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Access to Ultra-High-Molecular Weight Poly(ethylene) and Activity Boost in the Presence of Cyclopentene With Group 4 Bis-Amido Complexes

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Zr^{IV} complexes of the type [Me_2Si{(NR)(6-{2-(diethylboryl)phenyl}pyridyl-2-yl-N)}$ZrCl_2\cdot$thf] (R = *t*Bu (**4**), adamantyl (**7 a**); thf = tetrahydrofuran), [Me_2Si{(NAd)(6-{2-(diphenylboryl)phenyl}pyridyl-2-yl-N)}$ZrCl_2$] (Ad = adamantyl (**7 b**)), the nonbridged half-titanocene complexes of the type [(N-{6-(2-diethylborylphenyl)pyrid-2-yl}-NR)Cp′$TiCl_2$] (R = Me, Cp′ = C_5H_5 (**12**), Cp′ = C_5Me_5 (**13**)), and the titanium(IV)-based metallocene-type complex [bis{N-(6-{2-(diethylboryl)phenyl}pyrid-2-yl)NMe}$TiCl_2$] (**14**) have been synthesized. The structures of complexes **7 b**, **12**, and **13** were determined by single-crystal X-ray diffraction analysis. In solution, complex **4** slowly rearranges to [Me_2Si{(N-*t*Bu)(6-{2-(diethylboryl)phenyl}pyridyl-2-yl-N)}$_2$Zr] (**4 a**), the structure of which was unambiguously confirmed by single-crystal X-ray crystallography. Similarly, reaction of $HfCl_4$ with Me_2Si({RNLi}{6-[2-(diethylboryl)phenyl]pyridyl-2-ylNLi}) yielded the corresponding Hf^{IV} complexes [Me_2Si{(NR)(6-{2-(diethylboryl)phenyl}pyridyl-2-ylN)}$_2$Hf] (R = *t*Bu (**8**) and Ad (**9**)). Upon activation of these complexes with methylalumoxane (MAO), complexes **4**, **7 a**, **7 b**, and **12**–**14** showed activities up to 750 kg of polyethylene (PE)/$mol_{cat.}$ bar h in the homopolymerization of ethylene (E), producing mainly linear PE (high-density PE, HDPE) with molecular weights in the range of $1\,800\,000 < M_n < 4\times10^6$ g mol^{-1}. In the copolymerization of E with cyclopentene (CPE), the polymerization activities of complexes **4**, **7 a**, and **7 b** can be enhanced by a factor of 140 up to 7500 kg PE/$mol_{cat.}$ bar h, which produced PE-*co*-poly(CPE) containing 3.5 mol % of CPE. This dramatic increase in polymerization activity for E in the presence of CPE can be attributed to an involvement of CPE in the polymerization process rather than to solvent polarity.

Introduction

Olefin polymerization by homogeneous transition-metal complexes is considered to be a mature field of polymer chemistry, especially when using early-transition metals.[1–6] Over the past twenty years it has emerged that Group 4 transition-metal complexes containing amide ligands are promising systems in olefin polymerization catalysis.[2] In particular, a large number of metallocene complexes have been developed for the copolymerization of ethylene (E) with cycloolefins.[7,8] Metallocene catalysts, particularly zirconium complexes, are effective catalytic systems for the copolymerization of E with different cycloolefins such as norborn-2-ene (NBE) or cyclopentene (CPE).[1] The copolymerization of E with NBE has been investigated with various metallocene catalysts, and the resulting polymers were found to be amorphous solids with high transparency.[2–7] Compared to C_2-symmetric catalyst systems, for example, [$Me_2Si(Ind)_2ZrCl_2$] or [$Ph_2Si(Ind)_2ZrCl_2$] (Ind = indenyl), C_s-symmetric catalyst systems, for example, [$Me_2C(Flu)(C_5H_5)ZrCl_2$] or [$Ph_2C(Flu)(C_5H_5)ZrCl_2$] (Flu = 9-fluorenyl), are well suited for the synthesis of amorphous copolymers with high glass-transition temperatures ($T_g \leq 180°$).[8] Nomura et al.[9,10] reported on nonbridged (anilido)(cyclopentadienyl)titanium(IV) complexes of the type [{N(2,6-$Me_2C_6H_3$)(R)}Cp′$TiCl_2$] (Cp′ = C_5Me_5, 1,3-$Me_2C_5H_3$, (C_5H_5)Cp; R = $SiMe_3$) for olefin polymerization, in which [(C_5Me_5)$TiCl_2${N(2,6-$Me_2C_6H_3$)($SiMe_3$)}], in particular, exhibited moderate activity (180 kg PE/$mol_{cat.}$ bar h) in E polymerization. In the copolymerization of E with NBE by various nonbridged (aryloxo)(cyclopentadienyl)$TiCl_2$-type complexes of the general formula [Cp′$TiCl_2$(OAr)] (Cp′ = indenyl, C_5Me_5, *t*BuC_5H_4, 1,2,4-$Me_3C_5H_2$; OAr = O-2,6-(2-Pr)–C_6H_3) the catalytic activity and incorporation of NBE was found to be highly dependent on the substituent on the cyclopentadienyl ring. In particular, indenyl-based Ti complexes showed high activity and efficient incorporation of NBE in PE-*co*-poly(NBE). These complexes were also active in the copolymerization of ethylene with CPE, however, incorporation of CPE was less effective than that of NBE.[2,11]

We recently reported on [$Me_2Si(\eta^5$-Me_4C_5)(6-{2-(diethylboryl)phenyl}pyrid-2-ylamido)$TiCl_2$],[12] [$Me_2Si(DbppN)_2ZrCl_2\cdot$thf] (thf =

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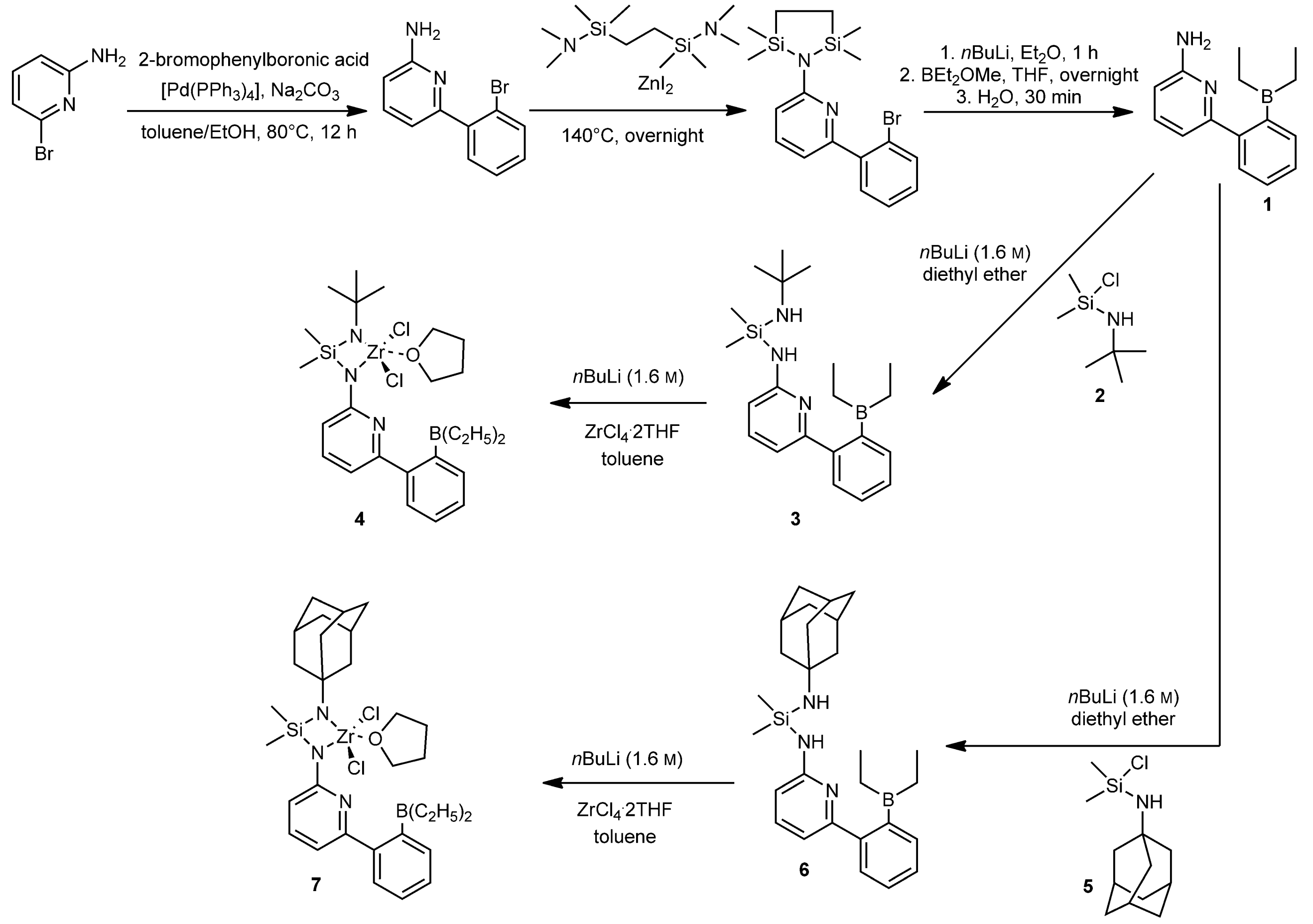
tetrahydrofuran), and [$Me_2Si(DbppN)_2HfCl_2$·thf] (DbppN = 6-[2-(diethylboryl)phenyl]pyrid-2-ylamido), which were, after activation with methylalumoxane (MAO), capable of forming both vinyl-insertion polymerization (VIP)- and ring-opening metathesis polymerization (ROMP)-derived, narrowly distributed ($1.05 <$ polydispersity index (PDI) < 2.0), high-molecular-weight copolymers ($M_n \leq 1\,500\,000$ g mol^{-1}) from, for example, norborn-2-ene and E containing multiple blocks of both ROMP- and VIP-derived structures within one single polymer chain. Herein, we report on the use of novel Ti^{IV}, Zr^{IV}, and Hf^{IV} complexes containing the 6-[2-(diethylboryl)phenyl]pyrid-2-ylamido motif and their use in the homopolymerization of E to yield ultra-high-molecular-weight (UHMW) poly(ethylene) (PE). Furthermore, we report on the copolymerization of E with CPE and the dramatic effect of high concentrations of CPE on polymerization activity.

Results and Discussion

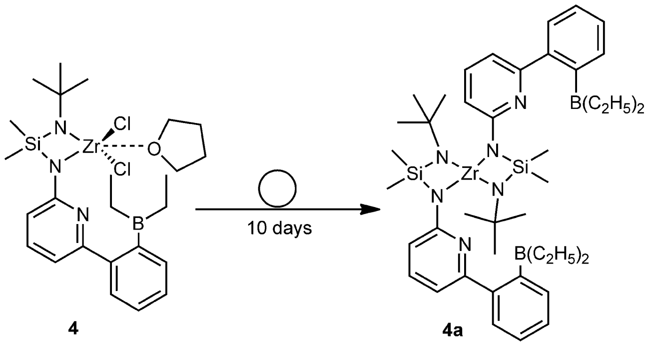
Synthesis of compounds 2–14

The ligand 6-[2-(diethylboryl)phenyl]pyrid-2-ylamine (**1**) was prepared as described in the literature.[12,13] Deprotonation with butyllithium in diethyl ether and reaction with *N*-(chlorodimethylsilyl)-*N*-*tert*-butylamine (**2**) yielded NH-*t*Bu-{6-[2-(diethylboryl)phenyl]pyrid-2-yl}NH (**3**) (Scheme 1). Deprotonation and reaction with $ZrCl_4$·2 thf yielded [Me_2Si{(N-*t*Bu)(6-{2-(diethylboryl)phenyl}pyridyl-2-yl-N)}$ZrCl_2$·thf] (**4**). Similarly, deprotonation of **1** and reaction with *N*-(chlorodimethylsilyl)-*N*-adamantylamine (**5**) yielded NH-Ad-{6-[2-(diethylboryl)phenyl]-pyrid-2-yl}NH (**6a**). Deprotonation of **6a** with butyllithium and reaction with $ZrCl_4$·2 thf yielded [Me_2Si{(N-Ad)(6-{2-(diethylboryl)phenyl}-pyridyl-2-yl-N)}$ZrCl_2$·thf] (**7a**).

6-[2-(Diphenylboryl)phenyl]pyrid-2-ylamine (**1b**) was prepared in analogy to compound **1**. Deprotonation with butyllithium in diethyl ether and reaction with *N*-(chlorodimethylsilyl)-*N*-adamantylamine (**5**) yielded NH-Ad-{6-[2-(diphenylboryl)-phenyl]-pyrid-2-yl}NH (**6b**) (Scheme 1). Deprotonation of **6b** with butyllithium and reaction with $ZrCl_4$·2 thf yielded [Me_2Si{(N-Ad)(6-{2-(diphenylboryl)phenyl}pyridyl-2-yl-N)}$ZrCl_2$] (**7b**, Scheme 2). Storage of precatalyst **4** in solution for a prolonged time resulted in a rearrangement of the ligand sphere around the zirconium ion resulting in the formation of [Me_2Si{(N-*t*Bu)(6-{2-(diethylboryl)phenyl}pyridyl-2-yl-N)}$_2$Zr] (**4a**, Scheme 2). Compound **4a** (Figure 1) crystallizes in the orthorhombic space group Pca_2 with $a = 2594.48(12)$ pm, $b = 1069.84(5)$ pm, $c = 3099.50(15)$ pm, $\alpha = \beta = \gamma = 90°$, $Z = 8$ with Zr1A–N4A 205.0(4) pm, Zr1A–N2A 206.4(4) pm, Zr1A–N6A



Scheme 1. Syntheses of compounds **2**–**7**.



Scheme 2. Rearrangement of **4** into **4 a**.

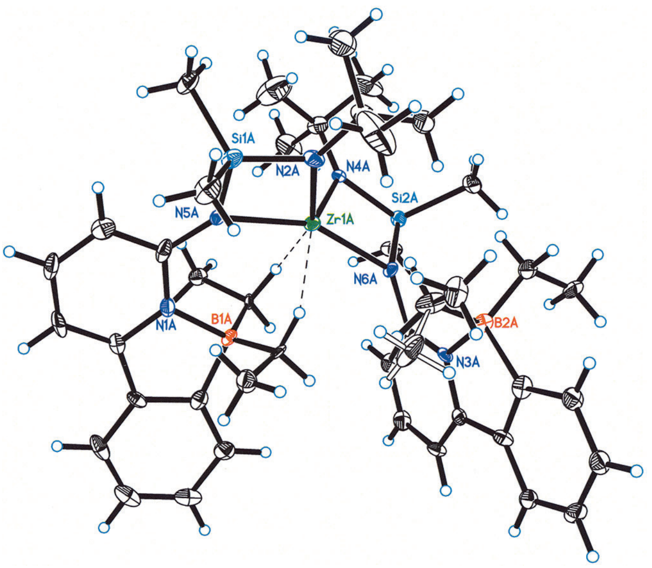
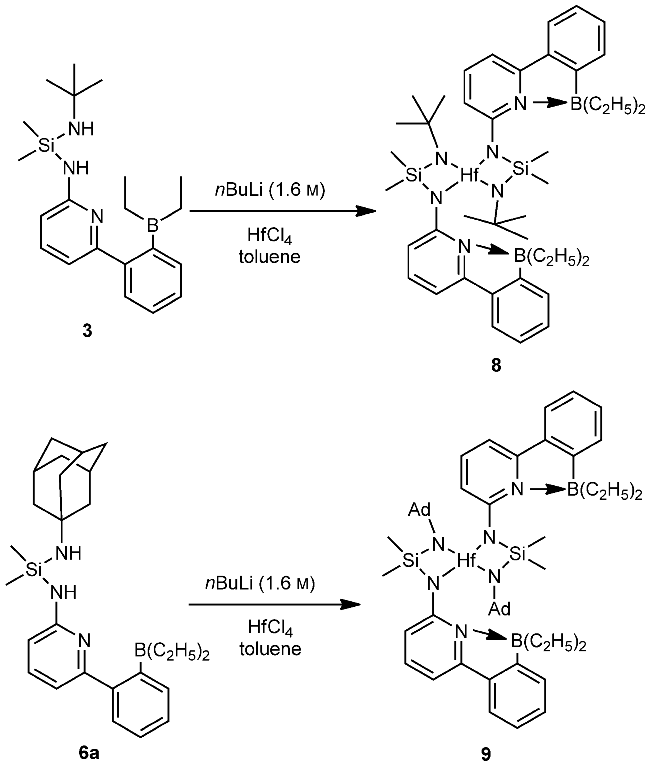


Figure 1. Single-crystal X-ray structure of compound **4 a**.



Scheme 3. Synthesis of compounds **8** and **9**.

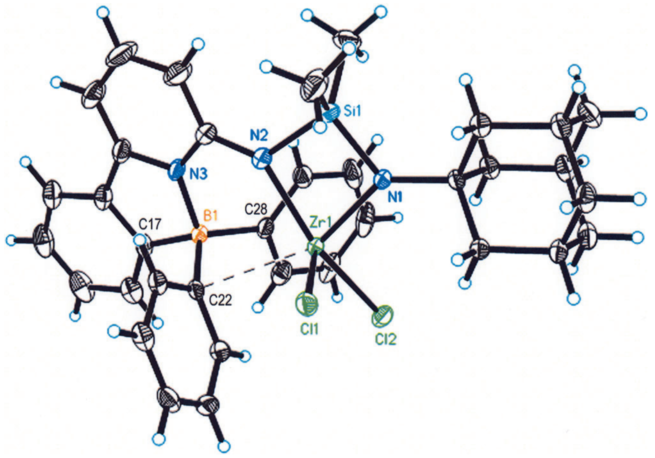
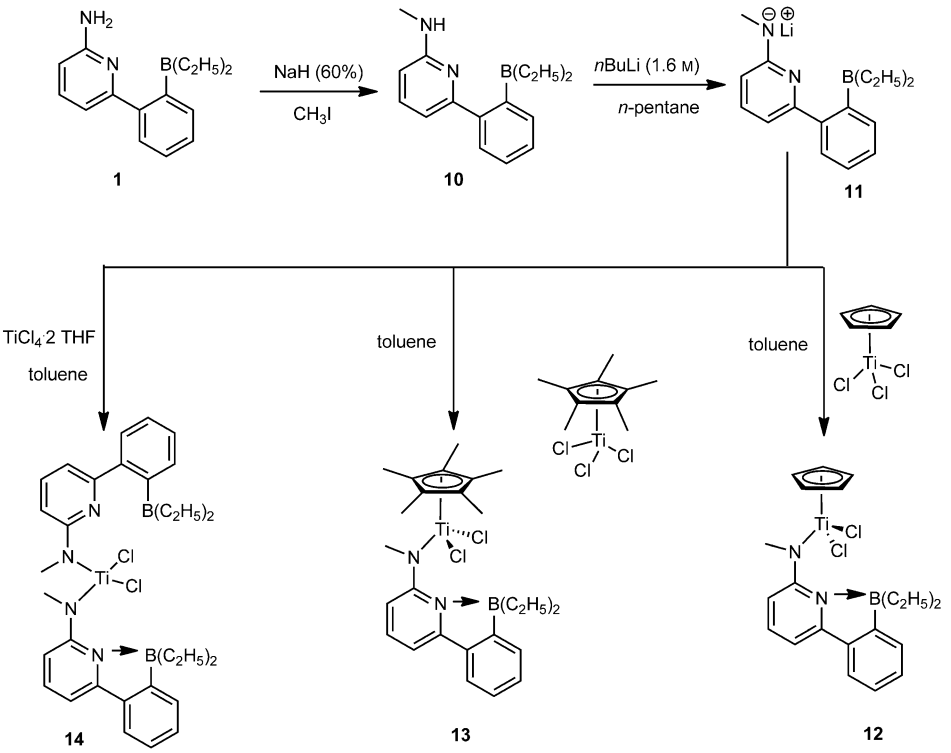


Figure 2. ORTEP drawing of complex **7 b** (50 % thermal ellipsoids). Selected bond lengths [pm] and angles [°]: Zr1–N1 201.78(16), Zr1–N2 213.41(16), Zr1–Cl1, 240.75(5), Zr1–Cl2 241.97(5), B1–N3 159.1(3), B1–C17 162.1(3), B1–C28 164.2(3), B1–C22 165.4(3); N1-Zr1-N2 74.52(6), N1-Zr1-Cl1 94.59(5), N2-Zr1-Cl1 104.66(5), N1-Zr1-Cl2 101.11(5), N2-Zr1-Cl2 152.51(5), Cl1-Zr1-Cl2 102.731(18), N3-B1-C17 97.80(14), N3-B1-C28 111.38(15), C17-B1-C28 111.88(16), N3-B1-C22 109.28(16), C17-B1-C22 108.67(15), C28-B1-C22 116.24(14).

215.4(4) pm, and Zr1A–N5A 215.9(4) pm with almost square-planar arrangements of the Zr1A-N4A-Si2A-N6A and Zr1A-N2A-Si1A-N5A planes. Reaction of ligands **3** and **6 a**, respectively, with $HfCl_4$ resulted in the structurally similar compounds [Me_2Si\{(N-*t*Bu)(6-\{2-(diethylboryl)phenyl\}pyridyl-2-yl-N)\}$_2$Hf] (**8**) and [Me_2Si\{(N-Ad)(6-\{2-(diethylboryl)phenyl\}pyridyl-2-yl-N)\}$_2$Hf] (**9**) (Scheme 3). Complex **7 b** crystallizes in the tetragonal space group $I\bar{4}$ with $a = b = 1870.84(6)$ pm, $c = 2214.38(7)$ pm, $\alpha = \beta = \gamma = 90°$, $Z = 8$. Figure 2 shows the X-ray structure of this complex as well as relevant bond lengths and angles. In the solid state, the nitrogen is coordinated to boron with a B–N distance of 150.1(3) pm.

The Ti-based complexes [(N-\{6-(2-diethylborylphenyl)pyrid-2-yl\}-N-Me)Cp′$TiCl_2$] (Cp′ = C_5H_5 (**12**), C_5Me_5 (**13**)) and [$TiCl_2$(N-\{6-(2-diethylborylphenyl)pyrid-2-yl\}-N-Me)$_2$] (**14**) were synthesized in a three-step procedure according to Scheme 4. First, *N*-\{6-[2-(diethylborylphenyl)pyrid-2-yl]\}-*N*-methylamine (**10**) was synthesized by the reaction of **9** with NaH (60 wt % in mineral oil) in dimethylformamide (DMF) at 0 °C followed by treatment with CH_3I and was isolated in high yield (90 %). Compound **10** was then deprotonated using *n*BuLi (1.6 M) in *n*-pentane and the corresponding Li salt (**11**) was isolated by filtration. Finally, **11** was reacted with Cp′$TiCl_3$ (Cp′ = C_5H_5 and C_5Me_5, respectively) in toluene at room temperature for 12 h and the corresponding Ti complexes **12** and **13** were isolated in moderate yields (50–55 %). The Ti complex **14** was synthesized in an anal-



Scheme 4. Syntheses of complexes **10–14**.

ogous manner using $TiCl_4$·2thf (0.5 equiv) in toluene.[14] Complexes **12** and **13** were crystallized from a mixture of toluene and pentane (2:8) at −36 °C. The structures of complexes **12** and **13** and selected bond lengths and angles are shown in Figures 3 and 4.

Complex **12** crystallizes in the monoclinic space group $P2_1/n$, $a=1099.79(11)$ pm, $b=1613.18(19)$ pm, $c=1233.24(11)$ pm, $\alpha=\gamma=90°$, $\beta=106.79°$, $Z=4$. Complex **13** crystallizes in the triclinic space group $P\bar{1}$, $a=925.38(4)$ pm, $b=1151.35(5)$ pm, $c=1277.79(6)$ pm, $\alpha=77.233°$, $\beta=81.007°$, $\gamma=72.946°$, $Z=2$. In both **12** and **13**, Zr adopts a tetrahedral geometry around the metal center and the pyridine nitrogen is coordinated to the diethylboryl group, at least in the solid state. The Ti–N distances in **12** (188.91 pm) and **13** (192.59 pm) are slightly longer than those previously reported for Ti complexes[15,16] (186.7–187.8 pm) but still shorter than the estimated value (202 pm) of a Ti–N single bond according to Pauling's radii. The average bond length of the Ti–Cl in **12** (226.7 pm) and **13** (227.19 pm) are shorter than those reported for [$CpTiCl_2${N(2,6-*i*Pr-C_6H_3)Me}] (227.5 pm; $Cp=C_5H_5$), [Cp^*TiCl_2{N(2,6-*i*Pr-C_6H_3)Me}] (228.5 pm; $Cp^*=C_5Me_5$), and [Cp^*TiCl_2{N(2,6-Me-C_6H_3)Me}] (228.1 pm),[16] and longer than the reported value for [Cp^*TiCl_2{N(Me)Cy}] (230.3 pm).[15] The N1-Ti1-Cl1 angle is almost the same in both **12** (106.22°) and **13** (106.26°); a subtle difference was observed in the bond angles of N1-Ti1-Cl2 in **12** (100.95°) and **13** (99.61°). The bond angles

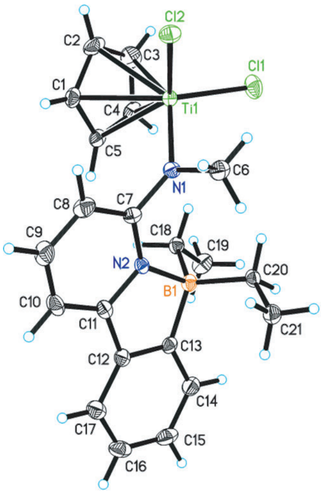


Figure 3. ORTEP drawing of complex **12** (50% thermal ellipsoids). Bond lengths [pm] and angles [°]: Ti1–N1 188.91, Ti1–C1 235.5, Ti1–Cl1 226.01, Ti1–C2 235.8, Ti1–Cl2 227.39, Ti1–C3 233.7, N1–C6 149.0, Ti1–C4 233.4, N1–C7 141.3, Ti1–C5 234.59, B1–N2 169.4, N2–C7 136.0; N1-Ti1-Cl1 106.22, C7-N1-Ti1 136.20, N1-Ti1-Cl2 100.95, C6-N1-Ti1 108.79, Cl1-Ti1-Cl2 103.71, C7-N1-C6 111.17.

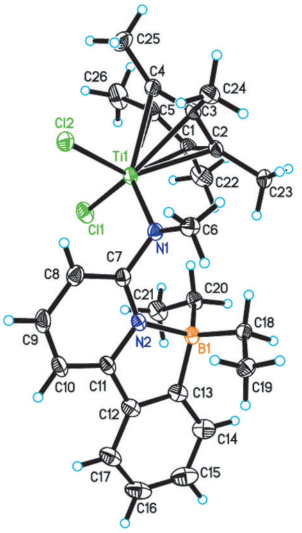


Figure 4. ORTEP drawing of complex **13** (50% thermal ellipsoids). Bond lengths [pm] and angles [°]: Ti1–N1 192.59, Ti1–C3 237.24, Ti1–Cl1 225.71, Ti1–C4 237.95, Ti1–Cl2 228.68, Ti1–C5 238.74, N1–C6 147.79, C1–C22 149.91, N1–C7 142.42, C2–C23 150.15, B1–N2 168.00, C3–C24 150.05, Ti1–C1 236.70, C4–C25 149.35, Ti1–C2 238.42, C5–C26 150.34; N1-Ti1-Cl1 106.26, C7-N1-Ti1 117.28, N1-Ti1-Cl2 99.61, C6-N1-Ti1 126.24, Cl1-Ti1-Cl2 101.225, C7-N1-C6 109.85.

Cl1-Ti1-Cl2 (103.71° in **12** and 101.22° in **13**) are slightly smaller than those in [CpTiCl$_2${N(2,6-*i*Pr-C$_6$H$_3$)Me}] (105.22°) and [Cp*TiCl$_2${N(2,6-*i*Pr-C$_6$H$_3$)Me}] (104.91°).

Homopolymerization of ethylene (E)

Group 4 bis-amido complexes are known to present active precatalysts for olefin homo- and copolymerization.[17–19] Whereas nonbridged bis-amido complexes showed only low activities (<20 kg of polymer/mol$_{\text{cat.}}$ h bar), the bridged analogues allowed for high activities in the polymerization of 1-olefins, with typical values for PE and PP in the range of 3.5–5300 and 7–320 kg mol^{-1}$_{\text{cat.}}$ h bar.[20–25] In all these polymerizations, both the polymerization kinetics and the activity are strongly influenced by the chelate ring size.[23]

The homopolymerization of E by the action of precatalysts **4**, **7 a**, **7 b**, and **12**–**14**, activated by MAO, yielded PE with melting points in the range of $115 < T_m < 133$ °C (Table 1). Particularly with precatalyst **14**, activities up to 750 kg mol^{-1}$_{\text{cat.}}$ bar h were observed. Notably, high molecular weights in the range of $1\,800\,000 < M_n < 4\,000\,000$ g mol^{-1} were accessible with all precatalysts. With precatalysts **4**, **7 a**, **7 b**, **13**, and **14**, an increase in temperature resulted in an increase in activity. With increasing polymerization temperature, the resulting polymer molecular weights decreased dramatically, except for **7 a** and **7 b**. This decrease in molecular weight can be attributed to β-hydride elimination (see below).[26] It appears that the large adamantyl group in **7 a** effectively impedes both α- and β-agostic interactions and prevents any of the aforementioned elimination reactions, which allows for the synthesis of UHMWPE with M_n values up to 4 000 000 g mol^{-1}. A further increase in the steric bulk at the borane, that is, switching from ethyl substituents in **7 a** to the phenyl substituent in **7 b** prevents reactivity and also results in lower molecular weights. In addition, pentyl side groups are observed (see below), which indicate substantial chain walking. Although precatalyst **12** allows for comparably low PDIs (1.65 < PDI < 2.7), broad molecular-weight distributions were observed for all other precatalysts (Table 1). For a representative GPC profile of **14**/MAO-derived PE prepared at various temperatures, please refer to Figure S30 in the Supporting Information.

Table 1. Results of E homopolymerization by the action of **4**, **7 a**, **7 b**, **12**, **13**, or **14** activated by MAO.[a]

Entry	Cat.	T [°C]	Activity[b]	M_n [g mol^{-1}][c]	PDI[c]	T_m [°C][d]
1	**4**	50	53	1 800 000	9	133
2	**4**	65	54	1 000 000	11	130
3	**4**	90	185	900 000	8	132
4	**7 a**	50	93	325 000	11	133
5	**7 a**	65	105	630 000	3.4	134
6	**7 a**	90	188	4 000 000	7	132
7	**7 b**	65	14	121 000	7.7	124
8	**7 b**	80	90	340 000	2.3	125
9	**12**	50	13	1 800 000	1.65	130
10	**12**	65	19	900 000	2.7	115
11	**12**	90	6	800 000	2.1	130
12	**13**	50	13	3 000 000	17	132
13	**13**	65	16	n.d.	n.d	136
14	**13**	90	16	1 500 000	6	134
15	**14**	50	300	2 700 000	3.4	131
16	**14**	65	750	700 000	4.7	130
17	**14**	90	750	600 000	6	134

[a] Polymerization conditions: 500 mL autoclave; total volume of the reaction mixture: 250 mL; catalyst/MAO 1:2000; $p = 4$ bar of E; toluene; $t = 1$ h. [b] kg mol^{-1}$_{\text{cat.}}$ bar h. [c] GPC data in 1,2,4-trichlorobenzene versus PS. [d] Measured by DSC. n.d. = not determined owing to poor solubility.

Polymer structure

In the homopolymerization of E with Zr-based **4** and **7 a** and Ti-based **12**–**14**, highly linear PE (HDPE) was obtained as evidenced by high-temperature ^{13}C NMR spectroscopy measurements and the high melting temperatures (T_m values 130–136 °C) determined by differential scanning calorimetry (DSC).[27] A representative ^{13}C NMR spectrum of PE obtained through the action of **4**/MAO is shown in Figure 5. In contrast to **7 a** (Figure 6b), precatalyst **7 b** yields pentyl-branched PE with about 60 branches per 1000 carbon atoms (Figure 6a). Also, vinyl end groups derived from β-hydride elimination become visible.

Copolymerization of E with cyclopentene (CPE)

The copolymerization of E with CPE was carried out with Zr complexes **4**, **7 a**, and **7 b** at various temperatures and with varying CPE content in the polymerization mixture (Table 2). Generally, activities increased with increasing temperature. For all precatalysts investigated and in particular for the Zr-based precatalyst **4**, a dramatic increase in activity was observed with increasing concentrations of CPE. Thus, by increasing the CPE concentration from 0 to 40 vol% at $T = 50$ °C, the activity increased from 53 to 7500 kg PE/mol$_{\text{cat.}}$ bar h (Table 2, entries 1–5), which corresponds to an activation factor of greater than 140. With increasing temperature, the number-average molecular weight of the resulting polymer decreased from 900 000 to 50 000 g mol^{-1}. The PDI was in the range of 1.6 to 2.5, with melting points in the range $127 < T_m < 134$ °C observed.

With **4**/MAO, no CPE incorporation was detected by NMR spectroscopy up to 20 vol% of CPE; 40 vol% of CPE in the reaction mixture yielded up to 3.5 mol% of incorporated CPE (Figure 7, Table 2, entry 5). Apart from the signal for linear PE at $\delta = 29.8$ ppm, the signals at $\delta = 32.0$ (C$_{4',5'}$), 40.5 (C$_{1',3'}$), and 40.9 ppm (C$_{2'}$) are typical resonances for 1,3-incorporated CPE units[28] that are formed by means of 1,2-insertion of CPE followed by β-hydride elimination and subsequent reinsertion.[1,29–30] The signals at $\delta = 23.0$ (C$_4$), 30.9 (C$_{3,5}$), and 43.0 ppm (C$_{1,2}$) can be assigned to isolated 1,2-incorporated CPE units.[28,31]

The effect of CPE on polymerization activity was less pronounced for **7 a** and only minor for **7 b**. It appears that the bulky adamantyl group in **7 a** and **7 b** and an additional bulky diphenylboryl group in **7 b** impede the coordination of CPE. To shed light onto the role of CPE in this copolymerization, we

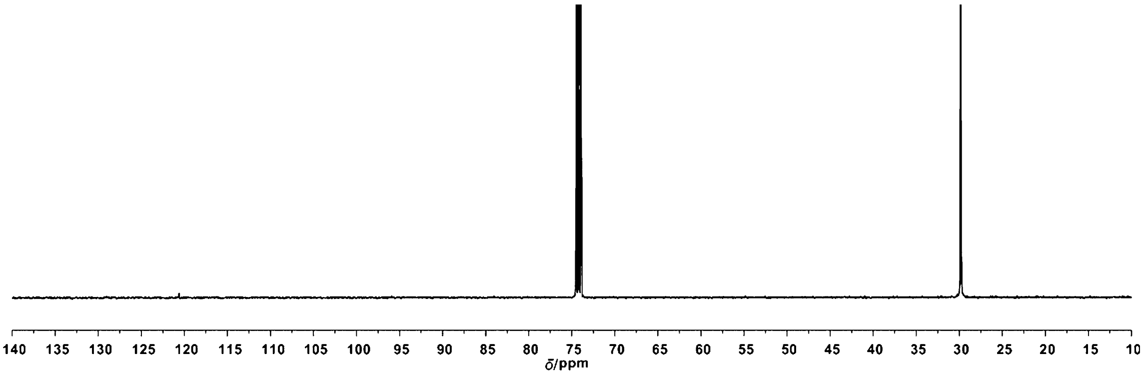


Figure 5. ^{13}C NMR spectrum of PE produced by the action of **4/MAO** at 90 °C using 4 bar of E (Table 1, entry 3 in 1,1,2,2-[D$_2$]tetrachloroethane). The signal at $\delta = 120.64$ ppm is a solvent impurity.

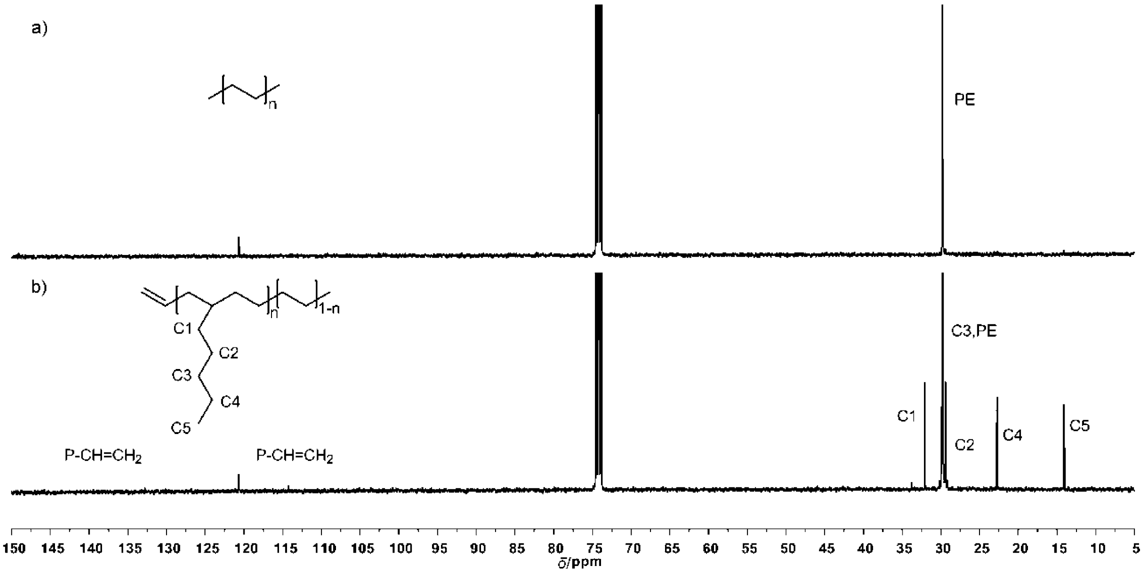


Figure 6. ^{13}C NMR spectrum (1,1,2,2-[D$_2$]tetrachloroethane) of PE produced by the action of a) **7 b**/MAO and b) **7 a**/MAO (Table 1, entries 6 and 13). The signal at $\delta = 120.64$ ppm is a solvent impurity.

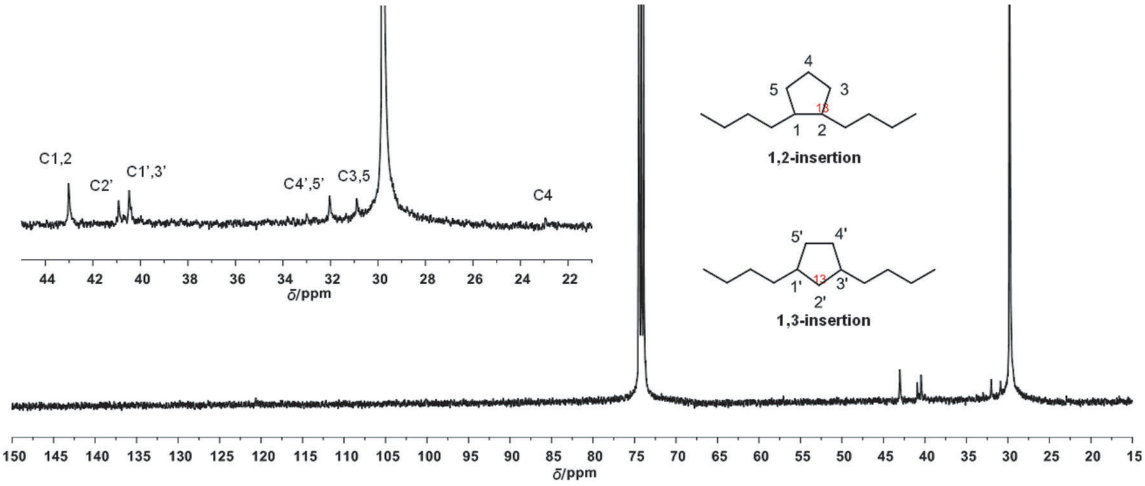


Figure 7. ^{13}C NMR spectrum of **4**/MAO-derivedPE-*co*-poly(CPE) using 40 vol % of CPE (Table 2, entry 5 in 1,1,2,2-[D$_2$]tetrachloroethane).

Table 2. Results of E/CPE copolymerization by the action of complexes **4**, **7b**, and **7b** activated by MAO.[a]

Entry	Cat.	CPE [vol%]	T [°C]	Activity[b]	M_n [g mol^{-1}][c]	CPE[d] [mol%]	PDI[c]	T_m [°C][e]
1	***4***	*0*	*50*	*53*	*1800000*	*0*	*9*	*133*
2	**4**	2	50	575	900000	<0.5	2.3	132
3	**4**	5	50	3000	600000	<0.5	1.6	134
4	**4**	20	50	2250	100000	<0.5	2.7	128
5	**4**	40	50	7500	50000	3.5	2.5	127
6	***7a***	*0*	*50*	*93*	*325000*	*0*	*11*	*133*
7	**7a**	3.5	50	1050	443000	<0.5	2.0	135
8	**7a**	3.5	65	2250	298000	<0.5	1.8	133
9	**7a**	2	70	5250	190000	<0.5	1.6	135
10	**7a**	0	80	130	551000	0	4.2	135
11	**7a**	0.1	80	250	280000	<0.5	2.0	135
12	**7a**	3.5	80	4000	92000	<0.5	2.3	134
13	**7b**	3.5	50	275	534000	<0.5	1.6	135
14	**7b**	44	50	385	180000	0.6	1.7	131
15	***7b***	*0*	*65*	*14*	*121000*	*0*	*7.7*	*124*
16	**7b**	3.5	65	575	240000	<0.5	1.9	132
17	**7b**	3.5	80	1265	226000	<0.5	1.7	134

[a] Polymerization conditions: 500 mL autoclave; total volume of the reaction mixture: 250 mL; $p=4$ bar of E; catalyst/MAO 1:2000; toluene; $t=1$ h. [b] kg mol$^{-1}_{\text{cat.}}$ bar h. [c] GPC data in 1,2,4-trichlorobenzene versus PS. [d] CPE content in the copolymer as estimated by ^{13}C NMR spectroscopy. [e] Measured by DSC. For GPC traces refer to Figure S31, for DSC traces refer to Figure S32. Data printed in italics are taken from Table 1.

prepared [^{13}C]cyclopent-1-ene and used it on an 8 vol% level in the **7a**/MAO-triggered copolymerization with E (Figure 8). Again, the above-described signals for 1,2- and 1,3-incorporated CPE are present, among other unassigned ones. These data clearly show an otherwise undetectable incorporation of CPE (<0.5 mol%) in the copolymerization with E even at low CPE concentrations in the reaction mixture and clearly prove the involvement of CPE in the entire polymerization process. Since CPE becomes incorporated into the polymer chain even at lower concentration and increases the activity at any volume level (Table 2), it must act in some way as a stabilizing agent. Interestingly, and in contrast to E homopolymerization, no vinyl end groups are visible in any of the copolymers. Scheme 5 shows the proposed role of CPE. Because any β-hydride elimination or transfer to monomer would result in terminal alkenes, we propose that CPE coordinates to the metal and promotes alkyl transfer to the aluminum atom of MAO. This pathway accounts for the finding that no terminal alkenes were visible in the polymer. It also explains the decrease in molecular weights with increasing CPE content in the polymerization mixture, which promotes coordination of CPE to the metal center. Finally, it seems reasonable to propose such a coordination, since the concentration of CPE in toluene even at a 2 vol% level is already six times higher than that of ethylene (ca. 0.3 M versus 0.05 M).[32] A simple polarity effect, caused by the polarity of CPE at high CPE concentration, can be ruled out in view of the effect of even low CPE concentrations (Table 2). It was additionally ruled out by running experiments with a mixture of toluene/heptane (60:40). No increase in polymerization activity was observed.

Conclusion

Novel Group 4 bis-amido complexes bearing the 6-[2-(diethylboryl)phenyl]pyrid-2-ylamido motif, including nonbridged half-titanocene complexes and a titanium(IV)-based metallocene-type complex, have been synthesized and their structures have been determined by single-crystal X-ray diffraction analysis. Corresponding Hf^{IV} complexes were also obtained. Upon activation of these zirconium and titanium complexes with MAO, they showed activities up to 750 kg of PE/mol$_{\text{cat.}}$ bar h in the

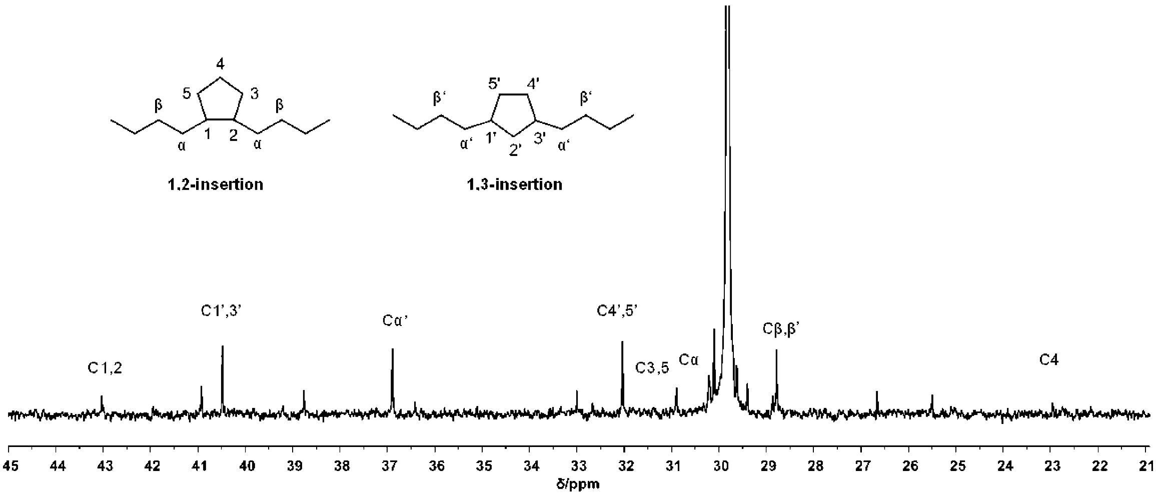
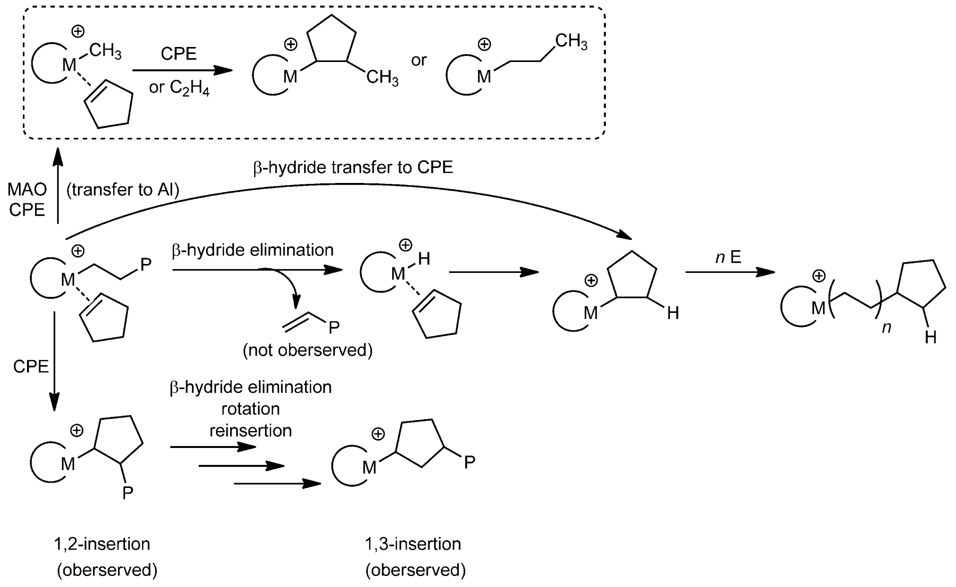


Figure 8. ^{13}C NMR spectrum of PE-*co*-poly(CPE-1-^{13}C) in 1,1,2,2-[D$_2$]tetrachloroethane produced by the action of **7a**/MAO (8 vol% of CPE-1-^{13}C in the polymerization mixture). The signal at $\delta=120.64$ ppm is a solvent impurity.



Scheme 5. Role of CPE in the (co-)polymerization with E (P = polymer chain).

homopolymerization of E, producing mainly linear HDPE with molecular weights in the range of $1\,800\,000 < M_n < 4 \times 10^6$ g mol^{-1}. In the copolymerization of E with CPE, the polymerization activities of complexes **4**, **7a**, and **7b** can be enhanced by a factor of 140 up to 7500 kg PE/mol$_{cat.}$ bar h, which produced PE-*co*-poly(CPE) containing 3.5 mol% of CPE. This dramatic increase in polymerization activity for E in the presence of CPE can be attributed to an involvement of CPE in the polymerization process rather than to solvent polarity.

Experimental Section

General remarks

Except where noted, all manipulations were conducted in the absence of oxygen and water under an atmosphere of nitrogen, either by the use of standard Schlenk techniques or within a nitrogen-filled MBraun glovebox utilizing glassware that was oven-dried and evacuated while hot prior to use. Toluene, diethyl ether, pentane, thf, and dichloromethane were dried and deoxygenated by means of degassing with nitrogen, followed by passage through a triple-column solvent-purification drying system (MBraun SPS). Deuterated NMR spectroscopy solvents were degassed with freeze–pump–thaw cycles. [D$_6$]Benzene, [D$_8$]toluene, and [D$_8$]tetrahydrofuran were dried and distilled from Na/benzophenone; CD_2Cl_2 and $CDCl_3$ were dried and distilled from CaH_2. MAO and triisobutylaluminum (1.1 M solution in toluene) were purchased from Aldrich Chem. Co. Trimethylaluminum was removed from commercial MAO (10 wt% solution in toluene, Aldrich Chem. Co.) by means of drying under vacuum (8 h, 70 °C) and the obtained solid MAO was redissolved in toluene to make a 2.0 M solution, which was stored in the dry box. Ethylene (Air Products) was dried by passing through columns filled with a Cu-based catalyst (BASF catalyst R3-11) and then through molecular sieves (3 Å) before use. Cyclopentene (95%, Fluka) was dried over calcium hydride, vacuum transferred, and stored in the glovebox. [^{13}C]cyclopent-1-anol (99 atom%) was purchased form Sigma–Aldrich (München, Germany). 85% phosphoric acid and potassium pyrosulfate were obtained from Merck (Karlsruhe, Germany). Purchased chemicals were used without further purification.

NMR spectroscopy data were obtained at 250.13 or 600.25 MHz for proton and at 62.5 or 100.6 MHz for carbon in the indicated solvent at 25 °C on a Bruker Spectrospin 250 and are listed in parts per million downfield from tetramethylsilane for proton and carbon. High-resolution mass spectra (ESI) were recorded on an APEX II FTICR mass spectrometer, Bruker Daltonics. Infrared spectra were recorded from 4000–400 cm^{-1} on a PerkinElmer 881 spectrometer using ATR technology.

Homopolymerization of E and copolymerizations of E with CPE were performed in a Büchi–Uster pressure reactor (polyclave) equipped with a Huber thermostat (Unistat Tango Nuevo). The monomer feed of the gaseous monomer was kept constant with a Büchi pressflow bpc 6010 flow controller. The reaction was monitored by a bdsmc Büchi data system.

GC–MS investigations were carried out on a Shimadzu GCMS-QP2010S equipped with an AOC-20i autosampler using a SPB fused silica (Rxi-5MS) column (30 m × 0.25 mm × 0.25 μm film thickness). Molecular weights and molecular-weight distributions were measured by high-temperature gel chromatography (HT-GPC) on a Polymer Standards HT-GPC system with triple detection (refractive index, light-scattering at 15 and 90°, viscosimetry) using three consecutive Waters Styragel HR4 4.6 × 300 mm columns in 1,2,4-trichlorobenzene at 145 °C. The flow rate was set to 1 mL min^{-1}. Narrow polystyrene standards in the range $162 < M_n < 6\,035\,000$ g mol^{-1} (Easi Vial-red, yellow and green) were purchased from Polymer Labs. DSC data were recorded by heating under a nitrogen atmosphere on a DSC7 PerkinElmer differential scanning calorimeter.

Syntheses

Methoxydiphenylborane: In a 100 mL Schlenk flask, $PhSiMe_3$ (25 g, 0.17 mol) was added dropwise to BBr_3 (20.8 g, 0.08 mol) under nitrogen at 0 °C. After addition was complete, the mixture was gradually warmed to room temperature and then placed into an oil bath preheated to 125 °C. The mixture was then slowly heated to 200 °C and left at reflux for 16 h. During this time, bromotrimethylsilane was allowed to distil off through a 30 cm Vigreux column. Fractionated distillation allowed for the separation of 10% byproduct (dibromophenylborane). Finally, diphenylbromoborane (11 g, 80%) was collected.[33] ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 7.52$ (m, 4H), 7.64 (m, 2H), 8.02 ppm (m, 4H); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 128.0$, 133.2, 137.6 ppm; GC–MS (EI, 70 eV): *m/z* calcd for $C_{12}H_{10}BBr$: 244.92; found: 244.1.

Under stirring, a solution of methoxytrimethylsilane (4.68 g, 4.50 mmol) in toluene (8 mL) was added dropwise at −78 °C to a solution of diphenylbromoborane (11 g, 4.50 mmol) in toluene (20 mL). The reaction mixture was slowly warmed to room temperature and stirred overnight. All volatiles were removed from the reaction mixture under vacuum and the crude oily product was extracted with *n*-hexane. Yield of methoxydiphenylborane: 7.1 g (81 %).[34] ^{1}H NMR (400.13 MHz, C_6D_6): $\delta = 7.24$ (m, 6H), 7.66 ppm (m, 4H); ^{13}C NMR (100.62 MHz, C_6D_6): $\delta = 128.4$, 130.5, 134.7 ppm; GC–MS (EI, 70 eV): *m/z* calcd for $C_{13}H_{13}BO$: 196.05; found: 196.1.

Ligand 1 b: *n*-Butyllithium (1.6 M in hexanes, 9.6 mL, 15.3 mmol) was added to a solution of 2-(2-bromophenyl)-6-(2,2,5,5-tetramethyl-1,2,5-azadisilolidin-1-yl)pyridine (5.0 g, 12.8 mmol) in diethyl ether (50 mL) at −78 °C and the mixture was stirred for 2 h at this temperature. Diphenylmethoxyborane (2 M in thf, 10 mL, 10 mmol) was then added and the resulting mixture was stirred for a further 1 h at −78 °C. The mixture was allowed to warm to room temperature overnight and was then poured into iced water and was stirred for 15 min. The organic phase was isolated and the water phase was extracted twice with ethyl acetate. The combined organic phases were washed with brine and dried over $MgSO_4$. After removal of the solvents, the residue was subjected to chromatography on silica gel eluting with EtOAc/pentane (1:10, containing 3 drops of triethylamine per 1000 mL of eluent). Yield: 3.1 g (73 %); ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 4.95$ (s, 2H), 6.42 (d, $^{3}J(\mathrm{H,H}) = 8.3$ Hz, 1H), 7.16 (m, 2H), 7.22 (m, 5H), 7.35 (m, 5H), 7.52 (d, $^{3}J(\mathrm{H,H}) = 7.1$ Hz, 1H), 7.74 ppm (t, $^{3}J(\mathrm{H,H}) = 7.9$ Hz, 2H); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 106.2$, 108.5, 121.2, 125.8, 125.9, 127.7, 130.0, 130.1, 133.5, 136.2, 141.3, 154.8, 157.1 ppm; FTIR (ATR): $\tilde{\nu} = 3502$ (s), 3397 (s), 3060 (s), 1636 (s), 1496 (s), 1425 (s), 1305 (m), 1174 (s), 863 (m), 805 (m), 757 (s), 702 cm^{-1} (s); ESI-MS: *m/z* calcd for $C_{23}H_{19}BN_2$: 334.22; found: 334.2.

Ligand 2: Triethylamine (14.5 g, 143.5 mmol) and *tert*-butylamine (10 g, 136.7 mmol) were added to a solution of dichlorodimethylsilane (17.6 g, 136.7 mmol) in *n*-pentane (50 mL) at 0–5 °C, and the resulting reaction mixture was stirred at room temperature for 16 h, then filtered to remove the salts (triethylammonium hydrochloride). The filtrate was transferred into a distillation apparatus to remove both triethylamine and pentane until a reflux temperature of 50 °C was reached. The remaining liquid was determined to be a pure product (10 g, 44 %). ^{1}H NMR (C_6D_6, 250 MHz): $\delta = 0.29$ (s, 6H; $\mathrm{Si}(\mathit{CH}_3)_2$), 0.96 (br, 1H; *NH*), 1.08 ppm (s, 9H; $\mathrm{C}(\mathit{CH}_3)_3$); ^{13}C NMR ($C_6D_6$, 250 MHz): $\delta = 4.4$, 33.1, 50.2 ppm; GC–MS: *m/z* calcd for $C_6H_{16}ClNSi$: 165.07; found: 164.9 [$M^{\bullet+}$]; elemental analysis calcd (%) for $C_6H_{16}ClNSi$: C 43.48, H 9.73, N 8.45; found: C 43.26, H 9.85, N 8.63.

Ligand 3: A solution of *n*BuLi (0.73 mL of 1.6 M in hexanes, 0.69 mmol) was added to a solution of **1** (150 mg, 0.63 mmol) in diethyl ether (20 mL) at −37 °C. The reaction mixture was warmed to room temperature for 2 h. Then, **2** (0.103 mg, 0.63 mmol) dissolved in diethyl ether (10 mL) was added slowly to the reaction mixture and stirred at room temperature for 16 h. The reaction mass was filtered over Celite and the filtrate was removed under vacuum to obtain **3** (200 mg, 86 %) as a white solid. ^{1}H NMR (C_6D_6, 250 MHz): $\delta = 0.21$ (s, 6H; $\mathrm{Si}(\mathit{CH}_3)_2$), 0.71 (br, 1H; *t*-butyl–*NH*), 0.87–0.93 (t, $J(\mathrm{H,H}) = 7.5$ Hz, 6H; $\mathrm{B}(\mathrm{CH}_2\mathit{CH}_3)_2$), 1.11 (s, 9H; *t*-butyl), 1.26–1.38 (m, 2H; $\mathrm{B}(\mathit{CH}_2\mathrm{CH}_3)_2$), 1.45–1.60 (m, 2H; $\mathrm{B}(\mathit{CH}_2\mathrm{CH}_3)_2$), 5.98 (br, 1H; Ar–*NH*), 6.67–6.71 (dd, $J(\mathrm{H,H}) = 0.75$ Hz, 1H; ArH), 6.88–6.91 (d, 1H; ArH), 7.13–7.19 (t, $J(\mathrm{H,H}) = 7.5$ Hz, 1H; ArH), 7.3–7.36 (ddd, $J(\mathrm{H,H}) = 1$ Hz, 1H; ArH), 7.48–7.54 (ddd, $J(\mathrm{H,H}) = 1$ Hz, 1H; ArH),7.70–7.73 (d, $J(\mathrm{H,H}) = 7.5$ Hz, 1H; ArH), 7.90–7.93 ppm (d, $J(\mathrm{H,H}) = 7.5$ Hz, 1H; ArH); ^{13}C NMR (C_6D_6, 250 MHz): $\delta = 1.4$, 8.8, 14.1, 31.7, 48.3, 104. 3, 106.9, 119.6, 124.1, 127.9, 128.7, 136.4, 138.1 ppm; GC–MS: *m/z* calcd for $C_{21}H_{34}BN_3Si$: 367.2; found: 338.2 $[M-C_2H_5]^+$.

Complex 4: A solution of *n*BuLi (1.6 M in hexanes, 0.73 mL, 1.14 mmol) was added to a solution of **3** (200 mg, 0.544 mmol) in *n*-pentane (15 mL) at −37 °C. A large amount of white precipitate formed during the addition. The reaction mixture was warmed to room temperature and was stirred for 3 h. The resulting precipitate was collected on a frit, washed with cold *n*-pentane (10 mL) and dried under vacuum to give the pure Li salt of **3** (160 mg), which was used without any further analysis.

The Li salt of **3** (160 mg, 0.42 mmol) was dissolved in toluene (20 mL) and added to a solution of $ZrCl_4{\cdot}2\,thf$ (160 mg, 0.42 mmol) in toluene (15 mL) at −37 °C and the resulting reaction mixture was stirred at room temperature for 6 h. Then the mixture was filtered through Celite and the solvent was removed under reduced pressure. *n*-Pentane was added and the solution was stored in a glovebox freezer for 24 h to precipitate the Zr complex **4** (200 mg, 80 %) as a white solid. ^{1}H NMR (C_6D_6, 250 MHz): $\delta = 0.52$ (s, 3H; $\mathrm{Si}(\mathit{CH}_3)_2$), 0.7–0.80 (m, 9H; $\mathrm{Si}(\mathit{CH}_3)_2$, $\mathrm{B}(\mathrm{CH}_2\mathit{CH}_3)_2$), 1.05–1.14 (m, 4H; $\mathrm{B}(\mathit{CH}_2\mathrm{CH}_3)_2$), 1.29–1.40 (m, 4H; thf), 1.62 (s, 9H; *t*-butyl), 4.29 (br, 4H; thf), 6.70–6.73 (d, $J(\mathrm{H,H}) = 7.5$ Hz, 1H; ArH), 6.95–6.98 (d, $J(\mathrm{H,H}) = 7.5$ Hz, 1H; ArH), 7.17–7.24 (t, $J(\mathrm{H,H}) = 7.5$ Hz, 1H; ArH), 7.30–7.37 (ddd, $J(\mathrm{H,H}) = 2.5$ Hz, 1H; ArH), 7.49–7.56 (ddd, $J(\mathrm{H,H}) = 0.75$ Hz, 1H; ArH), 6.67–6.70 (d, $J(\mathrm{H,H}) = 7.75$ Hz, 1H; ArH), 7.77–7.74 ppm (d, $J(\mathrm{H,H}) = 7.25$ Hz, 1H; ArH); ^{13}C NMR (C_6D_6, 250 MHz): $\delta = 5.2$, 5.6, 10.9, 11.7, 20.2, 25.0 (thf), 35.16, 57.5, 78.0 (thf), 107.2, 115.7, 121.0, 125.5, 129.1, 129.6, 137.8, 139.0, 158.1, 160.8 ppm; elemental analysis calcd (%) for $C_{25}H_{40}BCl_2N_3OSiZr$: C 50.08, H 6.72, N 7.01; found: C 50.37, H 7.08, N 7.34.

Ligand 5: A solution of *n*BuLi (1.6 M in hexanes, 22 mL, 34.68 mmol) was slowly added to a solution of 1-adamantylamine (5.0 g, 33.05 mmol) in pentane (100 mL) at −60 °C. A large amount of white precipitate formed during the addition. The reaction mixture was warmed to room temperature and was stirred for 4 h. The resulting precipitate was collected on a frit, washed with cold *n*-pentane (10 mL), and dried under vacuum to give pure lithium 1-adamantylamide (5.0 g, 99 %), which was used for the next reaction without any analysis.

Dichlorodimethylsilane (10.25 g, 79.49 mmol) was stirred in thf (75 mL) and lithium-1-adamantylamide (5.0 g, 31.79 mmol) in thf (50 mL) was added slowly and the resulting reaction mixture was allowed to stir for 2.5 h at room temperature. Then, all volatiles were removed under vacuum and the residue was extracted with pentane and evaporated under reduced pressure to isolate **5** as a white solid (6.0 g, 75 %). ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.44$ (s, 6H; $\mathrm{Si}(\mathit{CH}_3)_2$), 1.24 (br, 1H; *NH*), 1.59 (s, 6H; Ad–CH_2), 1.70 (s, 6H; Ad–CH_2), 2.02 ppm (s, 3H; Ad–*CH*); ^{13}C NMR ($CDCl_3$, 250 MHz): $\delta = 4.6$, 29.8, 36.1, 46.5, 50.5 ppm; GC–MS: *m/z* calcd for $C_{12}H_{22}ClNSi$: 243.1; found: 243.1 [M^+]; elemental analysis calcd (%) for $C_{12}H_{22}ClNSi$: C 59.11, H 9.09, N 5.74; found: C 58.86, H 8.96, N 5.62.

Ligand 6 a: A solution of *n*BuLi (1.6 M in hexanes, 0.73 mL, 1.14 mmol) was added to a solution of **1** (250 mg, 1.05 mmol) in diethyl ether (20 mL) at −37 °C. The reaction mixture was warmed to room temperature for 2 h. Then, **5** (0.25 mg, 1.05 mmol), dissolved in diethyl ether (10 mL), was added slowly to the reaction mixture and the mixture was stirred at room temperature for 16 h. After filtration and evaporation of the solvent under vacuum, **6 a** (420 mg, 90 %) was obtained as a white solid. ^{1}H NMR (C_6D_6, 250 MHz): $\delta = 0.29$ (s, 6H; $\mathrm{Si}(\mathit{CH}_3)_2$), 0.79 (br, 1H; Ad–*NH*), 0.90–0.96 (t, $J(\mathrm{H,H}) = 7.5$ Hz, 6H; $\mathrm{B}(\mathrm{CH}_2\mathit{CH}_3)_2$), 1.28–1.43 (m, 2H; $\mathrm{B}(\mathit{CH}_2\mathrm{CH}_3)_2$), 1.48–1.57 (m, 2H; $\mathrm{B}(\mathit{CH}_2\mathrm{CH}_3)_2$), 1.57–1.6 (t, 6H; Ad–$\mathit{CH}_2$), 1.74–1.75 (d, $J(\mathrm{H,H}) = 2.5$ Hz, 6H; Ad–CH_2), 2.0 (m, 3H; Ad–*CH*), 6.05 (br, 1H; Ar–NH), 6.75–6.79 (d, $J(\mathrm{H,H}) = 10$ Hz, 1H; ArH), 6.92–6.95 (d, *J*(H,H) = 7.5 Hz, 1 H; ArH), 7.20–7.26 (t, *J*(H,H) = 7.5 Hz, 1 H; ArH), 7.33–7.39 (t, *J*(H,H) = 7.5 Hz, 1 H; ArH), 7.51–7.57 (t, *J*(H,H) = 7.5 Hz, 1 H; ArH), 7.72–7.75 (d, *J*(H,H) = 7.5 Hz, 1 H; ArH), 7.93–7.96 ppm (d, *J*(H,H) = 7.5 Hz, 1 H; ArH); ^{13}C NMR (C_6D_6, 250 MHz): $\delta = 0.46$, 10.3, 15.4, 30.1, 36.3, 46.9, 50.1, 105.7, 108.5, 121.0, 125.4, 129.3, 130.0, 137.9, 139.5, 156.2, 157.5 ppm.

Ligand 6b: *n*-Butyllithium (1.6 M in hexanes, 2 mL, 3.1 mmol) was added to a solution of **1b** (1 g, 3 mmol) in diethyl ether at −37 °C. The pale yellow solution was allowed to warm to room temperature and was then stirred for another 1 h. The precipitate was collected by filtration, washed with cold diethyl ether/pentane (1:10, v/v), and dried under vacuum to give a pure yellow Li salt of **1b** (1.1 g, 92 %) , which was used without further analysis.

Compound **5** (0.66 g, 2.7 mmol) was added to a suspension of the lithium salt of **1b** (1.1 g, 2.7 mmol) in diethyl ether at −37 °C. The solution was allowed to warm to room temperature and was stirred for 4 h. Afterwards, the solution was filtered over Celite and was washed with diethyl ether. The volatiles were removed under vacuum and the crude product was recrystallized from diethyl ether/pentane. Yield 1.2 g, 86 %. ^{1}H NMR (400.13 MHz, CD_2Cl_2): $\delta = -0.03$ (s, 3 H), 0.91 (s, 1 H), 1.15 (t, ^{3}J(H,H) = 7.0 Hz, 6 H), 1.37 (d, ^{3}J(H,H) = 2.5 Hz, 6 H), 1.44 (d, ^{3}J(H,H) = 11.2 Hz, 3 H), 1.53 (d, ^{3}J(H,H) = 12.1 Hz, 3 H), 1.86 (s, 3 H), 3.43 (q, ^{3}J(H,H) = 7.0 Hz, 4 H), 5.19 (s, 1 H), 6.99 (d, ^{3}J(H,H) = 8.5 Hz, 1 H), 7.10 (m, 2 H), 7.17 (m, 4 H), 7.28 (m, 6 H), 7.34 (d, ^{3}J(H,H) = 7.5 Hz, 1 H), 7.48 (d, ^{3}J(H,H) = 6.8 Hz, 1 H), 7.77 ppm (m, 2 H); ^{13}C NMR (100.62 MHz, CD_2Cl_2): $\delta = 0.3$, 15.7, 30.5, 36.6, 46.9, 50.4, 66.2, 106.3, 110.9, 121.5, 126.1, 126.2, 127.9, 129.6, 130.8, 133.7, 137.4, 141.1, 156.7, 157.2 ppm; FTIR (ATR): $\tilde{\nu} = 3120$ (s), 3080 (w), 2905 (s), 1626 (s), 1569 (s), 1493 (s), 1454 (m), 1382 (m), 1305 (m), 1261 (m), 1171 (s), 1140 (s), 1097 (m), 1034 (s), 1005 (m), 877 (s), 836 (s), 760 (s), 731 (s), 703 cm^{-1} (s); ESI-MS: *m/z* calcd (%) for $C_{35}H_{40}BN_3Si$: 541.61; found: 541.32.

Complex 7a: A solution of *n*BuLi (1.6 M in hexanes, 1.28 mL, 2.0 mmol) was added to a solution of **6a** (420 mg, 0.94 mmol) in *n*-pentane (40 mL) at −37 °C. A large amount of white precipitate formed during the addition. The reaction mixture was warmed to room temperature and was stirred for 12 h. The resulting precipitate was collected on a frit, washed with cold *n*-pentane (10 mL), and dried under vacuum to give the pure Li salt of **6a** (350 mg), which was used without any analysis.

The Li salt of **6a** (350 mg, 0.76 mmol) was dissolved in toluene (20 mL) and added to a solution of $ZrCl_4 \cdot 2\,thf$ (0.29 g, 0.76 mmol) in toluene (30 mL) at −37 °C and the resulting reaction mixture was allowed to stir at room temperature for 16 h. Then the reaction mixture was filtered through Celite and all volatiles were removed under reduced pressure. The crude product was dissolved in *n*-pentane (10 mL) from which **7a** (280 mg, 45 %) crystallized as an off-white solid. ^{1}H NMR (C_6D_6, 250 MHz): $\delta = 0.62$ (s, 3 H; Si(CH_3)$_2$), 0.78–083 (t, *J*(H,H) = 5 Hz, 6 H; B(CH_2CH_3)$_2$), 0.89 (s, 3 H; Si(CH_3)$_2$), 1.1 (br, thf), 1.3–1.46 (m, 4 H; B(CH_2CH_3)$_2$), 1.67–1.91 (m, 6 H; Ad–CH_2), 2.28 (s, 3 H; Ad–*CH*), 2.37 (s, 6 H; Ad–CH_2), 4.30 (br, thf), 6.7–6.8 (d, *J*(H,H) = 10 Hz, 1 H; ArH), 6.97–7.00 (d, *J*(H,H) = 7.5 Hz, 1 H; ArH), 7.20–7.23 (d, *J*(H,H) = 7.5 Hz, 1 H; ArH), 7.32–7.39 (ddd, *J*(H,H) = 2.5 Hz, 1 H; ArH), 7.51–7.58 (ddd, *J*(H,H) = 2.5 Hz, 1 H; ArH), 7.70–7.73 (d, *J*(H,H) = 7.5 Hz, 1 H; ArH), 7.76–7.79 ppm (d, *J*(H,H) = 7.5 Hz, 1 H; ArH); ^{13}C NMR (C_6D_6, 250 MHz): $\delta = 5.7$, 6.3, 11.2, 11.8, 20.5, 25.1 (coordinated thf), 30.7, 36.6, 48.0, 58.9, 78.6 (coordinated thf), 107.3, 115.9, 121.1, 125.6, 129.1, 129.7, 138.0, 139.1, 158.2, 160.9 ppm; elemental analysis calcd (%) for $C_{31}H_{46}BCl_2N_3OSiZr$: C 54.94, H 6.84, N 6.20; found: C 55.39, H 7.39, N 5.88.

Complex 7b: A solution of *n*-butyllithium (1.6 M in hexanes, 1.7 mL, 2.8 mmol) was added to a solution of **6b** (0.6 g, 1.1 mmol) in pentane (15 mL) at −37 °C. The reaction mixture was warmed to room temperature and was stirred for 3 h. The resulting precipitate was collected on a frit, washed with cold pentane, and dried under vacuum to give a pure Li salt of **6b** (0.57 g, 73 %) , which was used without any further analysis.

The Li salt of **6b** (0.57 g, 0.8 mmol) was dissolved in tetrahydrofuran (10 mL) and added dropwise to a solution of $ZrCl_4 \cdot 2\,thf$ (0.31 g, 0.8 mmol) in tetrahydrofuran (20 mL) at −37 °C and the resulting reaction mixture was allowed to stir at room temperature for 6 h. After removal of the solvent, toluene was added and the mixture was stirred for half an hour. It was then filtered through Celite and the filtrate was concentrated under vacuum. The obtained oily product was recrystallized from dichloromethane/pentane at −37 °C to give colorless crystals. Yield: 0.2 g, 31 %. ^{1}H NMR (400.13 MHz, CD_2Cl_2): $\delta = 0.68$ (s, 3 H), 1.16 (t, ^{3}J(H,H) = 7.0 Hz, 3 H), 1.56 (s, 6 H), 1.82 (d, ^{3}J(H,H) = 3.0 Hz, 6 H), 1.97 (s, 3 H), 3.44 (q, ^{3}J(H,H) = 7.0 Hz, 2 H), 6.72 (d, ^{3}J(H,H) = 8.4 Hz, 1 H), 7.19 (t, ^{3}J(H,H) = 7.5 Hz, 1 H), 7.26 (t, ^{3}J(H,H) = 7.3 Hz, 1 H), 7.38 (d, ^{3}J(H,H) = 7.5 Hz, 1 H), 7.42–7.45 (m, 6 H), 7.61–7.68 (m, 2 H), 7.93–7.98 ppm (m, 5 H); ^{13}C NMR (100.62 MHz, CD_2Cl_2): $\delta = 3.6$, 15.7, 31.0, 36.6, 46.4, 61.0, 66.3, 107.3, 113.7, 122.0, 126.9, 128.9, 131.2, 132.0, 132.1, 136.0, 136.4, 142.6, 157.4, 159.7 ppm; elemental analysis calcd (%) for $C_{35}H_{38}BCl_2N_3SiZr \cdot 0.5\,C_4H_{10}O \cdot 0.5\,CH_2Cl_2$: C 57.65, H 5.69, N 5.38; found: C 57.84, H 5.84, N 5.36.

Complex 8: A solution of *n*BuLi (1.6 M in hexanes, 0.73 mL, 1.14 mmol) was added to a solution of **3** (200 mg, 0.544 mmol) in *n*-pentane (15 mL) at −37 °C. A large amount of white precipitate formed during the addition. The reaction mixture was warmed to room temperature and was stirred for 3 h. The resulting precipitate was collected on a frit, washed with cold *n*-pentane (10 mL), and dried under vacuum to give the pure Li salt of **3** (160 mg), which was used without any further analysis.

The Li salt of **3** (240 mg, 0.632 mmol) was dissolved in toluene (15 mL), this solution was added to a solution of $HfCl_4$ (202 mg, 0.632 mmol) in toluene (20 mL) at −37 °C and the resulting reaction mixture was stirred at room temperature for 9 h. Then it was filtered through Celite and all volatile materials were removed under reduced pressure. *n*-Pentane was added and the solution was stored in a glovebox freezer for 24 h to precipitate **8** (200 mg, 51 %) as a white solid. ^{1}H NMR (C_6D_6, 250 MHz): $\delta = 0.54$ (s, 3 H; Si(CH_3)$_{2)}$, 0.74–0.83 (m, 9 H; Si(CH_3)$_2$, –B(CH_2CH_3)$_2$), 1.26–1.58 (m, 4 H; B(CH_2CH_3)$_2$), 1.64 (s, 9 H; *t*-butyl), 6.73–6.76 (dd, *J*(H,H) = 0.75 Hz, 1 H; ArH), 6.94–6.98 (dd, *J*(H,H) = 0.5 Hz, 1 H; ArH), 7.19–7.25 (t, *J*(H,H) = 7.5 Hz, 1 H; ArH), 7.31–7.38 (ddd, *J*(H,H) = 1 Hz, 1 H; ArH), 7.50–7.56 (ddd, *J*(H,H) = 0.75 Hz, 1 H; ArH), 7.68–7.72 (d, *J*(H,H) = 7.75 Hz, 1 H; ArH), 7.76–7.78 ppm (d, *J*(H,H) = 7.25 Hz, 1 H; ArH); ^{13}C NMR (C_6D_6, 250 MHz): $\delta = 5.4$, 5.91, 11.3, 12.0, 12.5, 19.7, 35.9, 56.9, 107.7, 117.0, 121.3, 125.8, 129.4, 130.0, 138.1, 139.3, 158.4, 161.6 ppm; elemental analysis calcd (%) for $C_{42}H_{64}B_2HfN_6Si_2$: C 55.48, H 7.09, N 9.24; found: C 55.45, H 7.20, N 9.19.

Complex 9: A solution of *n*BuLi (1.6 M in hexanes, 0.73 mL, 1.14 mmol) was added to a solution of **6a** (200 mg, 0.544 mmol) in *n*-pentane (15 mL) at −37 °C. A large amount of white precipitate formed during the addition. The reaction mixture was warmed to room temperature and was stirred for 3 h. The resulting precipitate was collected on a frit, washed with cold *n*-pentane (10 mL), and dried under vacuum to give the pure Li salt of **6a** (160 mg), which was used without any further analysis. The Li salt of **6a** (400 mg, 0.87 mmol) was dissolved in toluene (20 mL) and added to a solution of $HfCl_4$ (280 mg, 0.87 mmol) in toluene (20 mL) and the resulting reaction mixture was stirred at room temperature for 9 h. Then it was filtered through Celite and all volatiles were removed under reduced pressure. *n*-Pentane (20 mL) was added to the crude and the solution was stored in a glovebox freezer for 24 h to precipitate the Hf complex **9** (380 mg, 50 %) as a white solid. ^1H NMR (C_6D_6, 250 MHz): $\delta = 0.50$ (s, 3 H; Si(CH_3)$_2$), 0.67–0.79 (m, 9 H; Si(CH_3)$_2$, –B(CH_2CH_3)$_2$), 1.28–1.79 (m, 10 H; B(CH_2CH$_3$)$_2$, Ad–CH_2), 2.18 (s, 3 H; Ad–CH), 2.25 (s, 6 H; Ad–CH_2), 6.67–6.70 (d, J(H,H) = 7.5 Hz, 1 H; ArH), 6.84–6.87 (d, J(H,H) = 7.5 Hz, 1 H; ArH), 7.09–7.12 (d, J(H,H) = 7.5 Hz, 1 H; ArH), 7.21–7.27 (t, J(H,H) = 7.5 Hz, 1 H; ArH), 7.40–7.46 (t, J(H,H) = 7.5 Hz, 1 H; ArH), 7.58–7.61 (d, J(H,H) = 7.5 Hz, 1 H; ArH), 7.64–7.67 ppm (d, J(H,H) = 7.5 Hz, 1 H; ArH); ^{13}C NMR (C_6D_6, 250 MHz): $\delta = 5.9$, 6.6, 11.4, 12.0, 20.1, 31.0, 36.9, 48.8, 58.0, 107.7, 117.1, 121.3, 125.8, 129.40, 130.0, 138.2, 139.3, 158.4, 161.5 ppm; elemental analysis calcd (%) for $C_{54}H_{76}B_2HfN_6Si_2$: C 60.87, H 7.19, N 7.89; found: C 60.79, H 7.80, N 7.15.

Ligand 10: A solution of **1** (750 mg, 3.15 mmol) in DMF (20 mL) was cooled to 0–5 °C and NaH (60 wt % in mineral oil, 125 mg, 3.15 mmol) was added portionwise over 15 min and the resulting reaction mixture was stirred at 0–5 °C for 2 h. Then, CH_3I (0.894 mg, 6.3 mmol) in DMF (2 mL) was added. After 30 min, the reaction was quenched with ice, and the mixture was extracted with ethyl acetate (2×20 mL). The combined organic layers were washed with water (3×25 mL) and brine solution (20 mL) and then dried over Na_2SO_4. Finally, the solvent was removed under reduced pressure. The crude product was purified by column chromatography (60–120 silica gel) using ethyl acetate/petroleum ether (3:97) and **10** (720 mg, 90 %) was obtained as a white solid. ^1H NMR ($CDCl_3$, 600 MHz): $\delta = 0.34$–0.36 (t, J(H,H) = 6 Hz, 6 H; B(CH$_2$$CH_3$)$_2$), 0.66–0.72 (m, 2 H; B($CH_2CH_3$)$_2$), 0.84–0.90 (m, 2 H; B($CH_2CH_3$)$_2$), 3.01–3.02 (d, J(H,H) = 6 Hz, 3 H; N–CH$_3$), 5.76 (br, 1 H; ArNH), 6.39–6.40 (d, J(H,H) = 6 Hz, 1 H; ArH), 7.17–7.18 (d, J(H,H) = 6 Hz, 1 H; ArH), 7.23–7.25 (t, J(H,H) = 6 Hz, 1 H; ArH), 7.35–7.38 (t, J(H,H) = 6 Hz, 1 H; ArH), 7.52–7.53 (d, J(H,H) = 6 Hz, 1 H; ArH), 7.7–7.72 ppm (t, J(H,H) = 6 Hz, 2 H; ArH); ^{13}C NMR ($CDCl_3$, 250 MHz): $\delta = 9.9$, 14.3, 29.7, 102.5, 104.8, 120.9, 125.1, 128.9, 129.5, 137.3, 140.4, 155.6, 157.0 ppm; elemental analysis calcd (%) for $C_{16}H_{21}BN_2$: C 76.21, H 8.39, N 11.11; found: C 76.23, H 8.33, N 11.10.

Ligand 11: A solution of *n*BuLi (1.6 M in hexanes, 2.72 mL, 4.36 mmol) was added to a solution of **10** (1.0 g, 3.96 mmol) in *n*-pentane (40 mL) at −37 °C. A large amount of precipitate formed during the addition. The reaction mixture was warmed to room temperature for 3 h and the resulting precipitate was collected on a frit, washed with cold *n*-pentane (10 mL), and dried under vacuum to give the pure lithium salt of **11** (800 mg, 79 %) as yellow powder. ^1H NMR (C_6D_6, 600 MHz): $\delta = -0.38$–0.32 (m, 2 H; B(CH_2CH$_3$)$_2$), 0.51–0.57 (m, 2 H; B(CH_2CH$_3$)$_2$), 0.62–0.64 (t, J(H,H) = 6 Hz, 6 H; B(CH$_2$$CH_3$)$_2$), 2.68 (s, 3 H; N–CH$_3$), 6.18–6.19 (d, J(H,H) = 6 Hz, 1 H; ArH), 6.50–6.51 (d, J(H,H) = 6 Hz, 1 H; ArH), 7.13–7.16 (t, 1 H; ArH), 7.20–7.23 (ddd, J(H,H) = 0.6 Hz, 1 H; ArH), 7.36–7.38 (t, J(H,H) = 6 Hz, 1 H; ArH), 7.61–7.65 ppm (m, 2 H; ArH).

Complex 12: Ligand **11** (100 mg, 0.387 mmol) in toluene (10 mL) was added to a solution of cyclopentadienyl titanium(IV) trichloride (85 mg, 0.387 mmol) in toluene (10 mL) at −37 °C and the resulting reaction mixture was stirred at room temperature for 16 h. Then the mixture was filtered through Celite and all volatiles were removed under reduced pressure. Crystallization from *n*-pentane allowed **12** (120 mg, 70 %) to be isolated as a red powder. ^1H NMR (C_6D_6, 250 MHz): $\delta = 0.75$ (br, 6 H; B(CH$_2$$CH_3$)$_2$), 0.89–1.02 (m, 2 H; B($CH_2CH_3$)$_2$), 1.18–1.33 (m, 2 H; B($CH_2CH_3$)$_2$), 4.11 (s, 3 H; N–CH$_3$), 5.86–5.89 (d, J(H,H) = 7.5 Hz, 1 H; ArH), 6.01 (s, 4 H), 6.8–6.9 (ddd, J(H,H) = 1.75 Hz, 1 H; ArH), 7.02–7.05(d, J(H,H) = 7.75 Hz, 1 H; ArH), 7.19–7.26 (ddd, J(H,H) = 1.25 Hz, 1 H; ArH), 7.35–7.41 (ddd, J(H,H) = 1 Hz, 1 H; ArH), 7.56–7.58 (d, J(H,H) = 5 Hz, 1 H; ArH), 7.75–7.78 ppm (d, J(H,H) = 8.25 Hz, 1 H; ArH); ^{13}C NMR (C_6D_6, 250 MHz): $\delta = 10.8$, 15.2, 50.7, 114.8, 118.4, 120.4, 121.5, 123.0, 125.4, 130.0, 130.8, 135.7, 140.9, 159.2, 168.2 ppm; elemental analysis calcd (%) for $C_{21}H_{25}BCl_2N_2Ti$: C 57.98, H 5.79, N 6.44; found: C 58.35, H 5.88, N 6.41; crystals suitable for single-crystal X-ray analysis were obtained by means of recrystallization from toluene/pentane.

Complex 13: Ligand **11** (100 mg, 0.386 mmol) in toluene (20 mL) was added to a solution of pentamethylcyclopentadienyltitanium(IV) trichloride (0.112 g, 0.386 mmol) in toluene (20 mL) at −37 °C and the resulting reaction mixture was allowed to stir at room temperature for 16 h. Then it was filtered through Celite and all volatiles were removed under reduced pressure. Crystallization from *n*-pentane allowed **13** (170 mg, 87 %) to be isolated as a red powder. ^1H NMR (C_6D_6, 250 MHz): $\delta = 0.97$–1.03 (t, J(H,H) = 1.75 Hz, 6 H; B(CH$_2$$CH_3$)$_2$), 1.15–1.29 (m, 2 H; B($CH_2CH_3$)$_2$), 1.39–1.54 (m, 2 H; B($CH_2CH_3$)$_2$), 2.00 (s, 15 H; Cp′), 3.77 (s, 3 H; N–CH$_3$), 7.06–7.20 (m, 3 H; ArH), 7.316–7.381 (ddd, J(H,H) = 1.25 Hz, 1 H; ArH), 7,50–7.56 (ddd, J(H,H) = 1 Hz, 1 H; ArH), 7.67–7.70 (d, J(H,H) = 7.75 Hz, 1 H; ArH), 8.00–8.03 ppm (d, J(H,H) = 7.25 Hz, 1 H; ArH); ^{13}C NMR (C_6D_6, 250 MHz): $\delta = 10.9$, 13.6, 16.5, 49.0, 115.0, 120.9, 121.6, 125.5, 129.9, 130.7, 133.0, 136.4, 140.7, 159.5, 166.6 ppm; elemental analysis calcd (%) for $C_{26}H_{35}BCl_2N_2Ti$: C 61.82, H 6.98, N 5.55; found: C 61.52, H 7.08, N 5.64; crystals suitable for single-crystal X-ray analysis were obtained by means of recrystallization from toluene/pentane.

Complex 14: Ligand **11** (700 mg, 2.72 mmol) was added to a solution of $TiCl_4 \cdot 2\,thf$ (454 mg, 1.36 mmol) in toluene (25 mL) at −37 °C and the resulting reaction mass was stirred for 16 h at room temperature. Then it was filtered through Celite and all volatiles were removed under reduced pressure. Crystallization from *n*-pentane, and washing with cold diethyl ether (3 mL) allowed **14** (500 mg, 30 %) to be obtained as a red powder. ^1H NMR ($CDCl_3$, 600 MHz): $\delta = 0.43$–0.46 (t, J(H,H) = 6 Hz, 12 H; B(CH$_2$$CH_3$)$_2$), 0.84 (br, 4 H; B($CH_2CH_3$)$_2$), 1.04 (br, 4 H; B($CH_2CH_3$)$_2$), 3.58 (s, 6 H; N–$CH_3$), 7.29–7.31 (t, J(H,H) = 6 Hz, 2 H; ArH), 7.35–7.36 (d, J(H,H) = 6 Hz, 2 H; ArH), 7.42–7.45 (t, J(H,H) = 6 Hz, 2 H; ArH), 7.61–7.62 (d, J(H,H) = 6 Hz, 2 H; ArH), 7.83–7.84 (d, J(H,H) = 6 Hz, 2 H; ArH), 7.86–7.87 (d, J(H,H) = 6 Hz, 2 H; ArH), 8.03–8.05 ppm (t, J(H,H) = 6 Hz, 2 H; ArH); ^{13}C NMR ($CDCl_3$, 600 MHz): $\delta = 10.5$, 15.8, 42.3, 115.5, 119.8, 121.4, 125.4, 129.3, 130.3, 135.7, 141.6, 160.0, 162.6, 165.2 ppm.

[^{13}C]cyclopent-1-ene: [^{13}C]cyclopent-1-anol (10 g, 0.12 mol), 85 % phosphoric acid (44 g), potassium pyrosulfate (27 g), and a stirring bar were placed in a 100 mL pear-shaped flask. The flask was fitted with a small condenser connected to a receiving vessel, which was immersed in a liquid-nitrogen bath. [^{13}C]cyclopent-1-ene began to distil at 50 °C, and after initial frothing had subsided, the temperature of the contents was raised from 90 to 140 °C.[35,36] The [^{13}C]cyclopent-1-ene distillate (6.0 g, 76 % yield) was dried over calcium hydride, and kept in the refrigerator. ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 1.83$ (m, 2 H), 2.32 (m, 4 H), 5.73 (m, 1 H), 5.76 ppm (m, 1 H); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 22.9$, 32.5, 130.8 ppm; GC–MS (EI, 70 eV): *m/z* calcd for C_5H_8: 69.12; found: 69.1; $t_R = 1.92$ min.

General procedure for ethylene homopolymerization

The homopolymerization of E was carried out in a 500 mL Büchi glass autoclave, equipped with a monitor stirrer, external temperature control jacket, and pressure gauge. The reactor was heated up to 100 °C under vacuum for 2 h before starting an experiment. A mixture of prescribed amount of monomer and MAO (235 mL) was introduced into the Ar-purged reactor followed by a solution of prescribed amount of catalyst in toluene (15 mL), and heated to the desired temperature. The reaction was started by the addition of ethylene gas. Polymerizations were stopped by closing the ethylene valve and introducing methanol (10 mL) into the reactor. The polymer was precipitated upon pouring the whole reaction mixture into methanol (200 mL) to which concentrated hydrochloric acid (20 mL) had been added. The polymer was collected by filtration, washed with methanol, and then dried under vacuum at 40 °C overnight.

General procedure for ethylene copolymerization

Polymerizations and workup were carried out as described above except that a defined amount of CPE and 2.0 M solution of MAO in toluene were jointly introduced into the reactor followed by a solution of the precatalyst in toluene (5 mL).

Copolymerization of ethylene with [^{13}C]cyclopent-1-ene

Copolymerization of ethylene with [^{13}C]cyclopent-1-ene was carried out in a 50 mL pressure tube equipped with an oil bath, vacuum lines, and pressure gauge. A mixture of the catalyst/MAO/CPE = 1:2000:4000 in toluene (5 mL) was introduced into a pressure tube inside a glovebox. The pressure tube was removed from the glovebox and charged with ethylene gas. Polymerization was stopped by closing the ethylene valve and introducing methanol (10 mL) into the pressure tube. The polymer was precipitated from methanol (50 mL) to which concentrated hydrochloric acid (2 mL) had been added. The polymer was collected by filtration, washed with methanol, and then dried under vacuum at 40 °C overnight.

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