CYCLOPROPENE POLYMERIZATION AND ENYNE METATHESIS CATALYZED BY HIGH OXIDATION STATE MOLYBDENUM ALKYLIDENES

by

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ABSTRACT

Chapter 1
An olefin metathesis reaction between Mo(NAr)(CHCMe2Ph)(OCMe(CF3)2)2 (Ar = 2,6-diisopropylphenyl) and trans-1,4-divinylbenzene or trans,trans-1,4-di-buta-1,3-dienylbenzene (5) results in the formation of bimetallic ROMP initiators [(DME)((CF3)2MeCO)2(ArN)MoCH]2-1,4-C6H4 (DME = 1,2-dimethoxyethane; 1a) and [(DME)((CF3)2MeCO)2(ArN)MoCHCHCH]2-1,4-C6H4 (6), respectively. An X-ray study of [(THF)((CF3)2MeCO)2(ArN)MoCH]2-1,4-C6H4 (THF = tetrahydrofuran; 1b), which is closely related to 1a, showed it to be the expected bimetallic species in which each end is approximately a trigonal bipyramidal monoadduct of a syn alkylidene with the THF coordinated to the NOO face of the metal trans to the Mo=C bond. Treatment of 1a with lithium-t-butoxide yielded [(Bu-t-O)2(ArN)MoCH]2-1,4-C6H4 (2). Addition of four equivalents of Me3CCH2MgCl to 1a produced the bimetallic species [(Me3CCH2)2(ArN)MoCH]2-1,4-C6H4 (3), which upon treatment with 2,6-dimethylphenol generated a diastereomeric mixture of [(DME)(ArO)(Me3CCH2)(ArN)MoCH]2-1,4-C6H4 (4). The solid state structure of 3 revealed a "syn/syn" bimetallic species related to 1b. In solution two resonances can be observed in the alkylidene region of the 1H NMR spectra for the "syn/anti" isomer of 1a, 1b, 2, 3, 4 and 5. The total amount of the "syn/anti" isomer varies between 4 and 20% of the total. Bimetallic species 1a, 2, and 6 initiate at both ends upon addition of less than ten equivalents of 4,5-dicarbomethoxyborbormadiene (DCMNBD), and afford homopolymers of DCMNBD and methyltetrcyclododecene (MTD) in a living fashion. MALDI-TOF mass spectra of ferrocene-containing homopolymers have been obtained that are consistent with the polymerization process being living. Triblock copolymers MTDxDCMNBDyMTDx were prepared by adding y equivalents of DCMNBD to the bimetallic ROMP initiators followed (after consumption of DCMNBD) by 2x equivalents of MTD. These triblocks were shown to be of relatively high purity (free of homopolymer and diblock copolymer) and to have a relatively low polydispersity index.

Chapter 2
A series of monomers with side chain liquid crystals (SCLCs) were synthesized for ring opening metathesis polymerization (ROMP). The liquid crystals (LCs) used were 4-hydroxybenzoic acid 4-methoxyphenyl ester (MPOB-H), which is known to exhibit a
nematic liquid crystalline phase, and biphenyl-4-carboxylic acid 4-(1-butoxy carbonylethoxy)phenyl ester (BPP4-H), which is known to exhibit a smectic phase. The side chains differed in spacer length, spacer type, and the nature of the LC. Monomers were polymerized using a bimetallic ROMP initiator [(Bu-t-O)2(ArN)MoCH]2-1,4-C6H4 (where Ar = 2,6-diisopropylphenyl); both homopolymers and ABA type triblock copolymers, where the B block is the LC functional monomer, and A is methyltetracyclodocene (MTD) were prepared. The polymers displayed unimodal peak distributions with polydispersities < 1.22. Incorporation of a polyoxyethylene spacer decreased the glass transition temperature (Tg) of the polymer block to -25 from +20 °C, the Tg when an alkyl spacer was used. Although no distinct LC phase was observed with the polyoxyethylene spacer when MPOB was used, use of BPP4 in conjunction with a polyoxyethylene spacer displayed a distinct liquid crystalline transition. Polymers with an alkyl spacer exhibited liquid crystalline behavior and good phase segregation on the basis of differential scanning calorimetry and small-angle X-ray scattering studies.

Chapter 3
Molybdenum imido alkylidene complexes supported by 2,6-diisopropylphenyl, 2,6-dimethylphenyl, 1-adamantyl, or 2-trifluorophenyl that contain relatively electron-withdrawing phenolate (pentafluoro), binaphtholate (3,3'-bis(9-anthracenyl), 3,3'-bis(pentafluorophenyl), or 3,3'-bis(3,5-bis(trifluoromethyl)phenyl)) or biphenolate (3,3'-distert-butyl-5,5'-bistrifluoromethyl-6,6'-dimethyl-1,1'-biphenyl) ligands have been prepared to be tested in olefin metathesis reactions. A series of new monomeric pyrrolide complexes, Mo(NR)(CHCMe2R')(2,5-dimethylpyrrolide)2 (where R' = Me or Ph) and Mo(NAd)(CHCMe2Ph)(2,4-dimethylpyrrolide)2, were also synthesized and treated with alcohols, biphenols or binaphthols in order to generate Mo(NR)(CHCMe2Ph)(diolate) species. In several cases the new alkylidene complexes could be prepared only through reaction of two equivalents of pentafluorophenols or an equivalent of binaphthol (3,3'-bis(pentafluorophenyl)binaphthol or 3,3'-bis(3,5-bis(trifluoromethyl)phenyl binaphthol) with a bis(2,5-dimethylpyrrolide) complex. The pyrrolide approach can be employed either to isolate catalysts on a preparative scale or to generate catalysts in situ. Several simple preliminary ring-closing metathesis reactions show that the new complexes are catalytically competent.

Chapter 4
Living ring opening metathesis polymerization of cyclopropenes using Mo(NAr)(CHCMe2R)(O-t-Bu)2 (where R = Me; 1a or R = Ph; 1b) and Mo(NAr)(CHCMe2Ph)(OCMe(CF3)2)2 (2) has been achieved. The polydispersity indices of the polymers generated are recorded to be < 1.10 for 1a and 1b based on gel permeation chromatography (GPC). Living polymerization of 3-methyl-3-phenyleyclopentene (MPC) by t-butoxide derived molybdenum imido alkylidene initiators is utilized in the synthesis of block copolymers. Diblock copolymers MPCxDCMNBDy (where DCMNBD = 2,3-dicarbomethoxynorbornadiene and x and y are the number of equivalents of MPC and DCMNBD, respectively) were prepared in quantitative yield with unimodal peak distribution via sequential addition of monomers to the initiator 1b. Triblock copolymers MPC100MEMC100MPC100 and
MTD<sub>100</sub>MEMC<sub>100</sub>MTD<sub>100</sub> were prepared using [(O-t-Bu)(ArN)MoCH]<sub>2</sub>-1,4-C<sub>6</sub>H<sub>4</sub> (1c) as an initiator. The block copolymers revealed good phase segregation based on the differential scanning calorimetry (DSC). ROMP of MPC by molybdenum imido alkylidene initiators containing electron-withdrawing diolates resulted in highly tactic polymers as determined by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. IR spectroscopy of all MPC<sub>100</sub> revealed absorptions at 963 and/or 982 cm<sup>-1</sup> of approximately equal intensity that are most consistent with a trans structure.

**Chapter 5**

Addition of one equivalent of ROH to Mo(NAr)(CHCMe<sub>2</sub>Ph)(2,5-dimethylpyrrolide)<sub>2</sub> (Ar = 2,6-diisopropylphenyl) in diethyl ether or THF yielded Mo(NAr)(CHCMe<sub>2</sub>Ph)(OR)(2,5-dimethylpyrrolide) species where R = (CH<sub>3</sub>)<sub>3</sub>C (1), (CH<sub>3</sub>)<sub>2</sub>CH (2), Ar (3), (CF<sub>3</sub>)<sub>2</sub>CH (4), (CF<sub>3</sub>)<sub>2</sub>MeC (5), (Bu-t-O)<sub>3</sub>SiO (6) or C<sub>6</sub>F<sub>5</sub>0 (7). Treatment of an equivalent of PMe<sub>3</sub> to 5 resulted in the formation of (Me<sub>3</sub>P)Mo(NAr)(CHCMe<sub>2</sub>Ph)(OCMe(CF<sub>3</sub>)<sub>2</sub>)(PyrMe) (Me<sub>3</sub>P-5), which showed trans binding of PMe<sub>3</sub> with respect to 2,5-dimethylpyrrolide ligand as determined by the <sup>1</sup>H NOESY spectrum. The solid state structure of 3 depicts a pseudo-tetrahedral geometry around the metal center with the 2,5-dimethylpyrrolide ligand bound η<sup>1</sup> to the metal center. Complexes 1-6 show rapid reaction when treated with one atmosphere of ethylene and catalyze ring-closing metathesis reactions. Heterogenous analogs of 6, Mo(NAr)(CHCMe<sub>2</sub>Ph)(PyrMe)(OSi<sub>surf</sub>) (10a), Mo(NAd)(CHCMe<sub>2</sub>Ph)(PyrMe)(OSi<sub>surf</sub>) (10b) and Mo(NArF)(CHCMe<sub>2</sub>Ph)(PyrMe)(OSi<sub>surf</sub>) (10c) (Ad = 1-adamantyl and ArF = 2-trifluoromethylphenyl) showed great enhancement in the catalytic activity when employed in self-metathesis of propene and ethyloleate. Ring-closing enyne metathesis catalyzed by 1 - 6 leads to cyclic products that arise through initial addition of the triple bond to a methylene species (initially neophyldene) to yield an α- or a β-substituted metallacyclobutene intermediate.

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<tr>
<th>Abbreviation</th>
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<td>Ad</td>
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<tr>
<td>Anal. Calcd.</td>
<td>elemental analysis calculated</td>
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<td>anti</td>
<td>alkylidene rotamer with hydrogen directed towards the imido group</td>
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<tr>
<td>Ar</td>
<td>2,6-diisopropylphenyl</td>
</tr>
<tr>
<td>Ar'</td>
<td>2,6-dimethylphenyl</td>
</tr>
<tr>
<td>ArCl</td>
<td>2,6-dichlorophenyl</td>
</tr>
<tr>
<td>ArF</td>
<td>2-trifluoromethylphenyl</td>
</tr>
<tr>
<td>BPP4</td>
<td>biphenyl-4-carboxylic acid 4-(1-butoxycarbonyl-ethoxy)-phenyl ester</td>
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<td>H2(Biphen)</td>
<td>rac-3,3'-di-tert-butyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diol (racemic, unless otherwise noted)</td>
</tr>
<tr>
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</tr>
<tr>
<td>H2(BinaphCF3)</td>
<td>3,3'-bis(3,5-bis(trifluoromethyl)phenyl)-1,1'-binaphthyl-2,2'-diol (R-configuration)</td>
</tr>
<tr>
<td>H2(BinaphCF6)</td>
<td>3,3'-bis(perfluorophenyl)-1,1'-binaphthyl-2,2'-diol (R-configuration)</td>
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<td>H2(BinaphCF8)</td>
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<td>CM</td>
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<td>CBw10MPOB</td>
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</tr>
<tr>
<td>DME</td>
<td>1,2-dimethoxyethane</td>
</tr>
<tr>
<td>i-Pr</td>
<td>isopropyl</td>
</tr>
<tr>
<td>J_{1AB}</td>
<td>coupling constant between nuclei A and B through n bonds</td>
</tr>
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<tr>
<td>K_a</td>
<td>acid dissociation constant</td>
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<tr>
<td>k_i</td>
<td>rate constant for initiation step</td>
</tr>
<tr>
<td>k_p</td>
<td>rate constant for propagation step</td>
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<tr>
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<tr>
<td>MAP</td>
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<tr>
<td>MDP</td>
<td>Molybdenum imido alkylidene dipyrrrole</td>
</tr>
<tr>
<td>MEMC</td>
<td>3-(2-methoxyethyl)-3-methylecyclopropene</td>
</tr>
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<td>mmol</td>
<td>millimole</td>
</tr>
<tr>
<td>mol</td>
<td>mole</td>
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<tr>
<td>MPC</td>
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<tr>
<td>MPCC</td>
<td>methyl 1-phenylcycloprop-2-ene-carboxylate</td>
</tr>
<tr>
<td>MPOB-H</td>
<td>4-hydroxy-benzoic acid 4-methoxy-phenyl</td>
</tr>
<tr>
<td>EXSY</td>
<td>Exchange Spectroscopy</td>
</tr>
<tr>
<td>NOESY</td>
<td>The Nuclear Overhauser Enhancement Spectroscopy</td>
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</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
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<tr>
<td>--------</td>
<td>------------</td>
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<td>NBwO1MPOB</td>
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</tr>
<tr>
<td>NBwO1BPP4</td>
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<tr>
<td>POV-ray</td>
<td>The Persistence of Vision Raytracer</td>
</tr>
<tr>
<td>OTf</td>
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</tr>
<tr>
<td>p-</td>
<td>\textit{para}-</td>
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<td>PDI</td>
<td>polydispersity index</td>
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<tr>
<td>ROMP</td>
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<tr>
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<td>( S)-configuration</td>
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<td>SiO\textit{surf}</td>
<td>surface silica</td>
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<td>( syn)</td>
<td>alkylidene rotamer with hydrogen directed away from imido</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>( T_g)</td>
<td>glass transition temperature</td>
</tr>
<tr>
<td>TON</td>
<td>turnover number</td>
</tr>
<tr>
<td>TMS</td>
<td>trimethylsilyl</td>
</tr>
<tr>
<td>TRIP</td>
<td>2,4,6-tri-\textit{iso}-propylphenyl</td>
</tr>
<tr>
<td>triflate</td>
<td>trifluoromethylsulfonate</td>
</tr>
<tr>
<td>Ts</td>
<td>tosyl, \textit{para}-tolylsulfonate</td>
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GENERAL INTRODUCTION
Olefin metathesis has come a long way to establish itself as an important reaction for carbon-carbon double bond manipulation since its inception in the form of an interesting anomaly. An olefin metathesis reaction involves an exchange of the olefinic components (Equation GI.1).

\[
2 \text{RCH=CHR} \rightleftharpoons \text{R'CH=CHR'}
\]

The classical catalyst systems for olefin metathesis involves mixtures of inorganic compounds such as MoO_3, WCl_6, W(O)Cl_6 and Re_2O_7 in the presence of aluminum/tin-based alkylating agents or alumina in ethanol or chlorobenzene. Despite the high turnover rate \((10^3 \text{ min}^{-1})\), short catalyst lifetime coupled with the poor selectivity and the lack of tolerance towards functional groups marred the development of the classical olefin metathesis catalyst system. Furthermore, lack of insight about the active component(s) in the classical catalyst system precluded modification and application of these catalysts in organic reactions.

The discovery and development of well-defined olefin metathesis catalysts was greatly influenced by work in the area of metal-carbon multiple bonds. Chauvin proposed that the exchange of the olefinic components occurred via a carbene/metallacyclobutane intermediate even before the relationship between the metal-carbon double bonded species and olefin metathesis was ascertained. The key step in olefin metathesis reaction is a \([2+2]\) cycloaddition of the olefin to a metal-carbon double bond to form a metallacyclobutane intermediate, which undergoes cycloreversion to yield
either the starting material or a new metal-carbon double bond and a different olefin (Equation GI.2).\(^6\)

\[
[M]=CHR \quad \leftrightarrow \quad \begin{array}{c}
\text{RCH}=CHR' \\
\text{RCH}=CHR’
\end{array} \quad \leftrightarrow \quad [M]=CHR' \
\quad \leftrightarrow \quad \begin{array}{c}
\text{RCH}=CHR' \\
\text{RCH}=CHR
\end{array}
\]

A class of organometallic complexes that have seen extensive use in olefin metathesis reactions are molybdenum imido alkylidene complexes of the type Mo(NR)(CHR')(OR’’)\(_2\) (Figure GI.1).\(^7\) The general architecture of these complexes comprises an imido ligand and alkoxide ligands in the molybdenum-carbon double bond framework. The imido ligand provides steric protection to the metal center thereby discouraging bimolecular decomposition, and the alkoxide ligands make the metal center Lewis acidic thereby enhancing catalytic activity. Finally, the metal center that resides in the highest oxidation state stabilizes electrons of the incoming olefin in the metal-based LUMO orbital as a consequence of the high positive charge of the metal.\(^8,\)\(^6\)_b

Figure GI.1. Molybdenum imido alkylidene complex of the type Mo(NR)(CHR')(OR’’)\(_2\).
In four-coordinate Mo(NR)(CHR')(OR'')₂ complexes the d orbital that is involved in the formation of metal-carbon double bond lies perpendicular to the Nₐ–Mo–Cipso plane due to the pseudo-triple bond that exists between the metal center and the imido nitrogen atom (Figure G1.2). In this situation, two isomers of the molybdenum imido alkylidene complexes are feasible. A syn isomer results when the alkylidene substituent points toward the imido ligand while in an anti isomer the alkylidene substituent points away from the imido ligand. The two isomers can interconvert in the absence of an olefin only if the d orbital used to form the dative bond from the imide nitrogen becomes available in order to stabilize an alkylidene ligand that has rotated by 90°. Syn and anti isomers also can form during a metathesis reaction itself. The syn isomer is often the lower energy species due to stabilization gained through an agostic interaction of the metal with the C-Hₐ bond. The interconversion of syn and anti isomers as well as the difference in the rates of reaction between the two isomers are intriguing aspects of molybdenum alkylidene catalysts but are often difficult to quantify and have been probed by theoretical studies. The conversion between syn and anti isomers can be

**Figure G1.2.** Schematic representation of the orbital orientation in syn and anti isomers.
induced by irradiating the alkylidene complexes at 360 nm; in complexes of the type Mo(NAr)(CHCMe₂Ph)(OR)₂ when R = CMe(CF₃)₂, the isomer interconversion is slow (10⁻⁵ to 10⁻⁶ s⁻¹) whereas a relatively fast (~ 1 s⁻¹) interconversion between the isomers is recorded when R = t-Bu.⁹

The molybdenum imido alkylidene species can be detected easily by using NMR techniques. Resonances for the alkylidene protons appear between 9 – 14 ppm: the syn proton isomer appears 1 – 2 ppm upfield of its anti form.⁷ An unequivocal differentiation between a syn and an anti isomer can be made by calculating the JCH values of the alkylidene resonance – a coupling constant of < 130 Hz is assigned to a syn isomer while that of > 140 Hz is associated with an anti isomer.

**Figure G1.3.** Synthesis of bicyclic β-lactam carboxylates.

Two molybdenum-based olefin metathesis catalysts that have been used extensively, in part because of their commercial availability, are the molybdenum imido
alkylidene bishexafluoro-t-butoxide complex and the t-butoxide analog. One of the uses of hexafluoro-t-butoxide derived catalyst has been realized in the preparation of a variety of bicyclic β-lactam carboxylates. The same investigation has deemed the Ru-based olefin metathesis catalysts inferior to molybdenum catalysts in presence of sulfur and phosphane functional groups. Ten mol% of the catalyst is utilized in a key step in the synthesis of a pharmaceutically relevant molecule, which cannot be synthesized efficiently otherwise (Figure GI.3). A less Lewis acidic molybdenum complex bearing t-butoxide ligands has found its niche in living polymerization. Various forms of the bis-t-butoxide derived catalyst have been used with great success in preparing block copolymers of norbornene- and cyclobutene-based monomers via ring opening metathesis polymerization (ROMP). Molybdenum complexes bearing t-butoxide ligands have been utilized in the preparation of substituted polyenes of various chain lengths via cyclopolymerization of 1,6-heptadiynes.

One of the most fascinating revelations in the ROMP of norbornadiene-based monomers has been the relationship between the catalyst structure (syn versus anti) and the polymer microstructure. For the polymers derived from 2,3-bistrifluoromethylnorbornadiene, it was established that the cis double bonds in the polymer backbone arise from syn alkylidenes while trans double bonds arise from anti isomers. Along this line, the bis-t-butoxide complex was found to react with 2,3-dicarbomethoxynorbornadiene monomer to yield all trans and highly tactic polymers (Figure GI.4). The tacticity was determined by incorporating a chiral group in the polymer backbone such that the magnitude of the coupling of the olefinic protons could be used to differentiate between an isotactic and a syndiotactic polymer. ROMP of
norbornadienes containing chiral substituents (R*) yielded polymers that lacked coupling between the two adjacent olefinic protons, which suggested syndiotactic microstructure.\textsuperscript{18}

![Figure GI.4. Stereospecific ROMP of norbornadiene-based monomer.](image)

The modular design of the molybdenum-based olefin metathesis catalysts, especially the imido and the alkoxide ligands that remain intact during the course of the metathesis reaction, make steric as well as electronic variations to the metal complex easy to accomplish. So far, chiral alkoxides have been employed with great success and have produced a library of active asymmetric olefin metathesis catalysts.\textsuperscript{19} The chiral diolates that have been used thus far have mainly been based on biphenolate, binaphtholate and octahydrobinaphtholate ligands (Figure GI.5). Likewise, the imido ligand has been varied in order to alter the reactivity of the metal complex.\textsuperscript{19,20} Some of the widely used imido ligands are shown in Figure GI.5.
Various imido and diolate ligands used in the preparation of molybdenum imido alkylidenes.

Asymmetric catalysts of this type can result in excellent enantioselectivity for the formation of a variety of ring containing products. An example of such a transformation is shown in Figure G1.6. The biphenolate-based catalyst undergoes ring opening/cross metathesis with the triene to form the heterocycle in excellent yield and with excellent ee (Figure G1.6).

Ring opening/cross metathesis employing molybdenum imido alkylidene catalyst containing a biphenolate ligand.

Figure G1.5.

Figure G1.6.
Polymer-supported variations of well-defined Mo catalysts have been explored for olefin metathesis reactions. These catalysts were found to promote asymmetric olefin metathesis reactions effectively; an example of asymmetric ring opening/cross metathesis is shown in Figure GI.7. Rate with these solid supported catalysts were relatively slow in comparison to the corresponding homogenous analogs, but similar levels of enantioselectivity were observed. What was most impressive about these catalysts was that they could be recycled, although reactivity decreased by the third cycle. However, the enantioselectivity remained high. Additionally, the product isolated using these solid supported catalysts contained fewer metal impurities in comparison that obtained using a corresponding homogenous catalyst.

![Attachment]

**Figure GI.7.** Asymmetric olefin metathesis catalyzed by polymer-supported catalyst.

Thus, the goal for the metathesis project in our laboratory is the development of catalysts that are more active, long-lived and stereoselective in various olefin metathesis reactions by controlling the decomposition pathways – namely, coupling of alkylidene species and rearrangement of metallacyclobutanes that result in metathetically inactive species. Ultimately, it will be highly desirable to be able to regenerate the
metathetically active species.\textsuperscript{25} The ability of the molybdenum imido alkylidene catalyst system to accommodate functionalities validates the modular design of the molybdenum-based olefin metathesis catalysts (Figure G1.8). Chapter 1 will deal with the modification of the alkylidene ligand in order to generate bifunctional ROMP initiators, which are employed for the preparation of triblock copolymers with side chain liquid crystals (Chapter 2). Variations of the alkoxide ligands in the form of electron-withdrawing biphenolate- and binaphtholate-based ligands are reported in chapter 3. Living ROMP of cyclopropenes is addressed in chapter 4 along with the stereospecific polymerization of 3-methyl-3-phenylcyclopropene. Finally, a new type of olefin metathesis catalyst prepared by replacing one of the alkoxide ligands with a pyrrolide ligand will be discussed in chapter 5 along with the catalysis of enyne metathesis reactions using these species.

\textbf{Figure G1.8.} Exploration of modular design of molybdenum imido alkylidene complexes.
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CHAPTER 1

Bifunctional Ring-Opening Metathesis Polymerization Initiators for the Synthesis of ABA Triblock Copolymers

A portion of this chapter has appeared in print:

INTRODUCTION

Ring-opening metathesis polymerization (ROMP) is a method of making polymers utilizing ring strain of cyclic olefins. The initial step in ROMP involves an electrophilic interaction between the cyclic olefin and the alkylidene ligand to generate the metallacyclobutane intermediate upon [2+2] cycloaddition (Figure 1.1). Upon cycloreversion of the metallacyclobutane intermediate, a new alkylidene ligand is generated with the monomer incorporated in a growing chain. Repetition of these steps generates a polymer that can be easily cleaved off from the metal center using various quenching reagents.

![Figure 1.1. Ring-opening metathesis polymerization.](image)

Block copolymers are of interest to us because of their ability to "microphase separate" forming periodic nanostructures. A range of morphologies can be formed, such as lamellae, bicontinuous gyroids, hexagonal packed cylinders and cubic packed spheres, by varying either block sizes or processing techniques used to building these materials. Commercially relevant block copolymers include ABS plastic (acetonitrile-butadiene-styrene), SBR (styrene-butadiene), SIS (styrene-isoprene-styrene) and ethylene-vinyl acetate block copolymers. We are specifically interested in ABA triblock copolymers for applications such as thermoplastic elastomers.
Imido alkylidene complexes of Mo and W that are amenable to living polymerization have been used to prepare block copolymers of various types.7 The two important criteria for a well-behaved living process are 1) comparable rate constants for the initiation and the propagation steps and 2) stable intermediates on the time scale of polymerization.1b The relative rates of initiation and propagation can be easily examined by measuring the quantity of remaining initiator upon addition of a few equivalents of monomer (see experimental for details).8 Likewise, the stability of the reactive intermediates during the course of polymerization can be examined through GPC studies of the polymers. The unimodal distribution of the polymer in the GPC profile can be attributed to the stable intermediates but the lack of such can be associated with unstable intermediates.9

ABA type triblock copolymers have been prepared via sequential addition of monomers to a monometallic initiator or by coupling of living homopolymers with a bifunctional central oligomer or polymer. These methods of block copolymer synthesis usually result in the formation of homopolymer or diblock copolymer impurities due to incomplete coupling or catalyst degradation during the sequential addition of monomers to yield ABA triblock copolymers. Thus, a purification step becomes essential in order to obtain relatively pure triblock copolymers. ABA triblock copolymers have also been prepared by employing bifunctional initiators in an “inside out” mechanism as shown in Figure 1.2.10 The process involves a reaction between a bifunctional initiator with monomer B generating a central polymer block with the linker molecule employed in the construct of the bifunctional initiator situated roughly in the middle of the central block. After the complete consumption of monomer B, monomer A is added to form the outer
blocks with same average chain length. Under the given reaction conditions, if the polymerization reaction employing the bifunctional initiator and the monomers A and B are living, pure ABA triblocks copolymers should result. The first example of bifunctional ROMP initiator based on titanacyclobutane was reported by Grubbs. Molybdenum based bifunctional initiators were first reported by our lab in 1993 - 

\[
\text{[((CF}_3\text{)}_2\text{MeCO})_2(\text{ArN})\text{MoCHCH}_2\text{CH(OMe)}]_2-1,4-\text{C}_6\text{H}_4, \\
\text{[(DME)((CF}_3\text{)}_2\text{MeCO})_2(\text{ArN})\text{MoCHCHCH}]_2, \\
\text{[(quin)((CF}_3\text{)}_2\text{MeCO})_2(\text{ArN})\text{MoCHCHCH}]_2, \text{ and } \text{[(DME)((CF}_3\text{)}_2\text{MeCO})_2(\text{ArN})\text{MoCH}]_2-1,4-\text{C}_6\text{H}_4) (where } \text{Ar = 2,6-diisopropylphenyl, quin = quinuclidine, DME = 1,4-dimethoxyethane).}\]

These ROMP initiators were explored in the polymerization of 2,3-dicarbomethoxynorbornadiene monomer. However, no block copolymers were prepared using these bifunctional ROMP initiators. Grubbs later reported analogous Ru bifunctional ROMP initiators and used them successfully to prepare triblock copolymers. Buchmeiser used some bi- and trifunctional Mo and Ru initiators to prepare homo – and triblock copolymers of 1,6-heptadiynes and norbornene based monomers. This chapter reports the re-examination of the earlier published chemistry of Mo based bifunctional ROMP initiators in the preparation of ABA triblock copolymers. Several new bifunctional ROMP initiators prepared for the synthesis of triblock copolymers will also be discussed.
RESULTS AND DISCUSSION

1.1 Synthesis of bifunctional ROMP initiators

1.1.1 Synthesis of bifunctional initiators containing 1,4-divinylbenzene

A metathesis reaction between 1,4-divinylbenzene and Mo(NAr)(CHCMe₂Ph)(OCMe(CF₃)₂)₂ or Mo(NAr)(CHCMe₃)(OCMe(CF₃)₂)₂ in DME generates [(DME)((CF₃)₂MeCO)₂(ArN)MoCH]₂-1,4-C₆H₄ (1a) (equation 1) in 75% yield. The compound is isolated as a crystalline, bright orange solid which is soluble in DME and THF and poorly soluble in other common solvents (diethyl ether, dichloromethane, benzene). The ¹H NMR spectrum of the bifunctional ROMP initiator in C₆D₆ revealed a single alkylidene peak at 12.64 ppm with Jₐₗ = 125 Hz, which is consistent with a syn disposition of the alkylidene with respect to the imido ligand. The ¹³C NMR spectrum was not viable due to poor solubility of the complex. A solid state structure of a closely related complex, [(THF)((CF₃)₂MeCO)₂(ArN)MoCH]₂-1,4-C₆H₄
(1b), also depicted syn configuration of the alkylidene ligand with respect to the imide (vide infra). In the $^1$H NMR spectrum, two minor peaks of equal intensity (each ~ 10% of the total) were observed at 12.81 ppm and 12.84 ppm. We ascribed these alkylidene resonances to an isomer of 1a in which the configuration at one metal center is different from the other, i.e. orientation at the metal centers is such that the alkylidene is syn at one metal center and anti at the other. This hypothesis has been supported by the $J_{CH}$ coupling constants in a related complex, $\{((CF_3)_2MeCO)_2(ArN)Mo[CH(C_5H_4)]\}_2Fe$, which show similar isomeric distribution in $^1$H NMR spectrum. Diethyl ether does not displace the DME ligand in 1a, suggesting that DME is a preferred stabilizing ligand for the benzylidene complexes. Interestingly, the alkylidene containing products isolated in each of the reactions discussed above are obtained in good yield in spite of the fact the alkylidene is relatively small and therefore could decompose in a bimolecular reaction to yield dimers.  

$$\text{Me}$$

$$\text{RF}_6\text{Mo-O-Me}$$

$$0.5$$

$$\text{DME}$$

$$\text{NAr}$$

$\text{ArN} (1.1)\text{RF}_6\text{O}$,$\text{Ph Me-O-Mo Ar}=2,6-i-\text{Pr}_2\text{C}_6\text{H}_3$, OR$_{F6}=\text{OCMe(CF}_3)_2$: la

A THF adduct $[(\text{THF})((\text{CF}_3)_2\text{MeCO})_2(\text{ArN})\text{MoCH}]_{2-1,4-\text{C}_6\text{H}_4}$ (1b) can be isolated in virtually quantitative yield by dissolving 1a in THF followed by removal of the volatiles. The $^1$H NMR spectrum of 1b in C$_6$D$_6$ reveals a sharp alkylidene resonance

39
at 12.88 ppm, which is assigned to a syn orientation of the alkylidene with respect to the imide based on the $J_{CH}$ of 125 Hz. Single crystals suitable for X-ray studies were obtained by cooling the saturated heptane solution of 1b to –30 °C.

Figure 1.3. A POV-ray diagram of
[(DME)((CF$_3$)$_2$MeCO)$_2$(ArN)MoCH]$_2$-1,4-C$_6$H$_4$ (1b) Thermal ellipsoids are displayed at 50% probability level. Hydrogen atoms are omitted for clarity; Mo(1)-N(1) = 1.717(2) Å, Mo(1)-C(1) = 1.931(3) Å, Mo(1)-O(1) = 1.9395(18) Å, Mo(1)-O(2) = 1.9618(18) Å, Mo(1)-O(3) 2.3995(19) Å, N(1)-Mo(1)-C(1) = 100.03(11) °, N(1)-Mo(1)-O(1) = 115.83(9)°, C(1)-Mo(1)-O(1) = 102.01(10)°, N(1)-Mo(1)-O(2) = 114.27(9)°, C(1)-Mo(1)-O(2) = 98.30(9)°, O(1)-Mo(1)-O(2) = 120.81(8)°, N(1)-Mo(1)-O(3) = 87.22(9)°, C(1)-Mo(1)-O(3) = 172.49(9)°, O(1)-Mo(1)-O(3) = 76.23(7)°.
The solid state structure of 1b (Figure 1.3) revealed an expected bifunctional complex in which each end possesses a pseudo trigonal bipyramidal geometry about the metal center with the THF and the alkylidene ligand occupying axial positions. The alkylidene ligand depicts a syn orientation with respect to the imido ligand, consistent with the solution state structure. A THF molecule is coordinated to the NOO face of the metal center. Two independent molecules were found in the unit cell, the bond lengths and angles for each are similar; data for only one molecule is represented in figure 1.3 caption. To the best of our knowledge, this is the first structurally characterized example of a five-coordinate imido alkylidene complex in which the base is coordinated to an NOO face, although adducts of this type have been characterized in solution by $^1$H NMR spectroscopy.\(^{17}\)

The coordinated THF in 1b can be removed upon a prolonged exposure of the complex to vacuum,\(^{14b}\) consistent with the weak coordination of NOO base adducts and fairly long Mo(1)-O(3) (2.3995(19) Å) bond length. The THF is essentially trans to the alkylidene ligand (C(1)-Mo(1)-O(3) = 172.39(9)°) in 1b. The imido and two alkoxide ligands are slightly bent towards the THF ligand, leading to O(3)-Mo-L angles of less than 90° (87.22(9)° when L = N(1), 76.23(7)° and 76.77(7)° when L is O(1) or O(2), respectively). The Mo(1)-C(1) bond length (1.931(3) Å) and Mo(1)-C(1)-C(2) angle (141.6(2)°) as well as other bond lengths and angles are within the norm for general complexes of this type.\(^{18}\) Efforts to prepare 1b directly via metathesis reaction between Mo(NAr)(CHCMe₂Ph)(OCMe(CF₃)₂)₂ or Mo(NAr)(CHCMe₃)(OCMe(CF₃)₂)₂ and half an equivalent of 1,4-divinylbenzene require a prolonged reaction time for an appreciable product yield.\(^{14b}\)
[(Bu-t-O)₂(ArN)MoCH]₂-1,4-C₆H₄ (2) could not be prepared by adding half an equivalent of 1,4-divinylbenzene to Mo(NAr)(CHCMe₂Ph)(O-t-Bu)₂ or Mo(NAr)(CHCMe₃)(O-t-Bu)₂ due to the incomplete reaction even after 48 h at 60 °C. 2 can be prepared successfully in good yield by reacting 1a with four equivalents of LiO-t-Bu (equation 2). The ¹H NMR spectrum of 2 recorded in C₆D₆ revealed the alkylidene resonance at 11.91 ppm with J(CH) = 123 Hz which is assigned to the syn orientation of the alkylidene ligand with respect to the imide. Resonances for two isomers of 2 were identified at 12.10 ppm and 12.36 ppm (14% of the total), which are assigned to syn-anti disposition of the alkylidene ligand with respect to the imide.

The chemistry of bifunctional initiators has also been extended to the molybdenum imido dialkyl system. Reacting 1a with four equivalents of neopentyl magnesiumchloride in diethyl ether yields [(Me₃CCH₂)₂(ArN)MoCH]₂-1,4-C₆H₄ (3) in 62% yield. The ¹H NMR spectrum of 3 recorded in C₆D₆ reveals an alkylidene resonance at 10.68 ppm, which is assigned to the syn isomer based on the J(CH) coupling constant (J(CH) = 120 Hz). The characteristic doublet resonances for CH₂ moieties are observed at 2.24 ppm and 1.04 ppm.
X-ray quality crystals of 3 were grown from a concentrated toluene solution of the complex set aside at $-30^\circ$C. (Figure 1.4). 3 is the only structurally characterized high oxidation state molybdenum dialkyl complex. The metal centers display tetrahedral geometry, which is also corroborated by the bond angles and distances of the complex in solid state (see caption for Figure 1.4). The alkylidene ligand displays syn orientation with respect to the imide, which is consistent with the solution state structure.

**Figure 1.4.** A POV-ray diagram of $[(\text{Me}_3\text{CCH}_2)_2(\text{ArN})\text{MoCH}]_2-1,4$-$\text{C}_6\text{H}_4$ (3). Thermal ellipsoids are displayed at 50% probability level. Hydrogen atoms are omitted for clarity; Mo(1)-N(1) = 1.717(3) Å, Mo(1)-C(41) = 1.879(3) Å, Mo(1)-C(21) = 2.129(3) Å, Mo(1)-C(31) = 2.148(4) Å, Mo(1)-N(1) = 1.717(3)$^\circ$, Mo(1)-C(41) = 1.879(3)$^\circ$, Mo(1)-C(21) = 2.129(3)$^\circ$, Mo(1)-C(31) = 2.148(4)$^\circ$. 
Alcoholysis of 3 with two equivalents of 2,6-diisopropylphenol in C₆D₆ yields equal quantities of diastereomers of [(Me₃CCH₂)(ArO)(ArN)MoCH]₂-1,4-C₆H₄ (4a and 4b) as determined by the ¹H NMR spectrum (equation 3): presumably one displaying a Cᵢ symmetry (4a) and the other displaying a C₂ symmetry (4b).

1.1.2 Synthesis of bifunctional ROMP initiators containing 1,4-di-buta-1,3-dienylbenzene

One of the challenges in achieving living ROMP lies in controlling the rate constant for the propagation step (k_p) versus the rate constant for the initiation step (k_i). Ideally, k_i ≥ k_p is desired such that the rate constant for the initiation step is greater than that for the propagation step. Such control over k_i and k_p have been successfully achieved.
in cyclopolymerization of 1,6-heptadiynes by employing vinyl alkylidene complexes such as Mo(NAr)(CHCH₂CHCH₂CH₃)(OCMe₃)₂.²⁰ A new series of ROMP bifunctional initiators that are linked by trans,trans-1,4-di-buta-1,3-dienyl-benzene were targeted to improve the initiation properties.

Trans,trans-1,4-di-buta-1,3-dienyl-benzene (5) was prepared by reacting the stoichiometric mixture of Cp₂Zr(H)Cl and HCCCH₂SiMe₃ with half an equivalent of p-carboxydialdehyde in CH₂Cl₂, followed by the addition of a catalytic amount of AgClO₄ to the reaction mixture (Scheme 1.3).²¹ 5 is metastable at room temperature as it decomposes readily over a few days even in the solid state to yield a highly insoluble light yellow powder. Freshly prepared 5 is soluble in most organic solvents.

![Scheme 1.3. Synthesis of 1,4-di-buta-1,3-dienyl-benzene.](image)

A metathesis reaction between Mo(NAr)(CHCMₑ₂Ph)(OCMe(CF₃)₂)₂ and half an equivalent of 1,4-di-buta-1,3-dienyl-benzene in DME resulted in the bifunctional initiators, [(DME)((CF₃)₂MeCO)₂(ArN)MoCHCHCH]₂-1,4-C₆H₄ (6) (equation 4). 6 can be characterized by ¹H NMR spectroscopy, which revealed an alkylidene resonance at
12.77 ppm with a $J_{HH}$ value of 9.99 Hz indicative of a syn-syn orientation of the alkylidenes with respect to the imido ligands. Two minor resonances (~4%) of equal intensities at 12.96 ppm ($J_{HH} = 13.99$ Hz) and 12.65 ppm ($J_{HH} = 8.99$ Hz) were also observed. These resonances are assigned to inequivalent alkylidene protons corresponding to a syn-anti alkylidene rotamer of the same molecule.

Despite the coordination of a DME molecule in 6, these complexes decompose in solution at room temperature to generate new complexes as determined by the $^1$H NMR spectrum. After 12 h at room temperature, new resonances were observed in the $^1$H NMR spectrum of 6 in CD$_2$Cl$_2$. One set of the resonances matches those for 1a, indicating a “back-biting” reaction as a possible pathway for decomposition. It is likely that the smaller alkylidene coupled with the “exposed” vinyl carbons in the linker molecule facilitate the decomposition reaction.
1.2 Initiation studies

In a living polymerization it is essential to establish that the rate of initiation is approximately equal to or greater than the rate of propagation and both ends of the initiator participate in the polymerization reaction. The initiation properties of the bifunctional ROMP initiators were investigated by adding aliquots of two equivalents of DCMNBD (4,5-dicarbomethoxynorbornadiene) to solutions of the initiators, and monitoring the alkylidene region by $^1$H NMR spectroscopy. Addition of aliquots of DCMNBD to 1a in C$_6$D$_6$ led to the disappearance of the initial alkylidene proton resonances and appearance of broadened alkylidene resonances at 12.69 ppm (−15%) and 12.10 ppm, which are assigned to the growing polymer chain. Only eight equivalents of DCMNBD (four per Mo) were required in order to consume all of the initiator when the alkoxide ligands were hexafluoro-t-butoxide. The resonance at 12.69 ppm is proposed to correspond to the anti isomer, while that at 12.10 ppm is attributed to that of the syn isomer of the propagating chain. Likewise, addition of 4 equivalents of DCMNBD (2 per Mo) to 2 in C$_6$D$_6$ revealed the consumption of initial alkylidene resonance, which was replaced by two doublet alkylidene resonances at 11.71 and 11.66 ppm (2.5:1) as determined by the $^1$H NMR spectrum. A similar alkylidene resonance pattern was observed when a monometallic initiator, Mo(NAr)(CHCMe$_2$Ph)(O-t-Bu)$_2$, was used in the initiation study with DCMNBD. Since the number of cis and trans double bonds in polymer derived from DCMNBD is approximately the same, we believe that the two alkylidene resonances can be ascribed to the syn and anti isomers of the propagating polymer chain. The alkylidene itself is likely to be the average of rapidly equilibrating anti and syn isomers in NMR timescale. The main point is that initiation appears to be
facile for both t-butoxide and hexafluoro-t-butoxide complexes, and only 4-8 equiv of **DCMNBD** are needed in order to initiate polymerization at both metal sites.

Likewise, initiation studies of 6 showed clean and complete initiation of both alkylidene groups after the addition of eight equivalents of **DCMNBD** (four per Mo) per bifunctional ROMP initiator. The new alkylidene resonances were observed at 12.71 ppm and 12.15 ppm. Despite good initiation properties, 6 was deemed unsuitable for the preparation of block copolymers due to low stability of the complex in solution.

### 1.3 Polymerization Studies, Including Analyses by MALDI-TOF.

<table>
<thead>
<tr>
<th>Initiator (I)</th>
<th>Monomer</th>
<th>M/I a</th>
<th>PDI b</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>DCMNBD</td>
<td>100</td>
<td>&lt;1.10</td>
<td>95</td>
</tr>
<tr>
<td>1a</td>
<td>DCMNBD</td>
<td>300</td>
<td>&lt;1.10</td>
<td>97</td>
</tr>
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<td>&lt;1.10</td>
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</tr>
<tr>
<td>2</td>
<td>MTD</td>
<td>100</td>
<td>&lt;1.10</td>
<td>97</td>
</tr>
</tbody>
</table>

**Table 1.1.** Gel permeation chromatography data for homopolymers prepared from 2,3-dicarbomethoxy norbornadiene (**DCMNBD**) or methyltetracyclododecene (**MTD**) using bifunctional ROMP initiators [[(DME)((CF<sub>3</sub>)<sub>2</sub>MeCO)<sub>2</sub>(ArN)MoCH]<sub>2</sub>-1,4-C<sub>6</sub>H<sub>4</sub> (1a) and [(Bu-t-O)<sub>2</sub>(ArN)MoCH]<sub>2</sub>-1,4-C<sub>6</sub>H<sub>4</sub> (2).  

*a* See experimental for procedural details. 

*b* Polydispersities were obtained using an RI detector versus polystyrene standards.
Homopolymers and ABA triblock copolymers were prepared using initiators 1a and 2 in toluene (Figure 1.5). A typical polymerization reaction involved addition of a monomer solution to a stirred solution of initiator in one portion. The polymerization reaction mixture was stirred at room temperature for 1 h. To prepare triblock copolymers, a second monomer solution was then added to the reaction mixture, which was stirred for another hour. In all cases, the polymerization reactions were quenched through addition of benzaldehyde or ferrocenecarboxaldehyde, and the polymers were precipitated in methanol (see experimental for details). Polymers were analyzed by $^1$H and $^{13}$C NMR spectroscopies and gel permeation chromatography (GPC); the data are summarized in Table 1.1.

![Figure 1.5](image)

**Figure 1.5.** A representative polymerization showing the synthesis of MTD$_{50}$DCMNBD$_{100}$MTD$_{50}$ using a bifunctional initiator.
DCMNBD\textsubscript{100} prepared using \textit{1a} as initiator had a low polydispersity index (PDI = 1.04) in contrast to MTD\textsubscript{100} (PDI = 1.58) as determined by GPC studies performed versus polystyrene standards. High-PDI polymers also resulted when the monometallic hexafluoro-\textit{tert}-butoxide complex was used as an initiator in the polymerization of MTD and are believed to result from circumstances where \( k_\text{p} \gg k_\text{i} \). Triblock copolymers, MTD\textsubscript{50}DCMNBD\textsubscript{100}MTD\textsubscript{50}, synthesized using \textit{1a} as initiator showed a small amount of homopolymer of DCMNBD based on the \(^1\text{H} \) NMR spectrum (also verified by the GPC trace) along with the major triblock copolymer (Table 1.2). Such low molecular weight homopolymer impurity was also observed when norbornene (NB) was used as the outside block in the preparation of NB\textsubscript{50}DCMNBD\textsubscript{100}NB\textsubscript{50} (PDI of triblock copolymer was 1.12). Decomposition of "active" initiating ends after formation of the inside block is proposed to be the reason for formation of low molecular weight homopolymer.

\begin{tabular}{|c|c|c|c|c|}
\hline
\textbf{Initiator (I)} & \textbf{1\textsuperscript{st} Monomer (eqv.)\textsuperscript{a}} & \textbf{2\textsuperscript{nd} Monomer (eqv.)\textsuperscript{a}} & \textbf{PDI\textsuperscript{b}} & \textbf{Yield (%)} \\
\hline
\textit{1a} & DCMNBD (100) & MTD (100) & 1.21\textsuperscript{c} & 95 \\
\hline
\textit{1a} & DCMNBD (100) & NB (100) & 1.12\textsuperscript{c} & 97 \\
\hline
\textbf{2} & DCMNBD (100) & MTD (100) & 1.12 & 97 \\
\hline
\textbf{2} & DCMNBD (100) & NB (100) & <1.10 & 96 \\
\hline
\end{tabular}

Table 1.2. Gel permeation chromatography data for triblock copolymers prepared from 2,3-dicarbomethoxy norbornadiene (DCMNBD), norbornene (NB) and methyltetracyclododecene (MTD) prepared using bifunctional ROMP initiators \(((\text{DME})((\text{CF}_3)_2\text{MeCO})_2(\text{ArN})\text{MoCH})_2\text{-1,4-C}_6\text{H}_4 \text{ (1a)} \) and \(((\text{Bu-t-O})_2(\text{ArN})\text{MoCH})_2\text{-1,4-C}_6\text{H}_4 \text{ (2)} \).\textsuperscript{a} See experimental for procedural details. \textsuperscript{b}Polydispersity indices were calculated versus polystyrene standards. \textsuperscript{c}Calculated for the major peak.
Initiator 2 was used to prepare homopolymers and triblock copolymers in a similar manner as described for 1a. The GPC data are tabulated in Table 1.1 and Table 1.2. 2 afforded polymers with a lower PDI compared to 1a as determined by GPC studies; for example, MTD100 prepared by 2 revealed a PDI of 1.04 compared to a PDI of 1.58 recorded for the same polymer prepared by 1a. Furthermore, MTD50DCMNBD100MTD50 and NB50DCMNBD100NB50 prepared by 2 did not contain any homopolymer impurities and the polydispersity indices were 1.12 and 1.09, respectively, as determined by the GPC studies. Therefore, 2 was the initiator of choice for the preparation of ABA triblock copolymers.

Several samples of DCMNBDx (100 ≤ x ≤ 50) were examined by MALDI-TOF mass spectroscopy. The three matrixes that were investigated for MALDI included 2,5-dihydroxybenzoic acid (DHB), dithranol (DT), and trans-3-indoleacrylic acid (IAA). Dopants included Na⁺ (source = NaI), K⁺ (source = KCl), and Ag⁺ (source = silver trifluoroacetate). After several sample preparations and optimization, DT was found to be the most appropriate matrix for the polymers of this type. DCMNBD30 prepared using 2 as an initiator revealed extremely weak signals in the MALDI-TOF spectrum when the quenching reagent was benzaldehyde. However, after quenching the polymers with ferrocenecarboxyaldehyde significant improvement in the signals was observed (Figure 1.6). A single distribution (Mn = 6.8 x 10³ g/mol) with the molecular weight centered around the theoretical molecular weight (6.7 x 10³ g/mol) was recorded in the MALDI spectrum. The distance between peaks corresponded approximately to the mass of the monomer (DCMNBD = 208.21 g/mol), and the PDI was 1.08.
Polymerization of 100 equivalents each of DCMNBD and MTD using a mixture of 4a and 4b in THF resulted in quantitative yield of the polymers, however the polydispersity indices were 1.98 and 2.09, respectively, as determined by GPC. The high PDI values can be attributed to the differential polymerization rates demonstrated by the two diastereomers with the monomers resulting in a large distribution of average molecular weights of the polymers.

![Figure 1.6](image)

**Figure 1.6.** A representative MALDI-TOF spectrum for $\text{C}_5\text{H}_3\text{FeC}_5\text{H}_4\text{HC=DCMNBD}_3\text{=CHC}_5\text{H}_4\text{FeC}_5\text{H}_5$.

**CONCLUSIONS**

This chapter details the synthesis and reactivity of several bifunctional ROMP initiators (1a, 2, 4, 6) to be used for the preparation of ABA triblock copolymers. Among the initiators studied, 2 displayed properties that can be best matched with the living polymerization behavior. The homopolymers and triblock copolymers prepared using 2 revealed unimodal distributions with low PDI values based on GPC studies.
TOF mass spectroscopy on the polymer prepared by 2 showed a low PDI (1.04), which further corroborates the living polymerization behavior. Also, the complete initiation of 2 by DCMNBD required only four equivalents (two per Mo center) of the monomer. 2 will be used to prepare various block copolymers to access thermoplastic elastomers as discussed in chapter 2.

1a showed clean initiation by eight equivalents of DCMNBD (four per Mo center) however the triblock copolymers, MTD$_{50}$DCMNBD$_{100}$MTD$_{50}$ and NB$_{50}$DCMNBD$_{100}$NB$_{50}$, prepared using the initiator were contaminated by low molecular weight homopolymers of DCMNBD. The diastereomeric mixture of 4a and 4b used in the ROMP of DCMNBD and MTD resulted in homopolymers with PDI values of ~ 2, presumably due to differential polymerization rates demonstrated by the two diastereomers with the monomers. Instability of 6 to yield 1a in solution prevented us from studying the bifunctional initiator for polymerization studies despite very favorable initiation properties for living polymerization – eight equivalents of DCMNBD resulted in the complete initiation of 6 in C$_6$D$_6$. 
EXPERIMENTAL

General. All manipulations were performed in oven-dried (140 °C) glassware under an atmosphere of nitrogen in a Vacumm Atmospheres glovebox or using standard Schlenk techniques unless otherwise stated. HPLC-grade solvents were purified by passage through an alumina column and stored over 4 Å Linde-type molecular sieves prior to use. Deuterated solvents were degassed and distilled from CaH₂ or sodium benzophenone ketyl. Commercial reagents were used without purification unless stated otherwise. Methyltetrcyclododecene (MTD) and norbornene (NB) were dried over CaH₂ and vacuum distilled. 1,4-Divinylbenzene was purified as suggested in the literature and stored at – 30 °C. Benzaldehyde was vacuum distilled and stored over molecular sieves. Mo(NAr)(CHCMe₂Ph)(OCMe(CF₃)₂)₂ and 4,5-dicarbomethoxynorbonadiene (DCMNBD) were synthesized according to published procedures.

NMR spectra were recorded on a Varian INOVA 500 spectrometer. ¹H NMR chemical shifts are given in ppm versus residual protons in the deuterated solvents as follows: δ 7.27 CDCl₃, 7.16 C₆D₆, 5.32 CD₂Cl₂, and 2.09 CD₃C₆D₅. MALDI-TOF mass spectra were recorded on a Bruker Omni-Flex MALDI-TOF, and data were analyzed using Xtof Software Version 5.1.5 by Bruker Daltonics, Inc. Matrix solutions were prepared as 10 mg/mL solutions in THF. Samples were prepared as 0.1 to 1 mg/mL solutions in THF, and the matrix:sample ratio was 10:1. Dopant concentration when applicable was approximately 0.1 mg/mL. GPC analyses were carried out on a system equipped with two Waters Styragel HR 5E columns (300 mm length × 7.8 mm inner diameter) in series. HPLC grade THF was supplied at a flow rate of 1.0 mL/min with a Knauer HPLC pump K501. A Wyatt Technology mini Dawn light-scattering detector
coupled with a Knauer differential refractometer was employed. Data analysis was carried out using Astrette 1.2 software (Wyatt Technology). PDI values for polymers were obtained using $dn/dc = 0.110 \text{ mL/g}$.

**X-ray Crystallography.** Mounting of the crystals and refinement of X-ray diffraction data was performed by Dr. Adam S. Hock. Low temperature diffraction data were collected on a Siemens Platform three-circle diffractometer equipped with a CCD or Bruker Apex-CCD detector at low temperature. Mo Kα radiation ($\lambda = 0.71073 \text{ Å}$) was used. Integration was performed using the SAINT package and corrected for absorption effects with SADABS, unless otherwise noted. The initial solutions were obtained using direct methods, unless otherwise noted, and refined against $F^2$ on all data using full-matrix least squares using the SHELXTL package. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the $U$ value of the atoms they are linked to, except for methyl groups, which were fixed at 1.5.

$[(\text{DME})((\text{CF}_3)_2\text{MeCO})_2(\text{ArN})\text{MoCH}]_2$-1,4-\text{C}_6\text{H}_4$ (1a). To a stirred solution of Mo(NAr)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$ (1.2 g, 1.6 mmol) in 40 mL of DME was added $p$-divinylbenzene (125 mg, 0.96 mmol), and the reaction mixture was allowed to stir at room temperature for 12 h. The solvent was removed in vacuo, and the residue was crystallized from pentane to yield orange product (1.0 g, 76%): $^1\text{H NMR}$ (C$_6$D$_6$, 500 Mhz) $\delta$ 12.84 (s, 1, Mo=CH, syn/anti isomer, 10%), 12.81 (s, 1, Mo=CH, syn/anti isomer, 10%), 12.64 (s, 2, Mo=CH, $J_{CH} = 125 \text{ Hz}$, syn/syn isomer, 80%). The following peaks are
reported for the major isomer only: 7.0-6.8 (m, 10, Ar), 3.42 (sept, 4, \textit{CH(CH₃)₂}), 3.31 (s, 8, \textit{DME}), 3.12 (s, 12, \textit{DME}), 1.19 (s, 12, \textit{OCCH₃(CF₃)₂}), 1.02 (d, 24, \textit{CH(CH₃)₂}); \textsuperscript{19}F NMR (CD₂Cl₂, 300 MHz) δ - 76.54, - 76.86. Due to the low solubility of the complex in common deuterated solvents (C₆D₆, CD₂Cl₂) \textsuperscript{13}C NMR spectrum could not be recorded. Anal. Calcd for C₅₆H₇₂F₂₄Mo₂N₂O₈: C, 43.42; H, 4.69; N, 1.81. Found: C, 43.28; H, 4.59; N, 1.76.

\[(\text{THF})((\text{CF₃})₂\text{MeCO})₂(\text{ArN})\text{MoCH}][₂\text{-1,4-C₆H₄} \text{(1b)}. \text{1a} \text{ (30 mg, 0.019 mmol)} \text{ was dissolved in 8 mL of THF, and the solution was stirred at room temperature for 2 h. The volatile components were removed in vacuo to obtain orange powder (24.3 mg, 83% yield): } \textsuperscript{1}H NMR (C₆D₆, 500 MHz) δ 13.63 (s, 1, Mo=CH, \textit{syn/anti} isomer, 7%), 13.09 (s, 1, Mo=CH, \textit{syn/anti} isomer, 7%), 12.88 (s, 2, Mo=CH, \textit{syn/syn} isomer, 86%, \textit{J}_{CH} = 125 Hz). The following peaks are reported for the major isomer only: 7.05-6.98 (m, 10 \textit{Ar}), 3.66 (sept, 4, \textit{CH(CH₃)₂}), 3.65 (s, 4, \textit{THF}), 1.29 (s, 4, \textit{THF}), 1.18 (s, 12, \textit{OCCH₃(CF₃)₂}), 1.06 (d, 24, \textit{CH(CH₃)₂}); \textsuperscript{19}F NMR (CD₂Cl₂, 300 MHz) δ - 76.54, -76.86. Anal. Calcd for C₅₆H₆₈F₂₄Mo₂N₂O₆: C, 44.45; H, 4.53; N, 1.85. Found: C, 44.49; H, 4.59; N, 1.78.

\[\text{(t-BuO)₂(NAr)MoCH}][₂C₆H₄ \text{(2). Lithium tert-butoxide (78.8 mg, 0.985 mmol)} \text{ was added to a suspension of 1a (300 mg, 0.193 mmol) in CH₂Cl₂, and the reaction mixture was stirred at room temperature for 2 h. As the reaction progressed, the color changed from orange to dark red, and a more homogeneous solution formed. The volatiles were removed in vacuo, and the product was crystallized from pentane as a powdery red solid (162 mg, 89%): } \textsuperscript{1}H NMR 500 MHz (C₆D₆) δ 12.36 (s, 1H, \textit{MoCHR, syn/anti} isomer,
7%), 12.10 (s, 1H, MoCHR, syn/anti isomer, 7%), 11.91 (s, 2H, MoCHR, syn/syn isomer, 86%). The following peaks are reported for the major isomer only: 7.14-7.05 (m, 10H, Ar), 3.95 (sept, 4H, CH(CH₃)₂), 1.28 (s, 12H, O(CH₃)₃), 1.16 (d, 24H, CH(CH₃)₂); ¹³C NMR (C₆D₆, 125 MHz) δ 247.01 (Mo=CH, J_CMₐ =123 Hz). Anal. Calcd for C₄₈H₇₆Mo₂N₂O₄: C, 61.23; H, 7.98; N, 3.04. Found: C, 61.37; H, 8.08; N, 3.06.

[(Me₃CCH₂)(ArN)MoCH]₂-1,4-C₆H₄ (3). Neopentylmagnesium chloride (0.325 mL, 0.517 mmol, 1.59 M) was added drop-wise to the stirring solution of 1a (200.3 mg, 0.219 mmol) in DME (3 ml) and Et₂O (6 ml) at -30 °C. The reaction was allowed to come to room temperature and stirred for 12h. The solvent was removed under vacuum, and the crude product was extracted with pentane. The pentane solution was concentrated and crystallization at -30 °C gave dark red product (80 mg, 62%). ¹H-NMR (C₆D₆, 500MHz) δ 10.68 (s, 2, Mo=CH, J_CMₐ = 120 Hz) 7.07 (m, 6, Ar), 6.92 (m, 4, Ar), 3.98 (sept, 4, CH(CH₃)₂), 2.24 (d, 4, CH₂CMc₃), 1.19 (d, 24, CH(CH₃)₂), 1.04 (d, 4, CH₂CMc₃), 1.14 (s, 36, CH₂CMc₃); ¹³C NMR (CD₂Cl₂, 125 MHz) δ 237.87 (Mo=CH, J_CMₐ =120 Hz), 153.87, 144.36, 143.17, 127.29, 126.73, 123.35, 80.60, 34.62, 34.02, 28.69, 23.95. Anal. Calcd for C₄₈H₇₆Mo₂N₂O₄: C, 67.22; H, 9.11; N, 3.02. Found: C, 67.46; H, 9.08; N, 3.09.

Observation of [(Me₃CCH₂)(ArO)(ArN)MoCH]₂-1,4-C₆H₄ (4a and 4b) by ¹H NMR. To a 30 mM solution of [(Me₃CCH₂)(ArN)MoCH]₂-1,4-C₆H₄ (20 mg, 0.022 mmol) in C₆D₆ (0.7 mL) taken in a J-Young NMR tube, 2,6-Pr₂C₆H₃OH (8 mg, 0.044 mmol, 7 µL) was added via a syringe. The reaction mixture was thoroughly mixed at which point
the solution became deep red: $^1$H NMR (C$_6$D$_6$, 300 MHz) $\delta$ 12.87 (s, 1, Mo=CH), 12.85 (s, 1, Mo=CH).

**trans,trans-1,4-di-buta-1,3-dienyl-benzene (5).**$^{21}$ HCCCH$_2$SiMe$_3$ (0.720 ml, 4.00 mmol) was added via a syringe into the suspension of Cp$_2$Zr(H)Cl (1.00 g, 3.88 mmol) in 15 mL of CH$_2$Cl$_2$ to obtain a yellow solution after 15 min. Terephthalaldehyde (218 mg, 1.94 mmol) was added to the reaction solution followed by AgClO$_4$ (40 mg, 0.18 mmol). The reaction was stirred at room temperature for 3 h. The reaction solution was then poured into the saturated solution of NaHCO$_3$ and the organic layer was separated, washed with brine and dried over MgSO$_4$. Removal of the volatiles in vacuo yielded a light yellow solid (271 mg, 77 %): $^1$H-NMR (DMSO, 500 MHz) $\delta$ 7.45 (s, 4, Ar), 6.94 (dd, 2, (H$_2$CCHCHCH)$_2$C$_6$H$_4$), 6.64 (d, 2, (H$_2$CCHCHCH)$_2$C$_6$H$_4$), 6.52 (tt, 2, (H$_2$CCHCHCH)$_2$C$_6$H$_4$), 5.38-5.19 (dd, 4, (H$_2$CCHCHCH)$_2$C$_6$H$_4$)

[(DME)((CF$_3$)$_2$MeCO)$_2$(ArN)MoCHCHCH]$_2$-1,4-C$_6$H$_4$ (6). To a stirred solution of Mo(NAr)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$ (200 mg, 0.26 mmol) in 8 mL of DME, a solution of 5 (30 mg, 0.17 mmol) in 2 mL of DME was added. The reaction was stirred at room temperature of 5 h, during which time the color of the solution changed from yellow to dark red. The volatiles were removed in vacuo, and addition of pentane to the crude solid resulted in the precipitation of the product as an orange solid (100 mg, 50 %): $^1$H NMR (CD$_2$Cl$_2$, 500 MHz) $\delta$ 12.96 (d, 2, anti Mo=CH, 2% $J_{HH}$ = 13.99 Hz), 12.79 (d, 2, 2%), 12.77 (d, 2, syn Mo=CH, 96% $J_{HH}$ = 9.99 Hz), 8.43 (dd, 2, Mo=CHCH), 7.34-7.13 (m, 10, Ar), 5.74 (d, 2, Mo=CHCHCH), 3.62 (sept, 4, CH(CH$_3$)$_2$), 3.50 (s, 8, DME), 3.33 (s, 12, DME) 1.44 (s, 12, OCM$_3$), 1.22 (d, 24, CH(CH$_3$)$_2$); $^{19}$F-NMR 300Mhz (CD$_2$Cl$_2$) $\delta$ -
78.67 ppm; Due to the low solubility of the complex in common deuterated solvents (C₆D₆, CD₂Cl₂) the ¹³C NMR spectrum could not be recorded.

Initiation studies. To a stirred solution of initiator at room temperature, an aliquot of monomer was added and the reaction solution was stirred for 15 min before it was transferred to an NMR tube. The reaction was analyzed by ¹H NMR spectroscopy.

A representative example for initiation of 2 by DCMNBD. To a stirred solution of 2 (10 mg, 9.35 x 10⁻³ mmol) in 0.7 mL of CD₂Cl₂ at room temperature, four equivalents of DCMNBD (14.2 µL, 2.85 µM) were added. After 15 min, the reaction solution was transferred into a J. Young NMR tube and the ¹H NMR spectrum was recorded. The ¹H NMR spectrum revealed complete consumption of the initial alkylidene resonance indicating good initiating properties of 2.

General procedure for polymerization in the synthesis of triblock copolymers. The first monomer (inside block) in a given solvent was added in one portion to the catalyst solution in toluene, and the solution was stirred at room temperature for 1 h. Then a solution of the second monomer (outside block) in toluene was added in one portion and the reaction stirred for another hour. Benzaldehyde was added, and the solution was stirred for 45 min to 1 h. The polymer was precipitated by addition of methanol, filtered, and dried under vacuum.

A representative example of polymerization of MTD with 1a. A solution of DCMNBD (130 mg, 0.625 mmol) in 1 mL of toluene was added in one portion to the stirred solution of 1a (10.1 mg, 6.46 x 10⁻³ mmol) in 10 mL of toluene. The solution was
stirred for 1 h at room temperature. Benzaldehyde (200 μL) was added to quench the reaction, and the solution was allowed to stir for another hour. The polymer was precipitated in methanol (100 mL) and isolated by filtration as a white polymer (127 mg, 96%).

A representative example of polymerization of MTD and DCMNBD with 1a. To the stirred solution of 1a (10 mg, 6.46 \times 10^{-3} \text{ mmol}) in toluene (10 mL) was added a solution of DCMNBD (132 mg, 0.631 mmol) in 2 mL of toluene in one portion. The solution was stirred for 1 h at room temperature. A solution of MTD (117 mg, 0.672 mmol) in 2 mL of toluene was added in one portion, and the solution was stirred for another hour. Benzaldehyde (200 μL) was added to quench the reaction, and the solution was allowed to stir for an additional hour. The polymer was precipitated in methanol (100 mL) and isolated by filtration as a white polymer (245 mg, 98%).
Crystal data and structure refinement for [(DME)((CF$_3$)$_2$MeCO)$_2$(ArN)MoCH]$_2$-1,4-C$_6$H$_4$ (1b)

Identification code 04227

Empirical formula C$_{56}$H$_{68}$F$_{24}$Mo$_2$N$_2$O$_6$

Formula weight 1513.00

Temperature 100(2) K

Wavelength 0.71073 Å

Crystal system Triclinic

Space group P1

Unit cell dimensions
\[ a = 13.0696(19) \, \text{Å} \quad \alpha = 110.582(3)^\circ \]
\[ b = 15.465(2) \, \text{Å} \quad \beta = 93.113(2)^\circ \]
\[ c = 16.682(3) \, \text{Å} \quad \gamma = 91.248(2)^\circ \]

Volume 3149.0(8) Å$^3$

Z 2

Density (calculated) 1.596 Mg/m$^3$

Absorption coefficient 0.518 mm$^{-1}$

F(000) 1532

Crystal size 0.28 x 0.12 x 0.04 mm$^3$

Θ range for data collection 1.41 to 26.37°

Index ranges - 16 ≤ h ≤ 16, - 19 ≤ k ≤ 18, 0 ≤ l ≤ 20

Reflections collected 55205

Independent reflections 12827 [R(int) = 0.0391]

Completeness to Θ = 26.37° 99.7 %

Absorption correction Empirical

Max. and min. transmission 0.9796 and 0.8685

Refinement method Full-matrix least-squares on F$^2$

Data / restraints / parameters 12827 / 0 / 819

Goodness-of-fit on F$^2$ 1.064

Final R indices [I>2σ(I)] R1 = 0.0364, wR2 = 0.0925

R indices (all data) R1 = 0.0505, wR2 = 0.1031

Largest diff. peak and hole 1.371 and -0.492 e.Å$^{-3}$
Crystal data and structure refinement for [(Me₃C₂H₂)(ArN)MoCH]₂-1,4-C₆H₄ (3)

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REFERENCES


CHAPTER 2

ABA Triblock Copolymers Containing Side Chain Liquid Crystals via Ring-Opening Metathesis Polymerization: Structural and Functional Investigations for Thermoplastic Elastomers

A portion of this chapter has appeared in print:

INTRODUCTION

Liquid crystals (LCs) have been a subject of intensive study because of their interesting properties and their wide range of applications, especially in optoelectronics that include displays, memory devices and sensors. The molecular property consisting of a rigid component coupled with some degree of anisotropy result in “liquid crystalline” phases between the solid state and the isotropic state make these molecules amenable to various applications. Traditionally, application of LCs has been limited to small molecules or LC homopolymers due to the fast response time of these molecules or polymers, respectively. Recent work in various laboratories has set the precedent to combine LCs in the block copolymers architecture, mainly to take advantage of surface stabilization caused by the inter-material dividing surface (IMDS) of the block copolymer microstructures. One of the methods to incorporate ways that has been proven successful in incorporating LCs in a block copolymer domain is via a side chain liquid crystalline polymer (SCLCP) – a technique that was first made popular by Finkelmann and Ringsdorf.

Block copolymers that contain a SCLCP block coupled to an amorphous block or blocks offer a unique combination of liquid crystalline and block copolymer properties. This combination is a result of liquid crystal (LC) order confined within the microphase segregated domains. Phase segregated triblock copolymers in particular are of significant interest because of potential applications as thermoplastic LC elastomers. Incorporation of LC side chains within the soft domains of a phase segregated thermoplastic elastomer (TPE) can produce liquid crystal thermoplastic elastomers
(LCTPE) with interesting properties, which can be altered and enhanced through processing.

Ring-opening metathesis polymerization (ROMP) has emerged as a powerful tool for preparing polymers with predictable molecular weights. The living nature of several ROMP processes has been utilized successfully to prepare block copolymers. Bicycloheptene derived polymers are the most common polymers prepared via ROMP because of the relative ease in preparation, modification, and their often living characteristics. In most cases, the block copolymers were obtained via sequential addition of monomers to monometallic initiators. Recently, we reported a series of bifunctional ROMP initiators with two initiation sites that allow symmetric ABA triblock copolymers to be synthesized through a two-step addition of monomer.

We are particularly interested in ABA triblock copolymers where the A block is amorphous and the B block is a SCLC block with a glass transition temperature ($T_g$) well below room temperature. Successful synthesis of such triblock copolymers could yield a room temperature LCTPE. Monomers based on bicycloheptenes with SCLC containing nematic LC have been synthesized and polymerized to prepare homopolymers and their properties have been studied. The general architecture of these monomers consists of a polymerizable unit (a bicycloheptene or a cyclobutene) and a LC, which are coupled by a spacer. Generally, longer spacers lower the $T_g$ of the polymer block, and influence the LC phase behavior and stability of nematic and smectic phases. Bicycloheptene and cyclobutene based LC side chains containing alkyl spacers have been explored. However, polyoxyethylene spacers have not been investigated in polymers synthesized via ROMP despite their success in lowering the $T_g$ of the polymer blocks in
other systems. In addition, triblock copolymers prepared by ROMP from monomers that contain polyoxyethylene spacers have not been reported in the literature. In this chapter synthesis of various bicycloheptene and cyclobutene-based monomers with both alkyl and polyoxyethylene spacers and with 4-hydroxy-benzoic acid 4-methoxy-phenyl (MPOB-H) and biphenyl-4-carboxylic acid 4-(1-butoxycarbonyl-ethoxy)-phenyl ester (BPP4-H) as the LCs are discussed. Thermal, optical and mechanical properties of these polymers, along with their morphologies are discussed in order to evaluate the possibilities of preparing a room temperature TPE that contains a SCLC block.

RESULTS AND DISCUSSION

2.1 Bicycloheptene monomer system

2.1.1 Synthesis and polymerization of bicycloheptene based monomers

A series of five monomers that contain the MPOB (Scheme 2.1 and Scheme 2.2), and one monomer that contain the BPP4 (Scheme 2.3) have been synthesized. Monomers NBw9MPOB, NBw11MPOB, NBwO2MPOB and NBwO1MPOB were synthesized as shown in Scheme 2.1 by reacting the appropriate reagent – 9-bromononan-1-ol for NBw9MPOB, 11-bromo-undecan-1-ol for NBw11MPOB, 2-[2-(2-chloro-ethoxy)-ethoxy]-ethanol for NBwO2MPOB, and 2-(2-chloro-ethoxy)-ethanol for NBwO1MPOB – with 4-hydroxy-benzoic acid 4-methoxy-phenyl ester (MPOB-H) followed by esterification of the terminal alcohol with 5-norbornene-2-carboxylic acid chloride. NBwO3MPOB was synthesized by reacting 5-((2-(2-chloroethoxy)ethoxy)methyl)bicyclo[2.2.1]hept-2-ene (V) with p-phenol allyl ester, followed by alkylation at the terminal chloro-position, cleavage of the allyl group and
finally the coupling of the resulting acid with p-methoxy phenol (Scheme 2.2). 

**NBwO1BPP4** was synthesized by alkylating 4'-hydroxy-biphenyl-4-carboxylic acid with 2-(2-chloro-ethoxy)-ethanol followed by coupling with 2-(4-hydroxy-phenoxy)-propionic acid butyl ester, and finally esterification of the alcohol with 5-norbornene-2-carboxylic acid chloride (Scheme 2.3). All the norbornene based monomers displayed endo:exo = 4:1 isomeric distribution in CDCl₃.

![Scheme 2.1. Synthesis of monomers NBw9MPOB, NBw11MPOB, NBwO2MPOB, NBwO1MPOB; (i) KI (cat.), K₂CO₃, DMSO, 65 °C; (ii) Et₃N, THF, reflux.](image-url)
Scheme 2.2. Synthesis of NBwO3MPOB; (i) NaH, THF, -78 °C (ii) K₂CO₃, DMSO, 65 °C; (iii) Pd(PPh₃)₄, PPh₃, Pyrrolidine, CH₂Cl₂; (iv) DCC, DMAP, p-methoxy phenol, CH₂Cl₂.

Scheme 2.3. Synthesis of NBwO1BPP4; (i) NaOH, EtOH, reflux (ii) DCC, DMAP, CH₂Cl₂ (iii) Et₃N, THF, reflux.

The monomers were polymerized by the bifunctional ROMP initiator [(Bu-t-O)(ArN)MoCH]₂-1,4-C₆H₄ (where Ar = 2,6-diisopropylphenyl) in THF at room
temperature to yield polymers in > 95 % yield. The synthesis of homopolymers involved addition of monomer solution into the rapidly stirred initiator solution. In all cases, methyltetrayclocodocene (MTD) was used as the glassy outer block for the ABA type triblock copolymers. In triblock copolymers, the percentage of the liquid crystalline block of the polymer was maintained between 70-80 %. Benzaldehyde was used to quench the polymerization in a Wittig-like fashion to give benzylidene-capped polymers, which were isolated in > 95 % yield. The details about the synthesis and living nature of this bifunctional ROMP initiator is discussed in chapter 1.\textsuperscript{15} Gel permeation chromatography (GPC) studies on the triblock copolymers display a unimodal peak distribution (see Supporting Info) and low polydispersities (Table 2.1). Lack of any homopolymer components in the GPC traces of the triblock copolymers indicates quantitative re-activation of the bifunctional initiator for the second step of polymerization yielding ABA triblock copolymers. To determine the end group of the polymers, a polymer chain prepared using the bifunctional ROMP initiator was quenched with ferrocene aldehyde. MALDI-TOF analysis of the polymer revealed the presence of two ferrocenyl moieties (one on each side).\textsuperscript{15} This result also supports that there is virtually quantitative re-activation of the bifunctional initiator for the second step of polymerization. It should also be noted that in all cases the theoretical average molecular weight was significantly lower than the calculated molecular weight as they were calculated versus the polystyrene standards. The ability of these bifunctional ROMP initiators to synthesize polymers with predictable molecular weight has been verified by MALDI-TOF analysis as discussed in chapter 1.\textsuperscript{15}
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Table 2.1. Gel permeation chromatography data of homopolymers and triblock copolymers in $^a$THF or $^b$CH$_2$Cl$_2$ calculated versus polystyrene standards.

$^c$ref. Scheme 2.1, 2.2 and 2.3

$^d$M$_n$ calculated versus polystyrene standards

2.1.2 Thermal studies

Differential scanning calorimetry (DSC) was used in order to determine the glass transition temperatures ($T_g$) and LC transitions of homopolymers ($NBw9MPOB$_{100}$,
NBw11MPOB_{100} and MTD_{100}) and triblock copolymers (MTD_{100} NBw9MPOB_{200} MTD_{100} and MTD_{100} NBw11MPOB_{200} MTD_{100}), which are reported in Figure 2.1 and Table 2.2. A distinct $T_g$ was observed for the MTD homopolymer at 210 °C. The first and subsequent DSC heating scans were essentially identical and all heating and cooling scans showed good reversibility. Thermal studies on the triblock copolymers revealed $T_g$s that were consistent with those of the respective homopolymers, which is indicative of good phase segregation (Figure 2.1). MTD_{100} NBw9MPOB_{200} MTD_{100} exhibited two distinct $T_g$s at 20 °C and 200 °C, which corresponds with the homopolymer $T_g$s. Similarly, MTD_{100} NBw11MPOB_{200} MTD_{100} displayed two $T_g$s at 15 °C and 200 °C also consistent with their respective homopolymers. A slight broadening of nematic to isotropic LC transitions was observed for the triblock copolymers in comparison to the corresponding homopolymers. We ascribe such broadening of the transitions to the interaction of the LC phase with the inter-material dividing surface (IMDS) of the MTD block.

The DSC scans for monomers NBw9MPOB and NBw11MPOB displayed sharp nematic to isotropic liquid crystalline transitions at 60 °C and 70 °C, respectively (Figure 2.1 and Table 2.1). In NBw11MPOB_{100}, a liquid crystalline phase transition was observed at 75 °C, which correspond to a 5 °C increase relative to its monomer. Similarly, NBw9MPOB homopolymer displayed a liquid crystalline transition 20 °C above the transition in the monomer. Polarized optical microscopy (POM) further confirmed the LC transitions of the homopolymers as well as the triblock copolymers. POM data was in good agreement with DSC data for homopolymers and triblock copolymers containing NBw9MPOB (Figure 2.2) and NBw11MPOB (Figure 2.3).
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<td>GLC – 25</td>
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<tr>
<td>NBwO3MPOB</td>
<td>-</td>
<td>-</td>
<td>GLC – 25</td>
</tr>
<tr>
<td>NBwO1MPOB</td>
<td>-</td>
<td>-</td>
<td>GLC – 25</td>
</tr>
<tr>
<td>NBwO1BPP4</td>
<td>N 60 I</td>
<td>I 60 N</td>
<td>GLC 25 Sc* 60 I</td>
</tr>
</tbody>
</table>

Table 2.2. Differential scanning calorimetry data of ABA triblock copolymers with methyltetrayclododecene (MTD) as the outer blocks.

a-ref. Scheme 2.2 and 2.3
Figure 2.1. Differential scanning calorimetry scans of monomer (top), homopolymer, triblock copolymer and methyltetrayclododecene homopolymer (bottom)
Figure 2.2. Polarized optical micrographs of the polymers containing NBw9MPOB observed on heating (i) triblock copolymer at 60 °C; (ii) triblock copolymer at the isotropic state 100 °C.

Figure 2.3. Polarized optical micrographs of the polymers containing NBw11MPOB observed on heating (iii) triblock copolymer at 60 °C; (iv) triblock copolymer at the isotropic state 100 °C
2.1.3 SAXS and DMA studies

Small angle X-ray scattering (SAXS) studies\textsuperscript{28} were performed on triblock copolymers containing NBw9MPOB and NBw11MPOB to investigate the morphology of the block copolymer and liquid crystalline mesophases (Figure 2.4). Both polymers exhibited a scattering peak at approximately 40 nm, which is characteristic of the block copolymer domain spacing of phase segregated polymers. In both triblock copolymers, a weak second order peak at $\sqrt{7}$ nm is observed, which is typically indicative of hexagonal cylindrical phase morphology of the block copolymer. As the higher order peaks are not well defined, it is concluded that a disordered cylindrical morphology is being observed.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{saxs_dia.png}
\caption{Small angle X-ray diffraction of triblock copolymers containing 9 (NBw9MPOB) and 11 (NBw11MPOB) alkyl spacers}
\end{figure}
It was concluded from the DSC studies that the polymers are well phase segregated as the glass transition temperatures of the block copolymer are very similar to those of the respective homopolymers. However, due to the high $T_g$ of the MTD block, annealing could not take place to allow for the block copolymer to reach its equilibrium conformation without degrading the polymer, which resulted in the lack of long range ordering and thus the disordered cylindrical morphology is observed.

Dynamic mechanical analysis (DMA) studies on the triblock copolymers containing NBw9MPOB and NBw11MPOB confirmed the $T_g$s of the center liquid crystalline blocks (Figure 2.5). Oscillations of 25 μm were applied to films of the samples in tension at a frequency of 1 Hz and heated from -20 °C at a rate of 3 °C/min. The $T_g$s of the liquid crystalline polymers were observed near 35 °C for the polymers containing NBw9MPOB and NBw11MPOB. It should be noted that it is typical to observe thermal transitions at higher temperatures (by 10 - 20 °C) with DMA as compared to other techniques such as DSC. Two elastic plateaus were observed for each sample; the first precedes a "glassy" transition and lies below the $T_g$ of liquid crystalline polymer block, while the second indicates a rubber elasticity plateau of the triblock copolymer and exists between the $T_g$ of the LCP and the MTD blocks. In the case of the triblock copolymer MTD$_{100}$NBw9MPOB$_{200}$MTD$_{100}$, the elastic plateau persisted up to 200 °C, indicating rubber-like elasticity. Additionally, the MTD$_{100}$NBw11MPOB$_{200}$MTD$_{100}$ triblock copolymer shows a broader transition in the DMA, which is believed to be a superposition of the LCP $T_g$ and the dynamic decoupling of the nematic mesogen from the polymer backbone. This second transition results in an elastic plateau of MTD$_{100}$NBw11MPOB$_{200}$MTD$_{100}$ that is nearly two orders lower than
that of $\text{MTD}_{100}\text{NBw9MPOB}_{200}\text{MTD}_{100}$. It is thought that the dynamic decoupling of the polymer backbone from the nematic mesogen allows the backbone to move more independently of the attached mesogen. Thus, the polymer with the longer spacer has a lower modulus, as the polymer backbone with the shorter spacer is supported by the stronger interaction with the nematic mesogen.

**Figure 2.5.** Dynamic mechanical analysis of triblock copolymer containing (a) 9 (NBw9MPOB) and (b) 11 (NBw11MPOB) alkyl spacers.
Shape memory alloys are materials that can take on a new shape when molded under a given set of conditions, and then revert back to their original shape on introduction of an outside stimulus, which may be heat, light, or an external electric or magnetic field.\textsuperscript{29} Shape memory polymers (SMPs) are particularly important technologies in this area due to their light weight and ease of processing, along with their mechanical strength and relatively high percentage of deformation. An investigation of shape memory effect\textsuperscript{30} on MTD\textsubscript{100}NBw9MPOB\textsubscript{200}MTD\textsubscript{100} shows promise; almost complete shape recovery occurs after deformations of at least 100\% strain when cycled in a temperature loop (Figure 2.6).

There was no significant difference in the $T_g$s of the homopolymers obtained by increasing the spacer length by two alkyl units (NBw9MPOB vs. NBw11MPOB) (Figure 2.1). Thus, increasing the alkyl spacer is not a viable method to obtain a $T_g$ lower than 0 °C, as suggested by the inverse relationship between the $T_g$ and the number of
methylene units in the alkyl spacer, which levels out after 10 or 11 methylene units. In addition, increasing the spacer length decouples the LC moiety from the polymer backbone, decreasing the influence of the LC on the polymer backbone and lowering the rigid rod aspect ratio and overall stability of the LC, which are important for the proposed applications of these triblock copolymers. Therefore, a new type of spacer that could lower the \( T_g \) of the polymer, maintain LC stability at room and higher temperatures, and give significant coupling between the LC and the polymer backbone was required.

Polymers such as polyoxyethylene \([-\text{CH}_2\text{-CH}_2\text{-O-}]_n\] that have relatively flexible chains because of easy rotation about main chain bonds have been reported to have low values of \( T_g \). We chose to investigate the influence of polyoxyethylene spacers in the \( T_g \) of the resulting polymers. The first series of polymers prepared containing polyoxyethylene spacers were \( \text{NBwO2MPOB}_{100} \) and \( \text{NBwO3MPOB}_{100} \) (Scheme 2.1 and Scheme 2.2); with ester and ether functional moieties, respectively, that connected the polymer backbone and spacers. DSC studies on the homopolymers of these monomers yielded a \( T_g \) of -25 °C in both cases (Table 2.2), showing no difference between the two connecting moieties in terms of their \( T_g \)s. Unfortunately, neither a distinct nematic to isotropic phase transition, nor birefringence between the temperature range of 30 °C and 200 °C were observed for either of these homopolymers. The lack of a clear LC transition is due to the destabilization of the LC phase by the polyoxyethylene spacer; in such cases, the LC clearing point effectively overlaps with the \( T_g \) of the polymer backbone, rendering it impossible to detect. The lowering of the LC transition phase temperature has been observed in other systems where a polyoxyethylene spacer was employed, but the lack of any direct evidence in our system did not allow us to confirm
the same. A monomer with a shorter polyoxyethylene spacer, NBwO1MPOB (Scheme 2.2), was synthesized to examine its effect on the LC phase transition. A $T_g$ of -25 °C was also observed for the homopolymer of NBwO1MPOB based on DSC studies, with a weak LC clearing transition near the $T_g$ (-15 °C). This was a first direct evidence of a polyoxyethylene spacer lowering the LC transition phase in our system. A more distinct LC clearing transition was observed when BPP4, which has shown stable high temperature smectic phases in various systems, was used with the polyoxyethylene spacer. NBwO1BPP4100 (Scheme 2.3) exhibited a $T_g$ of the LC block of 25 °C with another broad transition at ~ 60 °C. We assign this broad transition to the smectic to isotropic phase transition. We noticed that introduction of the BPP4 side chain (NBwO1BPP4100) elevated the $T_g$ of the polymer backbone in comparison to MPOB (NBwO1MPOB100) by 50 °C (-25 °C to 25 °C). Compared to the alkyl spacer, incorporation of polyoxyethylene spacers decreased the smectic to isotropic phase transition by 80 °C in the BPP4 system ($T_{iso}$ with alkyl spacer = 140 °C$^{28}$ and $T_{iso}$ with polyoxyethylene spacer = 60 °C), which is consistent with the lowering of the LC transition phase due to polyoxyethylene spacers. The DSC studies on the triblock copolymer containing NBwO1BPP4 resulted in a $T_g$ for the liquid crystalline block at the same temperature range as its homopolymer (25 °C), suggesting phase segregation, but the smectic to isotropic transition was not prominent. This observation can be explained by considering interactions between IMDS of the MTD block and the LC phase block, as observed for the alkyl spacers. In summary, use of polyoxyethylene spacers in the monomers lowered the $T_g$s of their polymers along with the LC transitions, which were broad and overlapped with the $T_g$ of the polymer backbone for NBwO2MPOB and
**NBwO3MPOB.** Such overlap was distinct in the case of homopolymers of NBwO1MPOB and NBwO1BPP4. The LC transitions in the triblock copolymer were further broadened due to the stabilization of MTD block by the ordering of the LCs.

In the polyoxyethylene spacer system, birefringence was not observed for the homopolymers NBwO2MPOB, NBwO3MPOB and NBwO1MPOB between the temperature range of 30 °C and 200 °C as determined by POM. Homopolymer of NBwO1BPP4 revealed birefringence until 60 °C, which coincides with the LC transition as determined by DSC studies. In all triblock copolymers containing polyoxyethylene spacer, birefringence was observed over a broad temperature range without any distinct isotropization point, which is attributed to IMDS of the MTD block stabilizing the LC phases. The DSC scans of monomer NBwO1BPP4 revealed a LC transition at 60 °C, which is also supported by the observation of birefringence at the same temperature. Due to the lack of distinct LC transitions in bicycloheptene based monomers containing polyoxyethylene spacer, further mechanical and diffraction studies were not successful.

A different polymer backbone (cyclobutene based polymer) was explored to be used as the LCP block such that a $T_g < 0 \, ^\circ C$, as well as a clear LC clearing point may be achieved.

### 2.2 Synthesis and polymerization of cyclobutene based monomers

**CBw10MPOB** was synthesized as shown in Scheme 2.4 by reacting 10-bromo-decan-1-ol with 4-hydroxy-benzoic acid 4-methoxy-phenyl ester (MPOB-H) followed by etherification. A homopolymer of CBw10MPOB was prepared using the bifunctional ROMP initiator, [((Bu-\text{t}-O))_2(ArN)MoCH]_2-1,4-CH_4, and isolated in 98% yield with a
polydispersity index of < 1.10. The DSC studies on the homopolymer revealed a $T_g$ of 15 °C with a sharp nematic to isotropic phase transition at 90 °C, which was also corroborated by the OM. Monomer **CBw10MPOB** was not used in the preparation of triblock copolymers in lieu of the high $T_g$ demonstrated by its homopolymer. Cyclobutene based monomers containing the polyoxyethylene spacers connecting the polymerizable unit and the smectic LC moiety have also been polymerized by Dr. Andrea J. Gabert, which resulted in a polymer with a low $T_g$ (-20 °C), but lacked a LC clearing point.$^{31}$

![Chemical structure](image)

**Scheme 2.4.** Synthesis of **CBw10MPOB**: (i) K$_2$CO$_3$, KI (cat.), DMSO, 90 °C; (ii) TsCl, Et$_3$N, CH$_2$Cl$_2$; (iii) NaH, DMSO.

**CONCLUSIONS**

A series of monomers for ROMP with SCLCs that vary in spacer length, spacer type and LC have been synthesized. These monomers were polymerized using a molybdenum bifunctional ROMP initiator to yield homopolymers and ABA triblock copolymers with MTD as the A block in high yield and with low polydispersities. Triblock copolymers with alkyl spacers connecting the polymer backbone and the LC showed good phase separation as verified by DSC and SAXS studies. Incorporation of
polyoxyethylene spacers in the monomers resulted in polymers with lower $T_g$s in comparison to the related alkyl spacers; however, absence of a sharp nematic to isotropic phase change did not allow for further characterization of these polymers. The presence of a distinct LC transition in the homopolymer of NBwO1BPP4 showed the possibility of using polyoxyethylene spacers with BPP4 LCs. SAXS studies on triblock copolymers consisting of NBw9MPOB and NBw11MPOB revealed phase segregation of the polymers. Presence of a higher order peak in both triblock copolymers suggested hexagonal cylindrical morphology of the block copolymer domains in each case. The lack of long range order is ascribed to the high melting temperature of the MTD block, which inhibits the attainment of equilibrium morphology. DMA studies of the triblocks containing NBw9MPOB and NBw11MPOB showed an elastic plateau above the liquid crystalline polymer $T_g$ suggestive of rubber elasticity in these samples. This finding was encouraging mainly because this shows the possibility for similar materials to be used as TPEs.

Lowering the $T_g$ of LCP block was attempted by using cyclobutene as the polymer backbone. Polymers prepared from CBw10MPOB afforded a polymer with $T_g$ of 15 °C, which did not meet the desired temperature for the inside block. Polyoxyethylene spacer contain monomers have also be studied for the purpose, but the lack of LC clearing point in the polymers did not allow us to study this class of monomers in the preparation of triblock copolymers. These results suggest the need to investigate into a new type of polymer backbone which not only affords a low $T_g$, but also a distinct LC transition.
EXPERIMENTAL

General. All polymerizations were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox. 2-Norbornene-5-carboxylic acid chloride (exo:endo = 1:4),\textsuperscript{32} 4-hydroxy-benzoic acid 4-methoxy-phenyl ester,\textsuperscript{33} 4-hydroxy-benzoic acid 4-(1-butoxycarbonyl-ethoxy)-phenyl ester, bicyclo[2.2.1]hept-5-en-2-yl-methanol, cyclobut-2-enylmethanol\textsuperscript{34} and [(Bu-t-O)\textsubscript{2}(ArN)MoCH]\textsubscript{2}-1.4-C\textsubscript{6}H\textsubscript{4} were prepared as described in the literature. 1-chloro-2-[2-(2-chloro-ethoxy)-ethoxy]-ethane and 2-[2-(2-chloro-ethoxy)-ethoxy]-ethanol were purchased from TCI America, and 11-bromo-undecan-l-ol, 9-bromo-nonan-1-ol, 10 bromo-decan-1-ol and 2-(2-chloro-ethoxy)-ethanol were purchased from Aldrich and used as received.

NMR spectra were recorded on 500 MHz or 300 MHz Varian spectrometers. \textsuperscript{1}H NMR chemical shifts are reported in ppm versus residual protons in the deuterated solvents as follows: \$7.27 \text{CDCl}_3; \$7.16 \text{C}_6\text{D}_6; \$2.50 \text{(CD}_3\text{)}_2\text{SO. NMR chemical shifts are reported for the major isomer. The relative molecular weights were determined by gel permeation chromatography (GPC) at room temperature in THF (1mL/min) or CH\textsubscript{2}Cl\textsubscript{2} (1mL/min) using a system equipped with two Jordi-Gel DVB mixed bed columns (250 mm length x 10 mm inner diameter) assembled in series. A Wyatt Technology mini Dawn light-scattering detector coupled with a Knauer differential refractometer was also employed for the purpose. The GPC columns were calibrated using polystyrene standards (Polymer Laboratories Ltd.). The polymer samples were cast from a concentrated toluene solution onto a Teflon coated sheet, which was then air-dried for 24 h. A TA Instrument Q1000 differential scanning calorimeter (DSC) was used to determine the thermal transitions, which were read as the maxima and minima of the
endothermic and exothermic peaks, respectively. All heating and cooling scans were performed at the rate of 5 °C/min. Glass transition temperatures (T_g) were read as the middle of the change in the heat capacity. A Zeiss Axioskop2 polarized light microscope with a Zeiss AxioCam HRc digital camera was used to measure the thermal transitions and to analyze the anisotropic textures. The samples were heated using a Linkam THMS 600 hot stage at the rate of 5 °C/min. A TA instrument Q800 was used for Dynamic Mechanical Analysis (DMA). The heating rate was maintained at 3 °C/min, and an oscillation amplitude of 25 μm and 0.02 MPa of tension at a frequency of 1 Hz were employed. Small angle X-ray scattering data were collected with a Siemens 2-D SAXS detector. The X-rays were Cu-Kα radiation with a wavelength of 0.1542 nm set at 40 kV and 0.66 mA. Silver behenate was used to calibrate the distance between the sample and the detector with a first order scattering vector q of 1.076 nm⁻¹ (with q = (4πsinθ)/λ, where 2θ is the scattering angle and λ is the wavelength).

**Synthesis of Monomers**

The synthesis of monomers NBw9MPOB, NBw11MPOB, NBwO2MPOB and NBwO1MPOB is outlined in Scheme 2.1.

**4-(11-Hydroxy-undecyloxy)-benzoic acid 4-methoxy-phenyl ester (II)** A 250 mL round bottom flask was charged with 4-Hydroxy-benzoic acid 4-methoxy-phenyl ester (5.00 g, 2.05 x 10⁻² mol), K₂CO₃ (5.67 g, 4.10 x 10⁻² mol), KI (100 mg) and anhydrous DMSO (100 mL). 11-bromo-undecan-1-ol (5.14 g, 2.05 x 10⁻² mol) was added to the flask and the contents were heated to 90 °C for 12 h. The
reaction solution was cooled to room temperature and diluted by adding 100 mL of ethyl acetate. The diluted solution was washed with distilled water. The organic layer was separated and dried over anhydrous MgSO₄. The volatiles were removed in vacuo, and the product was precipitated in diethyl ether as a white solid (7.10 g, 83 %): ¹H NMR (C₆D₆, 300 MHz) δ 8.81 (d, 2, Ar), 7.08 (d, 2, Ar), 6.77 (d, 2, Ar), 6.69 (d, 2, Ar), 3.52 (t, 2, CH₂OC₆H₄), 3.37 (t, 2, CH₂OH), 3.24 (s, 3, OCH₃), 1.6-1.2 (m, 18, (CH₂)₉); ¹³C-NMR (CDCl₃, 125MHz) δ 165.5, 163.6, 157.3, 144.6, 132.4, 122.7, 114.6, 114.4, 68.43, 63.15, 55.75, 32.93, 29.74, 29.68, 29.66, 29.58, 29.50, 29.24, 26.13, 25.90.

I, III, IV were prepared using a method similar to that described for the preparation of II.

4-(9-Hydroxy-nonyloxy)-benzoic acid 4-methoxy-phenyl ester (I) The yield was 76 %: ¹H NMR (C₆D₆, 300 MHz) δ 8.81 (d, 2, Ar), 7.08 (d, 2, Ar), 6.77 (d, 2, Ar), 6.69 (d, 2, Ar), 3.52 (t, 2, CH₂OPh), 3.37 (t, 2, CH₂OH), 3.24 (s, 3, OCH₃), 1.6-1.2 (br m, 14, (CH₂)₇); ¹³C-NMR (CDCl₃, 125 MHz) δ 165.5, 163.4, 157.3, 144.6, 132.4, 122.5, 114.6, 114.4, 68.43, 63.15, 55.55, 32.93, 29.54, 29.68, 29.63, 29.58, 26.13, 25.90.

4-{2-[2-(2-Hydroxy-ethoxy)-ethoxy]-ethoxy}-benzoic acid 4-methoxy-phenyl ester (III) The yield was 68 %: ¹H NMR (C₆D₆, 300 MHz) δ 8.24 (d, 2, Ar), 7.06 (d, 2, Ar), 6.51 (d, 2, Ar), 6.69 (d, 2, Ar), 3.65 (t, 2, CH₂OC₆H₄), 3.42-3.34 (m, 10, CH₂CH₂O), 3.24 (s, 3, OMe); ¹³C-
NMR (CDCl$_3$, 125 MHz) $\delta$ 165.4, 163.2, 157.4, 144.7, 132.6, 132.5, 132.4, 122.3, 114.7, 114.5, 69.71, 69.69, 69.59, 69.56, 67.79, 63.33, 55.79.

4-[2-(2-Hydroxy-ethoxy)-ethoxy]-benzoic acid 4-methoxy-phenyl ester (IV) The yield was 70%: $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 8.15 (d, 2, Ar), 7.12 (d, 2, Ar), 6.97 (dd, 4, Ar), 4.45 (t, 2, CH$_2$OPh), 3.85 (t, 2, CH$_2$OCH$_2$), 3.83 (s, 3, OMe), 3.80 (t, 2, HOCH$_2$), 3.71 (t, 2, CH$_2$OCH$_2$); $^{13}$C-NMR (CDCl$_3$, 125 MHz) $\delta$ 165.4, 163.0, 157.3, 144.6, 132.4, 122.6, 114.6, 114.5, 72.79, 69.54, 67.70, 61.85, 55.73.

Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid 11-[4-(4-methoxy-phenoxy carbonyl)-phenoxy]-undecyl ester (NBw11MPOB). Bicyclo[2.2.1]hept-5-ene-2-carbonyl chloride (1.90 g, 1.21 x $10^{-2}$ mol) was added dropwise to a refluxing solution of 4-(11-hydroxy-undecyloxy)-benzoic acid 4-methoxy-phenyl ester (II) (5 g, 1.21 x $10^{-2}$ mol) and Et$_3$N (1.70 mL, 1.21 x $10^{-2}$ mol) in 40 mL of THF, and the reaction was refluxed for 12 h. The reaction solution was cooled to room temperature and diluted by adding 50 mL of diethyl ether. The reaction solution was washed with water and the organic layer was dried over anhydrous MgSO$_4$. After removal of the volatiles in vacuo, the crude organic product was purified by column chromatography using silica as the stationary phase and hexanes:ethyl acetate (2:1) as the eluent. The product was obtained as a white solid (5.30
g, 80%): $^1$H NMR (C$_6$D$_6$, 500 MHz) δ 8.26 (d, 2, Ar), 7.03 (d, 2, Ar), 6.68 (dd, 4, Ar), 6.06 (s, 2, HC=CH), 4.0 (tt, 2, CH$_2$CO$_2$), 3.47 (t, 2, CH$_2$OPh), 3.19 (s, 3, OCH$_3$), 3.15 (s, 1, HCCCH(CH$_2$)CH), 2.75 (quin, 1, CHCO$_2$), 2.59 (s, 1, HCCCH(CH)(CH$_2$)), 1.8-1.0 (m, 17, CH$_2$s and one bridging CH$_2$ of norbornene), (d, 1, one bridging CH$_2$ of norbornene, $J_{HH} = 8$ Hz); $^{13}$C-NMR (CDCl$_3$, 125 MHz) δ 174.9, 165.4, 163.5, 157.3, 144.6, 137.8, 132.5, 132.3, 122.6, 114.5, 114.3, 68.37, 64.41, 55.67, 49.73, 45.83, 43.50, 42.64, 29.63, 29.61, 29.48, 29.34, 29.27, 29.21, 28.79, 26.10, 26.06; HRMS (ESI) Calcd for C$_{33}$H$_{42}$O$_6$ [M+Na]: 557.2879 Found: 557.2889.

NBw9MPOB, NBwO2MPOB and NBwO1MPOB were all prepared in the same manner as described for NBw11MPOB.

Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid 9-[4-(4-methoxy-phenoxycarbonyl)-phenoxy]-nonyl ester (NBw9MPOB) The yield was 86%: $^1$H NMR (C$_6$D$_6$, 500MHz)

$^1$H NMR (C$_6$D$_6$, 500 MHz) δ 8.26 (d, 2, Ar), 7.03 (d, 2, Ar), 6.68 (dd, 4, Ar), 6.06 (s, 2, HC=CH), 4.0 (tt, 2, CH$_2$CO$_2$ (endo/exo)), 3.47 (t, 2, CH$_2$OPh), 3.19 (s, 3, OCH$_3$), 3.15 (s, 1, HCCCH(CH$_2$)CH), 2.75 (quin, 1, CHCO$_2$), 2.59 (s, 1, HCCCH(CH$_2$)CH$_2$)), 1.8-1.0 (m, 15, CH$_2$s and one bridging H of norbornene), (d, 1, one bridging H of norbornene , $J = 8.1$Hz); $^{13}$C-NMR (CDCl$_3$, 125 MHz) δ 175.0, 158.8, 158.4, 137.9, 133.6, 133.3, 132.5, 127.8, 114.9, 114.3, 68.16, 64.48, 55.44, 49.78, 45.88, 43.51, 42.69, 29.72, 29.67, 29.57, 29.47, 29.39, 29.32, 28.84, 26.23, 26.12; HRMS (ESI) Calcd for C$_{31}$H$_{38}$O$_6$ [M+Na]: 529.2561 Found: 529.2541.
Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid 2-(2-{-2-[4-(4-methoxy-phenoxy carbonyl)-phenox y]-ethoxy}-ethoxy)-ethyl ester (NBwO2MPOB) The yield was 78 %: \(^1\text{H NMR}\) (C\textsubscript{6}D\textsubscript{6}, 500MHz) \(\delta\) 8.24 (d, 2, \(\text{Ar}\)), 7.06 (d, 2, \(\text{Ar}\)), 6.51 (d, 2, \(\text{Ar}\)), 6.10 (m, 2, \(\text{HCCH}\) (norbornene)), 4.1 (tt, 2, \(\text{HCCH}_2\text{CHCO}_2\)), 3.90 (q, 1, \(\text{CHCO}_2\)), 3.65 (t, 2, \(\text{CH}_2\text{OC}_6\text{H}_4\)), 3.47 (t, 2, \(\text{CH}_2\text{CO}_2\)), 3.42-3.34 (m, 10, \(\text{CH}_2\text{CH}_2\text{O}\)), 3.24 (s, 3, \(\text{OMe}\)), 3.19 (m, 1, \(\text{CO}_2\text{HCCH}\)), 2.6 (m, 1, \(\text{CH}_2\text{CH}\)) 1.04 (d, 1, \(\text{H}\) on bridging \(\text{C}\)), 0.93 (d, 1, \(\text{H}\) on bridging \(\text{C}\), \(J = 7\text{Hz}\)); \(^{13}\text{C-NMR}\) (CDCl\textsubscript{3}, 125 MHz) \(\delta\) 174.9, 165.4, 163.2, 157.4, 144.7, 138.3, 138.1, 138.0, 135.9, 132.6, 132.5, 132.4, 122.3, 114.7, 114.5, 69.71, 69.69, 69.59, 69.56, 67.79, 63.33, 55.79, 49.79, 45.94, 43.42, 42.74, 29.45; HRMS (ESI) Calcd for [M+Na]: 519.1995 Found: 519.1920.

Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid 2-[2-[4-(4-methoxy-phenoxy carbonyl)- phenox y]-ethoxy]-ethyl ester (NBwO1MPOB) The yield was 70 %: \(^1\text{H NMR}\) (CDCl\textsubscript{3}, 500 MHz) \(\delta\) 8.14 (d, 2, \(\text{Ar}\)), 7.12 (d, 2, \(\text{Ar}\)), 7.00 (d, 2, \(\text{Ar}\)), 6.11 (dd, 1, \(\text{HC=CH}\)), 5.94 (dd, 1, \(\text{HC=CH}\)), 4.23 (t, 2, \(\text{COOC}_2\)), 3.92 (t, 2, \(\text{CH}_2\text{CH}_2\text{O}\)), 3.83 (s, 3, \(\text{OMe}\)), 3.76 (m, 2, \(\text{CH}_2\text{OPh}\)), 3.71 (m, 2, \(\text{PhOCH}_2\text{CH}_2\)), 2.80 (br s, 1 \(\text{CH=CHCH}\)), 2.39 (br s, 1, \(\text{CH=CHCH}\)), 1.80 (m, 1, \(\text{CHCO}_2\)), 1.42 (dd, 1, bridging \(\text{H}\) of norbornene), 1.24 (d, 2, \(\text{CH}_2\text{CHCO}_2\)), 0.45 (dd, 1, bridging \(\text{H}\) of norbornene); \(^{13}\text{C-NMR}\) (CDCl\textsubscript{3}, 125MHz) \(\delta\) 174.8, 165.3, 163.1, 157.3, 144.6, 137.8, 132.4, 132.3, 122.3, 122.1, 114.5, 114.4,
70.98, 70.65, 69.65, 69.37, 67.72, 63.33, 55.66, 49.68, 45.82, 43.29, 42.62, 29.33.
HRMS (ESI) Calcd for C_{26}H_{28}O_{7} [M+Na]: 475.1727 Found: 475.1718.

The synthesis of NBwO3MPOB is outlined in Scheme 2.2, the detailed experimental of which is described below.

**5-{2-[2-(2-Chloro-ethoxy)-ethoxy]-ethoxymethyl}-bicyclo[2.2.1]hept-2-ene (V)**

To a flask containing a suspension of NaH (610.8 %, 1.60 g, 6.62 x 10^{-2}) at -78 °C in 20 mL of THF, bicyclo[2.2.1]hept-5-en-2-yl-methanol (5.0 g, 4.03 x 10^{-2}) dissolved in 20 mL of THF was added dropwise. After the complete addition, the reaction solution was brought to room temperature and stirred for 1 h. After effervescence ceased, the solution was transferred to a flask containing a solution of 1-chloro-2-[2-(2-chloro-ethoxy)-ethoxy]-ethane (15.1 g, 8.06 x 10^{-2} mol) in 20 mL of THF via a cannula. The reaction solution was stirred at room temperature for 3 h, and then diluted with 50 mL of distilled water. The mixture was extracted with diethyl ether (3 aliquots of 100 mL). The organic layers were combined, dried over anhydrous MgSO_{4}, and the volatiles were removed in vacuo. Purification by column chromatography using silica as the stationary phase and hexane:ethyl acetate (2:1) as the eluent yielded the product as a light yellow oil (8.50 g, 77 %): \textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}, 500 MHz) \textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}, 500 MHz) \delta 6.08 (dd, 1, CH=CH), 5.98 (dd, 1, CH=CH), 3.43 (m, 6, CH\textsubscript{2}OCH\textsubscript{2}CH\textsubscript{2}), 3.33 (m, 4, CH\textsubscript{2}CH\textsubscript{2}Cl), 3.16 (m, 4, OCH\textsubscript{2}CH\textsubscript{2}O), 2.68 (br s, 1, HC=CHCH), 2.68 (br s, 1, HC=CHCH), 2.37 (br s, 1, HC=CHCH), 1.68 (m, 1, CHCH\textsubscript{2}O), 1.45 (dd, 1, bridging H on norbornene), 1.12 (m, 2, CH\textsubscript{2}CHCH\textsubscript{2}O), 0.45 (m, 1, bridging H norbornene); \textsuperscript{13}C-NMR (CDCl\textsubscript{3}, 125 MHz) \delta 136.8, 132.2, 74.69, 71.09,
4-(2-{2-[2-(Bicyclo[2.2.1]hept-5-en-2-ylmethoxy)-ethoxy]-ethoxy}-ethoxy)-benzoic
acid vinyl ester (VI) A 250 mL flask was charged with 4-Hydroxy-benzoic acid allyl
ester (1.95 g, 1.10 x 10^-2 mol), K₂CO₃ (2.50 g, 1.82 x 10^-2 mol), 5-{2-[2-(2-
chloro-ethoxy)-ethoxy]-ethoxy methyl}-bicyclo[2.2.1]hept-2-ene (2.50 g, 9.1 x 10^-3 mol)
and 50 mL of DMSO and the contents were heated at 90 °C for 12 h. The reaction
solution was cooled to room temperature and 100 mL of distilled water was added to it.
The diluted solution was then extracted with diethyl ether (3 aliquots of 100 mL). The
organic fractions were combined and dried over anhydrous MgSO₄. Removal of volatiles
and column chromatography using silica as the stationary phase and hexane:ethylacetate
(2:1) as eluent yielded the product as a colorless oil (2.50 g, 70 %): ^1^H NMR (C₆D₆, 500
MHz) δ 8.14 (d, 2, Ar), 6.69 (d, 2, Ar), 6.02 (dd, 1, CH=CH), 5.96 (dd, 1, CH=CH), 5.80
(m, 1, CH=CH₂), 5.16, 4.98 (dd, 2, CH=CH), 4.64 (d, 2, CH₂CH), 3.64 (m, 6,
CH₂OCH₂CH₂), 3.50 (m, 4, CH₂CH₂OPh), 3.41 (m, 4, OCH₂CH₂O), 2.61 (br s, 1,
HC=CHCH), 2.68 (br s, 1, HC=CHCH), 2.37 (br s, 1, HC=CHCH), 1.68 (m, 1,
CHCH₂O), 1.45 (dd, 1, bridging H on norbornene), 1.12 (m, 2, CH₂CHCH₂O), 0.45 (m,
1, bridging H norbornene); ^1^C-NMR (C₆D₆, 125 MHz) δ 166.0, 163.4, 137.5, 133.4,
132.4, 123.7, 118.0, 114.9, 75.57, 71.54, 71.44, 71.14, 69.96, 68.01, 65.56, 50.01, 44.75,
42.95, 39.58, 29.72.
4-(2-{2-[2-(Bicyclo[2.2.1]hept-5-en-2-ylmethoxy)-ethoxy]-ethoxy}-ethoxy)-benzoic acid (VII) A solution of pyrrolidine (2.53 mL, 0.041 mol) dissolved in 25 mL of CH$_2$Cl$_2$ was added to an ice-cooled solution containing 4-(2-{2-[2-(bicyclo[2.2.1]hept-5-en-2-ylmethoxy)-ethoxy]-ethoxy}-ethoxy)-benzoic acid vinyl ester (16.8 g, 0.039 mol), Pd(Ph$_3$P)$_4$ (1.13 g, 9.8x10$^{-4}$ mol), and PPh$_3$ (0.511 g, 1.95x10$^{-3}$ mol) in 150 mL of CH$_2$Cl$_2$. The reaction solution was stirred for 1h at room temperature and then diluted with 150 mL of ethyl acetate. The volatiles were removed in vacuo to yield a white solid, which was used in the next step without further purification; Yield 10.6 g, 70%. $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 8.02 (d, 2, Ar), 6.94 (d, 2, Ar), 6.20 (dd, 1, HC=CH ), 5.96 (dd, 1, HC=CH ) 4.78 (d, 2, CH$_2$CHCO$_2$-), 4.19-3.67 (m, 12, (CH$_2$CH$_2$)$_3$O), 3.22 (br s, 1, HCCCH(CH$_2$)CH), 2.98 (quin, 1, CHCO$_2$-), 2.91 (br s, 1, HCCCH(CH$_2$)CH$_2$)), 1.21 (d, 1, one bridging H of norbornene), 1.40 (d, 1, one bridging H of norbornene, $J$ = 7.1Hz).

4-methoxyphenyl 4-(2-(2-((bicyclo[2.2.1]hept-5-en-2-yl)methoxy)ethoxy)ethoxy) benzoate (NBwO3MPOB) A solution of DCC (9.74 g, 0.04 mol) dissolved in 15 mL of CH$_2$Cl$_2$ was added to a stirred solution of Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid 2-{2-[2-(4-carboxy-phenoxy)-ethoxy]-ethoxy}-ethyl ester (9.2 g, 0.02
mol), DMAP (0.29 g, 2.3 x 10^{-3} mol) and \( p \)-methoxy phenol (3.07 g, 0.02 mol) in 30 mL of \( \text{CH}_2\text{Cl}_2 \) at room temperature. The mixture was stirred for 12h. The resulting precipitate was filtered off and the volatiles were removed in vacuo. Purification of the crude product by column chromatography using silica as the stationary phase and ethyl acetate:hexanes (2:1) as the eluent afforded a yellow oil (10.6 g, 76%): \( ^1 \)H NMR (\( \text{C}_6\text{D}_6 \), 500 MHz) \( \delta \) 8.23 (d, 2, \( Ar \)), 7.06 (d, 2, \( Ar \)), 6.74 (d, 2, \( Ar \)), 6.69 (d, 2, \( Ar \)) 6.10 (m, 1, \( HC=CH \)), 5.92 (m, 1, \( CH=CH \)), 3.67 (t, 2, \( \text{CH}_2\text{OC}_6\text{H}_4 \)), 3.42-3.34 (m, 10, \( (\text{CH}_2\text{CH}_2)3\text{O} \)), 3.25 (s, 1, \( \text{OMe} \)), 2.62 (m, 1, \( \text{CH}_2\text{CH} \)), 2.36 (m, 1, \( \text{CO}_2\text{HC} \)), 1.68 (m, 1, \( \text{CO}_2\text{HC} \)), 1.45 (m, 1, \( H \) on bridging C of norbornene), 1.21 (\( CH_2\text{CHCO}_2 \)) 0.93 (d, 1, \( H \) on bridging C of norbornene); \( ^{13} \)C-NMR (\( \text{CDCl}_3 \), 125 MHz) 174.94, 165.42, 163.15, 144.66, 138.28, 138.08, 137.97, 135.88, 132.58, 132.53, 132.40, 122.70, 114.65, 114.53, 69.71, 69.69, 69.59, 69.56, 67.79, 63.33, 55.79, 49.79, 46.56, 46.49, 45.94, 45.87, 43.42, 43.26, 43.24, 42.73, 29.45, 29.30, 21.25, 14.39; HRMS (ESI) Calcd for \( \text{C}_{35}\text{H}_{4\text{O}}\text{O}_8 \) [M+Na]: 611.2615 Found: 611.2639.

The synthesis of NBwO1BPP4 is shown in Scheme 2.3 and described below.

4'-[2-(2-Hydroxy-ethoxy)-ethoxy]-biphenyl-4-carboxylic acid 4-(1-butoxycarbonyl-ethoxy)-phenyl ester (VIII) A solution of DCC (5.12 g, 2.48 x 10^{-2} mol) dissolved in 20 mL of \( \text{CH}_2\text{Cl}_2 \) was added dropwise to a stirred solution of 4'-[2-(2-hydroxy-ethoxy)-ethoxy]-biphenyl-4-carboxylic acid (3.0 g, 9.92 x 10^{-3} mol), 4-hydroxy-benzoic acid 4-(1-butoxycarbonyl-ethoxy)-phenyl ester (2.36 g, 9.92 x 10^{-3} mol) and DMAP (303 mg, 2.48 mol).
x $10^{-3}$ mol) in 50 mL of CH$_2$Cl$_2$. The reaction was stirred for 12 h, during which time a white precipitate formed. The reaction solution was washed with water (3 x 20 mL aliquots) and the organic layer was dried over anhydrous MgSO$_4$. The volatiles were removed in vacuo, and the residue was purified by column chromatography with silica as the stationary phase and ethyl acetate:hexanes (1:2) as the eluent. The product was isolated as a white solid (2.9 g, 56 %): $^1$H NMR (DMSO, 500 MHz) $\delta$ 8.14 (d, 2, Ar), 7.86 (d, 2, Ar), 7.74 (d, 2, Ar), 7.21 (d, 2, Ar), 7.09 (d, 2, Ar), 6.95 (d, 2, Ar), 5.01 (q, 1, CHCH$_3$), 4.16 (m, 2, CH$_2$OPh), 3.77 (m, 2, CH$_2$OH), 3.52 (m, 4, CH$_2$OCH$_2$), 1.71 (m, 2, CO$_2$CH$_2$), 1.61 (m, 2, CH$_3$CH$_3$), 1.53 (d, 3, CH$_3$CH), 1.25 (m, OCH$_2$CH$_2$CH$_2$CH$_3$), 0.86 (t, 3, CH$_2$CH$_3$).

4'-{2-[2-(Bicyclo[2.2.1]hept-5-ene-2-carbonyloxy)-ethoxy]-ethoxy}-biphenyl-4-carboxylic acid 4-(1-butoxycarbonyl-ethoxy)-phenyl ester (NBwO1BPP4)

Bicyclo[2.2.1]hept-5-ene-2-carbonyl chloride (600 mg, 3.82 x $10^{-3}$ mol) was added dropwise to a refluxing solution of 4'-{2-(2-hydroxy-ethoxy)-ethoxy}-biphenyl-4-carboxylic acid 4-(1-butoxycarbonyl-ethoxy)-phenyl ester (2 g, 3.82 x $10^{-3}$) and Et$_3$N (532 µL, 3.82 x $10^{-3}$) in 40 mL of THF. After 12 h, the reaction solution was cooled to room temperature and washed with distilled water (3 x 20 mL aliquots). The organic fraction was dried over anhydrous MgSO$_4$. The volatiles were removed in vacuo and the crude product was purified by column chromatography with silica as a stationary phase and hexanes:ethylacetate (2:1) as the eluent. The product was obtained as a colorless oil.
(1.54 g, 65 %): $^1$H NMR (CDCl$_3$, 500MHz) δ 8.22 (d, 2, Ar), 7.69 (d, 2, Ar), 7.61 (d, 2, Ar), 7.13 (d, 2, Ar), 7.04 (d, 2, Ar), 6.93 (d, 2, Ar), 6.18 (dd, 1, CH=CH), 5.95 (dd, 1, CH=CH), 4.75 (q, 1, OCHCH$_3$), 4.31-4.17 (m, 5, OCH$_3$ + norbornene CH$_2$), 3.90 (t, 2H, CH$_2$O), 3.78 (t, 2H, CH$_2$CH$_2$O), 3.23 (br s, 1H, norbornene), 2.98 (tt, 1H, CHCO$_2$), 2.91 (br s, 1H, norbornene), 1.90 (d, 1H, bridging norbornene), 1.64 (d, 3H, CHCH$_3$); $^{13}$C-NMR (CDCl$_3$, 125MHz) 172.08, 165.46, 160.43, 156.33, 146.40, 146.08, 137.55, 132.97, 131.40, 129.1, 128.68, 127.2, 123.47, 116.35, 115.58, 70.98, 70.65, 69.65, 69.37, 67.72, 63.33, 55.66, 49.68, 45.82, 43.29, 42.62, 39.51, 35.50, 33.15, 31.10, 30.41, 30.01, 29.38, 26.80, 19.52, 18.97.

4-methoxyphenyl 4-(10-hydroxydecyloxy)benzoate (IX). A 250 mL flask was charged with 4-Hyroxy-benzoic acid 4-methoxy-phenyl ester (5.00 g, 2.05 x 10$^{-2}$ mol), K$_2$CO$_3$ (5.67 g, 4.10 x 10$^{-2}$ mol), KI (100 mg), 100 mL of anhydrous DMSO and 10-Bromo-decan-1-ol (5.14 g, 2.05 x 10$^{-2}$ mol). The reaction mixture was heated at 90 °C for 12 h. The reaction solution was cooled to room temperature and diluted with 100 mL of ethyl acetate. The solution was washed with distilled water (3 times) and the organic fraction was dried over anhydrous MgSO$_4$. The volatiles were removed under vacuum, and the product was precipitated in diethyl ether as a white solid (7.10 g, 83 %). $^1$H NMR (C$_6$D$_6$) δ 8.81 (d, 2, Ar), 7.08 (d, 2, Ar), 6.77 (d, 2, Ar), 6.69 (d, 2, Ar), 3.52 (t, 2, CH$_2$OC$_6$H$_4$), 3.37 (t, 2, CH$_2$OH), 3.24 (s, 3, OCH$_3$), 1.60-1.20 (m, 16, (CH$_2$)$_8$). $^{13}$C-NMR (CDCl$_3$, 125Mhz) 165.5, 163.6, 157.3,
4-methoxyphenyl 4-(10-(tosyloxy)decyloxy)benzoate (X). TsCl (2.35 g, 1.25 x 10^{-2} mol) was added as a solid to a stirred solution of 4-methoxyphenyl 4-(10-hydroxydecyloxy)benzoate (IX) (5 g, 1.25 x 10^{-2} mol) and Et₃N (3.39 mL, 2.41 x 10^{-2} mol) in 50 mL of CH₂Cl₂ and the reaction solution was stirred at room temperature for 3 h. The reaction solution was then washed with 100 mL of water, and the organic layer dried over anhydrous MgSO₄. Removal of the volatiles under vacuum resulted in a brown solid, which was purified by crystallization in toluene to obtain a light yellow solid (6.0 g, 90 %). ¹H NMR (CDCl₃, 500 MHz) δ 8.13 (d, 2, Ar), 7.80 (d, 2, Ar Ts), 7.35 (d, 2, Ar Ts), 7.12 (d, 2, Ar), 6.95 (dd, 4, Ar), 4.04 (m, 4, OCH₂(CH₂)₈CH₂O), 3.83 (s, 3, OMe), 2.46 (s, 3, CH₃ of Ts), 1.82 - 1.23 (br m, 16, (CH₂)₈). ¹³C-NMR (CDCl₃, 125 MHz) 165.5, 163.6, 157.3, 144.8, 144.7, 132.4, 130.0, 128.0, 122.7, 114.6, 114.4, 70.87, 68.43, 55.76, 29.64, 29.56, 29.52, 29.50, 29.25, 29.08, 28.97, 26.14, 25.49, 21.81.

4-methoxyphenyl 4-(10-(cyclobut-2-enylmethoxy)decyloxy)benzoate (CBw10MPOB). A solution of cyclobut-2-enylmethanol (200 mg, 2.38 x 10^{-3} mol) in 5 mL of DMSO was added dropwise to a suspension of NaH (94 mg, 60.8 %, 3.92 x 10^{-3} mol) in 10 mL of DMSO and the reaction
was stirred at room temperature for 1 h. The solution was then transferred to a flask containing a solution of 4-methoxyphenyl 4-(10-(tosyloxy)decyloxy)benzoate (X) (1.00 g, 2.09 x 10^{-3} mol) in 20 mL of DMSO via a thin cannula. After stirring the reaction at room temperature for 12 h, the reaction solution was diluted by adding 50 mL of diethyl ether, washed with water (3 aliquots of 20 mL) and the organic layer was separated and dried over anhydrous MgSO₄. The product was purified by column chromatography using silica as the stationary phase and ethyl acetate:hexanes (1:2) as the eluent. (800 mg, 62%). ¹H NMR (CDCl₃, 300 MHz) δ 8.00 (d, 2, Ar), 6.85 (d, 2, Ar), 6.80 (s, 4, Ar), 6.18 (br s, 1, CH=CH), 6.12 (br s, 1, CH=CH), 4.29 (t, 2, CHCH₂O), 4.01 (t, 2, CH₂OPh), 3.85 (t, 2, CH₂O), 3.79 (s, 3, OMe), 3.22 (m, 1, CHCH₂), 2.68 (d, 1, CH=CHCH₂H), 2.38 (d, 1, CH=CHCH₂H), 1.8 - 1.3 (br m, 16, (CH₂)₈); ¹³C NMR (CDCl₃, 125MHz) δ 166.48, 162.96, 153.66, 153.30, 137.57, 137.28, 132.24, 131.60, 131.38, 122.58, 115.40, 114.60, 114.60, 113.89, 107.90, 80.46, 68.59, 68.30, 68.19, 67.39, 55.70, 42.48, 34.14, 29.56, 29.54, 29.44, 29.40, 29.16, 28.30, 26.11, 26.0324.84; HRMS (ESI) Calcd for C₂₆H₂₈O₇ [M+Na]: 391.1521 Found: 391.1520.

**General protocol for homopolymer synthesis:**

The homopolymers were prepared in a manner similar to that described for **NBw11MPOB**. A solution of **NBw11MPOB** (286 mg, 0.534 mmol) dissolved in 2 mL of THF was added in one portion to a solution of [(Bu-t-O)₂(ArN)MoCH]₂-1,4-C₆H₄ (5 mg, 5.34 x 10^{-3} mmol) in 10 mL of THF, and the reaction mixture was stirred at room temperature for 1 h. The polymerization was quenched through addition of
benzaldehyde (100 µL). After 1 h, the polymer was precipitated in methanol, and isolated by filtration (280 mg, 98%).

Homopolymers containing the polyoxyethylene spacer were glue-like, which made purification by precipitation the polymer in methanol impossible. Therefore these polymers were isolated by passing the polymer solutions through a layer of silica to remove the metal byproducts followed by removal of the volatile components in vacuo.

General protocol for triblock copolymer synthesis:
The triblock copolymers were prepared in the manner described for

\[
\text{MTD}_{100}\text{NBw11MPOB}_{200}\text{MTD}_{100} \quad \text{NBw11MPOB (572 mg, 1.07 mmol) dissolved in 2 mL of THF was added in one portion to a stirred solution of } \left[\text{(Bu-t-O)}_2\text{(ArN)}\text{MoCH}\right]_2-1,4\text{-C}_6\text{H}_4 (5 mg, 5.34 \times 10^{-3} \text{ mmol) in 10 mL of THF, and the reaction mixture was stirred at room temperature for 1 h. Methyltetracyclododecene (MTD) (180 mg, 1.07 mmol) dissolved in 2 mL of THF was added in one portion, and the resulting reaction mixture was stirred at room temperature. After 1 h, the reaction was quenched through the addition of benzaldehyde (100 µL) and the solution was stirred at room temperature for 1 h. The polymer was then precipitated in methanol (738 mg, 98%). The triblock copolymers containing polyoxyethylene spacers were precipitated in hexanes.}\n\]
REFERENCES


28. SAXS and DMA analysis was performed by Eric Verploegen (Hammond Group).


CHAPTER 3

Molybdenum Imido Alkylidene Complexes Supported by Highly Electron--Withdrawing Ligands

A portion of this chapter has appeared in print:

INTRODUCTION

The discovery and development of well-defined olefin metathesis catalysts have greatly enriched synthetic strategies in organic chemistry allowing for more facile, efficient and “green” approaches in the manipulation of unsaturated carbon-carbon bonds. Complexes of the type $M(NR)(CHR')(OR')_2$ or $M(NR)(CHR')(diolate)$ ($M = Mo$ or $W$) are well-established high oxidation state olefin metathesis catalysts. The modular nature of these complexes, mainly the imide and alkoxide ligands that remain intact during the course of metathesis reaction, make these motifs ideal platforms for designing catalysts with specific reactivity and selectivity profiles. Thus far, modification of the alkoxide ligands to incorporate chirality at the metal center has resulted in a library of active asymmetric olefin metathesis catalysts. Typical chiral diolates that have been employed successfully have mainly been based on biphenolate, binaphtholate and octahydrobinaphtholate ligands; examples are shown in Figure 3.1.2a

![Figure 3.1. Chiral olefin metathesis catalysts.](image)

One of the goals in olefin metathesis has been the development of new catalysts that outperform traditional catalysts, and also catalyze reactions that heretofore have been unsuccessful with traditional catalysts. Electron-withdrawing ligands (e.g., hexafluoro-$t$-butoxide, 2,6-dichlorophenyl imide) have been used to impart high electrophilic character to the
metal center.\textsuperscript{3} The initial step in olefin metathesis is postulated to involve interaction between the olefin and a metal in a position \textit{cis} to the alkylidene ligand.\textsuperscript{4} An electrophilic metal center can facilitate this step by forming a stronger interaction with the incoming olefin. Use of electron-deficient metal centers to impart higher reactivity has also been a part of the design strategy in Ru\textsuperscript{-5} and cationic Mo-based\textsuperscript{6} olefin metathesis catalysts. Along these lines we decided to explore the possibility of preparing Mo(NR)(CHR')(OR'\textsuperscript{2}) and Mo(NR)(CHR')(diolate) catalysts in which the alkoxides, biphenolate or binaphtholate ligands are significantly more electron-withdrawing than any employed thus far (Figure 3.2). The detailed syntheses of these ligands were recently reported.\textsuperscript{7} In several cases syntheses involve addition of the biphenol or binaphthol to bispyrrolide species, including new 2,5-dimethylpyrrolide complexes. The use of bispyrrolide species as catalyst precursors avoids complications\textsuperscript{8} in traditional catalyst syntheses in which triflate ligands are displaced by biphenolates or binaphtholates. Additionally these precursors allow catalysts to be prepared \textit{in situ}. In at least one synthesis reported here, the bispyrrolide approach was the only one found to be successful.

![Electron-withdrawing ligands](image)

R = 10-Anthracenyl, H\textsubscript{2}[Binaph\textsubscript{Anthryl}], C\textsubscript{6}F\textsubscript{5}, H\textsubscript{2}[Binaph\textsubscript{C6F5}], 3,5-CF\textsubscript{3}C\textsubscript{6}H\textsubscript{2}, H\textsubscript{2}[Binaph\textsubscript{CF3}].

\textbf{Figure 3.2.} Electron-withdrawing ligands.
RESULTS AND DISCUSSION

3.1 Molybdenum imido complexes supported by 2,5-dimethylpyrrolide ligands

3.1.1 Synthesis of 2,5-dimethylpyrrolide complexes

[Mo(NR)(CHCMe₂R')(C₄H₄N)₂]₂ was prepared previously by Dr. Adam S. Hock as shown in equation 3.1. Those complexes were found to react readily with various alcohols, binaphthols, and biphenols to yield Mo(NR)(CHCMe₂R'(OR")₂ or Mo(NR)(CHCMe₂R')(diolate) complexes in situ.⁹ This method is an attractive and mild way to prepare a variety of catalysts from a single precursor. In the solid state structure, an η⁵-pyrrolide ligand on one molybdenum atom was found to behave as a donor to the neighboring molybdenum atom. Consequently, the ¹H NMR spectra of [Mo(NR)(CHCMe₂R')(C₄H₄N)₂]₂ species show two alkylidene resonances at low temperature and a single alkylidene resonance at high temperatures as a consequence of fluxional processes that equilibrate both pyrrolide and two alkylidene ligands at each end of the dimer. This method of catalyst generation is very promising especially when it is employed to screen catalysts prepaid in situ. However, the two equivalents of pyrrole that are generated during the alcoholysis reaction may interact with the metal center thereby affecting the olefin metathesis reaction.¹⁰
We became curious about the 2,5-dimethylpyrrolide analog of [Mo(NR)(CHCMe₂R')(C₄H₄N)₂]₂ for the possibility of preparing monomeric complexes and exploring their use as catalyst precursors in similar fashion. Furthermore the 2,5-dimethylpyrrole that is generated during alcoholysis may not interact with the metal center to the same extent as pyrrole because of increased steric bulk about the nitrogen atom.

Addition of two equivalents of lithium 2,5-dimethylpyrrolide to a diethyl ether solution of Mo(NR)(CHCMe₂R')(OTf)₂(DME) [R = 2,6-diisopropylphenyl (Ar), 2,6-dimethylphenyl (Ar'), 1-adamantyl (Ad), 2-trifluorophenyl (ArF) or 2,6-dichlorophenyl (ArCl)] produced Mo(NR)(CHCMe₂R')(2,5-Me₂NC₄H₂)₂ (R' = Ph or Me) complexes (1a – 1e, equation 3.2). The ¹H NMR spectra of 1a – 1e in C₆D₆ display sharp alkylidene resonances at 13.30 ppm (1a), 13.19 ppm (1b), 12.94 ppm (1c), 13.19 ppm (1d) and 13.58 ppm (1e), but broad pyrrolide resonances as a consequence of hindered rotation about the Mo-Nₚyr bonds. ¹³C NMR spectra reveal alkylidene carbon resonances characteristic of syn isomers (JCH = 120 Hz).

Upon cooling a CD₂Cl₂ solution of 1a to – 80 °C, the alkylidene resonance in the ¹H NMR spectrum appears virtually unperturbed, but the resonances corresponding to the pyrrolide ligands become inequivalent, consistent with a molecule that possesses no symmetry element and an imide with locked rotation (Figure 3.3). We propose that the lowest energy species at this
temperature is one in which one of the 2,5-dimethylpyrrolide ligands is bound in an \( \eta^5 \) fashion and the other is bound in an \( \eta^1 \) fashion. The fluxionality observed at room temperature can therefore be explained by an equilibrium between two \( \eta^1, \eta^5 \)-enantiomers that interconvert via a \( C_s \) symmetric complex in which both 2,5-dimethylpyrrolide ligands are bound \( \eta^1 \) to the metal center.

![NMR spectra](image-url)

**Figure 3.3.** \(^1\)H NMR spectra of Mo(NAr)(CHMe\(_2\)Ph)(2,5-Me\(_2\)NC\(_4\)H\(_2\))\(_2\) (1a) in CD\(_2\)Cl\(_2\) (500MHz) and a scheme accounting for the equilibrium process observed at room temperature.
Figure 3.4. POV-ray diagram of Mo(NAd)(CHCMe$_2$Ph)(2,5-Me$_2$NC$_5$H$_2$)$_2$ (1c)

Thermal ellipsoids are displayed at 50% probability level. Hydrogen atoms and cocrystallized 2,5-dimethylpyrrole and pentane are omitted for clarity; Mo(1)-N(3) = 1.720(3) Å, Mo(1)-C(1) = 1.938(3) Å, Mo(1)-N(1) = 2.117(3) Å, Mo(1)-N(2) = 2.391(3) Å, Mo(1)-Pyr$_{cent}$ = 1.735 Å, N(3)-Mo(1)-C(1) = 101.65(14)$^\circ$, N(3)-Mo(1)-N(1) = 106.10(12)$^\circ$, C(1)-Mo(1)-N(1) = 100.07(12)$^\circ$, C(2)-C(1)-Mo(1) = 141.7(3)$^\circ$, Pyr$_{cent}$-Mo(1)-N(3) = 120.66$^\circ$

The solid state structure of 1c, depicting a psuedo-tetrahedral geometry, also corroborates $\eta^5$, $\eta^1$ binding of the 2,5-dimethylpyrrolide ligands (Figure 3.4). The alkylidene ligand adopts a
disposition with respect to the imido ligand, consistent with what is observed in solution.

Two "short" (Mo-C(22) = 2.358(2) and Mo-C(23) = 2.406(3) Å) and two "long" (Mo-C(24) = 2.472(3) and Mo-C(25) = 2.448(3) Å) Mo-C bond distances are observed to the carbon atoms in the π*-bound pyrrolide ring, although the C-N bond distances within the η5-pyrrolyl ring are essentially the same (C(25)-N(2) = 1.385(9) Å; C(22)-N(2) = 1.378(5) Å). Steric interactions are likely to be responsible for the slightly "slipped" nature of the η5-dimethylpyrrolide ligand. An 18-electron count is also reached in 1c.

3.1.2 Reaction of 1a – 1e with olefins

Compounds 1a – 1e do not react with simple olefins such as ethylene (1 atm at 60 °C) or diallylether, consistent with the reactivity observed for bisamido and [BINA(NR2)] complexes. Although steric factors may be significant, the primary reason for the observed lack of reactivity with simple olefins is believed to be due to the 18 electron count at the metal center rendering it electronically saturated. However, 100 equivalents of norbornene are polymerized instantaneously when added to a C6D6 solution of 1a – 1e. The polymer formed in each instance forms a gel like material, which displays very poor solubility in common organic solvents (THF, benzene, diethylether, chloroform) which might be ascribed to a high molecular weight was a consequence of poor initiation versus propagation. Low solubility (< 1 mg in 1 mL solvent) of the polymers in common organic solvents did not allow for the analysis by gel permeation chromatography (GPC). The 1H NMR spectra of the polymers recorded in C6D6 reveal various ratios of cis and trans polymer microstructures.
3.1.3 Reaction of 1a – 1e with alcohols

Compounds 1a – 1e were employed in alcoholysis reactions with alcohols and diols to compare the reactivity with [Mo(NR)(CHCMe₂R')(C₄H₄N)₂]. Upon reacting 5 mM C₆D₆ solutions of 1a – 1e with two equivalents of t-BuOH and (CF₃)₂MeCOH, facile conversion to the respective bisalkoxide species were observed within 15 min by ¹H NMR spectroscopy. There is no indication of any interaction between liberated 2,5-dimethylpyrrole and the metal complex as determined by ¹H NMR spectroscopy; i.e. the chemical shifts for the alkylidene protons are identical to those for the base free species isolated independently. Likewise, protonation of alkylidene and imido ligands was not observed during alcoholysis.

When reacting 5 mM C₆D₆ solution of 1a with commercially available binaphthol (BINAP) based ligands containing phenyl, iso-propyl and tert-butyl moities on the 3,3' positions, only the diols containing relatively small substituents (e.g. phenyl and isopropyl) reacted readily. Likewise, an octahydrobinaphthol (BITET) ligand containing a benzyl group in the 3,3' positions afforded facile alcoholysis, whereas trimethylsilyl and tert-butyl substituted BITET ligands did not (Table 3.1). Complexes 1b – 1d, which contain less sterically demanding imide ligands did not help in alcoholysis reactions with the aforementioned ligands. Likewise, 5 mM C₆D₆ solution of 1a – 1d gave no reaction with 3,3'-di-tert-butyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diol (H₂Biphen) in 2 days at room temperature as judged by the ¹H NMR spectra. Heating the reaction solution at 60 °C for 48 h did afford the desired product though in the case of 1e complete alcholysis was achieved in 50 h. It should be noted that this method of preparation of Mo(NAr₅)(CHCMe₃)(Biphen) is advantageous over the route that involves salt metathesis of the Mo(NAr₅)(CHCMe₃)(OTf)₂(DME) with Biphen⁻² as the latter has been shown to yield the alkylidyne species, Mo(CCMMe₃)(NHAr₅)(Biphen).¹³
<table>
<thead>
<tr>
<th>Diol</th>
<th>Time for full conversion&lt;sup&gt;a&lt;/sup&gt; (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BINAPH&lt;sub&gt;Ph-H&lt;/sub&gt;&lt;sub&gt;2&lt;/sub&gt;</td>
<td>15</td>
</tr>
<tr>
<td>BINAPH&lt;sub&gt;ipr-H&lt;/sub&gt;&lt;sub&gt;2&lt;/sub&gt;</td>
<td>15</td>
</tr>
<tr>
<td>BINAPH&lt;sub&gt;tBu-H&lt;/sub&gt;&lt;sub&gt;2&lt;/sub&gt;</td>
<td>No reaction</td>
</tr>
<tr>
<td>BITET&lt;sub&gt;CHPh&lt;sub&gt;2&lt;/sub&gt;-H&lt;/sub&gt;&lt;sub&gt;2&lt;/sub&gt;</td>
<td>15</td>
</tr>
<tr>
<td>BITET&lt;sub&gt;tBu-H&lt;/sub&gt;&lt;sub&gt;2&lt;/sub&gt;</td>
<td>No reaction</td>
</tr>
<tr>
<td>BITET&lt;sub&gt;TMS-H&lt;/sub&gt;&lt;sub&gt;2&lt;/sub&gt;</td>
<td>No reaction</td>
</tr>
</tbody>
</table>

Table 3.1. Alcoholysis of Mo(NAr)(CHCM<sub>2</sub>Ph)(2,5-Me<sub>2</sub>NC<sub>4</sub>H<sub>2</sub>)<sub>2</sub> (1a) by diols.

<sup>a</sup>As determined by<sup>1</sup>H NMR at 23 °C
3.2 Molybdenum imido complexes supported by 2,4-dimethylpyrrolide ligands

Inability of 1a – 1e to react with the biphensols and binaphthols containing bulky substituents in the 3, 3’-positions, in comparison to the unsubstituted pyrrolide complexes, led us to investigate their 2,4-dimethylpyrrrolide analogs. Addition of two equivalents of lithium 2,4-dimethylpyrrolide to a diethyl ether or toluene solution of Mo(NAr)(CHCMe2Ph)(OTf)2(DME) resulted in dark red crystals in < 20% yield. The $^1$H NMR spectrum of the complex was most consistent with Mo(NAr)2(2,4-dimethylpyrrolide)(CH2CMe2Ph). However, Mo(NAd)(CHCMe2Ph)(2,4-Me2NC4H2)2 was isolated in 76% yield by reacting lithium 2,4-dimethylpyrrolide with Mo(NAd)(CHCMe2Ph)(OTf)2(DME) in toluene (Equation 3.3). The $^1$H NMR spectrum of Mo(NAd)(CHCMe2Ph)(2,4-Me2NC4H2)2 (1f) depicted an alkylidene resonance at 11.62 ppm ($J_{CH} = 125.1$ Hz), which is assigned to the syn orientation of the alkylidene with respect to the imido ligand.

3.3 Synthesis of catalysts containing electron-withdrawing ligands

A reaction between 1a and two equivalents of C6F5OH in THF yielded Mo(NAr)(CHCMe2Ph)(OC6F5)2 (2) in 70% yield (Equation 3.4). The insolubility of 2 in diethyl ether, benzene, toluene and its low solubility in dichloromethane suggests that the complex may be dimeric in the solid state. Complex 2 is soluble in THF probably due to break-up of the dimer by THF. The $^1$H NMR spectrum recorded in CD2Cl2 revealed a broad alkylidene resonance at $\delta$
12.24 ppm ($J_{CH} = 124$ Hz), which is assigned to a syn alkylidene isomer. It should be noted that previous efforts to prepare 2 by salt metathesis reaction between Mo(NAr)(CHMe$_2$Ph)(OTf)$_2$(DME) and the alkali metal salt of the ligand were not successful.

Variable-temperature $^1$H NMR spectra of 2 recorded in THF-$d_8$ from –80 °C to 40 °C are shown in Figure 3.5. Two primary alkylidene resonances were observed at room temperature; the furthest downfield (δ 13.95 ppm) is assigned to an anti isomer based on the $J_{CH} = 144$ Hz and the one at δ 12.42 ppm is identified as a syn ($J_{CH} = 124$ Hz). Both are assumed to be THF adducts, based on the two sets of THF resonances observed for each alkylidene resonance at –40 °C. At 20 °C, the anti alkylidene resonance is relatively sharp suggesting a strong binding of THF, whereas the syn alkylidene resonance is broad, consistent with a slow equilibrium between a THF bound and a THF free species. At –40 °C, the syn alkylidene resonance becomes sharp due to a less facile equilibrium between a THF free and a THF bound species. Another anti alkylidene resonance (δ 13.90 ppm) appears at –40 °C that is believed to be due to THF binding on a different face (probably NOO face) of the metal center. Likewise, at –80 °C, a second minor alkylidene resonance for the syn isomer becomes visible, which can also be ascribed to the coordination isomer of the THF bound species. Upon warming the sample, the chemical shift for
the alkylidene resonance for the *anti* isomer is virtually unperturbed, indicating strong binding of THF to the metal center. The alkylidene resonance for the *syn* isomer, however, is broadened at 40 °C with an upfield shift, consistent with the generation of a THF free species that is in rapid equilibrium with the THF bound species. During the entire cooling and heating of the sample, no decomposition of the complex was observed.

![NMR spectra](image)

**Figure 3.5.** Variable temperature $^1$H NMR spectra of Mo(NAr)(CHCMe$_2$Ph)(OC$_6$F$_5$)$_2$ (2) in THF-d$_8$ (500 MHz).

Incorporation of diolates on the molybdenum imido alkylidene framework has mainly been limited to the reaction between Mo(NR)(CHCMe$_2$Ph)(OTf)$_2$(DME) and the alkali metal salts of the diols.$^{14, 15, 16, 17}$ Salt metathesis reactions between the dilithium salt of the ligands (generated *in situ* through deprotonation of the ligands with n-BuLi in THF) and Mo(NR)(CHCMe$_2$Ph)(OTf)$_2$(DME) ($R = Ar, Ar', Ad, ArF$) in THF failed due to ligand decomposition (for H$_2$[Binaph$_{Anthyl}$]), formation of undesired products for (H$_2$[Binaph$_{C6F5}$]) and
poor and inconsistent yields (for H2[BiphenCF3]). Therefore a related, but milder route that employs triethylamine as a base was pursued.

Mo(NAr)(CHCMe2Ph)(BinaphAnthryl)(THF) (3a) was synthesized in 90% yield through the reaction of Mo(NAr)(CHCMe2Ph)(OTf)2(DME) with H2[BinaphAnthryl] in the presence of ten equivalents of Et3N in THF (Equation 3.4). The 1H NMR spectrum of 3a in C6D6 revealed two broad resonances at δ 13.21 ppm (80%) and 11.70 ppm (20%) which are assigned to anti and syn alkylidene isomers, respectively. The resonances are broad as a consequence of THF dissociation from the metal. In the presence of 10 equivalents of THF sharp alkylidene resonances were observed at δ 13.20 ppm and 12.34 ppm. Binding of THF is characteristic of binaphtholate compounds of this general type.2a The 1H NMR spectrum of 3a in CD2Cl2 displayed sharp resonances for both syn (δ 11.95 ppm, JCH = 117 Hz) and anti (δ 12.89 ppm, JCH = 145 Hz) isomers in the ratio of 85(anti):15(syn). Mo(NR)(CHCMe2Ph)(BinaphAnthryl)(THF), where R = Ar' (3b, 84% yield) or Ad (3c, 92% yield) were synthesized in a manner analogous to that described for 3a (Equation 3.5). Efforts to synthesize Mo(NArF)(CHCMe2Ph)(BinaphAnthryl)(THF) (3d) in a similar manner resulted in formation of unknown multiple products having multiple alkylidene resonances in the 1H NMR spectrum; therefore 3d could not be prepared using the same method shown in equation 3.4.
Attempts to generate THF-free versions of $3a - 3d$ ($3a' - 3d'$) in reaction between $H_2[\text{BinaphAnthryl}]$ and $1a - 1d$ in $C_6D_6$ resulted in $< 20\%$ conversion after 12 h. Likewise, $[\text{Mo}(NAr)(\text{CHCM}_2\text{Ph})(\text{C}_4\text{H}_4\text{N})_2]_2$ did not react readily or cleanly with $H_2[\text{BinaphAnthryl}]$ in $C_6D_6$. We ascribe these slow reactions to the sterically demanding characteristics of the $[\text{BinaphAnthryl}]^{2-}$ ligand.

Single crystals of $3a$ suitable for X-ray crystallography were obtained by slow diffusion of pentane into a THF solution at $-30$ °C (See Figure 3.6). The overall structure of $3a$ depicts a trigonal bipyramidal geometry; the THF molecule O1S and one of the binaphtholate oxygen atoms (O1) occupy the axial positions, while the alkylidene carbon (C1), imide nitrogen (N1), and binaphtholate oxygen atom (O2) are located in the equatorial positions. The THF molecule is bound to a CNO face of the tetrahedral Mo(NAr)(CHCM$_2$Ph)(BinaphAnthryl) core. This is the most often observed geometry of base adducts of this type.$^{14}$ The alkylidene displays an *anti* configuration with respect to the imido ligand, which is consistent with the solution behavior as determined by the $^1$H NMR spectrum. The dihedral angle between the anthracenyl and the binaphthyl planes is $68.5\degree$. All bond angles and bond distances observed are consistent with the five-coordinate complexes of this type (see caption to Figure 3.6).
Figure 3.6. POV-ray diagram of Mo(NAr)(CHCMe2Ph)(BinaphAnthryl)(THF) (3a). Thermal ellipsoids are displayed at 50% probability level. Hydrogen atoms and cocrystallized THF molecules are omitted for clarity; Mo(1)-N(1) = 1.736(3), Mo(1)-C(1) = 1.941(4) Å, Mo(1)-O(2) = 1.994(2) Å, Mo(1)-O(1) = 2.025(2) Å, Mo(1)-O(1S) = 2.235(2) Å, N(1)-Mo(1)-C(1) = 96.94(18)°, N(1)-Mo(1)-O(2) = 131.98(12)°, C(1)-Mo(1)-O(2) = 128.22(16)°, N(1)-Mo(1)-O(1) = 102.22(11)°, C(1)-Mo(1)-O(1) = 96.02(14)°, O(2)-Mo(1)-O(1) = 89.74(9)°, N(1)-Mo(1)-O(1S) = 85.39(11)°, C(1)-Mo(1)-O(1S) = 91.30(14)°, O(2)-Mo(1)-O(1S) = 78.95(9)°, O(1)-Mo(1)-O(1S) = 168.68(9)°, C(2)-C(1)-Mo(1) = 125.7(4)°, C(11)-N(1)-Mo(1) = 159.8(2).
Efforts to prepare 4a – 4d (Equation 3.5) through a reaction between H₂[Biphen₆F₅] and Mo(NR)(CH₃Me₂Ph)(OTf)₂(DME) [R = Ar, Ar', Ad, ArF] in the presence of excess Et₂N in THF were not successful. However, reactions between the bispyrrolide complexes (1a - 1d) and one equivalent of H₂[Biphen₆F₅] in THF yielded the respective complexes 4a - 4d in >84% yield as THF adducts (Equation 3.6). The ¹H NMR spectra of 4a, 4b, and 4c contained alkylidene resonances only for anti isomers in C₆D₆, according to their JₜCH values (> 140 Hz). The ¹H NMR spectrum of 4d in C₆D₆ depicted two resonances in the alkylidene region at 14.08 ppm (anti, 60%) and 13.36 ppm (syn, 40%), which correlate with ¹³C NMR resonances at 320.4 ppm and 307.1 ppm. Compound 4a should be compared with the previously reported anti-(R)-Mo(NAr)(CH₃Me₂Ph)(Binaphth)(THF) (δ 13.65 ppm in C₆D₆, JₜCH = 150 Hz). The ¹⁹F NMR spectra of these complexes display ten aryl fluoride resonances, consistent with pentafluorophenyl groups that do not rotate faster than the NMR timescale at room temperature.

\[
\begin{align*}
\text{R} &= 2,6-i-Pr_2C₆H₃ (4a); \\
&= 2,6-Me_2C₆H₃ (4b); \\
&= 1-Adamantyl (4c); \\
&= 2-CF₃C₆H₄ (4d).
\end{align*}
\]

Variable-temperature ¹H NMR spectra of 4a in toluene-d₈ from -80 °C to 90 °C are shown in Figure 3.7. At 20 °C, only the Hₐ resonance for the anti isomer (JₜCH = 146 Hz) is observed at 13.81 ppm. Upon cooling the sample to -40 °C, new minor alkylidene resonances (<5% total) are observed at 13.26 ppm and 12.69 ppm, which are proposed to be diastereomeric...
syn-THF adducts. Warming the sample to 60 °C generates a broad upfield resonance that is the result of equilibration of syn THF-free and syn-THF adducts on the NMR timescale. The resonance for the anti THF adduct is broad for similar reasons, but does not shift upfield since relatively little THF-free anti isomer is generated. At 90 °C broadening of the anti and the syn alkylidene resonances may also be the result of interconversion of anti and the syn isomers through rotation about the Mo=C bond. After heating the sample to 90 °C, some decomposition of 4a was observed.

![NMR spectra](image)

**Figure 3.7.** Variable temperature $^1$H NMR spectra of Mo(NAr)(CHCMe$_2$Ph)(Binaphc$_6$F$_5$)(THF) (4a) in toluene-$d_8$ (500 MHz).

Mo(NR)(CHCMe$_2$Ph)(Binaph$_{CF_3}$)(THF) complexes [R = Ar, Ar', Ad, Ar$_F$] (5a - 5d) can be prepared by treating bispyrrolide complexes 1a - 1d with H$_2$[Binaph$_{CF_3}$] in THF (Equation 3.7). For example Mo(NAr)(CHCMe$_2$Ph)(Binaph$_{CF_3}$)(THF) (5a) was isolated in 37% yield. The $^1$H NMR spectrum of 5a in C$_6$D$_6$ revealed alkylidene resonances at 13.77 ppm ($J_{CH} = 140$ Hz) for the anti isomer and at 12.23 ppm (5%) for the syn isomer. The presence of only two $^{19}$F
resonances for each isomer is a consequence of free rotation of the 3,5-
bis(trifluoromethyl)phenyl groups on the NMR time scale at room temperature. Compounds 5b – 5d could be observed to form cleanly as shown in equation 3.6. However, none could be
crystallized from solution. In C₆D₆ essentially one alkylidene resonance was found at 13.79 ppm
for 5b, 12.42 ppm for 5c, and 13.91 ppm for 5d. Generation of BinaphCF₃²- containing
complexes through alcoholysis of Mo(NR)(CHCMe₂Ph)(OTf)₂(DME) [R = Ar, Ar', Ad, ArF]
with the ligand in the presence of ten equivalents of triethylamine resulted in clean conversion
only in the case of the complex containing the 1-adamantyl imido ligand (δHα = 13.18 ppm).

![Equation 3.7]

The THF-free versions of 5a – 5d (5a' – 5d') could be prepared in C₆D₆. The reaction
between 1a and H₂[BinaphCF₃] proceeds in 15 min to generate "syn-
Mo(NAr)(CHCMe₂Ph)(BinaphCF₃)" (5a'; δHα = 10.83 ppm). The 2,5-dimethylpyrrole
resonances are not shifted from where they are observed in the free pyrrole, therefore we will
designate 5a' as a dimethylpyrrole-free species. This method of in situ catalyst generation also
can be employed to prepare Mo(NR)(CHCMe₂Ph)(BinaphCF₃) species 5b' (R = Ar'), 5c' (R =
Ad), and 5d' (R = ArF). Conversion was rapid (< 15 min) in the case of 5b' and 5c', but 5d'

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required one hour for full conversion at 22 °C at a concentration of 23 mM. Compounds 5a',
5b', and 5c' consisted of mostly the syn isomer (δHα = 10.83 ppm, 10.81 ppm, and 10.62 ppm,
respectively) while 5d' consisted of approximately an equal ratio of syn (δ 10.73 ppm) and anti
(δ 13.71 ppm) isomers. Upon addition of THF to samples that contain 5a' - 5d', the THF
adducts (5a - 5d) are formed immediately.

Addition of H₂[BiphenCF₃] to a THF solution of Mo(NAr)(CHCMe₂Ph)(OTf)₂(DME) in
the presence of ten equivalents of triethylamine yielded rac-
Mo(NAr)(CHCMe₂Ph)(BiphenCF₃)(THF) (6a) in 50% yield (Equation 3.8). It should be noted
that the analogous Mo(NAr)(CHCMe₂Ph)(Biphen) species does not crystallize with one
equivalent of THF bound to the metal.¹⁴ In fact, the only other crystalline THF adduct of a
[Biphen]²⁻ complex is Mo(NArCl)(CHCMe₂Ph)(Biphen)(THF), where it is believed the 2,6-
dichlorophenylimido ligand creates a more electrophilic metal center.¹⁷ Coordination of THF
in 6a is also consistent with a more electrophilic metal center.

\[
\begin{align*}
\text{Me} & \text{OTf} \quad \text{Ph} \\
\text{Me} & \text{OTf} \\
\begin{array}{c}
\text{O} \\
\text{Me}
\end{array} & \begin{array}{c}
\text{N} \\
\text{R}
\end{array} \\
\begin{array}{c}
\text{F₃C} \\
\text{CH₂Ph}
\end{array} & \begin{array}{c}
t-\text{Bu} \\
t-\text{Bu}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\text{F₃C} & \text{OH} \\
\text{F₃C} & \text{OH}
\end{align*}
\]

\[
\text{10 Et₃N} - 2 \text{Et₃NHOTf} \\
\text{THF} - \text{DME}
\]

(3.8)

R = 2,6-\text{i-Pr}_₂\text{C₆H₃} (6a);
2,6-\text{Me}_₂\text{C₆H₃} (6b);
1-Adamantyl (6c).

Proton, carbon, and fluorine NMR spectra of 6a in C₆D₆ at 20 °C are all consistent with a
70:30 mixture of syn and anti isomers being present. At higher and lower temperatures, behavior
analogous to that for 4a is observed (Figure 3.8). Such fluxionality has been observed in a
variety of previous biphenolate or binaphtholate complexes explored to date. Interestingly at -60 °C, four alkylidene proton resonances are observed for what we propose are four diastereomeric THF adducts (largely two of the anti isomer at 14.15 and 14.25 ppm). It is not known whether five-coordinate rearrangements of diastereomers can take place at some point without THF dissociation or whether base-free syn and anti isomers can interconvert on the NMR time scale through rotation about the Mo=C bond. During the entire cooling and heating of the sample, no decomposition of the complex was observed.

![Variable temperature ¹H NMR spectra of Mo(NAr)(CHCMe₂Ph)(BiphencF₃)(THF) (6a) in toluene-d₈ (500 MHz).](image)

**Figure 3.8.** Variable temperature ¹H NMR spectra of Mo(NAr)(CHCMe₂Ph)(BiphencF₃)(THF) (6a) in toluene-d₈ (500 MHz).

Mo(NR)(CHCMe₂Ph)(BiphencF₃)(THF) complexes (R = Ar' (6b) or R = Ad (6c)) were prepared in a manner analogous to the synthesis of 6a from Mo(NAr')(CHCMe₂Ph)(OTf)₂(DME) and Mo(NAd)(CHCMe₂Ph)(OTf)₂(DME), respectively (Equation 3.11). The ¹H NMR spectrum of 6b in C₆D₆ showed it to be a mixture of anti (14.10 ppm, JCH = 146 Hz, ~75%) and syn
isomers (12.41 ppm, $J_{CH} = 117$ Hz, ~25%). The $^1$H NMR spectrum of 6c in C$_6$D$_6$ revealed only one broad alkylidene resonance at 12.14 ppm.

Figure 3.9. POV-ray diagram of Mo(NAd)(CHCMe$_2$Ph)(Biphen$_{CF_3}$)(THF) (6c). Thermal ellipsoids are displayed at 50% probability level. Hydrogen atoms are omitted for clarity; Mo-C(1) = 1.8825(19) Å, Mo-N(1) = 1.7280(16) Å, Mo-O(1) = 1.987(2) Å, Mo-O(2) = 2.027(2) Å, Mo-O(1T) = 2.2206(13) Å, Mo-C(1)-C(2) = 146.73(15)$^\circ$, Mo-N(1)-C(11) = 162.04(13)$^\circ$, C(1)-Mo-N(1) = 105.19(8)$^\circ$, C(1)-Mo-O(1) = 109.13(14)$^\circ$, C(1)-Mo-O(2) = 102.14(17)$^\circ$, N(1)-Mo-O(1T) = 92.62(6)$^\circ$, N(1)-Mo-O(1) = 144.54(14)$^\circ$, N(1)-Mo-O(2) = 95.06(12)$^\circ$, N(1)-Mo-O(1T) = 92.62(6)$^\circ$, O(1)-Mo-O(2) = 86.35(14)$^\circ$, O(1)-Mo-O(1T) = 78.15(12)$^\circ$, O(2)-Mo-O(1T) = 162.21(17)$^\circ$. 

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Single crystals of 6c suitable for X-ray crystallography were grown from a diethyl ether solution at -30 °C (Figure 3.9). The overall structure is a trigonal bipyramid in which the syn alkylidene carbon (C1), the imide nitrogen (N1), and the biphenolate oxygen (O1) share the equatorial plane, while O2 of the biphenolate ligand and THF occupy axial positions. All bond angles and bond distances observed are typical for five-coordinate complexes of this type (see caption to Figure 3.9).

Reactions between 1a - 1c and H2[BiphenCF3] showed < 10% conversion at room temperature in 12 h in C6D6 at concentrations of ~ 25 mM. Upon heating the samples to 70 °C complete conversion was achieved in 18 h. There was no change in the rates of conversion when the reaction was performed in CD2Cl2. However, THF-free syn complexes containing the [BiphenCF3]2- ligand could be generated in situ readily in C6D6 when the dipyrrrolide precursors, [Mo(NR)(CHCMe2Ph)(NC4H4)2]2 (R = Ar or Ad) were employed instead of 1a or 1c. Addition of one equivalent of THF to an NMR sample of syn-Mo(NAr)(CHCMe2Ph)(BiphenCF3) (6a'; δHα = 11.31 ppm) generated in this manner produced a spectrum consistent with formation of the anti THF adduct 6a (δHα = 14.24 ppm).

Likewise, a stoichiometric reaction between 1f and H2[BiphenCF3] in C6D6 (17 mM) resulted in five new resonances in the alkylidene region (13.74 ppm (10%), 13.59 ppm (25%), 13.21 ppm (8%), 11.82 (24%) and 11.22 ppm (33%)) with complete consumption of 1f as determined by the 1H NMR spectrum. After 6h at room temperature, only two resonances were observed in the alkylidene region (13.59 ppm (90%) and 11.90 ppm), neither of which matched the alkylidene resonance recorded for the isolated Mo(NAd)(CHCMe2Ph)(BiphenCF3) (12.14 ppm). The product(s) in the reaction have not been elucidated.
Synthesis of complexes 2 – 6 gives us a unique opportunity to compare the electrophilicity of metal centers of these complexes with that of previously reported complexes (Table 3.2). In complexes of general type Mo(NR)(CHR')(OR')₂, the chemical shift of the alkylidene resonance can be taken as a diagnostic test for the electrophilicity of the metal center among the same rotamers; a more downfield shift of the alkylidene resonance is associated with the more electrophilic metal center. Comparing the alkylidene resonance for 6a with that of its non-fluorinated analog, it becomes apparent that the former has a more downfield shifted resonance for the alkylidene proton. Also, a molecule of THF is bound to the metal center in the case of 6a, which is consistent with a more electrophilic metal center. Likewise, among the metal complexes ligated by the substituted binaphtholate ligands, 4a demonstrates the most electron deficient metal center as judged by the chemical shift of the alkylidene proton. All these observations are consistent with the increase in electrophilicity of the metal center with the incorporation of highly electron-withdrawing ligands in the metal complex.

<table>
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<th>Catalyst</th>
<th>Syn (δ ppm, %)</th>
<th>Anti (δ ppm, %)</th>
</tr>
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<tbody>
<tr>
<td>Mo(NAr)(CHCMe₂Ph)(Biphen)</td>
<td>10.98, 100</td>
<td></td>
</tr>
<tr>
<td>Mo(NAr)(CHCMe₂Ph)(Biphen₃CF₃)(THF)</td>
<td>11.46, 70</td>
<td>14.17, 30</td>
</tr>
<tr>
<td>Mo(NAr)(CHCMe₂Ph)(BinaphPh)(THF)</td>
<td>10.85, 10</td>
<td>13.65, 90</td>
</tr>
<tr>
<td>Mo(NAr)(CHCMe₂Ph)(Binaph₃Anthryl)(THF)</td>
<td>11.70, 20</td>
<td>13.21, 80</td>
</tr>
<tr>
<td>Mo(NAr)(CHCMe₂Ph)(Binaph₃CF₃)(THF)</td>
<td>12.23, 5</td>
<td>13.77, 95</td>
</tr>
<tr>
<td>Mo(NAr)(CHCMe₂Ph)(Binaph₆CF₅)(THF)</td>
<td>13.81, 100</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2. Comparison of alkylidene resonances of various diolate based molybdenum imido alkylidene complexes.
3.4 Metathesis reactions

Ring-closing metatheses of diallylether were carried out in C₆D₆ with ~ 4% catalyst loading (14 mM) and product yield was determined through ¹H NMR studies (see experimental section for details). Of the compounds examined (2, 3a – 3c, 4a – 4d, 5a, 6a – 6c), only 2 and the BiphenCF₃²⁻ complexes (6) were successful. In 15 min 2 and 6a afforded the ring-closed product, dihydrofuran, in essentially 100% yield, while 6b and 6c yielded 80% and 50% ring-closed product, respectively, in the same time period. No BINAPH-based catalyst (3, 4, or 5) produced any significant amount of product (< 1% based on ¹H NMR) in 12 h, even though resonances for the first metathesis product (3,3-dimethyl-3-phenyl-1-propene) were observed in ¹H NMR spectra. No product was observed upon heating reactions to 60 °C.

In contrast, diallyltosylamine can be ring-closed with BINAPH based catalysts to yield the ring closed product in good yields. Catalysts 3a, 3b and 3c produced 15%, 65% and 6% product after 15 min, and 90%, 100% and 50%, respectively, at 40 °C in 3 h. Catalyst 4a completely ring-closed diallyltosylamine in 3 h, while 4b – 4d produced 86%, 29% and 25%, respectively, of the ring closed product after 3 h. Interestingly, "in situ" catalysts 5a' – 5d' in C₆D₆ produced 77%, 60%, 43%, and 20%, respectively, of the ring closed product in 15 min.

We ascribe the inability of BINAPH-based catalysts to ring-close diallylether to coordination of the oxygen atom of the ring closed product to the more accessible metal center, thereby slowing metathesis significantly. The ether oxygen can coordinate in either diallylether itself, or in a Mo=CHCH₂OCH₂CHCH₂ intermediate or the product. In the case of diallyltosylamine, the nitrogen does not coordinate strongly enough to inhibit metathesis to any significant degree.
CONCLUSIONS

Several new molybdenum imido alkylidene complexes containing highly electron-withdrawing aryloxide, biphenolate or binaphtholate ligands are detailed in this chapter. All of these ligands were successful in supporting isolable and well-defined complexes. Incorporation of electron-withdrawing ligands in the molybdenum imido alkylidene framework was only successful via alcoholysis reaction either between Mo(NR)(CHCMe₂Ph)(OTf)₂(DME) and the ligand in presence of a base (Et₃N) or Mo(NR)(CHCMe₂Ph)(2,5-Me₂NC₄H₂)₂ and the ligand. Mo(NR)(CHCMe₂Ph)(2,5-Me₂NC₄H₂)₂ complexes could be isolated in excellent yield and serve, along with known [Mo(NR)(CHCMe₂Ph)(NC₄H₄)₂]₂ complexes, as precursors to many in situ generated catalysts. Reactions between Mo(NR)(CHCMe₂Ph)(2,5-Me₂NC₄H₂)₂ complexes and H₂[BiphencF₃] were slow and incomplete compared to reactions between [Mo(NR)(CHCMe₂Ph)(NC₄H₄)₂]₂ complexes and H₂[BiphencF₃], most likely for steric reasons. Mo(NAr)(CHCMe₂Ph)(OC₆F₅)₂ and two new types of Mo(NR)(CHCMe₂Ph)(diolate) complexes could be prepared and isolated only via a reaction between alcohols/diols and bispyrrolide complexes. Simple ring-closing metathesis reactions demonstrate the potential of catalysts supported by electron withdrawing ligands, although coordination of donor functionality to the metal may limit activity in certain circumstances.
EXPERIMENTAL

General. All manipulations were conducted under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using Schlenk techniques. All glassware was oven-dried prior to use. Ether, pentane, toluene, dichloromethane, toluene and benzene were sparged with nitrogen and passed through activated alumina columns. Dimethoxyethane was vacuum distilled from a dark purple solution of sodium benzophenone ketyl, and degassed by three successive freeze-pump-thaw cycles. All dried and deoxygenated solvents were stored over molecular sieves in a nitrogen-filled glovebox.

C₆D₆, CD₂Cl₂, and C₆D₅CD₃ were dried over 4 Å Linde-type molecular sieves prior to use. CDCl₃ was used as received. NMR spectra were recorded on a Varian 300 MHz or 500 MHz spectrometer at room temperature unless otherwise noted. Chemical shifts for ¹H and ¹³C spectra were referenced to the residual ¹H/¹³C resonances of the deuterated solvent (¹H: CDCl₃, δ 7.26; C₆D₆, δ 7.16; CD₂Cl₂, δ 5.32; C₆D₅CD₃, δ 2.09 (methyl); ¹³C: CDCl₃, δ 77.23; C₆D₆, δ 128.39; CD₂Cl₂, δ 54.00) and are reported as parts per million relative to tetramethylsilane. The following abbreviations refer to observed peak multiplicities: s = singlet, d = doublet, t = triplet, sept = septet, q = quartet, m = multiplet, br = broad signal. Elemental Analyses were performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany.

Mo(NAr)(CHCMe₂Ph)(OTf)₂(DME),¹⁸ Mo(NAr')(CHCMe₂Ph)(OTf)₂(DME),¹⁹ Mo(NAd)(CHCMe₂Ph)(OTf)₂(DME),¹⁹ Mo(NArF)(CHCMe₂Ph)(OTf)₂(DME)¹⁹ and Mo(NArCl)(CHCMe₂Ph)(OTf)₂(DME)¹² (Ar = 2,6-diisopropylphenyl; Ar' = 2,6-dimethylphenyl; Ad = 1-adamantyl; ArF = 2-trifluorophenyl; ArCl = 2,6-dichlorophenyl) were prepared as described in the literature. LiNC₄H₄ and Li-2,5-Me₂NC₄H₂ were prepared by treating the respective pyrrole (Aldrich) with n-BuLi in diethylether.
X-ray Crystallography. Mounting of the crystals and refinement of X-ray diffraction data was performed by Dr. Peter Müller. Low temperature diffraction data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), performing φ- and ω-scans. All structures were solved by direct methods using SHELXS,20 and refined against R2 on all data by full-matrix least squares with SHELXL-97.21 All non-hydrogen atoms, were refined anisotropically. Except for the hydrogen atoms on carbon atoms binding directly to molybdenum, which have been taken from the difference Fourier synthesis and refined semi-freely with the help of distance restraints, all hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups).

Mo(NAr)(CHCMe2Ph)(2,5-Me2NC4H2)2 (1a). Lithium 2,5-dimethylpyrrolide (103 mg, 1.01 mmol) was added to a -30 °C solution of Mo(NAr)(CHCMe2Ph)(OTf)2(DME) (400 mg, 0.511 mmol) in 30 mL Et2O. The reaction was warmed to room temperature during which time the solution changed from yellow to red. After 3 h, all volatiles were removed in vacuo, and the crude solid was extracted with 40 mL of toluene. Removal of the volatiles in vacuo yielded a dark red solid. Addition of pentane to the red solid produced a yellow powder that was collected by filtration (270 mg, 90%).1H NMR (C6D6, 300 MHz) δ 13.30 (s, 1, syn Mo=CH, JCH = 120 Hz), 7.37 (d, 2, Ar), 7.14 (m, 3, Ar), 7.03 (d, 1, Ar), 6.97 (d, 2, Ar), 5.94 (br s, 2, NC4H2) 3.54 (sept, 2, CHMe2), 2.02 (s, 12, Me2NC4H2), 1.72 (s, 6, HCMe2Ph), 1.69 (br, 12, CHMe2); 13C NMR (CD2Cl2, 125 MHz) δ 315.16 (Mo=CH), 151.88, 149.32, 128.72, 127.83, 126.85, 126.44,
124.13, 105.64, 70.77, 58.22, 31.61, 27.99, 25.19, 24.13, 22.79, 18.17; Anal. Calcd for C_{34}H_{43}MoN_3: C, 69.02; H, 7.67; N, 7.10. Found: C, 69.01; H, 7.60; N, 7.14.

**Mo(NAr')\{(CHCMe_2)Ph}_{2}(2,5-Me_2NC_4H_2)_2** (1b). The synthesis was analogous to that for 1a; yield 83%: $^1$H NMR (C_6D_6, 300 MHz) $\delta$ 13.19 (s, 1, $\text{syn Mo=CCH}$, $J_{\text{CH}}$ = 120 Hz), 7.29 (d, 2, $Ar$), 7.07 (t, 3, $Ar$), 7.03 (d, 1, $Ar$), 6.77 (s, 2, $Ar$), 5.94 (br s, 2, NC_4H_2) 2.16 (s, 6, Me_2C_6H_3), 2.02 (s, 12, Me_2NC_4H_2), 1.61 (s, 6, CHMe_2Ph); $^{13}$C NMR (CD_2Cl_2, 125 MHz) $\delta$ 314.41 (Mo=CH), 154.34, 149.20, 136.61, 128.76, 128.70, 128.60, 128.96, 126.88, 126.29, 105.91, 57.53, 31.03, 19.64, 17.90; Anal. Calcd for C_{30}H_{37}MoN_3: C, 67.28; H, 6.96; N, 7.85 Found: C, 67.34; H, 7.08; N, 7.74.

**Mo(NAd)(CHCMe_2)Ph}_{2}(2,5-Me_2NC_4H_2)_2** (1c). The synthesis was analogous to that for 1a; yield 86%: $^1$H NMR (C_6D_6, 300 MHz) $\delta$ 12.94 (s, 1, $\text{syn Mo=CCH}$, $J_{\text{CH}}$ = 120 Hz), 7.38 (d, 2, $Ar$), 7.10 (t, 3, $Ar$), 6.98 (d, 1, $Ar$), 5.96 (br s, 2, NC_4H_2) 2.22 (br s, 12, Me_2NC_4H_2), 1.77 (s, 3, adamantyl), 1.53 (s, 6, CHMe_2Ph), 1.45 (s, 6, adamantyl), 1.34 (s, 6, adamantyl); $^{13}$C NMR (CD_2Cl_2, 125 MHz) $\delta$ 306.87 (Mo=CH), 151.05, 128.47, 127.81, 126.10, 74.40, 54.91, 44.45, 36.13, 30.16, 30.10. Anal. Calcd for C_{32}H_{43}MoN_3: C, 67.95; H, 7.66; N, 7.43. Found: C, 68.09; H, 7.60; N, 7.28.

**Mo(NArF)\{(CHCMe_2)Ph}_{2}(2,5-Me_2NC_4H_2)_2** (1d). The synthesis was analogous to that for 1a; yield 82%: $^1$H NMR (C_6D_6, 300 MHz) $\delta$ 13.19 (s, 1, $\text{syn Mo=CCH}$, $J_{\text{CH}}$ = 120 Hz), 7.30 (d, 2, $Ar$), 7.20 – 6.85 (m, 5, $Ar$), 6.64 (t, 1, $Ar$), 6.44 (t, 1, $Ar$), 6.02 (br s, 2, NC_4H_2), 2.08 (br s, 12, Me_2NC_4H_2), 1.59 (s, 6, CHMe_2Ph); $^{13}$C NMR (CD_2Cl_2, 125 MHz) $\delta$ 317.76 (Mo=CH), 152.73, 149.45, 132.85, 132.05, 128.63, 127.15, 126.59, 126.39, 126.16, 125.20, 123.04, 122.83, 120.86, 59.12, 31.33, 17.99; $^{19}$F NMR (C_6D_6, 471 MHz) $\delta$ – 60.42. Anal. Calcd for C_{29}H_{32}F_3MoN_3: C, 60.52; H, 5.60; N, 7.30. Found: C, 60.46; H, 5.52; N, 7.24.
Mo(NArCl)(CHCMe₃)(2,5-Me₂NC₄H₂)₂ (1e). The synthesis was analogous to that for 1a; yield 76%: ¹H NMR (C₆D₆, 300 MHz) δ 13.58 (s, 1, syn Mo=CH, JCH = 122 Hz), 6.72 (d, 2, Ar), 6.15 (t, 1, Ar), 6.08 (br, 2, NC₄H₂), 2.19 (br s, 12, Me₂NC₄H₂), 1.24 (s, 9, CMe₃); ¹³C NMR (CD₂Cl₂, 125 MHz) δ 323.68 (Mo=CH), 149.72, 129.23, 128.99, 127.14, 106.99, 51.14, 32.41, 19.99; Anal. Calcd for C₂₄H₃₂Cl₂MoN₃: C, 54.45; H, 6.09; N, 7.94. Found: C, 54.61; H, 6.07; N, 7.77.

Mo(NAd)(CHCMe₂Ph)(2,4-Me₂NC₄H₂)₂ (1f) Lithium 2,4-dimethylpyrrolide (100 mg, 1.02 mmol) was added as a solid to the stirred and chilled solution of Mo(NAd)(CHCMe₂Ph)(OTf)₂(DME) in 30 mL of toluene at –30 °C. The reaction mixture was stirred at room temperature for 2 h, during which time the reaction solution turned into dark orange from light yellow. The volatiles were removed in vacuo, and the crude solid was extracted with 20 mL of toluene. Removal of the volatiles in vacuo followed by crystallization out of the cold pentane solution resulted in the product as a yellow solid (253 mg, 76%): ¹H NMR (CD₂Cl₂, 500 MHz) δ 12.73 (s, 1, syn Mo=CH, JCH = 125 Hz), 7.42 (d, 2, Ar), 7.30 (t, 2, Ar), 7.20 (t, 1, Ar), 6.46 (s, 2, Pyr), 5.88 (s, 2, Pyr), 2.09 (br s, 3, Ad), 2.05 (s, 6, PyrMe), 2.01 (br s, 6, Ad), 1.82 (s, 6, PyrMe), 1.72 (s, 6, CHMe₂Ph), 1.65 (br, 6, Ad); ¹³C NMR (CD₂Cl₂, 125 MHz) δ 303.7, 150.5, 143.9, 128.6, 127.1, 126.2, 125.6, 123.0, 108.6, 74.78, 44.47, 36.28, 31.75, 30.17, 30.07, 16.56; Anal. Calcd for C₃₃H₄₆MoN₃: C, 68.26; H, 7.98; N, 7.24. Found: C, 68.58; H, 7.27; N, 7.58.

Mo(NAr)(CHCMe₂Ph)(OC₆F₅)₂ (2). To a stirred solution of Mo(NAr)(CHCMe₂Ph)(2,5-Me₂NC₄H₂)₂ (75 mg, 0.127 mmol) in 20 mL of THF was added C₆F₅OH (48 mg, 0.260 mmol) and the reaction stirred at room temperature for 1 h. The volatiles were removed in vacuo and
addition of pentane to the residue resulted in formation of a yellow precipitate (110 mg, 70%):

$^1$H NMR (300 MHz, CD$_2$Cl$_2$) $\delta$ 12.19 (s, 1, syn Mo=CH, $J_{CH} = 124$ Hz), 7.25 (br, 3, Ar), 7.01-6.89 (br, 5, Ar), 3.94 (br sep, 2, CHMe$_2$), 1.29 – 1.27 (br, 18, Me); $^{19}$F NMR (282 MHz, C$_6$D$_6$) $\delta$ –163.11, -168.24, -173.95; $^{13}$C NMR (125 MHz, CD$_2$Cl$_2$) $\delta$ 307.68 (Mo=CH), 149.94, 148.90, 142.03, 140.09, 137.39, 135.63, 133.75, 130.32, 129.29, 128.76, 126.66, 126.29, 124.59, 123.95, 57.03, 30.10, 29.30, 24.57. Anal. Calcd for C$_{34}$H$_{29}$F$_{10}$MoNO$_2$: C, 53.07; H, 3.80; N, 1.82. Found: C, 52.88; H, 3.72; N, 1.85

$\text{Mo(NAr)(CHCMe}_2\text{Ph)(BinaphAnthryl)(THF)}$ (3a). To a 50 mL round-bottom flask charged with $\text{Mo(NAr)(CHCMe}_2\text{Ph)(OTf)}_2$(DME) (200 mg, 0.252 mmol), H$_2$[Binaph$_{\text{Anth}}$] (162 mg, 0.252 mmol), THF (15 mL) and Et$_3$N (0.175 mL, 1.26 mmol), and the reaction stirred at room temperature for 12 h. The volatiles were removed in vacuo, and addition of pentane to the crude solid caused formation of a yellow powder. The yellow powder was isolated by filtration. Recrystallization from a mixture of THF and pentane (2:4) solvent mixture to yield yellow crystals (250 mg, 90%): $^1$H NMR (CD$_2$Cl$_2$, 500 MHz) $\delta$ 12.89 (s, 1, anti Mo=CH, $J_{CH} = 147$ Hz), 11.95 (s, 1, syn Mo=CH, $J_{CH} = 116$ Hz), anti isomer 8.47 – 8.38 (m, 3, Ar), 8.11 – 7.85 (m, 10, Ar), 7.58 – 7.50 (m, 3, Ar), 7.42 – 7.22 (m, 10, Ar), 7.15 – 7.11 (m, 2, Ar), 6.94 – 6.86 (m, 3, Ar), 6.76 (t, 2, Ar), 6.41 (d, 2, Ar), 6.16 (t, 1, Ar), 3.66 (br, 4, THF), 3.12 (sept, 2, CHMe$_2$), 1.34 (s, 3, CHMe$_2$Ph), 1.35 (s, 3, CHMe$_2$Ph), 0.81 (d, 3, CHMe$_2$), 0.65 (d, 3, CHMe$_2$), 0.62 (s, 4, THF) 0.34 (d, 3, CHMe$_2$), 0.05 (d, 3, CHMe$_2$); $^{13}$C NMR major isomer (CD$_2$Cl$_2$, 125 MHz) $\delta$ 317.15 (Mo=CH), 164.77, 162.07, 155.16, 150.45, 145.83, 143.16, 137.29, 136.42, 135.83, 135.58, 133.54, 132.49, 132.43, 132.13, 131.82, 131.69, 131.40, 131.29, 131.02, 130.67, 130.54, 130.28, 130.16, 129.34, 129.04, 128.77, 128.72, 128.67, 128.51, 128.46, 128.44, 128.37, 128.33, 128.26,
127.56, 127.23, 127.18, 126.49, 126.45, 126.39, 126.02, 125.97, 125.84, 125.81, 125.76, 125.71, 125.52, 125.33, 125.20, 125.06, 124.09, 123.07, 123.04, 122.62, 122.13, 119.90, 68.60, 51.03, 47.38, 29.12, 28.07, 27.34, 27.18, 25.76, 24.75, 22.35, 21.99, 21.89, 21.81. Anal. Calcd for C\textsubscript{74}H\textsubscript{65}MoNO\textsubscript{3}: C, 79.91; H, 5.89; N, 1.26. Found: C, 80.09; H, 5.81; N, 1.24.

\textbf{Mo(NAr)(CHCM\textsubscript{2}Ph)(BinaphAnthryl)(THF)} (3b). Compound 3b was prepared in a manner similar to 3a and isolated in 84\% yield: \textsuperscript{1}H NMR (CD\textsubscript{2}Cl\textsubscript{2}, 500 MHz) δ 12.73 (s, 1, \textit{anti} Mo=CH) 12.05 (s, 1, \textit{syn} Mo=CH), \textit{major isomer} 8.47 – 8.40 (m, 3, \textit{Ar}), 8.10 – 7.87 (m, 10, \textit{Ar}), 7.52 – 7.24 (br m, 13, \textit{Ar}), 7.11 (br s, 2, \textit{Ar}), 7.01 – 6.93 (m, 3, \textit{Ar}), 6.60 (t, 2, \textit{Ar}), 6.42 (d, 2, \textit{Ar}), 6.22 (br, 1, \textit{Ar}), 3.12 (br s, THF), 1.37 (br s, 3, Me), 1.34 (br s, 3, Me), 0.91 (m, 4, THF), 0.74 (s, 3, CHMe\textsubscript{2}Ph), 0.66 (s, 3, CHMe\textsubscript{2}Ph); \textsuperscript{13}C NMR \textit{major isomer} (CD\textsubscript{2}Cl\textsubscript{2}, 125 MHz) δ 315.15, 168.90, 168.77, 164.30, 164.09, 162.57, 162.25, 156.32, 155.37, 151.73. 150.29, 150.11, 137.11, 135.95, 135.68, 135.49, 135.12, 134.99, 134.44, 133.70, 133.57, 133.31, 132.51, 132.27, 132.08, 131.97, 131.93, 131.77, 131.67, 131.54, 131.37, 131.26, 130.94, 130.74, 129.85, 129.64, 129.47, 129.19, 129.06, 128.98, 128.90, 128.62, 128.54, 128.49, 128.44, 128.34, 128.22, 128.08, 127.90, 127.79, 127.73, 127.70, 127.62, 126.82, 126.66, 126.50, 126.45, 126.30, 126.22, 126.08, 126.00, 125.93, 125.89, 125.83, 125.74, 125.66, 125.57, 125.15, 125.05, 124.84, 124.75, 124.17, 123.36, 123.16, 123.03, 122.93, 122.36, 119.89, 50.85, 47.36, 32.55, 28.46, 25.11, 19.99. Anal. Calcd for C\textsubscript{70}H\textsubscript{57}MoNO\textsubscript{3}: C, 79.61; H, 5.89; N, 1.26. Found: C, 80.09; H, 5.81; N, 1.24.

\textbf{Mo(NAd)(CHCM\textsubscript{2}Ph)(BinaphAnthryl)(THF)} (3c). Compound 3c was prepared in a manner similar to 3a and isolated in 92\% yield: \textsuperscript{1}H NMR (CD\textsubscript{2}Cl\textsubscript{2}, 500 MHz) δ 12.60 (br s, 1, Mo=CH), 8.44 (br s, 4, \textit{Ar}), 8.01 – 7.69 (m, 13, \textit{Ar}), 7.44 – 7.10 (m, 12, \textit{Ar}), 6.92 (br s, 2, \textit{Ar}), 6.75 (br s, 2, \textit{Ar}), 3.13 (t, 4, THF), 2.08 (br s, 1, adamantanyl), 1.87 (br s, 1, adamantanyl), 1.72 (br s, 2, adamantanyl), 1.42 (br s, 4, adamantanyl), 1.34 (br s, 6, CHMe\textsubscript{2}Ph), 1.09 (s, 2, adamantanyl), 0.49 (br s,
4, THF); $^{13}$C NMR major isomer (CD$_2$Cl$_2$, 125 MHz) $\delta$ 291.73 (Mo=CH), 178.08, 166.48, 160.38, 150.09, 137.53, 136.64, 135.87, 135.28, 133.67, 132.69, 131.98, 131.87, 131.44, 131.12, 130.71, 129.93, 129.31, 129.05, 128.81, 128.43, 128.38, 128.32, 128.23, 128.17, 127.92, 127.28, 126.65, 126.38, 125.80, 125.66, 125.38, 122.99, 122.57, 122.22, 122.15, 121.28, 120.64, 119.68, 117.15, 113.99, 76.74, 72.93, 49.93, 47.43, 43.55, 36.07, 32.19, 29.81, 25.86, 24.31, 22.89.

Mo(NAr)(CHCMe$_2$Ph)(Binaph$_{C6F5}$)(THF) (4a). H$_2$[Binaph$_{C6F5}$] (209 mg, 0.340 mmol) was dissolved in 2 mL of THF and added dropwise to a stirred solution of 1a (200 mg, 0.340 mmol) in 20 mL of THF at –30 °C. The solution was allowed to warm to room temperature and stir for 2 h. All volatiles were removed in vacuo and addition of pentane afforded a yellow powder (310 mg, 84%): $^1$H NMR (C$_6$D$_6$, 300 MHz) $\delta$ 13.81 (s, 1, anti Mo=CH, $J_{CH}$ = 140 Hz), 7.80 (s, 1, Ar), 7.76 (s, 1, Ar), 7.73 (s, 1, Ar), 6.70 (s, 1, Ar), 7.41 (d, 1, Ar), 7.15 – 7.06 (m, 6, Ar), 6.99 – 6.80 (m, 7, Ar), 3.78 (br s, 1, CHMe$_2$), 3.10 (d, 4, THF), 1.72 (s, 3, CHMe$_2$Ph), 1.46 (s, 3, CHMe$_2$Ph), 0.95 – 0.78 (br, 12, CHMe$_2$), 0.42 (br, 4, THF); $^{19}$F NMR (C$_6$D$_6$, 282MHz) $\delta$ –133.14, –136.40, –139.28, – 142.21, – 157.80, – 158.21, – 162.19, –162.99, –163.88, –165.17; $^{13}$C NMR (CD$_2$Cl$_2$, 125 MHz) $\delta$ 319.64 (Mo=CH), 161.83, 160.07, 154.29, 150.47, 146.57, 146.17, 145.62, 144.60, 144.21, 143.66, 141.70, 139.55, 138.90, 137.50, 136.92, 136.20, 135.61, 132.55, 131.88, 132.55, 131.88, 129.53, 128.94, 128.85, 128.73, 128.57, 127.91, 127.19, 126.93, 126.68, 126.29, 125.85, 123.64, 123.44, 121.88, 119.68, 117.08, 114.36, 106.22, 75.66, 52.13, 29.57, 28.77, 27.98, 27.10, 26.40, 25.64, 22.96. Anal. Calcd for C$_{58}$H$_{47}$F$_{10}$MoNO$_3$: C, 63.80; H, 4.34; N, 1.28. Found: C, 63.65; H, 4.36; N, 1.23.

Mo(NAr)(CHCMe$_2$Ph)(Binaph$_{C6F5}$)(THF) (4b). Compound 4b was prepared using the same protocol as that employed for 4a and was isolated in a yield of 86%: $^1$H NMR (C$_6$D$_6$, 500MHz)
δ 13.65 (s, 1, *anti* Mo=CH, *J*<sub>CH</sub> = 140 Hz), 7.87 – 7.76 (m, 4, *Ar*), 7.46 (d, 1, *Ar*), 7.32 (d, 1, *Ar*), 7.19 – 7.12 (m, 6, *Ar*), 6.98 (t, 2, *Ar*), 6.89 (t, 1, *Ar*), 6.84 (br s, 1, *Ar*), 6.72 – 6.61 (m, 2, *Ar*), 3.31 (br s, 2, THF), 2.91 ( br s, 2, THF), 2.24 (s, 3, Me), 1.70 (s, 3, Me), 1.49 (s, 3, HC(Me)Me), 1.42 (s, 3, HC(Me)Me), 0.77 (br s, 2, THF), 0.69 (br s, 2, THF); ¹⁹F NMR (C₆D₆, 282MHz) δ – 130.49, – 134.11, – 137.29, – 140.40, – 156.41, – 157.09, – 161.30, – 162.59, – 162.79 – 163.53;
¹³C NMR major isomer (CD₂Cl₂, 125 MHz) δ 318.99 (Mo=CH), 161.27, 159.94, 155.90, 154.59, 150.34, 149.47, 146.36, 145.47, 144.39, 143.50, 141.67, 141.34, 139.49, 138.71, 136.76, 135.50, 135.22, 133.16, 132.49, 131.91, 129.17, 128.87, 128.82, 128.68, 128.34, 128.20, 128.02, 127.18, 126.95, 126.77, 126.67, 126.43, 126.34, 125.95, 124.01, 123.68, 122.22, 120.08, 119.71, 119.65, 116.63, 113.98, 76.44, 52.08, 28.60, 27.40, 25.32, 19.39, 17.74. Anal. Calcd for C₅₄H₃₉F₁₀MoNO₃: C, 62.62; H, 3.80; N, 1.35. Found: C, 62.80; H, 3.73; N, 1.28.

**Mo(NAd)(CHCMε₂Ph)(BinaphC₆F₅)(THF) (4c).** Compound 4c was prepared using the same protocol as that employed for 4a and the yield was 85%: ¹H NMR (C₆D₆, 500MHz) δ 12.59 (br s, 1, Mo=CH), 7.99 (br s, 1, *Ar*), 7.84 (br s, 1, *Ar*), 7.76 (br s, 1, *Ar*), 7.71 (d, 2, *Ar*), 7.55 (br s, 1, *Ar*), 7.27 (d, 2, *Ar*), 7.08 (t, 1, *Ar*), 6.98 (br, 2, *Ar*), 6.87 (t, 1, *Ar*), 6.82 – 6.72 (br, 3, *Ar*), 2.85 (br, 4, THF), 1.94 – 1.83 (br, 6, adamantyl), 1.46 (br s, 3, adamantyl), 1.44 (br s, 3, adamantyl), 1.18 (br s, 3, adamantyl), 0.64 (br, 4, THF); ¹⁹F NMR (C₆D₆, 282MHz) δ – 130.49, – 134.11, – 137.29, – 140.40, – 156.41, – 157.09, – 161.30, – 162.59, – 162.79 – 163.53 ¹³C NMR major isomer (CD₂Cl₂, 125 MHz) δ 294.06, 166.26, 159.40, 149.57, 146.64, 146.23, 145.69, 144.59, 144.26, 143.75, 141.41, 139.36, 137.39, 136.00, 135.40, 132.25, 131.72, 128.89, 128.76, 126.89, 126.80, 126.48, 123.56, 123.16, 121.73, 121.07, 119.91, 118.90, 116.31, 115.51, 77.95, 73.61, 49.97, 44.23, 36.35, 30.08, 24.81, 22.93. Anal. Calcd for C₅₆H₄₅F₁₀MoNO₃: C, 63.10; H, 4.26; N, 1.31. Found: C, 62.88; H, 4.18; N, 1.26.
Mo(NArF)(CHCMe₂Ph)(BinaphC₆F₅)(THF) (4d). Compound 4d was prepared using the same protocol as that employed for 4a and the yield was 84%. ¹H NMR (C₆D₆, 500MHz) δ 14.08 (s, 1, anti Mo=CH), 13.36 (br s, 1, syn Mo=CH), anti isomer 7.86 (s, 1, Ar), 7.78 – 7.69 (m, 4, Ar), 7.46 (t, 1, Ar), 7.34 (d, 1, Ar), 7.24 – 7.06 (m, 6, Ar), 6.55 (t, 2, Ar), 6.53 (t, 1, Ar), 6.40 (br s, 1, Ar), 6.02 (d, 2, Ar), 3.41 (q, 2, THF), 2.84 (q, 2, THF), 1.59 (s, 3, CHMe₂Ph), 1.37 (s, 3, CHMe₂Ph), 0.88 (q, 4, THF); ¹⁹F NMR major isomer (C₆D₆, 282MHz) δ –60.61, –132.57, –136.45, –139.07, –143.09, –158.10, –158.96, –163.01, –164.80, –165.34; ¹³C NMR (CD₂Cl₂, 125 MHz) δ 320.44 (anti Ca), 307.09 (syn Ca); Anal. Calcd for C₅₃H₃₄F₁₃MoNO₅: C, 59.17; H, 3.19; N, 1.30. Found: C, 59.32; H, 3.26; N, 1.32.

Mo(NAr)(CHCMe₂Ph)(BinaphCF₃)(THF) (5a). H₂[BinaphCF₃] (240 mg, 0.338 mmol) was added as a THF solution (2 mL) to a stirred solution of 1a (200 mg, 0.338 mmol) in 20 mL of THF and the reaction stirred at room temperature for 1 h. Removal of volatiles in vacuo afforded a yellow residue which dissolved in pentane (2 mL). Cooling of the pentane solution to –30 °C resulted in precipitation of a yellow powder (150 mg, 37%): ¹H NMR (C₆D₆, 300 MHz) δ 13.77 (s, 1, anti Mo=CH), 12.23 (s, 1, syn Mo=CH), 8.13 (s, 1, Ar), 8.12 (s, 1, Ar), 7.90 (s, 1, Ar), 7.82 – 7.71 (m, 3, Ar), 7.64 – 7.47 (m, 4, Ar), 7.29 (d, 1, Ar), 7.23 – 7.02 (m, 10 Ar), 6.90 (t, 1, Ar), 6.81 (d, 2, Ar), 3.29 (br, 2, CHMe₂), 3.25 (br, 4, THF), 1.85 (s, 3, CHMe₂Ph), 1.34 (s, 3, CHMe₂Ph), 1.12 (d, 6, CHMe₂), 1.09 (d, 6, CHMe₂), 0.70 (br, 4, THF); ¹⁹F NMR (C₆D₆, 282MHz) δ –61.92, –62.19 (anti), –61.99, –62.30 (syn); ¹³C NMR anti isomer (CD₂Cl₂, 125 MHz) δ 317.90 (Mo=CH). Anal. Calcd for C₆₂H₅₃F₁₂MoNO₅: C, 62.89; H, 4.51; N, 1.81. Found: C, 62.76; H, 4.61; N, 1.09.
Spectroscopic observation of Mo(NAr')(CHCMe₂Ph)(Binaph₃CF₃) (5b'). H₂[Binaph₃CF₃] (9 mg, 0.013 mmol) was added as a solid to a solution of 1 (10 mg, 0.013 mmol, 0.024 M) in 1 mL of C₆D₆. The solution was transferred to a J-Young tube and the spectrum recorded within 15 min. Mo(NAd)(CHCMe₂Ph)(Binaph₃CF₃) (5c') and Mo(NArF)(CHCMe₂Ph)(Binaph₃CF₃) (5d') were observed spectroscopically in a similar manner.

Mo(NAr)(CHCMe₂Ph)(Binaph₃CF₃)(THF) (6a). To a 100 mL round-bottom flask charged with Mo(NAr)(CHCMe₂Ph)(OTf)₂(DME) (500 mg, 0.632 mmol), H₂[BiphencF₃] (292 mg, 0.632 mmol) and THF (60 mL), was added Et₃N (0.890 mL, 6.32 mmol) via a syringe, and the reaction stirred at room temperature for 12 h. The volatiles were removed in vacuo, and the residue extracted into 60 mL of pentane. Concentration of the pentane solution resulted in precipitation of a yellow solid (300 mg, 50%): ¹H NMR (C₆D₆, 500MHz) δ 14.17 (s, 1, anti Mo=CH, JCH = 147 Hz), 11.46 (br s, 1, syn Mo=CH, JCH = 121 Hz), 7.90 (s, 1, Ar), 7.78 (s, 1, Ar), 7.28 (br s, 2, Ar), 7.12 (t, 2, Ar), 7.00 (t, 1, Ar), 6.91 (m, 3, Ar), 3.62 (br, 2, CHMe₂), 3.48 (br, 4, THF), 2.13 (s, 6, CHMe₂Ph), 1.68 (s, 3, BiphencMe), 1.57 (s, 3, BiphencMe), 1.43 (s, 9, Biphenc-t-Bu), 1.37 (s, 9, Biphenc-t-Bu), 1.20 (br, 4, THF), 1.11 (d, 12, CHMe₂); ¹³F NMR (C₆D₆, 282MHz) δ -58.21, -58.40, -58.77, -58.90; ¹³C NMR (CD₂Cl₂, 125 MHz) both isomers δ 322.00 (anti, C₀, JCH = 147 Hz), 290.30 (syn, C₀, JCH = 121 Hz), 154.54, 154.00, 150.61, 149.81, 136.08, 135.28, 134.99, 131.38, 131.07, 130.17, 128.92, 128.88, 128.83, 128.65, 127.95, 126.78, 126.74, 126.70, 126.67, 126.64, 123.85, 123.56, 35.96, 35.87, 35.52, 35.49, 30.96, 30.81, 30.48, 30.38, 30.03, 29.48, 29.43, 25.91, 24.54, 24.45, 23.44, 16.00, 15.89. Anal. Calcd for C₅₀H₆₃F₆MoNO₃: C, 64.16; H, 6.78; N, 1.50. Found: C, 64.04; H, 6.85; N, 1.48.
**Mo(NAr')(CHCMe₂Ph)(BiphencF₃)(THF)** (6b). Complex 6b was prepared in a manner analogous to 6a and isolated in 60% yield: ^1^H NMR (C₆D₆, 500MHz) δ 14.10 (s, 1, anti Mo=CH, JCH = 146 Hz), 12.41 (br, 1, syn Mo=CH, JCH = 117 Hz), 7.93 (s, 1, Ar), 7.72 (s, 1, Ar), 7.39 (d, 2, Ar), 7.18 (t, 1, Ar), 7.10 – 6.96 (m, 2, Ar), 6.71 (d, 2, Ar), 6.63 (t, 1, Ar), 3.45 (br s, 4, CH₂OCH₂), 2.16 (s, 3, CMe₂Ph), 2.15 (s, 3, ArMe) 2.08 (s, 3, CMePh), 2.05 (s, 3, ArMe), 2.02 (s, 3, BiphenMe), 1.66 (s, 3, BiphenMe), 1.53 (s, 3, BiphenMe), 1.47 (s, 8, Biphen-t-Bu), 1.33 (s, 9, Biphen-t-Bu), 0.98 (br s, 4, CH₂CH₂); ^1^F NMR (C₆D₆, 282MHz) δ -58.2, -58.3, -58.8; ^1^3C NMR (C₆D₆, 125 MHz) major isomer δ 320.48 (Mo=CH), 168.31, 165.48, 156.67, 156.21, 150.76, 149.46, 136.50, 135.45, 134.92, 132.22, 131.99, 131.15, 129.87, 128.99, 128.92, 127.42, 127.28, 126.96, 126.68, 126.32, 126.01, 125.70, 124.84, 124.03, 120.83, 75.40, 55.21, 53.72, 35.85, 35.74, 35.69, 34.80, 32.33, 31.16, 30.98, 30.79, 30.68, 30.63, 28.60, 27.22, 25.21, 23.10, 20.11, 19.03, 16.76, 16.60, 16.15, 14.66. Anal. Calcd for C₄₆H₅₅F₆MoNO₃: C, 62.79; H, 6.30; N, 1.59. Found: C, 62.88; H, 6.38; N, 1.62.

**Mo(NAd)(CHCMe₂Ph)(BiphencF₃)(THF)** (6c). Complex 6c was prepared in a manner analogous to 6a and isolated in 71% yield: ^1^H NMR (C₆D₆, 500MHz) δ 12.14 (br, 1, syn Mo=CH), 7.92 (s, 1, Ar), 7.86 (s, 1, Ar), 7.26 (d, 2, Ar), 7.15 (t, 2, Ar), 7.01 (t, 1, Ar), 3.42 (br s, 4, THF), 2.11 (s, 3, CHMe₂Ph), 2.08 (s, 3, CHMe₂Ph), 1.78 (br s, 6, adamantyl), 1.71 (br s, 3, adamantyl), 1.66 (s, 3, BiphenMe), 1.59 (s, 3, BiphenMe), 1.47 (s, 9, Biphen-t-Bu), 1.42 (s, 9, Biphen-t-Bu), 1.33(br s, 6, adamantyl), 1.23 (m, 4, THF); ^1^F NMR (C₆D₆, 282 MHz) δ -58.36, -58.52; ^1^3C NMR (CD₂Cl₂, 125 MHz, – 40 °C) both diastereomers δ 309.11 (Mo=CH), 295.71 (Mo=CH), 171.06, 168.30, 165.96, 165.39, 148.92, 147.95, 135.02, 134.32, 134.10, 133.91, 132.55, 131.26, 130.70, 130.01, 129.72, 128.35, 126.50, 126.98, 126.22, 126.14, 125.96, 125.86, 124.81, 124.70, 123.84, 123.34, 123.15, 118.46, 117.33, 77.42, 76.93, 74.97, 73.83, 51.13, 50.37.
44.24, 44.08, 35.68, 35.57, 35.12, 34.84, 34.37, 32.47, 31.78, 30.80, 30.32, 30.15, 29.83, 29.69, 29.52, 29.42, 29.28, 25.88, 25.65, 22.77, 15.98, 15.75, 15.62, 14.30. Anal. Calcd for C$_{48}$H$_{61}$F$_6$MoNO$_3$: C, 63.36; H, 6.76; N, 1.54. Found: C, 63.26; H, 6.71; N, 1.47.

Representative ring-closing metathesis reactions. Diallylether (0.225 mmol, 28 μL) was added via syringe to a stirred solution of 3a (10 mg, 0.009 mmol) in 1 mL of C$_6$D$_6$. The solution was transferred to a J. Young NMR tube and $^1$H NMR spectra recorded after the stated time interval at the stated temperatures. A similar procedure was employed for the ring-closing reaction of diallyltosylamine.
Crystal data and structure refinement for Mo(NAd)(CHCMe\textsubscript{2}Ph)(2,5-Me\textsubscript{2}NC\textsubscript{4}H\textsubscript{2})\textsubscript{2} (1c).

Identification code 07163
Empirical formula C\textsubscript{40.50}H\textsubscript{58}MoN\textsubscript{4}
Formula weight 696.85
Temperature 100(2) K
Wavelength 0.71073 Å
Crystal system Triclinic
Space group P\textbar
Unit cell dimensions
\begin{align*}
a &= 9.468(3) \text{ Å} & \alpha &= 92.682(5)^\circ \\
b &= 10.102(3) \text{ Å} & \beta &= 102.986(5)^\circ \\
c &= 20.072(6) \text{ Å} & \gamma &= 97.859(5)^\circ \\
\end{align*}
Volume 1847.1(9) Å\textsuperscript{3}
Z 2
Density (calculated) 1.253 Mg/m\textsuperscript{3}
Absorption coefficient 0.388 mm\textsuperscript{-1}
F(000) 742
Crystal size 0.25 x 0.15 x 0.02 mm\textsuperscript{3}
\(\Theta\) range for data collection 2.04 to 28.28°
Index ranges -12 ≤ h ≤ 12, -13 ≤ k ≤ 13, 0 ≤ l ≤ 26
Reflections collected 9130
Independent reflections 9132 [Nonmerohedral twin]
Completeness to \(\Theta = 28.28^\circ\) 99.6%
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.9923 and 0.9093
Refinement method Full-matrix least-squares on F\textsuperscript{2}
Data / restraints / parameters 9132 / 459 / 448
Goodness-of-fit on F\textsuperscript{2} 1.034
Final R indices [I>2\sigma(I)]
\begin{align*}
R1 &= 0.0494, wR2 = 0.0965 \\
R1 &= 0.0612, wR2 = 0.1029 \\
\end{align*}
Largest diff. peak and hole 0.828 and -1.080 e.Å\textsuperscript{-3}
Crystal data and structure refinement for Mo(NAr)(CHCMe\textsubscript{2}Ph)(Binaph\textsubscript{Anthryl})(THF) (3a).

Identification code: 06240

Empirical formula: C\textsubscript{88.60}H\textsubscript{94.18}MoNO\textsubscript{6.65}

Formula weight: 1375.31

Temperature: 100(2) K

Wavelength: 0.71073 Å

Crystal system: Monoclinic

Space group: P2(1)

Unit cell dimensions:

- a = 12.245(3) Å, \(\alpha = 90^\circ\)
- b = 15.001(4) Å, \(\beta = 93.793(4)^\circ\)
- c = 19.710(5) Å, \(\gamma = 90^\circ\)

Volume: 3612.5(15) Å\textsuperscript{3}

Z: 2

Density (calcd): 1.264 Mg/m\textsuperscript{3}

Absorption coefficient: 0.239 mm\textsuperscript{-1}

\(F(000)\): 1456

Crystal size: 0.25 x 0.15 x 0.15 mm\textsuperscript{3}

\(\Theta\) range for data collection: 1.71 to 29.08°

Index ranges:

-16 \(\leq\) h \(\leq\) 16, -20 \(\leq\) k \(\leq\) 20, -26 \(\leq\) l \(\leq\) 26

Reflections collected: 78198

Independent reflections: 19293 \([R(int) = 0.0721]\)

Completeness to \(\Theta = 29.08^\circ\): 100%

Absorption correction: Semi-empirical from equivalents

Max. and min. transmission: 0.9651 and 0.9427

Refinement method: Full-matrix least-squares on \(F^2\)

Data / restraints / parameters: 19293 / 1155 / 1066

Goodness-of-fit on \(F^2\): 1.036

Final R indices [I>2\(\sigma(I)\)]: R1 = 0.0461, wR2 = 0.1203

R indices (all data): R1 = 0.0551, wR2 = 0.1263

Absolute structure parameter: 0.00(2)

Largest diff. peak and hole: 0.768 and -0.825 e Å\textsuperscript{-3}
Crystal data and structure refinement for Mo(NAd)(CHCMe$_2$Ph)(Biphen$_{CF3}$)(THF). (6a)

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<td>Empirical formula</td>
<td>C$<em>{48}$H$</em>{61}$F$_6$MoNO$_3$</td>
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<td>Formula weight</td>
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<td>c = 15.7794(19) Å, γ = 61.683(3)°</td>
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<td>Z</td>
<td>2</td>
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<td>Density (calculated)</td>
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<td>Index ranges</td>
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<td>Independent reflections</td>
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<td>Completeness to Θ = 29.57°</td>
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<td>Max. and min. transmission</td>
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<td>Refinement method</td>
<td>Full-matrix least-squares on F$^2$</td>
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<td>Data / restraints / parameters</td>
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<td>R indices (all data)</td>
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<td>Largest diff. peak and hole</td>
<td>0.872 and -0.308 e.Å$^{-3}$</td>
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REFERENCES


CHAPTER 4

Living Ring-Opening Metathesis Polymerization of Cyclopropenes and Stereoregular Polymer of 3-Methyl-3-phenylcyclopropene

Portions of this chapter have appeared in print:


INTRODUCTION

The development of initiators for the ring-opening metathesis polymerization (ROMP) of cyclic olefins has opened a new chapter in the field of controlled-architecture polymers.¹ Living ROMP is a powerful method to synthesize a variety of polymers and block copolymers with precise molecular weights, low polydispersities and unique properties.² In many cases, polymers prepared via living ROMP are derived from bicycloheptenes or bicyclooctenes.³ One of the reasons for the interest in ROMP of monocyclic olefins is the possibility of preparing block copolymers with elastomeric properties.⁴ However, lack of diversity of monocyclic substrates suitable for living ROMP has limited the progress in this field. In particular, there is no mention of ROMP of cyclopropenes⁵ in the literature despite the high ring strain of these monomers,⁶ which is surprising as the release of the ring strain is believed to be the driving force in ROMP. The closest example is a report by Risse and co-workers, who observed ring-opened polymers of cyclopropenes as a side product when disubstituted cyclopropenes were treated with Pd(II) complexes in efforts to prepare cyclopropane polymers.⁷ Likewise, 3,3-diphenylcyclopropenes have been used successfully as a carbene source in the generation of metathetically inactive W(VI) vinyl alkylidene species (Equation 4.1).⁸

![Equation 4.1](image-url)
One class of ROMP initiators that has been employed successfully for the polymerization (often living) of strained cyclic olefins are molybdenum alkylidene complexes of the type $\text{Mo(NR)(CHR')(OR')}_2$. Two important requirements for a well-behaved living process are that the rate of initiation be approximately same as the rate of propagation, and that the alkylidene intermediates be stable on the time scale of the polymerization. It is also desirable to prepare polymers with a single structure in order to probe the relationship between structure and bulk properties of polymeric materials. Polymers prepared via ROMP of cyclic olefins can result in two types of isomers. The first is based on the configuration of the double bonds ($\text{cis}$ or $\text{trans}$) between repeat units, while the second is the consequence of the stereochemical differentiation that arises from the relative configuration of the neighboring repeat units. In order to produce a long range order in polymers prepared via ROMP it is not only necessary to control $\text{cis}$ versus $\text{trans}$ linkages, but also the tacticity of the repeating units. Enantiomeric site control with chiral (racemic or enantiomerically pure) initiators has been used most efficiently to prepare highly tactic polymers via ROMP of norbornadienes, although regular microstructures have also been achieved through chain-end control. The tacticities of two highly tactic polymers derived from certain bicycloheptadienes have been proven through introduction of an enantiomerically pure group in the monomer that is polymerized.

Since monosubstituted cyclopropenes are reported to be unstable at room temperature, we focused our attention in the ROMP of 3,3-disubstituted cyclopropenes. In particular, we were interested in 3-methyl-3-phenylecyclopropene ($\text{MPC}$) as our initial target molecule for polymerization (Figure 4.1). ROMP of $\text{MPC}$ would yield propagating alkylidenes that are similar to the relatively stable neopentyldene or neophylidene initiators of the type $\text{Mo(NAr)(CHR)(OR')}_2$. Likewise, since the substituents in the 3-position of $\text{MPC}$ are different
the tacticity of these polymers can also be explored. This chapter reports the first living ROMP of cyclopropenes and also the preparation of tactic, as well as atactic polymer derived from ROMP of MPC using high oxidation state molybdenum imido alkylidene initiators.

![Cyclopropenes used in the ROMP studies.](image)

**Figure 4.1.** Cyclopropenes used in the ROMP studies.

**RESULTS AND DISCUSSION**

4.1 Living ROMP of cyclopropenes

![Ring opening metathesis polymerization of 3-methyl-3-phenyl cyclopropene.](image)

**Scheme 4.1.** Ring opening metathesis polymerization of 3-methyl-3-phenyl cyclopropene.

ROMP of MPC in THF at room temperature using 1a, 1b, or 2 (Scheme 4.1) produced polymers in virtually quantitative yield. A typical polymerization involved addition of 100 equivalents of MPC to each initiator. Polymerizations were allowed to run for one hour and
were then quenched with ten equivalents of benzaldehyde. The resulting polymers were precipitated in methanol and analyzed by gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and $^1$H and $^{13}$C NMR spectroscopy. Characterization data are shown in Table 4.1.

Proton and carbon NMR spectra of the polymers prepared with initiators 1a, 1b and 2 revealed virtually identical resonances for the olefinic proton and carbon, while the quaternary carbon resonance appeared between 46 – 47 ppm (as shown for several samples in Figure 4.7). The IR spectra of a thin film of MPC$_{100}$ prepared using 1a, 1b and 2 revealed absorptions at 963 and/or 982 cm$^{-1}$ of approximately equal intensity that are not present in the spectrum of MPC, and that are most consistent with a trans structure (Figure 4.2). In MPC$_{100}$ prepared with 1a and 1b the 982 cm$^{-1}$ absorption is dominant.

**Figure 4.2.** IR spectroscopic studies of (3-methyl-3-phenylcyclopropene)$_{100}$ prepared using Mo(NAr)(CHCMe$_2$Ph)(O-t-Bu)$_2$ (1b) and Mo(NAr)(CHCMe$_2$Ph)(OR$_{F6}$)$_2$ (Ar = 2,6-i-Pr$_2$C$_6$H$_3$, OR$_{F6}$ = OC(CF$_3$)$_2$Me) (2).

Gel permeation chromatography (GPC) studies on the polymers revealed a unimodal peak distribution with a low polydispersity index (PDI) indicating a living polymerization except
in the case of 2 (Table 4.1). The calculated number-average molecular weights \( (M_n) \) (as determined by GPC versus the polystyrene standards) for the polymers were comparable with the theoretical molecular weights (Table 4.1). A linear relationship between the \( M_n \) values of \( \text{MPC}_x \) \((100 \geq x \geq 25)\) prepared using initiator 1a and the monomer to initiator ratio along with the PDI of \(< 1.10\) further supports the living ROMP of \( \text{MPC} \) as shown in Figure 4.3.

<table>
<thead>
<tr>
<th>Initiator&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Monomer</th>
<th>M/I</th>
<th>( M_n ) (theo.) (x 10&lt;sup&gt;3&lt;/sup&gt;)</th>
<th>( M_n ) (calcld.)&lt;sup&gt;b&lt;/sup&gt; (x 10&lt;sup&gt;3&lt;/sup&gt;)</th>
<th>PDI&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a MPC</td>
<td>80</td>
<td>10</td>
<td>9</td>
<td>&lt; 1.10</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td>1b MPC</td>
<td>100</td>
<td>13</td>
<td>12</td>
<td>&lt; 1.10</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td>2 MPC</td>
<td>100</td>
<td>13</td>
<td>13</td>
<td>1.50</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td>1b MEMC</td>
<td>100</td>
<td>11</td>
<td>10</td>
<td>&lt; 1.10</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td>2 MEMC</td>
<td>100</td>
<td>11</td>
<td>9</td>
<td>&lt; 1.10</td>
<td>95</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1. Gel permeation chromatography data of the homopolymers derived from cyclopropenes.

<sup>a</sup> Ref. Scheme 4.1

<sup>b</sup> Calculated versus the polystyrene standards
Figure 4.3. A correlation diagram between the number-average molecular weight of poly(3-methyl-3-phenylcyclopropene) and the monomer to initiator ratio. Polydispersity indices of polymers are also depicted.

An initiation experiment in which eight equivalents of MPC were added to 1a in C₆D₆ (Hₐ = 11.26 ppm), complete initiation (> 99%) of the initiator was observed with the new alkylidene resonance appearing at 11.35 ppm (Figure 4.4). Under similar reaction conditions, an identical resonance for the propagating alkylidene (11.35 ppm) was identified in the ¹H NMR spectrum upon addition of ten equivalents of MPC to 1b (Hₐ = 11.41 ppm). In contrast, addition of ten equivalents of MPC to initiator 2 in C₆D₆ (Hₐ = 12.16 ppm) resulted in multiple alkylidene resonances (11.96 ppm major), which were attributed to oligomeric insertion products with incomplete initiation (~ 50%). The higher PDI (1.50) observed for the MPC₁₀₀ prepared by 2 could potentially be due to its poor initiation ability.
Figure 4.4. $^1$H NMR spectra of the alkylidene region after the addition of (a) 10 equivalents of 2,3-dicarbomethoxynorbornadiene to Mo(NAr)(CHCMe$_2$Ph)(OR$_{c6}$)$_2$ (2) (b) 8 equivalents of 2,3-dicarbomethoxynorbornadiene to Mo(NAr)(CHCMe$_2$Ph)(O-t-Bu)$_2$ (1b) (c) 8 equivalents of 2,3-dicarbomethoxynorbornadiene to Mo(NAr)(CHCMe$_3$)(O-t-Bu)$_2$ (1a) (Ar = 2,6-i-Pr$_2$C$_6$H$_3$, OR$_{c6}$ = OC(CF$_3$)$_2$Me)

A Grubbs-type Ru initiator, (H$_2$IMes)(PCy$_3$)Cl$_2$RuCHC$_6$H$_5$ (H$_2$IMes = 1,3-dimesitylimidazolidine), was also investigated as an initiator for the polymerization of MPC. Addition of eighteen equivalents of MPC to a CD$_2$Cl$_2$ solution of (H$_2$IMes)(PCy$_3$)Cl$_2$RuCHC$_6$H$_5$ (15 mM) resulted in the consumption of the initial benzylidene species ($H_a$ = 19.09 ppm) to the extent of 54% after 1 h at room temperature, and four new resonances (16.70 ppm, 16.65 ppm, 16.63 ppm (major) and 16.58 ppm) appeared in the alkylidene region. The $^1$H NMR spectra of the same sample revealed 83% and 95% consumption of the initiator after 7 h and 15 h, respectively. Complete consumption of the monomer was achieved after 24 h. The reaction was slower in C$_6$D$_6$ as ten equivalents of MPC were polymerized in 34 h with ~75% of the initiator consumed in the process. Use of the second generation Hoveyda-Grubbs initiator, (H$_2$IMes)Cl$_2$RuCH(2-i-PrO)C$_6$H$_4$ (H$_2$IMes = 1,3-dimesitylimidazolidine) (13 mM), in the ROMP of MPC resulted in the complete consumption of twenty equivalents of monomer in 12 h with the initiation of < 5% of the initial alkylidene as determined by the $^1$HNMR spectrum.
Diblock copolymers comprising of MPC and 2,3-dicarbomethoxynorbornadiene (DCMNBD) were prepared by taking advantage of the living polymerization behavior of 1a and 1b. Two diblock copolymers were prepared for each initiator under identical conditions – the first through polymerization of MPC followed by DCMNBD, and the second in which the order of monomer addition was reversed. The polymerization reactions were quenched by adding excess benzaldehyde and the polymers were precipitated in methanol. The polymers were isolated in virtually quantitative yield, and revealed a unimodal peak distribution with narrow PDI (< 1.10) as revealed by GPC studies, which further corroborates the living polymerization of MPC by 1a and 1b (Table 4.2).

<table>
<thead>
<tr>
<th>Initiator• (I) Diblock copolymer</th>
<th>Mn (theor.) x 10^3</th>
<th>Mn (calcd.) x 10^3</th>
<th>PDI</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a MPC_75DCMNBD_200</td>
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<td>33</td>
<td>1.17</td>
<td>98</td>
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<td>1a DCMNBD_200_MPC_70</td>
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<td>39</td>
<td>&lt; 1.10</td>
<td>97</td>
</tr>
<tr>
<td>1b MPC_65DCMNBD_100</td>
<td>30</td>
<td>23</td>
<td>&lt; 1.10</td>
<td>93</td>
</tr>
<tr>
<td>1b DCMNBD_100_MPC_100</td>
<td>35</td>
<td>24</td>
<td>&lt; 1.10</td>
<td>96</td>
</tr>
</tbody>
</table>

Table 4.2. Gel permeation chromatography data of diblock copolymers.

• Ref. Scheme 4.1

• Calculated versus the polystyrene standards

ROMP of two new cyclopropenes, 3-(2-methoxyethyl)-3-methylocyclopropene (MEMC) and methyl 1-phenylcycloprop-2-ene carboxylate (MPCC), were also performed (Figure 4.1). MEMC was readily polymerized by 1b and 2 in THF to afford the corresponding homopolymers in virtually quantitative yield. Analysis of the polymers by GPC revealed unimodal peak distributions with polydispersity indices of < 1.10. However, MPCC could only
be polymerized by 2 in 90% yield. \textbf{MPCC}_{100} could not be analyzed by GPC due to its low solubility in THF, a common solvent used for GPC. \textbf{MEMC} was also used in the preparation of homopolymers and ABA triblock copolymers using the bifunctional ROMP initiator [(O-t-Bu)$_2$(ArN)MoCH]$_2$-1,4-C$_6$H$_4$\textsuperscript{15} (Ar = 2,6-i-Pr$_2$C$_6$H$_3$) (1c). Two ABA triblock copolymers, \textbf{MPC$_{100}$MEMC$_{100}$MPC$_{100}$} and \textbf{MTD$_{100}$MEMC$_{100}$MTD$_{100}$} (MTD = methyltetracyclododecene), were prepared by adding \textbf{MEMC} to 1c followed by the outer block monomer (MPC or MTD). The triblock copolymers were successfully isolated in > 92% yield and revealed unimodal peak distributions with narrow PDI (Table 4.2).

4.2 Thermal Analysis

Differential scanning calorimetry (DSC) was used in order to determine the glass transition temperature ($T_g$) of homopolymers (\textbf{MPC$_{100}$} and \textbf{MEMC$_{100}$}) and triblock copolymers (\textbf{MPC$_{100}$MEMC$_{100}$MPC$_{100}$} and \textbf{MTD$_{100}$MEMC$_{100}$MTD$_{100}$}). The first and subsequent DSC heating scans were essentially identical and all heating and cooling scans showed good reversibility. Thermal studies on \textbf{MPC$_{100}$MEMC$_{100}$MPC$_{100}$} revealed a homogeneous microphase with a broad transition centered at 0 °C, whereas \textbf{MTD$_{100}$MEMC$_{100}$MTD$_{100}$} displayed two distinct $T_g$s at −40 °C and 210 °C. The $T_g$s of the homopolymers of \textbf{MEMC$_{100}$} and \textbf{MTD$_{100}$}, prepared using 1c, were recorded at −42 °C and 215 °C, respectively. The appearance of both $T_g$s in the triblock copolymer very similar to those of their respective homopolymers is indicative of a well phase-segregated morphology. However, analysis of \textbf{MTD$_{100}$MEMC$_{100}$MTD$_{100}$} by small angle X-ray scattering (SAXS) did not produce any scattering peak, which made the identification of the triblock copolymer morphology unsuccessful.
Studies of thermal properties of the homopolymers of MPC and MEMC led to an interesting observation. An anomaly in the Tgs of MPC<sub>100</sub> and MEMC<sub>100</sub> was encountered as a function of the initiator used in the polymerization reactions. For example, MPC<sub>100</sub> and MEMC<sub>100</sub> prepared using 2 recorded the Tgs at 80 °C and –20 °C, respectively whereas MPC<sub>100</sub> and MEMC<sub>100</sub> prepared using initiator 1b revealed the Tgs at 40 °C and –30 °C, respectively. We tentatively assigned such discrepancies in the Tgs to differences in tacticity in the polymer microstructure.

4.3 Stereospecific polymerization of cyclopropene

4.3.1 Stereospecific polymerization of MPC

As suggested above, since the substituents on C(3) of MPC are different, the tacticity in the resulting polymers is possible. The possible configurations that can arise in polymer derived from MPC are shown in Figure 4.5. It should be possible to control the tacticity in MPC<sub>100</sub> and to determine the degree of tacticity through <sup>13</sup>C NMR studies, e.g., through analysis of the quaternary carbon resonance in the polymer backbone.

![Figure 4.5.](image)

Figure 4.5. Three possible orientation of poly(3-methyl-3-phenylcyclopropene).
Several initiators were screened for the polymerization of MPC in efforts to yield highly tactic polymers (Figure 4.6). In the case of 1b–4 tacticity would have to arise through chain-end control, while tacticity would most likely arise through enantiomorphic site control with 5–10. All initiators shown in Figure 4.6 are known in the literature except 7, which was prepared through addition of the in situ generated K₂[Binaph₅-Bu] (dipotassium 3,3',6,6'-tetra-t-butyl-2-binaphtholate) to (DME)Mo(NAr)(CHCMe₂Ph)(OTf)₂ in THF (Equation 4.2).

The ¹H NMR spectrum of 7 in CD₂Cl₂ showed a resonance at 10.71 ppm, which is assigned to the alkylidene proton in the syn isomer on the basis of a Jₘₙ value of 120 Hz. The relatively broad alkylidene resonance that is observed at 12.70 ppm (5%) is ascribed to an anti isomer to which THF is bound in the solid state. Compound 7 is largely THF-free, according to elemental analysis. Coordination of THF to binaphtholate catalysts (e.g., 9 or 10) is a common feature of their chemistry. Compound 7 is the first binaphtholate derivative which contains t-butyl groups in the 3 and 3' positions, which we believe to be the reason why even the anti isomer of 7 does not bind THF strongly. Analogous biphenolate species (e.g., 5 and 6) are isolated as THF-free species.

\[ 1.2 \text{ KH, THF, } -30^\circ C \]

\[ -2 \text{ H₂, } -2 \text{ KOTf} \]
Polymerizations of MPC were carried out in dichloromethane or THF through addition of 100 equivalents of the monomer to the initiator. Polymerizations were allowed to run for two hours to ensure complete polymerization and were then quenched with a large excess of benzaldehyde. The resulting polymers were precipitated in methanol and analyzed by GPC, DSC, and $^1$H and $^{13}$C NMR spectroscopy. Characterization data are shown in Table 4.3.

![Chemical Structures]

$\text{M} = \text{Mo, } R = \text{CMe}_3; 1b$
$\text{M} = \text{Mo, } R = \text{C(CF}_3)_2\text{Me}; 2$
$\text{M} = \text{Mo, } R = \text{C(CF}_3)_2\text{CF}_2\text{CF}_3; 3$
$\text{M} = \text{W, } R = \text{C(CF}_3)_3; 4$
$\text{R'} = \text{Me; 5}$
$\text{R'} = \text{t-Bu; 6}$
$\text{R''} = \text{t-Bu, } x = 0; 8$
$\text{R''} = \text{H, } \text{R'''} = \text{Ph, } x = 1; 9$
$\text{R''} = \text{H, } \text{R'''} = \text{Mesityl, } x = 1; 10$

Figure 4.6. Initiators screened for stereospecific polymerization of 3-methyl-3-phenylcyclopropene.

The $^1$H NMR spectra of the polymers prepared by 1b – 10 contained a broad olefinic proton resonance between 5 – 6 ppm, and the corresponding carbon resonances appeared between 135 – 139 ppm. The IR spectra of a thin film of MPC$_{100}$ prepared with 1b, 2, 5, 7 and
10 reveal a distinct IR absorptions at 963 cm\(^{-1}\) and/or 982 cm\(^{-1}\) of approximately equal intensity that are not present in the spectrum of MPC, and that are most consistent with a \textit{trans}\ structure.\(^{22}\) In MPC\(_{100}\) prepared with 1a and 5 the 982 cm\(^{-1}\) absorption dominates. Quaternary carbon resonances could be observed in the \(^{13}\)C NMR spectrum in the region between 46 and 47 ppm, as shown for several samples in Figure 4.7. Observation of multiple quaternary carbon resonances for each suggests that these MPC\(_{100}\) samples do not exhibit long range order. The polymer prepared employing 10 showed a bias (~ 80\%) toward a tactic polymer in which the quaternary carbon resonance appears at 46.05 ppm (Figure 4.7, top). The \(^1\)H NMR spectrum of the MPC\(_{100}\) samples prepared employing 10 was also sharper and well-resolved. DSC analyses revealed a range of T\(_g\) values – a T\(_g\) of 42 °C was observed for MPC\(_{100}\) prepared using 1b, whereas that prepared using 10 recorded a T\(_g\) of 95 °C.

![Figure 4.7. Quaternary carbon region in \(^{13}\)C NMR spectra of poly(3-methyl,3-phenylcyclopropene) prepared employing initiator 1b (bottom), 2, 5, and 10 (top).]
<table>
<thead>
<tr>
<th>Initiator (I)</th>
<th>M/I&lt;sup&gt;a&lt;/sup&gt;</th>
<th>PDI&lt;sup&gt;b&lt;/sup&gt;</th>
<th>T&lt;sub&gt;g&lt;/sub&gt; (°C)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>M&lt;sub&gt;n&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt; x 10&lt;sup&gt;3&lt;/sup&gt;</th>
<th>Yield (%)</th>
<th>Tacticity&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1b</td>
<td>100</td>
<td>1.50</td>
<td>42</td>
<td>13</td>
<td>97</td>
<td>atactic</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>&lt;1.10</td>
<td>85</td>
<td>12</td>
<td>95</td>
<td>atactic</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>1.12</td>
<td>60</td>
<td>18</td>
<td>90</td>
<td>atactic</td>
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<td>100</td>
<td>1.21</td>
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<td>14</td>
<td>60</td>
<td>atactic</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>&lt;1.10</td>
<td>85</td>
<td>12</td>
<td>95</td>
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<tr>
<td>rac-6</td>
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<td>&lt;1.10</td>
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<td>13</td>
<td>96</td>
<td>atactic</td>
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<td>rac-7</td>
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<td>1.18</td>
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<td>15</td>
<td>99</td>
<td>atactic</td>
</tr>
<tr>
<td>rac-10</td>
<td>100</td>
<td>&lt;1.10</td>
<td>95</td>
<td>14</td>
<td>98</td>
<td>80% tactic</td>
</tr>
</tbody>
</table>

Table 4.3. Poly(3-methyl-3-phenyl cyclopropene) prepared in dichloromethane.

<sup>a</sup> Ratio of monomer (M) to initiator (I).
<sup>b</sup> Determined by GPC in THF versus polystyrene standards.
<sup>c</sup> Determined by DSC. The T<sub>g</sub> was identical in heating and cooling transitions.
<sup>d</sup> Based on the <sup>13</sup>C NMR of the quaternary carbon.

In Figure 4.8 are shown several molybdenum species<sup>23</sup> that contain electron-withdrawing biphenolate or binaphtholate ligands. Polymerization of MPC using 11a generated a polymer with a sharp singlet resonance at 46.05 ppm and 137.23 ppm for the quaternary carbon and the olefinic carbon, respectively, which we ascribe to a highly tactic (> 99%) polymer microstructure. Strong IR absorptions at 963 and 982 cm<sup>-1</sup> for MPC<sub>100</sub> prepared with 11a suggest a trans structure. A typical <sup>13</sup>C NMR spectrum of a highly regular polymer structure is shown in Figure 4.9. The <sup>1</sup>H NMR spectrum of this tactic polymer was also sharp and well-
resolved. DSC studies on the polymer (Table 4.4) revealed a $T_g$ of 105 °C, presumably as a consequence of a highly regular stereochemistry, while the GPC profile displayed a unimodal peak with a PDI of 1.80. Polymerization in THF or decreasing the steric bulk of the imido ligand (in 11b or 11c) also led to tactic polymers but did not improve the PDI (Table 4.4). The polymer prepared using 11c revealed a high molecular peak (~ 40% of the total) in addition to that with $M_n$ of 12000.

![Chemical structures](image)

**Figure 4.8.** Initiators containing relatively electron-withdrawing diolate ligands.

Initiator 12a also afforded highly tactic (>99%) MPC$_{100}$ with a relatively low PDI on the basis of $^{13}$C NMR and GPC studies, respectively. A THF-free version of 12a (12a') could be prepared by reacting Mo(NAr)(CHCMe$_2$Ph)(2,5-Me$_2$NC$_6$H$_2$)$_2$ ($Ar = 2,6-i$-Pr$_2$C$_6$H$_3$; 2,5-Me$_2$NC$_6$H$_2$ = 2,5-dimethylpyrrolidine)$^{24}$ with one equivalent of H$_2$[Binaph$_{c65}$F$_5$] in CH$_2$Cl$_2$. The $^1$H and $^{13}$C NMR spectra of the polymer prepared using 12a' were identical to those of 12a,
although the PDI was somewhat higher. So at least in the case of the molybdenum initiator that contains the \([\text{Binaphc}_6\text{F}_5]^{2-}\) ligand, the presence of one equivalent of THF during polymerization had no effect on the polymer microstructure of \(\text{MPC}_{100}\). Polymerization of \(\text{MPC}\) with \(13\text{a}\) in \(\text{CH}_2\text{Cl}_2\) produced a 90% tactic polymer while \(\text{MPC}_{100}\) prepared using \(14\text{a}\) (generated \emph{in situ} by reacting \(\text{Mo(NAr)(CHCMe}_2\text{Ph}(2,5-\text{Me}_2\text{NC}_4\text{H}_2)_2\) with one equivalent of \(\text{H}_2[\text{Binaphc}_\text{CF}_3]\)) in THF generated an atactic polymer in 60% yield. The high PDI and low molecular weight of \(\text{MPC}_{100}\) prepared with \(14\text{a}\) might suggest that this polymerization is not well-behaved.

\[\text{Figure 4.9.}\] The \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectrum (\(\text{CD}_2\text{Cl}_2\)) of a tactic > 99% polymer of poly(3-methyl, 3-phenyl cyclopropene) prepared using \(\text{Mo(NAr)(CHCMe}_2\text{Ph)(Binaphc}_6\text{F}_5)(\text{THF})\) as the initiator in dichloromethane.
<table>
<thead>
<tr>
<th>Initiator</th>
<th>Solvent</th>
<th>$^a$PDI</th>
<th>$^b$T&lt;sub&gt;g&lt;/sub&gt;</th>
<th>$^a$M&lt;sub&gt;n&lt;/sub&gt; x 10&lt;sup&gt;3&lt;/sup&gt;</th>
<th>Yield(%)</th>
<th>$^c$Tactic</th>
</tr>
</thead>
<tbody>
<tr>
<td>11a</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.80</td>
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<td>12</td>
<td>95</td>
<td>99%</td>
</tr>
<tr>
<td>11a</td>
<td>THF</td>
<td>2.17</td>
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<td>11</td>
<td>96</td>
<td>99%</td>
</tr>
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<tr>
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<td>102 (100)</td>
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<td>90</td>
<td>&gt;99%</td>
</tr>
<tr>
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<td>THF</td>
<td>2.13</td>
<td>102 (100)</td>
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<td>1.18</td>
<td>107 (105)</td>
<td>14</td>
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<td>&gt;99%</td>
</tr>
<tr>
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<td>$^f$</td>
<td>$^f$ &lt;10</td>
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</tr>
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<td>&lt;1.10</td>
<td>102</td>
<td>13</td>
<td>90</td>
<td>90%</td>
</tr>
<tr>
<td>13b</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>&lt;1.10</td>
<td>102</td>
<td>15</td>
<td>95</td>
<td>90%</td>
</tr>
<tr>
<td>13c</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.90</td>
<td>$^f$</td>
<td>25</td>
<td>30</td>
<td>atactic</td>
</tr>
<tr>
<td>14a</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>3.35</td>
<td>87</td>
<td>6</td>
<td>60</td>
<td>atactic</td>
</tr>
</tbody>
</table>

Table 4.4. Poly(3-methyl-3-phenylcyclopropene)100 microstructure.

- $^a$ Determined by GPC in THF versus polystyrene standards
- $^b$ Determined by DSC. Heating and cooling transitions produced identical T<sub>g</sub>s, except where noted in parentheses for the cooling transition.
- $^c$ Based on the quaternary carbon resonance in the $^{13}$C NMR spectrum.
- $^d$ Generated in situ in CH<sub>2</sub>Cl<sub>2</sub> by reacting Mo(NAr)(CHCMe<sub>2</sub>Ph)(2,5-Me<sub>2</sub>NC<sub>4</sub>H<sub>2</sub>)<sub>2</sub> and H<sub>2</sub>[Binaph<sub>C6F<sub>5</sub></sub>] (Figure 4.2)
- $^e$ Generated in situ in THF by reacting Mo(NAr)(CHCMe<sub>2</sub>Ph)(2,5-Me<sub>2</sub>NC<sub>4</sub>H<sub>2</sub>)<sub>2</sub> and H<sub>2</sub>[Binaph<sub>CF<sub>3</sub></sub>] (Figure 4.2)
- $^f$ Not determined
In contrast to polymerizations with 11b or 11c, reducing the size of the imido ligand in initiators 12b, 12c, 13b, and 13c did not lead to highly tactic polymers. Only 13b afforded a polymer with a 90% tactic bias as determined by the $^{13}$C NMR spectrum. Initiators 12b, 12c, and 13c afforded atactic polymers in relatively low yields.

A subtle variation in the electronic environment of the initiators was the difference in their ability to afford an atactic and a tactic polymer. For example, use of 5 (Figure 4.6) as an initiator led to an all trans polymer (it is proposed) with little order (Table 4.3), while use of 11a (Figure 4.8), in which the methyl groups in the 5 and 5' positions of the biphenolate are fluorinated, led to highly tactic MPC$_{100}$ (Table 4.4). Direct attachment of fluorinated groups to the binaphtholate backbone (as in 12a) is also required for forming tactic MPC$_{100}$ (Table 4.4 and Figure 4.9). Finally, the nature of the imido group can have a dramatic impact on the stereoselective ROMP. Such intricate balance between the electronic environment around the tactic polymer can be better understood if we rationalize the possible pathways involved in the stereospecific polymerization of MPC. If we assume that trans linkages are produced, the monomer must add to the Mo=CHP (P = growing polymer) bond to yield a molybdabicyclopentane intermediate in which P and the cyclopropane ring are trans to one another, as shown in Figure 4.10. Base binding studies on four-coordinate molybdenum imido alkylidene complexes have indicated that for a productive metathesis to occur, a substrate has to approach the metal center via one of the two CNO faces. In an alkylidene complex ligated by a chiral ligand, the two CNO faces are inequivalent. Likewise, the two faces of the C=C bond in MPC are inequivalent and the Mo=CHP species that may generate either a syn or anti isomer further adds to the complexity of stereoregular ROMP. Therefore, for an all trans polymer, eight distinct (diastereomeric) propagating pathways appear to be possible from a single metal center,
which can be narrowed down to four pathways if the addition through one face of the cyclopropene is more selective for steric reasons (for example as shown in Figure 4.10). It should be noted that an initiator containing a racemic or an enantiomerically pure diolate ligand will yield a polymer with same microstructure as long as no chain transfer occurs between metal centers.

![Figure 4.10](image-url)

**Figure 4.10.** Addition of 3-methyl-3-phenylcyclopropene onto a metal carbon bond.

If the five-coordinate molybdabicyclopentane species does not rearrange before the intermediate opens to yield the new alkylidene, the Mo=CHP isomer that forms when a cyclopropene inserts will be the opposite of the initial isomer, i.e., a syn isomer would generate an anti isomer, or vice versa (Figure 4.10). The alkylidene then would have to rotate about the Mo=C bond in order to form the preferred (i.e., most reactive) syn or anti isomer for the next insertion. If this pathway is operative, then an isotactic polymer would result. The rate of rotation about the Mo=C bond has been shown to vary by several orders of magnitude among a collection of molybdenum imido alkylidene complexes containing bisalkoxide ligands, but quantitative data are not trivial to obtain. It has also been established that there are dramatic differences in the reactivities for most of the syn and anti isomers of molybdenum imido alkylidene complexes.
Owing to the aforementioned circumstances we were somewhat surprised that highly regular \( \text{MPC}_{100} \) was even possible. It is not intuitively obvious to what details of initiator behavior (including interconversion of \textit{syn} and \textit{anti} isomers and their likely different reactivities) lead to formation of tactic \( \text{MPC}_{100} \) in high yield. The experiments and data that we have managed to gather implicates a more electron poor and highly crowded metal centers favor the formation of \( \text{MPC}_{100} \) with a long range order. At this point it is not known which tacticity is responsible for the 46.05 ppm quaternary carbon resonance in the \( ^{13}\text{C} \) NMR spectrum of the polymer. Work is enroute to determine whether the polymer is isotactic or syndiotactic through methods related to those employed to determine tacticity in certain all \textit{cis} and all \textit{trans} polynorbornene derivatives.\(^{10b, 26}\)

### 4.3.2. Stereospecific polymerization of MPCC and MEMC

Initiators that afforded high tactic \( \text{MPC}_{100} \) were also screened in the ROMP of \( \text{MPCC} \) (Figure 4.1). Unfortunately, no polymer resulted upon treatment of 100 equivalents \( \text{MPCC} \) to the \( \text{CH}_2\text{Cl}_2 \) solution of \( 11\text{a, 12a or 13a} (~15\ \text{mM}) \). In a separate experiment, addition of ten equivalents of \( \text{MPCC} \) to the \( \text{CD}_2\text{Cl}_2 \) solution of \( 11\text{a} \) showed no evidence for the polymer formation despite the instantaneous consumption of the initial alkylidene as determined by the \(^1\text{H} \) NMR spectrum. It is believed that coordination of the ester functionality to the electron-deficient metal center inhibits the polymerization reaction after the first insertion step. In fact, among \( 1\text{a} – 10 \) only 2 and 7 were able to polymerize \( \text{MPCC} \) in 90% and 60% yield, respectively. The \( ^{13}\text{C} \) NMR spectra of \( \text{MPCC}_{100} \) revealed that polymer in both the instances lacked a long range order. Likewise, efforts to polymerize \( \text{MEMC} \) (Figure 4.1) using \( 11\text{a, 12a} \)
or 13a were not successful, presumably due to the coordination of the ether functionality to the highly electron deficient metal center.

CONCLUSION

Living ROMP of cyclopropenes has been achieved using high oxidation state molybdenum imido alkylidene initiators 1a, 1b and 2. The polymers were isolated in virtually quantitative yield and GPC studies revealed unimodal peak distributions with low PDI. Several block copolymers were also prepared utilizing the living polymerization of the MPC, MEMC and DCMNBD with monometallic (1a and 1b) as well as bimetallic ROMP initiator (1c) containing t-butoxide ligands. The block copolymers displayed good phase segregation as determined by DSC studies. Ruthenium-based ROMP initiators were also explored for the polymerization of MPC, however they showed slow reaction rates.

Identical olefinic proton and carbon resonances for MCP100 prepared with various initiators in the corresponding 1H and 13C NMR spectra coupled with strong IR absorptions for the polymer thin film at 963 and/or 982 cm⁻¹ were indicative of an all trans double bond.27 It should be noted that in MPC100 prepared with 1b and 5 the absorption at 982 cm⁻¹ dominates. The quaternary carbon resonances of MCP100 appeared in the region between 46 and 47 ppm (as shown for several samples in Figure 4.4), consistent with varying degrees of tacticity in the polymer microstructure. Stereospecific polymerization of MPC was achieved by using molybdenum imido alkylidene complexes containing electron withdrawing ligands (11a, 11b, 11c, 12a, 13a and 13b), however their non-fluorinated analogs afforded atactic polymer microstructure as determined by 1H and 13C NMR spectroscopy.
EXPERIMENTAL

General. All manipulations were conducted under a nitrogen atmosphere in a Nitrogen Atmospheres drybox or using Schlenk techniques. The glassware, including NMR tubes were oven-dried prior to use. Ether, pentane, toluene, dichloromethane, toluene and benzene were degassed with dinitrogen and passed through activated alumina columns. Dimethoxyethane was vacuum distilled from a dark purple solution of sodium benzophenone ketyl, and degassed three times by freeze-pump-thaw technique. All dried and deoxygenated solvents were stored over molecular sieves in a nitrogen-filled glovebox.

Proton, carbon and fluorine NMR spectra were acquired at room temperature unless otherwise noted using Varian spectrometers and referenced to the residual protio solvent resonances. Elemental Analyses were performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany. The relative molecular weights were determined by Waters gel permeation chromatography (GPC) equipped with 1 Styragel HT3 column (500-30 000 MW range), 1 Styragel HT4 column (5000-600 000 MW range), 1 Styragel HT5 column (50 000-4 x10^6 MW range), a refractive index detector, and a UV detector (254 nm) was used for molecular weight measurement relative to polystyrene standards at room temperature in THF (1 mL/min). A TA instruments Q1000 differential scanning calorimeter (DSC) was used to determine the thermal transitions, which were read as the maxima and minima of the endothermic peaks, respectively. All heating and cooling scans were performed at the rate of 5 °C/min.

(DME)Mo(NAr)(CHCMe2Ph)(OTf)2, (DME)Mo(NAr')(CHCMe2Ph)(OTf)2,

(DME)Mo(NAd)(CHCMe2Ph)(OTf)2 (Ar = 2,6-diisopropylphenyl; Ar' = 2,6-dimethylphenyl; Ad = 1-adamantyl), MPC, MEMC, MPCC, 1a, 1b, 1c, 2, 3, 4, 5, 6, 7, 9, 10, 11-14, and H2[Binaph-Bu] were prepared as described in the literature.
Mo(NAr)(CHCMe₂Ph)(Binapht₆-Bu) (8). A 100 mL round bottom flask was charged with a 20 mL THF solution of H₂[rac-Binapht₆-Bu] (300mg, 0.588 mmol), and KH (70 mg, 1.76 mmol) was added in small portions. After 1 h, the reaction solution was filtered through Celite into a round bottom flask containing the solution of Mo(NAr)(CHCMe₂Ph)(OTf)₂(DME) (465 mg, 0.588 mmol) in THF. The reaction was stirred for 12 h at room temperature, after which the volatile components were removed in vacuo. The crude solid was extracted with pentane (60 mL). Removal of pentane in vacuo, and addition of heptane (10 mL) resulted in the precipitation of orange solid (380 mg, 70%): ¹H NMR (CD₂Cl₂, 500MHz) δ 12.69 (br s, 1, anti Mo=CH), 10.73 (s, 1, syn Mo=CH), 8.18 (s, 1, Ar), 8.00 (s, 1, Ar), 7.97 (br s, 2, Ar), 7.86 (s, 2, Ar), 7.47 (d, 2, Ar), 7.43 (d, 1, Ar), 7.38 (d, 1, Ar), 7.32 (t, 2, Ar), 7.21 (t, 1, Ar), 7.13 (t, 1, Ar), 7.05 (d, 2, Ar), 6.69 (q, 2, Ar), 3.48 (sept, 2, Me₂CH), 3.48 (br, 4, THF), 1.87 (s, 3, neophyl Me), 1.70 (s, 9, t-Bu), 1.68 (s, 9, t-Bu), 1.45 (s, 9, t-Bu), 1.41 (s, 9, t-Bu), 1.24 (s, 3, neophyl Me), 1.07 (d, 6, Me₂CH), 0.98 (br, ), 0.78 (d, 6, Me₂CH); ¹³C NMR (CD₂Cl₂, 125 MHz): δ 278.79 (syn C₀) 156.98, 156.63, 153.87, 151.17, 148.65, 148.17, 147.32, 142.31, 140.61, 132.13, 131.98, 131.53, 130.61, 130.21, 130.08, 128.63, 128.05, 127.12, 126.36, 129.19, 125.86, 125.26, 125.13, 124.58, 124.30, 123.56, 120.76, 118.22, 36.58, 36.36, 35.25, 35.16, 33.23, 32.23, 31.75, 31.71, 30.82, 30.36, 28.97, 24.48, 24.24. Anal. Calcd for 95% C₅₈H₇₃MoNO₂ and 5% (8 + THF): C, 76.37; H, 8.07; N, 1.54. Found: C, 76.33; H, 8.08; N, 1.53.

General procedure for polymerization in the synthesis of homopolymers. To a stirred solution of initiator, the monomer solution is added in one portion and the reaction mixture is stirred at room temperature. Benzaldehyde is added to quench the reaction. The polymer is
precipitated in methanol, isolated by filtration and analyzed by $^1$H and $^{13}$C NMR spectroscopy, gel permeation chromatography and differential scanning calorimetry.

**A representative example of homopolymer synthesis.** MPC (251 µL, 2.60 M in CH$_2$Cl$_2$, 0.653 mmol) dissolved in 2 mL of CH$_2$Cl$_2$ was added in one portion to a stirred solution of 1a (4 mg, 6.53 µmol) in 4 mL of CH$_2$Cl$_2$ and the reaction was stirred at room temperature for 1 h. Benzaldehyde (500 µL) was added *via* a syringe to the reaction and the reaction mixture was stirred for 1 h. The polymer was precipitated in 100 mL of methanol, collected by filtration and dried in vacuo (85 mg, 98%).

**A representative example for the synthesis of tactic MPC$_{100}$ by 11a.** To a stirred solution of Mo(NAr)(CHCMe$_2$Ph)(Biphen$_{CF_3}$)(THF) (10 mg, 0.01 mmol) dissolved in 4 mL of CH$_2$Cl$_2$, a solution of MCP (132 mg, 1.00 mmol) in 2 mL of CH$_2$Cl$_2$ was added in one portion and the reaction mixture was stirred for 2 h. Benzaldehyde (500 µL) was added to the reaction and the reaction mixture was stirred at room temperature for 1 h. The polymer was precipitated in 100 mL of methanol, isolated by filtration and dried in vacuo (130 mg, 98%).

**Initiation studies.** To a stirred solution of initiator at room temperature, an aliquot of monomer was added and the reaction solution was stirred for 15 min before it was transferred to an NMR tube. The reaction was analyzed by $^1$H NMR spectroscopy.

**A representative example for initiation of 2 by MPC.** To a stirred solution of 2 (10 mg, 4.45 x $10^{-3}$ mmol) in 0.7 mL of CD$_2$Cl$_2$ at room temperature, ten equivalents of DCMNBD (35.5 µL, 2.85 µM) were added. After 15 min, the reaction solution was transferred into a J. Young NMR tube and the $^1$H NMR spectrum was recorded: the $^1$H NMR spectrum revealed 50% consumption.
of the initial alkylidene with the formation of multiple alkylidene resonance indicating poor initiating properties of 2.

**General procedure for polymerization in the synthesis of diblock copolymer.** To a stirred initiator solution, a monomer solution was added in one portion and the reaction mixture was stirred at room temperature. A second monomer solution was added to the reaction and the reaction was stirred at room temperature. Benzaldehyde was added to the reaction to quench the polymerization. The polymer was precipitated in methanol, isolated by filtration and dried in vacuo. The polymer was analyzed by $^1$H NMR spectroscopy and gel permeation chromatography.

**A representative example of diblock copolymer synthesis using 1a.** To a stirred solution of 1a (10 mg, 0.018 mmol) in 6 mL of THF, MPC (177 mg, 1.37 mmol) dissolved in 2 mL of THF was added in one portion and the reaction mixture was stirred for 1 h. 2,3-dicarbomethoxynorbornadiene (757 mg, 3.64 mmol) was added, and the reaction mixture was stirred for another hour. Benzaldehyde (500 µL) was added to the polymerization reaction, and after 1 h the polymer was precipitated in methanol. The polymer was isolated by filtration and dried in vacuo (915 mg, 98%).

**A representative example of triblock copolymer synthesis using 1c.** To a stirred solution of 1c (5 mg, 0.005 mmol) in 6 mL of THF, MEMC (3.75M, 0.562 mmol, 150 µL) was added in one portion, and the reaction mixture was stirred at room temperature. After 1 h, MPC (2.35M, 1.12 mmol, 500 µL) was added to the solution in one portion, and the reaction was stirred for another 1 h. Benzaldehyde (500 µL) was added to the reaction and the polymer was precipitated
in methanol (100 mL). The polymer was dried in vacuo to obtain a glue-like material (192 mg, 89%).
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CHAPTER 5

Reactivity and Catalysis of Molybdenum Imido Alkylidene Complexes
Supported by a Pyrrolide Ligand

Portions of this chapter have appeared in print:


INTRODUCTION

High oxidation state molybdenum imido alkylidene complexes have emerged as one of the two most important classes of olefin metathesis catalysts. The reactive unit in these catalysts is the metal-carbon double bond, which is supported by imide and alkoxide (or diolate) ligands. The modular architecture of these complexes allows for the fine control of the reactivity and functional group tolerance through appropriate choice of supporting ligands. Various combinations of imide and the alkoxide have resulted in a vast library of olefin metathesis catalysts with unique reactivities. One of the catalysts that has seen tremendous use in olefin metathesis reactions is Mo(N-2,6-i-Pr_2C_6H_3)(CHCMe_2Ph)(OC(CF_3)Me)_2 – the imido ligand imparts steric protection to the metal center, and the electron-withdrawing alkoxide ligands engender the metal center more Lewis acidic increasing the reactivity of the catalyst. Formation of a new smaller alkylidene species (usually methylidene) during the catalytic cycle creates pathways for the formation of catalytically inactive species that can eventually terminate the catalytic cycle. Recent work with imido alkylidene complexes of tungsten has shown that bimolecular coupling of alkylidene ligands to give reduced metal-metal bonded species can act as a major decomposition pathway in olefin metathesis reactions.

Molybdenum imido alkylidene dipyrrolide (MDP) complexes of the type Mo(NR)(CHR')Pyr_2 (Pyr = pyrrolide or 2,5-dimethylpyrrolide) have been reported recently by our laboratory. Interest in the MDP species initially stemmed from the possibility of generating bisalkoxide catalysts of the type Mo(NR)(CHR')(OR)_2 or Mo(NR)(CHR')(diolate) through addition of alcohols or a diol to the dipyrrolide complexes. Generation of catalysts in situ in this manner would be ideal for high
throughput screening of catalysts. It has been shown that MDP complexes are less reactive toward olefins than bisalkoxide species, but serve as effective precursors for the *in situ* generation of Mo-based bisalkoxides or diolates, which show similar and sometimes better activity in comparison to the isolated catalysts.\(^4,5\)

We became attracted to the possibility of intercepting molybdenum imido alkylidene alkoxide pyrrolide (MAP) species, Mo(NR)(CHR')(OR'')(2,5-Me\(_2\)NC\(_4\)H\(_2\))\(^2\)(2,5-Me\(_2\)NC\(_4\)H\(_2\) = 2,5-dimethylpyrrolide), which might prove to be of interest in their own right. The impetus for isolating MAP species partly arises from the high catalytic activities that have been observed for supported MAP species.\(^6\) Theoretical studies have also been carried out on pseudotetrahedral metal complexes that are asymmetric at the metal center, Mo(NAr)(CHCMe\(_3\))(OR)(CH\(_2\)CMe\(_3\)).\(^7\) In addition, by virtue of \(\eta^1, \eta^5\) ligation of the 2,5-dimethylpyrrolide ligands observed in Mo(NAr)(CHMe\(_2\)Ph)(2,5-Me\(_2\)NC\(_4\)H\(_2\))\(^2\),\(^4a\) it may be inferred that similar binding of the 2,5-dimethylpyrrolide ligand is possible in MAP complexes resulting in an equilibrium between a 14-electron species and an 18-electron species (Scheme 5.1). Accessibility of an 18-electron methylidene complex is desirable in maintaining the relative stability of these highly reactive species towards bimolecular decomposition.\(^8\) These new and/or stable catalysts may be utilized in effecting a new reaction, i.e. enyne metathesis.
Scheme 5.1. Proposed equilibrium of the methylidene species in MAP complexes.

Enyne metathesis is a bond reorganization reaction that involves an alkene and an alkyne to produce a 1,3-diene. In an enyne metathesis reaction, the substituent on the alkylidene ligand is introduced onto respective alkyne carbons, and the initial triple bond is converted into a single bond as illustrated in Figure 5.1.

Figure 5.1. Enyne metathesis reaction employing a molybdenum alkylidene complex.

The dienes thus formed can be used as versatile intermediates for further synthetic manipulations; for example, Diels-Alder reaction. In an enyne metathesis reaction, it has been proposed that the alkylidene first reacts with the alkyne and the resulting
alkylidene reacts with the alkene. Two distinct pathways become viable based on the approach of the alkyne of enyne substrate to the metal-carbon double bond. The alkyne can add to the metal-carbon double bond in either an α- or a β-fashion as shown in Figure 5.2. A smaller-ring product with vinyl olefin is formed when the approach of an alkyne is such that an α-substituted metallacyclobutene intermediate is formed, whereas formation of β-substituted metallacyclobutene intermediate results in formation of a larger-ring structure with an exo-methylene unit.

![Figure 5.2](image)

**Figure 5.2.** The bifurcated pathway involved in enyne metathesis reaction.

Enyne metathesis reactions can be catalyzed by metal carbenes or low-valent transition metal salts such as Pt(II) and Pd(II), which operate via a different mechanism. The first enyne metathesis reaction catalyzed by Ru-based olefin metathesis catalysts was reported in 1994 by Kinoshita and Mori. While ring-closing metathesis (RCM) or cross metathesis (CM) is an entropically driven process as a consequence of the release of ethylene, enyne metathesis has to rely on the stability of the resulting conjugated 1,3-diene produced as an enthalpic driving force. Over the last decade additional reports
have emerged along with several reviews on the subject.\textsuperscript{14} Molybdenum-based catalysts employed in enyne metathesis reactions have resulted in a large amount of polymer with no or very little products of enyne metathesis, and as a result, very few studies have emerged that include molybdenum species in their screens for enyne metathesis reactions.\textsuperscript{15}

As will be shown here, MAP complexes will not only turn out to have special reactivities in various olefin metatheses, but also in enyne metathesis reactions. MAP complexes that contain a chiral alkoxide ligand can be envisioned for applications in asymmetric olefin metathesis, as well as asymmetric enyne metathesis reactions. This chapter details the reactions of selected alcohols with MDP complexes to afford a new class of olefin metathesis catalysts (MAP). Catalytic activity of MAP catalysts in RCM as well as enyne metathesis reactions is discussed. Several MAP complexes containing a chiral alkoxide ligand have also been synthesized and used in asymmetric olefin metathesis reactions. Some results with silica-supported catalysts of the type Mo(NAr)(CHCMe\textsubscript{2}Ph)(OSi\textsubscript{surf})(2,5-Me\textsubscript{2}NC\textsubscript{4}H\textsubscript{2}) prepared in collaboration with Dr. Christophe Copéret in the Basset group at CNRS, Lyon will be mentioned. Unless otherwise stated, the imido group (NAr) used in this chapter is N-2,6-diisopropylphenyl, which offers maximum steric protection to the metal center compared to other widely used imido functionalities in the chemistry of Mo(NR)(CHR')(OR)\textsubscript{2} and Mo(NR)(CHR')(diolate) complexes.
RESULTS AND DISCUSSION

5.1 Synthesis of MAP complexes:

Alcoholysis of Mo(NAr)(CHCMe₂Ph)(2,5-Me₂NC₄H₅)₂ with an equivalent of ROH (R = Me₃C; (CH₃)₂CH; 2,6-i-Pr₂C₆H₅; (CF₃)₂CHC; (CF₃)₂CH₃C; C₆F₅; (Bu-t-O)₃Si) in diethyl ether or THF yields the corresponding Mo(NAr)(CHCMe₂Ph)(OR)(2,5-Me₂NC₄H₅) (R = Me₃C: 1; (CH₃)₂CH: 2; 2,6-i-Pr₂C₆H₅: 3; (CF₃)₂CHC: 4; (CF₃)₂CH₃C: 5; (Bu-t-O)₃Si: 6; C₆F₅: 7) complexes (Equation 5.1). Proton NMR spectra of 1 – 7 recorded in C₆D₆ revealed single alkylidene resonances at 12.24 ppm (1), 12.04 ppm (2), 12.29 ppm (3), 12.34 ppm (4), 12.45 ppm (5), 12.43 ppm (6), 12.78 ppm (7), which are assigned to the alpha proton of the syn (JCH ~ 120 Hz) alkylidene ligand. The ¹H NMR spectra of 1 - 7 are consistent with the molecules possessing C₁ symmetry as indicated by the inequivalent methyl protons for the neophylidene group. Anti isomers were not observed at room temperature as judged by the ¹H NMR spectra.

![Equation 5.1](image-url)
Figure 5.3. POV-ray diagram of Mo(NAr)(CHCMe₂Ph)(2,5-Me₂NC₄H₂)(OAr) (Ar = 2,6-diisopropylphenyl) (3). Thermal ellipsoids are displayed at 50% probability level. Hydrogen atoms are omitted for clarity; Mo(1)-N(2) = 1.7364(11) Å, Mo(1)-C(1) = 1.8921(13) Å, Mo(1)-O(1) = 1.9145(10) Å, Mo(1)-N(1) = 2.0373(11) Å, N(2)-Mo(1)-C(1) = 101.45(5)°, C(1)-Mo(1)-O(1) = 108.85(5)°, C(1)-Mo(1)-N(1) = 106.52(5)°, C(2)-C(1)-Mo(1) = 139.48(9)°, C(21)-N(2)-Mo(1) = 172.57(9)°.

Single crystals of 3 suitable for X-ray crystallography were grown from a saturated heptane solution at −30 °C. The solid state structure of 3 displays a pseudotetrahedral geometry about the molybdenum center with the alkylidene ligand in the syn
confirmation, consistent with the observed \( J_{\text{CH}} \) value in solution (Figure 5.3). The 2,5-dimethylpyrrolide ligand is bound \( \eta^1 \) to the metal center, even though an \( \eta^5 \)-2,5-dimethylpyrrolide ligand is feasible electronically. We presume that steric crowding is the primary reason for \( \eta^1 \) instead of \( \eta^5 \) binding. It is not known whether complexes that contain smaller alkoxide and/or alkylidene ligands could contain an \( \eta^5 \)-pyrrolide ligand. It is likely that there is a rapid equilibrium between \( \eta^1 \)- and \( \eta^5 \)-pyrrolide ligands in Mo(NAr)(CHCMe\textsubscript{2}Ph)(Me\textsubscript{2}Pyr)(OR), as observed for Mo(NAr)(CHCMe\textsubscript{2}Ph)(Me\textsubscript{2}Pyr).\textsuperscript{4b} The bond distances and the bond angles of the solid state structure are typical for a four coordinate complex of this type (see caption to Figure 5.3).\textsuperscript{7b}

Among the MAP complexes prepared thus far 7 was the least stable, presumably due to the smaller pentafluorophenoxide ligand. Compound 7 was isolated in 70% yield, which contained approximately 10% of Mo(NAr)(CHCMe\textsubscript{2}Ph)(2,5-Me\textsubscript{2}NC\textsubscript{4}H\textsubscript{2})\textsubscript{2} as an impurity (Figure 5.4). Efforts to recrystallize 7 from a concentrated diethyl ether solution resulted in a mixture of Mo(NAr)(CHCMe\textsubscript{2}Ph)(2,5-Me\textsubscript{2}NC\textsubscript{4}H\textsubscript{2})\textsubscript{2} and Mo(NAr)(CHCMe\textsubscript{2}Ph)(OC\textsubscript{6}F\textsubscript{5})\textsubscript{2}, which suggests that ligands scramble intermolecularly in solution. Based on the solid state structure of the related Mo(NAr)(CHCMe\textsubscript{3})(CH\textsubscript{2}CMe\textsubscript{3})(OC\textsubscript{6}F\textsubscript{5}) complex,\textsuperscript{7b} which exists as a centrosymmetric dimer architecture with the pentafluorophenoxide ligands bridging the two metal centers, it seems likely that 7 also contains bridging phenoxides in the solid state.
5.2 Studies involving base binding to Mo(NAr)(CHCMe₂Ph)(OC(CF₃)₂Me)(2,5-Me₂NC₄H₂)

The primary step in an olefin metathesis reaction is proposed to be an electrophilic interaction between the olefin and the metal center, which leads to the formation of a metallacyclobutane intermediate. There is scant evidence for an olefin adduct of an alkylidene. Since neutral Lewis base is a nucleophile similar to an olefin, base-binding studies involving molybdenum imido alkylidene complexes have been used as a crude approximation of the olefinic interaction with the metal center.

Addition of one equivalent of a neutral base to Mo(NR)(CHR')(OR'')₂ complexes has shown a preference for binding to the CNO face, although a complex having a THF molecule bound on the NOO face has also been crystallographically characterized.
Likewise, base-binding studies on the complexes of the type \( \text{Mo(NAr)(CH-t-Bu)(CH}_2\text{-t-Bu)(OR)} \) create an interesting predicament because the approach of a base \textit{trans} to the alkyl or the alkoxide ligands should be energetically different in such unasymmetric complexes. An X-ray structure of \((\text{Me}_3\text{P})\text{Mo(NAr)(CH}_t\text{-Bu)(CH}_2\text{-t-Bu)(OC}_6\text{F}_5)}\) revealed the coordination of the base \textit{trans} to the alkyl ligand, which has also been rationalized by theoretical studies.\textsuperscript{7b}

![Image of chemical structure]

The room temperature reaction of 1.2 equivalents of \( \text{PMe}_3 \) with \( \textbf{5} \) in \( \text{C}_6\text{D}_6 \) (21 mM) resulted in the appearance of the new alkylidene resonance within 15 min as determined by \( ^1\text{H} \) NMR spectroscopy (Equation 5.2). The new resonance was observed at 14.06 ppm, which was assigned to the \textit{syn} isomer of the \( \text{PMe}_3 \) adduct (\( \text{Me}_3\text{P}-\textbf{5} \)) on the basis of the CH coupling constant \( (J_{CH} = 124 \text{ Hz}) \). The alkylidene resonance is a doublet due to \( ^{31}\text{P} \) nucleus \( (^{2}J_{HP} = 3.51 \text{ Hz}) \). Two distinct methine resonances for the isopropyl groups were observed in the \( ^1\text{H} \) NMR spectrum of \( \textbf{5-PMe}_3 \), which is indicative of hindered rotation of the imido ligand on the NMR time-scale. A 2-D \( ^1\text{H}-^1\text{H} \) EXSY (NOESY) experiment revealed two sets of cross peaks with the same sign as the peaks appearing on the diagonal, which is characteristic of exchange of methyl groups as a

\[ \textbf{5-PMe}_3 \]
consequence of slow rotation of the imido ligand (Figure 5.5). The methyl resonances for the isopropyl groups were found at 1.35, 1.13, 1.05 and 0.79 ppm.

Figure 5.5. 2-D $^1$H-$^1$H EXSY (NOESY) of (Me$_3$P)Mo(NAr)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)(2,5-Me$_2$NC$_4$H$_2$) (Me$_3$P-5) in C$_6$D$_6$.

The doublet resonance for the bound PMe$_3$ was observed at 0.84 ppm ($^3J_{HP} = 8.7$ Hz). The $^{31}$P NMR spectrum displayed a single resonance at $-5.72$ ppm and the $^{19}$F NMR spectrum revealed two quartets at $-75.58$ ppm and $-77.12$ ppm as a consequence of the fluorine coupling between the inequivalent trifluoromethyl groups. Me$_3$P-5 can be isolated in 82% yield as a yellow precipitate upon mixing a stoichiometric amount of PMe$_3$ and Mo(NAr)(CHCMe$_2$Ph)(OC(CF$_3$)$_2$Me)(2,5-Me$_2$NC$_4$H$_2$) in pentane. The $^1$H, $^{31}$P, $^{19}$F and $^{13}$C NMR spectra of the isolated Me$_3$P-5 were identical to that of the compound generated in situ.
Figure 5.6. Selected region of the 500 MHz $^1$H NOESY spectrum of (Me$_3$P)Mo(NAr)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)(2,5-Me$_2$NC$_4$H$_2$) (Me$_3$P-5) in C$_6$D$_6$ (mixing time = 200 ms).

The coordination of PMe$_3$ to the metal center was elucidated by means of a $^1$H NOESY experiment; absence of cross peaks between the methyl resonances of the coordinated PMe$_3$ and the resonances for the pyrrolide ligand (the methyl groups and the backbone protons) infers trans binding of the Lewis base with respect to the 2,5-dimethylpyrrolide ligand (Figure 5.6). The cross peaks between the methyl group of the alkoxide ligand and the bound PMe$_3$ could not be used for validation of the proposed
geometry due to the overlap of the methyl resonance of the alkoxide ligand with the slow rotating methyl groups of the imide ligand. The solution-state structure is also consistent with a crystallographically characterized PMe$_3$ adduct of a related complex, Mo(NAr)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)(2,5-Ph$_2$NC$_4$H$_2$), which shows the base coordinated trans to the 2,5-diphenylpyrrolide ligand.$^{21}$ The $^1$H NMR spectrum of (Me$_3$P)Mo(NAr)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)(2,5-Ph$_2$NC$_4$H$_2$) at room temperature shows an equilibrium between the base-adduct (H$_\alpha$ = 14.76 ppm, 73%) and the base-free (H$_\alpha$ = 12.76 ppm, 27%) species, unlike Me$_3$P-5, which shows strong binding of PMe$_3$ to the metal center in solution.

5.3 Variation of the imido ligand of MAP complexes

The MAP complexes described thus far utilize a bulky 2,6-diisopropylphenylimido ligand, which produces complexes in which bimolecular decomposition is the slow compared with other imido ligands. Previous studies in the bisalkoxide catalyst systems containing 1-adamantylimido ligand have yielded significantly different results in terms of stability of alkylidene complexes and reactivity and selectivity towards olefins compared to that containing the 2,6-diisopropylphenyl imido ligands.$^{22}$ The potential for increased accessibility to MDP complexes containing a wide variety of imido ligands also serves as an incentive to explore MAP complexes with other imido functionalities.$^{4b}$

As our initial goal, 2,6-dimethylphenylimido and 1-adamantylimido ligands were targeted to be incorporated in the MAP complexes. The procedure to prepare MDP complexes containing 2,6-dimethylphenylimido and 1-adamantylimido ligands has been
detailed in chapter 3. Treatment of Mo(NAr')(CHCMe2Ph)(2,5-Me2NC6H4)2 (Ar' = 2,6-dimethylphenyl) with one equivalent of (CF3)2MeCOH or 2,6-i-PrC6H3OH in C6D6 (23 mM) afforded a mixture of the bisalkoxide complex and starting material. Identical results were obtained when the alcoholysis of Mo(NAd)(CHCMe2Ph)(2,5-Me2NC6H4)2 (Ad = 1-adamantyl) was attempted using (CF3)2MeCOH or 2,6-i-PrC6H3OH in C6D6 (20 mM). The inability to prepare MAP complexes containing 2,6-dimethylphenylimido and 1-adamantylimido ligands can be attributed to the smaller size of the imido ligands, which leave the intermediate monopyrroliide complexes susceptible to further rapid protonation. The importance of a sterically encumbering imido group can also be ascertained from the fact that mono-substitution of MDP complex derived from the unsubstituted pyrrolides was not successful due to the formation of bisalkoxide species.

5.4 Reaction of 1-7 with simple olefins (ethylene and 1,3-pentadiene)

In order to probe the metathetical reactivity towards olefins, the reaction of 1 – 7 with ethylene was examined. Upon exposure of 1 – 7 to 1 atmosphere of ethylene in C6D6 at room temperature, the yellow/orange solutions darkened immediately. The 1H NMR spectra of the reactions revealed complete consumption of the initial alkylidene within 15 min in all cases. The principal end products in each case were identified by 1H NMR spectroscopy as the respective methylidene (25 – 40%) and metallacycle species. The methylidene species seemed stable in solution at room temperature for 12 h as judged by 1H NMR spectroscopy. Complexes 3 and 5' (neopentyliide analog of 5) were chosen as candidates for the isolation of the corresponding methylidene species because of the bulky alkoxide/phenoxide ligands that could provide the steric protection required
for their successful isolation. Surprisingly, removal of the volatile components in vacuo after treating 3 and 5' with 1 atmosphere of ethylene in heptane for 12 h resulted in formation of the corresponding ethylene complex, 8 and 9 in 59% and 63% isolated yield, respectively (Equation 5.3). Proton NMR spectra of 8 and 9 in C₆D₆ revealed the bound ethylene resonances at 2.95 ppm, 2.60 ppm, 1.95 ppm and 2.74 ppm, 2.45 ppm, 2.16 ppm, respectively. Unimolecular decomposition of molybdacyclobutanes is proposed as the mechanistic pathway for the formation of the ethylene complex. Formation of ethylene complexes in reactions of alkylidenes and ethylene has also been documented for other catalysts.²³

![Chemical structures](image)

Similarly, a metathesis reaction between 1,3-pentadiene and 2 in C₆D₆ (23 mM) (Equation 5.4) results in formation of a new alkylidene complex that has an alkylidene resonance at 13.31 ppm with Jₜₜ of 9.3 Hz, which is consistent with the formation of the a syn vinyl alkylidene.²⁴ The vinyl alkylidene complex seemed stable in solution for 72 h at room temperature. However, efforts to isolate the vinyl alkylidene resulted in what
appears to be \([(i-\text{PrO})_2(ArN)\text{Mo}]_2\) in 23\% yield as determined by the $^1\text{H}$ NMR spectrum.\(^3\) The reaction pathway that accounts for the formation of such dimeric species is yet to be understood.

\[(5.4)\]

\begin{align*}
\text{C}_6\text{D}_6 & - \text{CHCHCMePh} \\
& \xrightarrow{\text{C}_6\text{D}_6 - \text{CHCHCMePh}} \quad \text{dihydrofuran}
\end{align*}

\subsection*{5.5 Ring-closing metathesis reactions}

The efficacy of MAP complexes as olefin metathesis catalysts for several ring-closing metathesis (RCM) reactions was investigated. Upon addition of fifty equivalents of diallylether to the C\(_6\)D\(_6\) solutions of 1 – 6 (15 – 20 mM), the ring-closed product, dihydrofuran, was formed in each instance within 15 -20 min as determined by the $^1\text{H}$ NMR spectra (Equation 5.5). To evaluate the potential of MAP complexes in the catalysis of nitrogen containing substrates, the RCM of N,N-diallyltosylsulfonamide was investigated. Treating 1 – 6 in C\(_6\)D\(_6\) (~10 mM) with fifty equivalents of N,N-diallyltosylsulfonamide readily yielded the ring-closed product along with ethylene within 15 -20 min as judged by the $^1\text{H}$ NMR spectra (Equation 5.5). It should be pointed out that 7 was not employed in these studies because of its tendency to generate the bisalkoxide species in solution \((\text{vide supra})\), preventing accurate evaluation of the reactivity of 7.
In a separate experiment, 3 was treated with ten equivalents of diallyl ether in C₆D₆ (23 mM) at room temperature for a total of ten times in sequence. Complete conversion of the substrate into the ring-closed product and ethylene was observed in less than 10 min at each stage according to ¹H NMR spectroscopy. In fact, the ring-closed product was produced within 10 min when ten equivalents of diallyl ether was added for the eleventh time to the sample that was kept at room temperature for 12 h. These observations suggest that MAP catalysts are relatively stable and long-lived. Compounds 3 and 5 were screened in the ring-closing metathesis reactions to form five-membered ether rings with increasing number of methyl groups on the resulting olefinic bond (Equation 5.6). The reactions were performed in C₆D₆ (5 mM) at room temperature and monitored by ¹H NMR spectroscopy. Complete conversion to the corresponding ring-closed products was observed in each case for both the catalysts (Table 5.2). Related catalysts, Mo(NAr)(CHCMe₃)(OAr)(CH₂CMe₃) and Mo(NAr)(CHCMe₃)(OC₆Fs)(CH₂CMe₃), afforded 93% and 73% conversion, respectively, in 6 minutes when 5 mol% of the catalyst loading was employed in the same reaction.³b
Table 5.1. Catalysis of the ring-closing metathesis reaction shown in equation 5.6 by Mo(NAr)(CHCMe₂Ph)(OAr)(2,5-Me₂NC₄H₂) (3) and Mo(NAr)(CHCMe₂Ph)(OCMe(CF₃)₂)(2,5-Me₂NC₄H₂) (5) complexes.

The introduction of two methyl groups on the olefinic bonds of the substrate results in the formation of trisubstituted cyclic olefin upon ring closure (Equation 5.7). 3 and 5 show complete conversion within 40 min when 2 mol% of catalyst loading is employed in the reaction (Table 5.3). Likewise, 5 mol% of both Mo(NAr)(CHCMe₃)(OAr)(CH₂CMe₃) and Mo(NAr)(CHCMe₃)(OC₆F₅)(CH₂CMe₃) showed 98% conversion in 6 min when employed in the same reaction.³ᵇ
### Table 5.2.
Catalysis of the ring-closing metathesis reaction shown in equation 5.7 by Mo(NAr)(CHCMe$_2$Ph)(OAr)(2,5-Me$_2$NC$_6$H$_4$)$_2$ (3) and Mo(NAr)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)(2,5-Me$_2$NC$_6$H$_4$)$_2$ (5) complexes.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cat. Loading (mol%)</th>
<th>Time (min)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>2</td>
<td>40</td>
<td>&gt; 99</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>40</td>
<td>&gt; 99</td>
</tr>
</tbody>
</table>

The successful RCM of $N$,N-diallyl tosylsulfonamide (Equation 5.5 and Table 5.1) led to the study of RCM of other amine-based substrates such as the one shown in Equation 5.8. Successful RCM of this substrate should result in a $N$-heterocycle containing disubstituted olefins, which are of interest due to the prevalence of such moieties in pharmaceutical drugs.$^{25}$ Complexes 3 and 5 were able to catalyze this reaction to completion with 2 mol% of the catalyst loading. Complete conversion of the substrate to the ring-closed product was observed in 6 min when 5 mol% of Mo(NAr)(CHCMe$_3$)(OAr)(CH$_2$CMe$_3$) or Mo(NAr)(CHCMe$_3$)(OC$_6$F$_5$)(CH$_2$CMe$_3$) were used in the reaction.$^{3b}$

\[\text{OMe}\]
\[\text{Mo(NAr)(CHCMe}_2\text{Ph)(OR)(PvrNle)Me}\]

\[\text{MeO}\]
\[\text{Mo(NAr)(CHCMe}_2\text{Ph)(OR)(PyTms)}\]

197
Table 5.3. Catalysis of the ring-closing metathesis reaction shown in equation 5.8 by Mo(NAr)(CHCMe₂Ph)(OAr)(2,5-Me₂NC₄H₂) (3) and Mo(NAr)(CHCMe₂Ph)(OCMe(CF₃)₂)(2,5-Me₂NC₄H₂) (5) complexes.

Substrates containing secondary amines have a low propensity to undergo ring-closing metathesis as these species are believed to promote catalyst decomposition. The protonation of the alkoxide groups on the catalyst along with the coordination of the amine nitrogen atom to the metal and possible proton migration are believed to be probable catalyst decomposition pathways. Treatment of 2 mol% of 5 in C₆D₆ (5 mM) to the substrate containing a secondary amine resulted in the ring-closed product within 30 min (Equation 5.9 and Table 5.5). Using 2 mol% of 3 (5 mM) in the same reaction only 25% conversion into the ring-closed product could be obtained in 45 min, with no improvement in the percent conversion over time. However, when 5 mol% of 3 (15 mM) was used, complete consumption of substrate and formation of the ring-closed product was observed in 15 min.
\[
\text{Table 5.4. Catalysis of the ring-closing metathesis reaction shown in equation 5.9 by Mo(NAr)(CHCMe}_2\text{Ph}(\text{OR})(\text{PyrMc}) \text{NH}_9) \text{ and Mo(NAr)}(\text{CHCMe}_2\text{Ph})(\text{OCMe(CF}_3)_2)(\text{2,5-Me}_2\text{NC}_4\text{H}_2) \text{ complexes.}
\]

Finally, attempts were made to synthesize polycyclic secondary amines incorporating a benzoazocine via RCM. There was no reaction when 2 mol\% of 3 or 5 in C\textsubscript{6}D\textsubscript{6} (5 mM) was used in the RCM reaction shown in figure 5.7. A clean mixture of the catalyst and the substrate was observed. Heating the sample at 60 °C for 18 h resulted in the consumption of the alkylidene resonance but no ring-closed product was observed by \textsuperscript{1}H NMR spectroscopy. It should be noted that previous efforts to catalyze this reaction using all of the diolate based molybdenum imido alkylidene catalysts were also unsuccessful.\textsuperscript{27}
5.6 Silica-supported molybdenum imido alkylidene complexes containing a pyrrolide ligand

The bimolecular decomposition of smaller alkylidene intermediates (methylidene species especially) that are generated during olefin metathesis reaction is one of the main routes for catalyst deactivation. Solid-supported catalysts have gained a lot of interest as a potential means to overcome shortcomings of homogenous catalysis – more specifically with regard to the issues concerning catalyst longevity and metal recovery (separation of products from the catalyst as well as minimizing metal contamination of the product). Initial efforts in our group have relied upon site-isolation of the reactive metal centers by immobilizing the catalysts on a polymer support to prevent bimolecular interactions that may deactivate the reactive components.

The underlying principle concerning silica-supported catalysts involves understanding of an intricate but important structure-reactivity relationship, which involves evaluation of the surface (silica) at a molecular level, generation of well-defined reactive sites and finally, evaluation of the catalytic property of the surface species. One of the main factors that dictate the choice of silica is the number of silanol groups (number of sites available for catalyst immobilization), which can be controlled in a relatively well-defined fashion based on the temperature at which the sample is heated under vacuum. It has been shown that dehydroxylation of commercially available
Degussa (fumed) silica at 700 °C under vacuum results in the availability of \( \text{ca.} \ 1 \ \text{per} \ \text{nm}^2 \) hydroxyl groups, which translates to one hydroxyl every 13 Å.\(^{32}\) This in turn allows site isolation of the reactive species on the surface minimizing the intermolecular deactivation processes.

![Graph](image)

**Table 5.5.** Silica-supported MAP catalysts for propene metathesis

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Propene(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TOF(^b)</td>
</tr>
<tr>
<td>10a</td>
<td>5.2</td>
</tr>
<tr>
<td>10b</td>
<td>8.3</td>
</tr>
<tr>
<td>10c</td>
<td>13.2</td>
</tr>
<tr>
<td>10a’</td>
<td>6.2</td>
</tr>
</tbody>
</table>

\(^a\)flow reactor of propene;

\(^b\)TOF is the initial turnover frequency measure after 5 min of reaction expressed in mol of substrate converted per mol of Mo per second;

\(^c\)maximum turn over number obtained in a flow reactor.

Previous work concerning silica impregnation by metal complexes, done in collaboration with Copéret group at CNRS, Lyon, established that \((\text{Re}(\text{C-t-Bu})(\text{CH-t-Bu})(\text{CH}_2\text{-t-Bu})(\text{OSi}_{\text{surf}})^{33}\) and \(\text{Mo(NAr)(CH-t-Bu)(CH}_2\text{-t-Bu})(\text{OSi}_{\text{surf}})^{34}\) are efficient silica-supported olefin metathesis catalysts. The recent discovery of new precursors \(\text{Mo(NAr)(CHCM}_{2}\text{Ph})(\text{Pyr})_2\) (where Pyr = pyrrolide or 2,5-dimethylpyrrrolide) allows us to study silica-supported catalysts that are prepared from these complexes.
The room temperature reaction of Mo(NAr)(CHCMe₂Ph)(2,5-Me₂NC₄H₂)₂ in pentane with SiO₂-(700) results in the formation of 10a, which consists of a mixture of Mo(NAr)(CHCMe₂Ph)(2,5-Me₂NC₄H₂)(OSi₉surf) (ca. 80%) and Mo(NAr)(CH₂CMe₂Ph)(2,5-Me₂NC₄H₂)₂(OSi₉surf) (ca. 20%).²⁸ The surface organometallic species can then be dried under vacuum, analyzed spectroscopically and by combustion analysis. When 10a is treated with propene in a flow reactor (ca. 400 mL min⁻¹; 4800 mol of propene. mol of Mo⁻¹.min⁻¹) ethene and 2-butenes are generated selectively with the initial rate of 5.2 s⁻¹ over the period of 1500 min with TON of 101000 (Table 5.5). The initial rate of this reaction is comparable to the unsubstituted pyrrolide system (10a': 6.2 s⁻¹, TON = 62000), however the stability of the catalyst has been greatly improved by switching from unsubstituted pyrrolides to 2,5-dimethylpyrrolides. The stability as well as the reactivity of 2,5-dimethylpyrrolide system becomes more apparent if one corrects the rates and the TON for the actual number of active sites in 10a (ca. 80%, initial ratecorr. and TONcorr. of 6.5 s⁻¹ and 126000, respectively). The dramatic improvement in the longevity of 10a is also evident in the self metathesis reaction of ethyl oleate (used as received without purification). In presence of 0.05 mol% of 10a self metathesis of ethyl oleate in toluene is equilibrated in 3 h with an initial rate of 0.05 s⁻¹ (only 10% conversion after 8 h was achieved when unsubstituted pyrrolide system (10a') was employed in the same reaction under similar reaction conditions; initial rate of reaction was recorded at 0.04 s⁻¹) (Table 5.6).
Another advantage of silica-supported catalyst system is the ability to alter imido ligands. Efforts to incorporate 2,6-dimethylphenyl or 1-adamantyl imido ligand in MAP complexes resulted in the formation of the corresponding bisalkoxide complexes as a consequence of double protonation of the pyrroline ligands (*vide supra*). Varying the imido ligand resulted in the similar mixture of surface complexes upon silica impregnation (1-Adamantyl: 10b and 2-CF3C6H4: 10c) as observed in the case of 10a. Use of 10b and 10c in the aforementioned reactions, however, greatly increased the catalytic performances of the catalysts (higher initial rates and TON). 10b was the most

### Table 5.6. Self metathesis of ethyl oleate

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ethyl oleatea</th>
<th>TOFb</th>
<th>Time (h)c</th>
</tr>
</thead>
<tbody>
<tr>
<td>10a</td>
<td>0.05</td>
<td>0.05</td>
<td>3</td>
</tr>
<tr>
<td>10b</td>
<td>0.5</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>10c</td>
<td>1.2</td>
<td>1.2</td>
<td>0.5</td>
</tr>
<tr>
<td>10’</td>
<td>0.04</td>
<td>0.04</td>
<td>(10%)d</td>
</tr>
</tbody>
</table>

- *Experimental conditions: 0.5 M solution of ethyl oleate in toluene, 0.05% mol% of Mo;*  
- *TOF is the turnover frequency measured after 5 min of reaction expressed in mol of substrate converted per mol of Mo per second;*  
- *time to reach the equilibrium conversion in h (ca. 50%);*  
- *the number in parentheses corresponds to the maximum conversion reached after 8 h.*
stable catalyst system for propene metathesis allowing 231000 turnovers to be achieved in 1500 min (TOF = 8.3 s\(^{-1}\)), while 10c allows 135000 turnovers before it gets deactivated (Table 5.5). Interestingly, the order of efficiency is different in the self metathesis of ethyl oleate when 10b and 10c were employed: with 0.05 mol% of catalyst loading, the reaction mixture is equilibrated in 1 h and 30 min for 10b and 10c, respectively. Likewise, the TOF was recorded at 0.5 s\(^{-1}\) and 1.2 s\(^{-1}\) for 10b and 10c respectively in self metathesis reaction of ethyl oleate (Table 5.6). In fact, ethyl oleate was equilibrated with only 0.01 mol% of 10c in 8 h.

5.7 Enyne metathesis reaction

Previous work from our laboratory on enyne metathesis employing high oxidation state molybdenum imido alkylidene catalysts have showed limited success. High reactivity coupled with the relative instability of the methylidene species of the molybdenum alkylidene complexes are presumed to have prevented the progress in this area of olefin metathesis reactions. The high reactivity and the longevity of the MAP catalysts observed in olefin metathesis reactions make this class of catalysts ideal candidates to be screened for enyne metathesis.

1 – 6 were examined as possible enyne metathesis catalysts; enynes 11-14 served as substrates in these studies (Figure 5.8). The reactions were carried out under nitrogen atmosphere in a J. Young NMR tube and monitored by \(^1\)H NMR spectroscopy (see experimental section for details). The results of these studies are summarized in Table 5.7. Substrate 11 was converted exclusively into 11β, the β-addition product in good isolated yield within 20 min using 4 or 5 (entries 4 and 5). However, 1, 2, or 3 did not
afford any ring-closed product under similar reaction conditions, even though the initial alkylidenes were consumed immediately as judged by the $^1$H NMR spectra. Ru-carbene catalysts have been reported to afford $11\alpha$ in this reaction.\textsuperscript{13}

Treating 12 with 5 mol % of 3 or 5 in C$_6$D$_6$ produced 12\(\beta\) exclusively (entries 8 and 10). In contrast, 12\(\alpha\) and 12\(\beta\) were both observed when 1, 2, 4 or 7 was employed. Ru-carbene complexes afford 12\(\alpha\) in this reaction.\textsuperscript{13} None of the expected ring-closed enyne metathesis products of substrate 13 was observed for 1 - 5 (entries 12 - 16).

Compounds 1 and 2 led to formation of ethylene and what appears to be a dimer or oligomeric mixture, the exact nature of which has not been elucidated (enteries 12 and 13). In the case of substrate 14, 4 and 5 yield mixtures of the two possible products (entries 19 and 20). One might expect this result since the difference between the two types of initial metallacyclobutenes is not as marked compared to substrates that contain a terminal triple bond. In contrast, 2 and 3 did not lead to any ring-closed product despite consumption of the initial alkylidene (entries 17 and 18).

\[ \text{EtO}_2\text{C-CO}_2\text{Et} \, R \rightarrow \text{EtO}_2\text{C-CO}_2\text{Et} \, \text{R} \]  

\[ \text{EtO}_2\text{C-CO}_2\text{Et} \, \text{R} \rightarrow \text{EtO}_2\text{C-CO}_2\text{Et} \, \text{R} \]

\[ (10+n)\alpha \]  

\[ (10+n)\beta \]

\[ 5 \text{ mol}\% \text{ catalyst} \]

\[ \text{C}_6\text{D}_6 \]

**Figure 5.8.** Enyne metathesis reaction of diethylmalonate-based substrate.
<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>RA</th>
<th>n</th>
<th>Catalyst</th>
<th>Time</th>
<th>Conv/Product (%)</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11</td>
<td>H</td>
<td>1</td>
<td>1</td>
<td>1.5 h</td>
<td>&lt; 5</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>11</td>
<td>H</td>
<td>1</td>
<td>2</td>
<td>1.5 h</td>
<td>&lt; 5</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>11</td>
<td>H</td>
<td>1</td>
<td>3</td>
<td>12 h</td>
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Table 5.7. Enyne reactions of various substrates using monopyrrolide monoaalkoxide catalysts

<sup>a</sup> ref. Figure 5.8

<sup>b</sup> ref. Equation 5.1

<sup>c</sup> based on the consumption of substrate as determined by H<sup>1</sup>NMR

<sup>d</sup> isolated yield

<sup>e</sup> isolated as a mixture of α and β products

<sup>f</sup> oligomer
The formation of both products (α-addition and β-addition) is consistent with the primary step in enyne metathesis reaction being addition of an alkyne onto the metal-carbon double bond followed by attack on the alkene. Initial attack of an alkene by the alkylidene only generates one (smaller ring) product. It should be noted that this is the first instance in which a β-addition product has been observed and isolated, and so also constitutes the direct experimental validation of the two pathways involved in enyne metathesis reactions for Mo(VI) catalysts. The t-butoxide containing MAP complex (1) facilitates α-addition pathway, whereas the hexafluoro-t-butoxide complex (5) favors β-addition pathway – an observation that shows striking similarity with cyclopolymerization of heptadiynes using bisalkoxide-based catalysts.35

The synthetic approach to MAP catalysts, i.e. from selective alcoholysis of MDP complexes, can be utilized in rapid and high throughput methodologies to synthesize a library of catalysts from a single precursor. This idea has been used effectively to generate several new MAP catalysts in situ that show catalytic activity in enyne metathesis. Dr. Yeon-Ju Lee in the laboratory of Professor Amir Hoveyda at Boston College is currently involved in screening the MAP catalysts (isolated as well as in situ generated) with various enyne substrates.36 Two examples of enyne metathesis catalyzed by 5 are reproduced in figure 5.9.
Figure 5.9. Formation of O-heterocycle and benzazepines via enyne metathesis.

5.8 Asymmetric ring-closing metathesis reaction

Molybdenum catalysts that contain enantiomerically pure biphenolates and binaphtholates have been used in metathesis reactions to affect chirality at a carbon center in an olefinic substrate. The asymmetric ring-closing metathesis reaction has been employed in making diverse natural products and pharmaceutically relevant molecules. Successful use of MAP complexes for asymmetric induction in organic transformations is dictated by fulfillment of one of the two requirements – chiral alcohols used to prepare these complexes should selectively yield one diastereomer or upon generation of a mixture of diastereomers, one diastereomer should be much more reactive than the other.
Initial efforts to incorporate a chiral alkoxide ligand in the molybdenum imido alkylidene pyrrolide framework were based on chiral alcohols shown in Figure 5.10. Alcoholysis of Mo(NAr)(CHCMe₂Ph)(2,5-Me₂NC₄H₂)₂ with an equivalent of 15-H in THF resulted in an equal mixture of Mo(NAr)(CHCMe₂Ph)(15)(2,5-Me₂NC₄H₂) (19) diastereomers in 70% yield (Equation 5.11). The ¹H NMR spectrum of 19 recorded in C₆D₆ displays two alkylidene resonances at 12.13 ppm and 12.24 ppm, which are assigned to the syn isomers based on the J₃H value of 123 Hz. Under similar reaction conditions, adding 16-H to one equivalent of Mo(NAr)(CHCMe₂Ph)(2,5-Me₂NC₄H₂)₂ did not afford Mo(NAr)(CHCMe₂Ph)(16)(2,5-Me₂NC₄H₂) (20). The inability of 16-H to protonate the 2,5-dimethylpyrrolide ligand in Mo(NAr)(CHCMe₂Ph)(2,5-Me₂NC₄H₂)₂ is attributed to the methyl groups in the 3-position of 16-H that hinder the access of the exo-alcohol to the metal center. Likewise, protonolysis of Mo(NAr)(CHCMe₂Ph)(2,5-Me₂NC₄H₂)₂ by an equivalent of 17-H in THF afforded an unequal distribution of two diastereomers of Mo(NAr)(CHCMe₂Ph)(17)(2,5-Me₂NC₄H₂) (20) in 43% yield (Equation 5.10). The alkylidene resonances for the diastereomers appear at 10.67 ppm (75%) and 11.79 ppm (25%) based on the ¹H NMR.
spectrum. It was interesting to note that unlike compound 19, the two diastereomers of 20 show more than a ppm difference in their alkylidene shifts.

In the reaction between Mo(NAr)(CHCMe₂Ph)(2,5-Me₂NC₄H₂)₂ and 18-H, Mo(NAr)(CHCMe₂Ph)(18)(2,5-Me₂NC₄H₂) (22a) is observed to form within 15 min as determined by the ¹H NMR spectrum in C₆D₆ (Hₐ = 11.45 and 10.76 in 2:1 ratio). However, efforts to isolate the complex resulted in an oily product. Similar reaction between Mo(NAd)(CHCMe₂Ph)(2,5-Me₂NC₄H₂) and 18-H in diethyl ether resulted in Mo(NAd)(CHCMe₂Ph)(18)(2,5-Me₂NC₄H₂) (22b) as a yellow crystalline material in 40% yield. The ¹H NMR spectrum of 22b in C₆D₆ revealed unequal distribution of the two diastereomers – 11.44 ppm (5%) and 10.74 ppm (95%). Recrystallization of 22b from the concentrated diethyl ether solution resulted in full enrichment of the major diastereomer. Heating the C₆D₆ solutions of 19, 21 and 22b (~20 mM) at 60 °C for a period of 48 h did not lead to any change in the diastereomic ratios. Likewise, interconversion of the diastereomers was not observed over 12 h at 70 °C when C₆D₆ solutions of 19, 21 and 22b (~ 20 mM) were treated with one equivalent of THF.
Addition of 1.8 equivalents of styrene to the C₆D₆ solution of 22b (17 mM) at room temperature resulted in the consumption of 20% of the initial alkylidene in 7 d and formation of two new alkylidene resonances at 11.60 ppm and 11.45 ppm. Upon heating the sample for 12 h at 60 °C, 40% consumption of the initial alkylidene was achieved as determined by the ¹H NMR spectrum. No further change in the consumption of the initial alkylidene was observed upon further heating of the sample for 12 h. The alkylidene resonance at 11.45 ppm is characterized as the other diastereomer of the initial alkylidene (vide supra), and the resonance at 11.60 ppm is proposed to be that of the benzylidene formed via the metathesis reaction between the initial alkylidene and styrene. Formation of the other diastereomer from the diastereotopically pure complex is consistent with the cycloreversion of the molybdacyclobutane intermediate, though the pathway leading to the formation of the products is not understood.

Compound 19 (diastereomeric mixture) exhibits non-differential reactivities for the two diastereomers as no enantiomeric excess (ee) was obtained for the product when the catalyst was used in the ring-closing metathesis reaction shown in equation 5.11 (Table 5.8). The complete conversion of the substrate into the ring-closed product was observed within 1 h at room temperature with the consumption of both the diastereomers as judged by the ¹H NMR spectrum. When employing 21 (3:1 diastereomic mixture) in the ring-closing metathesis reaction shown in equation 5.11, complete conversion to the product required 48 h at 50 °C as judged by the ¹H NMR spectrum. Interestingly, only one diastereomer (Hₐ = 11.79 ppm) was consumed during the catalysis. Despite the consumption of one diastereomer during the ring-closing reaction, a mediocre ee of 20% was obtained for the product (Table 5.8). It should be mentioned that Alejandro
Lichtscheidl has been able to obtain one diastereomer of 21 (H\textsubscript{a} = 11.79 ppm) via recrystallization, and use of the complex in the ring-closing metathesis reaction revealed no improvement in the reaction rates and/or the enantioselectivity. 22b was also employed in the RCM reaction shown in equation 5.11. The reaction was complete in 72 h at 50 °C, as monitored by the \textsuperscript{1}H NMR spectrum and an ee of 10\% was obtained for the product.

\[
\begin{align*}
\text{Ph} & \quad \text{N} & \quad \text{Ph} \\
\text{5 mol\% cat} & \quad \text{C}_6\text{D}_6 \\
\text{5.11}
\end{align*}
\]

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<td>22b</td>
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Table 5.8. Asymmetric ring closing metathesis depicted in equation 5.12 using 19, 21 and 22b.

It became apparent that cyclohexyl- and heterocycle-based chiral alkoxide ligands were not suitable ligands for MAP complexes to induce enantioselectivity in olefin metathesis reactions. Alcohols derived from monoprotected chiral diols were investigated in the preparation of MAP catalysts as the use of diolate ligands has been very successful in asymmetric olefin metathesis reactions.\textsuperscript{1b} A collaborative effort with
Hoveyda laboratory at Boston College resulted in MAP complexes derived from mono-protected biphenolates and octahydrobinaphtholates. An example of such complex is represented in Equation 5.12, which has been crystallographically characterized and utilized in the reaction depicted in equation 5.11. Using 1 mol% of the catalyst in C₆D₆ (12 mM), complete conversion of the substrate into the ring-closed product with > 96% ee was achieved in 30 min. Similar MAP catalysts containing a chiral alkoxide ligand have been used successfully to catalyze RCM reactions that were not successful with other reactive bisalkoxide catalysts to yield products in excellent yield and ee.

\[
\text{Br}^+ + \text{HO pentane} \rightarrow \text{Br} \quad \text{Br}
\]

5.9 Molybdenum imido alkylidene monoalkoxide complexes

The success of catalysts of the type Mo(NAr)(CHCMe₂Ph)(OR)(2,5-Me₂NC₄H₂) in olefin metathesis reactions as well as enyne metathesis reactions that were not feasible with bisalkoxide catalysts led us to investigate other molybdenum imido alkylidene complexes of the type Mo(NAr)(CHCMe₂Ph)(OR)(NR'₂). Reaction of Mo(NAr)(CHCMe₂Ph)(NPh₂)₂ with one equivalent of Me(CF₃)₂COH in THF afforded Mo(NAr)(CHCMe₂Ph)(OCMe(CF₃)₂)(NPh₂) (23) in 54% yield (Equation 5.13). The \( ^1 \)H NMR spectrum of 23 in C₆D₆ displays an alkylidene resonance at 11.74 ppm, which is assigned to the syn isomer based on a \( J_{CH} \) value of 124 Hz.

213
Reaction of Mo(NAr)(CHCMe₂Ph)(NC₄H₄)₂ with one equivalent of Me(CF₃)₂COH afforded a mixture of Mo(NAr)(CHCMe₂Ph)(OCMe(CF₃)₂)₂ and starting material instead of the desired Mo(NAr)(CHCMe₂Ph)(OCMe(CF₃)₂)(NC₄H₄) (24). Complex 24 was isolated as a DME adduct, (DME)Mo(NAr)(CHCMe₂Ph)(OCMe(CF₃)₂)(NC₄H₄) (24-DME), in 36% yield via salt metathesis between (DME)Mo(NAr)(CHCMe₂Ph)(OTf)(NC₄H₄) and an equivalent of LiOCMe(CF₃)₂ in diethyl ether (Equation 5.14). The synthesis of (DME)Mo(NAr)(CHCMe₂Ph)(OTf)(NC₄H₄) was developed by Annie Jiang by treating (DME)Mo(NAr)(CHCMe₂Ph)(OTf)₂ with one equivalent of LiNC₄H₄ in toluene.⁴³ The choice of solvent for the reaction is crucial as introduction of any coordinating solvent to the reaction mixture results in the formation of Mo(NAr)(CHCMe₂Ph)(NC₄H₄)₂ instead of (DME)Mo(NAr)(CHCMe₂Ph)(OTf)(NC₄H₄). The ¹H NMR spectrum of 24-DME in C₆D₆ revealed an alkylidene resonance at 12.65 ppm. In solution, 24-DME exists as the syn isomer as judged by the JCH value of 126 Hz for the alkylidene resonance. Despite the successful isolation of the 24-DME, the instability of the complex towards disproportionation in solution hampered recrystallization leading to isolation of Mo(NAr)(CHCMe₂Ph)(NC₄H₄)₂ and Mo(NAr)(CHCMe₂Ph)(OCMe(CF₃)₂)₂. Such
scrambling of the ligands in 24-DME is attributed to the labile nature of DME, which is required for the stability of the complex.

To determine the utility of 23 and 24-DME as metathesis catalysts, their reactivities in ring-closing metathesis reactions were examined. Upon addition of 20 equivalents of diallyl ether to C₆D₆ solutions of 23 or 24-DME (~ 15 mM), complete conversion to the ring-closed product was observed as determined by ¹H NMR spectroscopy. Treatment of 20 equivalents of enyne substrate 12 to the C₆D₆ solution of 23 (16 mM), revealed no reaction at room temperature. Heating the reaction mixture at 40 °C for 12 h resulted in the disappearance of the alkylidene species, but no significant quantity of substrate was consumed in the process based on the ¹H NMR spectrum. Likewise, no enyne metathesis product was observed upon addition of 12 to a C₆D₆ solution of 24-DME (20 mM) despite the instantaneous consumption of the initial alkylidene. It is likely that the dissociation of DME from 24-DME facilitates the scrambling reaction to form Mo(NAr)(CHCMe₂Ph)(NPh₂)₂ and Mo(NAr)(CHCMe₂Ph)(OCMe(CF₃)₂)₂ (vide supra), which are known not to catalyze enyne metathesis reactions.
**5.10 Silica-supported catalysts for enyne metathesis reaction**

The success of silica-supported catalysts in propene metathesis generated an interest in screening these catalysts for enyne metathesis. Treating enyne substrates 11, 12 or 14 with a suspension of 10a in C₆D₆ resulted in appreciable catalytic activity only in the case of substrate 12. Treating 1 mol% of 10a with 12 resulted in a mixture of α- and β-products in the ratio of 3:1 in 12 h. Evolution of ethylene, as a consequence of the dimerization of the α-product was also observed by ¹H NMR spectroscopy. Unfortunately, attempts to recycle the catalyst by adding a second aliquot of the substrate were not successful. The deactivation of the silica-supported catalysts is presumed to be due to unimolecular decomposition of molybdacyclobutanes and formation of ethylene complexes. The unreactive nature of the ethylene complex has been verified by treating 9 with the enyne substrate 12, which results in no reaction. Similarly, 1 mol% of 10b and 10c required 27 h and 5 h for the complete consumption of 12, respectively. A distribution of α- and β-products were observed in a ratio of 4:3 for 10b, and 1:1 for 10c.

**CONCLUSION**

A new class of molybdenum imido alkylidene complexes has been prepared via protonolysis of Mo(NAr)(CHCMe₂Ph)(2,5-Me₂NC₄H₂)₂ with one equivalent of an alcohol. Compounds 1 – 6 show instantaneous reaction with 1 atm of ethylene in room temperature to afford a mixture of corresponding methylidene species and metallacycle species. Attempts to isolate the methylene species by treating 3 or 5 with 1 atm of ethylene resulted in the isolation of ethylene complexes, 8 and 9 respectively. Rapid conversion of diallyl ether and diallyltosylsulfanamide into their respective ring-closed
products were achieved by using 2 mol% of 1 – 6. RCM reactions involving formation of trisubstituted cyclic olefins were also performed using 3 and 5. In one case, 2 mol% of 3 was able to ring-close a substrate containing a secondary amine to yield the trisubstituted cyclic olefin in 30 min. A $^1$H NOESY spectrum of the PMe$_3$ adduct of 5 (Me$_3$P-5) was consistent with a trans disposition of the base with respect to the 2,5-dimethylpyrrolide ligand.

The utility of the MAP catalysts is best realized in their ability to catalyze enyne metathesis reactions. The success of these catalysts in enyne metathesis reactions might be attributed to the high stability of the methylene species, which is the most reactive and least stable intermediate that is formed in a typical reaction involving a terminal olefin. Both $\alpha$- and $\beta$-addition products were obtained depending on the alkoxide ligands of the MAP catalysts. The factors responsible for the selectivity between $\alpha$- versus $\beta$-addition pathways are not fully understood. The results we have obtained thus far indicate that the more Lewis acidic and sterically crowded metal center favors the $\beta$-addition product when the enyne substrate consists of a terminal alkyne. Surprisingly, related complexes 23 and 24-DME do not catalyze enyne metathesis reactions despite their success in RCM reactions.

Heterogeneous analogs of the MAP catalysts supported on the silica surface were also prepared and their reactivities were studied in metathesis of propene and ethyloleate. The results obtained in this study showed enhance reactivity as well as stability compared to other silica-supported catalyst systems. Use of silica-supported catalysts in enyne metathesis reactions resulted in catalysis of only 12. Different ratios of $\alpha$- and $\beta$-addition products were realized based on the imido ligand of the solid-supported catalyst systems.
Dimerization of the product containing a vinyl olefin (α-addition) resulted in the evolution of ethylene, which seems to deactivate the alkylidene species, presumably due to the formation of an ethylene complex. No enyne metathesis was achieved when the silica-supported catalysts were recycled. Two ethylene complexes, 8 and 9, were isolated upon exposing 1 atmosphere of ethylene to 3 and 5', respectively. A lack of reactivity of ethylene complexes in enyne metathesis reactions was verified by treating 9 with 12, which resulted in the spontaneous release of the bound ethylene upon alkyne coordination as determined by the $^1$H NMR spectrum.

Chiral versions of MAP catalysts have also been prepared and analyzed in asymmetric olefin metathesis reactions. Neither 19, 21 nor 22b were able to induce high enantioselectivity in the RCM reaction depicted in equation 5.12 as evidenced by the poor ee recorded for the product. However, use of mono-protected chiral diols to generate MAP catalysts has shown remarkable enhancement in the distereomeric selectivity of complex formation and the reactivity as well as enantioselectivity in asymmetric RCM reactions.

The higher activity of MAP catalysts in various olefin metathesis reactions is believed to be due to the better selectivity and stability of this class of catalysts in comparison to bisalkoxide-based catalysts. Such balance of high reactivity, longevity and selectivity in one catalyst framework is very appealing, especially when we consider that these species can be generated rapidly using high throughput or combinatorial techniques. High reactivity of MAP catalysts is consistent with the theoretical study performed on similar type of complexes that are asymmetric at the metal center.$^{16a}$ The stability of MAP catalysts is believed to be influenced by the $\eta^5$ hapticity of 2,5-
dimethylpyrrolide ligand, providing steric as well as electronic protection towards decomposition of the methylidene species, thereby resulting in a catalyst system that is highly reactive, selective and long-lived.
EXPERIMENTAL

Material. All manipulations of air and moisture sensitive materials were conducted under a nitrogen atmosphere in a Vacuum Atmospheres drybox or on a dual-manifold Schlenk line. The glassware, including NMR tubes were oven-dried prior to use. Ether, pentane, toluene, dichloromethane, toluene and benzene were degassed with dinitrogen and passed through activated alumina columns and stored over 4 Å Linde-type molecular sieves. Dimethoxyethane was vacuum distilled from a dark purple solution of sodium benzophenone ketyl, and degassed three times by freeze-pump-thaw technique. The deuterated solvents were dried over 4 Å Linde-type molecular sieves prior to use. \(^1\)H, \(^{13}\)C spectra were acquired at room temperature unless otherwise noted using Varian spectrometers and referenced to the residual \(^1\)H/\(^{13}\)C resonances of the deuterated solvent (\(^1\)H: CDCl\(_3\), \(\delta\) 7.26; C\(_6\)D\(_6\), \(\delta\) 7.16; CD\(_2\)Cl\(_2\), \(\delta\) 5.32. \(^{13}\)C: CDCl\(_3\), \(\delta\) 77.23; C\(_6\)D\(_6\), \(\delta\) 128.39; CD\(_2\)Cl\(_2\), \(\delta\) 54.00) and are reported as parts per million relative to tetramethylsilane. \(^{19}\)F NMR spectra were referenced externally to fluorobenzene (\(\delta\) – 113.15 ppm upfield of CFC\(_3\)). High resolution mass spectrometry measurements were performed at the MIT Department of Chemistry Instrument Facility, and elemental analyses were performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany.

Mo(N-2,6-i-Pr\(_2\)C\(_6\)H\(_3\))(CHCMe\(_2\)Ph)(2,5-Me\(_2\)NC\(_4\)H\(_2\))\(_2\) was prepared as described in the literature.\(^{4a}\) Enyne substrates 11, 12 and 13 were prepared following the literature procedures.\(^{13}\) Chiral alcohols 15 and 16 were purchased from Aldrich and 17 and 18 were obtained as generous gifts from Dr. Tatiana Pilyugina and Steven Malcolmson (Boston College), respectively.
Mo(NAr)(CHCMe2Ph)(2,5-Me2NC4H2)(OCMe3) (1). A flask was charged with Mo(NAr)(CHCMe2Ph)(2,5-Me2NC4H2)2 (208 mg, 0.351 mmol) and 5 mL of THF. To the cooled solution (− 30 °C), t-butanol (26 mg, 0.351 mmol) dissolved in 2 mL of THF was added dropwise. The mixture was stirred for 30 min at room temperature and the volatiles were removed in vacuo. The residue was dissolved in 1mL of heptane and set aside at − 30 °C. The product was isolated as yellow crystals (46 mg, 22%): 1H NMR (500 MHz, C6D6) δ 12.24 (s, 1, syn Mo=CH, JCH = 120 Hz), 7.36 (d, 2, Ar), 7.15 (t, 1, Ar), 7.03 (s, 5, Ar), 6.16 (s, 2, Pyr), 3.78 (sep, 2, CHMe2), 2.37 (s, 6, PyrMe), 1.81 (s, 3, CMe2Ph), 1.59 (s, 3, CMe2Ph), 1.24 (d, 6, CHMe2), 1.14 (d, 6, CHMe2), 1.09 (s, 9, t-Bu); 13C NMR (125 MHz, CD2Cl2) δ 284.26, 153.09, 149.34, 147.25, 135.05, 128.68, 128.01, 126.47, 123.34, 108.27, 81.58, 32.10, 31.95, 30.09, 28.84, 23.96, 23.57, 17.51: Anal. Calcd for C32H46MoN2O: C, 67.35; H, 8.12; N, 4.91. Found: C, 67.23; H, 8.15; N, 4.87.

Mo(NAr)(CHCMe2Ph)(2,5-Me2NC4H2)(OCHMe2) (2). This compound was prepared in analogous fashion to 1 starting from Mo(NAr)(CHCMe2Ph)(2,5-Me2NC4H2)2 (230 mg, 0.389 mmol) and Me2CHOH (24 mg, 0.389 mmol). Upon crystallization from pentane, bright orange crystals were obtained (178 mg, 83%): 1H NMR (300 MHz, C6D6) δ 12.04 (s, 1, syn Mo=CH, JCH = 119 Hz), 7.34 (d, 2, Ar), 7.14 (t, 1, Ar), 7.02 (s, 5, Ar), 6.17 (s, 2, Pyr), 4.44 (sep, 1, Me2CHO), 3.73 (sep, 2, CHMe2), 2.36 (s, 6, PyrMe), 1.78 (s, 3, CHMe2Ph), 1.54 (s, 3, CHMe2Ph), 1.24 (d, 6, CHMe2), 1.14 (d, 6, CHMe2), 1.04 (d, 3, Me2CHO), 0.97 (d, 3, Me2CHO); 13C NMR (125 MHz, CD2Cl2) δ 283.83, 153.21, 149.32, 147.23, 128.69, 128.12, 126.62, 126.37, 123.47, 108.42, 79.92, 32.00, 30.16,
Mo(NAr)(CHCMe$_2$Ph)(2,5-Me$_2$NC$_4$H$_2$)(OAr) (3). A chilled solution (−30 °C) of 2,6-i-Pr$_2$C$_6$H$_3$OH (75 mg, 0.417 mmol) in 15 mL of diethyl ether was added dropwise to the solution of Mo(NAr)(CHCMe$_2$Ph)(2,5-Me$_2$NC$_4$H$_2$)$_2$ (247 mg, 0.417 mmol) in 20 mL of diethyl ether. After 30 min, the volatiles were removed in vacuo and the residue was dissolved in 2 mL of pentane and the solution was set aside at −30 °C. Dark red crystals (232 mg, 81%) were isolated by decanting off the mother liquor and dried in vacuo: $^1$H NMR (300 MHz, C$_6$D$_6$) δ 12.29 (s, 1, syn Mo=CH, $J_{CH} = 120$ Hz), 7.14 – 7.11 (m, 3, Ar), 7.02 (br s, 8, Ar), 6.06 (s, 2, Pyr), 3.80 (br, 1, Me$_2$CH), 3.28 (sep, 2, CHMe$_2$), 6.02 (s, 2, Pyr$_{Me}$), 1.59 (s, 3, CHCMe$_2$Ph), 1.58 (s, 3, CHCMe$_2$Ph), 1.28 (d, 12, CHMe$_2$), 1.14 (d, 12, CHMe$_2$); $^{13}$C NMR (125 MHz, C$_2$D$_2$Cl$_2$) δ 292.23 (syn Mo=CH), 161.74, 153.76, 148.72, 146.15, 136.87, 135.56, 128.76, 126.58, 126.08, 123.63, 123.56, 122.32, 109.21, 55.80, 32.59, 30.47, 29.33, 28.21, 24.00, 23.66, 23.62; Anal Calcd for C$_{40}$H$_{54}$MoN$_2$O: C, 71.19; H, 8.07; N, 4.15. Found: C, 71.36; H, 8.05; N, 4.19.

Mo(NAr)(CHCMe$_2$Ph)(2,5-Me$_2$NC$_4$H$_2$)(OCH(CF$_3$)$_2$) (4). This compound was prepared in an identical manner as 3 by reacting Mo(NAr)(CHCMe$_2$Ph)(2,5-Me$_2$NC$_4$H$_2$)$_2$ (361 mg, 0.610 mmol) and (CF$_3$)$_2$CHOH (103 mg, 0.610 mmol, 64 μL) in THF. Crystallization from the concentrated heptane solution afforded dark red crystals (183 mg, 45%): $^1$H NMR (300 MHz, C$_6$D$_6$) δ 12.34 (s, 1, syn Mo=CH, $J_{CH} = 120$ Hz), 7.23 (d, 2, Ar), 7.12 (t, 1, Ar), 6.96 (br s, 5, Ar), 5.71 (s, 2, Pyr), 4.22 (sep, 1, (CF$_3$)$_2$CH), 3.67 (br,
2, Me₂CH), 2.24 (s, 6, PyrMe), 1.68 (s, 3, CHMe₂Ph), 1.52 (s, 3, CHMe₂Ph), 1.22 (d, 6, CHMe₂), 1.16 (br s, 6, CHMe₂); ¹⁹F NMR (282 MHz, C₆D₆) δ -75.02, -75.53; ¹³C NMR (125 MHz, CD₂Cl₂) δ 298.88, 153.06, 148.44, 128.95, 127.83, 126.85, 126.26, 124.33, 124.17, 123.70, 107.33, 85.88, 55.75, 31.63, 30.69, 30.10, 30.08, 28.55, 28.00, 24.24, 23.87, 16.56; Anal Calcd for C₃₁H₃₈F₆MoN₂O: C, 56.03; H, 5.76; N, 4.22. Found: C, 55.88; H, 5.70; N, 4.18.

Mo(NAr)(CHCMe₂Ph)(2,5-Me₂N₄H₂)(OCMe(CF₃)₂) (5). This compound was prepared in a similar fashion as 3 via alcoholysis of Mo(NAr)(CHCMe₂Ph)(2,5-Me₂N₄H₂)₂ (310 mg, 0.525 mmol) and (CF₃)₂MeCOH (96 mg, 0.525 mmol) in 20 mL of THF. The product was isolated as dark red crystals (285 mg, 80%) from the concentrated solution in heptane at -30 °C: ¹H NMR (300 MHz, C₆D₆) δ 12.45 (s, 1, syn Mo=CH, JCH = 120 Hz), 7.26 (d, 2, Ar), 7.10 (t, 1, Ar), 6.98 (br s, 5, Ar), 6.02 (s, 2, Pyr), 3.49 (br, 2, Me₂CH), 2.27 (s, 6, PyrMe), 1.70 (s, 3, CHCMe₂Ph), 1.60 (s, 3, CHCMe₂Ph), 1.22 (d, 6, CHMe₂), 1.08 (br s, 9, CHMe₂ + CHCMe₂Ph); ¹⁹F NMR (470 MHz, C₆D₆) δ -78.66, -78.74; ¹³C NMR (125 MHz, CD₂Cl₂) δ 291.83 (syn Mo=CH), 153.38, 147.88, 135.15, 129.13, 128.76, 126.76, 126.26, 123.42, 109.04, 123.56, 55.83, 31.09, 29.83, 29.00, 23.54, 23.66, 23.62, 19.13; Anal Calcd for C₃₂H₄₀F₆MoN₂O: C, 56.64; H, 5.94; N, 4.13. Found: C, 56.37; H, 6.05; N, 4.06.

(Me₃P)Mo(NAr)(CHCMe₂Ph)(OCMe(CF₃)₂)(2,5-Me₂N₄H₂) (Me₃P-5) PMe₃ (31 µL, 23 mg, 0.295 mmol) was syringed into a solution of 5 (200 mg, 0.295 mmol) in 10 mL of pentane. The reaction mixture was stirred at room temperature for 30 min during which
time a yellow precipitation was observed. The product was isolated by filtration (180mg, 82%): $^1$H NMR (C$_6$D$_6$, 500 MHz) δ 14.07 (s, 1, syn Mo=CH, $J_{CH} = 122$ Hz), 7.27 (d, 2, Ar), 7.09 (t, 3, Ar), 7.00 (m, 3, Ar), 6.22 (s, 1, Pyr), 6.00 (s, 1, Pyr), 4.23 (br, 1, CHMe$_2$), 3.46 (br, 1, CHMe$_2$), 2.44 (s, 3, PyrMe), 2.78 (s, 3, PyrMe), 1.81 (s, 3, CHCMe$_2$), 1.52 (s, 3, CHCMe$_2$), 1.35 (br, 3, CHMe$_2$), 1.13 (br, 3, CHMe$_2$), 1.08 (s, 3, OCMe) 1.05 (br, 3, CHMe$_2$), 0.83 (d, 9, Mo(PMe$_3$)) 0.79 (br, 3, CHMe$_2$); $^{31}$P NMR (C$_6$D$_6$, 121 MHz) δ - 5.72; $^{19}$F NMR (C$_6$D$_6$, 282 MHz) δ = -75.58, -77.12; $^{19}$C NMR (CD$_2$Cl$_2$, 125 MHz) δ 309.55 (Mo=CH), 150.18, 149.24, 147.87, 144.47, 133.04, 132.93, 129.25, 128.89, 127.56, 127.39, 126.57, 126.21, 124.91, 124.28, 123.77, 121.98, 106.24, 81.88, 56.01, 32.43, 28.48, 28.34, 24.96, 24.12, 18.28, 16.46, 15.15, 13.92; Anal. Calcd for C$_{35}$H$_{49}$F$_6$MoN$_2$OP: C, 55.70; H, 6.54; N, 3.71. Found: C, 55.61; H, 6.39; N, 3.63.

**Mo(NAr)(CHCMe$_3$)(OSi(O-t-Bu)$_3$)(2,5-Me$_2$NC$_4$H$_2$) (6)** To the chilled (− 30 °C) solution of Mo(NAr)(CHCMe$_2$Ph)(2,5-Me$_2$NC$_4$H$_2$)$_2$ (200 mg, 0.367 mmol) in 30 mL of diethyl ether, (t-BuO)$_3$SiOH (97 mg, 0.367 mmol) was added as a solution in 2 mL of diether ether. The reaction mixture was stirred at room temperature for 30 min, during which time the yellow reaction solution turned dark orange. The volatiles were removed in vacuo and the crude solid was dissolved in 1 mL of pentane and set aside at − 30 °C for 12 h. Dark orange crystals were isolated by decanting the mother liquor and washing the crystals with cold (- 30 °C) pentane (186 mg, 73%): $^1$H NMR (300 MHz, C$_6$D$_6$) δ 12.46 (s, 1, syn Mo=CH, $J_{CH} = 126$ Hz), 7.03 (s, 3, Ar), 6.18 (s, 2, Pyr), 3.67 (br, 2, CHMe$_2$), 2.46 (s, PyrMe), 1.39 (s, 27, (O-t-Bu)$_3$), 1.31 (s, 9, CMe$_3$), 1.20 (br, 12, CHMe$_2$); $^{13}$C NMR (125 MHz, CD$_2$Cl$_2$) δ 288.71 (Mo=CH), 153.41, 147.59, 134.68, 128.09, 123.38, 108.39, 224
73.30, 49.24, 32.33, 31.81, 28.95, 23.95, 23.72, 17.39; Anal. Calcd for C$_{40}$H$_{64}$MoN$_2$O$_3$Si: C, 63.13; H, 8.48; N, 3.68. Found: C, 63.62; H, 8.31; N, 3.62.

**Mo(NAr)(CHCMe$_2$Ph)(OC$_6$F$_5$)(2,5-Me$_2$NC$_4$H$_2$) (7)** A flask was charged with Mo(NAr)(CHCMe$_2$Ph)(2,5-Me$_2$NC$_4$H$_2$)$_2$ (205 mg, 0.346 mmol), a stir bar along with 10 mL of diethyl ether, and the contents cooled to -30 °C. A solution of C$_6$F$_5$OH (64 mg, 0.346 mmol) in diethyl ether (2 mL) at -30 °C was added dropwise to the solution and, removed in vacuo and addition of pentane to the residue afforded yellow powder (168 mg, 72%), which was 95% pure by $^1$H NMR spectroscopy: $^1$H NMR (300 MHz, C$_6$D$_6$) $\delta$ 12.78 (s, 1, syn Mo=CH, $J_{CH} = 120$ Hz), 7.00 - 6.98 (br s, 8, Ar), 5.65 (s, 2, Pyr), 3.90 (br, 2, Me$_2$CH), 2.31 (s, 6, PyrMe), 1.53 (s, 3, Me), 1.37 (s, 3, Me), 1.25 (br d, 12); $^{19}$F NMR (282 MHz, C$_6$D$_6$) $\delta$ -161.64, -166.78, -172.48; Instability of the complex prevented $^{13}$C NMR spectroscopy and elemental analysis.

**Mo(NAr)(CH$_2$CH$_2$)(OAr)(2,5-Me$_2$NC$_4$H$_2$) (8)** A schlenk flask was charged with 3 (60 mg, 0.090 mmol), a stir bar and 2 mL of heptane. The solution was degassed by freeze pump thawing the solution (3 times) and 1 atm of ethylene was introduced to the solution. The reaction was stirred at room temperature for 15 min and set aside at -30 °C for 12 h. Removal of the volatiles in vacuo followed by addition of pentane to the residue afforded dark red precipitate (31 mg, 59%): $^1$H NMR (300 MHz, C$_6$D$_6$) $\delta$ 7.22 (d, 2, Ar), 7.02 (t, 1, Ar), 6.89 (s, 3, Ar), 5.78 (br, 2, Pyr), 3.57 (sep, 2, CHMe$_2$), 3.25 (br, 2, CHMe$_2$), 2.95 (m, 2, ethylene), 2.60 (m, 1, ethylene), 2.16 (s, 6, PyrMe), 1.95 (m, 1, ethylene), 1.25 – 1.13 (m, 24, CHMe$_2$); $^{13}$C NMR (125 MHz, C$_6$D$_6$) $\delta$ 163.84, 155.02, 143.74, 139.41, 128.68, 128.40, 128.30, 127.22, 123.96, 123.75, 120.77, 107.65, 60.24, 56.29, 28.39,
25.97, 25.18, 24.70, 24.57, 16.02; Anal. Calcd for C_{32}H_{46}MoN_{2}O: C, 67.35; H, 8.12; N, 4.91. Found: C, 67.56; H, 8.11; N, 4.97.

Mo(NAr)(CH_{2}CH_{2})(OCCMe(CF_{3})_{2})(2,5-Me_{2}NC_{4}H_{2}) (9) This compound was prepared in an analogous fashion as 8 by treating Mo(NAr)(CHCMe_{3})(OCCMe(CF_{3})_{2})(2,5-Me_{2}NC_{4}H_{2}) (235 mg, 0.347 mmol) with 1 atm ethylene in heptane. The complex was crystallized out in pentane at –30 °C as dark red crystals (123 mg, 57%): \(^1\)H NMR (300 MHz, C_{6}D_{6}) \(\delta\) 6.19 – 6.81 (m, 3, Ar), 5.51 (br, 2, Pyr), 3.48 (sep., 2, CHMe_{2}), 2.77 (m, 2, ethylene), 2.45 (m, 1, ethylene), 2.16 (m, 1, ethylene), 2.10 (s, 6, Pyr_{Me}), 1.65 (s, 3, OCMMe) 1.10 (d, 6, CHMe_{2}), 1.06 (d, 6, CHMe_{2}); \(^{19}\)F NMR (282 MHz, C_{6}D_{6}) \(\delta\) – 75.20, –77.80; \(^{13}\)C NMR (125 MHz, C_{6}D_{6}) \(\delta\) 154.24, 145.74, 128.68, 128.27, 123.79, 110.15, 105.39, 56.34, 54.12, 28.09, 25.35, 23.62, 20.37, 16.26; Anal. Calcd for C_{24}H_{32}F_{6}MoN_{2}O: C, 50.18; H, 5.61; N, 4.88. Found: C, 50.26; H, 5.31; N, 4.67.

Mo(NAr)(CHCMe_{2}Ph)(2,5-Me_{2}NC_{4}H_{2}) (15) (19). A flask was charged with a stir bar, Mo(NAr)(CHCMe_{2}Ph)(2,5-Me_{2}NC_{4}H_{2})_{2} (145 mg, 0.245 mmol) and 50 mL of diethyl and the contents chilled to –30 °C. 15-H (67 mg, 0.240 mmol) dissolved in 2 mL of diethyl ether was added dropwise to the solution and the reaction mixture stirred at room temperature for 1 h. The volatiles were removed in vacuo and the residue was dissolved in 1 mL of pentane. Yellow crystals (80 mg, 43%) were obtained by setting aside the pentane solution at –30 °C for 3 d: \(^1\)H NMR (300 MHz, C_{6}D_{6}) \(\delta\) 11.79 (s, 1, syn Mo=CH, 25%), 10.66 (s, 1, Mo=CH, 75%); \(^{13}\)C NMR (125 MHz, CD_{2}Cl_{2}) \(\delta\) 287.44 (Mo=CH,

Mo(NAr)(CHCMe₂Ph)(2,5-Me₂NC₄H₂)(17) (21) A flask was charged with a stir bar, Mo(NAr)(CHCMe₂Ph)(2,5-Me₂NC₄H₂)₂ (145 mg, 0.245 mmol) and 50 mL of diethyl ether and the contents chilled to –30 °C. The chiral alcohol (H-17) (67 mg, 0.240 mmol) dissolved in 2 mL of diethyl ether was added dropwise to the solution and the reaction mixture stirred at room temperature for 1 h. The volatiles were removed in vacuo and the residue was dissolved in 1 mL of pentane. Yellow crystals (80 mg, 43%) were obtained by setting aside the pentane solution at –30 °C for 3 d. ¹H NMR (300 MHz, C₆D₆) both diastereomers δ 11.79 (s, 1, Mo=CH, 25%), 10.66 (s, 1, Mo=CH, 75%); Anal. Calcd for C₄₄H₅₇ClMoN₂O: C, 69.41; H, 7.55; N, 3.68. Found: C, 69.25; H, 7.48; N, 3.63.

Mo(NAd)(CHCMe₂Ph)(2,5-Me₂NC₄H₂)(18) (22b) Compound 22b was prepared in a similar manner as described for 21 via alcoholysis of Mo(NAr)(CHCMe₂Ph)(2,5-Me₂NC₄H₂)₂ (336 mg, 0.594 mmol) by the chiral alcohol (H-18) (178 mg, 0.594 mmol) in 50 mL of diethyl ether. The product was crystallized in a concentrated diethyl ether solution at –30 °C (208 mg, 46%) as a 3:1 diastereomeric mixture. Recrystallization in diethyl ether resulted in the diastereomerically pure complex (180 mg, 39%): ¹H NMR (300 MHz, C₆D₆) δ 10.75 (s, 1, syn Mo=CH, J₁₇H = 124 Hz); ¹⁹F NMR (282 MHz, CD₂Cl₂) δ –53.25; ¹³C NMR (125 MHz, CD₂Cl₂) δ 283.06 (Mo=CH), 150.26, 143.98, 135.00, 131.84, 130.93, 129.84, 128.41, 127.58, 127.40, 126.28, 107.85, 95.32, 76.64, 55.15, 52.61, 51.05, 49.39, 45.30, 44.54, 36.27, 34.09, 32.43, 31.47, 30.38, 28.26, 23.06,
Mo(NAr)(CHCMe₂Ph)(OCMe(CF₃)₂)(NPh₂) (23) To the solution of
Mo(NAr)(CHCMe₂Ph)(NPh₂)₂ (281 mg, 0.380 mmol) in 20 mL of THF, (CF₃)₂MeCOH
(47 µL, 69 mg, 0.380 mmol) was syringed in and the reaction mixture was stirred for 30
min at room temperature. The volatiles were removed in vacuo, and the crude solid was
treated with 8 mL of pentane, which led to the precipitation of red powder (183 mg,
70%): ¹H NMR (300 MHz, C₆D₆) δ 11.78 (s, 1, syn Mo=CH, JCH = 123 Hz), 7.12 – 7.05
(m, 8, Ar), 7.01 – 6.96 (m, 8, Ar), 6.77 (t, 2, Ar), 3.80 (sept, 2, CHMe₂), 1.64 (s, 3,
OCMe), 1.40 (s, 3, CHCMe₂), 1.28 (d, 6, CHMe₂), 1.19 (s, 3, CHCMe₂), 1.05 (d, 6,
CHMe₂); ¹⁹F NMR (C₆D₆, 282 MHz) δ – 78.29, – 78.68; ¹³C NMR (125 MHz, CD₂Cl₂) δ
289.06, 155.23, 153.35, 148.20, 146.99, 143.72, 129.83, 129.70, 128.74, 128.17, 126.57,
126.27, 124.09, 123.36, 121.40, 118.13, 55.36, 32.45, 31.17, 29.77, 29.60, 28.85, 24.21,
23.57, 23.27, 19.54; Anal. Calcd for C₄₆H₄₉MoN₃: C, 74.68; H, 6.68; N, 5.68. Found: C,
74.63; H, 6.59; N, 5.71.

(DME)Mo(NAr)(CHCMe₂Ph)(OCMe(CF₃)₂)(NC₄H₄) (24-DME) A 100 mL round
bottom flask was charged with a stir bar, (DME)Mo(NAr)(CHCMe₂Ph)(OTf)(NC₄H₄)
(220 mg, 0.324 mmol), 30 mL of toluene and the contents were cooled to – 30 °C.
LiOCMe(CF₃)₂ (61 mg, 0.324 mmol) was added to the solution as a solid and the reaction
mixture was stirred for 1 h during which time white precipitate was observed. The
precipitate was removed by filtration and the volatiles were removed in vacuo. The
residue was extracted with 20 mL of pentane and passed through celite. The solution was concentrated to 2 mL and set aside at –30 °C for 12 h. Red crystals were isolated by filtration (110 mg, 36%): $^1$H NMR (300 MHz, C$_6$D$_6$) δ 12.65 (s, 1, syn Mo=CH, J$_{CH}$ = 126 Hz), 7.29 (d, 2, Ar), 7.11 (m, 3, Ar), 6.96 (s, 3, Ar), 6.82 (t, 2, Pyr), 6.42 (t, 2, Pyr), 3.63 (sep., 2, CHMe$_2$), 3.23 (s, 4, OCH$_2$CH$_2$O), 3.09 (s, 6, CH$_3$O), 1.63 (s, 1, CHCMe$_2$), 1.62 (s, 1, CHCMe$_2$), 1.26 (s, 3, OCMc), 1.19 (d, 6, CHMe$_2$), 1.13 (d, 6, CHMe$_2$); $^{19}$F NMR (C$_6$D$_6$, 282 MHz) δ –78.69, –78.77; $^{13}$C NMR spectroscopy could not be recorded and the compound could not be analyzed due to the instability of the complex.

**Diethyl 2-(pent-4-enyl)-2-(prop-2-ynyl)malonate (14)** A three-neck round bottom flask was charged with NaH (1.1 g, 28 mmol) and 80 mL of THF. The flask was chilled to 0 °C under an atmosphere of N$_2$. Diethyl 2-(prop-2-ynyl)malonate (4.95 g, 25 mmol) dissolved in 25 mL of THF was added dropwise to the cold suspension of NaH, and the reaction was stirred for 1 h. 5-Bromopent-1-ene (2.6 mL, 26 mmol) was added dropwise as a THF (25 mL) solution, and the reaction mixture was heated at 70 °C for 12 h. After the reaction was cooled to room temperature, it was poured into a flask with 100 mL water and extracted with 200 mL of diethylether. The ether layer was separated and dried over MgSO$_4$. The volatiles were removed and the crude product was purified by column chromatography using silica as the stationary phase and hexane: ethyl acetate (20:1) as the eluent leaving a colorless oil (4.89 g, 73%): $^1$H NMR (500 MHz, C$_6$D$_6$) δ 5.68 (m, 1, CH$_2$CH), 4.94 (dd, 2, CH$_2$CH), 3.94 (q, 4, CO$_2$CH$_2$), 3.04 (d, 2, CHCCH), 2.37 (m, 2, CH$_2$), 1.96 (q, 2, CH$_2$), 1.72 (t, 1, CCH), 1.38 (m, 2, CH$_2$), 0.90 (t, 6, CO$_2$CH$_2$CH$_3$); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 170.64, 138.76, 115.17, 79.57, 71.45,
General protocol for RCM reaction:
To a stirred solution of 5 (15 µL, 7.2 x 10^{-3} mmol, 0.48 M) in C_6D_6, dially ether (14 mg, 0.14 mmol) was added. The reaction mixture was transferred to a J. Young NMR tube and the ^1H NMR spectrum recorded.

General protocol for enyne metathesis reaction:
5 (15 µL, 7.2 x 10^{-3} mmol, 0.48 M) dissolved in 1 mL of C_6D_6 and 8 (36 mg, 0.14 mmol) were mixed in a J. Young NMR tube and the reaction was monitored by ^1H NMR spectroscopy. Upon completion of reaction, methanol was added to quench the reaction. The volatiles were removed in vacuo and the residue was treated with hexane, which was filtered through a layer of Silica to remove the metal impurities. The solution was then concentrated in vacuo and the product(s) were purified by flash column chromatography using silica as the stationary phase and hexane: ethyl acetate (9:1) as an eluent.

General protocol for silica-supported enyne metathesis reaction:
To a suspension of 10c (10 mg, 1.5 x 10^{-3} mmol) in 3 mL of C_6D_6 taken in a 5 mL scintillation vial, 12 (38 mg, 0.15 mmol) was added and the reaction solution was stirred gently. The reaction was monitored by ^1H NMR spectroscopy.
11β: $^1$H NMR (500 MHz, CD$_2$Cl$_2$) $\delta$ 6.18 (d, 1, b), 5.78 (m, 1, c), 4.85 (d, 2, a), 4.13 (m, 4, f), 2.83 (m, 2, e), 2.64 (m, 2, d), 1.21 (t, 6, g); $^{13}$C NMR (125 MHz, CD$_2$Cl$_2$) $\delta$ 171.24, 139.91, 129.19, 128.83, 127.25, 113.61, 61.94, 36.24, 31.38, 14.32; ESI-HRMS calc for C$_{13}$H$_{18}$O$_4$ [M+Na]$^+$: 261.1097. Found [M+Na]$^+$: 261.1103.

12β: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.09 (d, 1, b), 5.78 (m, 1, c), 4.94 (d, 2, a), 4.19 (m, 4, g), 3.00 (s, 2, f), 2.30 (s, 4, d + e), 1.25 (m, 6, h); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 171.86, 142.41, 133.08, 132.71, 118.07, 61.50, 57.35, 39.73, 33.82, 24.67, 14.26; ESI-HRMS calc for C$_{14}$H$_{20}$O$_4$ [M+Na]$^+$: 275.1254. Found [M+Na]$^+$: 275.1251.
Mixture of 12α and 12β: 1H NMR (300 MHz, CDCl₃) δ 6.35 (dd, 1, j), 5.70 (s, 1, k), 5.15 (d, 1, i), 4.96 (d, 1, i), 4.19 (q, 4, o), 2.68 (s, 2, n), 2.22 (s, 2, m), 2.13 (m, 2, l), 1.24 (t, 6, p); 13C NMR (125 MHz, CDCl₃) δ 171.66, 139.05, 127.88, 126.37, 110.92, 53.29, 50.88, 29.45, 27.53, 23.02, 14.21. 12β: 1H NMR (300 MHz, CDCl₃) δ 6.08 (d, 1, b), 5.77 (m, 1, c), 4.94 (d, 2, a), 4.19 (q, 4, g), 3.01 (s, 2, f), 2.31 (s, 4, d + e), 1.27 (t, 6, h); 13C NMR (125 MHz, CDCl₃) δ 171.86, 142.41, 133.07, 132.72, 118.07, 61.52, 57.34, 39.72, 33.81, 24.67, 14.26.

Mixture of 13α and 13β: 1H NMR (300 MHz, CD₂Cl₂) δ 5.78 (br s, 1, d), 4.90 (s, 1, a), 4.80 (s, 1, b), 4.14 (q, 4, g), 3.18 (d, 2, e), 3.09 (s, 2, f), 1.85 (s, 3, c), 1.21 (t, 6, h); 13C NMR (125 MHz, CD₂Cl₂) δ 171.72, 139.06, 132.70, 126.37, 110.91, 61.54, 40.62, 39.75, 29.00, 23.03, 14.22. 13β: 1H NMR (300 MHz, CD₂Cl₂) δ 5.60 (s, 1, l), 4.99 (s, 1, i), 4.82 (s, 1, j), 4.13 (q, 4, o), 2.84 (s, 2, m), 2.62 (s, 2, n), 1.79 (s, 3, k), 1.21 (t, 6, p); 13C NMR (125 MHz, CD₂Cl₂) δ 171.86, 142.42, 133.08, 125.92, 118.07, 61.50, 57.36, 53.31, 33.83, 24.69, 14.27.
Crystal data and structure refinement for Mo(NAr)(CHMe₂Ph)(OAr)(2,5-Me₂NC₄H₂) (3).

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<tr>
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<td>b</td>
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<td>R indices (all data)</td>
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<td>Largest diff. peak and hole</td>
<td>0.454 and -0.477 e.Å⁻³</td>
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</tbody>
</table>
REFERENCES


40. The complex was synthesized by Dr. B. C. Bailey and crystallography was performed by Mr. Keith Wampler.

41. Lichtscheidl, A.; Schrock, R. R. *Unpublished results*.

42. Malcolmon, S. J.; Meek, S. J.; Sattely, E. S.; Schrock, R. R.; Hoveyda, A. H. *Submitted*.

43. Jiang, A. J.; Schrock, R. R. *Unpublished results*.
HIGHLIGHTS

- Well versed in multi-scale synthesis utilizing glove box and Schlenk techniques
- Hands-on experience with various instrumental methods: GPC, DSC, POM, DMA, SAXS/WAXS, GC, HPLC, CD
- Extensive experience in NMR (variable temperature, COSY, gCOSY), IR, UV-Vis
- President (2003) and treasurer (2002) of international student club, Linfield College
- Part of several collaborations in multi-disciplinary research groups

EDUCATION

Doctor of Philosophy, Inorganic Chemistry
Massachusetts Institute of Technology, Cambridge MA
Thesis: “Cyclopropene polymerization and enyne metathesis catalyzed by high oxidation state molybdenum alkylidenes”
Advisor: Professor Richard R. Schrock
Collaborators: Professor Paula T. Hammond (Chem. Eng., MIT); Professor Amir H. Hoveyda (Chem., Boston College); Professor Christophe Coperet (Chem., ESCPE – France)

Bachelor of Science (Magna cum laude), Chemistry and Computer Science
Linfield College, McMinnville OR
Advisor: Professor James J. Diamond (Chemistry)
Professor Martin D. Tweneboah (Computer Science)

RESEARCH EXPERIENCE

Research Assistant, Chemistry, MIT, Cambridge, MA
2003 – present
Advisor: Professor Richard R. Schrock
- Synthesized a series of bimetallic ROMP initiators to prepare ABA triblock copolymers
- Synthesized various bicycloheptene monomers to prepare thermoplastic elastomers
- First successful living ROMP of cyclopropenes
- First successful preparation of tactic polymers derived from monocyclic olefins
- A new class of olefin metathesis catalysts
- First successful enyne metathesis reaction using molybdenum imido alkylidene catalysts

Research Assistant, Chemistry, Carnegie Mellon University, Pittsburgh PA
2002 (summer)
Advisor: Professor Bruce A. Armitage
- Studied the effect of PNA backbone modifications on cyanine dye binding to PNA-DNA duplexes using optical spectroscopy and molecular dynamics simulations

Research Assistant, Chemistry, University of Oregon, Eugene OR
2001 (summer)
Advisor: Professor James E. Hutchison
Collaborator: Pacific Northwest National Lab, WA
- Synthesized and characterized bicyclic malonamides with octyl moieties on amide nitrogens for Eu3+ ligation
Research Assistant, Chemistry, Linfield College, McMinnville OR
Advisor: Professor Elizabeth O. Atkinson 1999 - 2003
• Synthesized a homologous series of phthalocyanines with cinnamoyl moieties to study p-stacking upon UV-irradiation

TEACHING EXPERIENCE AND PROJECTS
Teaching Assistant/Grader, Chemistry, MIT
Organometallics 2004-2005
System Administrator, Chemistry, Linfield College 2002-2003
Simulated a chemical inventory database system, Linfield College 2002

SELECTED AWARDS, HONORS AND AFFILIATION
MIT Deans Fellowship 2004
Institute of soldier nanotechnology, Cambridge Science Foundation travel grants 2007, 2005
Luis Gunning best sophomore/junior chemistry student award, Linfield College 2002
Linfield International Merit Scholarship, Linfield College 1999 – 2003
Yamamoto Scholarship for academic excellence, Linfield College 2000 – 2001
Taylor Grant for Chemistry for outstanding chemistry student, Linfield College 2002 – 2003
Student member of American Chemical Society 1999 – present

SELECTED PUBLICATIONS
  R. Singh and R. R. Schrock, ‘Stereospecific Ring Opening Polymerization of 3-Methyl-3-Phenylcyclopentene’ Macromolecules, 2008, ASAP.
ACKNOWLEDGEMENTS

My pursuit of higher education in the United States of America has been a tremendous journey since I left Nepal nine years ago. It gives me incredible pleasure to be able to thank the people who have contributed to my growth.

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My undergraduate mentor Professor Elizabeth J. O. Atkinson was instrumental in honing my skills in experimental chemistry. I appreciate her guidance during the early days of my career and her invaluable help in securing summer internship positions with Professor James Hutchison at the University of Oregon and Professor Bruce Armitage at Carnegie Mellon University. I thank Professors Armitage and Hutchison for their mentorship that validated my interest in research. During my internship at the University of Oregon, my training under Dr. Robert Gilbertson set the stage for my interest in synthetic chemistry, for which his supervision is sincerely appreciated.

I would like to thank the inorganic chemistry faculty at MIT - Professors Richard Schrock, Steve Lippard, Dan Nocera, Kit Cummins and Joseph Sadighi, for teaching me most of what I know today about Inorganic chemistry. I am truly grateful to Professors Joseph Sadighi and Paula Hammond for their precious advice as members of my thesis committee. I thank Professor Jonas Peters for presiding over my thesis committee in my final year.

During my time in the Schrock laboratory, I was able to interact with highly motivated and brilliant group of individuals who created an excellent atmosphere for science. I thank all present and past Schrock group members for their input and assistance. I would like to acknowledge Professor Dimitry Yandulov for training me in Schlenk as well as glove-box techniques when I first joined the group. Zachary Tonzetich has been a great friend and an invaluable scientific resource. I have also been extremely fortunate to know the likes of Amritanshu Sinha and Stefan Arndt who have been amazing friends. Andrea Gabert, who worked with me on the polymer project, was a great colleague and I appreciate her optimism, especially when faced with disappointing results. I would like to thank Annie Jiang for her generosity for sharing some of the ring-closing substrates that are reported in this thesis. For assistance with crystallography, I would like to thank Adam Hock and Peter Müller.

I would like to pay tribute to various collaborators I have had an opportunity to work with during my graduate career. I had a fruitful collaboration with the Hammond group, Eric Verploegen in particular, and I would like to thank him for contributing to some of the work reported in this thesis. Professor Amir Hoveyda and his group have been instrumental in promoting olefin metathesis in various organic transformations and his suggestions at that end are highly appreciated. The collaborative work with the Coperet group has resulted in several highly reactive silica-supported olefin metathesis catalysts and I would like to acknowledge the work done by Frederic Blanc.

I am thankful to Smaranda Marinescu and Maggie Flook for proof-reading my entire thesis along with Zachary Tonzetich, Keith Wampler, Brad Bailey, Dennis
Hetterscheid, Alejandro Lichtscheidl and Corina Scriban for their valuable input on various chapters of this thesis. I would also like to thank Gretchen Guidess and Macall Coombs, who have always managed to do a fantastic job taking care of administrative duties that make for smooth working of any research group.

Finally, I would like to acknowledge my family for their love and support. My parents instilled in me the importance of education ever since my younger days and this thesis is rightfully dedicated to them. I feel immensely fortunate to have a kind and supportive sister, Suhani, in my life. These people have the major contribution towards my present state in life. I am and forever shall be grateful to them.