Abstract

Catalysts for Olefin Metathesis:
Ruthenium Alkylidene Complexes with Phosphine and N-Heterocyclic Carbene Ligands

The olefin metathesis reaction entails the metal-catalyzed redistribution of carbon–carbon double bonds. This area of catalysis is currently in a period of renaissance because of the success of well-defined ruthenium catalysts, which are characterized by excellent functional group compatibility, relatively easy handling, and a wide range of catalytic activity. Due to these properties, the applications of olefin metathesis have expanded dramatically during the past few years to include the synthesis of molecules in organic, inorganic, biochemical, polymer, and materials chemistry.

In this context, the objectives of the work described in this dissertation were twofold: (1) to further improve the activity and selectivity of ruthenium-based olefin metathesis catalysts, and (2) to obtain a better understanding of how these catalysts operate.

The first problem was addressed by varying the ligand sphere within the $L_2X_2Ru{=}CHR$ framework. Chapter 2 explores the metathesis of directly functionalized olefins, such as 1,1-difluoroethylene and acrylonitrile, which are challenging reactions. Detailed studies revealed that ruthenium alkylidene complexes react readily with these olefins but stop after a single turnover of the catalytic cycle. This effect is caused by electronically deactivating carbene substituents, which dramatically decrease the rate of phosphine dissociation from the metal center and thus prevent catalyst re-initiation. In some cases, this effect can be moderated by replacing the phosphine with more labile pyridine ligands.

Chapter 3 describes complexes where the L ligands are phosphines, N-heterocyclic carbenes (NHCs), imidazoles, or pyridines, where the X ligands are chlorides, and where the carbene moiety is either benzylidene or a cyclic moiety. Improved catalytic activity and selectivity were achieved with complexes containing a combination of phosphine and NHC ligands. The reactivity and stability profiles of these species can be tuned through the stereo-electronic properties of the NHC, *e.g.*, by varying the N-substituents from aryl to alkyl. To facilitate the use of NHCs in organometallic applications, a synthetic route was developed that employs NHC adducts to protect the reactive carbene centers.

Chapter 4 describes the reactions of ruthenium alkylidene complexes with alkynes. In the majority of cases, the metathesis polymerization of alkynes is unsuccessful because of competing reactions to form η^3-vinylcarbene and η^5-cyclopentadienyl derivatives. The η^3-vinylcarbene complexes are particularly interesting as models for the olefin-bound intermediate in the olefin metathesis catalytic cycle, and their structures demonstrate that it is possible for the chloride ligands to adopt a cis arrangement that places one of the chlorides trans to the L donor ligand.

The studies in Chapter 5 explore the stereoelectronic properties of phosphine and NHC ligands and provide valuable insights about electronic structure and bonding. This information was obtained by a variety of techniques, including structure–activity studies, kinetics, x-ray crystallography, heteronuclear NMR, infrared spectroscopy, and gas-phase UV photoelectron spectroscopy, which were performed on several series of ruthenium and molybdenum model complexes.