

This article describes new selectivities for Grubbs' first and second generation catalysts when occluded in a hydrophobic matrix of polydimethylsiloxane (PDMS). Occlusion of catalysts in mm-sized slabs of PDMS is accomplished by swelling with methylene chloride then removing the solvent under vacuum. The catalysts are homogeneously dissolved in PDMS yet remain catalytically active. Many substrates that react by olefin metathesis with Grubbs' catalysts freely dissolved in methylene chloride also react by olefin isomerization with occluded catalysts. Eleven examples of substrates that exhibit dual reactivity by undergoing olefin isomerization with occluded catalysts and olefin metathesis with catalysts dissolved in methylene chloride are reported. Most of these substrates have olefins with allylic phosphine oxides, carbonyls, or ethers. Control expts. demonstrate that isomerization is occurring in the solvent by decomn. of the catalyst from a ruthenium carbene to a proposed ruthenium hydride. This work was extended by heating occluded Grubbs' first generation catalyst to 100° in 90% MeOH in H₂O in the presence of various alkenes to transform the Grubbs' catalyst into an isomerization catalyst for unfunctionalized olefins. This work demonstrates that occlusion of organometallic catalysts in PDMS has important implications for their reactions and can be used as a method to control which reactions they catalyze.