Stereoselective Olefin Metathesis Processes Using Cyclometalated Ruthenium Alkylidene Complexes

Thesis by

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ABSTRACT

The recent development of a class of *Z*-selective ruthenium metathesis catalysts containing a crucial cyclometalated *N*-heterocyclic carbene (NHC) ligand has extended the applicability of ruthenium-mediated olefin metathesis to the production of a variety of useful *Z*-olefin-containing small molecules, polymers, and natural products. This thesis explores the synthesis and application of a number of novel *Z*-selective cyclometalated ruthenium alkylidene complexes displaying enhanced activity and selectivity across a range of metathesis transformations. Mechanistic investigations aimed at understanding and controlling stereoselectivity specifically in ring-opening metathesis polymerization (ROMP) are also detailed.

Chapter 2 describes the preparation of new *Z*-selective cyclometalated ruthenium metathesis catalysts via an improved method employing sodium carboxylates. Effects of the cyclometalated NHC ligand on catalyst activity and selectivity in several cross metathesis assays, as well as macrocyclic ring-closing metathesis and other industrially relevant transformations, are investigated.

Chapter 3 relates a story in two parts: the first details the synthesis and activity of a series of novel cyclometalated ruthenium alkylidenes displaying unprecedented *cis,syndio*-selectivity in the ROMP of norbornene- and norbornadiene-derived monomers. The second comprises an extensive study into the origins of stereoselectivity in ROMP in these and related cyclometalated ruthenium initiators. Experimental results are used in conjunction with a computational analysis of propagation transition states to develop a complete stereochemical model for *cis,syndio*-selctivity in these systems.

PUBLISHED CONTENT AND CONTRIBUTIONS

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L.E.R. participated in the conception of the project, synthesized and characterized the catalysts as well as evaluated them in homodimerization reactions, prepared and analyzed the data, and participated in the writing of the manuscript.

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L.E.R. participated in the conception of the project, synthesized and characterized the cyclometalated *N*-^{t}Bu-*N*-mesityl catalyst, synthesized the chiral norbornene, evaluated the catalysts in ring-opening metathesis polymerization (ROMP) reactions, prepared and analyzed the data, and participated in the writing of the manuscript.

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