Characterization of [4+2] Cycloaddition Catalyzed by Lewis Acid Penta-arylcylopentadienylzirconium (IV) Complexes

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Abstract

The preparation and characterization of the achiral Lewis acid catalyst pentaarylcylopentadienylichlorozirconium (I) and the analogous methyltartrate ligated complex (II) are reported. Results from [4+2] cycloaddition reactions of cyclic dienophiles with acrolein or methyl acrylate are guiding our current syntheses of alkoxide stoichiometry as well as dynamic behavior. These studies have allowed us to observe possible complexes with both mono/bis, fac/mer, syn/anti) which vary as the dienophile type and the aldehyde region of acrolein show signal splitting to catalyst-dienophile conformations. These findings prompted us to further investigate catalyst-dienophile interactions.

Introduction

Application of transition metal complexes as Lewis acid catalysts for asymmetric induction of [4+2] cycloaddition reactions is an intensely studied area. The simultaneous formation of four chiral sites makes this reaction one of the most important reactions in organic chemistry. The role of these organometallic compounds is to decrease activation energy via nucleophilic electron donation to the metal, thereby forming a complex. Zirconium complex II, a Lewis acid, has been employed in cycloaddition reactions to investigate the steric effect of the penta-arylcylopentadienylichlorozirconium ligand to the formation of endo-exo isomers. Details of catalyst-dienophile binding and structure have been studied with VT-1H NMR.

Equation 1. Diels-Alder [4+2] cycloaddition

Discussion

Diels-Alder product ratios in Table 1 demonstrate that low temperatures in I and II increase eno formation with methyl acrylate and increase exo formation with acrolein reactions. Low temperature reactions of methyl acrylate demonstrate that a catalyzed reaction favors endo formation. Acrolein reactions show that in catalyzed solutions the yield of endo product is doubled at 25°C. However, further studies of this reaction using 85°C and 85°C have given us little insight for better understanding of the effects of catalysts I and II. The small size of acrolein (compared to methyl acrylate) allows for more possible dienophile-catalyst conformations. These findings prompted us to further investigate catalyst-dienophile interactions.

Conclusion

Zirconium complexes I and II are effective catalysts of [4+2] cycloaddition reactions as they decrease the activation energy and favor the formation of a specific isomer. The nature of the dienophile used has a significant effect on the catalytic dynamics. VT-1H NMR spectra of solutions with different mole ratios of acrolein or methyl acrylate and II support the presence of different catalyst-dienophile complexes. These studies have prompted us to explore synthesis of chiral derivatives of II (tartrate ligated) and expand our studies to Niobium (V) complexes.

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