Isospecific Living Polymerization of 1-Hexene by a Readily Available Nonmetallocene C_2-Symmetrical Zirconium Catalyst

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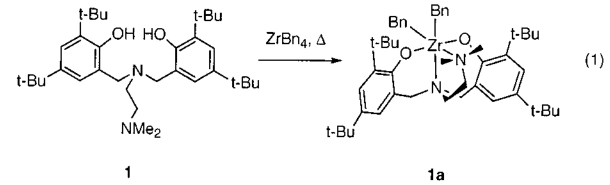
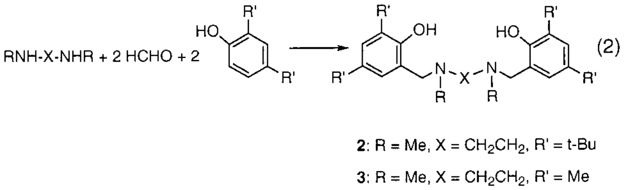
The search for new α-olefin polymerization catalysts based on transition metal complexes is a field of major interest involving many academic and industrial research groups. The ligands surrounding the metal play a crucial role in determining the activity as well as the stereospecifity of the catalyst, by affecting the steric and electronic properties at the metal. Over the last two decades, this field has been dominated by the metallocene complexes of group IV metals. Especially, *ansa*-metallocenes of C_2 symmetry were found to induce isospecificity in the resulting polymers.[1] Recently, there has been a growing interest in the development of *non*-cyclopentadienyl ligands for the polymerization of α-olefins.[2] Most attention was drawn to chelating di(amido) ligands,[3] some of whose group IV transition metal complexes induce polymerization in a *living* manner,[3a−c] whereas chelating di(alkoxo) ligands[4] drew a more limited attention. The number of nonmetallocene systems, which were found to induce tacticity in the resulting polymer, is, however, quite small.[5] In this communication we introduce a novel family of di(alkoxo) complexes, one member of which is the first nonmetallocene C_2-symmetrical complex, which, upon activation, leads to a highly isospecific living polymerization of 1-hexene.

Recently, we introduced the amine bis(phenolate) family of ligands to group IV transition metals.[6] We found that the presence of an extra donor group on a sidearm leads to octahedral $LigMX_2$-type complexes, in which the two labile X groups are forced into a cis geometry.[6a] Catalysts derived from these complexes (e.g. **1a**) lead to highly reactive 1-hexene polymerization catalysts.[6b]



The C_s-symmetry of **1a** allows olefin approach from the two possible directions in each active position without preference, thus the polymer obtained is atactic. Therefore, we aimed at complexes of a different symmetry which may induce tactic polymerization, that incorporate ligands having similar functional groups yet having a different connectivity. Our approach is based on replacing the "branched" mode of connectivity of donor atoms with a sequential connectivity mode, namely diamine bis(phenolate) ligands.

This new family of dianionic tetradentate chelating ligands is easily synthesized by a one-pot Mannich condensation between readily available di(secondary) amines, formaldehyde, and substituted phenols as demonstrated in eq 2. **2**, a structural isomer of **1**, was synthesized by mixing *N*,*N*′-dimethyl-ethylenediamine, 2 equiv of formaldehyde, and 2 equiv of 2,4-di-*tert*-butyl-phenol in methanol, and heating to reflux for 2 h. **2** precipitated as a colorless solid and was isolated in 70% yield.



Upon reaction with tetra(benzyl) zirconium, a sequential $[ONNO]^{2-}$ type ligand may wrap around the metal to afford several possible isomers, as shown in Figure 1.

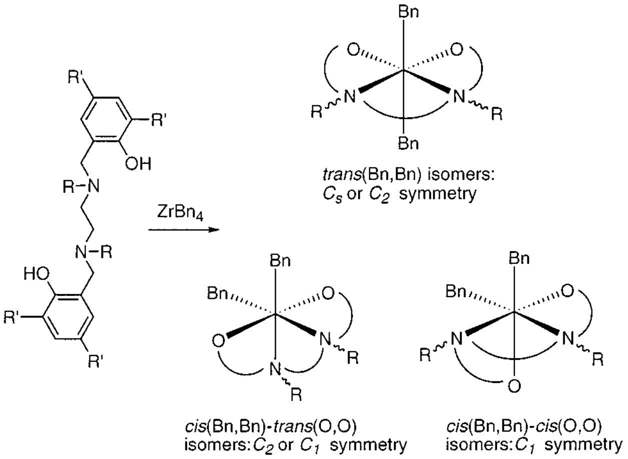


Figure 1.

trans(Bn,Bn) isomers (Figure 1), which are commonly obtained with salen-type ligands,[7] are less desired as catalysts for α-olefin polymerization. Two alternative chelating modes that feature two *cis*-benzyl ligands are the *cis*(Bn,Bn)-*trans*(O,O) mode,[8] which

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may result in either a C_1- or a C_2-symmetrical complex, and the *cis*(Bn,Bn)-*cis*(O,O) mode,[9] leading to C_1-symmetrical complexes (Figure 1). The preferred C_2-symmetrical complex may induce tacticity independently of polymeric chain rearrangement rate,[10a] and may therefore be considered an *ansa*-metallocene analogue.[1]

2 reacted cleanly with 1 equiv of tetra(benzyl) zirconium at 65 °C yielding a single isomer of a dibenzyl zirconium complex [ONNO]ZrBn$_2$, **2a**, quantitatively, as a yellow crystalline solid. The spectral data of **2a** indicated the formation of a C_2-symmetrical complex, evident from the symmetry-related phenolate rings, the symmetry-related benzyl groups, and the three AX spin systems which appear for three CH$_2$ units. The crystallographic analysis indicated that **2a** adopts the desired *cis*(Bn,Bn) C_2-symmetrical structure (Figure 2).

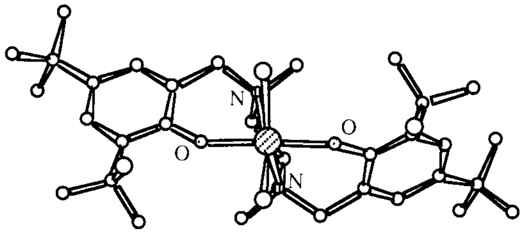
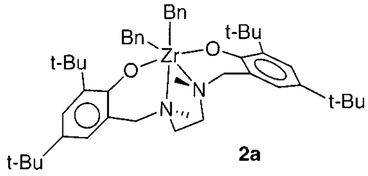


Figure 2. Molecular structure of **2a** exhibiting the C_2 symmetry and cis(Bn,Bn) geometry (one of two molecules in the asymmetric unit shown; H atoms and phenyl groups omitted for clarity). See Supporting Information for complete molecular structure.

The asymmetric unit contains two homochiral molecules of the slightly distorted octahedral complex, and three molecules of toluene. The two nitrogen donors are in a cis configuration, as expected, and the two oxygen atoms of the phenolate rings are in a trans configuration. The cis configuration between the two benzyl groups is evident from the C−Zr−C angle of 110.5°.



2a

Upon activation with tris(pentafluorophenyl)borane, **2a** was found to be an active 1-hexene polymerization catalyst. The addition of 32 μmol of **2a** and 1.1 equiv of B(C$_6$F$_5$)$_3$ to neat 1-hexene at room temperature yielded 300 mg of poly(1-hexene) after 30 min, corresponding to an activity of 18 g mmol$_{\text{cat}}^{-1}$ h^{-1}. Olefinic termination groups were not observed in the ^{1}H NMR spectra, and the polymer obtained had a molecular weight of M_w = 12 000 and a narrow PDI of M_w/M_n = 1.15. The narrow PDI and the linear dependence of the polymer molecular weight on the consumption of the monomer shown in Figure 3 suggest that the polymerization system is living. Furthermore, six narrow singlets in the ^{13}C NMR indicate an isospecific 1-hexene polymerization, affording >95% isotactic poly(1-hexene).[11]

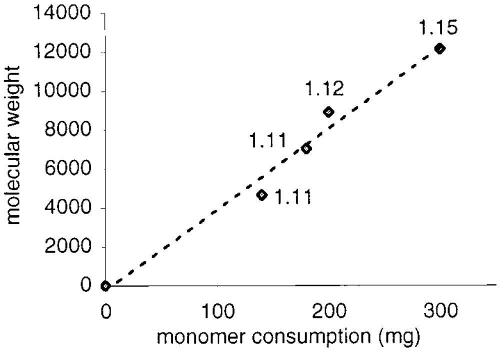


Figure 3. Dependence of polymer weight average molecular weight (M_w) on consumption of monomer (mg) using 32 μmol of **2a** and 1.1 equiv of B(C$_6$F$_5$)$_3$ in 10 mL of neat 1-hexene at room temperature and PDI values.

A possible source of this high isotacticity is the bulk of the *t*-Bu groups which direct the approaching olefin (Figure 2). To evaluate the effect of steric bulk on the tacticity, we synthesized the ligand precursor **3** in a similar manner (eq 1).

3 was obtained by mixing *N,N′*-dimethyl-ethylenediamine, 2 equiv of formaldehyde, and 2 equiv of 2,4-dimethylphenol in methanol, and heating to reflux for 2 h. **3** precipitated as a colorless solid and was isolated in 50% yield.

3 also reacted cleanly with 1 equiv of tetra(benzyl) zirconium at 65 °C yielding the dibenzyl complex [ONNO]ZrBn$_2$, **3a**, quantitatively as a yellow crystalline solid. The spectral data of **3a** indicated the formation of a single isomer having analogous symmetry to **2a**.

Upon activation with tris(pentafluorophenyl)borane, **3a** exhibits a somewhat higher activity in the polymerization of 1-hexene relative to **2a** of 35 g mmol$_{\text{cat}}^{-1}$ h^{-1}, leading to a polymer having a molecular weight of 23 000 and a PDI of M_w/M_n = 1.57. In contrast to the polymer obtained from **2a**, the polymer obtained from **3a** was atactic according to ^{13}C NMR.[11] Thus, the size of the substituents was shown to have a significant influence on the tacticity of the poly(1-hexene) produced using these C_2-symmetrical [ONNO]Zr-type catalysts.

To the best of our knowledge, this novel [ONNO] system is the first nonmetallocene C_2-symmetrical system which is active in isospecific and living polymerization of high-olefins.[10,12] Furthermore, this is a rare example of living polymerization of high-olefins at room temperature. The extreme ease of synthesis of a variety of ligand precursors and the resulting metal complexes make this new family of catalysts a potential alternative to the well-established *ansa*-metallocene family. We are currently studying the parameters responsible for the catalysts polymerization activity, as well as looking for further applications of this ligand family.

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Supporting Information Available: Synthesis and characterization of ligand precursors **2** and **3**, complexes **2a** and **3a**, and poly(1-hexene); crystal data, atomic coordinates and bond lengths and angles for **2a** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] See ^{13}C NMR spectra of isotactic poly(1-hexene) derived from **2a** and atactic poly(1-hexene) derived from **3a** in Supporting Information.

[12] 1-Octene was also polymerized by **2a**/B(C$_6$F$_5$)$_3$, yielding a highly isotactic poly(1-octene).