Recent Advances in Olefin Metathesis with Molybdenum and Tungsten Catalysts

Among the several important developments in the last five years in olefin metathesis chemistry employing Mo or W catalysts has been the synthesis and application of M(NR)(CHMe₂R')(OR)(Pyrrolide) (MonoAlkoxidePyrrolide or MAP) complexes, especially those in which OR is a sterically demanding terphenoxide such as 2,6-dimesitylphenoxoide (OHMT). MAP species under the right circumstances have proven to be Z-selective in a variety of olefin metathesis reactions, among them enantioselective ring-opening/cross-metatheses, ROMP to give highly stereoregular polymers, ethenolysis of internal olefins such as oleates, coupling of terminal olefins, cross coupling of terminal olefins, and synthesis of macrocyclic natural products. A second important development has been the synthesis of a variety of tungsten oxo alkylidene complexes. Oxo complexes can be "activated" by binding B(C₆F₅)₃ to the oxo ligand and are likely to be analogs of metathesis catalysts found in classical metathesis catalyst systems. Recent applications of metathesis include stereoregular ring-opening metathesis polymerization to give cis, isotactic or cis, syndiotactic polymers and alternating AB copolymers. Finally, it is now possible to employ olefins in metathesis reactions that have a halide or other electron withdrawing group directly attached to the olefinic carbon atom.