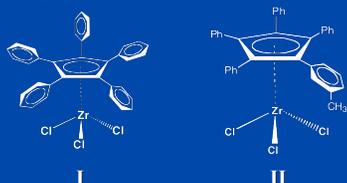


Characterization of [4+2] Cycloaddition Catalyzed by Lewis Acid Penta-arylcyclopentadienylzirconium (IV) Complexes

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Abstract

The preparation and characterization of the achiral Lewis acid catalysts pentaphenylcyclopentadienyltrichlorozirconium (I) and the analogous *m*-tolyltetraphenylcyclopentadienyltrichlorozirconium complex (II) are reported. Results from [4+2] cycloaddition reactions of cyclopentadiene with acrolein or methyl acrylate catalyzed by I or II under various conditions demonstrate that selectivity is dependent upon the nature of the dienophile and temperature. Low temperature (-15°C) cycloaddition of methyl acrylate resulted in an endo/exo ratio of 24.67 (4.85 for control), but at lower and elevated temperatures (-85°C and 85°C), endo/exo ratios are similar to the controls. VT-¹HNMR methods were used to investigate the relative stability of dienophile-catalyst complexes. The complexes formed show dienophile-dependent stoichiometry as well as dynamic behavior. These results are guiding our current syntheses of alkoxide derivatives of II and niobium Lewis acid complexes with chiral ligands.



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-arylcyclopentadienyl ligand in the formation of endo/exo isomers. Details of catalyst-dienophile binding and structure have been studied with VT-¹HNMR.

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

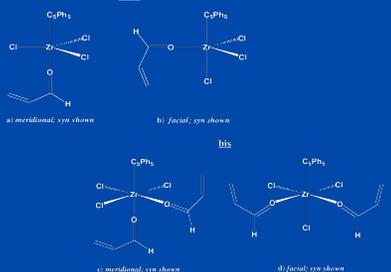
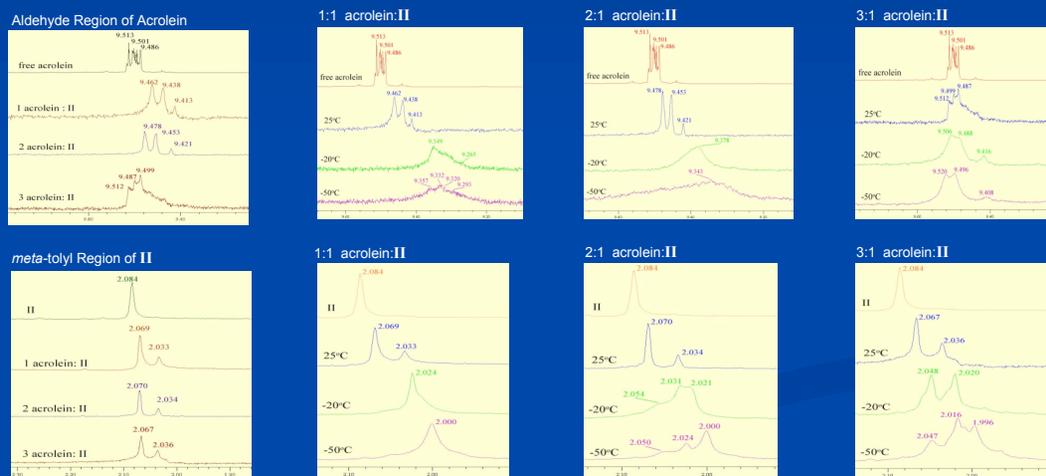


Table 1. Endo/Exo Product Formation Using I and II

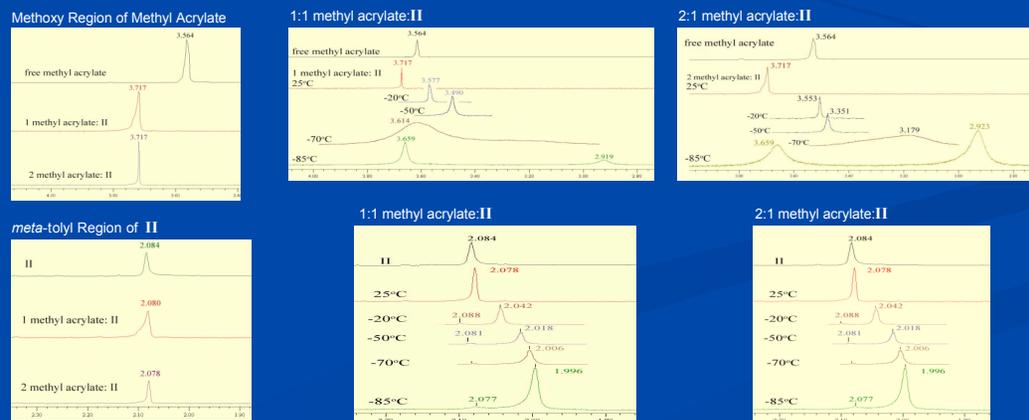
dienophile	temperature	cp* ^{Ph} ZrCl ₃ (I)		mt-cp* ^{Ph} ZrCl ₃ (II)		control	
		endo/exo	yield	endo/exo	yield	endo/exo	yield
acrolein	25°C	2.05 ± 0.05	100	2.09 ± 0.08	100	4.30 ± 0.02	100
	85°C ^b	1.72 ± 0.16	100	2.58 ± 0.13	100	2.65 ± 0.01	100
	-85°C ^a	2.80 ± 0.06	9.03	2.43 ± 0.47	62	3.36 ± 0.23	13
methyl acrylate	25°C	10.54 ± 0.87	100	17.71 ± 0.57	100	4.15 ± 0.03	90.47
	-15°C ^c	21.98 ± 0.40	88.2	24.67 ± 1.12	100	4.85 ± 0.13	15.08

^a Isomer ratios determined by GC (direct injection 0.4 µL, ZB-560 m x 0.53 mm x 1.50 µm) ^b 85°C reactions performed in a hot oil bath ^c reactions prepared over ice, then sealed and stored in -15°C freezer

Acrolein and II ¹HNMR Data



Methyl Acrylate and II ¹HNMR Data



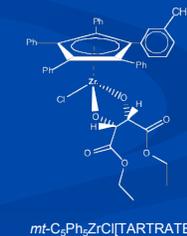
Discussion

Diels-Alder product ratios in Table 1 demonstrate that low quantities of I and II increase endo 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 exo 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 selectivity of 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.

¹HNMR studies of solutions containing catalyst to acrolein mole ratios of 1:1, 1:2, and 1:3 and methyl acrylate mole ratios of 1:1 and 1:2 have given us evidence that the dienophile is complexing to II. The *meta*-tolyl signal of II and the aldehyde region of acrolein show signal splitting and signal broadening; this indicates the presence of interchanging catalyst-dienophile complexes (such as monobis, fac/mer, syn/anti) which vary as the dienophile-to-catalyst mole ratio increases. Also, the downfield chemical shift of the methyl acrylate methoxy protons' signal demonstrates a deshielding effect that can be attributed to the electron donation, most likely via the carbonyl oxygen, to the Lewis acid. VT-¹HNMR spectra allow us to observe possible complexes with both dienophiles.

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-¹HNMR 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.



Acknowledgements

Linda Ye, Jin An, Akio Usuda, Tambi Wenj, Ali Jabalamei
\$\$\$
Petroleum Research Fund
Minority Biomedical Research Support Program (MBRS)