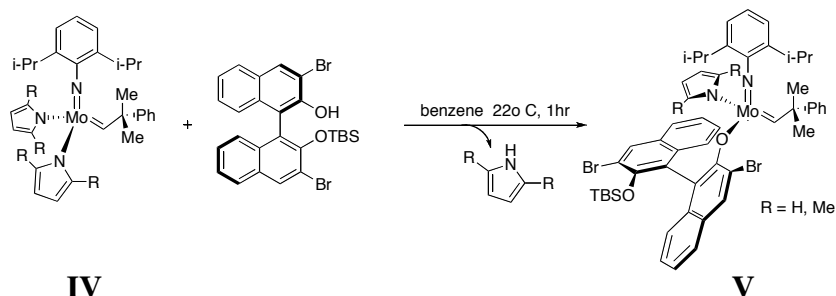


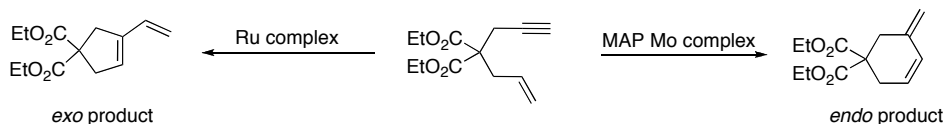


of achiral trienes to form cyclized products containing an all carbon stereocenter with up to 96% ee, requiring only 1 mol % catalyst. MAP catalysts demonstrate greater substrate compatibility with basic amines and promote the cyclization of trienes containing secondary and trialkylamines. These substrates proceed with low conversion with other available Mo- and Ru-catalysts.<sup>7</sup>



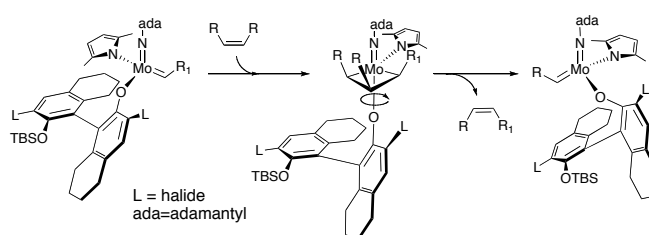
**Figure 2**

The highly reactive monoalkoxide monopyrrolyl Mo-alkylidenes are the first high oxidation state complexes that efficiently catalyze enyne ring-closing metathesis reactions. Nearly all previously reported enyne metathesis catalysts are complexes of ruthenium that, in most instances, provide *exo* products (Figure 3). In contrast, the MAP Mo-alkylidenes are the first complexes that allow for selective formation of *endo* products.<sup>5,9</sup> Additionally, the diastereomerically enriched MAP complex **V** promotes the first enantioselective enyne RCM reactions.



**Figure 3**

A major limitation of current metathesis catalysts is the inability to form *Z*-alkenes selectively. Schrock and Hoveyda recently reported a Mo-alkylidene complex that catalyzes ring-opening/cross-metathesis reactions that generate *Z*-olefins with high selectivity.<sup>10,11</sup> The selectivity is proposed to arise from the large, freely rotating aryl oxide ligand in the metallacyclobutane intermediate, which directs the R-groups of the metallacyclobutane toward the smaller adamantylimido ligand and favors the formation of the *Z*-alkene (Figure 4).



**Figure 4**

Complexes with stereogenic metal centers containing only monodentate ligands represents a new approach to the design of olefin metathesis catalysts. Chiral-at-metal monoalkoxide monopyrrolyl Mo-alkylidene complexes offer increased reactivity and unique selectivity when compared to traditional metathesis catalysts. Not only are they effective catalysts for enantioselective metathesis reactions, but they also offer

uncommon alkene stereoselectivity in enyne RCM and Z-selective ring-opening/cross metathesis reactions. The true scope of MAP Mo-alkylidene reactivity is yet to be discovered, and one should expect new developments in the near future.

## References

- 1) Grubbs, R. H. *Handbook of Metathesis*; Wiley-VCH: Weinheim, Germany, 2003.
- 2) Hoveyda, A. H.; Zhugralin, A. R. "The Remarkable Metal-Catalysed Olefin Metathesis Reaction." *Nature*. **2007**, 450, 243-251.
- 3) Hoveyda, A. H.; Schrock, R. R. "Catalytic Asymmetric Olefin Metathesis." *Chem. Eur. J.* **2001**, 7, 945-950.
- 4) Zhu, S. S.; Cefalo, D. R.; Jamieson, J. Y.; Davis, W. M.; Hoveyda, A. H.; Schrock, R. R. "Chiral Mo-Binol Complexes: Activity, Synthesis, and Structure. Efficient Enantioselective Six-Membered Ring Synthesis through Catalytic Metathesis." *J. Am. Chem. Soc.* **1999**, 121, 8251- 8259.
- 5) Singh, R.; Schrock, R. R.; Muller, P.; Hoveyda, A. H. "Synthesis of Monoalkoxide Monopyrrolyl Complexes Mo(NR)(CHR')(OR')(pyrrolyl): Enyne Metathesis with High Oxidation State Catalyst." *J. Am. Chem. Soc.* **2007**, 129, 12654-12655.
- 6) Poater, A.; Sonlans-Monfort, X.; Clot, E.; Coperet, C.; Eisenstein, O. "Understanding d<sup>0</sup>-Olefin Metathesis Catalysts: Which Metal, Which Ligands?" *J. Am. Chem. Soc.* **2007**, 129, 8207-8216.
- 7) Malcolmson, S. J.; Meek, S. S.; Sattely, E. S.; Schrock, R. R.; Hoveyda, A. H. "Highly Efficient Molybdenum-based Catalysts for Enantioselective Alkene Metathesis." *Nature*. **2008**, 456, 933-937.
- 8) Sattely, E. S.; Meek, S. J. Malcolmson, S. J.; Schrock, R. R.; Hoveyda, A. H. "Design and Stereoselective Preparation of Chiral Olefin Metathesis Catalysts and Application to Enantioselective Synthesis of Quebrachamine: Catalyst Development Inspired by Natural Product Synthesis." *J. Am. Chem. Soc.* **2008**, 131, 943-953.
- 9) Lee, Y.; Schrock, R. R.; Hoveyda, A. H. "Endo-Selective Enyne Ring-Closing Metathesis Promoted by Stereogenic-at-Mo Monoalkoxide and Monoaryloxide Complexes. Efficient Synthesis of Cyclic Dienes Not Accessible through Reactions with Ru Carbenes." *J. Am. Chem. Soc.* **2009**, 131, 10652-10661.
- 10) Ibrahim, I.; Yu, M.; Schrock, R. R.; Hoveyda, A. H. "Highly Z- and Enantioselective Ring-Opening/Cross-Metathesis Reactions Catalyzed by Stereogenic-at-Mo Adamantylimido Complexes." *J. Am. Chem. Soc.* **2009**, 131, 3844-3845.
- 11) Flook, M. M.; Jiang, A. J.; Schrock, R. R.; Muller, P.; Hoveyda, A. H. "Z-Selective Olefin Metathesis Processes Catalyzed by a Molybdenum Hexasiopropylterphenoxide Monopyrrolide Complex." *J. Am. Chem. Soc.* **2009**, 131, 7962-7963