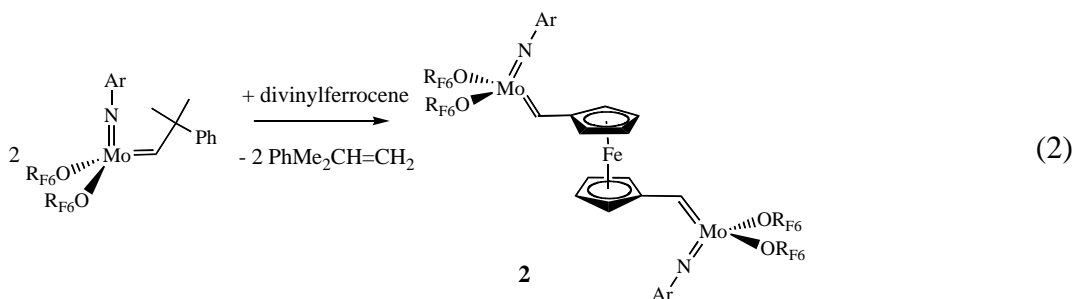
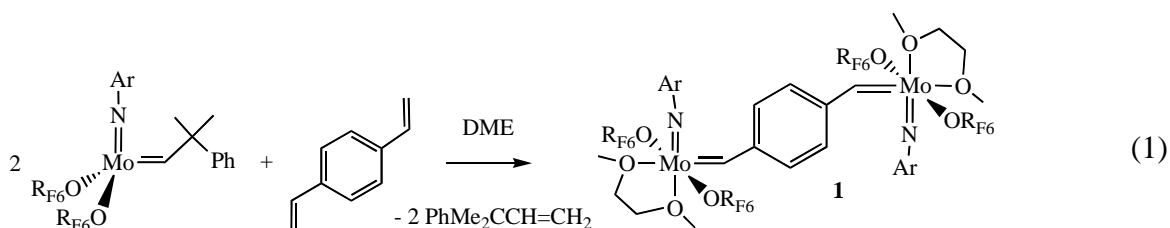


#### 4. The Living Polymerization of Cyclic Olefins and 1,6-Heptadiynes.

We are interested in controlling the primary structure (and therefore secondary structure and overall properties) of polymers in polymerization reactions that are initiated with high oxidation state alkylidene complexes. This project is divided into two parts, ROMP reactions and polymerization of 1,6-heptadiynes.

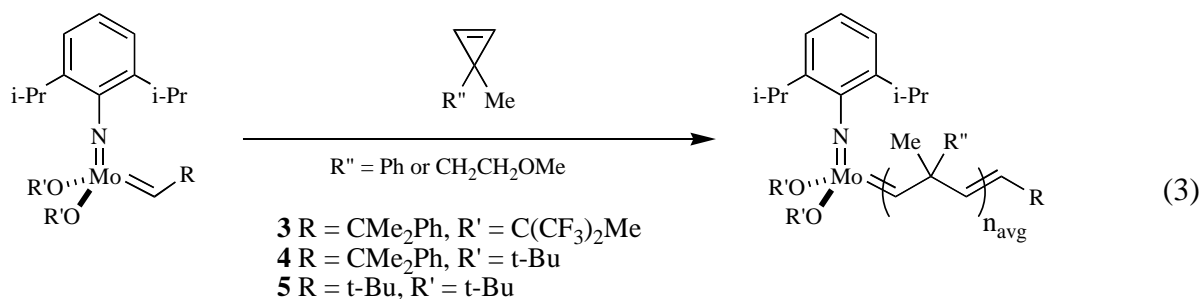
Ring-opening metathesis polymerization (ROMP) is catalyzed by a variety of alkylidene complexes. Imido alkylidene complexes of Mo or W that are living ROMP catalysts and that initiate at a rate comparable to the propagation rate are amenable to the synthesis of block copolymers. Some of the most interesting copolymers in terms of their physical properties are triblocks. Triblocks (e.g.,  $A_xB_yA_z$ , where x, y, and z are the average numbers of monomers of type A or B in each block) have been synthesized via a sequential or linear method (addition of A to an initiator, then B, then A again, allowing each to be consumed) or by coupling of living homopolymers with a bifunctional central oligomer or polymer. However, such methods often have limitations, most seriously the presence of homopolymer or diblock copolymer due to (e.g.) incomplete coupling or catalyst degradation during the linear  $A_xB_yA_z$  synthesis. Some purification step (e.g. selective precipitation) is then required in order to obtain relatively pure triblock. High purity triblocks are most desirable since the presence of homopolymer or diblock copolymer in a triblock copolymer can seriously degrade the properties that might be expected in a given triblock copolymer.



We began to focus on the formation of high purity triblock copolymers using bifunctional initiators. The method of synthesizing isolable bifunctional alkylidene initiators that we chose involved treating a neophylidene or neophylidene complex with a diene, as shown in equations 1 and 2. Triblock copolymers prepared from initiators of type **2** have been shown through MALDI-TOF spectroscopy to have exactly the chain structure that was proposed on the basis of the stoichiometry of the ROMP reaction. We are now in the process of preparing and employing other examples of bimetallic ROMP initiators for making other types of triblock copolymers.

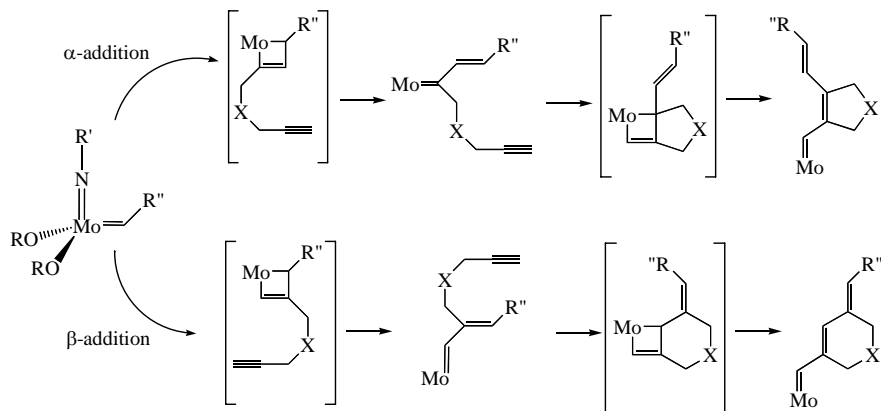
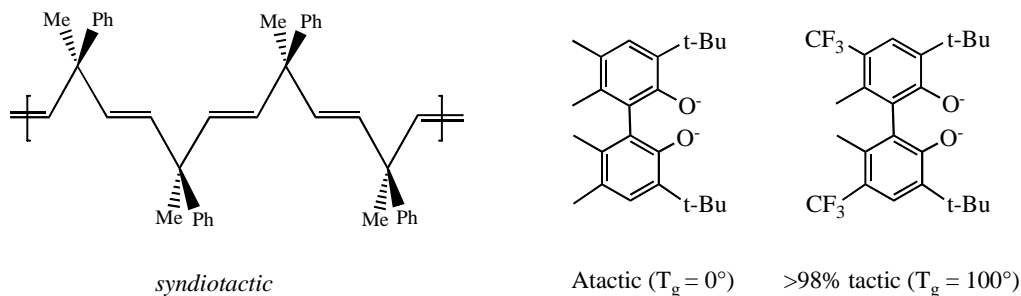
We became interested in the living ring-opening metathesis polymerization of cyclopropenes, in part because that reaction had never been reported. To the best of our knowledge, cyclobutenes are the only monocyclic olefins that have been polymerized successfully in a living manner *via* ROMP. We chose 3,3-disubstituted cyclopropenes as substrates for ROMP, in part because when 3,3-disubstituted cyclopropenes are opened to yield a new alkylidene, that alkylidene is similar to the relatively stable neophylidene or neophylidene

initiators of the type Mo(NAr)(CHR)(OR')<sub>2</sub> (equation 3). We have found that ROMP of



3-methyl-3-phenyl-cyclopropene in tetrahydrofuran at room temperature using the initiators **3**, **4**, or **5** (equation 3) produced ROMP polymers in 94-97% yield (100 equivalents in 10 min). Proton NMR spectra of the polymers showed that >99% *trans* double bonds were present, while carbon NMR spectra revealed that the polymers are atactic. In comparison to Mo, a Grubbs-type Ru initiator, [(H<sub>2</sub>IMes)(PCy<sub>3</sub>)Cl<sub>2</sub>RuCHC<sub>6</sub>H<sub>5</sub>] (H<sub>2</sub>IMes = 1,3-dimesitylimidazolidine), was found to have poor activity, with the reaction requiring hours to days.

Ring-opened cyclopropenes have tacticity if the substituents on C(3) are different. For example, the sequence shown below is syndiotactic, with all phenyl groups on one side of the extended chain. Tactic polymers can be prepared through the use of a new fluorinated Biphen ligand shown below. The glass transition temperatures vary dramatically with tacticity (structural regularity), as one might expect. We have not yet shown whether the polymer is syndiotactic or isotactic.



Scheme 1. Mechanisms of forming five- and six-membered rings from 1,6-heptadiynes.

The area of 1,6-heptadiyne polymerization revolves around controlling the formation of five- or six-membered rings in the polymer, while also controlling the polymer's molecular weight. The mechanisms for forming the two possible rings are shown in Scheme 1. Polymers that contain all five-membered rings are more desirable because of the lack of isomers and the high degree of conjugation and rigidity. We are understanding how to prepare polymers that contain all five-membered rings, and now also have learned how to prepare initiators that contain the type of five-membered ring found in the propagating species. As a consequence we can now control the molecular weight as well as the structure of poly[dialkyldipropargylmalonate]s.

The bimetallic initiator shown in Figure 1 not only allows us to incorporate polyene sequences into triblock copolymers, but serves as a Wittig-like reagent for the synthesis of polyenes that have a fixed length through stoichiometric reactions. For example, as shown in

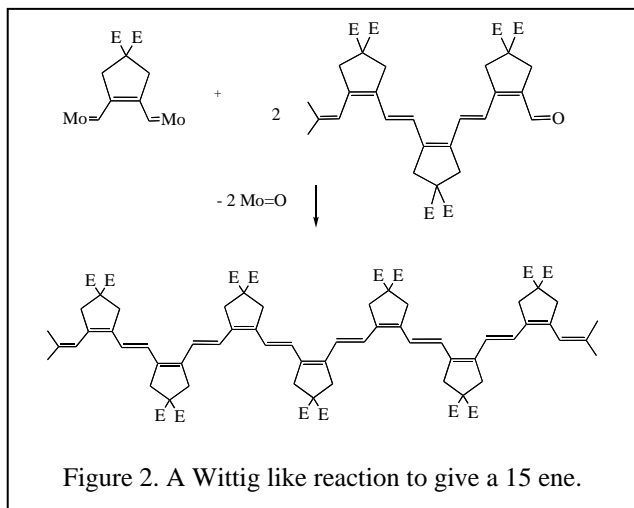
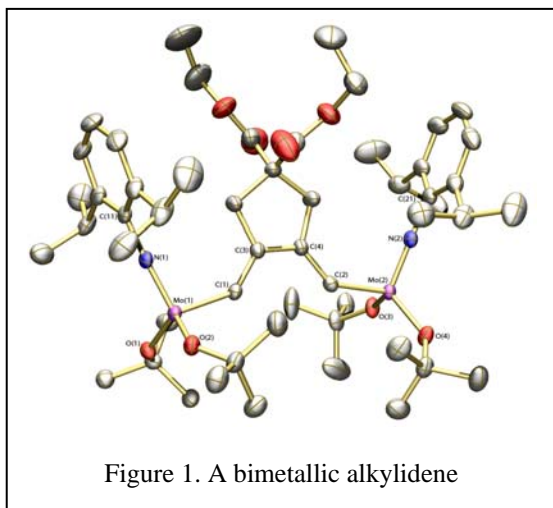


Figure 2, a Wittig-like reaction of the bimetallic species in Figure 1 with two equivalents of a "trimeric aldehyde" leads to formation of a polyene that contains fifteen double bonds. Polyenes that contain twelve or more double bonds are extremely rare. We hope that we will be able to prepare and study from a fundamental perspective a variety of polyenes of fixed chain length that contain a relatively large number of double bonds, studies that have not been possible before.

The following papers are relevant to this new area of research (see publication list): 413, 424, 429, 432, 436, 448, 451, 459.