

Synthesis and characterization of zirconium(IV) complexes containing the pentaphenylcyclopentadienyl ligand and dimethyl amido ligands

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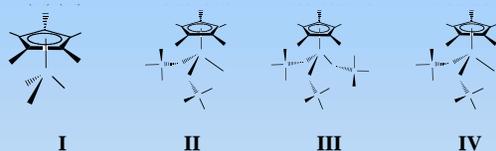
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INTRODUCTION

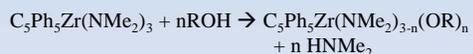
Chiral group 4 ansa-metallocenes have been exploited as stereoselective catalysts or reagents for a wide variety of reaction. Our work is directed towards developing chiral zirconocenes to promote the C-C bond formation reactions like [4+2] cycloaddition.

The high yield synthesis of the totally characterized intermediate, $C_5Ph_5Zr(N(CH_3)_2)_3$ (**I**) has been achieved by the reaction of HC_5Ph_5 with $Zr(N(CH_3)_2)_4$. **I** reacts with *R*-(+)-*sec*-phenethyl alcohols with ratio (1:3) and (1:2) to give the corresponding alkoxide complexes with loss of dimethyl amine. For **III**, cleavage of the remaining amido ligand can be achieved by mild protonolysis to give the chloride complexes **IV**.



RESULTS and DISCUSSION

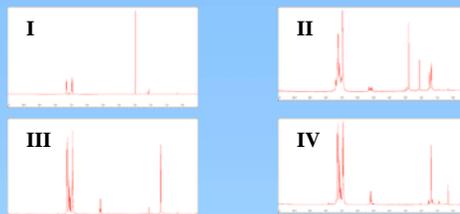
(a) SYNTHESSES



The reactions to make complexes where ROH is (*R*)-(+)-*sec*-phenethylalcohol and $n = 2$ (**II**), 3 (**III**) are shown above. Use of racemic *sec*-phenethylalcohol gave mixtures of diastereomers, with more complex NMR spectra. The diastereomers are formed in nearly equal quantities as determined from the integration of the 1H NMR spectra. Attempts to prepare the monosubstituted complex using a wide range of temperatures and addition rates led to the formation of mixtures that did not readily separate. Their 1H NMR showed the presence of **I**, **II** and **III**, as well as small amounts of the presumed monosubstituted complex.

(b) CHARACTERIZATION

1H -NMR (C_6D_6) for **I** to **IV**



X-ray structure

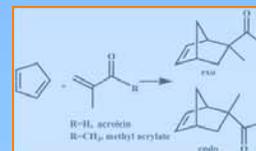


The bond distances and angles show that one of the dimethyl-amido ligands is not equivalent to the other two in the solid state. This is the amido ligand in which the plane containing N, and two carbon from methyl group is roughly parallel to the Zr-Cp centroid line, where the other amido ligands' planes are roughly orthogonal to that line. This uniqueness is noted by a shorter Zr-N1 distance (2.036 Å) longer N1-C distances (1.468 Å) and Zr-N1-C angles significantly different to the other two ligands (Cf. **Table 1**). These parameters suggest a stronger Zr-N1 bond than in the other two ligands. However, this distinction does not persist in solution as the proton NMR in solution shows a single resonance for methyl groups, suggesting either a different conformation in solution or fluxional behavior.

Table 1. Bond distances (Å) and angles (°).

Zr-N1	2.036	Zr-N2	2.052	Zr-N3	2.055
N1-C	1.468	N2-C	1.448	N3-C	1.434
C36-N1-Zr	143.7	C38-N2-Zr	127.8	C40-N3-Zr	129.1
C37-N1-Zr	107.4	C39-N2-Zr	123.3	C41-N3-Zr	122.0

(c) REACTIVITY



For the reactive dienophile, acrolein, and catalyzed reaction, At loading of 1.0 mol % *endo:exo* ratio of (**I**; 3.55: **II**; 5.84: **III**; 2.76: **IV**; 3.14) were obtained when cyclopentadiene is added to

solution containing the catalyst and acrolein at 294K (cf. control: 4.3±0.02).

Reaction at lower temperature (-15°C) for 15 h with 1.0 mol % loading, *endo:exo* ratio of (**I**; 4.01: **II**; 7.27: **III**; 4.00: **IV**; 6.33) were obtained. The ratios are higher than the control of the similar reaction with uncatalyzed (3.75±0.05).

Methyl acrylate cycloaddition shows different selectivity. At the room temperature, the control reaction runs about 15 h, with *endo:exo* ratio of (**I**; 5.94: **II**; 9.02: **III**; 5.84: **IV**; 6.14) (cf. contrl: 4.15±0.02). However, the presence of **I**, **II**, **III**, **IV** increases the *endo:exo* ratio. Best results in this work came from adding cyclopentadiene to a solution containing the dienophile and catalyst. At 1.0 mol % **II**, *endo:exo* ratio of 10.29 with 24.6 % conversion at lower temperature (-15°C) was obtained. The uncatalyzed reaction mixture had an *endo:exo* ratio of 4.85±0.13 with only 15 % consumption of methyl acrylate at -15°C after 18 h.

CONCLUSION

New piano-stool Zr complexes **I** to **IV** containing amido and alkoxide ligands were synthesized and characterized. Studies of the activity of **I**, **II**, **III** and **IV** in [4+2] cyclization of cyclopentadiene and the dienophiles acrolein and methyl acrylate showed modest acceleration and little enhancement of selectivity.

ACKNOWLEDGEMENT

Petroleum Research Fund
NIH-Minority Biochemistry Research Support Program