CONTROLLING OLEFIN METATHESIS THROUGH CATALYST AND MONOMER DESIGN

Thesis by

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Abstract

The olefin metathesis reaction has become a widely used method for the construction of new carbon–carbon double bonds. The development of well-defined, ruthenium-based catalysts with high air- and moisture-stability and functional group tolerance has allowed synthetic chemists to exploit this reaction in many areas. The main goal of this thesis was to better understand the impact of changes in catalyst and monomer structure on the olefin metathesis reaction.

The introduction of chelating alkylidene ligands to olefin metathesis catalysts has resulted in systems with high activity and stability. For the most part, these catalysts have included ether donors and are active at or below room temperature. However, for some applications, catalysts that react only at higher temperatures are desirable. Chapter 2 describes the synthesis of olefin metathesis catalysts with chelating alkylidenes with a range of donor ligands: including phosphines, pyridines, imines, amines, and thioethers. The nature of the donor ligand was found to have a large impact on the catalyst initiation rate. These results show that chelating a neutral donor is an effective method of synthesizing latent catalysts.

Catalysts with chelating alkylidenes are believed to operate by a mechanism where the neutral donor ligand dissociates prior to olefin binding. Chapter 3 describes mechanistic studies of the initiation of this family of chelated catalysts. In all cases, the rate-limiting step of catalyst initiation was found to be association of the incoming olefin, not dissociation of the donor ligand. Further investigations support a mechanism where dissociation of the chelated ligand occurs prior to olefin coordination, but is fast and reversible. Implications of these observations on future catalyst design are discussed.

Chapter 4 presents a detailed study of the ring-opening metathesis polymerization (ROMP) of low-strain monomers with ruthenium-based catalysts. The effects of monomer concentration and catalyst dependence are described for unsubstituted cycloolefins. The ROMP of low-strain olefins with polar substituents is also examined, and a predictive model for ROMP feasibility is proposed.

The success of olefin metathesis has spurred the intense investigation of new catalysts for this transformation. With the development of many different catalysts, however, it becomes increasingly difficult to compare their efficiencies. Appendix 1 introduces a set of six reactions with

specific reaction conditions to establish standards for comparing olefin metathesis catalysts. The reactions were selected on the basis of their ability to provide a maximum amount of information describing catalyst activity, stability, and selectivity, while being operationally simple. Seven of the most widely used ruthenium-based olefin metathesis catalysts were evaluated using these standards. These conditions are useful tools for the comparison and evaluation of new olefin metathesis catalysts.

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