkylidyne, has been reported, however this molybdenum alkylidyne is not a suitable precursor in the synthesis of tris-pyrrolyl or other new molybdenum alkylidyne, and therefore was not employed as a starting material in these studies.

<table>
<thead>
<tr>
<th>Compound number</th>
<th>L=</th>
<th>Grace silica</th>
<th>Degussa silica</th>
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<tbody>
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<td>time</td>
<td>% complete</td>
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<td>NMe2</td>
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</tr>
<tr>
<td>10b</td>
<td>ORF6</td>
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<td>-</td>
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</tbody>
</table>

Table 1.5: Reaction of supported tungsten alkylidyne complexes with 50 eq 1-pentyne. % complete det’d by integration of relevant GC peaks. Pyr = 2,5-dimethylpyrrolyl, ORF6 = hexafluoro-t-butoxide
Although a tris-pyrrolyl molybdenum neopentylidyne could not be isolated cleanly, it was found that the known molybdenum alkylidyne Mo(CCMe_3)(O-t-Bu)_3 (12, Figure 1.3) can be grafted onto silica in the manner described in Table 1.4. The expected one equivalent of tert-butanol was observed by GC, using toluene as internal standard. In solution, 12 does not metathesize 3-heptyne to the expected equilibrium mixture of alkynes, while the more electron-deficient metal center of Mo(CCMe_3)[OCMe(CF_3)_2]_3 will catalyze this reaction within minutes. Once supported on the silica surface, however, 12si will metathesize 3-heptyne in less than three minutes, comparable to the supported tungsten analogue.

The unexpectedly high reactivity of the supported species 12si compared to 12 can possibly be explained by the poorer electron donating ability of the supported siloxide ligand compared to an alkoxide donor. However, as was the case for most supported tungsten alkylidynes used in this study, all metathesis activity of 12si was lost after the catalyst was used once.

Surprisingly, when exposed to 50 equivalents of 1-pentyne under dynamic vacuum, 12si was able to catalyze the production of 70% of the expected coupled product 4-octyne (Table 1.6). One explanation for the high activity of 12si in terminal alkyne metathesis is the lower...
stability of molybdenum vs. tungsten metallacylclobutadienes. If the molybdenum metallacycle breaks up before another equivalent of alkyne can add, metathesis can be favored over polymerization of acetylene or the starting alkyne, thus avoiding the polymerization route described in Scheme 1.2.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>3-heptyne conversion</th>
<th>1-pentyne conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% complete</td>
<td>time</td>
</tr>
<tr>
<td>12</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>12_{Si}</td>
<td>100^a</td>
<td>&lt;3 min</td>
</tr>
</tbody>
</table>

Table 1.6: Reaction of 12 and 12(Si) with alkynes percent complete calculated by 100((hexyne+[octyne])/[heptyne]) as determined by integration of relevant GC peaks percent complete calculated by 100([octyne]/([octyne]+[pentynel]), where 100% complete would be complete conversion of 1-pentyne to 4-octyne

CONCLUSIONS

Tungsten alkylidyne compounds containing pyrrolide, amide, and alkoxide ligands have proven to be viable precursors for surface-supported alkyne metathesis catalysts. While the resulting dipyrrolyl silica-supported compound 2_{Si} can successfully metathesize 3-heptyne at room temperature, it is not as active as existing surface-supported or homogeneous catalysts. It appears that a competing polymerization reaction both impedes the catalyst’s ability to completely metathesize alkyne substrates and prevents the catalyst from being reused for metathesis after isolation.

To more fully understand these catalytic systems, it would be useful to prepare homogeneous analogs of each of the heterogeneous catalysts developed. Moore has developed an unsupported analog of his supported molybdenum complex, incorporating one or two POSS (polyhedral oligomeric silsesquioxane) ligands in place of a surface silanol. The POSS ligand, or another bulky siloxide ligand such as silox (tri-tert-butyilsiloxide), could potentially be incorporated into these tungsten alkylidyne compounds to develop a new homogeneous alkyne metathesis catalyst. Smaller alcohols such as tert-butanol and adamantanol react more than once with 2 and 3, making the monoalkoxide product difficult to isolate from the bisalkoxide and trisalkoxide products.

If a surface-supported tungsten alkylidyne are to be successful terminal alkyne metathesis catalysts, a procedure to remove acetylene from the reaction mixture will have to be
developed. Acetylene is polymerized by the supported tungsten species, and polyacetylene could interfere with the activity of the catalyst by physically blocking its access to the solution.

The results presented in this chapter demonstrate that although a number of group VI silica-supported neopentylidynes are active for the metathesis of internal alkynes, the activity of such complexes seems to be limited by the same factors that have always been proposed to limit the metathesis of terminal alkynes and the development of stable and reusable alkyne metathesis catalysts. According to the results presented here, molybdenum may be the metal of choice for developing catalysts that selectively perform alkyne metathesis over alkyne polymerization. In order to proceed with a detailed study of the electronic effects of ligand variation on molybdenum neopentylidynes towards metathesis, a more synthetically viable and versatile molybdenum alkylidyne precursor would have to be developed.

**EXPERIMENTAL**

**General Details.** All manipulations of air sensitive materials or reactions were performed under nitrogen in a drybox or using Schlenk techniques. All glassware was oven-dried and allowed to cool under vacuum before use. Ether, pentane, and toluene were sparged with nitrogen and passed through activated alumina. All solvents were stored over molecular sieves in a nitrogen atmosphere. All deuterated solvents were dried over molecular sieves. Alkyne substrates were dried over calcium hydride, degassed, and distilled. NMR spectra were obtained on Varian spectrometers operating at 300 MHz (\(^{1}\)H) or 125 MHz (\(^{13}\)C). NMR chemical shifts are reported as ppm relative to tetramethylsilane, and were referenced to the residual proton or \(^{13}\)C signal of the solvent (\(^{1}\)H C\(_6\)D\(_6\): 7.16 ppm, \(^{13}\)C C\(_6\)D\(_6\): 128.06). W(=CCMe\(_3\))Cl\(_3\)(dme)\(^{17}\), (3,5-Me\(_2\)C\(_6\)H\(_3\)NCH\(_2\)CH\(_2\))\(_3\)N\(^{25}\), Mo(=CCMe\(_3\))Cl\(_3\)(dme)\(^{23}\), W(=CCMe\(_3\))(O-t-Bu)\(_3\) (\(6\)\(^{17}\), W(=CCMe\(_3\))(NMe\(_2\))\(_3\) (\(8\)\(^{17}\), and W(=CCMe\(_3\))OAr\(_2\)(CH\(_2\)CMMe\(_3\)) (\(9\)\(^{22}\), W(=CCMe\(_3\))(ORF\(_6\))\(_3\)(dme) (\(10a\)\(^{17}\), W(C\(_3\)Et\(_3\))(ORF\(_6\))\(_3\) (\(10b\)\(^{17}\), and Mo(=CCMe\(_3\))(O-t-Bu)\(_3\) (\(12\)\(^{23}\) were prepared according to the literature. Type 1 silica was obtained from Grace Davison, Inc. (product name Sylopol 948), and type 2 silica was obtained from Degussa (product name Aerosil 200).

\[\{(3,5-Me_2C_6H_3NCH_2CH_2)_3N\}W(\text{CCMe}_3).\] (1) Li\(_3\)[(3,5-Me\(_2\)C\(_6\)H\(_3\)NCH\(_2\)CH\(_2\))\(_3\)N] (0.617 g, 1.29 mmol was prepared through addition of 1.1 eq n-butyllithium to H\(_3\)[(3,5-Me\(_2\)C\(_6\)H\(_3\)NCH\(_2\)CH\(_2\))\(_3\)N] in ether at -25 °C. The resulting white solid was isolated by filtration and suspended in 50 mL
toluene, and the mixture was chilled to -25 °C. W(CMe₃)Cl₃(dme) (0.582 g, 1.29 mmol) was added in one portion to the stirred suspension. The reaction was stirred for 12 h as it warmed to room temperature, during which time it became orange/red and a precipitate formed. The reaction was filtered through a plug of Celite to remove the white precipitate, and all volatiles were removed in vacuo. The resulting red oil was dissolved in a minimum amount of diethyl ether/ DME (2:1) and cooled to -25 °C, affording 0.450 g (0.635 mmol, 49%) of yellow blocks.

1H NMR (C₆D₆, 300 MHz) δ 7.13 (s, 6 H, H₆), 6.62 (s, 3 H, H₃), 3.75 (t, 6 H, CH₂), 2.25 (t, 6 H, CH₂), 2.25 (s, 18 H, 3,5-Me₂), 0.74 (s, 9 H, W(CMe₃); 13C{¹H} NMR (C₆D₆, 125 MHz) δ 297.88 (W ≡ C, JC₇W = 255 Hz), 165.49, 136.77, 124.08, 122.65, 58.34, 52.63, 49.06 (WCCMe₃, JC₇W = 38 Hz), 30.77, 21.63. Anal. Calcd for C₃₅H₄₈N₄W: C, 59.32; H, 6.83; N, 7.91. Found: C, 59.18; H, 6.75; N, 7.78.

W(CMe₃)(2,5-Me₂C₄H₂N)₃. (2) W(CMe₃)Cl₃(dme) (0.154 g, 0.342 mmol) was dissolved in 40 mL diethyl ether, and the solution was chilled to -25 °C. Li(2,5-Me₂C₄H₂N) (0.1037 g (1.026 mmol, 3 equiv), prepared by the addition of 1.1 eq n-butyllithium to 2,5-dimethylpyrrole in ether at -25 °C, was added as a solid in one portion to the stirred blue solution. The reaction was stirred for 1 h as it warmed to room temperature, during which time it became orange and a precipitate formed. The reaction mixture was filtered through a plug of Celite to remove the white precipitate, and all volatiles were removed in vacuo. The resulting orange solid was recrystallized from a minimum amount of pentane at -25 °C, yielding 0.084 g (0.1605 mmol, 47%) of orange needles: 1H NMR (C₆D₆, 300 MHz) δ 5.97 (s, 6 H, NC₄H₂), 2.18 (s, 18 H, 2,5-Me₂), 1.25 (s, 9 H, WCCMe₃); 13C{¹H} NMR (CD₂Cl₂, 125 MHz) δ 327.06 (W ≡ C, JC₇W = 254 Hz), 135.70, 111.99, 91.79 (WCCMe₃, JC₇W = 37 Hz), 33.18, 16.72. Anal. Calcd for C₂₃H₃₃N₃W: C, 51.60; H, 6.21; N, 7.85. Found: C, 51.43; H, 6.16; N, 7.74.

W(CMe₃)(NPh₂)₃. (3) W(CMe₃)Cl₃(dme) (0.1193 g, 0.2655 mmol) was dissolved in 40 mL of THF and the solution was chilled to -25°C. LiPh₂·Et₂O (0.1986 g, 0.7965 mmol, 3 eq) was dissolved in 10 mL THF and the solution was chilled to -25°C and added in one portion to the stirred W(CMe₃)Cl₃(dme) solution. The color immediately changed from blue to green/brown, to red/orange, and finally to yellow. The reaction was allowed to stir for 1.5 h and warm to room
temperature. All volatiles were removed in vacuo, and the resulting yellow residue was extracted into ether and the extract was filtered through Celite to remove a white precipitate. Pale yellow crystals were grown from minimal ether at -25 °C in two crops (0.1394 g, 0.1780 mmol, 67%): \( ^1H \) NMR (C\(_6\)D\(_6\), 300 MHz) \( \delta \) 7.05–6.82 (m, 30 H, Ar), 0.443 (s, 9 H, WCCMe\(_3\)). \( ^{13}C \{ ^1H \} \) NMR (C\(_6\)D\(_6\), 125 MHz) \( \delta \) 308.66 (W \( \equiv \) C, \( J_{CW} \) = 288 Hz), 129.60, 128.17, 124.89, 53.45 (WCCMe\(_3\), \( J_{CW} \) = 41 Hz), 30.10. Anal. Calcd for C\(_{41}\)H\(_{39}\)N\(_3\)W: C, 65.00; H, 5.19; N, 5.55. Found C, 64.88; H, 5.26; N, 5.60.

\( W(C\text{CMe}_3)(2,5\text{-Me}_2\text{C}_4\text{H}_2\text{N})_2(\text{OAd}) \): (7) \( W(C\text{CMe}_3)(2,5\text{-Me}_2\text{C}_4\text{H}_2\text{N})_3 \) (0.1066 g, 0.1991 mmol) was dissolved in 30 mL toluene and the solution was chilled to -78 °C. Adamantanol (0.0303 g, 0.1991 mmol, 1 eq) was dissolved in 20 mL of toluene, and the solution was added dropwise to the stirred orange solution. After ten minutes, the reaction was warmed to 0 °C and stirred for an additional 1 h, after which it was warmed to room temperature. All volatiles were removed in vacuo. The resulting orange oil was then exposed to a vacuum of ~10 mTorr at 50 °C for 1 h to remove the remaining 2,5-dimethylpyrrole. Pentane (10 mL) was added, and the mixture was filtered through a plug of Celite to remove a pale solid. (By \( ^1H \) NMR the pale solid appears to be \( W(C\text{CMe}_3)(2,5\text{-Me}_2\text{C}_4\text{H}_2\text{N})(\text{OAd})_2 \).) Orange crystals were grown from a solution prepared with minimal pentane after sitting at -25 °C for 3 days; yield 0.0115 g (0.0194 mmol, 10%): \( ^1H \) NMR (C\(_6\)D\(_6\), 300 MHz) \( \delta \) 6.13 (s, 4 H, NC\(_4\)H\(_2\)), 2.34 (s, 12 H, 2,5-Me\(_2\)), 2.00 (s, 3 H, AdO), 1.82 (s, 6 H, AdO), 1.45 (s, 6 H, AdO), 1.22 (s, 9 H, WCCMe\(_3\)). Sufficient quantities of pure compound could not be isolated for \( ^{13}C \) NMR or further analysis.

Representative procedure for reactions of catalyst precursors with silica. **Procedure 1, for \( ^1H \) NMR quantitation of liberated ligand:** \( W(C\text{CMe}_3)(2,5\text{-Me}_2\text{C}_4\text{H}_2\text{N})_3 \) (0.0563 g) was dissolved in 1.0 mL C\(_6\)D\(_6\), and 100 µL (0.0108 mmol) of the solution was added dropwise to a stirred suspension of silica in 0.5 mL of C\(_6\)D\(_6\). After stirring the mixture for 5 min, the orange solid was isolated by filtration and rinsed with C\(_6\)D\(_6\). Ferrocene (91 µL, 0.0108 mmol, 1 eq per W of a 0.1184 M C\(_6\)D\(_6\) solution) was added to the supernatant as an internal \( ^1H \) NMR standard. A small amount of the supernatant mixture was transferred to a J-young tube, and the \( ^1H \) NMR spectrum was recorded.
Procedure 2, for isolation of silica-supported compound for use in metathesis reactions: W(CMe\textsubscript{3})(2,5-Me\textsubscript{2}C\textsubscript{4}H\textsubscript{2}N)\textsubscript{3} (0.0220 g, 0.0420 mmol) was dissolved in pentane, and added dropwise to a stirred suspension of silica in 30 mL of pentane. The mixture was stirred for 5 min and the pale peach-orange solid was collected by filtration, rinsed with pentane, and dried in vacuo; the filtrate was colorless.

Representative reaction of supported compounds with 3-heptyne: A 20 mg sample of 2\textsubscript{Si} (0.00132 mmol W) was suspended in 5 mL of pentane in a 20 mL vial, 20 µL 5-decene was added as internal standard, and the mixture was stirred vigorously. 3-heptyne (8.65 µL, 6.35 mg, 0.066 mmol, 50 eq) was added via syringe, at which point the stirring solid became bright red. Aliquots were taken at regular intervals by filtering 0.2 mL of the reaction mixture through Celite to remove the solid catalyst, and were analyzed by gas chromatography. Equilibrium was taken to be a 1:2:1 mixture of hexyne : heptyne : octyne.

Representative reaction of homogeneous catalysts with 3-heptyne: Compound 2 (10 mg, 0.0187 mmol) was dissolved in 10 mL pentane in a 20 mL vial. 3-heptyne (120 µL, 100 mg, 0.934 mmol, 50 eq) was added to the stirred orange solution all at once, at which point the solution became bright red. Aliquots were taken at regular intervals by passing 0.2 mL of the reaction mixture through a plug of alumina and rinsing the plug with pentane. The aliquots were analyzed by gas chromatography.

Representative procedure for reaction of supported compounds with 1-pentyne: A 33 mg sample of 2\textsubscript{Si} (0.0022 mmol W) was suspended in 10 mL of mesitylene in a 20 mL vial capped with a rubber septum and stirred vigorously. The mixture was exposed to a dynamic vacuum through the septum via a needle connected to a vacuum pump, and 11 µL 1-pentyne (0.11 mmol, 50 eq) was added in one portion via syringe through the septum. The solid immediately became bright red, and the solution become yellow. The mixture was filtered through Celite to remove the solid and was analyzed by gas chromatography.
REFERENCES


13 Tsai, Y.-C.; Diaconescu, P. L.; Cummins, C. C. Organometallics. 2000, 19, 5260.


Chapter 2

Z-Selective Olefin Metathesis with Molybdenum Imido Alkylidene Complexes that Contain Achiral Bulky Alkoxides

Portions of this chapter have appeared in print:

INTRODUCTION

Since the discovery of high oxidation state Group VI olefin metathesis catalysts, there has been an ongoing push towards developing catalysts that are more active, more stable, and more selective in a wide range of metathesis processes.\(^1\) Recent work in our group has moved away from the traditional bisalkoxide catalysts of the type \(\text{M(CHR)}(\text{NR'}){(\text{OR})''}\), and focused on the development of “MonoAlkoxideMonoPyrrolide,” or “MAP” catalysts of the type \(\text{M(CHR)}(\text{NR'}){(\text{pyr}){(\text{OR})''}}\) (pyr = 2,5-dimethylpyrrolide or pyrrolide).\(^2\) MAP catalysts are prepared easily by the addition of one equivalent of an alcohol, silanol, or phenol to bispyrrolide complexes of the type \(\text{M(CHR)}(\text{NR'}){(\text{pyr})}_2\), and have emerged as a highly active alternative to bisalkoxide Group VI imido alkylidene complexes. One of the initial examples of the unique activity of MAP complexes in olefin metathesis was the first example of metathesis of en-yne substrates to afford exclusively the \textit{endo}-product.\(^3,4\)

Recent reports involving MAP complexes from our group have focused on compounds that contain an enantiomerically pure phenoxide ligand, often a mono-protected binaphtholate derivative such as 3,3'-dibromo-2'-(\((\text{tert}-\text{butyldimethylsilyl})\text{oxy}\))\(5,5',6,6',7,7',8,8'\)-octahydro-[1,1'-binaphthalen]-2-olate (BrBitet-TBS, Scheme 2.1, compound 1a). MAP compounds containing enantiomerically pure binaphtholate ligands such as the one shown in Scheme 2.1
have shown impressive enantioselectivity in a number of olefin metathesis processes, including the ring-closing metathesis of substrates that did not react with existing chiral metathesis catalysts.\textsuperscript{5,6}

In addition to the unprecedented enantioselectivity shown by MAP catalysts, another recent report has found that MAP catalysts such as 1a can catalyze the ring opening/cross metathesis of a bicyclic olefin with styrene to form the expected product in excellent yield and enantioselectivity, but also in very high selectivity for the \textit{cis} olefin.\textsuperscript{7}

The ability to selectively form \textit{cis} olefins over \textit{trans} olefins has been a goal in the development of new olefin metathesis catalysts, and the result described in Scheme 2.2 represents a significant advancement towards this goal. The authors postulated that the \textit{Z}-selectivity of the ring opening/cross metathesis reaction was related to the use of the relatively bulky phenoxide ligand, although at the time of the publication this hypothesis was only speculation. We decided to investigate the activity of MAP compounds in other potentially \textit{Z}-selective olefin metathesis processes and possibly gain insight into the mechanism of selectivity with MAP compounds such as 1a. A new class of MAP catalyst will be described in this chapter, along with their activity in a number of potentially \textit{Z}-selective metathesis processes. The ring opening metathesis polymerization activity of the compounds described in this chapter will be described in upcoming chapters.

\textbf{Scheme 2.2: \textit{Z}-selective ring opening/ cross metathesis with 1c}

95:5 enantiomeric ratio
\textgreater 98:2 Z:E
RESULTS AND DISCUSSION

I. Z-selective metathesis with MAP complexes containing the hexaisopropylterphenoxide ligand

I. A. Synthesis of MAP complexes containing the hexaisopropylterphenoxide ligand

While the result described above concerning successful Z-selective ring opening/cross metathesis of cyclic olefins with MAP catalysts employed a catalyst containing chiral phenoxide ligands (such as 1a, Scheme 2.1), we suspected that the Z-selectivity was unrelated to the enantioselectivity. Therefore, we set out to investigate the use of achiral bulky phenoxides as ligands for promoting Z-selective metathesis processes. As initial observations in our group had indicated that the Z-selectivity in ring opening/cross metathesis arises from the extreme steric bulk of the phenoxide ligand, our initial investigations focused on achiral versions of 1 that were of similar steric bulk. The phenoxide ligand of 1 is essentially a 2,6-disubstituted phenoxide. Therefore, we decided to investigate 2,6-disubstituted achiral phenoxides as ligands in MAP complexes. We first turned our attention toward the synthesis of MAP complexes containing the 2,6-bis-(2,4,6-triisopropyl)terphenoxide (HexaisopropylTerphenoxide, HIPTO) ligand. The corresponding phenol, hexaisopropylterphenol (HIPTOH) has been reported.\(^8\) When one equivalent of HIPTOH is added to Mo(NAd)(CHCMe\(_2\)Ph)(NC\(_4\)H\(_4\))\(_2\), one equivalent of pyrrole is released and 2a can be isolated as a yellow solid in 45\% yield. While 2a can be isolated as a solid, the \(^1\)H NMR spectrum of the crude reaction mixture displays only a single alkylidene resonance, suggesting that 2a is the only alkylidene-containing species formed in the reaction.

![Scheme 2.3: Synthesis of 2a](image-url)
and that precipitation from pentane is not necessary to obtain pure compound. The reaction of other phenols with bispyrrolide alkylidene complexes of the type Mo(NR)(CHCMe₂Ph)(pyr)₂ (pyr = pyrrolide or 2,5-dimethylpyrrolide) often results in the formation of several alkylidene products, often including the corresponding bisalkoxide alkylidene complex. Even upon the addition of excess HIPTOH to 2a, no new alkylidene species is observed by ¹H NMR spectroscopy, suggesting that the phenol is too sterically demanding to displace a second equivalent of pyrrole to form Mo(NAd)(CHCMe₂Ph)(HIPTO)₂. The fact that only one equivalent of HIPTOH reacts with Mo(NAd)(CHCMe₂Ph)(pyr)₂ and that essentially pure 2a forms in this reaction means that 2a can be prepared in situ and used as a metathesis catalyst from the appropriate starting materials without formation of deleterious side products.

![Diagram of Mo(Ad)(CHCMe₂Ph)(pyr)₂ reaction with HIPTOH](image)

**Table 2.1: Synthesis of molybdenum imido alkylidene complexes containing the hexaisopropyl terphenoxide ligand.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>R'</th>
<th>Time/ Temperature</th>
<th>Mo=CH ¹H NMR δ =</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>Ad</td>
<td>H</td>
<td>RT, 1h</td>
<td>11.95</td>
</tr>
<tr>
<td>2b</td>
<td>Ad</td>
<td>Me</td>
<td>60 °C, 5d</td>
<td>12.16</td>
</tr>
<tr>
<td>3b</td>
<td>Ar'</td>
<td>H</td>
<td>RT, 3h</td>
<td>12.49</td>
</tr>
<tr>
<td>3a</td>
<td>Ar</td>
<td>H</td>
<td>60 °C, 2h</td>
<td>12.76</td>
</tr>
<tr>
<td>3a</td>
<td>Ar</td>
<td>Me</td>
<td>100 °C, 3d*</td>
<td>---*</td>
</tr>
</tbody>
</table>

Variations of 2a involving a variety of different imido and pyrrolide ligands were prepared according to Table 2.1 by the addition of one equivalent of HIPTOH to a variety of bispyrrolide precursors of the type Mo(NR)(CHCMe₂Ph)(pyr)₂ (pyr = pyrrolide or 2,5-dimethylpyrrolide) in toluene or benzene, and monitoring the progress of the protonolysis reaction by ¹H NMR spectroscopy.
The synthesis of Mo(NAr')(CHCMe₂Ph)(NMe₂C₆H₄)₂ (Ar' = 2,6-dimethylphenyl) (precursor to 3b) has not previously been reported in the literature, so attempts were made at synthesizing this new bispyrrolide compound as displayed in Scheme 2.4.

When two equivalents of lithium pyrrolide were added to Mo(NAr')(CHCMe₂Ph)(OTf)₂(dme), an isolable yellow solid was obtained whose ¹H NMR contained broad resonances that resembled that expected for Mo(NAr')(CHCMe₂Ph)(pyr)₂ (see Figure 2.1), however the material did not appear to be completely pure. The broadness of the resonances suggests that in solution, Mo(NAr')(CHCMe₂Ph)(pyr)₂ does not contain exactly the structure depicted in Scheme 2.4 and instead undergoes various fluctional processes, possibly forming a dimeric complex in solution as has been seen in Mo(NAr)(CHCMe₂Ph)(pyr)₂. The few sharp signals in the alkylidene region that are observed likely correspond to minor impurities in the sample.

Unfortunately, repeated attempts at crystallization from both coordinating and non-coordinating solvents did not improve the purity of Mo(NAr')(CHCMe₂Ph)(pyr)₂. Fortunately, when one equivalent of HIPTOH was added to Mo(NAr')(CHCMe₂Ph)(pyr)₂, the ¹H NMR of the resulting mixture displayed resonances corresponding to Mo(NAr')(CHCMe₂Ph)(pyr)(HIPTO), indicating the formation of the MAP compound 3b that could be used as an in situ generated catalyst. Mo(NAr)(CHCMe₂Ph)(NC₆H₆)(HIPTO) (3a) and Mo(NAd)(CHCMe₂Ph)(NMe₂C₆H₂)(HIPTO) (2b) were made by the addition of one equivalent of HIPTOH to the corresponding bispyrrolide precursor. In each case, only one alkylidene resonance was observed, and the rest of the ¹H NMR resonances suggested a Mo(NR)(CHCMe₂Ph)(pyr)(OR') structure as opposed to a Mo(NR)(CHCMe₂Ph)(OR')₂ structure. Attempts to scale up the syntheses and isolate 2b and 3a were unsuccessful, presumably due to the high solubility the HIPTO ligand imparts on the compounds, leading to difficulty in crystallization of products.
Scheme 2.4: Attempted synthesis of Mo(NAr)(CHCMe₂Ph)(pyr)₂. Reaction carried out at -25 °C in Et₂O.

Figure 2.1: "H NMR of "Mo(NAr')(CHCMe₂Ph)(pyr)₂" in C₆D₆.
In the reactions described in Table 2.1, the rate of protonolysis was dependent on the steric properties of the pyrrolide and the imido ligands: dimethylpyrrolide is displaced more slowly than pyrrolide, and diisopropylphenyl imido complexes undergo alcoholysis more slowly than dimethylphenyl or adamantyl imido complexes. Steric factors help explain why the protonolysis of the dimethylpyrrolide ligand of Mo(NAr)(CHCMe₂Ph)(MePyr)₂ and Mo(NAr')(CHCMe₂Ph)(MePyr)₂ with HIPTOH was too slow to be synthetically practical. ¹H NMR resonances corresponding to bisalkoxide complexes such as Mo(NAr')(CHR)(OHIPT)₂ (alkylidene resonances expected between 10-11.5 ppm) were not observed, indicating that this very bulky ligand is too sterically demanding to be installed twice.

II. B. Reactions of MAP complexes containing the HIPTO ligand with olefins

The excellent cis-selectivity of MAP complexes such as 1 in ring-opening/cross metathesis reactions led to our interest in the potential applications of compounds 1a-3b towards other potentially Z-selective olefin metathesis processes. When 50 equivalents each cis-3-hexene and cis-4-octene are added to a pentane solution of various MAP compounds, a 1:2:1 mixture of hexenes:heptenes:octenes is formed after the times listed in Table 2.2. Ar₃-hexene and 4-octene were also subjected to the same conditions using Mo(NAr)(CHCMe₂Ph)[OCMe(CF₃)₂]₂ (4a) as catalyst. 4a converts a mixture of 50 equivalents each of 3-hexene and 4-octene to the expected 1:2:1 mixture of hexenes:heptenes:octenes, and the cis content of 3-heptene is only about 20%. Also, the starting material cis-4-octene is isomerized to a 20:80 mixture of trans:cis 4-octene (while the GC peaks corresponding to cis and trans 3-hexene are not distinct enough under these conditions to distinguish between the two, it would be expected that isomerization of the starting cis-3-hexene occurs as well). Under the same conditions, Mo(NAd)(CHCMe₂Ph)(pyr)(HIPTO) (2a) reacts more slowly than 4a, forming the expected equilibrium mixture only after 8 hours at room temperature, however it does so with excellent cis selectivity. According to integration of the GC peaks, approximately 95% of the heptenes and octenes present in solution after 8 hours are cis. When the reaction mixture was allowed to stir for longer, trans 3-heptene and 4-octene eventually formed, leading to a 40% cis olefins mixture after three days (Figure 2.3).
### Table 2.2: Cross-metathesis of 3-hexene and 4-octene with molybdenum imido alkylidene complexes.

<table>
<thead>
<tr>
<th>Compound number</th>
<th>R</th>
<th>R’</th>
<th>OR”</th>
<th>cis content of 3-heptene</th>
<th>Time to conversion to 1:2:1 ratio of products</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>Ad</td>
<td>H</td>
<td>OHIPT</td>
<td>95%</td>
<td>8 h</td>
</tr>
<tr>
<td>3b</td>
<td>Ar’</td>
<td>H</td>
<td>OHIPT</td>
<td>50%</td>
<td>5 h</td>
</tr>
<tr>
<td>3a</td>
<td>Ar</td>
<td>H</td>
<td>OHIPT</td>
<td>30%</td>
<td>24 h</td>
</tr>
<tr>
<td>1a</td>
<td>Ad</td>
<td>Me</td>
<td>OBr₂₂₆₆t-TBS</td>
<td>70%</td>
<td>2 d</td>
</tr>
<tr>
<td>4a</td>
<td>Ar</td>
<td>N/A</td>
<td>OCMe(CF₃)₂</td>
<td>20%</td>
<td>&lt;10 min</td>
</tr>
</tbody>
</table>

Table 2.2: Cross-metathesis of 3-hexene and 4-octene with molybdenum imido alkylidene complexes.

**Figure 2.3:** Cross metathesis of 3-hexene and 4-octene with 1a. Y-axis normalized so that 1.0 = 1:2:1 mixture of hexenes: heptenes: octenes, as measured by GC.
The eventual formation of *trans* olefins from the *cis* starting materials simply suggests that although the mixture has reached a 1:2:1 equilibrium, all olefins in solution are constantly being metathesized and hexenes are reformed in the presence of active catalyst. Assuming *cis* olefins react with 2a more rapidly than *trans* olefins due to steric reasons, it is not surprising that the equilibrium is eventually driven towards the production of *trans* olefins. The slight decrease of the GC integration of the total amount of 3-heptene present in solution over time is simply due to evaporation of the products; the peak corresponding to hexenes decreased noticeably faster than that due to heptenes or octenes. As displayed in Table 2.2, increasing the size of the imido group to 2,6-dimethylphenyl (3b) or 2,6-diisopropylphenyl (3a) led to decreased selectivity for the *cis* olefins in this reaction as compared to the adamantyl imido version (2a).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion</th>
<th>Time</th>
<th><em>cis</em>-content^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>20%</td>
<td>20 min</td>
<td>95%</td>
</tr>
<tr>
<td>4a</td>
<td>&gt;90%</td>
<td>&lt;10 min</td>
<td>25%</td>
</tr>
<tr>
<td>3b</td>
<td>76%</td>
<td>20 min</td>
<td>40%</td>
</tr>
</tbody>
</table>

Table 2.3: Homocoupling of 1-hexene to 5-decene in C₆D₆. *Cis* content and conversion determined by ^13C and ^1H NMR, respectively.

While the selective formation of *cis*-3-heptene through internal olefin cross-metathesis is an exciting result, the selective formation of *cis* internal olefins from terminal olefins would be of even greater synthetic use. The coupling of 1-hexene to form 5-decene was attempted using 4a, 2a and 3b, as described in Table 2.3.

When 50 equivalents 1-hexene were added to 4a in a 20-mL vial and transferred to a sealable NMR tube, full conversion to 5-decene was observed in the time required to record an NMR spectrum (10 minutes). No ethylene was observed in solution, suggesting that all that had formed had the opportunity to escape into the atmosphere before the reaction mixture was transferred to the NMR tube. The internal olefin product was found by ^13C NMR to be approximately 25% cis. The formation of 5-decene is necessarily coupled with the formation of ethylene, as shown in the reaction described in Table 2.3. If ethylene is not completely removed
from the reaction mixture, it can react with the catalyst, either reforming the starting terminal olefin, or destroying the catalyst.

When homocoupling of 1-hexene (Table 2.3) was attempted using 2a as catalyst, only 20% of the expected 5-decene was formed, and a significant amount of free ethylene was observed in the reaction mixture. Surprisingly, the 5-decene that was formed was found by $^{13}$C NMR to be 95% cis. The homocoupling of 1-hexene with 2a to form 95% cis 5-decene represented at the time of the experiment, to our knowledge, the first example of highly Z-selective metathesis homocoupling of a terminal olefin.

We suspected that the low conversion of 1-hexene to 5-decene with 2a likely was a result of the presence of ethylene in the reaction mixture. Efficient removal of ethylene from this system would both drive the reaction towards full conversion to decene, as well as avoid any catalyst decomposition due to reaction with ethylene. When a C$_6$D$_6$ solution of 2a is exposed to 1 atm of ethylene for 10 minutes, followed by removing all volatiles in vacuo, 2 doublets can be observed at 11.97 and 11.65 ppm in the $^1$H NMR spectrum corresponding to the methylidene protons of Mo(NAd)(CH$_2$)(pyr)(HIPTO). Upon standing at one hour, however, the $^1$H NMR methylidene resonances disappear, and a complex product mixture is observed, suggesting decomposition of the alkylidene species. Decomposition of Mo(NAd)(CH$_2$)(pyr)(HIPTO) might account for the lack of complete conversion of 1-hexene to 5-decene described above. The formation of metathesis-inactive ethylene complexes from the reaction of alkylidene compounds with ethylene has been documented recently.$^{10}$

The proposed theory for the formation of all-cis 5-decene from 1-hexene is shown in Figure 2.4. As seen in Figure 2.4, in the two possible metallacyclobutanes, the substituents of the olefin will be directed either towards the axial imido ligand or the axial phenoxide. The bulk of the HIPTO ligand forces the substituents to point towards the relatively small imido ligand, making the all-cis metallacycle more favorable than the cis, trans, trans-metallacycle. The all-cis metallacycle will break up to afford a new cis internal olefin and generate a new syn alkylidene. In the absence of a sterically demanding phenoxide ligand, as in 4a, a trans olefin is generally favored due to the decreased steric hindrance between substituents on a trans olefin relative to a cis olefin. In the homocoupling of 1-hexene, as well as in a variety of other olefin metathesis processes, 4a and other traditional molybdenum imido alkylidene catalysts will generally afford a mixture of ~80:20 trans:cis olefins.

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II. Catalyst variation for Z-selective olefin metathesis processes

While the Z-selectivity of 2a in homocoupling and internal olefin cross metathesis was spectacular, the instability of 2a towards ethylene led us to pursue more stable catalyst systems. In an effort to identify a MAP compound that maintains the Z-selectivity of 2a but is more stable in the presence of ethylene, a number of new MAP complexes were developed using a variety of bulky phenoxide ligands. We also hoped that catalyst development and screening would give insight into the proposed mechanism of Z-selectivity in this system.

II. A. Synthesis of new terphenoxide ligands and associated molybdenum alkylidene complexes

One simple variation on 2a is the replacement of the HIPTO ligand with the less bulky hexamethylterphenoxide (HMTO). When one equivalent of hexamethylterphenol (HMTOH) was added to Mo(NAd)(CHCMe₂Ph)(NC₄H₄)₂ in toluene, yellow crystalline Mo(NAd)(CHCMe₂Ph)(NC₄H₄)(HMTO) (2d, Figure 2.5) can be isolated in good yield. The corresponding dimethylpyrrolide version, 2d, could also be observed by ¹H NMR spectroscopy.
upon the addition of one equivalent of HMTOH to Mo(NAd)(CHCMe2Ph)(NMe2C2H4)2, however no attempts were made to scale-up and isolate 2d. To test the importance of the substituents of the flanking terphenyl rings of the phenoxide ligand, 5 was prepared by the addition of one equivalent of 2,3,5,6-tetraphenylphenol (OTPP) to Mo(NAd)(CHCMe2Ph)(Me2NC4H2)2 in toluene and isolated by precipitation from pentane.

Scheme 2.5: Synthesis of terphenol ligands: steric variations on HIPTOH
Other steric variations on the HIPTOH ligand were prepared by adaptation of terphenol syntheses described in the literature (Scheme 2.5). The terphenols described in Scheme 2.5 were prepared either according to the literature (TMTOH and TIPTOH), or were prepared by analogy to the literature procedure starting from either 3,5-di-tert-butylbromobenzene (in the case of TBTOH) or 2,6-di-iso-propyl-4-tert-butylbromobenzene in the case of TIPTBTOH (details available in Experimental section).

Addition of one equivalent of the appropriate phenol from Scheme 2.5 to Mo(NAd)(CHCMe₂Ph)(NC₄H₄)₂ afforded the four corresponding MAP complexes 6(a-c) and 7. 6a (MoNAd(CHCMe₂Ph)(pyr)(TMTO)) and 7 (MoNAd(CHCMe₂Ph)(pyr)(TBTO)) were isolated as orange crystalline solids in good yield and recrystallized from ether/pentane. 6b-c were prepared on a NMR scale and were >98% pure as observed by ¹H NMR spectroscopy. Bisalkoxide complexes were not observed in the syntheses of compounds 6a-c and 7.

![Figure 2.6: MAP complexes containing various bulky terphenoxide ligands](image)

- R₁ = Me, R₂ = H: 6a
- R₁ = i-Pr, R₂ = H: 6b
- R₁ = i-Pr, R₂ = tBu: 6c
- R = Br: 8a
- R = NO₂: 8b
In addition to the steric variations described above, electronic variations on the terphenoxide ligands were also investigated. A simple electronic variation for a phenol ligand is the introduction of an electron-withdrawing group \textit{para} to the hydroxyl. The addition of a nitro group in the 4-position of phenol itself lowers its pK\textsubscript{a} from 9.99 to 7.18, and the addition of a bromide in the 4-position lowers it to 9.36, suggesting that the introduction of these groups would have an effect on the electron-donating ability of the corresponding ligands (and that any effect would be more drastic for a nitro-containing ligand than a bromide-containing one).\textsuperscript{12} To test this hypothesis, both 4-bromo-2,6-dimesitylphenol (BrHMTOH) and 4-nitro-2,6-dimesitylphenol (NO\textsubscript{2}HMTOH) were prepared. Both were isolated as white crystalline solids by the addition of either one equivalent of bromine or nitric acid, respectively, to HMTOH in acetic acid (details available in Experimental section).

The associated MAP compounds \textbf{8a} and \textbf{8b} can be prepared by the addition of one equivalent of the appropriate phenol to Mo(NAd)(CHCMe\textsubscript{2}Ph)(pyr)\textsubscript{2}. The formation of \textbf{8a} proceeded as expected and only a single alkylidene peak was observed by \textsuperscript{1}H NMR upon addition of the 4-bromohexamethylterphenol to Mo(NAd)(CHCMe\textsubscript{2}Ph)(pyr)\textsubscript{2} in toluene-d\textsubscript{8}. However, when one equivalent of 4-nitrohexamethylterphenol was added to Mo(NAd)(CHCMe\textsubscript{2}Ph)(pyr)\textsubscript{2} at a metal concentration of 78 mM in toluene, the solution immediately became dark brown/black, and more than twenty peaks were observed in the alkylidene region of the \textsuperscript{1}H NMR spectrum, consistent with either formation of multiple protonation products or decomposition of the expected MAP compound to unidentified products. Fortunately, the expected MAP complex \textbf{8b} could be observed in \textgt;95\% purity by \textsuperscript{1}H NMR when the molybdenum concentration was reduced to 11 mM and the spectrum was recorded after only 2 minutes at room temperature. After the initial formation of the expected MAP complex, the formation of multiple unidentified alkylidene resonances could be observed after only minutes at 11 mM, suggesting that \textbf{6b} is not stable in solution even at lower concentration. The initial formation of clean expected MAP compound was promising, and therefore catalysis with \textbf{8b} was attempted using compound freshly prepared at concentrations below 3 mM to avoid decomposition.
II. B. Synthesis of molybdenum alkylidene complexes containing bulky siloxide and alkoxide ligands

While all of the alkoxide variations for MAP catalysts up to this point have focused on bulky phenoxide ligands containing substituents in the 2- and 6-positions, we were also interested in the synthesis and reactivity of MAP complexes bulky alkoxides and siloxides. While it is difficult to envision a siloxide or alkoxide that completely mimics the steric bulk of the HIPTO ligand, nevertheless a number of complexes were prepared containing relatively bulky tertiary alkoxides or siloxides, as depicted in Figure 2.7.

![Figure 2.7: Molybdenum MAP complexes containing bulky siloxides and alkoxides. TMS = trimethylsilyl, Napth = 1-napthyl, Ar = 2,6-diisopropylphenyl](image)

The compounds shown in Figure 2.7 were prepared by the addition of one equivalent of the appropriate alcohol or silanol to the corresponding bispyrrolide molybdenum alkylidene complex, as outlined in Table 2.1. Compounds 9a, 9b, and 10a were isolated as yellow solids by recrystallization from solutions of diethyl ether/pentane, and 11 and 10b were observed in C₆D₆ solution by ¹H NMR spectroscopy. There was no evidence for formation of bisalkoxide complexes in the synthesis of compounds 9-11.

II. C. Reactions of new MAP alkylidene complexes with terminal olefins

With compounds 3-11 in hand, we were interested in comparing the activity and Z-selectivity of the various catalysts against that of 2a. Although initial results were obtained with 1-hexene as the substrate, we chose 1-octene as a new standard test substrate due to ease in differentiation of the cis and trans internal olefin products by ¹H NMR. Screening results for the homocoupling of 1-octene to 7-tetradecene are presented in Table 2.4.
<table>
<thead>
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<th>#</th>
<th>R</th>
<th>R'</th>
<th>OR''</th>
<th>time</th>
<th>% conversion</th>
<th>% Z</th>
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<tr>
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<td></td>
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<td>51</td>
<td>50</td>
</tr>
<tr>
<td>6a</td>
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<td>TMTO</td>
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<td>55</td>
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<td></td>
<td></td>
<td></td>
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<td>10</td>
</tr>
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<td>H</td>
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<tr>
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<tr>
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<tr>
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<td>Me</td>
<td>Ph₃CO</td>
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<td>Ad</td>
<td>H</td>
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<td></td>
<td></td>
<td></td>
<td>10 min</td>
<td>45</td>
<td>50</td>
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</tbody>
</table>

Table 2.4: Screening of MAP catalysts for homocoupling of 1-octene at 2% catalyst loading. Conversion and % Z det’d by ¹H NMR. **Results with compound 5 were obtained with 1-hexene as substrate and % Z measured by ¹³C NMR. *prepared in situ from corresponding bispyrrolide complexes
The homocoupling reactions described in Table 2.4 were performed as follows: the catalyst was dissolved in toluene at a concentration of ~2 mM. 50 equivalents of 1-octene were added to the stirring catalyst solution via syringe. Aliquots were obtained at regular intervals by transferring 5 drops of the reaction mixture to an NMR tube containing bench top CDCl₃, which contains sufficient quantities of water and oxygen to quench the reaction immediately. As seen in Table 2.4, none of the catalysts developed in this chapter were able to catalyze the homocoupling of 1-octene to 5-decene with as high Z-selectivity as 2a, although with the exception of 6c and 9b, the MAP catalysts tested here showed improved conversion to 7-tetradecene as compared to 2a. The times and conversions listed here represent the maximum conversion for each case; it should be noted that a number of reactions achieved maximum conversion after only 10 minutes.

In almost all cases described in Table 2.4, the Z-selectivity at low conversions was higher than the Z-selectivity at maximum conversion. This increase in trans content over time suggests that cis-7-tetradecene is the kinetically favored product in most cases, but as the reaction proceeds, 7-tetradecene isomerizes to form more trans olefin, which is the thermodynamically favored product.

Inspired by the work reported in this chapter, further catalyst improvement for the Z-selective homocoupling of terminal olefins has been carried out by other members of our group and has resulted in a number of publications.¹³ ¹⁴ The most Z-selective MAP catalysts reported in these publications incorporate a large phenoxide ligand (often HIPTO) combined with a smaller imido ligand. The researchers found that tungsten-based MAP compounds generally give higher Z-selectivity than molybdenum-based compounds, likely due to the overall decreased reactivity of tungsten complexes and the very rapid isomerization of olefins with molybdenum complexes.

II. D. Photolysis studies of molybdenum MAP complexes containing bulky phenoxides

When considering MAP compounds for Z-selective metathesis reactions, the assumption is that only syn alkylidenes are present during the reaction, and that rotation of the alkylidene is not a competitive process during the reaction. The alkylidene resonances of the ¹H NMR spectra of compounds 1-11 reported here all exhibit a JCH between 117-123 Hz, indicative of syn-alkylidenes. It was originally thought that the bulk of the HIPTO and HMTO ligands in 2a and 2c would prevent the formation of anti alkylidenes. This hypothesis was investigated by actively pursuing the formation of anti alkylidenes in the MAP compounds through photolysis at 366 nm,
photolysis of syn-2a/c to anti-2a/c

Scheme 2.6: Photolysis of syn-2a/c to anti-2a/c

A technique that has been used extensively in our group. Toluene-D₈ solutions of both 2a and 2c were exposed to 366 nm UV radiation for 3h at -78 °C as described in Scheme 2.6, and the solutions were monitored by low-temperature ¹H NMR spectroscopy. In the case of 2a, after photolysis, the sample was placed in a pre-cooled -60°C NMR probe and ¹H NMR spectra were recorded. The alkylidene region of the resulting spectrum is displayed in Figure 2.8.

The photolyzed sample displayed both the resonance for the syn alkylidene species at 11.8 ppm as well as a resonance at 13.4 ppm, with a JCH of 148.2 Hz, indicative of an anti alkylidene (anti species is 42% of total). Observation of the anti species was surprising, as it was previously assumed that the bulk of the phenoxide would prevent the formation of anti alkylidenes. Decay of the anti species at -60 °C was not observed, so the sample was warmed to -40 °C, at which point decay of the anti alkylidene was observed. The decay was found to observe first-order kinetics, as determined by a plot of the natural log of the initial concentration divided by the concentration over time (Figure 2.9). This experiment was repeated at -30 °C and -20 °C to obtain rate constants at each temperature.

Figure 2.8: Alkylidene region of ¹H NMR spectrum of 2a photolyzed at 366 nm at -78 °C. Recorded at -60 °C in toluene-D₈
From the slopes of the plots displayed in Figure 2.9, the rate constants for the conversion of *anti* to *syn* (k<sub>a/s</sub>) were determined to be 0.21 x 10<sup>-3</sup> s<sup>-1</sup> at -40 °C, 0.78 x 10<sup>-3</sup> s<sup>-1</sup> at -40 °C, and 4.62 x 10<sup>-3</sup> s<sup>-1</sup> at -20 °C. An Eyring plot of these data (Figure 2.10) shows a linear relationship between ln(k/T) and 1/T, and from this plot, ΔH<sup>f</sup> and ΔS<sup>f</sup> can be calculated to be (respectively) 17.6 kcal/mol and 0.4 eu. For comparison, the rate constant for the decay of *anti*-Mo(NAd)(CHCMe<sub>2</sub>Ph)[OCMe(CF<sub>3</sub>)<sub>2</sub>] is reported to be 5.75 x 10<sup>-4</sup> at -31.4 °C.\textsuperscript{15}

A similar study was undertaken with a sample of Mo(NAd)(CHCMe<sub>2</sub>Ph)(pyr)(HMTO) (2c) in toluene-D<sub>8</sub>. The alkylidene region of the <sup>1</sup>H NMR of the sample after photolysis showed a new resonance (13.3 ppm) in the alkylidene region, corresponding to the *anti* alkylidene (J<sub>CH</sub> = 147.4 Hz), along with the starting *syn* alkylidene at 10.5 ppm (*anti* species is 11% of total). After warming to -40 °C, the resonance corresponding to the *anti* species began to decay. A plot of the natural log of the initial concentration divided by the concentration vs. time showed a linear relationship, suggesting the first-order decay of *anti*-2c.

The rate constant for decay of *anti*-2c, as determined by the slope of this plot, was determined to be 2.5 x 10<sup>-3</sup> s<sup>-1</sup> at -40 °C, which is an order of magnitude faster than the decay of *anti*-2a at -40 °C. The known compound *anti*-Mo(NAd)(CHCMe<sub>2</sub>Ph)[OCMe(CF<sub>3</sub>)<sub>2</sub>] decays at -38.5 °C at a rate of 2.26 x 10<sup>-4</sup> s<sup>-1</sup>, which is an order of magnitude slower than *anti*-2c at approximately the same temperature.\textsuperscript{15} Photolysis results are summarized in Table 2.5.
Figure 2.10: Eyring plot for the decay of anti-2a to syn-2a.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature</th>
<th>$k_{a/s}$ (x 10^{-4} s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(NAd)(CHCM\text{e}_2\text{Ph})[OCMe(\text{CF}_3)\text{2}]_2 (4a)</td>
<td>-31.4 °C</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td>-38.5 °C</td>
<td>2.3</td>
</tr>
<tr>
<td>Mo(NAd)(CHCM\text{e}_2\text{Ph})(pyr)(HIPTO) (2a)</td>
<td>-20 °C</td>
<td>46.2</td>
</tr>
<tr>
<td></td>
<td>-30 °C</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td>-40 °C</td>
<td>2.1</td>
</tr>
<tr>
<td>Mo(NAd)(CHCM\text{e}_2\text{Ph})(pyr)(HMTO) (2c)</td>
<td>-40 °C</td>
<td>25.0</td>
</tr>
</tbody>
</table>

Table 2.5: Rate constants for decay of anti-alkylidenes. Rate constants for 4a are from Ref (15) and presented here for comparison.

The data presented in this section show that anti alkylidenes are indeed accessible, even in complexes containing a very bulky phenoxide ligand such as HIPTO and HMTO. The hexamethyterphenoxide-based alkylidene compound anti-2c decays to syn-2c at -40 °C significantly faster than the hexaisopropylterphenoxide-based compound anti-2a to syn-2a at -30 °C. Based on steric alone, it was originally assumed that an anti alkylidene would be less stable in the hexaisopropyl version 2a than in the less crowded 2c; the fact that anti-2c decays faster suggests that steric is in fact not the determining factor in anti/syn interconversion rates, and instead perhaps the subtle electronic differences between 2a and 2c account for the difference in
decay rates between anti-2a and anti-2c. Discussion of the reactivity of anti- and syn-2a towards olefin metathesis substrates is available in Chapter 3.

CONCLUSIONS

A number of molybdenum alkylidene compounds containing bulky alkoxide ligands have been synthesized and characterized, many of which are based on the hexaisopropylterphenoxide ligand. The first very highly Z-selective homocoupling of terminal olefins is reported here, a striking result when compared to other traditional olefin metathesis catalysts, which generally give a ~1:4 mixture of cis and trans olefins. Ligand variation for the Z-selective metathesis processes reported here gave little improvement in Z-selective homocoupling as compared to 2a, stressing the importance of the hexaisopropylterphenoxide ligand in this reaction. The excellent Z-selectivity of 2a reported here has provided the inspiration for a number of other highly Z-selective catalyst systems reported recently in our group.

The activity of MAP compounds 1-11 in other Z- and E-selective olefin metathesis processes, mainly ring opening metathesis polymerization, will be discussed in further detail in later chapters.

EXPERIMENTAL

General Details. All manipulations of air-sensitive compounds or reactions were performed under nitrogen in a drybox or using Schlenk techniques. All glassware was oven-dried and allowed to cool under vacuum or nitrogen before use. Ether, pentane, and toluene were sparged with nitrogen and passed through activated alumina. All solvents were stored over molecular sieves in a nitrogen atmosphere. Deuterated solvents were degassed and passed through activated alumina before use and stored over molecular sieves. Nitrobenzene was dried with calcium hydride, then distilled and stored under nitrogen. NMR spectra were obtained on Varian spectrometers operating at 300 MHz or 500 MHz. NMR chemical shifts are reported as ppm relative to tetramethylsilane, and were referenced to the residual proton or $^{13}$C signal of the solvent ($^1$H CDCl$_3$: 7.26 ppm, $^1$H C$_6$D$_6$: 7.16 ppm, $^1$H toluene-d$_8$: 2.08 ppm, $^1$H acetone-D$_6$: 2.05 ppm, $^{13}$C C$_6$D$_6$: 128.06 ppm, $^{13}$CDCl$_3$: 77.16 ppm). 4a-b$^{16}$, HMTOH$^{17}$, 2,6-iPr$_2$-4-tBu-bromobenzene$^{18}$, TBTI$^8$, Mo(NAd)(CHCMe$_2$Ph)(NC$_4$H$_4$)$_2$$^9$, HIPTOH$^{11}$, Mo(NAd)(CHCMe$_2$Ph)(NMe$_2$C$_4$H$_2$)$_2$$^{19}$, Mo(NAr')(CHCMe$_2$Ph)(OTf)$_2$(dme)$^{15}$,
Mo(NAr)(CHCMe₂Ph)(NC₄H₄)₂, Mo(NAr)(CHCMe₂Ph)(NMe₂C₄H₂)₂, 2,6-Xy1₂Pheno1, Naph₅SiOH, and TMS₃SiOH were synthesized according to published procedures. Lithium pyrrolide was prepared by addition of 1.1 equivalents of n-BuLi to an ether solution of pyrrole and isolation of the resulting white solid by filtration and washing with cold ether. Organic substrates were dried with sodium/benzophenone and distilled. Unless otherwise noted, all other reagents were obtained from commercial sources and used as received.

5'-bromo-2,2'',4,4'',6,6''-hexamethyl-[1,1':3',1''-terphenyl]-2'-ol (4-Br-HMTOH):

2,6- Mes₂Pheno1 (1.7 g, 0.00514 mol) was dissolved in 100 mL acetic acid with vigorous stirring. Bromine (290 μL, 1.1 eq) was added via syringe dropwise – with each addition, the solution immediately became orange, then the color disappeared within seconds. The color persisted after the last few drops due to the slight excess of bromine. The mixture was allowed to stir for 5 minutes, then poured into a 50 mL saturated aqueous solution of sodium thiosulfate to quench excess bromine. The cloudy white mixture was extracted into dichloromethane, and the organic layer was washed with water and brine, dried with magnesium sulfate, filtered, and the volatiles were removed by rotary evaporation to afford a pale yellow solid. The sample was purified by short-column chromatography on silica using hexanes as eluent to first remove an unidentified high-Rf compound, followed by washing the desired product from the column with dichloromethane and isolation as a white solid. The solid was further purified by recrystallization from Et₂O. ¹H NMR (C₆D₆, 500 MHz) δ 7.11 (s, 2H, Ar), 6.77 (s, 2H, Ar), 4.45, (s, 1H, OH), 2.13 (s, 6H, p-Me), 1.99 (s, 12H, o-Me); ¹³C NMR (CDCl₃, 500 MHz) δ 149.48, 149.2, 138.09, 137.07, 132.14, 131.95, 129.21, 128.69, 21.26, 20.37; HRMS (ESI) Calcd for [M+H]: 409.1162 Found 409.1166.
2,2",4,4",6,6"-hexamethyl-5'-nitro-[1,1':3',1"'-terphenyl]-2'-ol (4-NO₂-HMTOH): 2,6-
Mes₂Phenol (1.6 g, 0.00484 mol) was dissolved in 100 mL acetic acid with vigorous stirring. 1 mL nitric acid (68% aqueous solution, ~0.01 mol, ~2eq) was added to the solution and allowed to stir 18 h at room temperature until thin layer chromatography showed complete consumption of the starting material. Aqueous sodium bicarbonate solution was added to neutralize excess nitric acid, then the mixture was extracted with Et₂O. The organic layer was washed with water and brine, dried with magnesium sulfate, filtered, and the volatiles were removed by rotary evaporation to afford a dark brown oil which solidified upon sitting. Pale brown crystalline solid was isolated by recrystallization from Et₂O/hexanes mixture, which was recrystallized a second time from Et₂O to afford white crystalline solid. ¹H NMR (CDCl₃, 300 MHz) δ 8.03 (s, 2H, Ar), 7.01 (s, 2H, Ar), 5.24, (s, 1H, OH), 2.35 (s, 6H, p-Me), 2.06 (s, 12H, o-Me); ¹³C NMR (CDCl₃, 500 MHz): 155.64, 141.59, 138.55, 136.89, 130.82, 128.81, 128.00, 125.80, 21.16, 20.19; HRMS (ESI) Calcd for [M+H]: 376.1907 Found 376.1913.

4,4"-di-tert-butyl-2'-iodo-2,2",6,6"-tetraisopropyl-1,1':3',1"'-terphenyl (tBuIPhI): 5.05 g (0.017 mol) of 2,6-iPr₂-4-tBu-bromobenzene were dissolved in THF and added to a 50 mL THF suspension of magnesium turnings (1.1 eq/ 454 mg, activated by dry spinning for 12 hours under a nitrogen atmosphere). The mixture was heated to reflux for 18 hours, after which the pale green solution was cooled to room temperature. In a separate flask, 2.32 g (0.0085 mol, 0.5 eq) 2,6-
dichloriodobenzene was dissolved in 25 mL THF and cooled to 0 °C. Ethyl magnesium bromide (3.1 mL of 3M solution in ether, 1.1 eq) was added to the chilled dichloriodobenzene solution via syringe. The mixture was allowed to stir for 2 hours then was added via cannula to the diisopropyl-t-butylphenyl grignard solution. The resulting mixture was heated to reflux for two hours then cooled to room temperature. Iodine (5.0 g, 0.020 mol, 2.3 eq) dissolved in dry...
THF was added via syringe until the red color of the iodine solution persisted for 30 minutes. Excess iodine was quenched with an aqueous sodium thiosulfate solution until the mixture became yellow/brown. 100 mL water was added and the aqueous layer was extracted with Et₂O. The combined organic layers were washed with water and brine, followed by drying with magnesium sulfate, filtering, and removing all volatiles by rotary evaporation. White feathery crystals were isolated by recrystallization from ethanol (1.03 g, 19% yield). ¹H NMR (CDCl₃, 500 MHz) δ 7.38 (t, 1H, Ar); 7.20 (s, 4H, Ar); 7.14 (d, 2H, Ar); 2.53 (sept, 4H, CHMe₂); 1.37 (s, 18H, t-Bu); 1.21 (d, 12H, CHMe₂); 1.09 (d, 12H, CHMe₂).

4,4''-di-tert-butyl-2,2'',6,6''-tetraisopropyl-[1,1':3',1''-terphenyl]-2'-ol (tBuiPrPhOH): 485 mg (0.762 mmol) tBuiPrPhI was dissolved in 15 mL Et₂O under nitrogen atmosphere and cooled to 0 °C. n-BuLi (2.5 M in Et₂O, 335 μL, 1.1 eq) was added to the solution via syringe and the mixture was allowed to warm to room temperature and stirred for 20 min. The aryl lithium solution was cooled again to -78 °C and nitrobenzene (469 μL, 4.6 mmol, 6 eq) was added via syringe. The dark red/brown solution was stirred for 10 minutes, then 15 mL methanol were added and the mixture was allowed to warm to room temperature. The mixture was poured into 100 mL water, and the aqueous layer was separated and acidified with HCl until neutral pH. The aqueous layer was extracted with Et₂O, and the combined organic layers were washed with water and brine, followed by drying with magnesium sulfate, filtering, and removing all volatiles by rotary evaporation giving a brown oil. The oil was purified by short column chromatography on silica with 1% ethyl acetate in hexanes to give an orange oil. Methanol was added and a pale orange solid formed which was isolated on a frit and washed with cold methanol. The solid was further purified by recrystallization from dry diethyl ether to afford 252 mg of pale solid (0.478 mmol, 53% yield). ¹H NMR (CDCl₃, 500 MHz) δ 7.25 (s, 4H, Ar); 7.09 (d, 2H, Ar); 7.01 (dd, 1H, Ar); 4.52 (s, 1H, OH); 2.74 (sept, 4H, CHMe₂); 1.37 (s, 18H, t-Bu); 1.14 (d, 12H, CHMe₂); 1.09 (d, 12H, CHMe₂); ¹³C NMR (CDCl₃, 500 MHz) δ 150.98, 147.31, 130.63, 130.15, 126.55, 120.04, 119.97, 35.05, 31.62, 30.89, 24.47, 24.15; HRMS (ESI) Calcd for [M+Na]: 549.4067 Found 549.4084.
3,3',5,5'-tetra-tert-butyl-[1,1':3',1''-terphenyl]-2'-ol (TBTOH): 1.85 g (3.19 mmol) of 3,3',5,5'-tetra-tert-butyl-2'-iodo-1,1':3',1''-terphenyl (TBTI) was dissolved in 15 mL Et₂O in a 100-mL Schlenk flask under nitrogen. The solution was cooled to -78 °C, and 2.2 mL of a 1.6 M hexane solution of n-BuLi (3.5 mmol, 1.1 eq) was added to it via syringe. The mixture was allowed to warm to room temperature and stir for 4 hours. The resulting pale orange solution was cooled again to -78 °C and nitrobenzene (1.6 mL, 15.9 mmol, 5 eq) was added via syringe. The dark red/brown solution was allowed to stir for 5 minutes, after which 30 mL of methanol was added via syringe and the mixture was warmed to room temperature and let stir for 10 h. The mixture was poured into 100 mL water, and the aqueous layer was separated and acidified with HCl until neutral pH. The aqueous layer was extracted with Et₂O, and the combined organic layers were washed with water and brine, followed by drying with magnesium sulfate, filtering, and removing all volatiles by rotary evaporation. Excess nitrobenzene was distilled from the resulting brown oil by vacuum distillation. The desired product was isolated by column chromatography on silica using 10% dichloromethane in hexanes, followed by 30% dichloromethane in hexanes as a white foam (130 mg, 9%). ¹H NMR (C₆D₆, 500 MHz) δ 7.45 (t, 2H, Ar), 7.39 (d, 4H, Ar), 7.30 (d, 2H, Ar), 7.07 (t, 1H, Ar), 5.56 (s, 1H, OH), 1.36 (s, 36H, t-Bu).

Mo(NAd)(CHCMε₂Ph)(pyr)(HIPTO) (2a): Mo(NAd)(CHCMε₂Ph)(NC₄H₄)$_2$ (153 mg, 0.300 mmol) was dissolved in 20 mL Et₂O and chilled to -25 °C. 2,2",4,4",6,6"-hexaisopropyl-[1,1':3',1''-terphenyl]-2'-ol (HIPTOH) (150 mg, 0.300 mmol, 1eq) was added in one portion as a solid. The mixture became orange after 10 minutes, and was allowed to warm to room temperature and stir for 1h. All volatiles were removed in vacuo. The resulting solid was dissolved in 5 mL pentane, which was removed under vacuum. Pentane was added and removed three times to remove residual pyrrole. The resulting yellow solid was obtained in quantitative yield and can be used without further purification. A yellow solid was isolated after allowing a pentane solution to stand at -25 °C over three nights. 145 mg (45%) isolated. ¹H NMR (C₆D₆, 300 MHz) δ 11.95 (s, 1H, Mo=CH, J$_{CH}$ = 119.4 Hz ), 7.33-6.85 (mult, 8H, Ar), 6.33 (t, 2H, NC₂H₄), 6.45 (t, 2H, NC₂H₄), 3.04 (sept, 2H, CHMe₂), 2.96 (sept, 4H, CHMe₂), 1.78, 1.60, 1.58,
1.55, 1.23, 1.38-1.34, 1.20-1.16, 1.11 (57H, Mo=CHCMe2Ph, NAd, (CHMe2)6). 13C NMR (C6D6, 500 MHz) δ 288.11, 159.34, 149.85, 147.87, 147.35, 147.28, 134.73, 133.70, 131.75, 131.32, 127.24, 126.21, 121.48, 121.45, 109.85, 76.30, 52.46, 43.92, 35.81, 34.46, 32.85, 32.06, 31.40, 31.33, 29.81, 25.01, 24.65, 24.52, 24.37, 24.27, 23.70. Anal. Calcd for C60H80MoN2O: C, 76.56; H, 8.57; N, 2.98. Found: C, 76.21; H, 8.61; N, 2.92.

*only alkylidene resonances are listed for in situ generated complexes*

**In situ generation of Mo(NAd)(CHCMe2Ph)(MePyr)(HIPTO) (2b):**

Mo(NAd)(CHCMe2Ph)(NMe2C4H2)2 (6.7 mg, 0.018 mmol) was dissolved in 1 mL C6D6, and to it was added HIPTOH (5.9 mg, 0.0118 mmol). The entire reaction mixture was transferred to a J. Young NMR tube and heated to 60 °C over 5 days. The catalyst was used in situ in further reactions. 1H NMR (C6D6, 300 MHz) δ 12.16 (s, 1H, Mo=CH), 7.4-6.8 (mult, 12H, Ar), 6.13 (s, 2H, NC4H2Me2), 3.05 (sept, 4H, CHMe2), 2.93 (sept, 2H, CHMe2), 1.94 (s, 6H, NC4H2Me2), 1.76, 1.62, 1.52, 1.36-1.14 (NAd, CMe2Ph, CHMe2, mult, 42H).

**Mo(NAd)(CHCMe2Ph)(Pyr)(HMTO) (2c):** Mo(NAd)(CHCMe2Ph)(NC4H4)2 (193 mg, 0.378 mmol) was dissolved in 20 mL toluene and chilled to -25 °C. 2,2",4,4",6,6"-hexamethyl-[1,1':3',1"-terphenyl]-2'-ol (HMTOH) (125 mg, 0.378 mmol, 1eq) was added in one portion as a solid. The mixture became orange after 10 minutes, and was allowed to warm to room temperature and stir for 1h. All volatiles were removed in vacuo affording an orange oil. 3 mL portions of pentane were added and removed several times to remove residual pyrrole. The resulting yellow foamy solid was obtained in quantitative yield and can be used without further purification. Orange feathery crystals were obtained after recrystallization from a 1:3 mixture of Et2O: pentane over several days at -25 °C. 1H NMR (C6D6, 500 MHz) δ 11.04 (s, 1H, Mo=CH, JCH = 121.8 Hz), 7.28-6.75 (m, 12H, Ar), 6.73 (t, 2H, NC2H4), 6.50 (t, 2H, NC2H4), 2.20 (s, 6H, mesityl CH3), 2.04 (s, 6H, mesityl CH3), 2.02 (s, 6H, mesityl CH3), 1.78 (br t, 3H, NAd), 1.66 (s, 3H, CHCMe2Ph), 1.62 (br, 3H, NAd), 1.53 (br, 3H, NAd), 1.48 (s, 3H, CHCMe2Ph), 1.38 (br s, 6H, NAd). 13C NMR (C6D6, 125 MHz) δ 285.10 (Mo=C), 158.21, 149.44, 137.13, 136.86, 136.60, 136.24, 132.23, 131.93, 130.05, 129.43, 128.87, 128.61, 128.43, 128.35, 126.82, 126.19,
Anal Calcd for C_{48}H_{56}MoN_{2}O: C, 74.59; H, 7.30; N, 3.62. Found: C, 74.47, H, 7.36, N, 3.57.

**In situ generation of Mo(NAd)(CHCMe_{2}Ph)(Me_{2}Pyr)(HMTO) (2d):**

Mo(NAd)(CHCMe_{2}Ph)(Me_{2}NC_{4}H_{2})_2 (23.3 mg, 0.0412 mmol) was dissolved in 1 mL toluene-D_8 in a J. Young type NMR tube and heated to 80 °C for 8 hours. The NMR spectrum showed full conversion to the expected compound. ¹H NMR (toluene-D_8, 500 MHz) δ 11.08 (s, 1H, Mo=CH, J_{CH} = 120.9 Hz).

**In situ generation of Mo(NAr)(CHCMe_{2}Ph)(Pyr)(HIPTO) (3a):**

Mo(NAr)(CHCMe_{2}Ph)(Pyr)_2 (9.2 mg, 0.0172 mmol) was dissolved in 1 mL C_6D_6 and 8.6 mg (0.0172 mmol) 2,6-(Trip)_{2}Phenol was added to it. The entire reaction mixture was transferred to a J. Young NMR tube and heated to 60 °C for 2h. The catalyst was used *in situ* for further reactions. ¹H NMR (C_6D_6, 300 MHz) δ 12.76 (s, 1H, Mo=CH).

**In situ generation of Mo(NAr')(CHCMe_{2}Ph)(NC_{4}H_{4})(HIPTO) (3b):**

0.5673 g (0.7712 mmol) Mo(NAr')(CHCMe_{2}Ph)(OTf)_2(dme) was suspended in 50 mL Et_2O and chilled to -25 °C. Li(NC_{4}H_{4}) was added slowly as a solid, and the suspension immediately becomes homogeneous and orange/red. After stirring 10 minutes, the mixture became brown yellow. The solution was allowed to warm to room temperature and stir for 1 h, after which the volatiles were removed in vacuo, leaving a yellow solid. The solid was extracted with toluene and filtered through Celite to remove a pale solid. All volatiles were removed in vacuo, and the remaining oily solid was dissolved in 1:1 Et_2O:pentane (20 mL), and chilled to precipitate an orange solid, which was isolated on a frit and dried under vacuum. 251 mg isolated (0.523 mmol, 68%). ¹H NMR of major resonances of Mo(NAr')(CHCMe_{2}Ph)(NC_{4}H_{4})_2 (~95% pure) (C_6D_6, 300 MHz) δ 13.45 (br s, 1H, Mo=CH), 7.42 (br s, 4H, pyr), 7.10-6.58 (mult, 8H, Ar), 6.5 (br s, 4H, pyr), 1.90 (br s, 6H, NMe_{2}Ph), 1.57 (s, 6H, CHCMe_{2}Ph).

“Mo(NAr')(CHCMe_{2}Ph)(NC_{4}H_{4})_2” (5.8 mg, 0.0121 mmol) was dissolved in 1 mL C_6D_6 and 6.0 mg (0.0121 mmol) 2,6-(Trip)_{2}Phenol was added to it. The entire reaction mixture was transferred to a J. Young NMR tube and let to sit at room temperature for 2h. The catalyst was used *in situ* for further reactions. ¹H NMR (C_6D_6, 300 MHz) δ 12.49 (s, 1H, Mo=CH).
**In situ** generation of Mo(NAr‘)(CHCMe₂Ph)(pyr)(HMTO) (3c): 72.8 mg (0.099 mmol) of Mo(NAr‘)(CHCMe₂Ph)(OTf)₂(dme) was suspended in 5 mL Et₂O and chilled to -25 °C. Lithium pyrrolide (14.5 mg, 0.198 mmol, 2 eq) was added to it in one portion as a solid. The mixture became homogeneous and dark orange. After stirring 20 min, all volatiles were removed by vacuum, leaving pale solids. 5 mL toluene was added, and the resulting brown cloudy mixture was filtered through Celite to remove white solid lithium triflate. All volatiles were removed *in vacuo*, leaving a brown oil. The oil was redissolved in 4 mL toluene, and 2,6-Mes₂Phenol (Mes = 2,4,6-Me₃C₆H₂) (32.7 mg, 0.099 mmol, 1 eq) was added as a solid. NMR spectroscopy showed complete conversion to the expected compound within minutes. **¹H NMR** (C₆D₆, 500 MHz) δ 11.50 (s, 1H, Mo=CH, JCH = 123.7 Hz).

**Mo(NAd)(CHCMe₂Ph)(Me₂Pyr)(OTPP) (5)**

Mo(NAd)(CHCMe₂Ph)(NMMe₂C₄H₂)₂ (0.1757 g, 0.311 mmol) was dissolved in 50 mL toluene and chilled to -25 °C. Ph₄PhOH (0.1238 g, 0.311 mmol) was dissolved in 10 mL toluene and chilled to -25 °C. The alcohol solution was added to the Mo solution in one portion, and the mixture was allowed to stir overnight, during which time the color changed to slightly deeper orange. All volatiles were removed *in vacuo*. The resulting solid was dissolved in 5 mL pentane, which was removed under vacuum. Pentane was added and removed three times to remove residual dimethylpyrrole. Yellow crystals were obtained from pentane after sitting at -25 °C overnight. 165 mg (61%) isolated in two crops. **¹H NMR** (C₆D₆, 300 MHz) δ 10.96 (s, 1H, Mo=CH, JCH = 121.8 Hz ), 7.32-6.92 (mult, 26H, Ar), 6.19 (s, 2H, NC₄H₂Me), 2.26 (s, 6H, NC₂H₂Me₂), 1.75 (s, 3H, NAd), 1.71 (br, 3H, NAd), 1.52 (6H, C=CHMe₂Ph), 1.30 (br, 6H, NAd), 1.24 (s, 3H, NAd). **¹³C NMR** (C₆D₆, 400 MHz) δ 284.31 (Mo=C), 160.7, 149.8, 142.9, 142.7, 138.5, 133.8, 52.1, 44.2, 36.2, 33.7, 30.3, 23.2, 18.0, 14.9. Anal Calcld for C₅₆H₅₆MoN₂O: C, 77.40; H, 6.50; N, 3.22. Found: C, 77.37, H, 6.75, N, 2.95.

**Mo(NAd)(CHCMe₂Ph)(Pyr)(TMTO) (6a):**

Mo(NAd)(CHCMe₂Ph)(NC₄H₄)₂ (53.6 mg, 0.1052 mmol) was dissolved in 2 mL C₆D₆. 2,2”,6,6”-tetramethyl-[1,1’:3’,1”-terphenyl]-2’-ol (TMTOH) (31.8 mg, 0.1052 mmol) was added to the solution as a solid, and the mixture was allowed to sit for 15 minutes at room temperature. All volatiles were removed under vacuum, and the resulting yellow foam was dissolved in
pentane/ether 10:1. Orange crystals were isolated after sitting overnight at -20 °C (26 mg, 33%).

$^1$H NMR (C$_6$D$_6$, 500 MHz) $\delta$ 10.99 (s, 1H, Mo=CH, $J_{CH} = 122.2$ Hz). 7.27-6.87 (mult., 14 H, Ar), 6.73 (t, 2H, pyr), 6.50 (t, 2H, pyr), 2.01 (s, 12H, HMTO methyl), 1.80 (s, 3H, NAd), 1.69 (s, 3H, CHCM$_2$Ph), 1.62 (br d, 3H, NAd), 1.50 (br d, 3H, NAd), 1.44 (s, 3H, CHCM$_2$Ph), 1.41 (s, 6H, NAd); $^{13}$C NMR (C$_6$D$_6$, 500 MHz) $\delta$ 285.44 (Mo=C) 151.61, 149.44, 139.10, 137.36, 137.16, 132.31, 131.90, 129.83, 129.73, 128.59, 128.39, 127.74, 127.86, 126.89, 126.19, 122.60, 121.16, 110.02, 75.99, 51.50, 43.99, 35.84, 32.57, 30.11, 29.90, 20.87, 20.57, 20.16; Anal Calcd for C$_{46}$H$_{52}$MoN$_2$O: C, 74.17; H, 7.04; N, 3.76. Found: C, 74.05, H, 6.94, N, 3.62.

**In situ generation of Mo(NAd)(CHCM$_2$Ph)(Pyr)(TIPTO) (6b):**

Mo(NAd)(CHCM$_2$Ph)(NC$_4$H$_4$)$_2$ (21.6 mg, 0.042 mmol) was dissolved in 1 mL C$_6$D$_6$. 2,2",6,6"-tetraisopropyl-[1,1':3',1"-terphenyl]-2'-ol (TIPTOH) (17.6 mg, 0.042 mmol) was added to the solution as a solid, and the entire mixture was transferred to a J. Young type NMR tube. The NMR spectrum showed full conversion to the expected compound within minutes. $^1$H NMR (C$_6$D$_6$, 500 MHz) $\delta$ 11.71 (s, 1H, Mo=CH, $J_{CH} = 122.3$ Hz).

**In situ generation of Mo(NAd)(CHCM$_2$Ph)(Pyr)(TIPTBTO) (6c):**

Mo(NAd)(CHCM$_2$Ph)(NC$_4$H$_4$)$_2$ (5.6 mg, 0.011 mmol) was dissolved in 2 mL C$_6$D$_6$. 4,4"-di-tert-butyl-2,2",6,6"-tetraisopropyl-[1,1':3',1"-terphenyl]-2'-ol (TIPTBTOH) (5.8 mg, 0.011 mmol) was added to the solution as a solid, and the entire mixture was transferred to a J. Young type NMR tube. The NMR spectrum showed full conversion to the expected compound within minutes. $^1$H NMR (C$_6$D$_6$, 500 MHz) $\delta$ 11.99 (s, 1H, Mo=CH, $J_{CH} = 120.8$ Hz).

**Mo(NAd)(CHCM$_2$Ph)(Pyr)(TBTO) (7):**

Mo(NAd)(CHCM$_2$Ph)(NC$_4$H$_4$)$_2$ (87.6 mg, 0.172 mmol) was dissolved in 5 mL toluene and to it was added a 5 mL solution of TBTOH (81.1 mg, 0.172 mmol) in toluene. The mixture immediately became deeper yellow, and was allowed to stir for 30 min before all volatiles were removed in vacuo. The resulting yellow foam was dissolved in 1:4 Et$_2$O: pentane, and large dark yellow crystals were isolated by decanting after sitting three days at -25 °C. The solid was recrystallized a second time at -25 °C from Et$_2$O/pentane and isolated as a yellow crystalline solid (113 mg, 72%). $^1$H NMR (C$_6$D$_6$, 500 MHz) $\delta$ 11.7 (s, 1H, Mo=CH, $J_{CH} = 118.9$ Hz), 7.70 (s, 4H, Ar), 7.53 (s, 2H, Ar),
7.35 (d, 2H, Ar), 7.11-6.95 (mult, 6H, Ar), 6.57(t, 2H, pyr), 6.37(t, 2H, pyr), 1.75 (s, 3H, NAd), 1.53 (s, 6H, NAd), 1.42 (s, 6H, CHCMe2Ph), 1.32 (br, 42H, tBu4, NAd). 13C NMR (C6D6, 125 MHz) δ 279.14 (Mo=C), 162.35, 151.30, 149.73, 139.84, 134.40, 132.18, 131.36, 126.72, 126.56, 125.33, 124.64, 122.47, 121.78, 76.77, 66.24, 52.06, 36.00, 35.39, 32.71, 32.03, 31.94, 31.21, 30.04. Anal Calced for C58H76MoN2O: C, 76.28; H, 8.39; N, 3.07. Found: C, 75.97; H, 8.74; N, 3.06.

**In situ generation of Mo(NAd)(CHCMe2Ph)(Pyr)(4-BrHMTO) (8a):**
Mo(NAd)(CHCMe2Ph)(NC4H4)2 (22.6 mg, 0.0444 mmol) was dissolved in 1 mL C6D6. 18.2 mg (1eq) Br-HMTO was added to the solution and the entire mixture was transferred to a J. Young type NMR tube. The NMR spectrum showed full conversion to the expected compound within minutes. 1H NMR (C6D6, 300 MHz) δ 10.91 (s, 1H, Mo=CH).

**In situ generation of Mo(NAd)(CHCMe2Ph)(Pyr)(4-NO2HMTO) (8b):**
Mo(NAd)(CHCMe2Ph)(NC4H4)2 (3.1 mg, 0.00608 mmol) was dissolved in 0.55 mL C6D6. 2.3 mg (1 eq) NO2-HMTO was added to the solution and the entire mixture was transferred to a J. Young type NMR tube. The NMR spectrum showed full conversion to the expected compound within 2 minutes. 1H NMR (C6D6, 500 MHz) δ 10.96 (s, 1H, Mo=CH)

**Mo(NAd)(CHCMe2Ph)(Pyr)(Ph3CO) (9a):** Mo(NAd)(CHCMe2Ph)(NC4H4)2 (193.2 mg, 0.3792 mmol) was dissolved in 10 mL toluene and chilled to -25 °C. 98.7 mg of HOCPh3 (0.3792 mmol, 1eq) was added in one portion as a solid. After stirring one hour at room temperature, the volatiles were removed by vacuum. The resulting yellow oil was recrystallized from 1:1 Et2O : pentane in one crop to give a yellow crystalline solid (119 mg, 45%). 1H NMR (C6D6, 300 MHz) δ 11.51 (s, 1H, Mo=CH), 7.4-7.0 (mult, 22H, Ar, pyr), 6.59 (t, 2H, pyr), 1.81 (mult, 9H, NAd), 1.65 (s, 3H, CHCMe2Ph), 1.56 (s, 3H, CHCMe2Ph), 1.36 (br s, 6H, NAd). 13C NMR (C6D6, 125 MHz) δ 280.72 (Mo=C), 149.83, 149.06, 148.47, 129.31, 128.93, 128.79, 128.50, 127.79, 127.38, 127.31, 127.11, 126.52, 110.84, 108.76, 92.50, 76.31, 51.81, 45.09, 36.44, 36.24, 32.88, 32.45, 31.73, 30.41, 30.26. Anal Calced for C43H46MoN2O: C, 73.49; H, 6.60; N, 3.99. Found: C, 73.32; H, 6.50; N, 4.08.
Mo(NAr)(CHCMe₃Ph)(NMe₂C₄H₂)(OCPh₃) (9b):
282 mg (0.4787 mmol) Mo(NAr)(CHCMe₃Ph)(NMe₂C₄H₂)₂ was dissolved in 40 mL Et₂O in a
100 mL round bottom flask and chilled to -25 °C. A 10 mL Et₂O solution of triphenylmethanol
was added dropwise to the stirring orange solution and allowed to stir 2 hours as it warmed to
room temperature. All volatiles were removed in vacuo and the orange oily residue was left
under vacuum at room temperature for one hour. 10 mL pentane was added and the resulting
yellow solid was isolated by filtration. A second crop of orange crystals was isolated from the
mother liquor after 24 h at -25 °C. 360 mg (0.475 mmol, 99%) ¹H NMR (C₆D₆, 500 MHz) δ
10.69 (s, 1H, Mo=CH), 7.24 (mult, 18H, Ar), 6.05 (br s, 2H, NC₄H₂), 3.72 (br s, 2H, CHMe₂),
2.10 (br s, 6H, NAdMe₂), 1.69 (s, 3H, Me), 1.51 (s, 3H, Me), 1.21 (d, 12H, i-Pr).
¹³C NMR (C₆D₆, 500 MHz) δ 285.85 (Mo=C), 154.04, 148.56, 129.21, 126.56, 123.64,
109.60, 92.46, 54.59, 31.90, 31.07.

Mo(NAd)(CHCMe₂Ph)(Pyr)(TMS₃SiO) (10a): Mo(NAd)(CHCMe₂Ph)(NC₄H₄)₂ (200.0 mg,
0.3925 mmol) was dissolved in 10 mL toluene and chilled to -25 °C. A 5 mL toluene solution of
TMS₃SiOH (103.9 mg, 0.3925 mmol) was added to it dropwise. The solution immediately
became orange. After stirring one hour at room temperature, the volatiles were removed by
vacuum. The resulting yellow foam was recrystallized from TMS in two crops to give yellow/orange crystalline solid (169 mg, 61%). ¹H NMR (C₆D₆, 500 MHz) δ 12.29 (s, 1H, Mo=CH, JCH =
117.6 Hz), 7.45 (d, 2H, Ar), 7.21 (dd, 2H, Ar), 7.08 (br, 1H, Ar), 7.08 (t, 2H, pyr), 6.56 (t, 2H,
pyr), 2.02 (s, 6H, NAd), 1.86 (br s, 3H, NAd), 1.84 (s, 3H, CHCMe₂Ph), 1.71 (s, 3H,
CHCMe₂Ph), 1.41 (s, 6H, NAd), 0.23 (s, 27H, OSiTMS₃). Anal Calcd for C₃₃H₅₈MoN₂O₅Si₄: C,
56.05; H, 8.27; N, 3.96. Found: C, 56.22; H, 8.32; N, 3.85.

In situ generation of Mo(NAd)(CHCMe₂Ph)(Me₂Pyr)(TMS₃SiO) (10b):
Mo(NAd)(CHCMe₂Ph)(Me₂NC₄H₂)₂ (8.3 mg, 0.0147 mmol) was dissolved in 0.5 mL toluene-
D₈ and chilled to -25 °C. A 0.5 mL toluene-D₈ solution of TMS₃SiOH was added to it, and the
entire mixture was transferred to a J. Young type NMR tube. The NMR spectrum showed full
conversion to the expected compound within minutes. ¹H NMR (toluene-D₈, 300 MHz) δ 12.17
(s, 1H, Mo=CH).


In situ generation of Mo(NAd)(CHCMe₂Ph)(Pyr)(Naphth₃SiO): (11)
Prepared from Mo(NAd)(CHCMe₂Ph)(NC₄H₄)₂ and (1-Naphthyl)₃SiOH in the same manner as 2a. ¹H NMR (Toluene-d₈, 300 MHz) δ 11.81 (s, 1H, Mo=CH).

Representative procedure for cross metathesis of hexane and octene: 4.4 mg (0.0046 mmol) 2a was dissolved in 5 mL pentane, and to it was added 230 μL of a 1M (each) pentane solution of cis 3-hexene and cis 4-octene. Aliquots were taken at regular intervals by passing 0.2 mL of the reaction mixture through a plug of alumina, and analyzed by gas chromatography.

Representative procedure for metathesis of 1-hexene: 8.3 mg (0.0108 mmol) 4b was dissolved in 1 mL C₆D₆, and to it was added 67 μL of 1-hexene (0.542 mmol, 50 eq.). The mixture was stirred for 1 min in a 20-mL vial, and the entire reaction mixture was transferred to a sealable NMR tube. ¹H NMR spectra were recorded at regular intervals to monitor the disappearance of 1-hexene, after which the ¹³C NMR spectrum was recorded to determine the ratio of cis/trans 5-decene (checked against authentic cis and trans 5-decene purchased from Aldrich).
REFERENCES


Chapter 3

Z-Selective and Syndioselective ROMP of Cyclic Olefins

Portions of this chapter have appeared in print:


INTRODUCTION

Ring opening metathesis polymerization (ROMP) of cyclic olefins has proven to be an extremely strong tool for the synthesis of polymers with finely controlled structures and molecular weights.\textsuperscript{1,2,3,4} The synthesis of polymers of regular structure has long been a goal in our research, as the physical properties of polymers tend to depend on their structure, making structure control important for the development of ROMP polymers for a variety of applications.\textsuperscript{1} Specifically, substituted norbornenes and norbornadienes have been studied extensively as ROMP monomers due to their high ring strain and ease of synthesis.

In ROMP polymers of substituted cyclic monomers, two factors determine the polymer structure: the \textit{cis}/\textit{trans} nature of the backbone double bonds, and the orientation of the repeating units relative to each other (tacticity). Taking these two factors into account, there are four possible isomers of a ROMP polymer derived from a 2,3-disubstituted cyclic norbornadiene: \textit{cis}-isotactic, \textit{cis}-syndiotactic, \textit{trans}-isotactic, and \textit{trans}-syndiotactic. Of the four regular ROMP polymer structures (Figure 3.1), two have been prepared in relatively pure form using Group VI imido alkylidene initiators and 2,3-dicarbomethoxynorbornadiene (DCMNBD) as the monomer, namely \textit{cis}-isotactic and \textit{trans}-syndiotactic. \textit{Cis}-isotactic polyDCMNBD has been prepared through enantiomorphic site control using initiators of the type Mo(NAr)(CHCMe\textsubscript{2}Ph)(O\textsubscript{2}R), (Ar = 2,6-(i-Pr)\textsubscript{2}Ph, O\textsubscript{2}R = bulky, chiral diolate).\textsuperscript{5}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.1.png}
\caption{The four possible regular structures of ROMP polymers of substituted norbornadienes}
\end{figure}
Group VI imido alkylidene complexes containing chiral diolate ligands such as those displayed in Figure 3.2 have been relatively well-studied, and are known to afford not only cis-isotactic ROMP polymers, but also to catalyze a number of other olefin metathesis processes enantioselectivity.⁶,⁷

Trans, syndiotactic polyDCMNBD has been reported using Mo(NAr)(CHCMe₂Ph)(OtBu)₂ as the initiator.⁸ The mechanism of trans-selective ROMP in this system has been studied in detail. It is proposed to occur through the syn addition of the monomer to an anti alkylidene initiator, as described in Scheme 3.1 (in this report, syn will refer to the orientation in which the substituents of the alkylidene or the incoming substrate are oriented towards the imido ligand, and anti will refer to the situation where the substituents point away from the imido ligand). Anti alkylidenes are generally less stable and more reactive than syn alkylidenes.⁹ According to the hypothesis proposed by the authors and described in Scheme 3.1, the syn isomer of Mo(NAr)(CHCMe₂Ph)(O-t-Bu)₂ does not react with DCMNBD relative to the rate at which the syn isomer rotates about the M=C bond to form anti initiator. The monomer then adds to the anti alkylidene in a syn orientation to form a new syn alkylidene propagating species. This new syn alkylidene again must convert to the anti before reacting with another equivalent of monomer. This process of syn monomer addition to an anti alkylidene forms exclusively trans linkages in the polymer.¹⁰
Scheme 3.1: Mechanism of formation of trans, syndiotactic polyDCMNBD using achiral bisalkoxide initiator. Ar = 2,6-i-Pr$_2$Ph, R = CO$_2$Me, R' = t-Bu, P = propagating polymer chain.

The cis/trans ratio of polyDCMNBD obtained with Mo(NAr)(CHCMe$_2$Ph)(O-t-Bu)$_2$ as initiator was also found to be temperature-dependent, which the authors attributed to the different temperature dependences of the alkylidene rotation (first order) and monomer insertion (second order). Syn/anti alkylidene interconversion has been found to be significantly more facile in bis-t-butoxide complexes as compared to bisalkoxide molybdenum alkylidene complexes containing fluorinated alkoxides. Since anti alkylidenes are less accessible in fluorinated complexes, Mo(NAr)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ affords mainly cis polymer in the ROMP of DCMNBD through the syn approach of the monomer to a syn alkylidene initiator. Clearly, the interplay between syn and anti alkylidenes is vital for the synthesis of polymers of solely cis or trans structure.

This chapter will explore the reactivity of a new class of molybdenum imido alkylidene MonoAlkoxide monoPyrrolide (MAP) initiators for ROMP of a variety of cyclic olefins, including substituted norbornadienes, norbornenes, cycloprenenes, and other monocyclic olefins. The unique “chiral at metal” nature of MAP compounds has the potential to yield a polymer with one or both of the previously unseen microstructures. We also hoped that ROMP would provide insight into the unique mechanism of activity of MAP complexes.
RESULTS AND DISCUSSION

I. ROMP of dicarboethoxynorbornadiene

I. A. Reaction of MAP initiators containing chiral phenoxides with DCMNBD

Strained monomers such as norbornenes and norbornadienes are well suited for ROMP, as the ring strain provides a driving force for the polymerization and reduces the likelihood that the reaction will be reversible. Both 2,3-disubstituted norbornenes and norbornadienes can be prepared simply and inexpensively. Therefore, our initial efforts focused on the ROMP of dicarboethoxynorbornadiene (DCMNBD, Scheme 3.2).

Due to the recent success in our group in enantioselective and Z-selective olefin metathesis with molybdenum MAP complexes containing enantiomerically pure chiral phenoxide ligands,\textsuperscript{12,13,14} we first set out to investigate these MAP compounds (shown in Scheme 3.2) as initiators in ROMP reactions. Since the initiator contains an enantiomerically pure chiral phenoxide, we initially expected that the outcome of the reaction would be determined through enantiomorphic site control, which in this case would be expected to afford isotactic polymer. One major difference between MAP compounds and biphenolate or binaphtholate ROMP initiators is that the metal center itself is chiral. Therefore, compounds \textbf{1a-d} are formed as a mixture of diastereomers. The two diastereomers of MAP compounds containing chiral phenoxide ligands can be observed by $^1$H NMR spectroscopy, and in some cases can be separated by recrystallization. Evidence from our group shows that the two four-coordinate...
diastereomers do not interconvert on their own. However, they can interconvert in a metathesis step through a metallacycle intermediate or through other 5-coordinate intermediates that are formed in the presence of two-electron donors. We did not know to what extent the presence of two diastereomers would alter the ROMP reaction, so before investigating the stereoselectivity of MAP catalysts in ROMP we first investigated the reaction of a mixture of two diastereomers of the initiator with ten equivalents of DCMNBD by $^1$H NMR.

When 1a is prepared from the reaction of one equivalent of HOBr$_2$Bitet-TBS (2',3-dibromo-3'-(OTBS)-5,5',6,6',7,7',8,8'-octahydro-[1,4'-binaphthalen]-2-olate, TBS = tert-butyldimethylsilyl) with Mo(NAd)(CHCMe$_2$Ph)(Me$_2$Pyr)$_2$ in C$_6$D$_6$, $^1$H NMR spectroscopy shows two diastereomers of 1a (12.52 and 12.88 ppm) to be present, along with significant amounts of Mo(NAd)(CHCMe$_2$Ph)(Me$_2$Pyr)$_2$ (12.94 ppm) and Mo(NAd)(CHCMe$_2$Ph)(OBr$_2$Bitet-TBS)$_2$ (12.68 ppm). The presence of both bispyrrolide and bisalkoxide complexes in the in situ prepared catalyst mixture is not surprising and has been

![Figure 3.3: Alkylidene region of $^1$H NMR spectrum of 1a, generated in situ from bispyrrolide and one equivalent of alcohol, before and after addition of DCMNBD](image-url)
observed in compounds of this type previously.\textsuperscript{14} The alkylidene regions of the \textsuperscript{1}H NMR spectra of in-situ prepared 1a before and after the addition of 10 equivalents of DCMNBD are shown in Figure 3.3.

The top spectrum of Figure 3.3 shows the alkylidene region of 1a generated in situ from Mo(NAd)(CHCMe\textsubscript{2}Ph)(Me\textsubscript{2}Pyr)\textsubscript{2} (Ad = 1-adamantyl, Me\textsubscript{2}Pyr = 2,5-dimethylpyrrolide) after addition of one equivalent of the corresponding phenol. After ten equivalents of DCMNBD were added to the initiator mixture, the \textsuperscript{1}H NMR spectrum was recorded; the resulting spectrum is shown at the bottom of Figure 3.3. As seen in this bottom spectrum, the resonances corresponding to the two diastereomers of 1a have been almost completely consumed, and the resonances corresponding to the bispyrrolide complex and the bisphenoxide complex remain. Two new broad doublets appear in the spectrum at 13.2 ppm and 12.3 ppm, likely corresponding to the two expected diastereomeric propagating alkylidene species. The integration of the peaks corresponding to the bispyrrolide and bisalkoxide complexes did not decrease relative to the internal standard, suggesting that although four species are present in the catalyst solution, the two MAP species are the only species active in polymerization.

When fifty equivalents DCMNBD were added to a toluene solution of 1a, the monomer was consumed (according to \textsuperscript{1}H NMR spectroscopy) within minutes, and resonances around 5.2 ppm appeared that correspond to the expected ROMP polymer. After quenching the reaction with benzaldehyde and adding the reaction mixture to methanol, a white solid polymer was isolated. The same polymerization procedure was repeated with compounds 1(b-d) as initiators. The results of these polymerizations are presented in Table 3.1.

All polymers obtained using initiators 1(a-d) contained mainly cis double bonds, which is not surprising considering that this type of catalyst has already been shown to exhibit very high Z selectivity in other metathesis processes.\textsuperscript{14} When the imido group was adamantyl, as in initiators 1a, 1c, and 1d, both diastereomers were completely consumed upon addition of the monomer (as observed by \textsuperscript{1}H NMR), and the expected white solid polymer was isolated in near 100\% yield. However, when the imido group was 2,6-diisopropylphenyl (initiator 1b) only trace amounts of the initiator were consumed upon addition of fifty equivalents of DCMNBD and polymer formation was extremely slow (~35\% yield of polymer was obtained after reaction at room temperature for 48 hours). The slow reaction of DCMNBD with 1b suggests that perhaps the combination of the bulky diisopropylphenyl imido group with a bulky phenoxide creates an
Table 3.1: ROMP of DCMNBD with chiral MAP initiators. Polymer structure determined by 13C NMR spectroscopy

<table>
<thead>
<tr>
<th>#</th>
<th>Initiator</th>
<th>% Initiation</th>
<th>Polymer Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R</td>
<td>R'</td>
<td>R''</td>
</tr>
<tr>
<td>1a</td>
<td>Ad</td>
<td>Me</td>
<td>Br</td>
</tr>
<tr>
<td>1b</td>
<td>Ar</td>
<td>Me</td>
<td>Br</td>
</tr>
<tr>
<td>1c</td>
<td>Ad</td>
<td>Me</td>
<td>Me</td>
</tr>
<tr>
<td>1d</td>
<td>Ad</td>
<td>H</td>
<td>CHPh₂</td>
</tr>
</tbody>
</table>

The major olefinic 13C NMR resonances (70% of total olefinic resonances) of polyDCMNBD obtained with 1a (polyDCMNBD₁₅) appeared at 131.5 ppm (identical to that of cis-isotactic polyDCMNBD), which suggests that the new polymer is 70% cis. When the alkoxide ligand was changed to 3,3'-Me₂Bitet-TBS (as in 1c) or 3,3'-(CHPh₂)₂Bitet-TBS (as in 1d), the cis content of the resulting polymer increased to 90% in both cases, and the cis portions of the polymers were 90% and 98% tactic, respectively. The sharp 13C resonance corresponding to the methylene carbon of poly-DCMNBD obtained with 1c and 1d appeared at 38.0 ppm (distinct from that of cis-isotactic-DCMNBD at 38.7 ppm), suggesting that the structure of the cis-portion of this polymer is different than the cis-isotactic DCMNBD reported in the literature. The 13C NMR spectra of polyDCMNBD₁₅ and polyDCMNBD₁₆ will be presented in the upcoming section.
I. B. MAP initiators containing achiral, bulky phenoxides and reactions with DCMNBD

The formation of highly tactic polyDCMNBD$_{1d}$ with a different structure than the known cis-isotactic polyDCMNBD reported in the literature suggests that the mechanism of tacticity control with MAP initiators is possibly more complicated than we originally proposed. If the chirality of the phenoxide ligand is the determining factor in the stereochemical outcome of the ROMP reaction, then the structure of the polymer would be expected to be isotactic as a consequence of enantiomorphic site control. Since the resulting polymer is not isotactic, efforts turned toward synthesis of polymer with a higher degree of tacticity and investigating the mechanism of stereoregular polymerization.

One advantage of ROMP over other asymmetric olefin metathesis processes is that it is not necessary to use an enantiomerically pure initiator to achieve stereocontrol; a racemic, chiral initiator is sufficient. An isotactic or syndiotactic polymer obtained from an (R)-initiator will have precisely the same structure as an isotactic or syndiotactic polymer obtained from an (S)-initiator, and a racemic mixture of the initiator should afford the same product as an isolated enantiomer or diastereomer. This means that a single structure could be formed using a racemic MAP catalyst containing an achiral alkoxide ligand. For example, if the olefin always approaches trans to the pyrrolide ligand (as has been suggested by theoretical calculations on this system) and the configuration at the metal inverts with every addition, these effects could potentially control the stereochemical outcome of the polymerization. It was suspected that

\[ R = H, R' = i-Pr: 2a \]
\[ R = Me, R' = i-Pr: 2b \]
\[ R = H, R' = Me: 2c \]
\[ R = Me, R' = Me: 2d \]

Scheme 3.3: ROMP of DCMNBD with initiators containing bulky terphenoxide ligands
perhaps the structure that gives rise to the 38.0 ppm $^{13}$C resonance in poly-DCMNBD$_{1d}$ is not a result of the presence of an enantiopure chiral ligand. Therefore, efforts moved towards MAP initiators that contained achiral phenoxide ligands.

The synthesis of Mo(NAd)(CHCMe$_2$Ph)(pyr)(HIPTO) (2a) has already been reported in Chapter 2 of this report. The excellent Z selectivity of 2a in acyclic olefin metathesis processes led us to investigate its use in potentially Z-selective and stereoselective ROMP. Polymerization of fifty equivalents of DCMNBD with 2a (Scheme 3.3) proceeded smoothly and near 100% yield of the expected white solid polymer was isolated after standard workup.

The $^1$H NMR and $^{13}$C NMR spectra of poly-DCMNBD$_{2a}$ showed sharp peaks corresponding to a polymer that is >98% cis and >98% tactic. As in the polymers obtained with 1c and 1d as initiators, the $^{13}$C NMR spectrum of poly-DCMNBD$_{2a}$ displayed a sharp C$_7$ (methylene) resonance at 38.0 ppm, instead of at 38.7 ppm as observed in existing cis, isotactic-polyDCMNBD. The alkyl regions of the $^{13}$C NMR spectra of poly-DCMNBD obtained with various initiators are shown in Figure 3.4.

The bottom spectrum in Figure 3.4, corresponding to the alkyl region of the $^{13}$C NMR spectrum of polyDCMNBD$_{2a}$ displays sharp peaks indicative of a highly tactic polymer. The tacticity responsible for the bottom spectrum appears to be the same as that responsible for the ~90% regular polymers shown in the middle two spectra, obtained with initiators 1b and 1d, and is different from that for the isotactic polymer (obtained with 12a, a chiral biphenolate molybdenum imido alkylidene as reported in the literature) shown in the top spectrum of Figure 3.4. The olefinic carbon signal in the $^{13}$C NMR spectrum of the new highly regular polyDCMNBD$_{2a}$ appears at 131.5 ppm, which is the same as that for cis, isotactic-polyDCMNBD, showing that the new polymer structure is also cis.
When 10 equivalents of DCMNBD are added to a CD$_2$Cl$_2$ solution of 2a, the starting alkylidene $^1$H NMR resonance at 11.9 ppm is completely consumed and replaced by a sharp doublet resonance at 11.65 ppm, corresponding to the expected propagating alkylidene. Unfortunately, cis-syndiotactic polyDCMNBD was insufficiently soluble in THF or DMF to determine its molecular weight distribution by gel permeation chromatography (GPC). However, the clean initiation of 2a with DCMNBD as determined by $^1$H NMR suggests that the system is highly living and likely exhibits a low PDI and predictable molecular weight. End group analysis by $^1$H NMR and $^{13}$C NMR confirms this as well: small sharp resonances are visible throughout the spectra (e.g. at 27.2 and 40.0 ppm in the $^{13}$C NMR, Figure 3.4) and integrate to ~2% of the total signals, as expected for the neophylidene and phenyl end groups of a 50-mer.

In an effort to determine the relative rates of anti and syn alkylidenes in the reaction of 2a with DCMNBD, initiation studies were performed with an initiator sample that had been photolyzed at 366 nm to generate a mixture of anti- and syn-2a (see Chapter 2 for further
Figure 3.5: $^1$H NMR spectrum (alkylidene region, toluene-D$_8$) of a mixture of anti- and syn-2a before and after the addition of 1.5 equiv. DCMNBD

The spectrum shows the initial initiator mixture with peaks at 31.07 and 100.00 ppm. After the addition of 1.5 equiv. DCMNBD, two doublets appear at 11.95 and 12.13 ppm. The olefinic region was too complex to determine the configuration about the double bonds of these two major species. While this experiment shows that both anti- and syn-2a are active in ROMP, the fact that no anti-2a is detected under normal ROMP conditions (room temperature, no photolysis) suggests that Z-selective ROMP with 2a proceeds through exclusively syn alkylidenes.

Differential scanning calorimetry (DSC) revealed that polyDCMNBD$_{2a}$ did not exhibit any thermal transitions (glass transition or melting point) below 250 °C, the temperature at which the polymers decompose. For comparison, cis-isotactic polyDCMNBD exhibits a glass transition at 115 °C. The difference in thermal properties between cis polyDCMNBD$_{2a}$ and cis-isotactic...
polyDCMNBD provides further evidence that the two structures are distinct from one another, and the polymer obtained using 2a as initiator has not been prepared before.

I. C. Determination of tacticity of polyDCMNBD

Since polyDCMNBD$_{2a}$ is a highly regular all-cis structure that is not isotactic, polyDCMNBD$_{2a}$ must be cis-syndiotactic. To provide further evidence for the cis, syndiotactic structure of polyDCMNBD$_{2a}$, a derivative containing a menthyl ester was polymerized with 2a. Incorporation of chiral, enantiopure menthyl groups into the carboxylate groups of the monomer (Scheme 3.4, DCMenthNBD) creates a monomer that is structurally similar to DCMNBD, but allows cis-isotactic and cis-syndiotactic polymer to be distinguished from one another.$^{17}$

As shown in Scheme 3.4, both cis, isotactic polyDCMNBD and cis, syndiotactic polyDCMNBD would be expected to exhibit only one olefinic resonance in their respective $^1$H NMR spectra. Addition of the (-)-menthyl group removes all mirror planes of symmetry in the polymer, and isotactic and syndiotactic polyDCMenthNBD can be distinguished from one another through $^1$H NMR spectroscopy. Cis, isotactic polyDCMenthNBD should exhibit two distinct olefinic proton $^1$H NMR resonances, and the protons should be coupled to each other, while cis, syndiotactic polyDCMNBD would exhibit resonance for two uncoupled olefinic protons. The same argument also applies for trans-syndiotactic (two uncoupled protons expected) and trans-isotactic polymers (two coupled protons expected).

The olefinic region of the $^1$H-$^1$H COSY NMR spectrum of polyDCMenthNBD prepared with 2a is shown in Figure 3.6. As expected, two resonances are present in the olefinic region of the $^1$H NMR spectrum of polyDCMenthNBD$_{2a}$ corresponding to H$_a$ and H$_b$ (Scheme 3.4). The lack of any cross peaks in this region of the $^1$H-$^1$H COSY NMR spectrum suggests that the olefinic protons do not couple, and therefore the polymer is cis, syndiotactic. By analogy to cis-syndiotactic polyDCMenthNBD$_{2a}$, polyDCMNBD$_{2a}$ is highly likely to also be syndiotactic. Pure cis-syndiotactic polyDCMNBD represents a structure of polyDCMNBD that previously had been unseen in the literature in pure form.
<table>
<thead>
<tr>
<th>Structure</th>
<th>Reaction</th>
<th>R</th>
<th>2% cat.</th>
<th>Structure</th>
<th>Reaction</th>
<th>R</th>
<th>2% cat.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂R</td>
<td></td>
<td></td>
<td></td>
<td>CO₂R*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DCMNBD</td>
<td></td>
<td></td>
<td></td>
<td>DCMenthNBD</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R = Me</td>
<td></td>
<td></td>
<td></td>
<td>R = (-)-Menthy</td>
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</table>

### cis, isotactic: one olefin signal
- DCMNBD: cis, isotactic: one olefin signal
- DCMenthNBD: cis, isotactic: two *coupled* olefin signals

### cis, syndiotactic: one olefin signal
- DCMNBD: cis, syndiotactic: one olefin signal
- DCMenthNBD: cis, syndiotactic: two *uncoupled* olefin signals

**Scheme 3.4:** Regular cis structures of polyDCMNBD and polyDCMenthNBD

**Figure 3.6:** $^1$H NMR spectrum (olefinic region) of polyDCMenthNBD obtained with 2a as initiator
The excellent Z selectivity in ROMP of DCMNBD with 2a is not unexpected, considering the results described in Chapter 2 with this catalyst in the Z-selective homocoupling of terminal olefins and cross metathesis of simple internal olefins. It can be assumed that the same mechanism for cis selectivity is active in the ROMP of DCMNBD as in the homocoupling of 1-hexene: the bulk of the hexaisopropylterphenoxide ligand forces the substituents of the metallacycle to point towards the relatively small imido group, leading to all-cis polymer (see Chapter 2 for discussion).

The origin of the syndioselectivity of 2a in ROMP is also of interest. A recent theoretical study on Group VI olefin metathesis catalysts has suggested that in complexes of the type M(NR)(CHR')(X)(Y), the lowest energy pathway for olefin attack is trans to whichever ligand (X or Y) is a better donor. In the case of a MAP complex, X and Y are a pyrrolide and an alkoxide. On the basis of electronegativity of O vs. N, the pyrrolide is assumed to be the better donor of the two. It follows that during an olefin metathesis process, the olefin associates to the complex on the Calkylidene-Nimido-Ophenoxide face, trans to the pyrrolide ligand. If the olefin both associates and dissociates on the same face of the catalyst, the configuration of the metal center will then invert exactly once with each productive metathesis step, as shown in Scheme 3.5.

![Scheme 3.5: Inversion of configuration in MAP complexes with a metathesis step. Ligands are indicated by atoms directly attached to Mo only. Figure adapted from reference 16.](image)

The mechanism described in Scheme 3.5 is in line with the observed syndioselectivity in ROMP of DCMNBD with 2a. If the orientation of the incoming monomer is determined by the configuration of the metal center, and the configuration inverts with each insertion, then it follows that the polymer should have an alternating, or syndiotactic structure. This type of stereocontrol (described in Scheme 3.6) is different from the enantiomorphic site control observed with molybdenum alkylidene initiators that contain a chiral diolate. It has the potential to be a strong determinant of the structure of a variety of highly regular polymers.
I. D. Catalyst variation for stereoselective ROMP of DCMNBD

The highly cis- and syndioselective ROMP of DCMNBD with 2a inspired exploration into catalyst variations in the hope of discovering other highly cis- and syndioselective catalysts for ROMP. A variety of MAP alkylidene complexes shown in Figure 3.7, which have been described in Chapter 2 were exposed to 50 or 100 equivalents of DCMNBD in toluene, and the structures of the resulting polymers are presented in Table 3.2. The initiators that are able to produce selectively cis, syndiotactic poly-DCMNBD in the same purity as 2a are those that contain the least steric variation from 2a. Moving to dimethylpyrrolide (2b, Scheme 3.3) from parent pyrrolide had no discernable effect on the regularity of the resulting polyDCMNBD. This result might be expected since the olefin binds to the metal center trans to the pyrrolide, and therefore the pyrrolide ligand is too remote for steric variations to have an effect on the orientation of the incoming monomer. Mo(NAd)(CHCMe2Ph)(pyr)(HMTO) (2c, HMTO = 2,4,6,2’,4’,6’-hexamethylterphenoxide) and Mo(NAd)(CHCMe2Ph)(pyr)(TMTO) (3c, TMTO = 2,6,2’,6’-tetramethylterphenoxide) were both able to afford highly cis, syndiotactic polyDCMNBD, suggesting that methyl groups provide sufficient steric bulk for the formation of cis double bonds in the ROMP of DCMNBD, and that the ortho-substituents of the flanking phenyl rings have more of an influence than the para-substituents. Removing all substituents on the flanking phenyl rings, however (as in initiator 6), reduced the cis- and syndioselectivity of ROMP of DCMNBD.

Increasing the sterics of the imido group of the initiator, as in compounds 3(a-b) leads to lowered Z selectivity in ROMP of DCMNBD. As the size of the imido group is increased from
adamantyl (2a) to dimethylphenyl (3a) to diisopropylphenyl (3b), the cis content of the resulting polymer decreases from >98% to 85% to 70%.

These results so far are consistent with the hypothesis that the small size of the adamantyl imido group and the large size of the phenoxide are necessary to facilitate cis selectivity in this system. However, this hypothesis is in part based on the assumption that polymerization proceeds through only syn-alkylidene intermediates. The magnitude of the $J_{\text{CH}}$ of the alkylidene $^1$H NMR resonances of all the initiators displayed in Table 3.2 suggests that all initiators are syn-alkylidenes. Also, only syn propagating alkylidenes have been observed by $^1$H NMR upon the addition of 1 or 10 equivalents of monomer to various initiators. Electronic differences in these catalyst systems could theoretically have a drastic impact on the availability of any anti species. However, for initiators that contain electronic variations of the HMTO ligand such as Br-HMTO and NO$_2$-HMTO, no decrease in cis- or syndioselectivity was observed in ROMP of DCMNBD with 14a or 14b as compared to polyDCMNBD$_{2a}$. The lack of a difference in cis selectivity when electronic variations of 2a are employed makes the use of steric-based mechanistic arguments more appropriate at this point.

When the aryloxide is replaced by the relatively bulky siloxide, TMS$_3$SiO, as in 8a and 8b, the resulting polymer maintained a high cis double bond content, but the syndioselectivity of the polymerization was reduced. Since the syndioselectivity of 2a is proposed to arise from the incoming olefin approaching the metal at the same C-alkylidene-Ophenoxide-Nimido face with each step, the reduced stereocontrol of 8a and 8b could be explained in light of the electronic differences between an aryloxide ligand and a siloxide ligand. As mentioned previously and described in a recent theoretical study on transition metal imido alkylidene compounds of the type M(NAr)(CHR)(X)(Y), the lowest energy transition state for approach of the olefin is trans to whichever X or Y ligand is the better donor. When X is a pyrrolide and Y is an aryloxide, the difference in donating ability of the two ligands is large (as suggested by the difference in pKa of the conjugate phenol (~9) or pyrrole (~23)), and the approach trans to the pyrrolide is favorable. However, when X is a pyrrolide and Y is a siloxide, the difference in donating ability between the two ligands is no longer quite as great (based on the relative electronegativities of silicon and carbon), and it is not surprising that the olefin might not exclusively bind trans to the pyrrolide. This breakdown in face selectivity would lead to the observed reduced stereoselectivity in polymerization with 8a and 8b.
Figure 3.7: Molybdenum alkylidene complexes for use as ROMP initiators. Ar = 2,6-i-Pr$_2$Ph, Ar' = 2,6-Me$_2$Ph, TRIP = 2,4,6-i-Pr$_3$Ph, Mes = 2,4,6-Me$_3$Ph
Table 3.2: ROMP of DCMNBD with molybdenum imido alkylidene MAP compounds. Cis content and tacticity determined by $^{13}$C NMR spectroscopy. Tacticity only listed for high-cis or high-trans polymers, and, with the exception of entry 5b, refers to a bias towards syndiotactic. *Prepared in situ as described in Chapter 2 of this report. **Compound 15 is tungsten-based.
Adamantyl imido molybdenum alkylidenes 7 and 10, which contain relatively bulky siloxides or alkoxides, also afford polyDCMNBD with reduced cis content and syndio-purity. Using Mo(NAr)(CHCMe₂Ph)(MePyr)[OCMe(CF₃)₂] (5b) as the initiator afforded polyDCMNBD that was composed of mostly cis double bonds, but the polymer was biased towards isotacticity rather than syndiotacticity, suggesting again that a small imido and a bulky phenoxide are both necessary to produce syndiotactic polymer. The corresponding bis-alkoxide complex Mo(NAr)(CHCMe₂Ph)[OCMe(CF₃)₂]₂ (4b) gives a similarly highly cis, isotactic polymer in this reaction.¹⁰

Compounds 9 and 11 both contain phenoxides that contain similar steric bulk to HIPTO, however, the bulk is distributed differently about the terphenoxide. The six isopropyl substituents of HIPTO are replaced by four tert-butyl groups in the TBTO ligand of 9, a change that completely reversed the selectivity of the initiator in ROMP of DCMNBD and afforded highly trans polymer. Moving to the 3,5-disubstituted version of HIPTO in 11, in which the flanking phenyl rings are oriented away from the metal center, also destroyed the Z-selectivity of the initiator in ROMP of DCMNBD. The lack of cis and syndioselectivity in ROMP of DCMNBD with 9 and 11 shows that the presence of substituents in the ortho position of the terphenyl rings is important in forcing the substituents of the substrate into a cis configuration. A tungsten analog of 2a, W(3,5-Me₂PhN)(CHCMe₂Ph)(pyr)(HIPTO) (15) has been reported previously.¹⁸ When 15 is employed in the ROMP of DCMNBD, the resulting polymer maintained the cis and syndioselectivity that had been observed with 2a.

I. E. ROMP of DCMNBD in the presence of Lewis bases

In a recent report from our group, it was found that while the R or S configuration of MAP complexes was stable in 4-coordinate complexes, the two enantiomers (or diastereomers in the case of a chiral OR* ligand) could interconvert upon addition of a two electron donor such as trimethylphosphine, as shown in Scheme 3.7.¹⁵
The current hypothesis concerning the stereoregularity in ROMP of DCMNBD with 2a assumes that the configuration of the metal at each monomer insertion step is crucial to the stereocontrol of the polymer, and that the inversion of configuration with each forward metathesis step leads to the syndiospecificity of the system. We thought that if we introduced a neutral 2-electron donor ligand such as PMe₃ to the system, the configuration of the metal could potentially be inverted before the insertion of a second equivalent of monomer, leading to reduced tacticity of the resulting polymer. The degree of enantiomer interconversion that occurs during polymerization would depend on the relative rates of interconversion and polymerization, providing the potential to finely tune the exact percent tacticity of the polymer by adjusting factors such as concentration of monomer and the number of equivalents of two-electron donor. The ability to “dial in” the percent tacticity of the polymer could lead to the ability to prepare polymers with a wide range of properties from a single catalyst/monomer combination.
When five equivalents of PMe₃ were added to 2a in benzene, complete consumption of the starting alkylidene resonance was observed in the ¹H NMR spectrum. A new alkylidene doublet resonance is observed at 12.3 ppm (Jₚₙ = 4.5 Hz), which likely corresponds to the expected 5-coordinate phosphine adduct. Two minor doublet resonances (~5% each) were also present at 12.2 and 13.2 ppm. The relevant region of the proton NMR spectrum is displayed in Figure 3.8. The minor resonances (13% of total) seen in Figure 3.8 likely are due to geometric isomers of the five-coordinate phosphine adduct complex. Due to the lack of a crystal structure or more complex NMR studies of the major species, the structure of each of these species is unknown. By analogy to similar crystallographically characterized MAP systems, it would be expected that the major species is a trigonal bipyramidal 5-coordinate complex with the imido group and alkoxide in the axial positions.¹⁵

The fact that no free 2a (alkylidene proton expected 11.9 ppm) is observed in solution at room temperature suggests that PMe₃ binds more strongly to the metal center of 2a at room

![Figure 3.8: ¹H NMR spectrum in C₆D₆ of 2a with 5 eq. PMe₃ (alkylidene region). Integrations are referenced to anthracene internal standard such that 1.0 = initial concentration of starting alkylidene.](image-url)
As shown in Table 3.3, in the systems with less than one equivalent of PMe₃, the polymerization proceeded in the same manner as in the base-free system. This is expected, considering that the four-coordinate neophyldiene would be much more active than the five-coordinate phosphine complex that requires the loss of base before reaction with olefins. When more than one equivalent of trimethylphosphine was used, the base bound strongly enough to completely deactivate the complex towards reaction with monomer.

Since the strategy described here requires the loss of coordinated base before the complex can bind and react with olefins, and since it appears that trimethylphosphine coordinates too strongly for dissociation to occur, efforts turned to a Lewis base that would be expected to bind less strongly, namely pyridine.
The results of ROMP reactions between DCMNBD and pyridine adducts of Mo(NAd)(CHCMe₂Ph)(pyr)(HIPTO) (2a) are displayed in Table 3.4. In contrast to the results described in Table 3.3 with trimethylphosphine, when the base used was pyridine, it appears that the five-coordinate pyridine adduct was in equilibrium with the active 4-coordinate complex, allowing polymerization to occur in the systems as described in Table 3.4.

<table>
<thead>
<tr>
<th>n</th>
<th>Time for consumption of 100 eq. DCMNBD</th>
<th>Structure of resulting polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.5 h</td>
<td>cis, syndiotactic</td>
</tr>
<tr>
<td>5</td>
<td>5h</td>
<td>cis, syndiotactic</td>
</tr>
<tr>
<td>20</td>
<td>12h</td>
<td>cis, syndiotactic</td>
</tr>
<tr>
<td>50</td>
<td>&gt;12h</td>
<td>cis, syndiotactic</td>
</tr>
<tr>
<td>neat</td>
<td>No reaction</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 3.4: ROMP of DCMNBD with pyridine adducts of 2a

In the presence of between one and fifty equivalents of pyridine, the resulting polymer was still >98% cis and syndiotactic, as observed by ¹H NMR spectroscopy. This suggests that although association and dissociation of the base is occurring on the polymerization time scale, interconversion of enantiomers is too slow in the pyridine systems to occur before dissociation of the base followed by ROMP. Not surprisingly, the use of neat pyridine as solvent completely shut down the reactivity of 2a towards ROMP of DCMNBD.

II. Stereoselective ROMP of other substituted norbornadiene monomers

II. A. ROMP of NBDF6 and formation of insoluble polymers

We were interested in exploring ROMP of other substituted norbornadiene monomers by 2a. The stereoselective ROMP of 2,3-bis(trifluoromethyl)norbornadiene (NBDF6) has been reported by our group as well as by others. A highly trans and tactic polymer is formed when 4a
is used as an initiator in the ROMP of NBDF6, and a highly cis, tactic polymer is formed when the initiator contains a chiral diolate such as in 13a-c.⁵

Although the tacticities of the two known regular NBDF6 polymers has not yet been proven directly, by analogy to the stereoselective ROMP of DCMenthNBD with 4a and 13a-c, it was originally proposed that cis-polyNBDF6₁₃ is isotactic and trans-polyNBDF6₄ₐ is syndiotactic.¹⁷ However, a 1995 report by Hubbard and coworkers found that >98% tactic cis-polyNBDF6₁₃ exhibited an unusually low dielectric constant, which they ascribed to the presence
of a structure in which the individual dipoles are oriented in an alternating manner, i.e. a syndiotactic structure.19

Hubbard and coworkers concede that the lack of a measured dipole moment in cis-polyNBDF6 could also be a consequence of an isotactic structure in which the polymer chain coils or otherwise orients itself in a way so as to cancel the individual dipole moments of the NBDF6 groups, and that without three-dimensional structural information, the value of some measured physical constant is not a perfect indicator of polymer structure. We were interested in pursuing the synthesis of new structures of polyNBDF6 and possibly shedding light on the conflicting structure assignments for the two existing regular polyNBDF6 structures, and therefore moved towards investigation of ROMP of NBDF6 with MAP initiators.

Addition of 100 equivalents of NBDF6 to 2a in toluene led to formation of a white solid within minutes. In contrast to cis-isotactic polyNBDF6,5 polyNBDF62a was found to be essentially insoluble in common organic solvents, including halogenated solvents such as 1,2-dichlorobenzene and α,α,α-trifluorotoluene at their respective boiling points. An insoluble white solid also was obtained when the polymerization of NBDF6 was carried out with 1d as the initiator. The insolubility of polyNBDF62a prevented solution NMR techniques from being employed in order to determine the degree of stereoregularity. Comparison of the IR spectrum of polyNBDF62a with the IR spectrum of what are proposed to be trans-syndiotactic polyNBDF64a and cis-isotactic polyNBDF613a, shown in Figure 3.10, suggests that polyNBDF62a has predominantly a cis structure. A strong absorption between 950 and 1000 cm⁻¹ corresponds to a C-H out of plane bending mode20 in trans, but not cis olefins, and is a good indicator of cis or trans structures of ROMP polymers.3

The insolubility of polyNBDF62a could at first glance be attributed to the presence of a polymer of very high molecular weight. However, a ¹H NMR spectrum of 2a in toluene-d8 after addition of 5 equivalents NBDF6 revealed that the alkylidene resonance at 11.9 ppm (for initiator 2a) disappeared and a doublet resonance appeared at 11.6 ppm
corresponding to the expected new alkylidene formed after insertion of NBDF6 to the initiator. Complete consumption of 2a by 5 equivalents NBDF6 suggests that the insolubility of polyNBDF62a is not simply due to incomplete initiation and the formation of very high molecular weight polymer, but is characteristic of the microstructure of polyNBDF62a itself. When 10 equivalents of NBDF6 are added to 2a in toluene, ~40% of the polymer formed is insoluble, suggesting that polyNBDF62a becomes insoluble when ~10 equivalents of monomer have been incorporated. A microstructure of polyNBDF6 with limited solubility has also been mentioned in the literature: Feast and coworkers found that when a mixture of molybdenum pentachloride/ tetramethyl tin was exposed to NBDF6 in chlorobenzene at -20 °C, an insoluble white polymer was isolated, which they ascribed to an insoluble polymer with a new structure.21

In an attempt to further characterize poly-NBDF6, 13C NMR spectra of the solid polymer were obtained in the solid state (CPMAS, 900MHz). The solid state 13C NMR spectrum of polyNBDF62a is displayed in Figure 3.11.
The peaks around 60, 70, 200, and 210 ppm were determined to be spinning side-bands (their chemical shift was dependent on the rate of spinning), and will be ignored in the discussion of these spectra. The $^{13}$C NMR spectrum of polyNBDF6$_{2a}$ shows the five expected peaks corresponding to polyNBDF6, each of a line width between 2-7 ppm. A minor resonance slightly downfield of the 44 ppm peak is likely to correspond to small amounts of trans olefin impurity. The same minor splitting is observed in the resonance around 35 ppm.

For comparison, the $^{13}$C CPMAS NMR spectra of the two known regular polymers (prepared with initiators 4a and 13b; trans and cis, respectively) were also obtained in the solid state and are displayed in Figure 3.12. The corresponding solution spectra are not shown, but the spectra of both trans polyNBDF6$_{4a}$ and cis polyNBDF6$_{13b}$ acetone-D$_6$ solution display the expected 5 sharp $^{13}$C NMR resonances corresponding to highly tactic polymers.
Figure 3.12: $^{13}$C MAS NMR spectra of tactic and trans polyNBDF$_{64}$, cis polyNBDF$_{13}$ obtained at 900 MHz and 16 kHz spin rate. Stars indicate spinning side bands.
One potential point of concern in the discussion of the spectra displayed in Figure 3.12 is that the peak around 50 ppm in trans, tactic polyNBDF6\textsubscript{4a} is split in the solid state $^{13}$C NMR spectrum, although it is not split in the solution $^{13}$C spectrum of the same polymer. Splitting in the solid state spectrum is not entirely unexpected, as different local environments in the polymer chain due to different chain conformations in the solid state have been shown to give rise to different NMR resonances.\textsuperscript{22} This unpredictable splitting and broadening of the solid state $^{13}$C NMR resonances limit the use of this technique for definitive proof of regular polymer structures in ROMP systems. Despite this limitation, however, information can still be gathered from these spectra. The chemical shifts (referenced to tetramethylsilane) of the major peaks of the solid state and solution $^{13}$C NMR spectra of the three polymers are listed in Table 3.5.

In spite of the minor splitting in the C\textsubscript{1} resonance of polyNBDF6\textsubscript{4a} and the C\textsubscript{7} resonance of polyNBDF6\textsubscript{2a}, the chemical shifts of the three polymers in Table 3.5 do suggest that there are three unique structures present. First, the C\textsubscript{1} chemical shifts vary with the cis or trans nature of the double bond in the solution spectra of the two soluble polymers. In the solid state spectra, the C\textsubscript{1} resonance of the first two polymers appears around 44 ppm, while the C\textsubscript{1} resonance in the polymer prepared with initiator 4\textsubscript{a} appears around 50 ppm.

![Catalyst Predicted Structure](image)

<table>
<thead>
<tr>
<th>Cat. Structure*</th>
<th>C1</th>
<th>C2</th>
<th>CF\textsubscript{3}</th>
<th>C6</th>
<th>C7</th>
</tr>
</thead>
<tbody>
<tr>
<td>ss</td>
<td>soln</td>
<td>ss</td>
<td>soln</td>
<td>ss</td>
<td>soln</td>
</tr>
<tr>
<td>2a</td>
<td>cis, syndio</td>
<td>44.2</td>
<td>---</td>
<td>139.3</td>
<td>---</td>
</tr>
<tr>
<td>13a</td>
<td>cis, iso</td>
<td>44.6</td>
<td>44.7</td>
<td>140.7</td>
<td>140.2</td>
</tr>
<tr>
<td>4a</td>
<td>trans, syndio</td>
<td>49.5</td>
<td>49.8</td>
<td>139.1</td>
<td>140.0</td>
</tr>
</tbody>
</table>

Table 3.5: Solid state and solution $^{13}$C NMR chemical shifts of polyNBDF6 (referenced to TMS). ss = solid state, soln = acetone-d\textsubscript{6} solution. *Cis/trans structure determined by IR spectroscopy, tacticity predicted by analogy to DCMenthNBD polymers.
The $C_1$ resonance of the insoluble polymer prepared from 2a lies very close to that of the polymer from 13a, suggesting that these two polymers have the same configuration about the double bond, and are therefore both cis. These cis and trans assignments are in accord with what was already suggested by IR spectroscopy (Figure 3.10).

The second piece of evidence for the presence of three distinct structures lies in the chemical shifts of carbon $C_7$. There is a distinct 2.5 ppm shift between the $C_7$ resonances in the two cis polymers, suggesting that two different microstructures are represented, presumably cis-isotactic and cis-syndiotactic. Unfortunately, due to the breadth of the $C_7$ resonance, it cannot be determined for certain if polyNBDF6$_{2a}$ is 100% this unique microstructure or if some other microstructure is present in low concentrations.

In an effort to prepare more soluble polymers for solution analysis, efforts turned to the synthesis of block copolymers with a first block from a monomer that is known to afford a more soluble polymer (e.g. DCMNBD or MPCP), and a second block of NBDF6 (discussion of the

<table>
<thead>
<tr>
<th>Monomer 1</th>
<th>n</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCMNBD</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>MPCP</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 3.6. $[\text{Mo}] = \text{Mo(Ad)(pyr)(HIPTO)}$, $P = \text{propagating polymer chain}$
ROMP of 3-methyl, 3-phenylcyclopropene (MPCP) will be discussed later. Attempts to prepare block copolymers that contain a more soluble polymer portion are shown in Table 3.6.

As described in Table 3.6, n equivalents of either DCMNBD or MPCP were added to a toluene solution containing initiator 2a, and after complete consumption of the monomer was observed by $^1$H NMR spectroscopy, m equivalents of NBDF6 were added to the reaction mixture. In each case described in Table 3.6, a white solid immediately precipitated from solution upon the addition of NBDF6. Even in the case of an 80:20 DCMNBD:NBDF6 ratio, the resulting polymers were insufficiently soluble to observe significant resonances due to polyNBDF6. The $^1$H NMR spectra of the resulting polymers in Table 3.6 were nearly identical to polyDCMNBD or polyMPCP, suggesting that any true block copolymers formed in this system were no more soluble than the NBDF6 homopolymer, and all that remained in solution were small amounts of the original homopolymer of monomer 1.

II. B. ROMP of Benzonorbornenes

Benzonorbornenes represent another class of norbornene-based monomer that can be synthesized easily through the Diels-Alder reaction between a benzyne and cyclopentadiene. When 100 equivalents of BenzNBE (Figure 3.13) are added to 2a in toluene, a white insoluble solid forms. Keeping in mind the difficulties with NMR characterization of insoluble NBDF6, several benzonorbornene derivatives were prepared that contain functional groups that would possibly form a more soluble ROMP polymer.

![Figure 3.13: Benzonorbornene monomers used in ROMP](image)

Much like in the case with BenzNBE, the ROMP of OMeBenzNBE with 2a led to the production of a white solid polymer that was essentially insoluble in common organic solvents. When only 10 equivalents of OMeBenzNBE were added to a CD$_2$Cl$_2$ solution of 2a, the $^1$H
NMR alkylidene resonance of the initiator was completely consumed and replaced by a number of new alkylidene peaks, suggesting that incomplete initiation leading to extremely long polymer chains is not the source of insolubility in this system. A white solid formed immediately upon addition of monomer, suggesting that even an oligomer of only 10 units is insoluble in dichloromethane. In an attempt to prepare a more soluble polymer, a monomer with even more polar functionalities, MOMBenzNBE, was synthesized by Dr. Xiaohui He. Addition of 100 equivalents of MOMBenzNBE to 2a in toluene led to complete consumption of the monomer and production of the expected polymer within an hour. While polyMOMBenzNBE obtained with 2a was sufficiently soluble in organic solvents, $^{13}$C NMR spectroscopy showed the resulting polymer to be atactic and composed of a mixture of cis and trans olefins. It is possible that the flexible pendant ether groups on MOMBenzNBE can coordinate to the metal center, forcing the monomer into orientations that compete with the orientations dictated by steric, thus disturbing the stereoregularity of the polymer. At this point, no soluble, regular ROMP polymers of benzonorbornenes have been prepared with MAP initiators.

III. ROMP of 3-methyl, 3-phenylcyclopropene

III. A. Stereoselective ROMP of MPCP with MAP Complexes

The first living ROMP of 3,3-substituted cyclopropenes has recently been reported by our group. If an initiator containing an electron-withdrawing chiral diolate ligand such as those in 12a-b and 13a-c is employed in the ROMP of 3-methyl-3-phenylcyclopropene (MPCP), a polymer with a single microstructure is produced; however, it is not yet known if the highly tactic polymer is syndiotactic or isotactic. We were interested in determining if regular polyMPCP could be obtained using a molybdenum MAP initiator and if the structure of the polymer obtained from MAP initiators would be identical to that described in the literature. Additionally, we aimed to determine the microstructure of all forms of tactic polyMPCP.
MPCP was added to 1% 2a in toluene, and after one hour, white solid was isolated after quenching the reaction with benzaldehyde adding the reaction mixture to methanol. Proton and carbon NMR spectroscopy revealed the solid to be highly regular polyMPCP. The aliphatic regions of the $^{13}$C spectra of polyMPCP prepared using various initiators are displayed in Figure 3.14.

As shown in Figure 3.14, resonances corresponding to C$_2$ and C$_3$ of polyMPCP prepared from initiators 2a and 12 are single peaks, suggesting that both are regular structures. However, the difference in the C$_2$ and C$_3$ chemical shifts in the two spectra suggests that the two structures are not identical. The polymer prepared with 4a appears to be $\sim$85% regular, while polyMPCP prepared from 4b is completely irregular.

The structure of tactic polyMPCP (as described recently$^{25}$) was proposed to be trans; however, recent close examination of the IR spectra of polyMPCP obtained with various initiators suggests instead that the configuration about the double bond in the tactic polymers is cis. In general, trans olefins can be distinguished from cis olefins through the presence of a sharp IR stretch between 950-1000 cm$^{-1}$ (present in trans, but not cis olefins), which corresponds to a C-H out of plane bending vibration.$^{26,27}$ This same IR analysis was employed in a recent
report to assign the structure of trans-polyMPCP obtained with a ruthenium-based initiator. In that report, the presence of an IR stretch at ~980 cm\(^{-1}\) led the authors to assign a trans configuration to the polymer. The IR spectra of polyMPCP prepared with various initiators are displayed in Figure 3.15.

There is a strong absorption in the IR spectrum of polyMPCP\(_{4a}\) that is not present in the spectra of either polyMPCP\(_{2a}\) or polyMPCP\(_{12}\). It is clear from examination of the olefinic resonances in the \(^{13}\)C NMR spectra of the polymers described in Table 3.1 that two classes of polymers are represented: one group with olefinic resonances around 136.5 ppm and another group around 137.5 ppm. A chemical shift difference of about 1 ppm is expected for cis vs. trans olefins in other ROMP polymers (such as polyDCMNBD, described in the previous section of this report). The IR spectra of each of these polymers confirm this grouping, as the polymers containing an olefinic \(^{13}\)C resonance around 136.5 (4a) exhibit a strong IR absorption around 980 cm\(^{-1}\) (characteristic of trans olefins), while the polymers containing an olefinic \(^{13}\)C resonance around 137.5 (2a and 12a) do not exhibit this absorption. Therefore, the structures of the two highly tactic polymers from initiators 2a and 12a are assigned as cis. The confusion about the

![Figure 3.15: IR spectra (thin film) of polyMPCP prepared with Mo(NAr)(CHCM\(_2\)Ph)(OtBu\(_2\)) (4a), Mo(NAr)(CHCM\(_2\)Ph)(Biphen-CF\(_3\)) (12a), and Mo(NAd)(CHCM\(_2\)Ph)(pyr)(HIPTO) (2a) as indicated in colored boxes.](image)

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*cis or trans* structure in the original report possibly arose from the fact that the *cis* polymers do exhibit weak IR stretches between 950-970 cm\(^{-1}\), but close examination of the spectra shows that these minor stretches are not significant enough to be indicative of a *trans* structure. A summary of the preceding analysis and *cis/trans* assignments are available in Table 3.7.

<table>
<thead>
<tr>
<th>Initiator</th>
<th>(^{13})C NMR olefinic resonance (ppm)</th>
<th>Presence of (\sim)980 cm(^{-1}) IR stretch?</th>
<th>Assigned structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a Mo(NAr)(CHCMe(_2)Ph)(O-t-Bu)(_2)</td>
<td>136.7*</td>
<td>yes</td>
<td><em>trans</em></td>
</tr>
<tr>
<td>13a Mo(NAr)(CHCMe(_2)Ph)(Binaph-C(_6)F(_5))</td>
<td>137.5</td>
<td>no</td>
<td><em>cis</em></td>
</tr>
<tr>
<td>2a Mo(NAd)(CHCMe(_2)Ph)(pyr)(HiptO)</td>
<td>137.7</td>
<td>no</td>
<td><em>cis</em></td>
</tr>
</tbody>
</table>

Table 3.7: Structure assignments for polyMPCP prepared with various initiators. \(^{13}\)C spectra recorded in CD\(_2\)Cl\(_2\) and referenced to TMS. *polyMPCP(4a) also contains \(-10\,\%\) other olefinic resonances

When only one equivalent of MPCP was added to 2a in benzene-d\(_6\), the proton NMR spectrum revealed several new alkylidene resonances along with a resonance for 2a (30\% of total alkylidene resonances). The olefinic region was complex, so we could not determine whether the first insertion product has the *cis* or *trans* configuration. When 5 equivalents of MPCP are added to 2a in benzene-d\(_6\), the proton NMR spectrum reveals that all 2a has been consumed and only one new propagating alkylidene (H\(_a\) singlet resonance at 11.68 ppm) is present. The ratio of propagation rate vs. initiation rate in ROMP polymerizations can be calculated from these NMR data: for a given initial monomer concentration \(M_0\), initial initiator concentration \(I_0\), and final initiator concentration \(I\), equation (1) holds true \((r = k_p/k_i)\).

\[
M_0/I_0 + r \ln(I/I_0) + (1-r)(I/I_0 - 1) = 0
\]  
(1)

For the ROMP of MPCP with 2a, \(I/I_0 = 0.30\) and \(M_0/I_0 = 1\), so according to equation (1), \(k_p/k_i = 0.60\), indicative of a system in which initiation is faster than propagation.

As shown in Figure 3.14, the two regular *cis* polymers obtained with initiators 2a and 12 have different microstructures, as the \(^{13}\)C resonance of the methyl carbon appears around 30 ppm in the former and 32 ppm in the latter. At this point, the tacticity of neither polymer is known for certain; however, by analogy with the results obtained with polyDCMenthNBD, polyMPCP obtained with 2a would be expected to be syndiotactic, and that obtained with 12 would be isotactic.
III. B. Efforts towards determination of polyMPCP tacticity

Since the stereoselective ROMP of 3,3-disubstituted cyclopropenes is a relatively new field, there is no system in place to distinguish between isotactic and syndiotactic polyMPCP. In the same way that a menthyl substituted norbornadiene was employed to determine the tacticity of DCMNBD, it would be useful to prepare a MPCP analog that contains a chiral tag so that the tacticities of polyMPCP$_2$a and polyMPCP$_{3a}$ could be determined as well. A few efforts towards this goal will be presented in this section.

It was of interest to develop an enantiomerically pure chiral cyclopropene monomer that was as structurally similar to MPCP as possible. Three candidates, MenthMPCP, BitetMPCP, and OMeMPCP are displayed in Figure 3.16. MenthMPCP maintains the 3-phenyl, 3-methylcyclopropene basic backbone, and by introducing the chiral group in the 4-position of the phenyl ring, keeps the electronics about the olefin as similar as possible to MPCP. Enantiomerically pure MenthMPCP was synthesized from commercially available L-menthone and 4-chloro-α-methylstyrene, following the general procedures for syntheses of related compounds described in the literature.\(^{30,31}\) The synthesis of MenthMPCP is outlined in Scheme 3.9.

**MenthMPCP-1** was synthesized by the CeCl$_3$-mediated addition of the Grignard of 4-chloro-α-methylstyrene to L-menthone. According to the $^1$H NMR spectrum of the crude product mixture, only $\sim$50% conversion to the expected alcohol product MenthMPCP-1 was obtained; however, the remaining starting materials can be easily removed by distillation at reduced pressure. By $^1$H NMR spectroscopy, it appears that only a single diastereomer of MenthMPCP-1 was formed, which by analogy to the results of Panev and Dimitrov\(^{31}\)
It should be noted that a similar approach was used in our group in an attempt to prepare a camphor-based derivative of MenthMPCP-1, however it was found that 4(magnesium chloride)-α-methylstyrene does not react with camphor under these conditions. MenthMPCP-1 was converted into its methoxy derivative MenthMPCP-2 through deprotonation with potassium hexamethyldisilazide followed by treatment with methyl iodide.

MenthMPCP was synthesized from MenthMPCP-2 as shown in Scheme 3.9 through cyclopropanation of MenthMPCP-2 with bromoform/NaOH to form MenthMPCP-3, followed by partial reduction with ethyl Grignard/Ti(O-i-Pr)₄ to give MenthMPCP-4 and subsequent dehydrohalogenation with potassium-tert-butoxide to give MenthMPCP, following the general procedure given by Rubin and Gevorgyan for the synthesis of MPCP. All intermediates in the synthesis of MenthMPCP are colorless or pale yellow oils and were purified by column chromatography. MenthMPCP itself is a colorless crystalline solid that was purified by recrystallization from hexane and isolated in 20% overall yield from the commercially available starting materials.

The ¹H NMR spectrum of MenthMPCP displays two distinct olefinic resonances around 6.8 ppm, as the incorporation of the chiral group eliminates any symmetry elements relating the
two olefinic protons. A ROMP polymer prepared from MenthMPCP also likely would contain protons whose $^1$H NMR signals were different from one another.

ROMP of MenthMPCP was carried out with several molybdenum imido alkylidene initiators through addition of 50 equivalents of monomer to a C$_6$D$_6$ solution of initiator. In general, initiators that afforded highly tactic polyMPCP also afforded relatively tactic polyMenthMPCP. When Mo(NAr)(CHMe$_2$Ph)(O-t-Bu)$_2$ (4a) was employed, the resulting polymer exhibited a single sharp $^{13}$C NMR resonance corresponding to the quaternary carbon at 46.4 ppm in CDCl$_3$, suggesting highly tactic polymer. Since 4a does not contain a chiral center, it can be assumed that the high level of tacticity arises entirely from chain-end control. A similar result in the polymerization of MPCP is obtained using 4a as an initiator, leading to polymer with a tactic bias that exhibits a $^{13}$C NMR resonance ~1 ppm downfield of that seen in polymers using chiral initiators. As found for the reported polymerizations of MPCP, when the ROMP of MenthMPCP$^{25}$ was carried out with an initiator containing the more electron-withdrawing hexafluoro-t-butoxide ligands, such as 4b, atactic polymer was obtained.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Polymer Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% tactic</td>
</tr>
<tr>
<td>4a</td>
<td>98%</td>
</tr>
<tr>
<td>4b</td>
<td>atactic</td>
</tr>
<tr>
<td>5a</td>
<td>98%</td>
</tr>
<tr>
<td>5b</td>
<td>atactic</td>
</tr>
<tr>
<td>12a</td>
<td>90%</td>
</tr>
<tr>
<td>12b</td>
<td>atactic</td>
</tr>
<tr>
<td>13a</td>
<td>70%</td>
</tr>
<tr>
<td>13b</td>
<td>atactic</td>
</tr>
</tbody>
</table>

Table 3.8: ROMP of MenthMPCP with Mo imido alkylidene initiators
Our attention then turned to the use of molybdenum imido alkylidene initiators containing electron-withdrawing diolates as initiators in ROMP of MenthMPCP. Molybdenum imido alkylidene complexes incorporating fluorinated binaphtholate and biphenolate ligands, (12 and 13a), catalyzed the formation of polyMenthMPCP whose $^{13}$C NMR spectrum revealed a sharp resonance at 45.7 ppm, suggesting highly tactic polymer of a different microstructure than that obtained with achiral initiators (with a $C_3$ resonance at 46.4 ppm). Unfortunately, neither polyMenthMPCP$_{12}$ nor polyMenthMPCP$_{13a}$ was 100% tactic. The aliphatic regions of the $^{13}$C spectra of polyMenthMPCP prepared with initiators 4a, 12a, 12b, and 13b are displayed in Figure 3.17.

Since polyMenthMPCP$_{12a}$ is relatively regular (as observed by $^{13}$C NMR), the corresponding $^1$H NMR spectrum should exhibit either two coupled olefinic protons or two uncoupled olefinic protons (if it is isotactic or syndiotactic, respectively). Unfortunately, while the $^{13}$C NMR spectrum of polyMenthMPCP$_{12a}$ showed it to be a relatively regular polymer, the corresponding $^1$H NMR spectrum showed only one broad olefinic resonance. The lack of differentiation between the expected two different olefinic protons suggests that the chiral tag in MenthMPCP is too remote to exert an influence on the chemical shift of the olefinic protons.
Efforts then turned to the syntheses of MPCP-based monomers containing other enantiomerically pure chiral tags. Another readily accessible chiral building block is the Bitet group ([Bitet = 5,5',6,6',7,7',8,8'-octahydro-[1,1'-binaphthalene]-2,2'-bis(olate)].) Starting from dimethyl-protected enantiomerically pure Bitet-OH₂, an isopropenyl group can be installed in the 3-position as described in Scheme 3.10.

**Scheme 3.10: Synthesis of BitetMPCP-2**

(i) Br₂, CH₂Cl₂, RT (ii) isopropenyl boronic acid, Pd(PPh₃)₂, K₂CO₃, 100 °C, toluene (iii) CHBr₃, NaOH, cetrimide (iv) Ti(O-i-Pr)₄, EtMgBr (v) tBuOK, DMSO

**BitetMPCP-1** can be obtained through treatment of (OMe)₂Bitet with one equivalent of Br₂ at 0 °C followed by column chromatography to separate the desired product from the dibromide and unbrominated products. **BitetMPCP-1** was then subjected to Suzuki coupling conditions with isopropenyl boronic acid to afford **BitetMPCP-2**. The desired cyclopropene **BitetMPCP** can be prepared in the same three-step synthesis outline by Rubin and Gevorgyan described in reference 30. **BitetMPCP** was obtained in gram quantities and purified through column chromatography on silica. With **BitetMPCP** in hand, it was then of interest to investigate the ROMP of this monomer in the presence of molybdenum imido alkylidene initiators.

When **BitetMPCP** is added to 1% 4a in toluene, complete consumption of the monomer can be observed by ¹H NMR spectroscopy over 4 days. In contrast, the same reaction with 1%
2a as initiator is only 50% complete after 4 days. After addition of benzaldehyde and precipitation from methanol, white solid polyBitetMPCP was isolated from both ROMP reactions. The $^1$H NMR spectra of both solids revealed broad resonances indicative of the expected polymer. However, the resonances corresponding to the olefinic protons of each polymer were much broader than what would be expected for even a completely irregular polymer. This led us to believe that the breadth of the resonances could possibly be due to hindered rotation of the very bulky Bitet moiety. To check this hypothesis, variable temperature $^1$H NMR spectra were recorded between 20 °C and 100 °C.

As shown in Figure 3.18, the olefinic region of the $^1$H NMR spectrum of polyBitetMPCP$_{4a}$ sharpens considerably with increasing temperature. This result suggests that the breadth of the resonance at room temperature could be ascribed to steric crowding and hindered rotation of the pendant groups of the polymer. Even at 100 °C, the olefinic resonance is not sufficiently sharp to draw any conclusions about the structure of the polymer. A similar sharpening of olefinic resonances was observed in the variable temperature $^1$H NMR spectra of polyBitetMPCP$_{2a}$. However, even in the 100 °C spectrum, the olefinic resonances were not sufficiently sharp to make any claims about the structure of the polymer.
It appeared that the structure of BitetMPCP deviates too much from the structure of MPCP to be a useful analog, so efforts turned to a cyclopropene-based monomer that contains a much smaller chiral tag in the hopes that the overall structure of the monomer more closely approximates that of MPCP. The first monomer synthesized along these lines was derived from commercially available (S)-propylene oxide. Installation of this chiral, enantiomerically pure tag begins with the addition of the Grignard reagent of α-bromostyrene to (S)-propylene oxide, as described in Scheme 3.11. The reaction proceeds only in the presence of catalytic amounts of copper (I) iodide, as described in literature reports of related reactions. 33

As shown in Scheme 3.11, the next step in the synthesis is the protection of OMeMPCP-1 through deprotonation with sodium hydride followed by reaction with methyl iodide to afford OMeMPCP-2. Both the alcohol and the methyl ether were purified by column chromatography on silica gel and isolated as colorless oils. The starting compounds in the synthesis of methyl, phenyl-substituted cyclopropene compounds as described by Rubin and Gevorgyan are methyl styrene derivatives similar in structure to OMeMPCP-2. Therefore, the next few steps to convert the styrene derivative OMeMPCP-2 to the cyclopropene compound were similar to those described in the literature for MPCP. 30

Following the three-step procedure described by Rubin and Gevorgyan, the cyclopropene OMeMPCP could be isolated in ~95% purity. Experimental details are described in the Experimental section. Unfortunately, the monomer decomposed upon attempted chromatography on silica gel and since it is an oil, it could not be recrystallized readily. Nevertheless, reactions of OMeMPCP with molybdenum imido alkylidene compounds were investigated.

![Chemical structure and reaction scheme]

Scheme 3.11: Synthesis of OMeMPCP; (i) cat. CuI, THF (ii) NaH, THF, 12 h 0 °C (iii) CHBr3, NaOH, cetrimide (iv) Ti(O-i-Pr)4, EtMgBr (v) tBuOK, DMSO

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When 5 equivalents of 95% pure OMeMPCP are added to a benzene solution of 2a, the initiator and monomer were completely consumed, and a number of new alkylidene and olefinic resonances were observed in the $^1$H NMR spectrum. While the spectrum is complex, a number of new sharp peaks could be observed in both the olefinic region and the region around 3 ppm (expected for the methoxy methyl peaks). These sharp peaks could represent either an extremely regular 5-unit long oligomer, or another unknown product (dimer or trimer) that is formed in a non-metathetical reaction between the monomer and initiator. A 500 MHz gCOSY spectrum showed coupling between the two olefinic resonances around 6 ppm, which suggests that the two distinct olefinic protons are indeed on the same C=C double bond.

The addition of 50 equivalents of OMeMPCP to 2a in benzene led to complete consumption of the monomer after stirring the reaction for 10 hours at room temperature. Upon addition of 50 equivalents of monomer, the resulting spectrum is, surprisingly, similar to the spectrum that resulted upon addition of only 5 equivalents of monomer. There do appear to be a number of very broad resonances in the spectrum, which could be evidence for the formation of some expected polyOMeMPCP. However, these peaks only account for a small percentage of the resulting product mixture. No polymer could be isolated upon attempted precipitation from various solvents. It appears that OMeMPCP forms an unexpected, non-metathesis product upon exposure to metathesis catalysts. Further investigation into the identity of the product was not pursued.

In a final attempt to determine the structure of the various highly tactic MPCP polymers, 5 equivalents of MPCP were added to 2a on a 700 mg scale in toluene. The polymerization reaction was quenched with ferrocenecarboxaldehyde in an attempt to cap the oligomers with ferrocene and make them more crystalline. After quenching the reaction and evaporating the solvent, the reaction mixture was purified by flash column chromatography on silica gel using 1% ethyl acetate in hexanes as the eluent. $^1$H NMR revealed the orange solid isolated after purification to be the expected MPCP oligomer capped with ferrocene. Although the isolated oligomer displayed only one spot by thin layer chromatography, it still may have contained oligomer chains of various lengths.

Since standard column chromatography was not sufficient to separate oligomers of different lengths preparative scale HPLC was explored. In collaboration with Dr. Jaclyn Murphy (Fu Group, MIT), various solvent and column conditions for analytical HPLC were attempted to
determine proper conditions for preparative scale chromatography. However, under all conditions with all columns tried, the orange solid only displayed one peak by HPLC. This result suggests that either HPLC was not sufficient to separate MPCP oligomers of various lengths, or that the mixture was composed of only oligomers of a single length. The fact that X-ray quality crystals could not be grown from the orange solid could be taken as evidence for the possible presence of various oligomers of different chain lengths in the solid.

IV. ROMP of unsubstituted monocyclic olefins

IV. A. ROMP of cyclooctenes

The scope of the cis selectivity of 2a was investigated further through the polymerization of cis,cis-1,5-cyclooctadiene (COD) and cis-cyclooctene (COE). 300 equivalents of monomer were employed in the following studies in order to afford polymer that is less soluble in organic solvents, and therefore easier to handle and isolate, as well as to be able to directly compare results to those reported in the literature.34 The polymerization reactions were monitored by 1H NMR spectroscopy, and quenched with benzaldehyde upon observation of complete consumption of the monomer. The polymers were isolated by repeated precipitation from methanol.

As seen in Table 3.9, using either 4b or 13c as initiators in the ROMP of COD leads to polymer with low cis content. As reported in the literature,35 13c affords all cis-isotactic

<table>
<thead>
<tr>
<th>Initiator</th>
<th>COD ROMP</th>
<th>COE ROMP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time</td>
<td>cis-content</td>
</tr>
<tr>
<td>4b</td>
<td>&lt;15min</td>
<td>15%</td>
</tr>
<tr>
<td>2a</td>
<td>1h</td>
<td>&gt;98%</td>
</tr>
<tr>
<td>13c</td>
<td>&lt;15min</td>
<td>50%</td>
</tr>
</tbody>
</table>

Table 3.9: ROMP of COD with Mo imido alkylidene initiators in CH2Cl2. Cis content determined by 13C NMR (CDCl3) resonances of olefinic carbon, cis: 129.5ppm, trans: 130.1ppm.34 n.d. = not determined.
polyDCMNBD, so the fact that it is not able to produce 100% cis-polyCOD is somewhat surprising. It is possible that cis polymer is originally formed, which then equilibrates to a mixture of cis and trans before the reaction is quenched.

When 300 equivalents COD are added to a CH₂Cl₂ solution of 2a, exclusively cis-polyCOD is formed after 1h. When the reaction mixture is allowed to stir at room temperature over 12h, not surprisingly, small ¹³C peaks at 130.2 and 129.4 ppm, (corresponding to tc and ct olefinic resonances, respectively)³⁴ appear in the resulting polymer spectrum. The first letter of olefin notation used for the discussion of polyCOD denotes the cis or trans structure of the double bond containing that carbon, and the second letter denotes the cis or trans structure of the adjacent double bond, as depicted in Figure 3.19 (dyad notation).

The ¹³C NMR spectra of polyCOD₄b and polyCOD₂a (both after reaction times of 1h and 18h) are displayed in Figure 3.19. The fact that small trans peaks appear in the 18h sample of polyCOD₂a suggests that although spectacular cis-selectivity is observed initially, the catalyst eventually isomerizes the C=C bonds in the cis-polymer to a mixture of cis and trans double bonds. This isomerization was not observed in the ROMP of more highly strained olefins such as DCMNBD, NBDF₆, or MPCP, described in earlier sections of this report. As shown in Figure 3.20, similarly high-cis polymer was obtained when the monomer employed was cis-cyclooctene (COE). PolyCOE with 20% cis content was obtained when 4b was employed as initiator, while 98% cis polyCOE was obtained using 2a as initiator.

When 10 equivalents of COD were added to a CD₂Cl₂ of 2a, the ¹H NMR spectrum of the sample showed that the monomer was consumed within 20 minutes. No significant amounts of the initiator were consumed, and no new resonances were observed in the alkylidene region of the ¹H NMR spectrum. Formation of a 10-mer of COD without significant consumption of the initiator suggests that kₚ is significantly larger than kᵢ in this system. A thorough study of the complex equilibrium processes involved in polymer and oligomer formation in ROMP of COD has been reported previously by Chauvin and coworkers.³⁶ Table 3.10 shows the thermodynamics of ROMP reactions for various cyclic olefins, which helps to explain why the ROMP of COD and COE are more reversible than the ROMP of norbornenes: the values of ΔG for the reactions are only -13 and -19 kJ/mol, compared to -47 kJ/mol for ROMP of norbornene.³
Figure 3.19: Olefinic region of $^{13}$C NMR spectra of polyCOD (CDCl$_3$) obtained using initiators 4b and 2a. First letter of olefin notation denotes cis/trans structure of the double bond containing that carbon, second letter denotes cis/trans structure of adjacent double bond.

Figure 3.20: Olefinic region of $^{13}$C NMR spectra (CDCl$_3$) of polyCOE obtained with initiators 4b and 2a
The thermal properties of any polymer with a new structure, such as cis-polyCOE and cis-polyCOD made by catalyst 2a, are expected to be different than those of polymers with a different structure. In the report by Feast, who investigated the structures of polyalkenamers made by ROMP, it was found that the melting point ($T_m$) of the polymers was roughly inversely proportional to the cis content.$^{34}$ By extrapolation of the thermal data of polymers of intermediate cis content, the approximate $T_m$ of 100% cis polycyclooctene (polyCOE) and polycyclooctadiene (polyCOD) was predicted. Investigation of the thermal properties of polyCOE and polyCOD by Differential Scanning Calorimetry (DSC), revealed that this predicted relationship did indeed hold for the ~100% cis polymers reported here (Table 3.11).

It is quite remarkable that cis-polyCOD, which is a viscous liquid at room temperature, did not undergo any observable phase transition above the lower limit of the DSC (-75 °C), suggesting that the freezing point of this polymer is below -75 °C, as predicted in the studies by

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Polymer Structure</th>
<th>$\Delta H$ kJ/mol</th>
<th>$\Delta S$ J/kmol</th>
<th>$\Delta G$ kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclobutene</td>
<td>$cis$</td>
<td>-121</td>
<td>-52</td>
<td>-105</td>
</tr>
<tr>
<td>Cyclopentene</td>
<td>$cis$</td>
<td>-15</td>
<td>-52</td>
<td>-0.3</td>
</tr>
<tr>
<td></td>
<td>$trans$</td>
<td>-18</td>
<td>-52</td>
<td>-2.6</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>$cis$</td>
<td>+2</td>
<td>-31</td>
<td>+6.2</td>
</tr>
<tr>
<td></td>
<td>$trans$</td>
<td>-2</td>
<td>-28</td>
<td>+7.3</td>
</tr>
<tr>
<td>Cyclooctene</td>
<td>1:1 c/t</td>
<td>-13</td>
<td>-9</td>
<td>-13</td>
</tr>
<tr>
<td>Cyclooctadiene</td>
<td>$cis$</td>
<td>-25</td>
<td>-5</td>
<td>-19</td>
</tr>
<tr>
<td></td>
<td>$trans$</td>
<td>-33</td>
<td>-5</td>
<td>-24</td>
</tr>
<tr>
<td>Norbornene</td>
<td>1:1 c/t</td>
<td>-62</td>
<td>-50</td>
<td>-47</td>
</tr>
</tbody>
</table>

Table 3.10: Thermodynamics of ROMP of cyclic monomers at 25 °C (table from reference 3)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Cis content</th>
<th>Predicted or reported $T_m$</th>
<th>Observed $T_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>polyCOE (4a)</td>
<td>20%</td>
<td>50 °C</td>
<td>35 °C</td>
</tr>
<tr>
<td>polyCOE (2a)</td>
<td>100%</td>
<td>-10 °C</td>
<td>-10 °C</td>
</tr>
<tr>
<td>polyCOD (4a)</td>
<td>20%</td>
<td>30 °C</td>
<td>20 °C</td>
</tr>
<tr>
<td>polyCOD (2a)</td>
<td>100%</td>
<td>-150 °C</td>
<td>not observed above -75 °C</td>
</tr>
</tbody>
</table>

Table 3.11: Thermal analysis of polyalkenamers, determined by DSC
Feast. While the exceptionally low melting points of cis-polyCOE and cis-polyCOD are at first glance very exciting, it should be noted that the non-living nature of these polymerizations means that the polymers are not true 300-mers and are more likely made up of oligomeric chains of various lengths. GPC analysis of cis-polyCOD$_{2a}$ showed the sample to be composed of mainly of chains less than 100 units long, with a PDI of 1.2. While a large $k_p/k_i$ could limit the use of polyCOD in applications that necessitate a polymer of finely controlled molecular weight, the fact that both polyCOD$_{2a}$ and polyCOE$_{2a}$ could be prepared through ROMP with only cis double bonds is still an important result.

IV. B. ROMP of cycloheptene and cyclopentene

When 300 equivalents of cycloheptene were added to a CD$_2$Cl$_2$ solution of 2a, 80% consumption of monomer and formation of polymer was observed by $^1$H NMR after 5 h. However, no further consumption of monomer was observed after stirring the reaction mixture a further 12 h under the conditions described here. The resulting polymer, once isolated, was only 80% cis. It is not known at this point why ROMP of cycloheptene should give lower cis content as compared to the ROMP of cyclooctene, but it is possible that isomerization occurs simultaneously with polymerization of cycloheptene.

When 300 equivalents of cyclopentene were added to a dichloromethane solution of 2a or 4a at 0.6 M monomer concentration, no cyclopentene was consumed. According to a recent report, for ROMP of cyclopentene to proceed, the monomer concentration must be greater than 1.5 M.$^{37}$ For this reason, ROMP of cyclopentene was attempted again with 2a and 4a at a concentration of 3 M. When 300 equivalents of cyclopentene (CPE) were added to the initiator solutions in dichloromethane at 3 M monomer concentrations, full consumption was observed in both cases, along with formation of the expected polyCPE. However, both polyCPE$_{2a}$ and polyCPE$_{4a}$ were composed of a mixture of both cis and trans olefins, suggesting that either ROMP of CPE with 2a is not Z-selective, or that the cis polymer isomerizes during polymerization to form cis and trans oligomers.

CONCLUSIONS

This chapter reports the synthesis of a new class of highly regular cis-syndiotactic ROMP polymers, including cis-syndiotactic polyDCMNBD, cis-syndiotactic polyNBDF6, cis-
syndiotactic polyMPCP, cis polyCOE, and cis polyCOD. The syndiotactic polymers are proposed to be formed through a unique type of control exerted by a chiral, racemic metal center whose chirality inverts with each monomer insertion. The most generally successful catalyst for the Z-selective and syndioselective ROMP was Mo(NAd)(CHCMe₂Ph)(pyr)(HIPTO), (2a), in which the bulky hexaisopropylterphenoxide ligand is proposed to force the substituents of the incoming monomer to point in the same direction with each insertion, making exclusively cis linkages.

While a number of enantioselective olefin metathesis processes have been reported using MAP compounds, all of these systems employ enantiomerically pure phenoxide ligands. Therefore, it is difficult (if not impossible) to separate the effects of the chiral ligand and the chiral metal center when considering the source of enantioselectivity in these reactions. It can be argued that because no chiral ligands are involved, the highly tactic ROMP systems described in this report with MAP compounds such as 2a represent the first examples of systems that truly exploits the chiral nature of the metal center in a stereoselective reaction.

The cis-syndioselective ROMP of cyclic monomers with MAP complexes has greatly expanded the scope of the types of polymers available through ROMP. In almost all cases described in this chapter (excluding cis-syndiotactic polyMPCP), the cis, syndiotactic polymers exhibited drastically different physical properties as compared to the corresponding cis-isotactic or trans-syndiotactic polymers. NMR-scale initiation studies suggest that the cis, syndioselective ROMP of strained cyclic olefins (i.e. DCMNBD, NBDF6, and MPCP) is highly living, which makes these monomers well suited for applications in which polymers of well-defined molecular weights are necessary. While the tacticity of polyMPCP₂a has yet to be explicitly proven, it can be assumed to be syndiotactic by analogy to the ROMP of bicyclic olefins with 2a.

Both very pure cis-polycyclooctadiene and highly cis-polycyclooctene have been reported here using 2a as initiator. NMR-scale initiation experiments and GPC analysis suggest that ROMP of these less-strained monomers is not living, due to poor catalyst initiation as well as the ability to perform unwanted metathesis on the polymer chain. These combined facts make ROMP polymers of unsubstituted monocyclic olefins such as COD and COE ill-suited for applications that call for polymers of controlled molecular weights. Nevertheless, the synthesis of both polyCOD and polyCOE in pure cis form through ROMP has not been reported in the
literature and represents another example of the unique activity and selectivity of MAP initiators in ROMP.

The results presented here represent only a fraction of the possible variations of MAP initiators that could potentially be used in ROMP. The modularity of all three ancillary ligands of MAP compounds allows for precise catalyst tuning, and should allow MAP catalysts to be employed in a wide variety of stereoselective ROMP and other selective olefin metathesis reactions.

EXPERIMENTAL

General Details. All manipulations of air-sensitive compounds or reactions were performed under nitrogen in a drybox or using Schlenk techniques. All glassware was oven-dried and allowed to cool under vacuum or nitrogen before use. Ether, pentane, toluene, benzene, tetrahydrofuran, and dichloromethane were sparged with nitrogen and passed through activated alumina. All solvents were stored over molecular sieves in a nitrogen atmosphere. Deuterated solvents were degassed and passed through activated alumina before use and stored over molecular sieves. Benzaldehyde was distilled and stored under nitrogen. NMR spectra were obtained on Varian spectrometers operating at 300 MHz or 500 MHz. NMR chemical shifts are reported as ppm relative to tetramethylsilane, and were referenced to the residual proton or $^{13}$C signal of the solvent ($^1$H CDCl$_3$: 7.26 ppm, $^1$H C$_6$D$_6$: 7.16 ppm, $^1$H acetone-D$_6$: 2.05 ppm, $^{13}$C C$_6$D$_6$: 128.06 ppm, $^{13}$CDCl$_3$: 77.16 ppm). DCMNBD$^{38}$, DCMenthNBD$^{17}$, NBDF$^{6,21}$, BenzNBE$^{39}$, OMeBenzNBE$^{40}$, MPCP$^{30}$, BitetMPCP-1$^{41}$, 1a$^{14}$, 1b$^{12}$, 4a-b$^{42}$, 5a-b$^{11}$, 12a-b$^{24}$, 13a-c$^{24}$ were synthesized according to published procedures. The syntheses of all other molybdenum imido alkylidene catalysts are reported in Chapter 2 of this report. Liquid monomers were dried with calcium hydride, freeze-pump-thaw degassed, and distilled before use. Solid monomers were dried under vacuum, passed as a toluene solution through activated alumina, and dried over molecular sieves before use. Unless otherwise noted, all other reagents were obtained from commercial sources and used as received.

Representative procedure for ROMP of cyclic olefins: DCMNBD (146.8 mg, 0.705 mmol, 50 eq) was dissolved in 0.7 mL C$_6$D$_6$, and to it was added a 0.5 mL C$_6$D$_6$ solution of 2a (0.0141 mmol) in one portion. The mixture immediately became deep red/brown. The mixture was
stirred for 1h, then transferred to a J-young tube and the progress of the reaction was monitored by $^1$H NMR spectroscopy. After the monomer was consumed, the reaction mixture was transferred to a vial, and 500 µL benzaldehyde was added. The reaction mixture became deep green within 5 minutes, and was stirred for one h. The entire mixture was added dropwise to 100 mL of vigorously stirring methanol. A fine white solid immediately formed, and the mixture was stirred for 12 h. The white or off-white polymers were isolated on a medium or fine porosity frit by filtration, rinsed with MeOH, and dried in vacuo.

cis-syndiotactic poly-DCMNBD: $^1$H NMR (C$_6$D$_6$, 300 MHz) $\delta$ 5.34 (m, 2H, C$_5$H, C$_6$H), 3.015 (m, 2H, C$_1$H, C$_4$H), 3.73 (s, 6H, CO$_2$Me), 2.52 (m, 1H, C$_7$H), 1.46 (m, 1H, C$_7$H). $^{13}$C NMR: (CDCl$_3$, 500 MHz) $\delta$ 165.37 (CO$_2$CH$_3$), 142.29 (C$_3$), 131.5 (C$_5$), 52.06 (CO$_2$CH$_3$), 44.44 (C$_4$), 38.01 (C$_7$).

cis, syndiotactic-polydicarbomenthoxynorbornadiene (polyDCMenthNBD): $^1$H NMR (CDCl$_3$) $\delta$ 5.34 (br, 1H, C$_5$H or C$_6$H), 5.29 (br, 1H, C$_5$H or C$_6$H), 4.75, 4.68, 2.13 (br, 1H), 2.03 (br, 1H), 1.93, 1.67, 1.47, 1.39, 1.02 (other resonances are overlapping).

cis-polycyclooctene: $^1$H NMR (CD$_2$Cl$_2$, 500 MHz) $\delta$ 5.38 (t, 1H, C=CH), 2.06 (m, 2H, CH$_2$), 1.34 (m, 4H, CH$_2$). $^{13}$C NMR: (CDCl$_3$, 500 MHz) $\delta$ 130.02 (C=CH), 29.91, 29.29, 27.38.

cis-polycyclooctadiene: $^1$H NMR (CD$_2$Cl$_2$, 500 MHz) $\delta$ 5.42 (t, 1H,C=CH), 2.12 (m, 2H, CH$_2$). $^{13}$C NMR: (CDCl$_3$, 500 MHz): $\delta$ 129.70 (C=CH), 27.53 (CH$_2$).

ROMP of DCMNBD in the presence of Lewis bases: Representative Procedure

2a (5.6 mg, 0.00589 mmol) was dissolved in 1.5 mL C$_6$D$_6$ in a 20-mL vial, and anthracene was added as an internal standard. 0.75 mL of the solution was transferred to a J-Young NMR tube as a standard, and 3 µL PMe$_3$ (5 eq, 0.0295 mmol) was added to the remaining solution, which was transferred to a second J-Young tube. $^1$H NMR spectra were recorded of both samples. The
trimethylphosphine-containing solution was transferred to a vial, 0.5 mL C₆D₆ solution of DCMNBD (123 mg, 100 eq) was added, and the reaction was monitored by ¹H NMR spectroscopy.

_Cis, syndiotactic–polyMPCP:_ ¹H NMR (CD₂Cl₂) δ 7.09 (s, 5H, Ar), 5.48 (s, 2H, C=C), 1.33 (s, 3H, CH₃); ¹³C {¹H} NMR (CD₂Cl₂) δ 152.0 (Cipso), 137.8 (C=C), 128.4 (Ar), 127.2 (Ar), 126.0 (Ar), 46.2 (Cquat), 30.0 (CH₃).

(1S,2S,5R)-2-isopropyl-5-methyl-1-(4-(prop-1-en-2-yl)phenyl)cyclohexanol (MenthMPCP-1)

Magnesium turnings (2.8 g, 0.115 mol) were suspended in 100 mL THF and to the stirring suspension was added dropwise 11.5 g (0.0753 mol) 4-chloro-α-methylstyrene via an addition funnel. The mixture was heated to reflux for 18 h after which it became a deep brown/green color. In a separate flask, 16 g (0.07 mol) CeCl₃ was suspended in 100 mL and 10.5 g (0.068 mol, 0.9 eq) L-menthone was added to it. The mixture became pale yellow and thicker, and was allowed to stir for 2 h at room temperature. The suspension was cooled to 0 °C and the Grignard solution was added to it via cannula. The green color of the Grignard solution immediately disappeared and the suspension became deeper yellow. The reaction mixture was allowed to warm to room temperature as it stirred for 1 h. 2M HCl (50 mL) was added, and the organic product was extracted with Et₂O and washed with NaHCO₃ followed by water and brine. The product was dried with magnesium sulfate and all volatiles were removed by rotary evaporation, leaving a pale yellow oil. Remaining starting materials were distilled from the mixture at 55 °C and 200 mTorr. The resulting yellow oil was sufficiently pure for use in the next step. Yield 9 g (0.033 mol, 48%). ¹H NMR (CDCl₃) δ 7.2-7.4 (mult., 4H, aromatic), 5.38 (mult., 1H, C=CH₂),
5.05 (mult., 1H, C=CH₂), 2.15 (s, 3H C₃H₂Me), 2.0-1.0 (m, 7H, cyclohexyl), 0.90 (d, 3H, CHCMₑ₂), 0.82 (d, 3H, CHCMₑ₂), 0.72 (d, 3H, CHCMₑ₂).

1-((1S,2S,5R)-2-isopropyl-1-methoxy-5-methylcyclohexyl)-4-(prop-1-en-2-yl)benzene (MenthMPCP-2)

MenthMPCP-1 (9 g, 0.033 mol) was added via syringe to a stirring suspension of potassium hexamethyldisilazide (9.9 g, 0.050 mol, 1.5 eq) in 50 mL THF. The suspension became peach/orange and homogeneous, and was allowed to stir for 30 min. Methyl iodide (3.1 mL, 0.050 mol) was added via syringe, after which a white precipitate immediately formed. The mixture was allowed to stir 18 h, after which all volatiles were removed in vacuo. To the remaining white paste were added 100 mL H₂O and 100 mL Et₂O. The layers were separated and the aqueous layer was extracted with Et₂O. The combined organic layers were washed with H₂O and brine, dried with magnesium sulfate and concentrated by rotary evaporation. A white precipitate, which by ¹H NMR appears to be 4,4’-di(prop-1-en-2-yl)biphenyl (a byproduct in the synthesis of MenthMPCP-1), was separated from the product by passing the oil through a small plug of Celite. The product was purified by column chromatography (1:20 Ethyl Acetate: Hexanes) and was isolated as a pale yellow oil. Yield 8.9 g (0.031 mol, 94%). ¹H NMR (CDCl₃) δ 7.47 (d, 2H, aromatic), 7.27 (d, 2H, aromatic), 5.41 (mult., 1H, C=CH₂), 5.06 (mult., 1H, C=CH₂), 3.16 (s, 3H, OMe), 2.17 (s, 3H C₃H₂Me), 2.0-1.0 (m, 7H, cyclohexyl), 0.95 (d, 3H, CHCMₑ₂), 0.88 (d, 3H, CHCMₑ₂), 0.60 (d, 3H, CHCMₑ₂).

1-(2,2-dibromo-1-methylcyclopropyl)-4-((1S,2S,5R)-2-isopropyl-1-methoxy-5-methylcyclohexyl)benzene (MenthMPCP-3):
A 100 mL flask was charged with the whole amount (8.9 g, 0.031 mol) of MenthMPCP-2, 6 mL CHBr₃, and 500 mg cetrimide (hexadecyltrimethylammonium bromide, phase transfer agent). To the stirring mixture was added dropwise 7 mL of a 50% aqueous NaOH solution. The mixture became off-white, heterogeneous and was stirred vigorously. The progress of the reaction was monitored by ¹H NMR, and was complete after 48 h. 100 mL CHCl₃ and 100 mL H₂O were added to the mixture, the layers were separated, and the aqueous phase was extracted with CHCl₃. The combined organic layers were washed with water, 2% HCl, and brine, and dried with magnesium sulfate. The extracts were concentrated by rotary evaporation and purified by column chromatography (1:50 Ethyl Acetate: Hexanes). Yield 11.0 g (0.024 mol, 77%) pale yellow oil. ¹H NMR (CDCl₃) δ 7.2 (mult., 4H, aromatic), 3.15 (s, 3H, OMe), 1.70 (sept, 1H CH₂Me₂), 1.55 (s, 3H C₃H₂Me), 2.16 (mult., 2H, C₃H₂) 2.0-1.0 (in, 6H, cyclohexyl CH₂), 0.95 (d, 3H, CH₂Me₂), 0.85 (dd, 3H, CH₂Me₂), 0.54 (d, 3H, CH₂Me₂).

1-(2-bromo-1-methylcyclopropyl)-4-((1S,2S,5R)-2-isopropyl-1-methoxy-5-methylcyclohexyl)benzene (MenthMPCP-4):

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MenthMPCP-3 (11.0 g, 0.024 mol) was dissolved in 100 mL Et₂O and 141 μL Ti(O-i-Pr)₄ (0.48 mmol, 2%) was added via syringe. 13.0 mL 3M ethereal EtMgBr (0.039 mol, 1.6 eq) was added dropwise to the stirring solution, resulting in the evolution of gas, which was vented to an oil bubbler. After stirring for 2h, 50 mL H₂O was added, followed by 20% aq H₂SO₄ until all solids dissolved (~20 mL). The organic layer was separated and the aqueous layer was extracted with Et₂O. The combined organic layers were washed with H₂O and brine, dried with magnesium sulfate, and concentrated by rotary evaporation. The product was purified by column chromatography (1:50 Ethyl Acetate: Hexanes). Yield 5.5 g (0.0145 mol, 60%).

$^1$H NMR (CDCl₃) δ 7.2 (mult., 4H, aromatic), 3.25 (mult., 3H, C₃H₂Br), 3.15 (s, 3H, OMe), 1.70 (sept, 1H, CHCMe₂), 1.64 (s, 3H C₃H₂Me), 2.0-1.0 (m, 6H, cyclohexyl CH₂), 0.95 (d, 3H, CHCMe₂), 0.88 (d, 3H, CHCMe₂), 0.60 (d, 3H, CHCMe₂).

1-((1S,2S,5R)-2-isopropyl-1-methoxy-5-methylcyclohexyl)-4-(1-methylcycloprop-2-en-1-yl)benzene (MenthMPCP):

Potassium tert-butoxide (1.95 g, 0.0174 mol) was suspended in 100 mL anhydrous DMSO and stirred at 50 °C for 30 min until the solution was pale yellow and homogeneous. MenthMPCP-4 (5.5 g, 0.0145 mol) was added to the mixture via syringe. The mixture became deep blue and heterogeneous after stirring 5 minutes, and was stirred vigorously for 30 min. The mixture was poured in one portion into 100 mL H₂O in a 0 °C ice bath and became pale yellow and heterogeneous. The mixture was extracted with hexanes and washed with H₂O and brine. The extracts was dried with magnesium sulfate, and concentrated by rotary evaporation, leaving an oily off-white solid. The solid was recrystallized in 2 crops from hot hexane at -20 °C giving off-white feathery crystals; yield 4.1 g (0.013 mol, 95%). $^1$H NMR (C₆D₆, 500 MHz) δ 7.3 (mult., 4H, aromatic), 6.849 (s, 1H, C₃H₂), 6.843 (s, 1H, C₃H₂), 3.06 (s, 3H, OMe), 1.75 (sept,
1H CHCMe₂), 1.55 (s, 3H C₃H₂Me), 2.0-1.5 (m, 6H, cyclohexyl CH₂), 1.18 (d, 3H, CHCMe₂), 0.93 (d, 3H, CHCMe₂), 0.69 (d, 3H, CHCMe₂).

2,2'-dimethoxy-3-(prop-1-en-2-yl)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthalene (BitetMPCP-2):

1) Synthesis of isopropenyl boronic acid: 2-bromopropene (1.96 g, 16.2 mmol) was added to a THF suspension of Mg(0) turnings (activated with I₂), and the mixture was heated to reflux for 1.5 h then cooled to room temperature. The entire mixture was added via cannula to a THF solution of trimethyl borate cooled to 0 °C. The mixture immediately became gray and cloudy. 2M HCl (~20 mL) was added until the mixture became clear and yellow. The aqueous layer was extracted with diethyl ether. The combined organic layers were washed with sodium bicarbonate, water, and brine, dried with MgSO₄, and volatiles were removed by rotary evaporation. The product was isolated in near-quantitative yield as a white foam and stored at -20 °C for less than one h before further use.

2) Suzuki Coupling: Pd(PPh₃)₄ (390 mg, 2.5%), K₂CO₃ (3.73, 27 mmol, 2 eq), BitetMPCP-1 (5.42 g, 13.5 mmol), and 100 mL toluene were combined in a 300 mL sealable flask. Freshly prepared isopropenyl boronic acid was added via syringe as a 10 mL toluene suspension. The flask was sealed and heated to 90-100 °C for 18h. Water (100 mL) was added, then the aqueous layer was extracted with diethyl ether. The combined organic layers were washed with water and brine, dried with MgSO₄, and all volatiles were removed by rotary evaporation. Column chromatography on silica with 1:50 ethyl acetate : hexanes afforded 4.0 g (82%) of expected product as a white solid. ¹H NMR (CDCl₃) δ 7.14 (d, 1H, Ar), 7.06 (s, 1H, Ar), 6.84 (d, 1H, Ar), 5.24 (m, 1H, C=CH₂), 5.20 (m, 1H, C=CH₂), 3.78 (s, 3H, OMe), 3.48 (s,
3-(2,2-dibromo-1-methylcyclopropyl)-2,2′-dimethoxy-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthalene (BitetMPCP-3):

\[
\begin{align*}
\text{(R)} & \\
\text{O} & \\
\text{O} & \\
\text{Br} & \\
\text{Br} &
\end{align*}
\]

5.6 g (0.0155 mol) of BitetMPCP-2 was dissolved in 5 mL CHBr₃, stirring vigorously and heating slightly to completely dissolve. Cetrimide (1-(hexadecyl)-trimethylammonium bromide) (100 mg) was added to the solution as a phase-transfer agent. 5 mL of a 50 % w/w NaOH solution was added to the vigorously stirred solution, cooling in a water bath to maintain the temperature around 20 °C. The mixture was stirred vigorously for 72 hours, after which extraction into CHCl₃, washing, and column chromatography (silica, 2% ethyl acetate in hexanes) gave 3.5 g (60%) of the expected product as a yellow oil (mixture of two diastereomers). \(^1\)H NMR (CDCl₃) δ (1:1 mixture of 2 diastereomers) 7.09 (dd, 1H, Ar), 6.78 (t, 1H, Ar), 6.75 (t, 1H, Ar), 3.75, 3.72 (s, 3H, OMe, 2 diast.) 3.48, 3.46 (s, 3H, OMe, 2 diast.), 2.76 (mult, 4H, bitet-CH₂), 2.2-0.8 (mult, 15H, bitet-CH₂ and cyclopropane-CH₃).

3-(2-bromo-1-methylcyclopropyl)-2,2′-dimethoxy-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthalene (BitetMPCP-4):
BitetMPCP-3 (3.5 g, 6.55 mmol) was dissolved in 100 mL diethyl ether in a 250-mL round bottom flask and 100 µL (0.34 mmol, 5%) of Ti(OiPr)$_4$ was added via syringe. The solution was chilled in an ice bath and 3.3 mL (9.8 mmol, 1.5 eq) of EtMgBr (3M in Et$_2$O) was added dropwise via syringe over 5 minutes. The mixture became deep brown and was allowed to stir for 2 h at room temperature. Extraction into ether, washing, and column chromatography (silica, 2% ethyl acetate in hexanes) gave 1.037 g (2.28 mmol, 35%) of the expected product as a white solid. $^1$H NMR (CDCl$_3$) δ 7.07 (d, 1H, Ar), 6.91 (s, 1H, Ar), 6.76 (d, 1H, Ar), 3.71 (d, 3H, OMe), 3.40 (d, 3H, OMe), 3.20 (dd, 1H, CH$_2$CHBr), 2.76 (mult, 4H, bitet-CH$_2$), 2.30 (mult, 4H, bitet-CH$_2$), 2.00 (mult, 4H, bitet-CH$_2$), 1.72 (mult, 4H, bitet-CH$_2$), 1.56 (s, 3H, CH$_3$), 0.97 (dt, 2H, CH$_2$CHBr).

2,2'-dimethoxy-3-(1-methylcycloprop-2-en-1-yl)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthalene (BitetMPCP):

Potassium tert-butoxide (306.5 mg, 1.2 eq) was dissolved in 100 mL DMSO in a 200 mL round bottom flask. To it was added a hexanes solution of monobromide BitetMPCP-4 (1.037 g, 2.28 mmol). The reaction was stirred vigorously, and became deep red-brown immediately. $^1$H NMR showed that the starting material was consumed after 5 h, after which the mixture was extracted.
into hexanes, washed with water and brine, dried with magnesium sulfate, filtered, and concentrated by rotary evaporation to give a pale yellow oil. The product was recrystallized from hexanes at -20 °C overnight. The aqueous layer was re-extracted with dichloromethane and washed and dried in the same manner as the hexane extracts to afford another 0.9 g of crude material (94% total). \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.61 (d, 1H, C\(_3\)H\(_2\), J\(_HH\) = 1.0 Hz), 7.56 (d, 1H, C\(_3\)H\(_2\), J\(_HH\) = 1.0 Hz), 7.04 (d, 1H, Ar), 6.90 (s, 1H, Ar), 6.74 (d, 1H, Ar), 3.68 (s, 3H, OMe), 3.47 (s, 3H, OMe), 2.74 (mult, 4H, bitet-CH\(_2\)), 2.23 (mult, 4H, bitet-CH\(_2\)), 2.00 (mult, 4H, bitet-CH\(_2\)), 1.63 (mult, 4H, bitet-CH\(_2\)), 1.53 (s, 3H, CH\(_3\)).

\((S)\)-4-phenylpent-4-en-2-ol (OMeMPCP-1):

\(\alpha\)-Bromostyrene (15 g, 0.0812 mol) was added via addition funnel to a 100 mL THF suspension of 5 g magnesium turnings (activated with I\(_2\)). The mixture refluxed spontaneously, and became deep reddish brown. After further heating to reflux for 2 hours, the solution was allowed to cool to room temperature. In a separate flask, 3 g (0.0162 mol, 0.2 eq) copper iodide was suspended in 50 mL THF under N\(_2\). To this flask was added 5.7 mL (0.0812 mol) (S)-propylene oxide (Alfa Aesar) via syringe, and the solution was cooled to 0 °C. The supernatant of the Grignard suspension was then added to the epoxide solution via cannula. The mixture immediately became deep green-brown and was warmed to room temperature and allowed to stir for one hour. Water (~50 mL) was added, and the cloudy mixture was filtered through filter paper to give a clear solution. The aqueous layer was separated and extracted with dichloromethane. The combined organic layers were washed with water and brine, dried with magnesium sulfate, and the volatiles were removed by rotary evaporation, leaving a yellow oil. The oil was purified by column chromatography first by eluting an impurity with 10% ethyl acetate in hexanes, followed by washing the product from the column with 1:1 isopropanol: hexanes. Yield 6.9 g (0.0422 mol, 51%) pale yellow oil. \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.41-7.29 (m, 5H, Ar), 5.40 (d, 1H, olefin), 5.16 (d, 1H, olefin), 3.84 (q, 1H, CHMe), 2.74 (m, 1H CH\(_2\)), 2.57 (m, 1H CH\(_2\)), 1.65 (s, 1H, OH), 1.20 (d, 3H, CH\(_3\)).
(S)-(4-methoxypent-1-en-2-yl)benzene (OMeMPCP-2):

(S)-4-Phenylpent-4-en-2-ol (OMeMPCP-1, 6.9 g, 0.0422 mol) was added to a 100 mL THF suspension of sodium hydride (1.5 eq, 0.063 mol, 2.53 g of 60% w/w oil dispersion) at 0 °C. The mixture was allowed to warm to room temperature and allowed to stir for 10 hours. Methyl iodide (3.9 mL, 0.063 mol, 1.5 eq) was added via syringe and the mixture was stirred for 2 hours. Water was added until the mixture became clear, then ether was added and the resulting aqueous layer was separated and extracted with ether. The combined organic layers were washed with water and brine, dried with magnesium sulfate, and the volatiles were removed by rotary evaporation, leaving a yellow oil. The product was purified by column chromatography with 5% ethyl acetate in hexanes. Unreacted starting alcohol could be recovered from the column after eluting with 20% isopropanol in hexanes. Yield 5.8 g (0.0329 mol, 78%) colorless oil. 'H NMR (CDCl₃) δ 7.43-7.26 (m, 5H, Ar), 5.31 (d, 1H, olefin), 5.13 (d, 1H, olefin), 3.36 (m, 1H, CHMe), 3.29 (s, 3H, OMe), 2.92 (dd, 1H, CH₂), 2.47 (dd, 1H, CH₂), 1.11 (d, 3H, CH₃).

(2,2-dibromo-1-((S)-2-methoxypropyl)cyclopropyl)benzene (OMeMPCP-3):

(S)-(4-methoxypent-1-en-2-yl)benzene (OMeMPCP-2, 5.8 g, 0.0329 mol) and 500 mg cetrimide (1-(hexadecyl)-trimethylammonium bromide) were dissolved in 10 mL bromoform in a 50 mL flask under air. 10 mL of a 50% sodium hydroxide solution was added to the mixture dropwise, which became deep brown and biphasic. The mixture was stirred vigorously for 10 hours, after which 'H NMR spectroscopy showed complete consumption of the starting material.
Chloroform and water were added (100 mL each) and the aqueous layer was separated and extracted with chloroform. The combined organic layers were washed with 2% HCl, followed by saturated sodium bicarbonate solution, water, and brine, dried with magnesium sulfate, and the volatiles were removed by rotary evaporation, leaving a brown oil. Residual bromoform was removed in vacuo at 40 °C and 200 mTorr. The resulting brown oil was purified by short-column chromatography, eluting with 10% ethyl acetate in hexanes. Yield 9.17 (0.0264 mol, 80%), isolated as pale orange oil. ¹H NMR (CDCl₃) δ 7.40-7.26 (m, 5H, Ar), 3.16, 3.15 (s, 2 diastereomers, 1H total, OMe), 3.0 (mult, 1H CH), 2.8-1.8 (multiple aliphatic peaks for 4 different CH₂ peaks in two diastereomers, 4H), 1.13, 1.03 (d, 2 diastereomers, 3H total, CHCH₃).

(2-bromo-1-((S)-2-methoxypropyl)cyclopropyl)benzene (OMeMPCP-4):

(2,2-dibromo-1-((S)-2-methoxypropyl)cyclopropyl)benzene (OMeMPCP-3, 9.2 g, 0.0264 mol) was dissolved in 50 mL ether under N₂, and 0.77 mL (2.64 mmol, 10%) Ti(OiPr)₄ was added via syringe. The solution was cooled to 0 °C and EtMgBr (11.4 mL of 3M solution in ether, 0.0343 mol, 1.3 eq.) was added via syringe. The mixture immediately became deep brown and gas evolution was observed. After stirring 10 hours, the reaction was quenched with dilute sulfuric acid until colorless. The aqueous layer was separated and extracted with ether. The combined organic layers were washed with saturated sodium bicarbonate solution, water, and brine, dried with magnesium sulfate, and the volatiles were removed by rotary evaporation, leaving a yellow oil. The oil was purified by short column chromatography (10% ethyl acetate in hexanes) to give a pale oil (6.1 g, 0.023 mol, 87%). ¹H NMR (CDCl₃) (mixture of 4 expected isomers) δ 7.39-7.20 (m, 5H, Ar), 3.21, 3.20, 3.19, 3.17 (4 isomers, OMe), remaining aliphatic resonances are too complicated to assign.

(S)-(1-(2-methoxypropyl)cycloprop-2-en-1-yl)benzene (OMeMPCP-1)
Potassium t-butoxide (3.08 g, 0.0275, 1.2 eq.) was dissolved in 75 mL anhydrous DMSO under N₂ (heated to 50 °C to completely dissolve, then cooled to room temperature). (2-Bromo-1-((S)-2-methoxypropyl)cyclopropyl)benzene (OMeMPCP-4, 6.1 g, 0.023 mol) was added to the pale yellow solution via syringe. The solution immediately became deep red/brown, then deep green/brown. After stirring at room temperature for one hour, the entire mixture was poured into 100 mL ice-cold water and became yellow and cloudy. The aqueous layer was separated and extracted with 10 x 75 mL hexanes. The combined organic layers were washed with water and brine, dried with magnesium sulfate, and the volatiles were removed by rotary evaporation, leaving a red/orange oil. The oil was purified by column chromatography (1:30 ethyl acetate: hexanes) and isolated as a colorless oil (2.13 g, 0.011 mol, 49%). ¹H NMR (C₆D₆) δ 7.22 (m, 5H, Ar), 6.96 (s, 1H, C₃H₂), 6.87 (s, 1H, C₃H₂), 3.11 (m, 1H, CMeH), 3.05, (s, 3H, OMe), 2.35 (dd, 1H, CH₂), 1.90 (dd, 1H, CH₂), 1.03 (d, 3H, CMeH).
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Chapter 4

Stereoselective ROMP of racemic and enantiomerically pure chiral monomers

Portions of this chapter have appeared in print:

INTRODUCTION

We recently reported the cis, syndiotactic ROMP of cyclic monomers using monoaryloxide monopyrrolide (MAP) imido alkylidene molybdenum initiators. The current hypothesis explaining the stereoselectivity of MAP catalysts in ROMP is that the configuration of the incoming monomer is determined by the chirality at the metal center, and that the configuration of the metal inverts with each productive metathesis step. These two factors lead to the production of syndiotactic polymer. Using the same argument, we predicted that this alternating configuration of the metal possibly could be exploited to polymerize a racemic mixture of a chiral monomer to produce a regular polymer structure in which the two enantiomers of the monomer alternate, as described in Scheme 4.1.

![Scheme 4.1: Potential ROMP of alternating enantiomers using a MAP initiator](image)

The process described in Scheme 4.1 could potentially lead to a regular polymer structure that is extremely rare – a literature search revealed only a single report of an ROMP polymer containing alternating enantiomers. The reported polymerization used 1-methylnorbornene as monomer and ReCl$_5$ as catalyst, however the exact mechanism of stereocontrol with this system was not understood and is likely monomer-derived. The authors point out that a 68% enantioenriched sample of 1-methylnorbornene could not be polymerized in good yield, suggesting that the reason for such high alternating selectivity in the ROMP of (rac)-1-methylnorbornene is that the homopolymerization of either enantiomer is not possible.
The goal of our project was development of a well defined, homogeneous ROMP system that is selective for the formation of polymers with alternating enantiomers through a logical mechanism such as the one described in Scheme 4.1. Due to our previous success in the selective ROMP of 2,3-disubstituted norbornadienes, we chose to begin our investigations with racemic 5,6-endo,exo-disubstituted norbornenes.

RESULTS AND DISCUSSION

I. Cis, Syndioselective alternating copolymerization of enantiomers

Molybdenum MAP compounds containing bulky phenoxides such as compounds 1a-b in Figure 4.1 have shown excellent selectivity in ROMP of cyclic monomers towards the synthesis of cis, syndiotactic polymers. 1 To form a polymer of a single structure that contains alternating enantiomers, the polymer must be tactic and composed of entirely cis or trans double bonds. Therefore, our initial efforts focused on MAP initiators 1a and 1b that form cis, syndiotactic ROMP polymers of substituted norbornadienes.

I. A. Stereoselective ROMP of (rac)-DCMNBE with MAP complexes

When 100 equivalents of (rac)-5,6-dicarbomethoxynorbornene (rac-DCMNBE, Scheme 4.2) was added to a toluene solution of 1b, 1H NMR spectroscopy showed only slow consumption of the monomer (~50% consumed after 48 hours at room temperature). The 1H

![Figure 4.1: Molybdenum alkylidene compounds used as ROMP initiators. Ad = 1-adamantyl, Ar' = 2,6-dimethylphenyl](image)
While it is unlikely that a racemic monomer could afford a polymer containing a single enantiomer, it could theoretically be possible through perfect kinetic resolution, and therefore a cis/isotactic/homopolymer structure cannot immediately be discarded for poly-rac-DCMNBE obtained with 1a. Fortunately, the presence of an isotactic structure here can be disproved by comparison of the new polymer with the known cis, isotactic poly-(+)-DCMNBE reported in the literature. The \( ^1\)H NMR spectrum of poly-rac-DCMNBE\(_{1a}\) contains olefinic resonances with chemical shifts within 0.05 ppm of the reported olefinic resonances of cis, iso-poly-(+)-DCMNBE, which is too similar to definitively claim that the two structures are different. To prove their difference, cis, isotactic-poly-(+)-DCMNBE was prepared independently by the ROMP of (+)-DCMNBE with \( \text{Mo(NAr')}(\text{CHCMe}_2\text{Ph})(\text{rac-3,3'-di-tert-butyl-5,5'-bis-trifluoromethyl-6,6'\text{-dimethyl-1,1'-biphenyl-2,2'-diolate})} \) (2, Ar’ = 2,6-dimethylphenylimido), a catalyst similar to that reported in the literature for isospecific ROMP of (+)-DCMNBE. The \( ^1\)H NMR spectrum of a physical mixture of the two polymers, obtained at 500 MHz in CDCl\(_3\), and displayed in Figure 4.4 shows that the olefinic protons in the two polymers are distinct.

![Figure 4.4: Olefinic region of \( ^1\)H NMR spectrum (CDCl\(_3\)) of a mixture of cis,syndio,alt-polyDCMNBE (obtained from ROMP of rac-DCMNBE with [Mo]NAd(pyr)(OHMT), indicated with blue stars) and cis,iso,sing-polyDCMNBE (indicated with red stars).](image-url)
NMR spectrum of the resulting polymer showed that it contained no long range structure. The inability of 1b to efficiently polymerize rac-DCMNBE can be ascribed to the extreme steric bulk of the catalyst combining with the bulk of the monomer to shut down reactivity. The 5-endo substituent of rac-DCMNBE is oriented in the direction of the metathesis-active double bond of the monomer than the 2- or 3-substituents of DCMNBD, meaning that DCMNBE is effectively a more sterically encumbered monomer. For this reason, a catalyst containing the less bulky phenoxide hexamethylterphenoxide, 1a, was investigated for the ROMP of rac-DCMNBE.

When rac-DCMNBE is added to a toluene solution containing 1% 1a, a white solid precipitate immediately forms. NMR spectroscopy showed complete consumption of the monomer within one hour. After quenching with excess benzaldehyde (~200 eq) and precipitation from methanol, a white solid polymer was isolated. The $^1$H NMR spectrum of the isolated polymer is displayed in Figure 4.2. Both the proton NMR (Figure 4.2) and $^{13}$C NMR spectra of poly-rac-DCMNBE obtained with 1a show sharp resonances corresponding to the resonances of a highly regular polymer. The olefinic region of the $^1$H NMR spectrum exhibits 2 pseudotriplet resonances, as expected for a polymer that contains two inequivalent olefinic protons. The two olefinic proton signals show coupling to each other, with a $J_{HH}$ of ~11 Hz, as expected for a cis double bond. The coupling between the two olefinic protons was confirmed though a proton/proton COSY spectrum (Figure 4.3).

![Figure 4.3: Proton-Proton COSY spectrum (CDCl$_3$, 500 MHz) of cis,syndio,alt-polyDCMNBE obtained with 1a (expanded olefinic region).](image-url)
There are eight possible regular structures that can be envisioned to arise from the ROMP of rac-DCMNBE, taking into account the following three factors: (1), structure about the double bond (cis vs. trans), (2), orientation of each monomer unit relative to the previous (syndiotactic vs. isotactic), and (3), whether each enantiomer of the monomer is followed by the same enantiomer or the opposite enantiomer (alternating copolymer of enantiomers vs. homopolymer of one enantiomer). The four structures containing trans double bonds can be discarded in our case, due to the cis-magnitude coupling constant between the olefinic protons. The four remaining cis structures are displayed in Scheme 4.3; of these, only two contain distinct olefinic protons that should be coupled to each other, namely cis/syndiotactic/alternating, and cis/isotactic/homopolymer.

Scheme 4.3: Four possible cis regular structures of ROMP polymers derived from racemic 5,6-disubstituted norbornenes
While it is unlikely that a racemic monomer could afford a polymer containing a single enantiomer, it could theoretically be possible through perfect kinetic resolution, and therefore a cis/isotactic/homopolymer structure cannot immediately be discarded for poly-rac-DCMNBE obtained with 1a. Fortunately, the presence of an isotactic structure here can be disproved by comparison of the new polymer with the known cis, isotactic poly-(+)-DCMNBE reported in the literature. The \(^1\)H NMR spectrum of poly-rac-DCMNBE\(_{1a}\) contains olefinic resonances with chemical shifts within 0.05 ppm of the reported olefinic resonances of cis, iso-poly-(+)-DCMNBE, which is too similar to definitively claim that the two structures are different. To prove their difference, cis, isotactic-poly-(+)-DCMNBE was prepared independently by the ROMP of (+)-DCMNBE with Mo(NAr')(CHCMe₂Ph)(rac-3,3'-di-tert-butyl-5,5'-bis-trifluoromethyl-6,6'dimethyl-1,1'-biphenyl-2,2'-diolate) (2, Ar' = 2,6-dimethylphenylimido), a catalyst similar to that reported in the literature for isospecific ROMP of (+)-DCMNBE. The \(^1\)H NMR spectrum of a physical mixture of the two polymers, obtained at 500 MHz in CDCl₃, and displayed in Figure 4.4 shows that the olefinic protons in the two polymers are distinct.

![Figure 4.4: Olefinic region of \(^1\)H NMR spectrum (CDCl₃) of a mixture of cis,syndio,alt-polyDCMNBE (obtained from ROMP of rac-DCMNBE with [Mo]NAd(pyr)(OHMT), indicated with blue stars) and cis,iso,sing-polyDCMNBE (indicated with red stars).](image-url)
The spectrum displayed in Figure 4.4 definitively proves that poly-rac-DCMNBE\textsubscript{1a} is in fact a new polymer structure that is distinct from the cis, isotactic poly-\textoplus{}-DCMNBE reported in the literature. Differential Scanning Calorimetry revealed a glass transition temperature of 85 °C for cis-isotactic poly-\textoplus{}-DCMNBE, however no thermal transitions were found for cis-syndiotactic poly-rac-DCMNBE below its decomposition temperature (generally around 250 °C for polynorbornenes in this report). Not surprisingly, when polymerization of rac-DCMNBE was performed using 2, the $^1$H NMR spectrum of the resulting polymer showed multiple broad olefinic resonances, which likely is due to an irregular polymer that contains random distribution of the two enantiomers, as expected for a catalyst of fixed chirality.

The broad resonance in the $^1$H NMR spectrum of poly-rac-DCMNBE in Figure 4.2 around 5.47 ppm is likely due to the presence of a small amount of trans double bonds in the polymer. The resonance integrates to ~2% of the total olefinic resonances, and assuming that this resonance represents only one of the expected two trans olefinic protons, the trans content of the polymer is estimated to be ~5% of the total. Polymerization of rac-DCMNBE with 1a at 0 °C and -15 °C did not lead to any change in the NMR spectrum of the polymer as compared to the sample prepared at room temperature. Efforts towards synthesis of a polymer that does not contain this small trans impurity will be presented later in this report and will be one aspect of future goals for this system.

I. B. Monomer scope in cis, syndiotactic ROMP of racemic monomers

The co-ROMP of enantiomers to form cis, syndiotactic alternating poly-rac-DCMNBE represents a new polymer microstructure available through ROMP, therefore we were interested in extending this new type of selectivity to other disubstituted norbornene-based monomers. The cis and syndioselectivity of 1a was first extended to the ROMP of (rac)-2,3-dicyanonorbornene (rac-DCNNBE). When 100 equivalents of rac-DCNNBE were added to a dichloromethane solution of 1a, the solution immediately became thick and cloudy.
After the usual workup, a white solid polymer was isolated that was insoluble in chloroform, methylene chloride, and toluene, and had limited solubility in acetone. A $^1$H NMR spectrum of sufficient quality (spectrum available in Experimental section) was obtained in acetone-$D_6$ at 50 °C, which exhibits the two pseudotriplet resonances expected for a cis, syndiotactic structure containing alternating enantiomers, showing that the selectivity of 1a in ROMP was successfully realized with rac-DCNNBE.

When 100 equivalents of endo,exo-5,6-dimethylnorbomene (rac-DMNBE) were added to a toluene solution of 1a, a white precipitate formed immediately. After quenching with benzaldehyde and washing with methanol, white solid polymer was isolated, which exhibited no observable $^1$H NMR signal in CDCl$_3$, toluene, acetone, CD$_2$Cl$_2$, THF, or cyclohexane. A weak signal could be observed in o-dichlorobenzene-$D_4$, but the $^1$H NMR spectrum showed only broad olefinic resonances, likely corresponding to polymer of no long-range structure. It is possible that the methyl groups of the monomer are not large enough for the catalyst to differentiate between the two enantiomers or to form selectively syndiotactic polymer. The lack of success in selective ROMP of rac-DMNBE led us to look towards racemic substituted norbornenes with larger 5,6 substituents and investigate their activity in ROMP.

In an effort to further extend the scope of cis-syndiotactic ROMP of racemic monomers, a number of ester, ether, and silyl ether-substituted 5,6-disubstituted norbornenes were prepared,
and are displayed in Figure 4.6. The syntheses of the racemic ester-substituted monomers rac-DCENBE and rac-DCTBuNBE have been reported and were prepared as described in the experimental section.

The addition of 100 equivalents of either (rac)-DCENBE or (rac)-DCTBuNBE to 1a led to the formation of polymers that exhibited the two pseudo-triplet resonances in the $^1$H NMR spectra expected for a highly $cis$, syndiotactic alternating structure, showing that the selectivity for $cis$-syndio-alt polymer is not limited to methyl ester substituted norbornenes. The $^1$H NMR spectra (available in Experimental Section of this report) of both poly-rac-DCENBE$_{1a}$ and poly-rac-DCTBuNBE$_{1a}$ each showed small broad resonances corresponding to $<5\%$ of $trans$ olefins.

The success of the alternating co-ROMP of enantiomers in the system described here lies in the preference of each enantiomer of the MAP catalyst for one or the other enantiomer of the monomer. The two steps shown in Scheme 4.1 show a situation that should lead to a $cis$, syndio, alt polymer: the S configuration of Mo ($S_{Mo}$) only reacts with the (+)-monomer, and the R configuration of Mo ($R_{Mo}$) only reacts with the (-)-monomer (it is not known which enantiomer of the catalyst reacts faster with either enantiomer of the monomer, therefore the favorable catalyst/monomer combinations are presented here only for purpose of argument). According to the proposal described in Scheme 4.1, the reaction of $S_{Mo}$ with (-)-monomer and the reaction of $R_{Mo}$ with (+)-monomer, referred to from now on as the “mismatched” cases, should be disfavored and therefore slow. In an effort to quantify the expected difference in rates between the mismatched and matched cases, kinetic studies were carried out on the ROMP of DCTBuNBE with 1a (precipitation of the highly regular polymers during polymerization prohibited similar kinetic evaluation of the ROMP of DCMNBE or DCENBE).

When fifty equivalents of rac-DCTBuNBE were added to 1a in toluene-$d_8$ at a monomer concentration of 29 mM at 20.2 °C, $^1$H NMR spectroscopy showed complete conversion of the monomer and production of the expected polymer within 4 minutes. Under the same conditions, 50 equivalents of enantiomerically pure (-)-DCTBuNBE required $>45$ minutes to achieve full consumption of monomer. The consumption of rac-DCTBuNBE and (-)-DCTBuNBE over time in the presence of 1a is shown in Table 4.1.
This observed difference in rates of reaction of the racemic and enantiomerically pure monomers is consistent with the mechanism described in Scheme 4.1. In the racemic case, both enantiomers of the catalyst are presented with a matching enantiomer of the monomer, and therefore each step is favorable. In contrast, in the enantiomerically pure case, the (-)-monomer is forced to react with both $R_{Mo}$ (favorable) and $S_{Mo}$ (unfavorable). The unfavorable "mismatched" step becomes the rate limiting step, making the ROMP of (-)-DCtBuNBE with 1a measurably slower than that of rac-DCtBuNBE.

Most of the highly regular cis, syndiotactic polymers presented up to this point have exhibited very limited solubility in organic solvents and have been insufficiently soluble in THF to determine their molecular weights by GPC. Fortunately, the highly cis, syndio, alt-poly-DCtBuNBE prepared here was more soluble in THF, allowing us to perform GPC analysis on the resulting polymer. The results of this analysis are presented in Table 4.2.
As seen in Table 4.2, up to 2000 equivalents of rac-DctBuNBE can be polymerized by 1a to give quantitative conversion to the expected polymer. All of the polymers represented in Table 4.2 were approximately 95% regular and exhibited the same cis,syndio,alt structure seen by 1H NMR spectroscopy in the 100-mer. The attempted polymerization of 4000 equivalents of rac-DctBuNBE in this system only afforded trace amounts of polymer, likely due to the presence of <0.05% water, acid, or oxygen impurities in the monomer or solvent. The PDI of each of the polymers of length under 400 n is less than 1.05, suggesting a highly living polymerization. Unfortunately, the 700-, 1000-, and 2000-mer polymers were insufficiently soluble in THF to determine their molecular weights and polydispersity by GPC in this solvent.

Another indication that the ROMP of rac-DctBuNBE with MAP catalysts is highly living is the linear relationship between the number of equivalents and the molecular weight of the polymers measured by GPC (polystyrene standards). A plot of this relationship is displayed in Figure 4.7. By analogy to the cis, syndiotactic, alternating ROMP of rac-DctBuNBE, the cis, syndiotactic, alternating ROMP of other substituted norbornene monomers can be assumed to also be highly living.
With the exception of rac-OTIPSNBE, the ether-substituted monomers presented in Figure 4.6 were prepared as reported in the literature by reduction of rac-DCMNBE to (rac)-endo,exo-5,6-(CH$_2$OH)$_2$norbornene with lithium aluminum hydride followed by protection with the appropriate silyl or methyl halide or triflate. Racemic OTIPSNBE was synthesized by analogy to reported preparations for similar compounds (details available in Experimental section). The results of polymerizations of ether-substituted norbornenes with 1a and Mo(NAd)(CHCMe$_2$Ph)(MePyr)(HMTO) (3a, MePyr = 2,5-dimethylpyrrolide) are presented in Table 4.3.

As seen in Table 4.3, relatively high, but not perfect cis-selectivity was observed in all cases when the catalyst used was 1a, and the cis portion in each exhibited the expected two pseudotriplets expected for a highly syndiotactic polymer that contains alternating enantiomers. Changing only the pyrrolide ligand to dimethylpyrrolide in 3a led to polymer with increased cis content in the polymerization of OMeNBE, but reduced cis content and syndioselectivity in both OTMSNBE and OTBSNBE.

The drastic change in polymer regularity associated with the seemingly small change in catalyst structure between the pyrrolide and dimethylpyrrolide ligands is surprising, but shows how sensitive the system is to minor steric changes. There was no clear trend in cis selectivity when the bulk on the monomer increased from trimethylsilyl to tert-butyldimethylsilyl to triisopropylsilyl-substituted norbornenes. It is possible that the steric bulk of the monomers presented in Figure 4.6 is sufficiently separated from the olefin by the flexible methylene linker,
<table>
<thead>
<tr>
<th>Monomer</th>
<th>Catalyst</th>
<th>Polymer Structure</th>
<th>% Cis</th>
<th>Bias towards syndio/alt?</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMeNBE</td>
<td>1a [Mo]NAd(pyr)(HMTO)</td>
<td></td>
<td>60</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td>3a [Mo]NAd(MePyr)(HMTO)</td>
<td></td>
<td>90</td>
<td>yes</td>
</tr>
<tr>
<td>OTMSNBE</td>
<td>1a [Mo]NAd(pyr)(HMTO)</td>
<td></td>
<td>85</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td>3a [Mo]NAd(MePyr)(HMTO)</td>
<td></td>
<td>75</td>
<td>no</td>
</tr>
<tr>
<td>OTBSNBE</td>
<td>1a [Mo]NAd(pyr)(HMTO)</td>
<td></td>
<td>90</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td>3a [Mo]NAd(MePyr)(HMTO)</td>
<td></td>
<td>50</td>
<td>no</td>
</tr>
<tr>
<td>OTIPSNBE</td>
<td>1a [Mo]NAd(pyr)(HMTO)</td>
<td></td>
<td>85</td>
<td>yes</td>
</tr>
</tbody>
</table>

Table 4.3: Polymerization results with various etherNBE monomers. Percent cis approximated by integration of 1H NMR spectrum of polymer. [Mo] = Mo(CHCMe_2Ph). 3a prepared in situ as described in Chapter 2.

meaning changes in the bulk so removed from the double bond do not make a difference on the stereochemistry of the polymerization.

I. C. Ligand Variation for Stereoselective ROMP

The results presented in the previous section have showed that no one catalyst is perfect; while 1a was able to produce >95% cis, syndiotactic poly-rac-DCMNBE and DCNNBE, the same catalyst polymerized a number of other monomers with only 60-90% cis content. The origin of the trans impurities in the polymers presented here was not obvious, however one option is that a small amount of “anti” alkylidenes are active during polymerization (“anti” referring to the orientation in which the alkylidene ligand is pointed away from the imido group, and “syn” when the alkylidene is pointed towards the imido ligand). Syn-anti rotation of the alkylidene has been observed to be highly dependent on the electron-donating ability of the ligands; for this reason, electronic variations on the hexamethylterphenol (HMTOH) ligand were investigated.

The syntheses of 4-bromohexamethylterphenol and 4-nitrohexamethylterphenol along with the syntheses of the associated MAP compounds 4a and 4b have been reported in Chapter 2.
of this report. It would be expected that if syn/anti alkylidene rotation was occurring on the time scale of polymerization, then the electronic differences between 4a/b and 1a would lead to a noticeable difference in poly-(rac)-DCMNBE structure obtained with each initiator.

Other ligand variations were attempted to investigate the influence of the ligand substituents on the outcome of the polymerization. The addition of one equivalent of 2,6-(2,6-dimethylphenyl)2phenol (XylPhOH, prepared according to the literature) to Mo(NAd)(CHCMe2Ph)(pyr)2 led to the expected MAP compound 1c (Figure 4.1).

While the variations presented in this report so far have focused only on changes in the pyrrolide or phenoxide ligands, one compound was prepared using an imido ligand other than adamantyl imido, namely 2,6-dimethylphenylimido. While the associated bispyrrolide complex, Mo(NAr')(CHCMe2Ph)(pyr)2 (Ar' = 2,6-Me2Ph) has not been isolated cleanly, it can be prepared and used in situ by addition of two equivalents of lithium pyrrolyde to Mo(NAr')(CHCMe2Ph)(OTf)2(dme). Using this method, 6a and 6b were prepared from in situ-generated Mo(NAr')(CHCMe2Ph)(pyr)2 upon the addition of one equivalent of HMTOH or HIPTOH. Details of this method are available in Chapter 2.

Addition of 100 equivalents of rac-DCMNBD to initiators 1c, 3b, 4a-b, 5a, and 6a in toluene led to the formation of the expected ROMP polymers. The results of these

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Polymer structure</th>
<th>% Cis</th>
<th>Pseudotriplet pattern in olefinic region of 1H NMR?</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a* [Mo]NAd(MePyr)(HMTO)</td>
<td></td>
<td>60</td>
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</tr>
<tr>
<td>5a [Mo]NAd(pyr)(TMS3SiO)</td>
<td></td>
<td>90</td>
<td>no</td>
</tr>
<tr>
<td>4a* [Mo]NAd(pyr)(BrHMTO)</td>
<td></td>
<td>95</td>
<td>yes</td>
</tr>
<tr>
<td>4b* [Mo]NAd(pyr)(NO2HMTO)</td>
<td></td>
<td>95</td>
<td>yes</td>
</tr>
<tr>
<td>1c [Mo]NAd(pyr)(XylPhO)</td>
<td></td>
<td>95</td>
<td>yes, reduced purity</td>
</tr>
<tr>
<td>6a* [Mo]NAr'(pyr)(HMTO)</td>
<td></td>
<td>95</td>
<td>yes</td>
</tr>
</tbody>
</table>

Table 4.4: ROMP of rac-DCMNBE with various MAP compounds. Cis content of polymer det. by 1H NMR. [Mo] = Mo(CHCMe2Ph). *Starred compounds prepared in situ as described in Chapter 2 of this report.
polymerizations are presented in Table 4.4; portions of the $^1$H NMR spectra of the resulting polymers are presented in Figure 4.8.

As seen in Table 4.4, changes in the pyrrolide or phenoxide ligand of MAP catalysts moving away from $\text{1a}$ have an effect on the stereochemistry of the resulting polymer, as expected. When the only change is from a pyrrolide ligand to the dimethylpyrrolide ligand, moving to $\text{Mo(NAd)(CHCMe}_2\text{Ph)(MePyr)(HMTO)}$ (3a) as the catalyst, both the cis selectivity and the syndioselectivity of the ROMP of $\text{rac-DCMNBE}$ are destroyed. It is somewhat surprising that such a seemingly small change in ligand structure would have such an effect on the resulting polymer, especially if the monomer truly does approach the metal trans to the pyrrolide ligand, meaning the methyl groups of the pyrrolide should never come in close contact with the incoming monomer. Perhaps instead of directly interacting with the monomer, the methyl groups of the dimethylpyrrolide ligand in 3a instead interact with the substituents on the phenoxide, forcing the phenoxide to adopt a different configuration than in the parent pyrrolide case $\text{1a}$.

Another steric change on the catalyst system is presented in Table 4.4: moving from the 2,6-bis-(2,4,6-trimethyl)terphenoxide (HMTO) ligand in initiator $\text{1a}$ to the 2,6-bis-(2,6-dimethyl)terphenoxide (abbreviated as XylPhO) in $\text{1c}$. The only change in $\text{1c}$ as compared to $\text{1a}$ is the removal of the two para methyl groups on the terphenoxide ligand. As shown in Table 4.4, this change had little effect on the cis-selectivity of the reaction, but did have an effect on the stereochemistry of the polymerization, as observed by a disruption of the expected pseudotriplet pattern in the olefinic region of the $^1$H NMR spectrum of the polymer. When this same initiator $\text{1c}$ is used to catalyze the polymerization of $\text{OTBSNBE}$, the resulting polymer contained ~90% cis olefins, but the cis portion of the polymer did not contain any clear long-range structure as seen by $^1$H NMR. It seems that changes in remote substituents such as the para-methyl groups of the phenoxide can in fact control either the syndioselectivity in this ROMP reaction, or the preference of the catalyst for a copolymer of alternating enantiomers. This result is in contrast with the results presented in Chapter 3 with initiator $\text{1c}$: removal of the para-methyl groups of the phenoxide did not have any effect on the stereochemical outcome of the cis, syndioselective ROMP of $\text{DCMNBD}$.

Overall, it appears that steric changes have a greater effect on selectivity of the ROMP of (rac)-$\text{DCMNBE}$ than electronic changes. When either BrHMTO or NO$_2$HMTO were used as
Figure 4.8: Olefinic regions of $^1$H NMR spectra (CDCl$_3$) of poly(rac)DCMNBE (various initiators as indicated)
supporting ligands in MAP compounds, the outcome of the polymerization was barely affected (Table 4.4). The only apparent difference in the structure of the resulting poly-rac-DCMNBE with 4a and 4b as compared to 1a is a very slightly increased trans content when the phenoxide is BrHMTO, and a very slightly decreased trans content in the case of NO₂HMTO, as calculated by integration of the broad resonance at 5.47 ppm in the ¹H NMR of the polymer. Since the differences in the selectivity of these catalysts are within the error of integration of the broad trans resonance and do not follow a clear trend, they will not be considered significant. A similar result was found when 4a and 4b were used to catalyze the polymerization of OTBSNBE: the bias towards cis, syndiotactic polymers with alternating enantiomers was not significantly changed between the three catalysts. The expected difference in electronics between HMTO and NO₂HMTO combined with the fact that no drastic change in polymer structure occurred when 4b was employed suggest that perhaps the electronic changes at the metal center are less important in controlling polymer structure than steric changes.

The compounds presented in the remaining entries in Table 4.4 represent compounds with both steric and electronic changes as compared to 1a and each showed reduced selectivity for the formation of cis, syndiotactic poly-(rac)-DCMNBE. 5a was able to catalyze the ROMP of rac-DCMNBE to form relatively high-cis, but atactic polymer, similar to the result obtained in the ROMP of DCMNBD with 5a reported in Chapter 3.

When Mo(2,6-Me₂PhN)(CHCMe₂Ph)(pyr)(HMTO) (6a) was exposed to the ROMP conditions described in Table 4.4, the polymer isolated exhibited the same cis, syndiotactic, alternating structure observed with 1a, however with a slightly increased trans content (again, within the error of integration of the ¹H NMR spectrum). The same result was obtained in the ROMP of OTMSNBE with 6a: the resulting polymer had the same structure as the polymer obtained using 1a as catalyst (~90% cis polymer, bias towards syndiotactic, alternating structure). These results suggest that moving from the adamantyl imido ligand to the dimethylphenylimido ligand has little to no effect on the polymer structure.

I. D. Alternating ROMP of two different monomers

The successful alternating copolymerization of enantiomers as described in the above section led us to pursue the alternating copolymerization of two different monomers using a similar strategy. We postulated that a physical mixture of the (+)-configuration of one monomer
and the (−)-configuration of a different monomer should be able to be copolymerized to give an alternating polymer in the same way that alternating polymer is formed from a mixture of (+)- and (−)-DCMNBE with MAP catalysts. If realized, the alternating ROMP of two different monomers could lead to the formation of a number of different polymer structures with drastically different physical properties than the corresponding homopolymers.

Reports of ROMP of two different monomers to give an alternating polymer have appeared in the literature. These reported alternating ROMP systems are generally monomer directed, i.e. the alternating structure is determined by chain end control with a pair of carefully selected monomers. In a few of these systems, a highly strained, but bulky monomer is combined with a less strained and less bulky monomer. After a single insertion of the strained, bulky monomer, steric effects prohibit the insertion of a second bulky monomer, and instead the less...
A recent report by Chen and coworkers has moved slightly away from this monomer-controlled system and towards a more catalyst-controlled alternating ROMP system. The catalyst reported in this study is a ruthenium-based carbene complex consisting of two diastereomeric forms, one of which preferentially reacts with norbornene and the other preferentially reacts with cyclooctene. An alternating polymer of cyclooctene and norbornene is formed in this system, although the polymer was not tactic nor highly cis or trans.9 We hoped that MAP catalysts such as 1a that are selective for the alternating copolymerization of enantiomers (described in the previous section) would also be selective for the alternating copolymerization of two different monomers, allowing for the potential synthesis of a wide range of new alternating polymers.
As described in Scheme 4.4, the ROMP of a mixture of (+)-X\textsubscript{2}NBE and (-)-Y\textsubscript{2}NBE theoretically should be polymerized by a MAP initiator to form a regular polymer with an alternating structure. Starting from either (-)-menthol (naturally occurring) or (+)-menthol (unnatural) as a chiral auxiliary, both (+)- and (-)-5,6-disubstituted norbornenes can be prepared according to the literature.\textsuperscript{10} To investigate if an alternating polymer of different monomers could be prepared by the method described in Scheme 4.4, a number of different enantiomerically pure monomers were synthesized and subjected to ROMP conditions in various combinations, as described in Table 4.5.

Unfortunately, all of the catalyst and monomer combinations shown in Table 4.5 afforded polymers that exhibited many broad resonances in the olefinic region of the corresponding $^1$H NMR spectra, suggesting that none of the polymers was completely regular. A representative $^1$H NMR spectrum of an irregular polymer prepared according to the conditions described in Table 4.5 is displayed in Figure 4.9, and the olefinic regions of the $^1$H NMR spectra of the remaining polymers are displayed in the Experimental Section.

![Figure 4.9: $^1$H NMR spectrum (CDCl\textsubscript{3}) of polymer obtained from 50 eq. (+)-DCMNBE and 50 eq. (-)-DCtBuNBE, catalyst is 1a at room temperature in toluene. Olefinic region is expanded in inset.]

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It is difficult to determine if the irregularity in polymer structures is due to a lack of cis-selectivity, a lack of syndioselectivity, or a lack of selectivity for one monomer over the other. Since the racemic forms of all three of the monomers presented in Table 4.5 will form cis, syndiotactic, alternating polymer, the most likely source of error is simply the lack of selectivity for one monomer over the other. In order for an alternating polymer to form, after a single insertion of the first monomer, the catalyst must selectively react with the second monomer; in all cases, however, the catalyst always has the option to react again with the first monomer instead. Although our current hypothesis suggests that a second insertion of the first monomer should be slow due to a “mismatch” of enantiomers, it might still be rapid enough to compete with the insertion of the second monomer. As long as the “mismatch” insertion of one monomer is competitive with the “matched” insertion of the other monomer, a fully alternating structure will not form.

It is possible that the alternating copolymerization of two different monomers will eventually be realized using MAP catalysts through extensive catalyst and monomer screening. An ideal monomer choice for this system would one in which the enantiomerically pure form of the monomer cannot be polymerized by MAP catalysts, meaning the insertion of a second equivalent of this monomer to the “mismatch” configuration of the catalyst is extremely slow and not competitive during polymerization. At this point, no such monomer has been discovered, and in fact the ROMP of enantiomerically pure norbornenes with MAP catalysts is quite readily achieved and will be discussed in the next section.

II. *Trans*, isoselective ROMP of enantiopure monomers

Due to the success in the selective polymerization of racemic monomers with MAP initiators presented in the previous section, we were curious about the activity of MAP compounds when exposed to a single enantiomer of a chiral monomer. The combination of a racemic initiator with an enantiomerically pure monomer makes this system more complicated than the case with a racemic monomer. In the racemic case, both enantiomers of the catalyst could react with whichever of the two enantiomers of the monomer was preferred, but switching to an enantiomerically pure monomer means one of the enantiomers of the catalyst is forced to react with the disfavored enantiomer of the monomer. We initially expected that either reactivity
would be completely shut down by this disfavored step, or that simply an irregular polymer would be formed.

II. A. ROMP of (+)-DCMNBE with MAP Complexes

When 100 equivalents of enantiomerically pure (+)-DCMNBE was added to a toluene solution of 1a, $^1$H NMR spectroscopy showed consumption of the monomer and production of the expected polymer within 30 minutes. After quenching with benzaldehyde and precipitation into methanol, a white solid polymer was isolated, and the $^1$H NMR spectrum of the resulting polymer surprisingly contained $\sim$70% trans double bonds. Although significant cis content was present, the resonances corresponding to the trans portion of the polymer exhibited a doublet of doublets pattern with a $J_{HH}$ of $\sim$16 Hz, suggesting a trans, isotactic configuration. Even more surprisingly, when 1% 1b was instead used as the catalyst in the polymerization of (+)-DCMNBE, the trans content of the resulting polymer was increased to 92%. The olefinic region of the $^1$H NMR spectrum of highly trans poly-(+)-DCMNBE obtained from the reaction of 1b with (+)-DCMNBE is shown in Figure 4.10.

![Figure 4.10: Olefinic region of $^1$H NMR spectrum (CDCl$_3$) of highly trans poly-(+)-DCMNBE](image-url)

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The spectrum shown in Figure 4.10 displays a clear “doublet of doublets” pattern as would be expected for a trans, isotactic polymer, in which the two olefinic protons are coupled to each other as well as the neighboring methyne protons of the cyclopentane rings. Although the olefinic region still shows minor resonances at 5.38 ppm and 5.17 ppm corresponding to cis double bonds in the polymer, the cis content is estimated through NMR integration to be only \(~8\%\) of the total.

At first glance, it is surprising that 1b, a catalyst that generally catalyzes the Z-selective metathesis of olefins, would afford such a highly trans polymer in the ROMP of (+)-DCMNBE. The key to explaining this phenomenon likely lies in the fact that the combination of an enantiopure monomer with a racemic catalyst necessarily leads to two distinct diastereomeric propagation steps. Taking these two distinct steps into account, one possible explanation for the trans configuration of poly-(+)-DCMNBE is described in Scheme 4.5.

Scheme 4.5: Possible mechanism for synthesis of trans-isotactic poly-(+)-DCMNBE using 1b.
The assumptions represented in Scheme 4.5 are as follows: First, the monomer always approaches the C_alkyldene-N_imido-O_phenoxide face of the catalyst with the C_7 methylene carbon of the cyclopentane ring pointed towards the alkyldene, and the configuration of the catalyst inverts with each metathesis step. Second, the monomer approaches one enantiomer of the metal (shown arbitrarily as (S_{Mo}) in Scheme 4.5) in a “syn” orientation (“syn” refers to the orientation in which the substituents of the monomer are closer to the imido ligand, and “anti” refers to when the substituents are pointed away from the imido ligand). Third, the monomer approaches the other enantiomer of the metal (shown arbitrarily as (R_{Mo}) in Scheme 4.5) in an “anti” orientation.

Points (1) and (2) carry over from previous studies, i.e. the cis, syndiotactic ROMP of rac-DCMNBE with MAP catalysts. It is not yet clear why point (3) would be true, however it would not be surprising for S_{Mo} and R_{Mo} to react differently with (+)-DCMNBE, as the two cases involve diastereomeric transition states. All of the assumptions described here and displayed in Scheme 4.5 would lead to the formation of the observed trans, isotactic structure, which, if made in pure form, would represent an entirely new ROMP polymer structure.

When 10 equivalents of (+)-DCMNBE were added to a toluene-D_8 solution of 1b, resonances corresponding to complete consumption of the monomer were observed in the ^1H NMR spectrum within 5 minutes. Only 37% of the alkyldene resonance of the initiator was consumed as compared to anthracene internal standard. The ratio of propagation rate vs. initiation rate in ROMP polymerizations can be calculated from this NMR data: for a given initial monomer concentration M_0, initial initiator concentration I_0, and final initiator concentration I, equation (1) holds true \( r = \frac{k_p}{k_i} \).

\[
\frac{M_0}{I_0} + r \ln \left( \frac{I}{I_0} \right) + (1-r)(I/I_0 - 1) = 0
\]  

For the ROMP of (+)-DCMNBE, \( I/I_0 = 0.63 \) and \( M_0/I_0 = 10 \), so \( k_p/k_i = 104 \), indicative of a system in which propagation is significantly faster than initiation. A similar treatment has been used to determine \( k_p/k_i \) for several highly living ROMP systems, including the ROMP of substituted norbornadienes with Mo(NAr)(CHCMe_2Ph)(OtBu)_2. GPC analysis of the polymer obtained using 100 equivalents of (+)-DCMNBE showed a molecular weight of 99,904 daltons (about four times the expected weight based on M_0/I_0) and a PDI of 1.21. The high PDI and unexpectedly high molecular weight are consistent with a poorly initiating system, consistent
with what is suggested by $^1$H NMR spectroscopy. The thermal properties of \textit{trans}, isotactic poly-(+)-DCMNBE will be reported later in this report.

\textbf{II. B. Catalyst variation for \textit{trans}-isoselective ROMP of enantiomerically pure monomers}

To investigate the proposed \textit{trans}, isotactic-selective mechanism and possibly discover an even more \textit{trans}-selective ROMP system, ROMP of (+)-DCMNBE was repeated with a number of MAP catalysts at various concentrations and temperatures, including compounds 1-6 and additional initiators presented in Figure 4.11. The syntheses of 7-9 (Figure 4.11) are reported in Chapter 2 of this report.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.11.png}
\caption{MAP and bisalkoxide compounds for ROMP of (+)-DCMNBE}
\end{figure}

The results of catalyst screening for ROMP of enantiomerically pure (+)-DCMNBE are presented in Table 4.6. There are a few notable results displayed in Table 4.6. As shown in entries 1-3, the \textit{cis}-selectivity of the ROMP of (+)-DCMNBE dramatically increases at low temperatures when the catalyst is 1a. The olefinic region of the $^1$H NMR spectrum of the polymer obtained at -20 °C displayed mainly (~70%) \textit{cis} olefinic resonances, inverting the \textit{cis}/\textit{trans} selectivity of the room temperature polymerization. Amazingly, the \textit{cis} portion of the polymer appeared to be highly biased towards \textit{cis}, syndiotactic-poly-(+)-DCMNBE, which would also represent a new structure if it could be made in pure form. The same temperature dependence was not observed when the catalyst was 1b, as seen in entries 4-6.
<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound number</th>
<th>M</th>
<th>R</th>
<th>R’</th>
<th>OR''</th>
<th>Temp</th>
<th>Polymer Structure</th>
<th>% Trans</th>
<th>Tacticity</th>
</tr>
</thead>
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<td>1a</td>
<td>Mo</td>
<td>Ad</td>
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<td></td>
<td>RT</td>
<td>HMTO</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>-20</td>
<td>syndio</td>
</tr>
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<td>3</td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<td>-78</td>
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<td>4</td>
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<td>Mo</td>
<td>Ad</td>
<td>H</td>
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<td>92</td>
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<td>HIPTO</td>
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</tr>
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<td>Ad</td>
<td>Mc</td>
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<td>HIPTO</td>
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<td>9</td>
<td>Mo</td>
<td>Ar</td>
<td>N/A</td>
<td>OtBu2**</td>
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<td></td>
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</tr>
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<td>H</td>
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<td></td>
<td>89</td>
<td>iso</td>
</tr>
<tr>
<td>17</td>
<td>1e*</td>
<td>Mo</td>
<td>Ad</td>
<td>H</td>
<td></td>
<td>DBTIPTO</td>
<td></td>
<td>89</td>
<td>iso</td>
</tr>
<tr>
<td>18</td>
<td>1d*</td>
<td>Mo</td>
<td>Ad</td>
<td>H</td>
<td></td>
<td>TIPTO</td>
<td></td>
<td>92</td>
<td>iso</td>
</tr>
</tbody>
</table>

Conditions: 0.24 M [monomer] in toluene, 1% catalyst. Trans content detd. by $^1$H NMR. Tacticity only listed if an obvious bias observed by $^1$H NMR. *Entry 7 run at 10x monomer concentration (2.4 M) and entry 8 run at 0.2x monomer concentration (0.045M), with monomer solution dripped in to catalyst solution slowly (1 drop/4 seconds).

**Entry 9 is bisalkoxide catalyst

Table 4.6: ROMP of (+)-DCMNBE with various Mo and W MAP compounds. *Starred compounds prepared in situ as described in Chapter 2 of this report.
It is possible that the small amount (8%) of cis impurities in the trans-isotactic polymer is formed due to undesired alkylidene rotation during polymerization. The proposed mechanism for formation of trans poly-(+)-DCMNBE as described in Scheme 4.5 does not invoke alkylidene rotation, therefore any rotation event would cause a mistake in the regularity of the olefin backbone. The rate of alkylidene rotation (first order) will not depend on the concentration of the reaction mixture, however the rate of polymer formation (second order) should depend on the concentration of monomer (assuming alkylidene rotation is not the rate-limiting step in the polymerization, as has been observed in at least one case\textsuperscript{13}). If alkylidene rotation was indeed the source of cis errors, the difference in concentration dependence of the two competing processes should cause the resulting polymer to have drastically different cis content when formed at different concentrations. Entries 7 and 8 in Table 4.6 show the results of concentration dependence studies. When the concentration was either increased from 0.24 M to 2.4 M in monomer (entry 7), or decreased to 0.045 M (entry 8), there was no significant difference in the structure of the resulting polymer, although the time for consumption of 100 equivalents of monomer was significantly shorter in the more concentrated case. This lack of a strong concentration dependence of the stereoselectivity of the ROMP of (+)-DCMNBE suggests that rotation of the alkylidene is not likely the major source of cis errors in this reaction.

Entries 9-18 in Table 4.6 show the results of catalyst variation on the structure of the resulting polymer. Changing the imido group to 2,6-dimethylphenyl imido (entries 9 and 10) or 3,5-dimethylphenyl imido (entry 11), or changing the pyrrolide to 2,5-dimethylpyrrolide (entries 13 and 14) decreased the trans selectivity of ROMP of (+)-DCMNBE. Moving to an analogous tungsten catalyst, W(CHCMe\textsubscript{2}Ph)(3,5-Me\textsubscript{2}PhN)(pyr)(HIPTO), (7b) afforded poly-(+)-DCMNBE with a high percentage of cis olefins, and the \textsuperscript{1}H NMR spectrum of the resulting polymer showed a bias towards syndiotactic polymer (entry 12). Increasing or decreasing the sterics of the para position of the flanking phenyls on the terphenoxide ligand of the catalyst (entries 16 and 17, compounds 1d and 1e) made essentially no difference on the stereochemical outcome of the ROMP of (+)-DCMNBE. Crystallographic studies in our group of MAP compounds containing
Figure 4.12: Olefinic regions of $^1$H NMR spectra (CDCl$_3$) of poly(+)-DCMNB (various initiators)
bulky terphenoxide ligands have suggested that the ortho substituents of the terphenoxide ligand play the biggest role in interacting with the substrate during metathesis, and that the para substituents are too far removed from the metal center to exert steric influence on the monomer. The results displayed in entries 16 and 17 of Table 4.6 are in accordance with this hypothesis, and suggest that any future variation in terphenoxide ligands in MAP complexes should focus on variations of the ortho substituents of the flanking phenyl rings.

II. C. Hydrogenation of regular ROMP polymers

With both trans-isotactic (92% pure) and cis-isotactic (>98% pure) poly-(+)-DCMNBE in hand, polymer hydrogenation studies were carried out to confirm that the two regular polymers were both isotactic. Upon hydrogenation, trans-isotactic and cis-isotactic polymers should have the same structure, and comparison of the $^1$H NMR and $^{13}$C NMR spectra of the two should confirm their similarity. Hydrogenations were carried out according to a method described in the literature: using the thermal decomposition of tosyl hydrazide as a stoichiometric source of N$_2$H$_2$, which decomposes to release one equivalent of N$_2$ and transfer one equivalent of H$_2$ to an olefin of the polymer.$^{14}$ As described in Table 4.7, poly-DCMNBE samples prepared using a number of different catalysts were subjected to the hydrogenation conditions described below.

The polymers described in Table 4.7 were hydrogenated in the following manner: the solid polymers were dissolved in dry xylenes under nitrogen, and 7 equivalents of tosyl hydrazide were added as a solid. The entire mixture was heated to 115 °C, at which point gas evolution was observed. The mixture was heated further to 130 °C until no further gas was evolved, usually 1-2 hours. After cooling, the solvents were removed under reduced pressure and the white solid polymer was precipitated from and washed with methanol. If no olefinic signals were observed by $^1$H NMR spectroscopy in the resulting polymer, the hydrogenation was deemed complete, however in several cases olefinic signals remained in the $^1$H NMR spectrum after a single hydrogenation batch. In the case of incomplete hydrogenation, the polymer was redissolved in xylenes and the entire hydrogenation procedure was repeated one to four times until the $^1$H NMR spectrum of the polymer exhibited no olefinic signals. In polymers that contained both cis and trans double bonds, it appeared that the trans olefins were hydrogenated more readily than the cis olefins; after a single hydrogenation batch, the sample that originally
Table 4.7: Hydrogenation of regular poly-DCMNBE polymers of various structures

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Monomer</th>
<th>Polymer Structure</th>
<th># of batches needed for full hydrogenation</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>[Mo]NAr'(Biphen-CF₃) (+)</td>
<td>&gt;98% Isotactic</td>
<td>2</td>
</tr>
<tr>
<td>1b</td>
<td>[Mo]NAd(pyr)(HIPTO) (+)</td>
<td>8% Isotactic</td>
<td>1</td>
</tr>
<tr>
<td>9</td>
<td>[Mo]NAr(O-t-Bu)₂ (+)</td>
<td>40% Atactic</td>
<td>1</td>
</tr>
<tr>
<td>1a</td>
<td>[Mo]NAd(pyr)(HMTO) (+)</td>
<td>75% Syndiotactic</td>
<td>2</td>
</tr>
<tr>
<td>1a</td>
<td>[Mo]NAd(pyr)(HMTO) (rac)</td>
<td>95% Syndiotactic/Alternating</td>
<td>5</td>
</tr>
</tbody>
</table>

Figure 4.13: $^1$H NMR spectra of trans, isotactic poly-(+)-DCMNBE before (top spectrum) and after (bottom spectrum) hydrogenation. Sharp resonances at 2.3 ppm, 3.5 ppm, and 7.2 ppm correspond to trace toluene and methanol.
contained 70% cis double bonds was converted to a partially hydrogenated polymer in which all of the remaining double bonds were cis. The increased difficulty in hydrogenating cis double bonds with this method could explain why five hydrogenation batches were needed to fully hydrogenate the cis, syndiotactic, alternating polymer described in the last entry of Table 4.7. The low solubility of cis, syndio, alt-poly-(rac)-DCMNBE in xylenes also could explain the difficulties in achieving complete hydrogenation.

The $^1$H NMR spectra of trans, isotactic poly- (+)-DCMNBE before and after hydrogenation are displayed in Figure 4.13.

As expected, the 1.0-3.5 ppm region of the $^1$H NMR spectrum of hydrogenated poly-DCMNBE contains 7 resonances, as compared to the 5 resonances exhibited in the spectrum of the polymer before hydrogenation. The $^1$H NMR spectrum of the hydrogenated polymer also does not contain any resonances corresponding to olefinic protons, suggesting that hydrogenation was complete (a small resonance at 5.3 ppm corresponding to trace dichloromethane can be observed). There was almost no observable difference observed in the $^1$H NMR spectra of the five different hydrogenated polymers described in Table 4.7, therefore we turned to $^{13}$C NMR spectroscopy to compare the various polymers. Expanded portions of the $^{13}$C NMR spectra of various hydrogenated (+)-DCMNBE polymers are displayed in Figure 4.14.

The spectra displayed in Figure 4.14 show fine structure corresponding to the differences between the various forms of hydrogenated poly- (+)-DCMNBE. Specifically, the resonances around 33 ppm, 38 ppm, and 42-43 ppm for C1, C2 and C4 show the most variation between the 4 polymer structures. Looking closely at the resonances between 42-43 ppm, it becomes clear that the resonance at 42.9 ppm in the top spectrum corresponds to the isotactic triad, while the major resonance at 42.1 ppm in the bottom spectrum corresponds to the same carbon in a syndiotactic triad. In the spectrum of the polymer derived from trans-isotactic polyDCMNBE, the major of the two resonances appears at 42.9 ppm, suggesting that as expected, the major tacticity in this polymer is isotactic. The small resonance in the second spectrum at 42.1 ppm, therefore, likely corresponds to a small percentage of syndiotactic impurity, which is consistent with the 8% impurity observed by $^1$H NMR in trans-isotactic poly- (+)-DCMNBE (Figure 4.10). The same analysis holds true for the C2 and C4 resonances: the chemical shifts of the major resonances in the spectrum of isotactic polyDCMNBE$^{1b}$ correlate well with the resonances for the isotactic
polymer in the top spectrum, suggesting that the major tacticity displayed in the second spectrum is also isotactic. The $^{13}$C NMR spectrum of hydrogenated cis,syndio,alt-poly-(rac)-DCMNBE (Figure 4.15) obtained with 1a also contained nine sharp singlets in the 30-55 ppm region. The $^{13}$C NMR resonances for C1 and C2 of hydrogenated cis-syndiotactic poly(rac)DCMNBE exhibited different chemical shifts from the corresponding resonances of any of the polymers obtained from enantiomerically pure (+)-DCMNBE, further confirming the unique structure of this alternating polymer.
With various saturated and unsaturated ROMP polymers of DCMNBE in hand, we set out to investigate the thermal properties of the various polymers. Glass transition temperatures (T_g) of DCMNBE ROMP polymers and their hydrogenated counterparts are shown in Table 4.8. The observed glass transition temperatures of unsaturated DCMNBE ROMP polymers range from 48.5 °C to 96.8 °C, and increase according to the regularity of the polymer backbone. The lowest T_g was observed in the atactic polymer, followed by an increased T_g in the two isotactic polymers, followed by an even further increased temperature for the two syndiotactic polymers. In the case of 95% cis-syndio-alt poly-(rac)-DCMNBE, no glass transition or melting was observed below the decomposition temperature of the polymer (~250 °C), a phenomenon which has been observed in all cis, syndiotactic poly-norbornenes prepared so far, and is therefore not surprising. As shown in the last column of Table 4.8, there was less variability in the glass transition temperatures of the hydrogenated polymers (temperatures ranged from 40 °C to 58 °C), however the same trend still held, with T_g highest in the syndiotactic polymers and lowest in the atactic polymer.
<table>
<thead>
<tr>
<th>Initiator</th>
<th>Polymer structure</th>
<th>Tc (^{(°C)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>[Mo]NAr(O-t-Bu)(_2)</td>
<td>40% atactic</td>
</tr>
<tr>
<td>2</td>
<td>[Mo]NAr'(Biphen-CF(_3))</td>
<td>&gt;98% iso</td>
</tr>
<tr>
<td>1b</td>
<td>[Mo]NAd(pyr)(HIPTO)</td>
<td>8% iso</td>
</tr>
<tr>
<td>1a</td>
<td>[Mo]NAd(pyr)(HMTO) (-20°C)</td>
<td>75% syndio</td>
</tr>
<tr>
<td>1a</td>
<td>[Mo]NAd(pyr)(HMTO)</td>
<td>95% syndio/alt</td>
</tr>
</tbody>
</table>

Table 4.8: Thermal properties of poly-DCMNBE of various structures. [Mo] = Mo(CHCMe\(_2\)Ph). Tc’s det’d by DSC

The lack of an observed glass transition in cis-syndio-alt poly-rac-DCMNBE could be ascribed to a highly crystalline polymer structure, although without an observed melting point in the DSC, it is difficult to directly determine percent crystallinity from the thermal data. In an attempt to obtain further evidence for a crystalline structure, Powder X-ray Diffraction was performed on both cis-syndiotactic-alt poly(rac)DCMNBE and trans-isotactic poly-(+)-DCMNBE and the resulting diffraction patterns are displayed in Table 4.9.

Table 4.9: Powder XRD of regular DCMNBE polymers prepared from MAP initiators

As seen in Table 4.9, the powder X-ray diffraction pattern of the tactic cis-syndiotactic polymer contains several relatively sharp features, indicative of a polymer that exhibits some crystallinity. The diffraction pattern of the tactic trans-isotactic polymer exhibits only a single...
broad feature (sharp peaks at 42 and 50 degrees theta correspond to the diffraction pattern of the aluminum/copper sample holder), confirming what was already determined by DSC, that \textit{trans-}

isotactic poly-(+)-DCMNBE is an amorphous polymer. The difference in powder diffraction patterns between these two highly tactic polymers is further evidence for the strong correlation between polymer structure and properties.

**CONCLUSION**

The alternating chirality of the metal center in a MAP complex has the unique ability to form polymers of regular structures that have not been previously reported. The two new polyDCMNBE structures reported in this chapter: \textit{cis/syndiotactic/alternating} and \textit{trans/isotactic} are both formed using molybdenum MAP initiators containing bulky phenoxide ligands. As suggested by the ligand and monomer variation studies reported in this chapter, while both regular polymerization processes can be extended to other monomers, the regularity of both systems can easily be disrupted by seemingly minor steric and electronic changes in the catalysts or monomers. The most selective catalysts in both cases contain an adamantyl imido ligand, an unsubstituted pyrrolide, and a bulky hexaalkylterphenoxide. According to the mechanism described in this report, this combination of a very bulky phenoxide and a relatively small imido group affords the highest Z-selectivity, therefore it is somewhat surprising that 1b produces such highly \textit{trans} poly-(+)-DCMNBE. Clearly the ROMP of an enantiopure monomer with a chiral catalyst creates a unique situation in which two distinct diastereomeric propagation steps are active, and the alternation of these two distinct steps creates a \textit{trans} polymer.

With a growing library of norbornene and norbornadiene-based polymer structures in hand, it is useful to be able to associate polymer structure with physical properties. The glass transition temperatures of a variety of \textit{trans} and \textit{cis} polyDCMNBE polymers derived from both (rac) and (+)-DCMNBE were found to correlate closely with polymer structure, with \textit{trans} polymers generally exhibiting lower Tg’s than \textit{cis} polymers, and isotactic polymers generally exhibiting lower Tg’s than syndiotactic polymers. The same trends hold true for hydrogenated polyDCMNBE polymers. This strong correlation between thermal properties and polymer structure reinforces the idea that the fine control of polymer structure is necessary for the synthesis of polymers with defined properties.
At this point, no catalyst/monomer combination has been found that can copolymerize two monomers to form a regular, alternating copolymer, however there is a large number of possible combinations of monomers and catalysts and it is possible that a system eventually will be developed that achieves this goal. The highly modular nature of MAP compounds could enable extension of cis/syndio/alternating and trans/isotactic polymerization to a large library of monomers in the future.

**EXPERIMENTAL**

**General Details.** All manipulations of air-sensitive compounds or reactions were performed under nitrogen in a drybox or using Schlenk techniques. All glassware was oven-dried and allowed to cool under vacuum or nitrogen before use. Ether, pentane, and toluene were sparged with nitrogen and passed through activated alumina. All solvents were stored over molecular sieves in a nitrogen atmosphere. Deuterated solvents were dried over molecular sieves. Benzaldehyde was distilled and stored under nitrogen. Nitrobenzene was dried with calcium hydride, then distilled and stored under nitrogen. NMR spectra were obtained on Varian spectrometers operating at 300 MHz or 500 MHz. NMR chemical shifts are reported as ppm relative to tetramethylsilane, and were referenced to the residual proton or $^{13}$C signal of the solvent ($^1$H CDCl$_3$: 7.26 ppm, $^1$H C$_6$D$_6$: 7.16 ppm, $^1$H acetone-D$_6$: 2.05 ppm, $^{13}$C C$_6$D$_6$: 128.06 ppm, $^{13}$CDCl$_3$: 77.16 ppm). 7a$^{15}$, 9a-b$^{16}$, Mo(3,5-Me$_2$PhN)(CHCMe$_2$Ph)(OTf)$_2$(dme)$^{17}$, (+)-DCMNBE$^3$, exo,endo-5,6-dicyanonorbornene$^{18}$, 5,6-dimethylnorbornene$^{10}$, endo,exo-5,6-dimethoxymethylnorbornene$^3$, endo,exo-5,6-bis(trimethylsilyl)norbornene$^{19}$, endo,exo-5,6-bis(t-butyldimethylsilyl)norbornene$^{20}$ were synthesized according to published procedures. The syntheses of all other molybdenum initiators have been reported in Chapter 2 of this report. Liquid monomers were dried with calcium hydride, freeze-pump-thaw degassed, and distilled before use. Solid monomers were dried under vacuum, passed as a toluene solution through activated alumina, and dried over molecular sieves before use.

(-)-Bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid was synthesized according to the published procedure for (+)-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid$^{10}$ but using (+)-menthol as the chiral starting material instead of the reported (-)-menthol. Lithium pyrrolide was prepared by
addition of 1.1 equivalents of \( n\)-BuLi to an ether solution of pyrrole and isolation of the resulting white solid by filtration and washing with cold ether. Monomers were dried with calcium hydride, degassed, and either distilled or filtered as a toluene solution through activated alumina before use. Unless otherwise noted, all other reagents were obtained from commercial sources and used as received.

*In situ* preparation of \( \text{Mo}(3,5\text{-Me}_2\text{PhN})(\text{CHCMe}_2\text{Ph})(\text{pyr})(\text{HIPTO}) \) (7b): \( \text{Mo}(3,5\text{-Me}_2\text{PhN})(\text{CHCMe}_2\text{Ph})(\text{OTf})_2\text{(dme)} \) (23.0 mg, 0.0313 mmol) was suspended in 2 mL \( \text{Et}_2\text{O} \) and chilled to -25 °C. Lithium pyrrolide (4.6 mg, 0.0625 mmol, 2 eq) was added to it in one portion as a solid. The mixture became homogeneous and orange. After stirring 45 min, all volatiles were removed by vacuum, leaving brown solids. 2 mL toluene was added, and the resulting brown cloudy mixture was filtered through celite to remove white solid lithium triflate. All volatiles were removed *in vacuo*, leaving a brown oil. The resulting oil, \( \text{Mo}(3,5\text{-Me}_2\text{PhN})(\text{CHCMe}_2\text{Ph})(\text{pyr})_2\text{(dme)} \) (11.0 mg, 0.0193 mmol) was redissolved in 2 mL toluene, and HIPTOH (9.6 mg, 0.0193 mmol, 1 eq) was added as a solid. NMR spectroscopy showed complete conversion to the expected MAP compound within minutes, however other minor resonances appear in the alkylidene region of the \( ^1\text{H} \) NMR spectrum, corresponding to minor impurities. \( ^1\text{H} \) NMR (\( \text{C}_6\text{D}_6 \), 500 MHz) (only alkylidene resonance is listed) \( \delta \) 12.30 (s, 1H, \( \text{Mo}=\text{CH} \), \( J_{\text{CH}} = 123 \text{ Hz} \)).

**dimethyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (rac-DCMNBE):** This compound has been reported previously\(^4\) and was prepared by an adapted procedure as follows: freshly distilled cyclopentadiene (14.7 g, 0.222 mol) was added to a 50 mL toluene suspension of dimethyl fumarate (28.9 g, 0.200 mol, 0.9 eq). The mixture was allowed to stir overnight, after which all volatiles were removed at 30 °C under reduced pressure. \( ^1\text{H} \) NMR (\( \text{CDCl}_3 \), 500 MHz) \( \delta \) 6.27 (mult., 1H, olefinic); 6.07 (mult., 1H, olefinic); 3.71 (s, 3H, \( \text{CO}_2\text{Me} \)); 3.64 (s, 3H, \( \text{CO}_2\text{Me} \)); 3.37 (t, 1H); 3.25 (s, 1H); 3.12 (s, 1H); 2.68 (d, 1H); 1.60 (d, 1H); 1.45 (d, 1H).

**diethyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (rac-DCENBE and (-)-DCENBE):** These compounds have been reported previously\(^4\) and were prepared by an adapted procedure as follows: Racemic bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid (1.09 g, 6.0 mmol) was
dissolved in 30 mL ethanol and concentrated sulfuric acid (4 mL of 95% aq soln, 71 mmol, 11.9 eq) was added. After stirring for 48 hours at room temperature, the mixture was extracted with hexanes. The organic layer was washed with aqueous sodium bicarbonate solution, followed by water and brine, then dried with magnesium sulfate. The hexane solution was filtered and all volatiles were removed under reduced pressure, leaving a colorless oil. The $^1$H NMR spectrum of the oil matched that of the reported compound. The enantiomerically pure version, (-)-DCENBE, was prepared in the same manner, starting from enantiomerically pure (-)-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid. $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 6.27 (mult, 1H, olefinic); 6.06 (mult., 1H, olefinic); 4.16 (mult., 2H, CO$_2$CH$_2$CH$_3$); 4.10 (mult., 2H, CO$_2$CH$_2$CH$_3$); 3.37 (t, 1H); 3.26 (s, 1H); 3.11 (s, 1H); 2.67 (d, 1H); 1.61 (d, 1H); 1.44 (d, 1H); 1.27 (t, 3H, CO$_2$CH$_2$CH$_3$); 1.23 (t, 3H, CO$_2$CH$_2$CH$_3$).

$^5$-$^6$-bis(((triisopropylsilyl)oxy)methyl)bicyclo[2.2.1]hept-2-ene (OTIPSNB): Bicyclo[2.2.1]hept-5-ene-2,3-diyldimethanol (2.4 g, 0.0156 mol) was dissolved in 75 mL dichloromethane under nitrogen. Triethylamine (5.4 mL, 2.5 eq) was added via syringe, followed by Tips triflate (10.5 mL, 2.5 eq) (triisopropylsilyl trifluoromethanesulfonate), and the mixture was allowed to stir for 18 hours. The pink-orange mixture was poured into aqueous saturated ammonium chloride solution, followed by extraction with dichloromethane. The organic layer was washed with water and brine, dried with magnesium sulfate, filtered, and the volatiles were removed by rotary evaporation to afford a pink oil. Thin layer chromatography showed only a single product, however the oil was purified by column chromatography (1:50 ethyl acetate: hexanes) on silica to remove a small amount of unidentified product with $^1$H NMR resonances at 3.4 ppm and 0.9 ppm and a very similar Rf to the desired product. OTIPSNB was isolated as a colorless oil (0.951 g, 2.03 mmol, 13%). $^1$H NMR (C$_6$D$_6$, 500 MHz) $\delta$ 6.18 (dd, 1H, olefinic), 6.10 (dd, 1H, olefinic), 3.88 (dd, 1H, C$_1$H), 3.64 (mult, 2H, CH$_2$OSi), 3.46 (t, 1H, C$_4$H), 2.97 (s, 1H, C$_2$H), 2.80 (s, 1H, C$_3$H), 1.97 (mult,1H, C$_3$H ), 1.51 (mult, 2H, CH$_2$OSi), 1.30 (mult, 1H, C$_7$H), 1.14 (mult, 42H, OSi-iPr$_3$); $^{13}$C NMR (CDCl$_3$, 500 MHz) $\delta$ 137.89, 134.30, 67.57, 67.09, 46.49, 46.27, 45.85, 44.21, 44.01, 18.21, 12.16; HRMS (ESI) Caled for [M+H]: 467.3735 Found 467.3737.

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Representative Polymerization Procedure: DCMNBE (130.6 mg, 0.621 mmol, 100 eq) was dissolved in 0.5 mL toluene, and added to a 1.5 mL toluene solution of 1a (4.8 mg, 6.21 μmol). The mixture immediately became thick and cloudy. The progress of the reaction was monitored by diluting aliquots of the reaction mixture in CDCl₃ and recording the ¹H NMR spectra. After consumption of the monomer was observed, 200 μL of benzaldehyde was added and the mixture was stirred for at least one h. The entire mixture was added dropwise to 100 mL of vigorously stirring methanol, affording a fine white solid. The white or off-white polymers were isolated on a medium or fine porosity frit by filtration, rinsed with MeOH, and dried in vacuo. Polymer yields were above 90% in all cases unless otherwise noted in the text.

Numbering system for polynorbornenes:

![Polynorbornene Structure]

**Cis, syndio, alt-poly-rac-DCMNBE:** ¹H NMR (CDCl₃, 500 MHz) δ 5.34 (dd, 1H, olefinic, J_HH = 10.4 Hz, 11.8 Hz), 5.23 (dd, 1H, olefinic, J_HH = 10.4 Hz, 11.8 Hz), 3.66 (s, 3H, CO₂Me), 3.61 (s, 3H, CO₂Me), 3.31 (m, 2H, C₄H, C₁H), 3.08 (m, 1H, C₅H), 2.98 (m, 1H, C₆H), 2.09 (m, 1H, C₇H), 1.36 (m, 1H, C₇H). ¹³C NMR (C₆D₆, 125 MHz) δ 174.22, 172.94 (CO₂Me), 133.23, 130.84 (C₂, C₃), 52.99, 52.50 (CO₂Me), 52.00, 51.73 (C₁, C₄), 42.24, 40.86 (C₅, C₆), 39.41 (C₇).

**Cis, syndio,alt-poly-rac-dicyanoNBE:** ¹H NMR (acetone-D₆, 500 MHz, 50 °C) δ 5.77 (dd, 1H, olefinic, J_HH = 10.4 Hz, 11.5 Hz), 5.67 (dd, 1H, olefinic, J_HH = 10.4 Hz, 11.5 Hz), 3.29 (t, 1H); 3.01 (mult., 2H); 2.80 (mult., 1H); 2.11 (t, 1H); 1.41 (s, 9H, CO₂tBu); 1.37 (s, 9H, CO₂tBu). ¹³C NMR (C₆D₆,

**Cis, syndio,alt-poly-rac-DCtBuNBE:** ¹H NMR (CDCl₃, 500 MHz) δ 5.30 (dd, 1H, olefinic, J_HH = 12.0 Hz, 10.1 Hz); 5.24 (dd, 1H, olefinic, J_HH = 12.0 Hz, 10.3 Hz); 3.29 (t, 1H); 3.01 (mult., 2H); 2.80 (mult., 1H); 2.11 (t, 1H); 1.41 (s, 9H, CO₂tBu); 1.37 (s, 9H, CO₂tBu). ¹³C NMR (C₆D₆,
125 MHz) δ 172.81, 171.98 (CO₂Me), 133.18, 130.63 (C₂, C₃), 80.51, 80.31, (CO₂CMe₂), 54.24, 53.12 (C₁, C₄), 41.60, 40.81 (C₅, C₆), 39.15 (C₇), 28.25, 28.16 (CO₂CMe₂).

**Cis,syndio,alt-poly-rac-DCENBE:** \(^1\)H NMR (CDCl₃, 500 MHz) δ 5.33 (dd, 1H, olefinic, J₉H = 11.7 Hz, 9.9 Hz); 5.23 (dd, 1H, olefinic, J₉H = 11.7 Hz, 10.4 Hz); 4.00-4.17 (mult., 4H, CO₂CH₂CH₃); 3.34 (mult.; 1H); 3.23 (t, 1H); 3.07 (mult., 1H); 2.95 (t, 1H); 2.10 (mult.; 1H); 1.36 (mult., 1H); 1.22 (t, 3H, CO₂CH₂CH₃); 1.19 (t, 3H, CO₂CH₂CH₃).

**Trans, isotactic-poly-(+)-DCMNBE:** \(^1\)H NMR (CDCl₃, 500 MHz) δ 5.49 (dd, 1H, olefinic, J₉H = 15.7 Hz, 7.7 Hz), 5.28 (dd, 1H, olefinic, J₉H = 15.7 Hz, 8.4 Hz), 3.66 (s, 3H, CO₂Me), 3.62 (s, 3H, CO₂Me), 3.25 (m, 1H, C₅H), 2.96 (m, 2H, C₆H, C₇H), 2.66 (m, 1H, C₄H), 1.97 (m, 1H, C₇H), 1.47 (m, 1H, C₇H). \(^1\)C NMR (CDCl₃, 125 MHz) δ 174.37; 173.33 (CO₂Me); 133.22; 130.28 (C₂, C₃); 52.29; 52.03 (CO₂Me); 51.86; 51.71 (C₁, C₄); 46.82; 44.39 (C₅, C₆); 39.29 (C₇).

**Representative Hydrogenation Procedure:** Poly-(+)-DCMNBE (72 mg, 0.343 mmol of olefinic groups) prepared using 1b as catalyst was suspended in 2 mL xylenes under a nitrogen atmosphere. Tosyl hydrazide (446 mg, 2.4 mmol, 7 eq per olefin) was added to the mixture. The mixture was heated to 100 °C, at which point the cloudy mixture became clear. After further heating to 115 °C, gas evolution was observed, and the mixture was heated to 130 °C for a further 90 minutes until gas evolution ceased. The solution was cooled to 50 °C and xylenes were removed under reduced pressure. Methanol was added to the resulting solid and the milky white methanol suspension was decanted off of the gooey solid polymer. The polymer was redissolved in minimum chloroform, and re-precipitated from methanol to give a stringy white solid which was isolated and rinsed with methanol. The entire hydrogenation procedure was repeated until \(^1\)H NMR spectroscopy showed complete disappearance of the olefin resonances.

**Hydrogenated isotactic-poly-(+)-DCMNBE:** \(^1\)H NMR (CDCl₃, 500 MHz) δ 3.67 (s, 6H, CO₂Me); 3.16 (mult, 1H); 2.79 (mult, 1H); 2.19 (br s, 1H); 1.99 (mult, 2H); 1.65 (br s, 1H); 1.36 (mult, 2H); 1.10 (mult, 2H) \(^1\)C NMR (CDCl₃, 125 MHz) δ 175.59; 174.74 (CO₂Me); 52.66; 52.08; 51.63; 50.97; 44.00; 42.98; 38.37; 33.87; 30.22.
Hydrogenated syndiotactic-poly- (+)-DCMNBE: (only major resonances reported) $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 3.67 (s, 6H, CO$_2$Me); 3.17 (mult, 1H); 2.80 (mult, 1H); 2.19 (br s, 1H); 2.01 (mult, 2H); 1.63 (br s, 1H); 1.38 (mult, 2H); 1.10 (mult, 2H) $^1$C NMR (CDCl$_3$, 125 MHz) $\delta$ 175.54; 174.60 (CO$_2$Me); 52.60; 52.03; 51.66; 50.97; 43.84; 42.13; 37.96; 33.21; 30.13.

Hydrogenated syndio, alt-poly-(rac)-DCMNBE: $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 3.67 (s, 6H, CO$_2$Me); 3.17 (mult, 1H); 2.80 (mult, 1H); 2.23 (br s, 1H); 1.99 (mult, 2H); 1.64 (br s, 1H); 1.35 (mult, 2H); 1.17 (mult, 1H); 1.08 (mult, 1H). $^1$C NMR (CDCl$_3$, 125 MHz) $\delta$ 175.52; 174.66 (CO$_2$Me); 52.52; 51.99; 51.61; 50.93; 43.83; 42.50; 38.12; 33.52; 30.09.

$^1$H NMR spectra (olefinic regions) of polymers (recorded in CDCl$_3$ unless otherwise noted) prepared from indicated initiators and monomers:
Mo(NAd)(CHCMe₂Ph)(MePyr)(HMTO) (1a)
(rac)-DCNNBE (recorded in acetone-D₆)

Mo(NAd)(CHCMe₂Ph)(pyr)(HMTO) (3a)
(rac)-DCMNBE

Mo(NAd)(CHCMe₂Ph)(pyr)(HMTO) (6a)
(rac)-DCMNBE

Mo(NAd)(CHCMe₂Ph)(pyr)(HMTO) (1a)
(rac)-DCF₆NBE

Mo(NAr')(CHCMe₂Ph)(pyr)(HMTO) (1a)
(rac)-DCtBuNBE
Mo(NAd)(CHCMe₂Ph)(pyr)(HMTO) (1a)  
(rac)-OMeNBE

Mo(NAd)(CHCMe₂Ph)(MePyr)(HMTO) (3a)  
(rac)-OMeNBE

Mo(NAd)(CHCMe₂Ph)(pyr)(HIPTO) (1b)  
(rac)-OMeNBE (* = DCM)

Mo(NAd)(CHCMe₂Ph)(pyr)(HMTO) (1a)  
(rac)-OTMSNBE recorded in tol-D₈

Mo(NAd)(CHCMe₂Ph)(MePyr)(HMTO) (3a)  
(rac)-OTMSNBE recorded in tol-D₈

Mo(NAd)(CHCMe₂Ph)(Pyr)(HMTO) (1a)  
(rac)-OTBSNBE
Mo(NAr)(CHCMe₂Ph)(O-t-Bu)₂ (9)
(+)-DCMNBE

Mo(NAd)(CHCMe₂Ph)(Pyr)(TBTO) (8)
(+)-DCMNBE
REFERENCES


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- Synthesis of molybdenum alkylidene complexes that contain bulky alkoxide ligands and studies towards their use in Z-selective olefin metathesis
- Synthesis and reactivity studies of surface-supported tungsten alkylidyne complexes

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Tufts Summer Scholars Fellowship (2005)

Peer-Reviewed Publications


Patents

Presentations


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My chemistry research experience began during my undergraduate years at Tufts in the lab of Elena Rybak-Akimova. Elena and her lab, specifically my graduate student mentor Sonia Taktak, provided a nurturing, yet stimulating environment for my first chemistry projects. Elena treated me as a graduate student almost immediately and respected my opinions and expected results from me as much as a she would from a more advanced student. Through striving to meet these expectations I learned a huge amount of chemistry and lab techniques which I brought with me to MIT.

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