Synthesis and Characterization of Pentaphenylcyclopentadienyltris(dimethylamido)Zirconium and Chloride Derivatives

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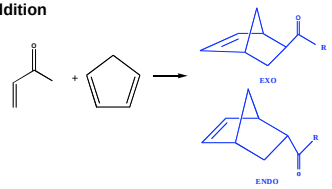
Abstract

We have prepared pentaphenylcyclopentadienyltris (dimethylamido) zirconium (C_5Ph_5)Zr(NMe_2)$_3$ (I) and a chloride derivative, (C_5Ph_5)Zr(NMe_2)$_2$Cl (II). The preparation of (C_5Ph_5)Zr(NMe_2)$_2$Cl$_2$ (III) is providing more challenges. I was synthesized by reacting pentaphenylcyclopentadiene (HC_5Ph_5) with tetra-kisdimethyl amidozirconium Zr(NMe_2)$_4$. Next, II was produced by reacting I with one equivalent of Me_2NH•HCl which was added using a slow addition method at room temperature. III was prepared by reacting (I) with two equivalents of Me_2NH• HCl which was added using the same slow addition method but at -78°C. The compounds were characterized by ^1H and ^{13}C NMR spectroscopy. They will be used in the synthesis of chiral Lewis acids, which will be catalysts in C-C bond formation reactions.

Introduction

We are interested in preparing chiral Lewis acids to act as catalysts in reactions such as [4+2] cycloaddition. Compounds of this sort are of significance in many industrial reactions such as petroleum, pharmaceutical and plastic production. These compounds act as catalysts by lowering activation energies of a reaction through coordination of a substrate to a metal (e.g. Zr). Ideally, we want these substances to catalyze the stereoselective formation of one enantiomer. This is important because different enantiomers may have biological activity that may not be understood or expected. We are developing methodologies to readily prepare many candidates for catalysts.

Diels-Alder [4+2] cycloaddition

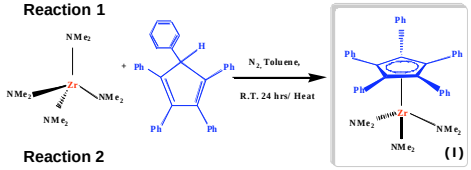


Method s

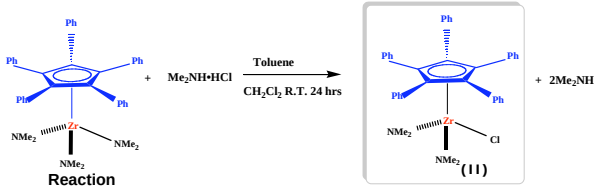
The preparation of pentaphenylcyclopentadienyltris (dimethylamido) zirconium (C_5Ph_5)Zr(NMe_2)$_3$ (I) was achieved by reacting pentaphenyl-cyclopentadiene with 1 equivalent of Zr(NMe_2)$_4$. Next, II was produced by reacting I with one equivalent of $HNMe_2$•HCl. $HNMe_2$• HCl was added to I using a slow addition method at room temperature. Compound III was prepared by reacting I with two equivalents of $HNMe_2$• HCl. $HNMe_2$ • HCl was added to I using a slow addition method at -78°C. All reactions were done under inert atmosphere.

Reactions

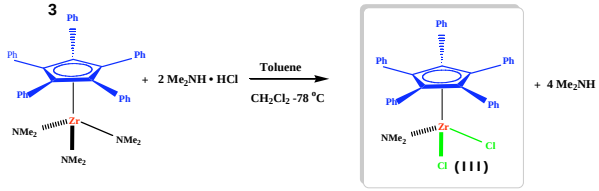
Reaction 1



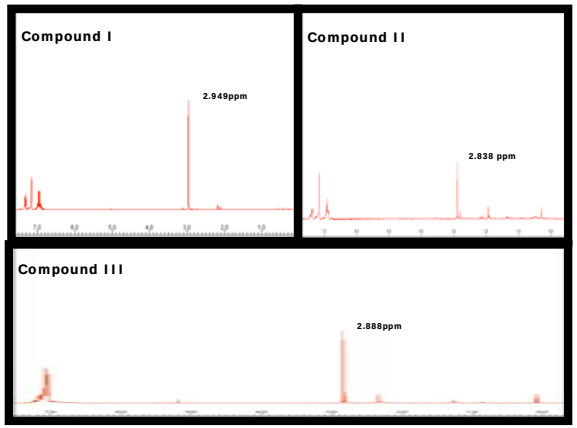
Reaction 2



Reaction 3

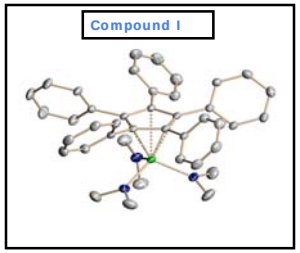


Proton NMR



Discussion

We have successfully synthesized pentaphenylcyclopentadientris-(dimethylamido)zirconium and one of its chloride derivatives. Compound I has been produced in 70 percent yield; the amido methyl signal is at 2.949ppm. The crystal structure of I is shown below. An agostic interaction is suggested with the N-methyl group by the Zr-H (located by HFIX) distance of 2.624 Å and the Zr-N-C angles, 143.7(3) and 107.4(3)°, compared to the 125.5(3)° average for the four other Zr-N-C angles. This interaction is dynamic, as only one amido methyl signal is observed at room temperature. Compound II, has been produced in 73% yield and has an amido chemical shift of 2.838 ppm. Initial results for the preparation of III show an amido chemical shift of 2.888ppm. However, the synthesis is still in optimization.



Future Plans

- Optimize synthesis of III
- Prepare phenyl ethyl alcohol (PEA) derivatives of II and III
- Investigate potential catalytic activity of PEA derivatives of II and III
- Optimize techniques to improve purity and yields

Acknowledgements

More Program

MARC U STAR*

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