Olefin Metathesis Ruthenium Catalysts Bearing Unsymmetrical Heterocylic Carbenes

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Abstract
Catalytic olefin metathesis has become a powerful tool for carbon–carbon bond formation in organic and polymer chemistry. The Grubbs' 1st generation catalyst 1 constitutes a highly efficient metathesis catalyst tolerating a wide variety of functional groups. The introduction of N-heterocyclic carbenes (NHCs) as ligands has afforded the more stable and active 2nd generation ruthenium catalyst 2. Several ruthenium metathesis initiators of the 2nd generation type have been prepared from various NHCs. Altering the steric and electronic properties of the ligand can control the activity and selectivity of the NHC coordinated catalysts. One of the reported modifications for the NHC-containing ruthenium metathesis initiators is the application of unsymmetrical NHC ligands. The unsymmetrical nature of these ligands may lead to the selective catalysts in different metathesis reactions. This survey highlights the developments in ruthenium catalysts coordinated with unsymmetrical NHC ligands and their trends in activity and selectivity on olefin metathesis. The discussion includes the description of ruthenium initiators coordinated with N-aryl-N′-alkyl NHCs, N-aryl-N′-aryl NHCs, and those coordinated with two unsymmetrical NHCs. Ruthenium complexes bearing chiral NHCs, cyclic (alkyl) (amino) carbenes (CAACs) as well as thiazol-2-ylidene ligands are also described.