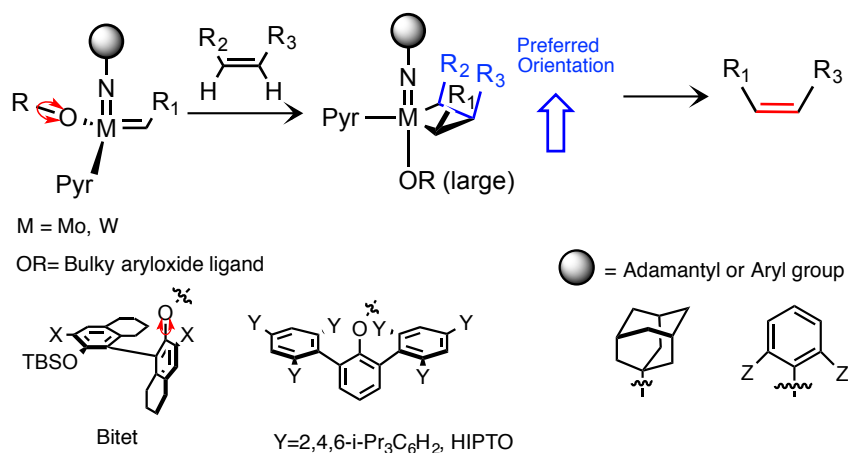


Olefin metathesis was first observed in industry in 1964 by Banks<sup>1</sup> who used heterogeneous catalysts to convert linear olefins to homologs of shorter and longer carbon chains. But it was not until three decades later that the transition metal catalysts were well developed and the olefin metathesis began to be widely used in organic synthesis, e.g. the ring opening metathesis polymerization (ROMP), the ring closing metathesis (RCM) and the cross metathesis (CM).

Because most of the steps in the metathesis reaction are often reversible and governed by thermodynamic factors, the newly formed alkenes often result in the thermodynamically favorable *E*-geometry or a mixture of *E/Z* isomers in many cases<sup>2,3</sup>. Forming *Z*-selective alkenes represents a great challenge and a number of approaches were revealed to achieve this goal. Before 2009 when Schrock<sup>4,5</sup> reported controlling *Z*-alkene formation through catalyst design, the approaches toward these intrinsically disfavored products were mainly through substrate control which lacks generality. In early 2009 the first *Z*-selective monoaryloxide-pyrrolide (MAP) metathesis catalyst was reported by the Schrock and Hoveyda group<sup>4</sup> and later a mechanism for the catalyst control stereochemistry was reported.

### Scheme 1 Proposed mechanism of *Z*-selectivity<sup>5</sup>



As shown in Scheme 1, the selectivity was controlled by the stereo of the MAP catalyst: the sufficient size difference between the imido- and aryloxide ligand. The bulky, free rotating aryloxide ligand forces the substituents ( $R_2$ ,  $R_3$ ) of the alkene to be away from it, resulting a metalocyclobutane intermediate which all substituents point toward the small imido ligand. Thus, the *Z*-olefin product is selectively formed. This catalyst control method enables *Z*-selectivity for a large range of substrates and the potential generality of the MAP catalyst was successfully demonstrated.

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