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Diastereomerically-Specific Zirconium Complexes of Chiral Salan Ligands: Isospecific Polymerization of 1-Hexene and 4-Methyl-1-pentene and Cyclopolymerization of 1,5-Hexadiene

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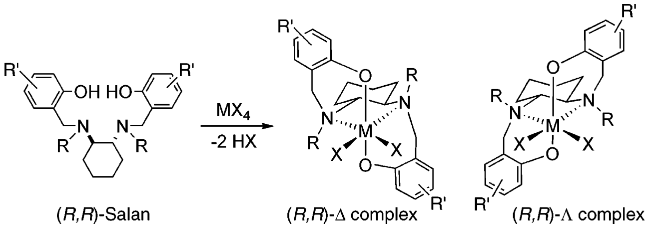
Chirality is an essential requirement of isospecific polymerization catalysts of α-olefins that operate by an enantiomorphic-site control mechanism. While conventional polymerizations employ racemic catalysts, there are several notable exceptions in which enantiomerically pure catalysts are required. These include the chiral cyclopolymerization of 1,5-hexadiene,[1] chiral oligomerization,[2] and kinetic resolution via polymerization.[3] Such catalysts may be prepared by resolution of the racemic complexes, as is achieved in the case of *ansa*-metallocenes,[4] or, preferably, by employing an enatiomerically pure ligand that would wrap in a well-defined way around the metal. Herein we describe the first highly diastereoselective formation of zirconium complexes of chiral Salan ligands and their application in polymerization of α-olefins leading to novel materials.

Recently, we introduced the family of Salan complexes of group 4 metals as α-olefin polymerization catalysts.[5] The dianionic tetradentate [ONNO]-type Salan ligands tend to wrap around an octahedral metal center in a *fac-fac* mode, so that the overall symmetry of the [ONNO]-MX_2 complex is C_2-chiral and the two labile X groups are cis-related, an essential requirement for polymerization catalysis. While achiral Salan ligands lead to racemic mixtures, introduction of chirality to the Salan backbone may lead to two C_2-diastereomers of *fac-fac* geometry. We have shown that chiral Salan ligands assembled around a *trans*-1,2-diaminocyclohexane bridge lead to titanium complexes with varying degrees of diastereoselectivity: several unsubstituted Salan ligands (bearing N-*H* groups) led to single diastereomers, whereas those bearing N-*Me* groups led to diastereomer mixtures (Scheme 1).[6] Unfortunately, unsubstituted Salan ligands are not inert enough for polymerization catalysis. We therefore turned to investigate the wrapping of chiral *N*-Me substituted Salan ligands around zirconium.

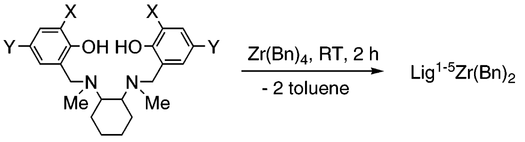
The ligand precursors described in this work were synthesized either in an enantiomerically pure form ($Lig^{1-4}H_2$) or as racemates ($Lig^{1-5}H_2$) following two possible synthetic schemes.[7] $Lig^{1,2}H_2$ featuring electron-withdrawing substituents and Lig^4H_2 featuring the bulky *tert*-Bu groups were described previously. Lig^3H_2 featuring nonbulky *ortho*-Me groups, and Lig^5H_2 featuring the very bulky *ortho*-adamantyl groups[8] are described herein for the first time. The ligand precursors were reacted with tetrabenzylzirconium in a toluene elimination reaction to produce the corresponding dibenzyl complexes $Lig^{1-5}Zr(Bn)_2$ in typical yields of 90% (Scheme 2).

In a sharp contrast to the titanium coordination chemistry that gave diastereomer mixtures for the *N*-Me ligands, all the zirconium complexes formed as single diastereomers, as evident from their ^1H NMR spectra. The number of peaks observed for all complexes supported the formation of a C_2-symmetric diastereomer. X-ray quality crystals of $Lig^3Zr(Bn)_2$ synthesized from *rac*-Lig^3H_2 were obtained from toluene, and an ORTEP representation is shown in Figure 1. The noncentrosymmetric space-group indicates that a conglomerate rather than a racemate crystallization had occurred.[6] The crystal structure of *rac*-$Lig^5Zr(Bn)_2$ that had crystallized in a centrosymmetric space group was of lower quality owing to disordered solvent molecules. Both structures indicated that the *fac-fac* isomers have formed and, most notably, that the wrapping of the ligands in both structures followed the same pattern; that is, an (*R,R*)-Salan ligand leads to a Δ-binding. This is the same wrapping preference that was observed for the titanium complexes of the nonsubstituted ligands. Furthermore, an X-ray structure of the di(*tert*-butoxide) zirconium complex *rac*-$Lig^3Zr(O\text{-}tert\text{-}Bu)_2$ that had also formed as a single diastereomer indicated an identical wrapping mode.[7] A possible explanation for the considerably higher diastereoselectivity found for zirconium in comparison to titanium is the higher covalent radius of zirconium enabling a less hindered fitting of the *N*-Me substituted ligands.

Scheme 1. The Possible *fac-fac* Wrapping Modes of Chiral Salan Ligands around Octahedral Group 4 Metal Centers



Scheme 2. Ligand Precursors Employed in This Work and Synthesis of Their Corresponding Dibenzylzirconium Complexes



Lig^1H_2: X,Y = Cl
Lig^2H_2: X,Y = Br
Lig^3H_2: X = Me, Y = H
Lig^4H_2: X,Y = *tert*-Bu
Lig^5H_2: X = 1-Adamantyl, Y = Me

All the dibenzylzirconium complexes were found to be active catalysts for 1-hexene polymerization at room temperature upon activation with tris(pentafluorophenyl)borane (eq 1). Their activities were found to follow those of the analogous catalysts derived from the nonchiral ligands: The three catalysts featuring nonbulky groups ($Lig^{1-3}Zr(Bn)_2$) led to atactic polymerization, whereas $Lig^{4,5}$Zr-

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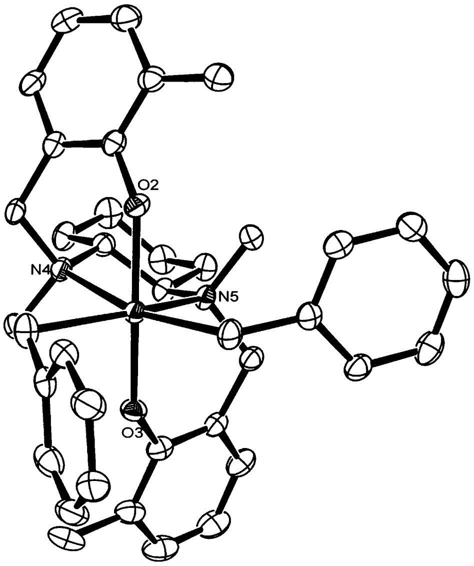

Figure 1. An ORTEP representation of *rac*-Lig^{3}Zr(Bn)$_2$, 50% probability.

(Bn)$_2$ led to highly isotactic poly(1-hexene).[9] Lig^{5}Zr(Bn)$_2$ is somewhat more active than Lig^{4}Zr(Bn)$_2$, and the ^{13}C NMR spectrum of its polymer shows no traces of any stereo-errors (e.g., mmmr), signifying a very high degree of isotacticity.[7,5,10] These results are consistent with those obtained with the analogous zirconium complex of the nonchiral ligand in propylene polymerization.[8] As expected, the two catalysts featuring the electron withdrawing groups (Lig^{1,2}Zr(Bn)$_2$) exhibited very high activities. In contrast to their analogues based on the nonchiral ligands,[5b] they led to high-molecular-weight polymers rather than to oligomers. This is tentatively attributed to their higher rigidity that may restrict conformations that favor termination events.

$$\text{1-hexene} \xrightarrow[\text{B}(\text{C}_6\text{F}_5)_3\text{, rt}]{\text{Lig}^{1-5}\text{Zr(Bn)}_2} \text{poly(1-hexene)} \qquad (1)$$

These catalysts were also found suitable for polymerization of the somewhat bulkier monomer, 4-methyl-1-pentene. This polymerization followed the trend observed for 1-hexene polymerization: The two complexes featuring electron-withdrawing phenolate substituents (Lig^{1,2}Zr(Bn)$_2$) gave rise to highly active catalysts, and to high-molecular weight stereoirregular polymers. On the other hand, the two complexes featuring the bulky phenolate substituents (Lig^{4,5}Zr(Bn)$_2$) led to catalysts of low activity and to crystalline polymers insoluble in common solvents at room temperature. ^{13}C NMR at an elevated temperature of these crystalline polymers indicated the formation of highly isotactic poly(4-methyl-1-pentene). Differential scanning calorimetry results for polymer samples synthesized from (*rac*)-Lig^{4}Zr(Bn)$_2$, (*R*,*R*)$-$(Δ)-Lig^{4}Zr(Bn)$_2$, and (*rac*)-Lig^{5}Zr(Bn)$_2$ supported their crystalline structure as evident from the presence of exothermal (crystallization) peaks on the cooling thermograms and endothermal (melting) peaks on the heating thermograms. The melting peak (second heating thermograms) temperatures are at 218.0, 216.7, and 222.7 °C, respectively.[7] The somewhat higher melting point of the polymer derived from (*rac*)-Lig^{5}Zr(Bn)$_2$ may signify a higher isotacticity. It is noteworthy that the first and the second heating thermograms of the polymer samples derived from the enantiomerically pure and the racemic varieties of Lig^{4}Zr(Bn)$_2$ are almost identical. Thus, although a presumable enantiomorphic-site control mechanism is expected to produce chains of single helicity from (*R,R*)$-$(Δ)-Lig^{4}Zr(Bn)$_2$ (assuming no helix-racemization prior to precipitation), no expected thermal effects associated with the helix racemization on melting-recrystallization were observed. Cyclopolymerization of 1,5-hexadiene may lead to main-chain chiral poly(methylene-1,3-cyclopentane) if the stereocontrol is trans-diisotactic.[1] All the complexes Lig$^{1-5}$Zr(Bn)$_2$ led to active catalysts for 1,5-hexadiene polymerization, their activity following the trend observed above, that is, highly active catalysis by the complexes featuring electron withdrawing phenolate substituents, low activity by the catalysts bearing bulky groups, and intermediate activity by Lig^{3}Zr(Bn)$_2$. While most samples were highly insoluble, ^{13}C NMR spectra at high temperature of a more soluble sample (prepared from (*R*,*R*)$-$(Δ)-Lig^{2}Zr(Bn)$_2$) featured only cyclopolymerization peaks, and no vinyl groups peaks or peaks attributed to cross-linking were observed. Peak integration aided by spectrum simulation of the C$_{4,5}$ peaks region of the ^{13}C NMR spectrum supported a preference for trans substituted rings ($1 - \sigma = 0.75$), and a mild isotactic preference ($\alpha = 0.75$).[1] The combination of these two properties should render this polymer chiral; however, its insolubility prevents a direct optical rotation assessment. Polymers prepared from Lig^{2}Zr(Bn)$_2$ and Lig^{3}Zr(Bn)$_2$ show clear melting peaks at ca. 100 °C and glass transition at ca. +5 °C (second heating thermograms), indicating a semicrystalline structure. In contrast, the polymers derived from Lig^{4}Zr(Bn)$_2$ and Lig^{5}Zr(Bn)$_2$ showed strong glass transitions at ca. -4 °C,[7] and no melting, indicating lack of crystallinity, which, combined with their insolubility, may suggest a higher degree of cross-linking.

In conclusion, we have introduced the first zirconium complexes of chiral Salan ligands. They were found to form as single diastereomers of predetermined chirality around the metal and led to active polymerization catalysts of higher α-olefins whose isotacticity induction depended on the ligands' bulk. We are currently investigating further polymerizations as well as other enantioselective transformations with these types of catalysts.

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Supporting Information Available: Details of the syntheses and characterization of the complexes, polymerization procedures, and polymer characterization; crystallographic data in text format for *rac*-Lig^{3}Zr(Bn)$_2$, *rac*-Lig^{5}Zr(Bn)$_2$, and *rac*-Lig^{3}Zr(O-*tert*-Bu)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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