Organometallics **2004,** *23,* 5291−5299

Diverse Structure−Activity Trends in Amine Bis(phenolate) Titanium Polymerization Catalysts

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Received May 24, 2004

The activity of amine bis(phenolate) Ti dibenzyl complexes in 1-hexene polymerization catalysis as a function of the phenolate substituents was investigated. Two series of Ti complexes carrying either a dimethylamino or a methoxy sidearm donor were prepared and characterized. In each series, the substituents on the phenolate rings were either alkyl groups of varying bulk or electron-withdrawing chloro groups. When activated with a suitable Lewis acid, all precatalysts have shown reactivity toward 1-hexene. Different structure−activity trends were observed in the two series: The activity of the catalysts of the “OMe” series was low to moderate and was almost independent of the phenolate substituents. In contrast, the activity of the “NMe_2” catalysts had a strong dependence on both the steric and electronic character of the phenolate substituents, ranging from mild to highly active. The difference in polymerization activity trends between the two series may be traced back to their different tendency toward misinsertions. A “NMe_2”-Ti complex having Cl groups in the ortho, para positions of the phenolate rings led to the most active catalyst and to a remarkably high-M_w polymer (>4 000 000) obtained within 1 h of polymerization at RT. The characterization of this ultrahigh-M_w *atactic* poly(1-hexene) by means of oscillatory rheometry and stress relaxation experiments indicated typical elastomeric behavior at RT.

Introduction

The recent exploration of group IV cyclopentadienyl-free α-olefin polymerization catalysts has yielded several systems that exhibited polymerization modes and activities unmatched by the traditional metallocene-type catalysts.[1] Some noteworthy examples include the living polymerization of high olefins at ambient temperatures,[2,3] the extremely active ethylene polymerization catalysts,[4] the living and isotactic polymerization of high olefins at RT,[5] and the living and syndiotactic polymerization of propylene.[6] Yet, due to their wide-ranging structures, the parameters responsible for the unique polymerization modes of the Cp-free systems are considerably less established. Deciphering of these parameters can lead to development of catalysts exhibiting new activity modes and consequently to polymeric materials exhibiting desired physical characteristics.

Recently, we introduced the family of amine bis(phenolate) ligands to group IV metals and studied the potential of the resulting complexes as precatalysts for polymerization of α-olefins.[7] The general structure of the ligand precursors $LigH_2$ (including a sidearm donor that was found essential for the formation of active catalysts) is depicted in Figure 1. These tetradentate ligands wrap around group IV metals forming C_s-symmetrical octahedral complexes in which the two labile groups (most commonly alkyl groups) are forced into a *cis* relationship, as required from an olefin polymerization precatalyst. All the ligands employed in group IV chemistry carried bulky (*t*-Bu) ortho substituents on the phenolate rings.[8]

Following activation with a strong Lewis acid such as tris(pentafluorophenyl)borane, the amine bis(pheno-

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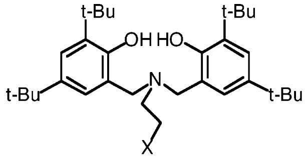
10.1021/om049630q CCC: $27.50



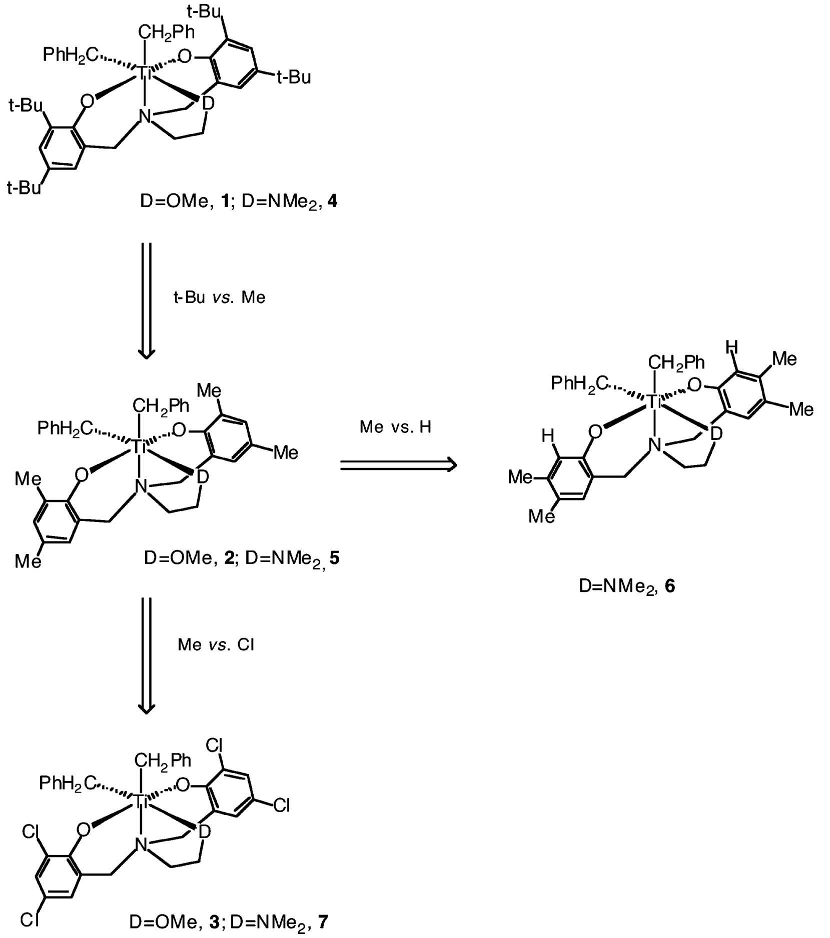
X=NMe_2, NEt_2, py, OMe, THF, furan, SMe

Figure 1. Amine bis(phenolate) ligand precursors carrying t-Bu substituents on the phenolate rings and varying sidearm donors D.

late) dialkyl complexes led to α-olefin polymerization catalysts whose activity, revealed thus far, depended mostly on the nature of the metal atom, with the following general order: Zr ≥ Hf ≫ Ti.[9] The most active Zr-based catalysts were derived from ligands bearing "strong" sidearm donors, such as OMe (ca. 50 000 g_{pol} $mmol_{cat}^{-1}$ h^{-1}), NMe_2, and THF (ca. 20 000 g_{pol} $mmol_{cat}^{-1}$ h^{-1} each).[7d,f] Typically, the molecular weight of the resulting poly(1-hexene) samples was around 100 000 g mol^{-1}, and the PDI was around 2.0.[7c,d,f] Employing the same ligands in titanium chemistry led to moderately active catalysts (10−35 g_{pol} $mmol_{cat}^{-1}$ h^{-1}),[7b,e,f] which exhibited, however, a living character for prolonged periods of time (up to several days)[7e,f] at room temperature, leading, in certain cases, to very high molecular weight polymers (up to 1 000 000 g mol^{-1}) and block copolymers. Looking for new structure−activity relationships and, possibly, discovering catalysts that would exhibit new activity modes, we turned to explore the influence of the phenolate substituents on the activity of titanium catalysts, namely, those expected to be affected mostly by steric influence. The effect of electron-withdrawing substituents on the polymerization activity was explored as well. Herein we describe two series of tetradentate amine bis(phenolate) ligand precursors (each having a specific sidearm donor), their respective dibenzyltitanium complexes, and their activity in polymerization of 1-hexene. We show that, unexpectedly, the activity of the complexes belonging to one of the series is almost uniform, whereas the activity of the complexes of the second series varies dramatically as a function of phenolate substituents. One such catalyst led to unprecedented high molecular weight polymer (under ambient conditions) that exhibited elastomeric properties.

Results

Synthesis and Structure. The dibenzyl titanium complexes of the ligands employed in this study are outlined in Figure 2. They are divided into two series, each featuring a different "strong" sidearm donor, i.e., either a dimethylamino or a methoxy group. Each series allows the estimation of steric effects on the resulting catalyst's reactivity, through a gradual decrease in the phenolate (ortho) substituents' size, and of electronic effects by the introduction of electron-withdrawing chloro groups. The synthesis and reactivity of the most sterically congested members of each series (**1** and **4**) that led to living polymerization catalysts at room temperature were described previously.[7b,c] All ligand



D=OMe, **1**; D=NMe_2, **4**

D=OMe, **2**; D=NMe_2, **5**

D=NMe_2, **6**

D=OMe, **3**; D=NMe_2, **7**

Figure 2. Dibenzylamine bis(phenolate) Ti(IV) complexes **1**−**7**.

Scheme 1

$$\mathrm{Lig^{X}H_2} \xrightarrow[\text{- 2 toluene}]{\mathrm{Ti(benzyl)_4}} \text{complex } \mathbf{X}$$

precursors were prepared by a Mannich condensation between the corresponding phenol, amine, and formaldehyde.[7b,e,8b]

The dibenzyl titanium complexes **1**−**7** were prepared by a straightforward toluene-elimination reaction of the ligand precursors with tetrabenzyltitanium as shown in Scheme 1. This reaction is of high yield and takes place readily when both reagents are mixed in toluene at RT. Employing this route generally eliminates the need for recrystallization and leads to sufficiently pure complexes following pentane washings of the crude products. All complexes were found to possess C_s-symmetry on the NMR time scale, according to the symmetry-related phenolate rings, distinct benzyl ligands, and AB pattern for the ligand benzyl protons.

The X-ray structures of complexes **1** and **4** were previously described.[7b,e] We carried out X-ray structure determinations for complexes **2**, **3**, **6**, and **7** (see Figures 3−6, and Supporting Information for the crystal structure data). These structures are closely related to each other and to previous structures of this family of ligands with group IV metals.[7] All complexes feature hexacoordinate titanium centers with the sidearm donor firmly attached. The phenolate oxygens are located mutually *trans*. The Ti−OPh bond lengths and the corresponding Ti−O−C(Ph) bond angles are common for the amine bis(phenolate) Ti complexes, lying in the narrow ranges of 1.851−1.875 Å and 143−146°, respectively. All benzyl ligands are coordinated to the metal in the usual η^1 fashion (105−117°), with the narrowest angle (105°) found for the "axial" benzyl group in the least sterically hindered complex **6** (ortho-H phenolate substituents). In complex **2** the "axial" benzyl ligand twists sideways and seems to undergo a CH-π interaction with the ortho-Me group on one of the phenolate rings.

The Ti−D bonds (D = sidearm donor) deserve special attention since their presence and strength were shown to be essential for olefin polymerization catalysis in the amine bis(phenolate) series. We have previously reported the solid-state structures of the dibenzyl complexes of the entire group IV triad with Lig^1 (OMe) and Lig^4 (NMe_2) ligands (the Ti structure with Lig^4 was of low quality).[7b−e] Very narrow ranges of M−D bond distances were observed in both series: M−O bond distances of 2.43−2.46 Å for the "OMe"-type complexes and M−N bond distances of 2.54−2.59 Å for the "NMe_2"-type complexes. The reduction of steric repulsion by replacement of the bulky t-Bu groups with smaller Me or H groups causes the Ti−NMe_2 bond lengths to contract (2.451 and 2.466 Å in **6** and **7**, respectively). Notably, the complexes of the "OMe" set present a dual behavior. No bond contraction is detected in **3** vs **1** (2.457 Å in **3** vs 2.433 Å for **1**), possibly due to the already low steric congestion in **1**: a methoxy group bears a *single* methyl substituent that experiences a small steric interaction with the t-Bu groups in **1** (and in the analogous Zr and Hf complexes). In contrast, **2** features a significantly shorter Ti−OMe bond length, which may result from the different arrangement of the "axial" benzyl ligand (see Figure 3 for details).

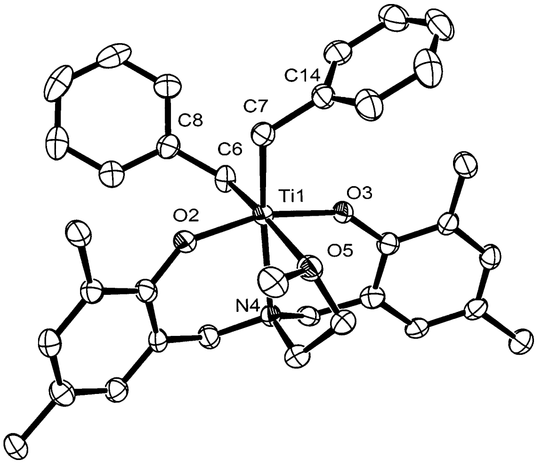


Figure 3. ORTEP representation of **2** (50% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Ti1−O2 1.856(3), Ti1−O3 1.854(3), Ti1−N4 2.385(3), Ti1−O5 2.339(3), Ti1−C6 2.129(4), Ti1−C7 2.128(4), O2−Ti1−O3 162.14(11), C6−Ti1−O5 173.46(13), C20−O2−Ti1 144.5(2), C36−O3−Ti1 145.4(2), C8−C6−Ti1 120.3(3), C14−C7−Ti1 120.7(3).

Reactivity in 1-Hexene Polymerization: "OMe" Series. Activation of **1** with $B(C_6F_5)_3$ at RT led to polymerization of 1-hexene that remained living for more than 24 h.[7e] The activity of this catalyst was moderate: 20−35 g_{pol} $mmol_{cat}^{-1}$ h^{-1}. Activation of deep red **2** in neat 1-hexene led to a similar low to moderate activity of 15−20 g_{pol} $mmol_{cat}^{-1}$ h^{-1}. In common with **1**, the less sterically congested **2** was active for a long period of time. However, in contrast to **1**, **2** does not promote a prolonged living polymerization, as revealed from the PDI values that are narrow (1.1−1.2) only in the first hour of the reaction (Table 1). Activation of the yellow-orange **3** with $B(C_6F_5)_3$ resulted in only slightly more active 1-hexene polymerization catalyst (34−44 g polymer $mmol_{cat}^{-1}$ h^{-1}). After 60 min the polymerization reaction yields poly(1-hexene) of M_w = 38 000 and PDI = 1.4 (Table 1). Thus, it appears that, surprisingly, neither steric nor electronic modification of the "OMe"-type ligands leads to any pronounced activity enhancement of the resulting polymerization catalysts, while the living character is lost, apparently due to an increase in the termination/propagation ratio.

The ^{13}C NMR spectra of the resulting polymers indicated that they are atactic, as expected to result from these C_s-symmetrical catalysts. The regioregularity aspect was more revealing. All the poly(1-hexene) samples derived from the catalysts of this series exhibited additional peaks at the ranges of 34.9−38.1 and 30.2−30.7 ppm that were previously reported to be indicative of regioirregular poly(1-hexene).[10] According to a DEPT-135 spectrum, the peaks at 34.9−35.9 and at 36.6−38.1 are CH-type carbons, while the peak at 30.2−30.7 ppm represents a CH_2-type carbon. An additional CH_2 peak, of relatively low intensity (ca. 20%

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(8) (a) A ligand bearing ortho Me groups led to a mixture of a bis(homoleptic) complex alongside the desired complex, see ref 7c. (b) The bulky t-Bu groups inhibited the reaction of the ligand precursors with pentabenzyltantalum, see: Groysman, S.; Goldberg, I.; Kol, M.; Genizi, E.; Goldschmidt, Z. *Organometallics* **2004**, *23*, 1880.

(9) Exceptionally, a hafnium catalyst based on a ligand bearing an −SMe sidearm donor was more active than its zirconium analogue; see ref 7d.

Table 1. Selected Polymerization Data for 2 and 3

no.	precat. (μmol)	$B(C_6F_5)_3$, μmol	1-hexene, g	polym. time, min[a]	polymer obtained, g	activity[b]	conversion, %	M_w	PDI
1	**2** (17)	28	3.37	20	0.081	14	2	7400	1.13
				60	0.261	15	8	17 300	1.18
				120	0.524	15	17	29 800	1.24
2	**2** (17)	17	26.92	48	*c*	*c*	*c*	20 300	1.09
				177	0.806	16	3	46 600	1.41
				240	1.448	21	5	43 700	1.62
				1522	6.860	16	26	54 000	1.98
3	**3** (14)	25	3.37	20	0.160	34	5	17 200	1.13
				60	0.572	41	17	38 200	1.36
				120	1.236	44	37	77 800	1.52

[a] Values represent aliquots taken out at the specified time in polymerization runs 1−3. [b] $g_{pol}\ mmol_{cat}^{-1}\ h^{-1}$. [c] The weight of the resulting polymer was too low to be determined precisely.

Table 2. Selected Polymerization Data in the “NMe_2” Series

no.	precat. (μmol)	$B(C_6F_5)_3$, μmol	1-hexene, g/ClPh, g	polym. time, min	polymer obtained, g	activity[a]	conversion, %	M_w	PDI
1[b]	**5** (14)	19	neat, 3.36	7.0	2.35	1,400	70	37,000	10.3
2	**5** (10)	15	4.04/26.57	12.5[c]	1.34	620	33	45,000	1.3
				26.5[c]	2.86	630	71	35,000	2.3
				52.3[c]	4.1	470	∼100	26,000	3.2
3[b]	**6** (12)	29	neat, 3.36	6.2	1.84	1,500	55	24,000	2.5
4	**6** (17)	17	4.04/26.57	15.0[d]	0.82	190	2	40,000	1.4
				28.0[d]	1.15	140	28	52,000	1.5
				52.0[d]	1.64	110	41	51,000	1.8
5[b]	**7** (12)	29	neat, 3.40	1.0	1.18	5,900	35	330,000	2.0
6[b]	**7** (15)	23	neat, 13.60	2.7	4.20	6,200	31	1,140,000	1.8[e]

[a] $g_{pol}\ mmol_{cat}^{-1}\ h^{-1}$. [b] A typical polymerization out of at least 3 runs. [c] Aliquots taken in run 2. [d] Aliquots taken in run 4. [e] Bimodal MWD.

compared to the peak at 30.2−30.7), is found at 35.9−36.6 ppm. On the basis of these data and the previous reports, we assigned the absorptions at 34.9−35.9 and at 36.6−38.1 to misinserted C2 carbons of H−H and T−T linkages (H = Head = C2; T = Tail = C1), while the large peak at ca. 30.2−30.7 was assigned as a regioirregular C1 carbon of a T−T linkage type. The degree of misinsertions could be estimated by integration of the irregular C1 peak relative to the “normal” (H−T) C1 peak (ca. 40.6 ppm).[10] Significantly, the extent of regioregularity was found to decrease as the bulk of the phenolate substituents decreased. The bulkiest precatalyst of this series, **1**, led to an almost regioregular poly(1-hexene), exhibiting ca. 4% misinsertions. However, the less bulky **2** and **3** led to a significantly higher number of regioerrors, with ca. 16% and 20% misinsertions, respectively.

Reactivity in 1-Hexene Polymerization: “NMe_2” Series. As previously described, activation of the sterically congested precatalyst **4** with $B(C_6F_5)_3$ led to a moderate activity of 30 $g_{pol}\ mmol_{cat}^{-1}\ h^{-1}$.[7b] A 30 min polymerization run led to poly(1-hexene) having M_w of several tens of thousands and a narrow PDI consistent with living polymerization. However, in a stark diversion from the almost uniform activity of the “OMe”-type catalysts, the less sterically congested complex **5** exhibits a dramatically higher activity. Following activation by $B(C_6F_5)_3$ its polymerization activity approached 1400 $g_{pol}\ mmol_{cat}^{-1}\ h^{-1}$, namely, an almost 2 orders of magnitude higher activity in comparison to **4** (Table 2). The fast polymerization caused the monomer to boil in the reaction vessel while being almost completely consumed. This is the first time a titanium catalyst of this family showed such a high activity, previously observed only for the Zr/Hf catalysts. In contrast to the Zr catalysts, **5**/$B(C_6F_5)_3$ yielded poly(1-hexene) of broad molecular weight distribution (PDI values of ca. 10; M_w = 30 000−40 000), possibly due to its lower thermal stability under these harsh conditions. Dilution of the monomer with chlorobenzene slowed the temperature rise, and consequently the PDI values narrowed to around 2, while the catalyst's activity decreased to ca. 600 $g_{pol}\ mmol_{cat}^{-1}\ h^{-1}$.

Interestingly, a further drop in steric congestion (Me to H ortho-substituents on the phenolate rings) caused only a minor increase in activity of the catalyst. Thus, following activation with $B(C_6F_5)_3$, red-brown **6** led to a highly active 1-hexene polymerization catalyst, with an activity of 1400−1900 $g_{pol}\ mmol_{cat}^{-1}\ h^{-1}$. The resulting polymer had a M_w of 40 000−50 000 and a broad molecular weight distribution. When the polymerization is performed in chlorobenzene, the polymer obtained has narrower PDI values (1.7−2.0), thereby supporting the single-site nature of the catalyst.

As a second diversion from the “OMe”-type catalysts, electronic factors were found to affect the reactivity of the “NMe_2”-type catalysts even more dramatically. Upon activation, purple-brown **7** led to a polymerization catalyst, whose activity (6000−8000 $g_{pol}\ mmol_{cat}^{-1}\ h^{-1}$) approaches that of the Zr catalysts of this family.[7c,d] As a matter of fact, this is one of the highest activities reported for 1-hexene polymerization by Cp-free Ti catalysts and is comparable to the activities of titanocenes[11] and constrained-geometry titanium catalysts.[12]

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Table 3. Large-Scale Polymerization with 7/$B(C_6F_5)_3$ (7, 4 μmol; $B(C_6F_5)_3$, 10 μmol; 1-hexene, 104 mL)

time (min)	polymer weight (g)	activity[a]	M_w	PDI
5	0.405	1200	660 000	1.5
10	0.693	1000	1 330 000	1.5
15	1.086	1100	1 930 000	1.6
20	1.857	1400	2 670 000	2.1
30	2.161	1100	3 200 000	2.7
40	2.572	1000	3 560 000	1.8
60	n.d.	n.d.	4 170 000	1.9
80	6.000	1100	4 340 000	2.0
120	8.748	1100	4 340 000	2.5

[a] g_{pol} $mmol_{cat}^{-1}$ h^{-1}.

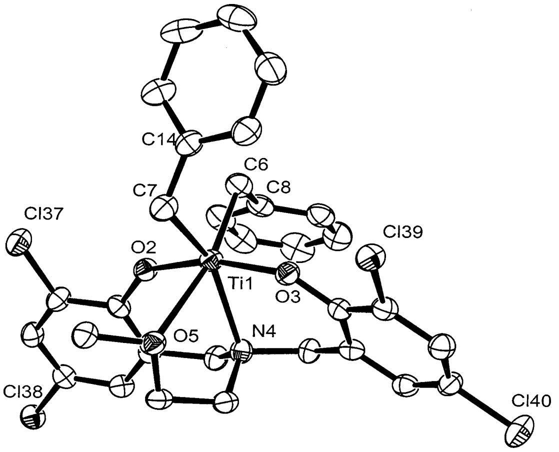

Figure 4. ORTEP representation of **3** (50% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Ti–O2 1.856(2), Ti1–O3 1.875(2), Ti1–N4 2.374(3), Ti1–O5 2.457(2), Ti1–C6 2.120(3), Ti1–C7 2.149(3), O2–Ti1–O3 162.8(1), C6–Ti1–O5 167.5(1), C20–O2–Ti1 144.5(2), C36–O3–Ti1 144.9(2), C8–C6–Ti1 108.7(2), C14–C7–Ti1 117.0(2).

Yet, the most unique feature of this catalytic system is the very high propagation-to-termination ratio, affording poly(1-hexene) of unusually high molecular weight. Relatively small-scale experiments (molar ratio ca. 3000/1 1-hexene/**7**) led to polymers having M_w values of several hundreds of thousands within 1 min and higher than 1 000 000 within 2.7 min. In larger-scale polymerization experiments, even though some reduction in catalytic activity was observed (to ca. 1000–2500 g_{pol} $mmol_{cat}^{-1}$ h^{-1}), polymers with even higher molecular weights of several millions were obtained. Thus, the combination of high activity and negligible termination resulted in an ultrahigh molecular weight polymer with a M_w value of more than 4 000 000, within less than 1 h (Table 3, Figure 7). To our knowledge, this is the highest M_w poly(1-hexene) ever prepared at RT under atmospheric pressure. It is also the highest M_w atactic poly(1-hexene) ever prepared under any conditions.

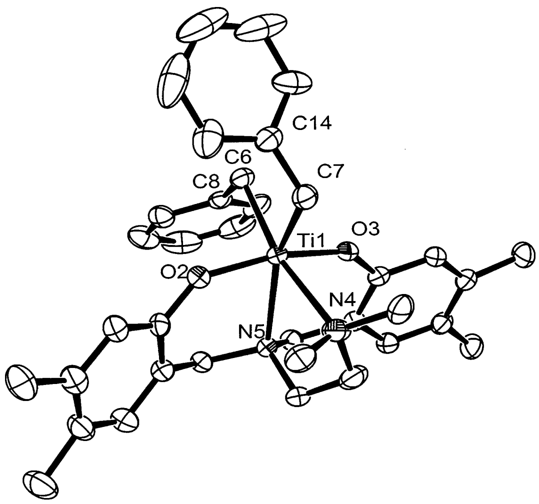

Figure 5. ORTEP representation of 6 (50% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Ti1–O2 1.851(2), Ti1–O3 1.852(2), Ti1–N4 2.451(3), Ti1–N5 2.437(2), Ti1–C6 2.153(3), Ti1–C7 2.174(3), O2–Ti1–O3 162.56(10), C6–Ti1–N4 166.32(11), C20–O2–Ti1 143.2(2), C37–O3–Ti1 146.17(19), C8–C6–Ti1 104.56(19), C14–C7–Ti1 120.5(2).

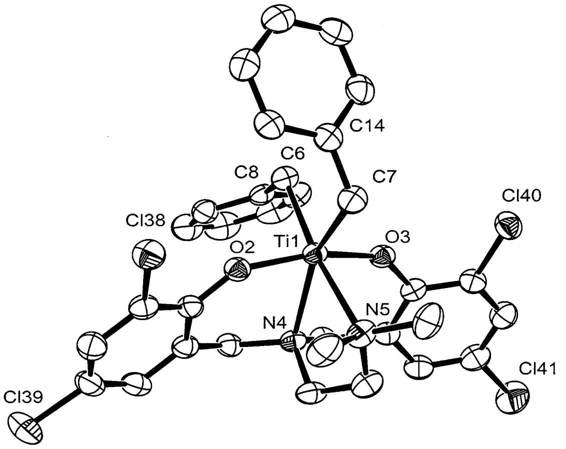

Figure 6. ORTEP representation of **7** (50% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Ti1–O2 1.857(2), Ti1–O3 1.864(2), Ti1–N4 2.414(2), Ti1–N5 2.466(2), Ti1–C6 2.154(3), Ti1–C7 2.175(3), O2–Ti1–O3 162.26(8), C6–Ti1–N5 170.08(9), C20–O2–Ti1 145.7 (2), C37–O3–Ti1 143.47(18), C8–C6–Ti1 109.1(2), C14–C7–Ti1 117.3(2).

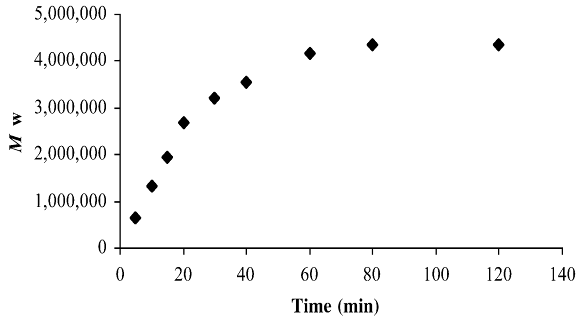

Figure 7. M_w evolution in the large-scale polymerization with **7**/$B(C_6F_5)_3$.

The ^{13}C NMR spectra of the polymer samples resulting from this series of catalysts revealed valuable information, especially when compared to the spectra of the polymers resulting from the "OMe"-type catalysts. As expected, all polymers were atactic. On the other hand, the degree of regioregularity induction was much higher for the "NMe$_2$"-type catalysts. Bulky **4** yielded essentially regioregular poly(1-hexene) (misinsertions < 1%). The reduction in steric bulk led to some regioirregularity; however, its extent was much lower than that observed for the "OMe"-type catalysts. Thus the

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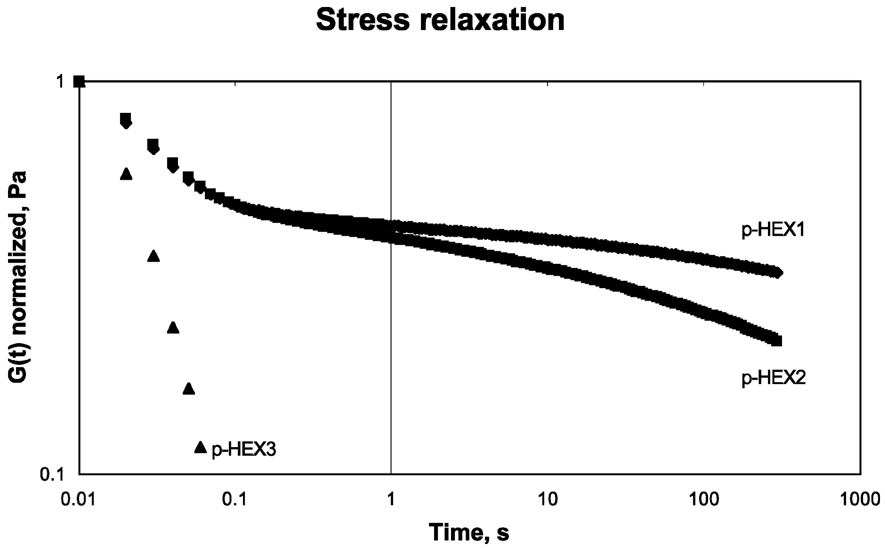

Figure 8. Stress relaxation plot for the p-HEX1, p-HEX2, and p-HEX3 samples.

polymer samples produced by catalysts **5**−**7** exhibited rather similar microstructures, with only 4−5% misinsertions, giving rise to a highly regioregular poly(1-hexene).

Characterization of the Ultrahigh M_w Polymer. The ultrahigh M_w polymer samples produced by complex **7** have the appearance of a solid elastomer rather than that of a sticky oil, typical of lower M_w atactic poly(1-hexene). The viscoelastic properties of two high-M_w samples (p-HEX1, M_w = 4 300 000, PDI = 2.5; p-HEX2, M_w = 1 500 000, PDI = 2.0) were characterized and compared with those of a low-M_w sample (p-HEX3 M_w = 50 000), produced by a Zr catalyst of this family.[7c] The loss modulus $G''(\omega)$ dependence (going through the minimum) and the storage modulus $G'(\omega)$ dependence (going through the plateau) of p-HEX1 and p-HEX2, measured in oscillatory tests, are typical of rubbery polymers having high-M_w and low PDI.[13] For both materials in the temperature range 296−463 K, $G''(\omega)$ was found to be lower than $G'(\omega)$, indicating that the elasticity dominates the rheological behavior of these polymers. For p-HEX3, on the contrary, $G'(\omega)$ is lower than $G''(\omega)$ even at room temperature, indicating a typical liquidlike behavior. To directly compare the viscoelastic properties of the high molecular weight p-HEX1 and p-HEX2 with those of the regular p-HEX3, stress relaxation experiments were performed at 296 K. Since the concept of a relaxation modulus $G(t)$ applies to liquids as well as to solids, it is well suited for this comparison. Figure 8 displays the normalized $G(t)$ curves for all three polymer samples. The relaxation modulus of p-HEX3 drops very fast to zero, showing a behavior typical of non-crosslinked and nonentangled polymer melts. For the high molecular weight samples p-HEX1 and p-HEX2, an initial fast relaxation is followed by a plateau zone in which the modulus decrease is very slow, and then the second drop occurs at substantially long times. The existence of a plateau for p-HEX1 and p-HEX2 is characteristic of polymers in the rubbery state and implies the presence of entanglements. The plateau moduli G_p and $G_p(t)$ were determined for p-HEX1 and p-HEX2 from both oscillatory and relaxation experiments,[14] and the entanglement molecular weights M_e were calculated. Notably, the M_e value obtained for both polymers was ca. 27 000, which is markedly different from the predicted value of 12 100 recently reported.[15,16] The full characterization of this material will be published elsewhere.

Discussion

This work further establishes that amine bis(phenolate) ligands bind in a uniform and rigid manner to early transition metals as apparent from spectroscopic and solid-state data. Variation of structural parameters such as phenolate ring substituents does not alter the overall binding of the ligand core to the metal and has only a minor effect on bond lengths and angles. Yet, as this and previous studies on these systems have shown, these minor structural changes have a major effect on reactivity, leading to a broad variety of olefin polymerization catalysts.

Contrary to our initial expectations, the dependence of activity on steric and electronic factors obeys a different trend for the two series of complexes: a strong dependence for the "NMe_2"-type catalysts and an almost negligible dependence for the "OMe"-type catalysts. The behavior of the "NMe_2"-type catalysts is more in line with our predictions. Comparing the low activity of **4** to the high activity of its zirconium analogue, we may assume that it is caused by steric congestion. Thus, the reduction of steric bulk by replacement of t-Bu groups with Me groups (**4** to **5**) indeed leads to a dramatic activity enhancement. An observed $Ti-NMe_2$ bond contraction supports the notion of strain relief at the metal center. Notably, the polymerization modes of **5**/$B(C_6F_5)_3$ and **6**/$B(C_6F_5)_3$ are very similar, indicating that "opening" the catalytic site beyond a certain value does not have a considerable effect on reactivity. However, **7**/$B(C_6F_5)_3$, carrying Cl substituents, exhibits a different behavior in terms of propagation vs termination rates and stability of the catalyst. In addition, the Cl substituents lead to a further increase in activity relative to the catalysts bearing small alkyl groups. Thus, the "positive" effect of the Cl substituents in the ortho and para positions of the phenolate rings should be assigned to their electron-withdrawing nature. A similar activity enhancement following introduction of electron-withdrawing F groups was reported for the phenoxyimine Ti catalysts.[17] In contrast, electron-withdrawing Cl or F substituents in the diamido/donor Zr/Hf complexes had a negative effect on the polymerization behavior by decreasing polymerization rate and increasing termination (β-hydride elimination), thus producing shorter polymeric chains.[18]

With the trend of the "NMe_2"-type catalysts in mind, the source of the indifference of the "OMe"-type catalysts to electronic and steric effects is at first glance unclear. Especially, the low activity of all the titanium catalysts of the "OMe"-type stands in sharp contrast to the extremely high activity of the zirconium and hafnium catalysts of this series. A possible explanation for this unexpected behavior is the unusually high ratio of regioerrors occurring in this series of catalysts, as observed in the ^{13}C NMR spectra. A misinsertion is expected to lower the rate of the following insertion step, by blocking the metal center.[19] Thus, the expected increase in insertion rate as the bulk of the phenolate substituents is reduced is compensated by the increased degree of regioerrors reducing the insertion rate. Altogether, a uniform behavior is observed along this series.

A further outcome of the current work is the insight into the requirements for living polymerization in this system. In both series of catalysts, only the members bearing t-Bu groups, namely, **4**/$B(C_6F_5)_3$ and **1**/$B(C_6F_5)_3$, led to living polymerization. Providing a more open metal center in both series led to acceleration of the termination processes even when the polymerization was run under conditions wherein the heat release was quenched. Thus, as previously observed for other systems,[2,5,7] steric crowding at the metal center seems to be an important requirement for living polymerization catalysis.

Conclusions

This work demonstrates that although the effects of structural parameters on reactivity are difficult to predict, highly successful catalysts of the amine bis(phenolate) family may be obtained. Such a catalyst featuring high activity and low termination allowed the preparation of ultrahigh-M_w poly(1-hexene) within a short time under ambient conditions. This work gives further evidence for the potential of Cp-free catalysts for production of specialty polymers not accessible by classical Ziegler–Natta or metallocene catalysts. We are currently exploring other types of polymerization employing these catalysts.

Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry nitrogen in a nitrogen-filled glovebox. Ether was purified by reflux and distillation under dry argon atmosphere from Na/benzophenone. Pentane was washed with HNO_3/H_2SO_4 prior to distillation from Na/benzophenone/tetraglyme. Toluene was refluxed over Na and distilled. Benzylmagnesium chloride, 1-hexene, and chlorobenzene were purchased from Aldrich Inc. Tris(pentafluorophenyl)borane was obtained from Strem Chemicals Inc. 1-Hexene and chlorobenzene were passed through activated alumina prior to use. Titanium tetrabenzyl was synthesized according to published procedures[20] and used shortly after its synthesis. The ligand precursors Lig^1H_2, Lig^2H_2, and Lig^4H_2–Lig^7H_2were prepared as previously described.[7c,8b] The preparation of complexes **1** and **4** was previously described.[7b,c]

NMR data of metal complexes were recorded on Bruker AC-200 and Bruker Avance AC-400 spectrometers and referenced to protio impurities in benzene-d_6 (δ 7.15) and to the ^{13}C chemical shift of benzene (δ 128.70). ^{13}C NMR data of poly(1-hexene) samples were recorded on a Bruker AM-500B spectrometer in $CDCl_3$ at 300 K and referenced to $CDCl_3$ (77.16 ppm). Scanned copies of all (7) ^{13}C NMR spectra discussed in the text may be found in the Supporting Information.

Elemental analyses were performed in the microanalytical laboratory of the Hebrew University in Jerusalem. The metal complexes were analyzed within a few hours of being taken out of the freezer of the glovebox. Though showing good H/N percentage, the analyzed complexes consistently showed low carbon percentage. This may stem from their extreme air-sensitivity, leading to an immediate hydrolysis upon contact with air.

The molecular weight of the poly(1-hexene) samples was determined by gel permeation chromatography (GPC) relative to polystyrene standards using tetrahydrofuran (HPLC grade, distilled and filtered under vacuum prior to use) as the eluting solvent and TSKgel GMHHR-M, TSKgel G 5000 HHR, and PSS SDV 10^8 Å columns set on a Jasco instrument equipped with a refractive index detector.

The X-ray diffraction measurements were performed on a Nonius Kappa CCD diffractometer system, using Mo Kα (λ = 0.7107 Å radiation). The analyzed crystals were embedded within a drop of viscous oil and freeze-cooled to ca. 110 K. The structures were solved by a combination of direct methods and Fourier techniques using SIR-92 software[21] and were refined by full-matrix least squares with SHELXL-97.[22] The crystal and experimental data are summarized in Table 4.

Polymer densities were measured at 296 K by means of hydrostatic weighing in ethanol. Storage $G'(\omega)$, loss $G''(\omega)$ and relaxation $G(t)$ shear moduli were measured using an ARES mechanical spectrometer (ex Rheometric) with a parallel plate geometry 25 mm in diameter. All poly(1-hexene) samples were studied under nitrogen atmosphere to prevent possible thermooxidative destruction of these unstabilized polymers.

Synthesis of Lig^3H_2 (2,2′-[[(2-Methoxyethyll)imino]bis(methylene)]bis(4,6-dichlorophenol)). A solution of 2,4-dichlorophenol (6.0 g, 36.7 mmol), (2-methoxy)ethylamine (0.901 g, 12 mmol), and 36% aqueous formaldehyde (2.1 mL, 24.4 mmol) in methanol (10 mL) was stirred and refluxed for 48 h. Upon cooling, the reaction mixture separated into two

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[15] (a) Entanglement molecular weights M_e were estimated from the measured plateau modulus values using the equation $M_e = \rho RT/G_p$; see ref 13. (b) In addition, M_e can be estimated from the absolute value of $G(t)$ in the plateau zone $G_p(t)$ using a similar equation: $M_e = \rho RT/G_p(t)$; see: Dealy, J.; Wissbrun, K. *Melt Rheology And Its Role in Plastics Processing;* Van Nostrand Reinhold: New York, 1990.

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Table 4. Crystallographic Data for 2, 3, 6, and 7

	2	**3**	**6**	**7**
formula	$C_{35}H_{41}NO_3Ti$	$C_{31}H_{29}Cl_4NO_3Ti$	$C_{36}H_{44}N_2O_2Ti$	$C_{32}H_{32}N_2O_2Ti{\cdot}C_4H_8O$
fw	571.59	653.25	584.63	740.42
a (Å)	11.1230(4)	13.9020(8)	8.8780(2)	10.3640(2)
b (Å)	13.5580(4)	12.2160(8)	11.5040(3)	17.5590(6)
c (Å)	19.8870(7)	17.3030(8)	16.2040(6)	20.3320(6)
α (deg)	90.00	90.00	90.050(1)	90.00
β (deg)	90.00	95.005(4)	96.651(1)	93.738(2)
γ (deg)	90.00	90.00	105.940(2)	90.00
cryst syst	orthorombic	monoclinic	triclinic	monoclinic
space group	$P2_12_12_1$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
V (Å^3)	2999.1(2)	2927.3(3)	1579.69(8)	3692.2(2)
D_c (g cm^{-1})	1.266	1.482	1.229	1.332
μ (cm^{-1})	0.321	0.692	0.305	0.558
Z	4	4	2	4
no. of measd reflns	5257	6947	6985	8858
no. of reflns [$I > 2\sigma(I)$]	4010	4273	4688	5623
R_1 [$I > 2\sigma(I)$]	0.0567	0.0613	0.0657	0.0541
wR_2 [$I > 2\sigma(I)$]	0.1016	1.1199	0.1601	0.1253
GOF	1.012	1.016	1.025	1.018

phases. The upper phase was decanted, and the remaining heavy oil containing the product, excess phenol, and the corresponding benzoxazine was triturated with cold methanol to give colorless crystals of the product (1.2 g, 28% yield). The filtrate was concentrated and left at room temperature for ca. 2 months, during which further crystals of the product had formed, increasing the reaction yield to a total of 60%. Mp: 115−116 °C (methanol). Anal. Calc for $C_{17}H_{17}NO_3$ (425.13): C, 48.03; H, 4.03; N, 3.29; Cl, 33.36. Found: C, 48.13; H, 4.02; N, 3.19; Cl, 33.13. ^{1}H NMR ($CDCl_3$): δ 8.09 (2H, bs), 7.27 (d, J = 2.5 Hz, 2H), 6.98 (d, J = 2.5 Hz, 2H); 3.81 (s, 4H), 3.61 (t, J = 5.0 Hz, 2H), 3.41 (s, 3H), 2.76 (t, J = 5.0 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 150.83 (2*C*), 128.82 (2*C*H), 128.46 (2*C*H), 124.49 (2*C*), 124.13 (2C), 121.58 (2*C*), 70.18 (2*C*H_2), 58.94 (*C*H_3), 55.78 (*C*H_2), 55.54, (*C*H_2). HRMS (DCI−CH_4): 424.0060 ($C_{17}H_{18}Cl_4NO_3$)(MH^+) (^{35}Cl).

Preparation of Complex 2. To a stirring dark red solution of $Ti(CH_2Ph)_4$ (35 mg, 0.085 mmol) in 1 mL of toluene was added dropwise Lig^2H_2 (26 mg, 0.076 mmol) in toluene (1 mL) at RT. After 2 h the solvent was evaporated, and the resulting red-orange solid was washed with a small amount of pentane and dried under vacuum. The final yield of **2** was 71% (31 mg, 0.054 mmol). Anal. Calc for $C_{35}H_{41}NO_3Ti$ (571.57): C, 73.55; H, 7.23; N, 2.45. Found: C, 71.23; H, 7.25; N, 2.42. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.48 (d, J = 7.4, 2H), 7.21 (t, J = 7.6 Hz, 2H), 7.01−6.77 (Ar-H, 7H), 6.59 (m, 1H), 6.52 (br s, 2H), 3.49 (s, 2H), 3.35 (s, 2H), 2.95 (d, J = 13.2 Hz, 2H), 2.74 (s, 6H), 2.57 (d, J = 13.6, 2H), 2.34 (s, 3H), 2.26 (m, 2H), 2.22 (s, 6H), 1.57 (m, 2H). ^{13}C NMR (C_6D_6, 50.29 MHz): δ 160.54 (*C*-O), 150.56 (*C*), 147.53 (*C*), 132.58 (*C*H), 129.72 (*C*H), 129.45 (*C*), 129.14 (*C*H), 128.99 (*C*), 128.88 (*C*), 128.84 (*C*H), 125.39 (*C*H), 125.69 (*C*H), 122.98 (*C*H), 122.92 (*C*H), 91.17 (*C*H_2), 86.00 (*C*H_2), 71.01 (*C*H_2), 63.46 (*C*H_2), 58.62 (*C*H_3), 49.24 (*C*H_2), 21.50 (*C*H_3), 17.83 (*C*H_3).

Preparation of Complex 3. To a stirring dark red solution of $Ti(CH_2Ph)_4$ (70 mg, 0.169 mmol) in 2 mL of toluene was added dropwise 65 mg (0.153 mmol) of Lig^3H_2 in toluene (1 mL) at RT. After 1 h the toluene was evaporated, and the resulting orange solid was washed with pentane (2 mL) and dried under vacuum. The final yield of **3** was 82% (82 mg, 0.126 mmol). **3** can be recrystallized from cold ether (−30 °C). ^{1}H NMR (C_6D_6, 200 MHz): δ 7.83 (d, J = 7.2 Hz, 2H), 7.39 (d, J = 2.5 Hz, 2H), 7.12 (m, 2H), 6.81 (t, J = 7.3 Hz, 2H), 6.74−6.66 (m, 4H), 6.62−6.56 (d, J = 2.5 Hz, and m, 3H), 3.53 (s, 2H), 3.24 (s, 2H), 2.58 (d, J = 13.7 Hz, 2H), 2.40 (d, J = 13.8 Hz, 2H), 2.32 (s, 3H), 2.07 (t, 5.1 Hz, 2H), 1.14 (br s, 2H). ^{13}C NMR (C_6D_6, 50.29 MHz): δ 157.86 (*C*-O), 14579 (*C*), 144.93 (*C*), 131.93 (*C*H), 130.79 (*C*H), 130.46 (*C*H), 129.64 (*C*H), 129.08 (*C*H), 124.79 (*C*H), 124.68 (*C*), 123.95 (*C*H), 123.23 (*C*), 92.36 (*C*H_2), 90.20 (*C*H_2), 69.36 (*C*H_2), 61.14 (*C*H_2), 58.99 (*C*H_3), 47.29 (*C*H_2).

Preparation of Complex 5. To a stirring dark red solution of $Ti(CH_2Ph)_4$ (58 mg, 0.141 mmol) in toluene (ca. 1 mL) was added dropwise Lig^5H_2 (49 mg, 0.138 mmol) in toluene (1 mL) at RT. After 2 h the solvent was evaporated, and the resulting dark red solid was washed with pentane (ca. 2 mL) and dried under vacuum. The final yield of **5** was 86% (69 mg, 0.118 mmol). Anal. Calc for $C_{36}H_{44}N_2O_2Ti$ (584.61): C, 73.96; H, 7.59; N, 4.79. Found: C, 69.58; H, 7.50; N, 4.90. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.58 (d, J = 7.9 Hz, 2H), 7.35 (t, J = 7.8 Hz, 2H), 7.03 (br s, 2H), 6.95 (m, 3H), 6.86 (t, J = 7.3 Hz, 2H), 6.62 (t, J = 7.1 Hz, 1H), 6.62 (t, J = 1.7 Hz, 2H), 3.21 (s, 2H), ca. 3.13 and 3.09 (d and s, 4H), 2.71 (s, 6H), 2.38 (d, J = 13.6 Hz, 2H), 2.23 (s, 6H), 1.69 (br s, 2H), 1.40 (s, 6H), 1.18 (m, 2H). ^{13}C NMR (C_6D_6, 50.29 MHz): δ 160.36 (*C*-O), 154.01 (*C*), 150.95 (*C*), 132.66 (*C*H), 129.01 (*C*H), 129.82 (*C*H), 128.65 (*C*H), 128.15 (*C*H), 127.81 (*C*H), 126.53 (*C*), 125.74 (*C*), 122.66 (*C*H), 122.29 (*C*H), 95.44 (*C*H_2), 89.46 (*C*H_2), 64.80 (*C*H_2), 60.18 (*C*H_2), 52.29 (*C*H_2), 46.95 (*C*H_3), 21.50 (*C*H_3), 17.97 (*C*H_3).

Preparation of Complex 6. To a stirring dark red solution of $Ti(CH_2Ph)_4$ (54 mg, 0.131 mmol) in toluene (1 mL) was added dropwise Lig^6H_2 (45 mg, 0.126 mmol) in toluene (1 mL) at RT. After 2 h the solvent was evaporated, and the resulting red-brown solid was washed once with pentane (ca. 3 mL) and dried under vacuum. The final yield of **6** was 98% (72 mg, 0.123 mmol). Anal. Calc for $C_{36}H_{44}N_2O_2Ti$ (584.61): C, 73.96; H, 7.59; N, 4.79. Found: C, 70.07; H, 7.52; N, 4.80. ^{1}H NMR (C_6D_6, 200 MHz) δ 7.70 (d, J = 7.5 Hz, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.25(s, 2H), 6.86 (t, J = 7.6 Hz, 2H), 6.61 (s and m, 3H), 3.27 (s, 2H), 3.10 (d, J = 13.4 Hz, 2H), 3.09 (s, 2H), 2.35 (d, J = 13.6 Hz, 2H), 2.18 (s, 6H), 2.11 (s, 6H), 1.65 (m, 2H), 1.49 (s, 6H), 1.22 (m, 2H). ^{13}C NMR (C_6D_6, 50.29 MHz): δ 162.29 (*C*-O), 154.16 (*C*), 150.34 (*C*), 138.74 (*C*), 131.69 (*C*H), 129.01 (*C*H), 128.69 (*C*H), 128.55 (*C*H), 128.04 (*C*H), 127.92 (*C*), 124.81 (*C*), 122.76 (*C*H), 122.33 (*C*H), 118.71 (*C*H), 95.33 (*C*H_2), 90.86 (*C*H_2), 64.39 (*C*H_2), 60.32 (*C*H_2), 52.17 (*C*H_2), 47.31 (*C*H_3), 20.62 (*C*H_3), 19.74 (*C*H_3).

Preparation of Complex 7. To a stirring dark red solution of $Ti(CH_2Ph)_4$ (57 mg, 0.138 mmol) in toluene (ca. 1 mL) was added dropwise Lig^7H_2 (55 mg, 0.125 mmol) in toluene (1 mL) at RT. After 1 h the solvent was evaporated, and the resulting purple-brown solid was washed with pentane (ca. 2 mL) and dried under vacuum. The final yield of **7** was 93% (77 mg, 0.116 mmol). Anal. Calc for $C_{32}H_{32}Cl_4N_2O_2Ti$ (666.29): C, 57.68; H, 4.84; N, 4.20. Found: C, 58.89; H, 4.96; N, 4.17. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.94 (d, J = 7.3 Hz, 2H), 7.42 (d, J = 2.1 Hz, 2H), 7.35 (t, J = 7.3 Hz, 2H), 7.00 (m, 1H), 6.7−6.5 (Ar-H, 6H), 3.21 (s, 2H), 3.14 (s, 2H), 2.65 (d, J = 13.9, 2H), 1.87 (d, J = 13.7, 2H), 1.35 (s, 6H), 1.21 (m, 2H), 0.90 (m, 2H). ^{13}C NMR (C_6D_6, 50.29 MHz): δ 158.27 (*C*-O), 154.06 (*C*), 150.03 (*C*), 130.89 (*C*H), 130.00 (*C*H), 128.99 (*C*H), 128.92 (*C*H), 128.60 (*C*H), 127.98 (*C*H), 124.57 (C), 123.76 (*C*H), 123.60 (C), 122.96 (CH), 101.68 (CH_2), 94.92 (CH_2), 63.34 (CH_2), 59.78 (CH_2), 52.18 (CH_2), 47.01 (CH_3).

Polymerization of Neat 1-Hexene with 2/B(C_6F_5)$_3$ and with 3/B(C_6F_5)$_3$. B(C_6F_5)$_3$ (17−28 μmol) was dissolved in ca. 1 mL of 1-hexene and added to a stirred solution of **2** (or **3**) (14−17 μmol) in 1-hexene. The resulting mixture was allowed to stir at RT. The polymerization was monitored by taking out a measured volume of the solution, evaporating to dryness, weighing, and analyzing by GPC.

Polymerization of Neat 1-Hexene with 5−7/B(C_6F_5)$_3$. B(C_6F_5)$_3$ (15−29 μmol) was dissolved in ca. 1 mL of 1-hexene and added to a stirred solution of **5** (or **6** or **7**) (10−17 μmol) in 1-hexene. The total volume of the solution was 5−15 mL. The resulting mixture was stirred for 1−9 min (until 1-hexene had started to boil). The remaining olefin was evaporated in vacuo, yielding poly(1-hexene) as a colorless sticky oil. The polymer was weighted and subjected to GPC analysis.

Polymerization in ClPh with 5/B(C_6F_5)$_3$ and with 6/B(C_6F_5)$_3$. 1-Hexene (6 mL, 4.04 g) was dissolved in 24 mL (26.57 g) of ClPh. B(C_6F_5)$_3$ (15−17 μmol) was dissolved in ca. 1 mL of the resulting mixture and added in one portion to the **5** (or **6**) (10−17 μmol) predissolved in the remaining solution. The polymerization process was monitored by taking out measured volumes, evaporating to dryness, weighing, and subjecting to GPC analysis.

Large-Scale Polymerization with 7/B(C_6F_5)$_3$. B(C_6F_5)$_3$ (9 μmol) was dissolved in ca. 1 mL of 1-hexene and added in one portion to a stirred solution of **7** (4 μmol) in 100−140 mL of 1-hexene. The polymerization process was monitored by taking out measured aliqouts, evaporating to dryness, weighing, and subjecting to GPC analysis.

To prepare p-HEX1, the polymerization process was allowed to proceed for at least 2 h, after which time methanol/HCl$_{aq}$ was added. The organic phase was separated, and the solvent (1-hexene) was removed under vacuum. The resulting white rubber-like solid was dried under vacuum for 3 h. According to GPC, the final polymer had M_w = 4 300 000, PDI = 2.5. To prepare p-HEX2, the polymerization was allowed to proceed for ca. 30 min (only a slight increase in the polymer weight was detected after 30 min). The resulting polymer was worked up as above. According to GPC, the final had M_w = 1 500 000, PDI = 2.0

Polymer Characterization. Specimens for density determination and viscoelastic parameter measurements (storage, loss, and relaxation shear moduli) were prepared by compression molding of the high molecular weight samples p-HEX1 and p-HEX2 into plates of about 1.8 mm thickness at 170 and 150 °C, respectively. Disks of 25 mm in diameter were cut from the plates and used in the viscoelasticity studies; small specimens having no sharp edges were also cut out of the plates and used in the density measurements. A sample of p-HEX3 (M_w = 50 000, PDI = 3.0), previously prepared by a Zr catalyst,[7c] required no specific preparation for the rheological testing.

Frequency sweeps were made at 2% strain (well below the linear viscoelasticity limit of more than 10%) in the frequency window from 5×10^{-2} to 16 Hz. The temperature ranged from 296 to 463 K for p-HEX1, from 296 to 443 K for p-HEX2, and from 296 to 323 K for p-HEX3. The isotherms of the high molecular weight poly(1-hexene) samples were shifted to obtain master curves at the reference temperature T_0 = 403 K using the Time-Temperature Superposition (TTS) module of the Orchestrator Software. A master curve for p-HEX3 was constructed for the reference temperature 323 K. The dynamic frequency sweep data were converted into relaxation time spectra using the Orchestrator Molecular Weight Distribution (MWD) module. Shear stress relaxation tests were made at 5% strain at 296 K.

Acknowledgment. This research was supported by the Israel Science Foundation, founded by the Israel Academy of Sciences and Humanities. We thank Elisheva Genizi (BIU) and Dalia Gut-Regev (TAU) for technical assistance.

Supporting Information Available: Crystallographic information files for compounds **2**, **3**, **6**, and **7**. ^{13}C NMR spectra of the polymers prepared by catalysts **1**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049630Q