Ruthenium metathesis precatalysts with unsymmetrical N-heterocyclic carbene (NHC) ligands

Abstract

Olefin metathesis is one of the most important chemical transformations for the formation of carbon-carbon double bonds. The possibility to build up highly funtionalised alkenes starting from simple olefins makes this reaction indispensable in modern organic synthesis, giving access to a wide range of molecules that would be barely obtained through other synthetic routes.

The success of metathesis is due to the development of new and efficient catalysts which can be used in a wide variety of research fields, both in industry and in academia. In this context, the research of the ‘perfect’ metathesis complex still impassions scientists all over the word, and several research papers regarding the development of new catalytic systems are published every year.

The group I am part of focuses its attention on the development of new ruthenium metathesis catalysts. Our interest lies in the influence that nature and configuration of substituents on the N-heterocyclic carbene (NHC) ligand could have on the performances of the corresponding metal complexes.

In this doctoral thesis, the field of unsymmetrical N-heterocyclic carbene (u-NHC) ruthenium catalysts will be explored. Synthesis and characterisation of several novel complexes will be discussed. Catalytic performances will be evaluated in model metathesis reactions as well as in more attractive metathesis transformations. The relationship between NHC structure and complexes’ behaviours will be investigated using NMR, X-Ray, IR, cyclic voltammetry and DFT calculations.

Chapters One and Two give an overview on olefin metathesis and on the most famous ruthenium-based systems.

In Chapter Three novel u-NHC ruthenium catalysts are investigated. Steric and electronic properties of the ligands are analysed in depth.

In Chapter Four, u-NHC ruthenium compounds are tested in homo- and copolymerisations.

In Chapter Five, the performances of a new series of u-NHC catalytic systems are studied. The application in various metathesis transformations, also involving renewable substrates, is investigated.

In Chapter Six, all the enantiomerically pure catalysts are tested in asymmetric metathesis transformations. A novel approach for the synthesis of enantiopure catalysts is also described.