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# Group IV complexes of an amine bis(phenolate) ligand featuring a THF sidearm donor: from highly active to living polymerization catalysts of 1-hexene

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### Abstract

A new amine bis(phenolate) ligand bearing a THF donor on a sidearm and several dialkyl complexes of the group IV triad are introduced. The crystal structures of a zirconium dibenzyl complex and a titanium dibenzyl complex were solved, and revealed a strong binding of the oxygen donor of the THF group to the metal center. Upon activation with tris(pentafluorophenyl)borane the zirconium and the hafnium dibenzyl complexes lead to highly active 1-hexene polymerization catalysts. In comparison, titanium complexes (a dibenzyl complex and a dimethyl complex) lead to slower but living polymerization of 1-hexene at room temperature. Polymerization of neat 1-hexene under high dilution conditions was found to be living for an exceptionally long time of 6 days, leading to poly(1-hexene) of  $M_w = 816000$  and PDI = 1.09. A block copolymerization of 1-hexene and 1-octene at room temperature could be obtained using the titanium catalysts.

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# 1. Introduction

In recent years there has been a broad interest in the developing of cyclopentadienyl-free catalysts based on group IV metals for polymerization of alpha olefins [1-3]. This interest was inspired, to a large extent, by the pioneering work of McConville [4] and Schrock [5] that reported for the first time a living polymerization of high-olefins at ambient temperatures employing diamido-type ligands. Several other important developments that followed include the living and isotactic polymerization of high-olefins at room temperature employing diamine diphenolate ligands [6], the living

and syndiotactic polymerization of propylene at room temperature [7], and the extremely active catalysts for polymerization of ethylene [8–11] employing imine phenolate ligands. These studies show that by careful design of the ligand system, a close control of the activity of the catalyst and the properties of the polymer may be achieved.

Recently we introduced the amine bis(phenolate) ligand family for group IV metals [12-17]. We found that for zirconium and hafnium, the presence of an extra donor on a sidearm was crucial for obtaining active polymerization catalysts, as complexes lacking it led to rapid catalyst deactivation [13,14]. The reactivity of these precatalysts could be tuned by varying the nature of this sidearm donor, and the most active zirconium catalyst was found to have a methoxy donor on the sidearm [15]. The corresponding titanium complexes exhibited a different mode of reactivity. Whereas the

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sidearm donor was not a prerequisite for an active catalyst, its presence led to living polymerization at room temperature [16]. Especially, a titanium complex of an amine bis(phenolate) ligand having a methoxy donor on the sidearm led to living polymerization of 1-hexene for an exceptionally long time of 31 h yielding a polymer of  $M_w$  of 450 000 and PDI of 1.12 [17]. These results led us to design a new amine bis(phenolate) ligand having a different oxygen donor: a THF group. In this work we describe the synthesis of dialkyl complexes of zirconium, hafnium, and titanium of this new ligand and their reactivity in polymerization of 1-hexene.

# 2. Experimental

### 2.1. General

All experiments were performed under an atmosphere of dry nitrogen in a nitrogen-filled glovebox. Ether and tetrahydrofuran were purified by reflux and distillation under dry argon atmosphere from Na/benzophenone. Pentane was washed with HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> prior to distillation from Na/benzophenone/tetraglyme. Toluene was refluxed over Na and distilled. Benzyl magnesium chloride, 1-hexene, 1-octene, and chlorobenzene were purchased from Aldrich Inc. Tris(pentafluorophenyl)borane was obtained from Strem Chemicals Inc. 1-Hexene and chlorobenzene were passed through alumina prior to use. Zirconium tetrabenzyl, hafnium tetrabenzyl, and titanium tetrabenzyl were synthesized according to published procedures [18,19]. Titanium tetrabenzyl was used shortly after its synthesis. NMR data were recorded on Bruker AC-200 and Bruker Avance AC-400 spectrometers and referenced to protio impurities in benzene- $d_6$  ( $\delta$  7.15) or TMS in CDCl<sub>3</sub> ( $\delta$ 0.00). Elemental analyses were performed in the microanalytical laboratory in the Hebrew University of Jerusalem. The metal complexes were analyzed within a few hours of being taken out of the freezer of the glove box. Poly(1-hexene) molecular weights were determined by gel permeation chromatography (GPC) using TSKgel GMHHR-M, TSKgel G 4000 HHR, and TSKgel G 5000 HHR columns set on a Jasco instrument equipped with a refractive index detector. Molecular weight determination was carried out relative to polystyrene standards using tetrahydrofuran (HPLC grade, distilled and filtered under vacuum prior to use) as the eluting solvent. The X-ray diffraction measurements were performed on a Nonius Kappa CCD diffractometer system, using Mo K $\alpha$  ( $\lambda = 0.7107$  Å radiation). The analyzed crystals were embedded within a drop of viscous oil and freeze-cooled to approximately 110 K. The structures were solved by a combination of direct methods and Fourier techniques using the SIR-92 software [20], and were refined by full-matrix least-squares with SHELXL-97 [21]. The crystals contain partly disordered solvent and partly disordered *tert*-butyl groups. Some of the benzyl groups also exhibit large-amplitude wagging motion. These give rise to a relatively large fraction of weak reflections below the intensity threshold, and affect to some extent the precision of the structure determination.

# 2.2. Synthesis of the ligand precursor $(LigH_2)$

A solution of 2,4-di-tert-butylphenol (6.0 g, 29 mmol), 2-(aminomethyl)tetrahydrofuran (1.0 ml, 9.7 mmol) and 36% aqueous formaldehyde (1.62 ml, 19.4 mmol) in methanol (10 ml) was stirred and refluxed for 40 h. The mixture was cooled and the supernatant solution decanted. The solid residue was triturated with ice cold methanol, filtered and washed thoroughly with cold methanol, to give the ligand precursor as a colorless powder (3.48 g, 67% yield), which could be further purified by recrystallization from ether-methanol. M.p. 160-161 °C. To the crude oil which remained after removal of the solvent, was added a small amount of methanol. The mixture was left standing at room temperature for 2 months, during which more of the product precipitated, increasing the yield to a total of 90%. C35H55NO3 (537.7): Calc. for C, 78.16; H, 10.31; N, 2.60. Found: C, 78.16; H, 10.29; N, 2.84%. <sup>1</sup>H NMR  $(CDCl_3)$ :  $\delta$  8.86 (bs, 2H), 7.20 (d, J = 2 Hz, 2H), 6.88 (d, J = 2 Hz, 2H), 4.27 (m, 1H), 4.01 (m, 1H), 3.89 (m, 1H), 3.77 (m, 4H), 2.61 (m, 1H), 2.51 (m, 1H), 1.90 (m, 3H), 1.57 (m, 1H), 1.40 (s, 18H), 1.27 (s, 18H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 153.02 (C), 140.63 (C), 136.05 (C), 124.95 (CH), 123.38 (CH), 121.43 (C), 77.54 (CH), 68.28 (CH<sub>2</sub>), 57.52 (CH<sub>2</sub>), 55.93 (CH<sub>2</sub>), 34.99 (CMe<sub>3</sub>) 34.10 (CMe<sub>3</sub>), 31.67 (CH<sub>3</sub>), 29.60 (CH<sub>3</sub>), 29.60 (CH<sub>2</sub>), 25.21 (CH<sub>2</sub>). HRMS (DCI-CH<sub>4</sub>): 537.418854 (C<sub>35</sub>H<sub>55</sub> NO<sub>3</sub>)  $(M^{+}).$ 

### 2.3. Synthesis of 1a

LigH<sub>2</sub> (60 mg, 0.11 mmol) was dissolved in approximately 1 ml of toluene and added dropwise to a bright yellow solution of ZrBn<sub>4</sub> (51 mg, 0.11 mmol) in toluene at room temperature. The solution was stirred at room temperature for 2 h. The solvent was removed in vacuo, and the resulting yellow solid was washed with pentane (ca. 2 ml). The final yield was 70 mg (78%). Single crystals of **1a** were grown from toluene (see Table 1 for crystallographic data). C<sub>49</sub>H<sub>67</sub>NO<sub>3</sub>Zr (809.3): Calc. C, 72.72; H, 8.35; N, 1.73. Found: C, 71.99; H, 8.12; N, 1.82%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz)  $\delta$  7.79 (d, J = 7.2 Hz, 2H), 7.59 (t, J = 2.4 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.02 (m, 5H), 6.77 (t, J = 7.4 Hz, 2H), 6.58 (t, J = 7.0 Hz, 1H), 3.5 (t, J = 13.8 Hz, 2H), 3.27 (m, 3H), 2.89 (s, 2H), 2.65 (m, 2H), 2.61 (s, 2H), 2.08 (t, 2H), 1.79 (s,

Table 1 Crystallographic data for **1a** and **3a** 

	$3\mathbf{a} \cdot 2\mathbf{C}_7\mathbf{H}_8$	$1a \cdot 2C_7H_8$
Empirical formula	C <sub>63</sub> H <sub>83</sub> NO <sub>3</sub> Ti	C <sub>63</sub> H <sub>83</sub> NO <sub>3</sub> Zr
Formula weight	950.20	993.52
Temperature (K)	110	110
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	14.8410(2)	14.6110(2)
b (Å)	15.3280(2)	15.3350(2)
<i>c</i> (Å)	25.3630(6)	25.8920(5)
β (°)	105.3950(6)	103.9060(6)
V (Å <sup>3</sup> )	5562.62(17)	5631.32(15)
Z	4	4
$D_{\text{calc}} (\text{g cm}^{-1})$	1.135	1.172
$\lambda$ (Å)	0.7107	0.7107
$\mu  ({\rm mm}^{-1})$	0.198	0.239
Reflections measured	12237	13 451
Independent reflections	7074	8302
$2\theta$ Range (°)	3.3-55.8	5.5-56.5
Dataset	0-19/0-16/-33-32	0-19/0-20/-33-33
$R_1 (I > 2\sigma(I))$	0.0900	0.0713
$wR_2 (I > 2\sigma(I))$	0.2112	0.1684
$R_1$ (all data)	0.1604	0.1322
$wR_2$ (all data)	0.2522	0.2044
Goodness-of-fit $(F^2)$	1.015	1.049

18H), 1.34 (s, 18H), 0.60 (m, 3H), -0.01 (m, 1H). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 50.29 MHz)  $\delta$  158.9 (*C*-O), 158.2 (*C*-O), 148.5 (*C*), 147.5 (*C*), 141.1 (*C*), 149.8 (*C*), 136.8 (*C*), 136.5 (*C*), 129.2 (*C*H), 128.6 (*C*H), 128.5 (*C*H), 128.2 (*C*H), 128.0 (*C*H), 125.6 (*C*H), 124.7 (*C*H), 124.6 (*C*H), 124.3 (*C*H), 122.4 (*C*H), 120.7 (*C*H), 80.5 (*C*H), 70.4 (*C*H<sub>2</sub>), 68.3 (*C*H<sub>2</sub>), 65.2 (*C*H<sub>2</sub>), 65.0 (*C*H<sub>2</sub>), 64.6 (*C*H<sub>2</sub>), 56.7 (*C*H<sub>3</sub>), 35.8 (*C*), 35.6 (*C*), 34.5 (*C*), 32.0 (*C*H<sub>3</sub>), 30.6 (*C*H<sub>3</sub>), 30.3 (*C*H<sub>3</sub>), 28.7 (*C*H<sub>2</sub>), 25.1 (*C*H<sub>2</sub>).

### 2.4. Synthesis of 2a

LigH<sub>2</sub> (149 mg, 0.28 mmol) was dissolved in toluene and added dropwise to a bright yellow solution of HfBn<sub>4</sub> (150 mg, 0.28 mmol) in 6 ml of toluene. The yellow color disappeared immediately and the solution became colorless. The solution was stirred at room temperature for two hours, and the solvent was removed under reduced pressure. The product was washed once with approximately 2 ml of pentane and dried in vacuo to give 2a as a white solid. The final yield was 209 mg (83%). C<sub>49</sub>H<sub>67</sub>NO<sub>3</sub>Hf (896.5): Calc. C, 65.64; H, 7.53; N, 1.56. Found C, 65.42; H, 7.61; N, 1.74%. <sup>1</sup>H NMR  $(C_6D_6, 200 \text{ MHz}) \delta$  7.73 (d, J = 7.2 Hz, 2H), 7.63 (t, J =2.2 Hz, 2H), 7.42 (t, J = 7.7 Hz, 2H), 6.95 (m, 5H), 6.82 (t, J = 7.7 Hz, 2H), 6.59 (m, 1H), 3.54 (m, 2H), 3.29 (m, 1H), 3.29 (m, 2H), 3.29 (m, 2H),3H), 2.66 (m, 2H), 2.64 (s, 2H, Ph $CH_2$ ), 2.50 (s, 2H, PhCH<sub>2</sub>), 2.10 (m, 2H), 1.88 (s, 18H), 1.35 (s, 18H), 0.57 (m, 3H), -0.02 (m, 1H). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 50.29 MHz) δ 158.9 (C-O), 158.2 (C-O), 149.2 (C), 148.9 (C), 140.9 (*C*), 140.8 (*C*), 137.4 (*C*), 137.1 (*C*), 128.8 (*C*H), 128.4 (*C*H), 128.0 (*C*H), 127.9 (*C*H), 125.4 (*C*H), 125.3 (*C*H), 124.9 (*C*H), 124.5 (*C*H), 124.6 (*C*H), 121.9 (*C*H), 120.8 (*C*H), 80.9 (*C*H), 75.0 (*C*H<sub>2</sub>), 71.6 (*C*H<sub>2</sub>), 70.8 (*C*H<sub>2</sub>), 64.7 (*C*H<sub>2</sub>), 64.3 (*C*H<sub>2</sub>), 56.7 (*C*H<sub>2</sub>), 35.7 (*C*), 35.6 (*C*), 34.5 (*C*), 32.0 (*C*H<sub>3</sub>), 30.6 (*C*H<sub>3</sub>), 30.3 (*C*H<sub>3</sub>), 28.5 (*C*H<sub>2</sub>), 25.2 (*C*H<sub>2</sub>).

## 2.5. Synthesis of 3a

LigH<sub>2</sub> (92 mg, 0.17 mmol) was dissolved in approximately 1 ml of toluene at room temperature and added dropwise to a stirring dark red solution of TiBn<sub>4</sub> in approximately 1 ml of toluene. The color of the solution remained dark red and it was stirred for 2 h at room temperature. The solvent was removed under reduced pressure yielding a red-brown solid, which was washed with approximately 2 ml of pentane and dried in vacuo. The final yield was 98 mg (75%). Crystals suitable for Xray analysis were grown from toluene-pentane mixture at -35 °C (see Table 1 for crystallographic data). C<sub>49</sub>H<sub>67</sub>NO<sub>3</sub>Ti (757.9): Calc. C, 76.83; H, 8.82; N, 1.83. Found: C, 76.55; H, 8.64; N, 1.93%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz)  $\delta$  7.94 (d, J = 7.6 Hz, 2H), 7.72 (bs, 2H), 7.42 (d, J = 7.8 Hz, 2H), 7.00 (m, 5H), 6.66 (t, J = 7.1 Hz, 2H), 6.48 (t, J = 7.2 Hz, 2H), 3.56 (m, 2H, CH<sub>2</sub>), 3.28 (m, 3H), 3.01 (m, 4H, PhCH<sub>2</sub>-Ti), 2.51 (dd, 2H, CH<sub>2</sub>), 2.20 (s, 18H, t-Bu), 1.86 (m, 2H), 1.37 (s, 18H, t-Bu), 0.55 (m, 3H), -0.05 (m, 1H). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 50.29 MHz) δ 161.43 (C-O), 160.80 (C-O), 154.94 (C), 141.45 (C), 141.31 (C), 136.34 (C), 129.73 (CH), 129.27 (CH), 128.51 (CH), 128.40 (CH), 128.12 (CH), 128.01 (CH), 126.90 (C), 126.84 (CH), 126.05 (C), 125.64 (CH), 125.19 (CH), 124.39 (CH), 124.22 (CH), 124.09 (CH), 122.18 (CH), 121.93 (CH), 99.26 (CH<sub>2</sub>), 84.54 (CH<sub>2</sub>), 78.54 (CH), 68.29 (CH<sub>2</sub>), 65.50 (CH<sub>2</sub>), 65.00 (CH<sub>2</sub>), 56.82 (CH<sub>2</sub>), 36.08 (C), 35.97 (C), 34.41 (C), 31.91 (CH<sub>3</sub>), 31.13 (CH<sub>3</sub>), 30.84 (CH<sub>3</sub>), 28.52 (CH<sub>2</sub>), 24.55  $(CH_2)$ .

### 2.6. Synthesis of 3b

50 mg (90 µmol) of LigH<sub>2</sub> and 19 mg (0.19 mmol) of Et<sub>3</sub>N were dissolved in 2 ml of THF and added dropwise at room temperature to 31 mg (90 µmol) of TiCl<sub>4</sub>(THF)<sub>2</sub> in 3 ml of THF. The reaction solution turned red slowly and was stirred at room temperature for 2 h. The solution was filtered through Celite (in order to remove Et<sub>3</sub>N·HCl) and cooled to -33 °C. MeMgBr (60 µl, 1.0 M in diethyl ether) was added to the reaction vial, and the solution turned brown immediately. The reaction was allowed to stir for 20 min, after which it was evaporated to dryness. **3b** was extracted from the crude product by pentane (ca. 1 ml). The final yield was 28 mg (50%). C<sub>37</sub>H<sub>59</sub>NO<sub>3</sub>Ti (613.7): **3b** gave low carbon percentage due to its extreme thermal and hydrolytic

sensitivity (Calc. C, 72.40; H, 9.69; N, 2.28. Found: C, 70.02; H, 9.42; N, 2.27%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz)  $\delta$  7.65 (bs, 2H), 6.99 (bs, 2H), 3.59 (m, 2H), 3.13 (m, 3H), 2.61 (m, 2H), 1.99 (s, 9H), 1.97 (s, 9H), 1.75 (s, 3H), 1.48 (s, 3H), 1.42 (s, 9H), 1.41(s, 9H), 0.62 (m, 3H), -0.05 (m, 1H). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 50.29 MHz)  $\delta$  161.61 (*C*-O), 160.61 (*C*-O), 140.76 (C), 136.35 (C), 135.93 (C), 128.73 (C-H), 79.08 (*C*H), 69.12 (*C*H<sub>2</sub>), 64.65 (*C*H<sub>2</sub>), 64.09 (*C*H<sub>2</sub>), 62.49 (*C*H<sub>2</sub>), 61.39 (*C*H<sub>3</sub>-Ti), 56.91 (*C*H<sub>3</sub>-Ti), 35.93 (*C*), 35.78 (*C*), 34.59 (*C*), 32.16 (*C*H<sub>3</sub>), 30.49 (*C*H<sub>3</sub>), 30.11 (*C*H<sub>3</sub>), 28.89 (*C*H<sub>2</sub>), 25.15 (*C*H<sub>2</sub>).

### 2.7. Polymerization of neat 1-hexene by 1a-2a

B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (15 mol) was dissolved in approximately 1 ml of 1-hexene and added to a stirred solution of **1a** (**2a**) (12 μmol) in 1-hexene. The total volume of the monomer was 20 ml. The resulting mixture was stirred for 20–40 min until 1-hexene had started to boil. The remaining olefin was evaporated in vacuo yielding poly(1-hexene) as a colorless sticky oil. Samples of poly(1-hexene) were analyzed by GPC. <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 40.39 (br, CH<sub>2</sub>), 34.40 (br, CH<sub>2</sub>), 32.41 (CH), 29.87 (br, CH<sub>2</sub>), 23.41 (CH<sub>2</sub>), 14.35 (CH<sub>3</sub>).

# 2.8. Polymerization of 1-hexene diluted in chlorobenzene by 1a-2a

A solution of  $B(C_6F_5)_3$  (15 µmol) in 1-hexene (1 ml) and chlorobenzene (4 ml) was added dropwise to a solution of **1a** (**2a**) (12 µmol) in 4 ml of 1-hexene and 16 ml of chlorobenzene. In a typical experiment the polymerization process was monitored by taking measured aliquots over a period of 20 min. The samples were evaporated to dryness, weighed and analyzed by GPC.

### 2.9. Typical polymerization of neat 1-hexene by 3a-3b

B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (ca. 15  $\mu$ mol) was dissolved in 1 ml of 1hexene and added to a stirred olefin solution of **3a** (**3b**) (ca. 12  $\mu$ mol). A typical volume of 1-hexene was in range of 40–500 ml. The polymerization process was followed by GPC.

# 2.10. Block copolymerization of 1-hexenel1-octene by 3a

16 mg (31 µmol) of  $B(C_6F_5)_3$  were dissolved in 0.43 ml of chlorobenzene and added to 20 mg (26 µmol) of **3a** in 1.00 ml of chlorobenzene. The reaction solution turned slowly yellow and was allowed to stir at room temperature for 1 h. 426 mg (5.2 mmol, 200 equiv.) of 1-hexene in 1.43 ml of chlorobenzene were added to the reaction vial, and the polymerization process was monitored by GPC. The second monomer (1-octene, 396 mg, 136 equiv.) was dissolved in 2.50 ml of chlorobenzene and

added to the polymerization vial after the complete consumption of 1-hexene. The duration of the whole experiment was approximately 30 h, after which a complete consumption of 1-octene was observed.

# 3. Results and discussion

### 3.1. Catalyst design through ligand design

The ligand precursor (Scheme 1) was prepared by a single step Mannich condensation between 2,4-di-tertbutylphenol, formaldehyde, and the corresponding amine (see Section 2 for details). The tetrahydrofuran ring is connected through the 2' position to the central nitrogen atom by a methylene bridge. The increased polarity of THF relative to ether (1.75 vs.  $\sim$  1.2 D) should promote a stronger binding of the THF oxygen to the metal atom. The rigidity of the THF group relative to the O-Me group should also contribute to its stronger coordination to the metal. The bulky *tert*-butyl groups ortho to the phenolic oxygen are required for the clean chemistry in the case of the large metal ions (Zr, Hf) [14]. The resulting dibenzyl octahedral complexes should possess  $C_1$  symmetry in contrast to all previously reported amine bis(phenolate) complexes (featuring  $C_s$ symmetry on the NMR timescale) due to an asymmetric carbon atom. The low symmetry of this ligand may direct the approaching monomer thus leading to a defined stereochemistry of the resulting polymer if it is expressed in the catalytic site ('enanthiomorphic site control').



Scheme 1. The amine bis(phenolate) THF ligand.

### 3.2. Synthesis and structure

The desired dibenzyl complexes of the group IV triad were prepared by protonolysis of a readily available precursor (M(CH<sub>2</sub>Ph)<sub>4</sub>) with the ligand precursor (Scheme 2). A different synthetic strategy had to be developed for preparing the dimethyl complex **3b**. Reacting TiCl<sub>4</sub>(THF)<sub>2</sub> with the ligand precursor in the presence of NEt<sub>3</sub> led to a clean mixture of two products that were not fully characterized [22,23] but were further reacted with 2 equiv. of MeMgBr (Scheme 3). The desired product was extracted with pentane giving a yellow-orange solid, in ca. 50% yield.

As previously mentioned, the low symmetry of this ligand must induce a low symmetry of the complex  $(C_1)$ .



Scheme 3. Synthesis of the titanium dimethyl complex.

This could be confirmed by four different benzyl protons and four different aromatic protons (observed as multiplets), as well as by two AB systems for the ligand methylenes (adjacent to the phenolate rings) for both of the titanium complexes (**3a** and **3b**). Interestingly, **3a** and **3b** differ from each other by the number of dissimilar *tert*-butyl groups: two for **3a** and four for **3b**. The zirconium and the hafnium complexes exhibit apparent 'higher' symmetry than the titanium complexes: the benzylic protons are observed as sharp singlets, and only two different *tert*-butyl groups could be identified. Hence, it may be concluded, that the influence of the formally low symmetry on the catalytic site is rather small, especially for the case of the larger metal atoms.

1a and 3a were recrystallized from cold toluene and their crystal structures were solved. ORTEP views of 1a and 3a are shown in Figs. 1 and 2, respectively. The crystallographic data, key bond distances and angles are listed in Tables 1-3.

The two X-ray structures indicate that the 'ligand core' remains symmetrical despite the formal absence of a mirror plane in the molecule. The molecules are of a distorted octahedral geometry, in which the two phenolic oxygens are in *trans* configuration, and the two benzyl groups are in *cis* configuration. According to our expectations, the Ti–O (THF donor) bond distance of



Fig. 1. Structure of **1a** (50% probability ellipsoids). H-atoms and solvent molecules are omitted for clarity. Key atoms are labeled. The elongated ellipsoids indicate partly disordered atoms. The disorder of the lower left *tert*-butyl group could not be resolved.



Fig. 2. Structure of **3a** (50% probability ellipsoids). H-atoms and solvent molecules are omitted for clarity. Key atoms are labeled.

Table 2 Selected bond distances (Å) and angles (°) for 1a

Bond distances		
Zr-O2	1.992(2)	
Zr-O3	1.998(2)	
Zr-O4	2.371(3)	
Zr-N5	2.444(3)	
Zr-C6	2.296(4)	
Zr-C7	2.297(4)	
Bond angles		
O2–Zr–O3	159.09(10)	
O4-Zr-N5	69.36(9)	
C6-Zr-C7	101.42(14)	
Zr-C6-C8	114.63(2)	
Zr-C7-C14	105.80(3)	

Table 3					
Selected bond distances	(Å) and	angles	(°)	for	3a

Bond distances		
Ti-O2	1.870(2)	
Ti-O3	1.880(2)	
Ti-O4	2.264(2)	
Ti–N5	2.359(3)	
Ti-C6	2.149(4)	
Ti-C7	2.197(3)	
Bond angles		
O2-Ti-O3	163.15(10)	
O4-Ti-N5	72.94(9)	
C6-Ti-C7	90.40(14)	
Ti-C6-C8	109.67(2)	
Ti-C7-C14	117.00(3)	

2.26 Å is considerably shorter than the Ti–O bond length of 2.42 Å found for a methoxyalkyl sidearm donor [17]. The same trend was observed for the Zr–O donor bond of 2.37 Å in **1a** versus 2.45 Å found for a related zirconium compound with the same methoxyalkyl sidearm [15]. The structural similarity between the cores of these complexes and those of previously reported complexes of that ligand family enables us to attribute different reactivities to minor changes in the ligand framework.

Precatalyst/solvent	Activity <sup>a</sup>	$M_{ m w}{}^{ m b}$	PDI
1a/neat	21 000	80	3.0
1a/ClPh	2000	118	2.1
2a/neat	4000	59	1.9
2a/ClPh	1000	60	1.5

Table 4 Polymerization data for  $1a/B(C_6F_5)_3$  and  $2a/B(C_6F_5)_3$ 

<sup>a</sup> Measured in g mmol<sub>cat</sub><sup>-1</sup>  $h^{-1}$ .

<sup>b</sup>  $10^3$  g mol<sup>-1</sup>.

### 3.3. Polymerization studies

For metallocenes, zirconium and hafnium catalysts are generally more active than the respective titanium systems [24]. For non-metallocene systems this tendency does not appear to be general. Nevertheless, the amine bis(phenolate) systems follow the same trend. Upon activation with approximately 1.2 equiv. of  $B(C_6F_5)_3$ , 1a was found to be highly active toward polymerization of 1-hexene. The highest activity was obtained in neat olefin (21 000 g mmol<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>) and was accompanied by boiling of the monomer. Diluting of 1-hexene in chlorobenzene reduced the excess heat release, thereby slowing various termination processes. Consequently, 1hexene was consumed totally, and a higher molecular weight and lower PDI value were obtained (see Table 4 for details). The PDI values are around 2.0 in this case, signifying that  $1a/B(C_6F_5)_3$  is a single site catalyst.

The hafnium-based catalysts are generally slightly less active than their zirconium analogues [25]. Activation of **2a** with approximately 1.2 equiv. of  $B(C_6F_5)_3$  resulted in the boiling of the monomer. As expected, the reaction was slower than in the case of **1a**, and the calculated activity was 4000 g mmol<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>. When diluted in chlorobenzene, complex **2a** led to poly(1-hexene) having significantly lower PDI values, without affecting the molecular weight appreciably (Table 4).

Complex **3a** was also found to be an active precatalyst for 1-hexene polymerization. Addition of  $B(C_6F_5)_3$  to a dark red solution of **3a** in neat 1-hexene resulted in a slow change of color to bright yellow. We propose that the color change results from the precatalyst's activation. The titanium-based catalyst is a moderate polymerization catalyst, and its activity was evaluated to be



Fig. 3. Living polymerization of 1-hexene by  $3a/B(C_6F_5)_3$ : dependence of  $M_w$  on time.



Fig. 4. Living polymerization of 1-hexene by  $3a/B(C_6F_5)_3$ : dependence of  $M_w$  on the polymer weight.

12 g mmol<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>. At the early stages of the polymerization (2-3 h) the PDI indices appear to be rather high (1.13-1.15) for a living process, but as the polymerization proceeds (Fig. 3), there is a substantial lowering of the PDI values (1.05). The lowering of the polydispersity, the linear dependence of molecular weight on time (Fig. 3), and the linear increase in molecular weight versus polymer produced (Fig. 4) all suggest that the polymerization is living and that its rate is constant under these conditions. When the initial amount of 1hexene is very high (more than 50000 equiv.), the polymerization remains living for an exceptionally long time: the  $3a/B(C_6F_5)_3$  system catalyzes 1-hexene polymerization at room temperature in a living fashion for up to 48 h: after that time the resulting polymer has a molecular weight of 316000 and a PDI value as low as 1.05 (Figs. 3 and 4).

The relatively high polydispersitiy at the early stages of the polymerization may result from slow activation of the precatalyst (abstraction of the benzyl group by the borane reagent). To try to improve the catalyst's performance at the early stage of the reaction we prepared **3b**. Adding  $B(C_6F_5)_3$  to **3b** in 1-hexene resulted in an immediate color change from dark red to bright yellow, apparently signifying a rapid activation of the precatalyst. As for **3a**, the polymerization of 1-hexene proceeded in a living manner, however, the initial PDI values were not reduced substantially. When high dilution conditions were employed (200 000 equiv.), the polymerization continued for 6 days giving poly(1hexene) of extremely high molecular weight. The final polymer had a molecular weight of 816000 and a PDI value of 1.09 (see Fig. 5 for details). We therefore



Fig. 5. 'Immortal' polymerization by  $3b/B(C_6F_5)_3$ : dependence of molecular weight  $(M_w)$  on time.



Fig. 6. Block copolymerization of 1-hexene and 1-octene by  $3a/B(C_6F_5)_3$ .

propose that the behavior of the catalyst is almost unaffected by the nature of original alkyl groups in a precatalyst, and that the polymerization in this system is practically 'immortal'. We attribute the eventual termination of the living polymerization process to technical sources, such as increased solution's viscosity or water/ oxygen traces in the glove box atmosphere.

The main application of living polymerization is the synthesis of well-defined block copolymers. A necessary condition for successful block copolymerization is the total consumption of the first monomer. The system should also be stable enough so as not to decompose prior to addition of the second monomer. In order to achieve a maximum activation of the precatalyst, the catalyst was preconditioned, i.e. **3a** and  $B(C_6F_5)_3$  were mixed in chlorobenzene for 1 h after which 200 equiv. of 1-hexene were added (Fig. 6). After the complete consumption of the first monomer, the resulting polymer had a molecular weight  $(M_w)$  of 22000 and a PDI value of 1.16. The higher than expected molecular weight (17000) could arise from a partial decomposition of the catalyst prior to 1-hexene addition or from incomplete catalyst activation. 1-Octene was added to the reaction mixture after the complete consumption of the first olefin, and immediate increase in molecular weight could be noticed (Fig. 6). The rise of  $M_{\rm w}$  was accompanied by retention of the polydispersity index (PDI = 1.16). After full consumption of the second monomer, the resulting block poly((1-hexene)-(1-octene) had an  $M_{\rm w}$  of 34000 (all actions were performed at room temperature).

Despite the formal  $C_1$  symmetry of the complexes, the polymers obtained by all of the catalysts were atactic, according to <sup>13</sup>C NMR [6].

In summary, we introduced a new amine bis(phenolate) ligand, featuring a THF donor on a sidearm. Dibenzyl complexes of the group IV triad with the ligand were obtained in a one-step reaction, and a dimethyl titanium complex was prepared in a simple 'one-pot' two-step procedure. The zirconium and the hafnium complexes showed an outstanding activity in high-olefin polymerization proving to be single-site catalysts. The titanium complexes promote an 'immortal' polymerization of neat 1-hexene at room temperature that led to a polymer having a molecular weight of  $816\,000$  (PDI = 1.09). To the best of our knowledge, this is the highest molecular weight ever obtained for polymerization of 1-hexene in the living fashion.

# 4. Supplementary material

Crystal structures of **1a** and **2a** in a cif format are available from the authors upon request.

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