

**Selectivity in Ruthenium Catalyzed Olefin Metathesis:
Applications and Origins**

Thesis by
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For Dad

(June 4, 1960 – October 30, 2010)

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Abstract

Ruthenium-based catalysts for olefin metathesis display high activity in the presence of common functional groups and have been utilized in a variety of chemical disciplines. This thesis describes the development of new catalysts with superior properties and mechanistic studies directed at understanding the factors governing catalyst activity and selectivity.

Chapter 2 describes the preparation of acid-activated olefin metathesis catalysts containing acetylacetonate (acac)-type ligands. The effect of ligand structure and the exogenous acid on catalytic activity was examined. The acid-activated catalysts were also combined with a photoacid generator (PAG), which resulted in a highly active system for photo-activated olefin metathesis.

Chapter 3 details the incorporation of mesoionic carbenes (MICs) into ruthenium metathesis catalysts. The activity of these catalysts in several metathesis assays was measured and correlated to their initiation rates. The protonolysis of a Ru-MIC bond and the incorporation of this reaction into an acid-activated catalyst are also described.

Chapter 4 explores the relationship between catalyst structure and degenerate metathesis. A ring-closing metathesis assay was used to measure the preference of different catalysts for productive or degenerate metathesis. The relationship between degenerate metathesis and reactions such as ethenolysis is also discussed.

Chapter 5 describes the study of ruthenacyclobutanes formed from the degenerate metathesis selective catalysts presented in Chapter 4. The rates of various chemical exchange processes were measured and correlated to catalyst structure. Kinetic parameters for the rate-limiting step in ring-closing metathesis were also measured and used to rationalize the

differences in productive/degenerate selectivity for various catalysts.

Chapter 6 details the preparation and study of C-H-activated ruthenium catalysts for *Z*-selective olefin metathesis. Ligand effects on catalyst activity and selectivity are explored along with the application of these catalysts in *Z*-selective cross-metathesis and ring-opening metathesis polymerization.

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