

Zirconium and Titanium Diamine Bis(phenolate) Catalysts for α -Olefin Polymerization: From Atactic Oligo(1-hexene) to Ultrahigh-Molecular-Weight Isotactic Poly(1-hexene)

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Summary: Aiming at higher activities of group IV diamine bis(phenolate) catalysts in olefin polymerization, ligands containing electron-withdrawing groups have been introduced. The dibenzyl Zr complexes of these ligands lead to highly active 1-hexene catalysts upon activation yielding, however, low-molecular-weight atactic poly(1-hexene). In contrast, the corresponding titanium complexes are highly active and lead to ultrahigh-molecular-weight poly(1-hexene) of different isotacticities, dictated by the size of the phenolate substituents.

Some of the most promising categories of well-defined catalytic systems for polymerization of α -olefins are cyclopentadienyl-free complexes of group IV metals.¹ Remarkable achievements have been made with such catalysts, including the living polymerization of high olefins at ambient temperatures,² the extremely active ethylene polymerization catalysts,³ and the living and syndiotactic polymerization of propylene.⁴ Recently we introduced the diamine bis(phenolate) tetradentate dianionic ligands to group IV metal chemistry.⁵ These ligands wrapped around an octahedral zirconium center in a *fac, fac* mode,⁶ leading to C_2 -symmetrical complexes in which the labile groups were in a *cis* disposition. A dibenzylzirconium complex of a ligand with ortho *t*-Bu substituents on the phenolate rings led to living and isotactic polymerization of 1-hexene at room temperature.^{7,8} The activity of this catalyst was not high: ca. 18 g mmol_{cat}⁻¹ h⁻¹ in neat 1-hexene.⁹ Reducing the bulk of the phenolate substituents (*o*-Me groups) led to loss

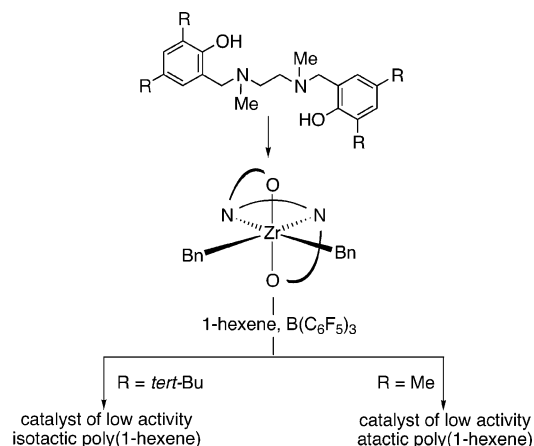


Figure 1. Synthesis, geometry, and activity of zirconium complexes of alkyl-substituted diamine bis(phenolate) ligands.

of the tacticity control, whereas the activity of the zirconium catalyst increased by a mere 2-fold (Figure 1). It therefore seemed that if highly active catalysts inducing tacticity control are desired, electronic effects should be addressed. In this communication we describe our efforts aimed in this direction.

Lig¹H₂, a diamine bis(phenolate) ligand precursor featuring 3,5-dichloro substitution, was synthesized by a Mannich condensation between 2,4-dichlorophenol, *N,N'*-dimethylethylenediamine, and formaldehyde.^{10,11} It reacted cleanly with tetrabenzylzirconium, leading to the corresponding dibenzyl complex Lig¹ZrBn₂, isolated as a yellow solid (for synthetic details and spectroscopic analyses of the ligands and the metal complexes, see the Supporting Information). ¹H NMR characterization supported the formation of a single isomer of C_2 sym-

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(8) A similar ligand design led to an isotactic styrene polymerization catalyst: Cappachione, C.; Proto, A.; Ebeling, H.; Mülhaupt, R.; Möller, K.; Spaniol, T. P.; Okuda, J. *J. Am. Chem. Soc.* **2003**, *125*, 4964.

(9) In comparison, the activity of the isomeric zirconium catalyst of the amine bis(phenolate) ligand bearing a sidearm dimethylamino group is at least 2 orders of magnitude higher: (a) Tshuva, E. Y.; Goldberg, I.; Kol, M.; Goldschmidt, Z. *Organometallics* **2001**, *20*, 3017. (b) Tshuva, E. Y.; Groysman, S.; Goldberg, I.; Kol, M.; Goldschmidt, Z. *Organometallics* **2002**, *21*, 662.

(10) For a general synthetic procedure of diamine bis(phenolate) ligands, see: Tshuva, E. Y.; Gendzeiuk, N.; Kol, M. *Tetrahedron Lett.* **2001**, *42*, 6405.

(11) An aluminum complex of this ligand employed in stereoselective lactide polymerization was described recently: Hornmür, P.; Marshall, E. L.; Gibson, V. C.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **2004**, *126*, 2688.

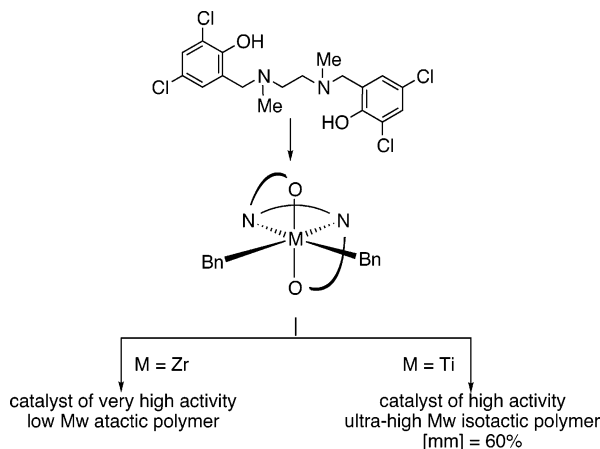


Figure 2. $\text{Lig}^1\text{ZrBn}_2$ vs $\text{Lig}^1\text{TiBn}_2$ catalytic activity.

metry, as apparent from the presence of three AX systems as well as the equivalence of the phenolate rings, the *N*-methyl groups, and the benzyl groups. On the basis of its activity (vide infra) and the structure of the previous zirconium complexes we propose that this complex is of the *fac, fac* geometry.

The addition of 1.2 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$ to 0.02 mmol of $\text{Lig}^1\text{ZrBn}_2$ in 20 mL of 1-hexene at room temperature initiated a fast polymerization reaction, accompanied by substantial warming, and yielded 9.0 g of a sticky product after 5 min. This corresponds to a very high activity of ca. 5400 g $\text{mmol}_{\text{cat}}^{-1} \text{h}^{-1}$. GPC analysis implied a low-molecular-weight polymer of $M_w = 9100 \text{ g mol}^{-1}$ and PDI value of $M_w/M_n = 1.7$ (see the Supporting Information). The broadened polydispersity and the substantial amount of polymer obtained relative to the quantity of catalyst employed and average M_w (corresponding to ca. 50 polymer chains per catalyst unit, assuming a complete activation of the precatalyst) clearly imply a nonliving catalyst under these conditions. This trend did not change when the polymerization was carried out under different conditions.¹² The microstructure of the polymer was investigated by ^{13}C NMR spectroscopy. There are six main peaks corresponding to the six different carbons of the polymer chain. The broadness and pattern of the methylene peaks support an essentially atactic polymer. In addition, peaks attributed to end groups (mostly of the vinylidene type) are observed. The lack of tacticity is consistent with our observation that bulky phenolate substituents are required for stereospecific olefin directing to the active site in these zirconium catalysts (Figure 2).⁵

Thus, we turned to a smaller group IV metal—titanium. The corresponding dibenzyltitanium complex $\text{Lig}^1\text{TiBn}_2$ was obtained by reaction between tetrabenzyltitanium and the ligand precursor. It requires a quick workup due to its apparent instability in solution, yet it is stable for several weeks in the solid state at -35°C . It is obtained in higher than 85% yield, and its ^1H NMR spectrum supports its assignment as the “normal” *fac, fac* geometrical isomer. While X-ray-quality crystals of $\text{Lig}^1\text{TiBn}_2$ have not been obtained yet, the X-ray structure of the analogous dipropoxy complex $\text{Lig}^1\text{Ti}(\text{OPr})_2$

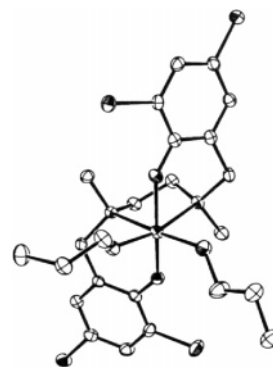


Figure 3. ORTEP representation of $\text{Lig}^1\text{Ti}(\text{OPr})_2$ (40% probability ellipsoids). Selected bond lengths (Å): $\text{Ti1}-\text{O6} = 1.922(2)$, $\text{Ti1}-\text{O7} = 1.900(2)$, $\text{Ti1}-\text{N10} = 2.316(2)$, $\text{Ti1}-\text{N11} = 2.326(2)$.

(OPr)₂ supported the overall wrapping mode of this ligand around titanium.¹³ As expected from the smaller radius of Ti vs Zr, the ligand O—Ti and N—Ti bonds are shorter by 5–8% relative to the Zr complex of the analogous Salan ligand (Figure 3); therefore, the ligand steric influence is expected to be more pronounced.⁵

Activation of $\text{Lig}^1\text{TiBn}_2$ with 1.2 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$ in neat 1-hexene at room temperature led to a highly active catalyst whose average activity was ca. 200 g $\text{mmol}_{\text{cat}}^{-1} \text{h}^{-1}$.¹⁴ The lower activity of $\text{Lig}^1\text{TiBn}_2$ relative to $\text{Lig}^1\text{ZrBn}_2$ is consistent with previous studies concerning the activity of the related amine bis(phenolate) complexes of these two metals.¹⁵ In sharp contrast to the zirconium catalyst, the titanium catalyst leads to ultrahigh-molecular-weight polymers. The polymerization has some living character in its initial stages: following a 20 mL polymerization run of neat 1-hexene by GPC indicated a constant rise of molecular weight as well as constant consumption of the monomer for 40 min and very narrow PDIs. After this period the polymer M_w exceeded 550 000 and the PDI was 1.2. A higher scale polymerization run, which was allowed to continue for a longer period of 19 h at room temperature, led to a polymer of an even higher molecular weight of ca. 1 900 000. At this point the molecular weight distribution had broadened but was still below 2.0. To our knowledge, this is one of the highest molecular weights reported for poly(1-hexene) under ambient pressure.¹⁶ The ^{13}C NMR spectra of these polymer samples (see the Supporting Information) give no evidence for chain end groups (as expected for high-molecular-weight polymers) or for regioerrors. Most importantly, in a clear distinction from the behavior of

(13) Crystal data for $\text{Lig}^1\text{Ti}(\text{O-Pr})_2$: $\text{C}_{24}\text{H}_{32}\text{Cl}_4\text{N}_2\text{O}_4\text{Ti}$, $M_r = 602.22$, monoclinic, space group $P2_1/c$, $a = 9.4100(2) \text{ Å}$, $b = 12.6650(3) \text{ Å}$, $c = 23.3470(5) \text{ Å}$, $V = 2775.63(11) \text{ Å}^3$, $Z = 4$, $D = 1.441 \text{ g/cm}^3$, $\mu = 0.726 \text{ mm}^{-1}$, 6255 independent reflections collected, 4348 unique reflections with $I > 2\sigma(I)$, $R1(I > 2\sigma(I)) = 0.0474$, $wR2(I > 2\sigma(I)) = 0.1138$, $R1(\text{all data}) = 0.0792$, $wR2(\text{all data}) = 0.1297$. Data were collected on a Kappa CCD diffractometer using Mo K α radiation ($\lambda = 0.710 73 \text{ Å}$) at 110 K. For full details concerning crystallographic analysis, see the Supporting Information.

(14) NMR measurements indicate that addition of $\text{B}(\text{C}_6\text{F}_5)_3$ to $\text{Lig}^1\text{TiBn}_2$ in C_6D_6 causes a fast decomposition. We thus propose that the active species is stable only in the presence of a monomer.

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(12) For example: a polymerization run of 5 mL of 1-hexene diluted in 20 mL of chlorobenzene led to a polymer having an M_w value of ca. 6000 and PDI of 1.6 after 60 min at room temperature.

the zirconium complex, the polymer obtained from the titanium catalyst is isotactically enriched. Integration of the peaks corresponding to the C3 carbon gives $[mm]$ of ca. 60% (fitting an enantioselectivity parameter, α , of ca. 0.84),¹⁷ signifying a low-to-medium degree of isospecificity.¹⁸ The relative intensity of the pentads corresponding to C3 (the *mrrm*-pentad peak is higher than the *mmrm*-pentad peak)¹⁸ implies that the mechanism responsible for this stereoselectivity is enantiomorphic site control, rather than chain end control, namely, that the symmetry of the complex is responsible for the microstructure of the polymer and not the last inserted monomeric unit. We propose that the stereoregions arise from enantiofacial misinsertion and not from chain epimerization reactions, since reducing the polymerization temperature to 0 °C did not affect the degree of isotacticity.¹⁹

It therefore appears that the steric bulk of the relatively small chloro substituents becomes significant when the diamine bis(phenolate) ligand wraps around the smaller titanium center. Following this lead, we synthesized Lig²H₂, featuring the bulkier 3,5-dibromo substituents on the phenolate rings, which was reacted with tetrabenzyltitanium to give the dibenzyltitanium complex Lig²TiBn₂. Spectroscopic data indicated that the structure of Lig²TiBn₂ is analogous to that of Lig¹TiBn₂. Its stability resembles that of Lig¹TiBn₂. The activity of Lig²TiBn₂ was found to be closely related to that of Lig¹TiBn₂: namely, a highly active 1-hexene polymerization catalyst (following activation with B(C₆F₅)₃ in the neat monomer at room temperature), having a typical activity of ca. 400 g mmol_{cat}⁻¹ h⁻¹.²⁰ Lig²TiBn₂ led to polymers of even higher molecular weight. Following a 100 mL polymerization run of neat 1-hexene by GPC indicated a constant rise of molecular weight as well as constant consumption of the monomer for 75 min and very narrow PDIs. After this period the polymer's M_w was ca. 1 750 000 and the PDI was 1.2. After 18 h the molecular weight had reached a value of ca. 4 000 000 and the PDI had broadened to 2.9 (probably due to the high viscosity of the polymerization mixture). Gratifyingly, a substantial increase in the stereochemical control (induced by an enantiomorphic

site control mechanism: *mrrm*-pentad peak present; *mmrm*-pentad peak absent) was evident from the ¹³C NMR spectra of these polymer samples: namely, $[mm]$ of ca. 80%, $\alpha = 0.93$ (see the Supporting Information).

To reveal whether the source of the high activity of the catalysts derived from Lig¹TiBn₂ and Lig²TiBn₂ was the reduction in ligand bulk (relative to *t*-Bu) or the metal electron deficiency, the dibenzyltitanium complex of the diamine bis(phenolate) ligand bearing 3,5-dimethyl substituents, Lig³TiBn₂ (the corresponding Zr complex led to atactic polymerization; vide supra),⁵ was synthesized from the corresponding ligand precursor and tetrabenzyltitanium and employed in the polymerization of 1-hexene. The isospecificity of the resulting poly(1-hexene) has improved beyond that of Lig²TiBn₂ ($[mm] = 90\%$, $\alpha = 0.97$), as may be expected for a ligand carrying bulkier methyl substituents relative to bromo substituents. The activity of Lig³TiBn₂ was found to be very low: ca. 3 g mmol_{cat}⁻¹ h⁻¹; namely, the high activity of Lig¹TiBn₂ and Lig²TiBn₂ is derived primarily from their electron deficiency.

In conclusion, group IV complexes of diamine bis(phenolate) ligands prove to be versatile precatalysts for olefin polymerization. Specifically, the combination of electron-withdrawing groups on the phenolate rings that cause an increase in activity and a small titanium center that is sensitive to ligand steric bulk leads to highly active high-olefin polymerization catalysts exhibiting varying degrees of stereocontrol.²¹ These catalysts exhibit a high propagation/termination ratio that leads to polymers of unusually high molecular weights under the ambient conditions employed.²² The development of further catalysts of this family and their applications in olefin polymerization in our laboratories is under way.

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Supporting Information Available: Text, tables, and figures giving synthetic procedures and spectroscopic characterization of the ligand precursors and the metal complexes, ¹³C NMR spectra of typical polymers, and crystallographic data for Lig¹Ti(OPr)₂. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(21) For the significance of producing polypropylene with varying degrees of isotacticity, see: Balboni, D.; Moscardi, G.; Baruzzi, G.; Braga, V.; Camurati, I.; Piemontesi, F.; Resconi, L.; Nifant'ev, I. E.; Venditto, V.; Antirucci, S. *Macromol. Chem. Phys.* **2001**, *202*, 2010 and references cited therein.

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