

rac-[Ethylenebis(2-(thexyldimethylsiloxy)indenyl)]zirconium dichloride: synthesis, molecular structure and olefin polymerization catalysis

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Abstract

The synthesis and molecular structure of *rac*-[ethylenebis(2-(thexyldimethylsiloxy)indenyl)]zirconium dichloride (**4**), is reported. In combination with methylaluminoxane (MAO), **4** forms an active catalyst system for homogeneous polymerization of ethylene and propylene. The high activity of **4**/MAO is retained at low [Al]:[Zr] ratios [(150–250):1]. Decreasing polymerization temperature or the [Al]:[Zr] ratio results in production of polyethylene having a high molecular weight shoulder in its molecular weight distribution (MWD). Deconvolution of the MWDs into a series of calculated Flory-distribution curves indicates that with this catalyst system ethylene is polymerized by three different types of active sites, whereas propylene is predominantly polymerized by two active sites. Complex **4** crystallizes in the indenyl-backward conformation. The ligand backbone adopts the expected C₂ symmetry. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Indenyl; Siloxy; Zirconium; *ansa*-Metallocene; Olefin polymerization

1. Introduction

Chiral group IV *ansa*-metallocene complexes are catalyst precursors for stereoselective polymerization of α -olefins [1]. The performance characteristics of these complexes are determined by their ligand substitution patterns, e.g. *racemic* dimethylsilylene-bridged 2,2'-di-alkyl-4,4'-diaryl-substituted bis(indenyl) zirconocenes produce, in combination with methylaluminoxane (MAO) or other activators, high-molecular-weight isotactic polypropylene [2]. Recently, we reported the preparation of the first siloxy substituted bis(indenyl)

and bis(tetrahydroindenyl) metallocene dichlorides and their application in olefin polymerization [3], e.g. the *rac*-[ethylenebis(2-(*tert*-butyldimethylsiloxy)indenyl)]zirconium dichloride (**1**)/MAO catalyst system homopolymerizes and copolymerizes α -olefins with high activity.

Variations in the siloxyindenyl metallocene structure can be performed in (1) the substitution patterns of the six-membered rings, (2) the interannular bridge [4], and (3) the size and position of the siloxy group [5]. Structural variations in the siloxy group are limited by stabilities of the corresponding silyl enol ethers toward organometallic reagents [6]. This paper continues our structure/performance studies on this new class of metallocene complexes, and reports the synthesis and molecular structure of the thexyldimethylsiloxy substituted analogue of **1** (thexyl = 1,1,2-trimethylpropyl),

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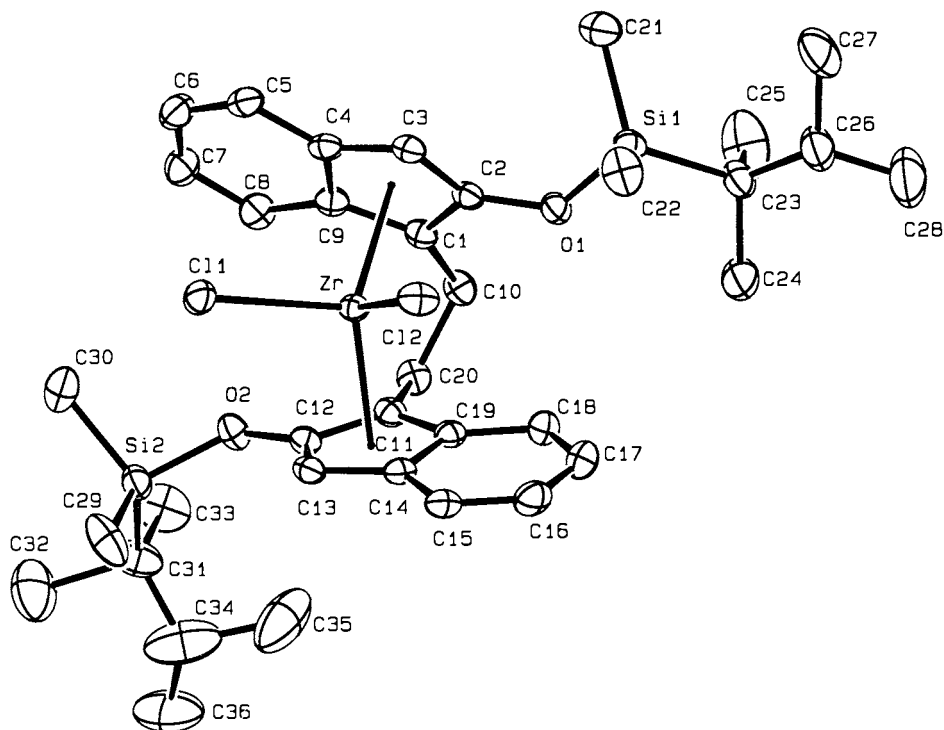


Fig. 1. Molecular structure of **4**. Thermal ellipsoids are drawn at 30% probability level. The hydrogen atoms are omitted for clarity.

rac-[ethylenebis(2-(thexyldimethylsiloxy)indenyl)]zirconium dichloride (**4**), and its activation with MAO for homogeneous polymerization of propylene and ethylene.

2. Results and discussion

2.1. Synthesis and molecular structure of **4**

Complex **4** was prepared according to an analogous procedure as described previously for **1** ([3]a). Reaction of 2-indanone with thexyldimethylchlorosilane and imidazole in DMF gave, after work-up and distillation, 2-(thexyldimethylsiloxy)indene (**2**) in 85% yield [7]. Compound **2** was converted to bis(2-(thexyldimethylsiloxy)-1-indenyl)ethane (**3**) in 55% yield by reaction of the corresponding lithium salt with 0.5 equivalents of dibromoethane in THF. Deprotonation of **3** with 2 equivalents of *n*-BuLi and subsequent reaction with ZrCl₄ in THF gave, after work-up and crystallization from CH₂Cl₂, the pure *racemic* diastereomer of **4** in 22% yield. The ¹H- and ¹³C-NMR spectra of **4** are consistent with C₂ symmetry. In the ¹H-NMR spectrum of **4**, hindered rotation of the Si–O bonds results in two singlets from the silylene methyl groups (0.26 and 0.25 ppm). The methyl groups of the thexyl moiety give two singlets (0.99 and 0.97 ppm), and two doublets (0.95 and 0.94 ppm). The resonance of the β-H of the five-membered ring (5.95 ppm) is comparable to that of **1** (5.93 ppm) ([3]a) and

rac-Et(2-(Me₂N)Ind)₂ZrCl₂ (5.99 ppm) [8], but shielded considerably compared to that of *rac*-Et(Ind)₂ZrCl₂ (6.58 ppm) [9]. A similar shielding effect was observed for the β-protons of *rac*-Me₂Si(2-(*t*-BuMe₂SiO)Ind)₂ZrCl₂ (6.22 ppm) ([3]d) and *rac*-Me₂Si(2-(Me₂N)Ind)₂ZrCl₂ (6.40 ppm) [10], compared to *rac*-Me₂Si(Ind)₂ZrCl₂ (6.90 ppm) [11]. In the ¹³C-NMR spectra of **4** and **1**, signals from the C(3) and C(13) carbon atoms (**4**: 98.54 ppm; **1**: 98.61 ppm ([3]a), for atomic numbering see Fig. 1) are strongly shielded compared to those of *rac*-Et(Ind)₂ZrCl₂ (110.83 ppm) [9].

The molecular structure of **4** is displayed in Fig. 1 with selected bond distances and angles in Table 1. The

Table 1
Selected intramolecular distances (Å) and angles (°) for **4**^a

Intramolecular distances			
Zr–Cl(1)	2.4365(8)	Si(1)–O(1)	1.691(2)
Zr–Cl(2)	2.4295(9)	Si(2)–O(2)	1.669(2)
Zr–Cen(1)	2.2468	C(2)–O(1)	1.357(3)
Zr–Cen(2)	2.2395	C(12)–O(2)	1.355(3)
Intramolecular angles			
Cl(1)–Zr–Cl(2)	97.90(3)	C(2)–O(1)–Si(1)	129.0(2)
Cen(1)–Zr	120.32	C(12)–O(2)–Si(2)	134.8
–Cen(2)			
Cp(1)–Cp(2) ^b	58.56		

^a Cen refers to the centroids of the C₅ rings.

^b Angle between the cyclopentadienyl planes.

Table 2
Polymerization of propylene over 4/MAO^a

T_p (°C)	P (bar)	[Al]:[Zr]	<i>A</i> (kg of PP/mol of Zr/h)	[<i>mmmm</i>] ^c (%)	M_w^d	M_w/M_n	T_m (°C)	X_c^e (%)
20	2.0	3000:1	2700	95	16 100	2.1	146	43
40	2.7	3000:1	8500	87	5 500	2.1	136	29
60	3.4	3000:1	6100	n.c. ^f	4 400	2.2	122	25
80	4.1	3000:1	3200	n.c.	2 500	1.9	114	6
40	2.7	250:1 ^b	11900	86	11 500	2.4	129	29
40	2.7	1000:1 ^b	12600	85	8 500	2.4	130	32
40	2.7	10000:1 ^b	7800	91	6 800	2.0	138	44

^a Polymerization time = 60 min; [metallocene] = 11 μ mol 200 ml⁻¹ of toluene.

^b Polymerization time = 30 min.

^c By ¹³C-NMR.

^d By GPC vs polystyrene.

^e Crystallinity by DSC.

^f Not calculated.

Zr–Centroid distances (2.247 and 2.240 Å) and average Zr–C bond length (2.551 Å) of **4** are nearly identical to the corresponding values for **1** (Zr–Cen, 2.254 Å; average Zr–C, 2.559 Å) ([3]a). The Centroid–Zr–Centroid angle (120.3°) and Cl–Zr–Cl angle (97.9°) of **4** are, however, smaller (for **1**: Cen–Zr–Cen, 125.9°; Cl–Zr–Cl, 99.3°). The η -carbon–oxygen bond lengths (1.357 and 1.355 Å) of **4** are comparable to those of **1** (1.362 Å) ([3]a) and its hydrogenated congener (1.376 Å) ([3]b). Increase in the Zr–Cl bond lengths (2.437 and 2.430 Å) of **4** compared to *rac*-Et(Ind)₂ZrCl₂ (2.388 Å) [9] is consistent with a decreased electrophilicity of the zirconium atom. Complex **4** adopts the indenyl-backward (Y) conformation, first described by Brintzinger for *rac*-Et(IndH₄)₂Ti(*O*-acetyl-*R*-mandelate)₂ [12], and recently observed by Jordan and coworkers for *rac*-Et(Ind)Hf(NMe₂)₂ [13], and by us for complex **1** ([3]a), and its hydrogenated congener ([3]b).

2.2. Polymerization catalysis

Precursor **4** was activated with MAO for homogeneous polymerization of propylene and ethylene. The results are presented in Tables 2 and 3 [14]. Fig. 2 shows a comparison of the propylene polymerization activities of **4**/MAO and **1**/MAO ([3]b) vs the polymerization temperature. For both catalyst systems high activities were obtained at reduced [Al]:[Zr] ratios [(150–250):1]. The conventional homogeneous metallocene catalysts require considerably higher ratios, usually (2500–10000):1, to achieve maximum polymerization activities ([1,2,14]a, [15]). Recently, Richardson et al. predicted that bulky ligands with electron-donating substituents could increase the catalyst activity by increasing the equilibrium amount of the solvent-separated cation, despite the reduced electrophilicity of the metallocenium ion [16]. Electron-donation from the siloxy group may have a stabilizing effect on the cationic active species resulting in easier alkylation of

the catalyst precursor and high activities at reduced cocatalyst concentrations. Decrease in the local Lewis acidity at the zirconium atom should also lower the tendency to β -elimination and increase the molecular weight of the produced polymer [2,17]. The observed decrease of the molecular weights obtained with the siloxy-indenyl metallocene/MAO catalysts results mainly from chain transfer to aluminum ([3]a, b). In the ¹³C-NMR spectra of the polypropylenes obtained with **4**/MAO the ratio of isopropyl/*n*-propyl end-group signal intensities increases with the [Al]:[Zr] ratio from 0.6 at [Al]:[Zr] = 250:1 and 1.9 at [Al]:[Zr] = 1000:1 to 4.5 at [Al]:[Zr] = (3000–10000):1. Weaker signals possibly resulting from isobutenyl end-groups can be observed at $T_p \geq 40^\circ\text{C}$. The stereoselectivity of **4**/MAO is similar to that of **1**/MAO. Exact estimation of the pentad distributions of the polypropylene samples is difficult due to the low molecular weights and the large amounts of weak overlapping signals. The molecular weights of the polypropylenes obtained with **4**/MAO are 15–40% lower than those produced with **1**/MAO under similar polymerization conditions. Only at [Al]:[Zr] = 10000:1 is higher M_w with **4**/MAO obtained. The difference is less pronounced in polymerization of ethylene, where **4**/MAO produces PE with 10–15% lower M_w compared with **1**/MAO. The molecular weights of the polymers decrease with increasing [Al]:[Zr] ratio and increasing T_p .

Polydispersities of the polypropylenes are close to two, as predicted by Schulz–Flory statistics for polymers arising from nearly identical catalyst centers ([1]c). The molecular weight distributions (MWDs) of the polyethylenes are, however, appreciably broadened, which at low T_p (Fig. 3) and low [Al]:[Zr] ratios (Fig. 4) is emphasized by an increasing high molecular weight shoulder. Similar behavior was observed for **1**/MAO ([3]b). Ethylene bridged *ansa*-metallocenes are known to fluctuate between their indenyl-backward (Y) and indenyl-forward (Π) chelate ring conformers [9,12,18].

Table 3
Polymerization of ethylene over 4/MAO^a

T_p (°C)	[Al]:[Zr]	A (Kg of PE/mol of Zr/h)	M_w^b	M_w/M_n	T_m (°C)	X_c^c (%)
20	150:1	3100	330 000	3.1	135	52
40	150:1	2200	320 000	3.7	135	61
60	150:1	2200	230 000	4.0	133	65
80	150:1	8000	150 000	3.3	133	67
40	250:1	2200	270 000	3.7	135	61
40	500:1	2000	240 000	3.4	136	62
40	3000:1	1700	210 000	3.2	135	61
40	10 000:1	1900	170 000	3.6	136	62

^a $P(C_2H_4) = 2.5$ bar; Polymerization time = 30 min; [metallocene] = 3 μ mol 200 g^{-1} of toluene.

^b By GPC vs polystyrene standards.

^c Crystallinity by DSC.

The bulky siloxy group may decrease the rate of this interconversion by steric interaction, especially in the activated cationic state. Mobilities of the cationic species may be severely restricted due to contact ion pairing between the zirconium alkyl cation and the MAO counter ion [19]. Hence, the different conformers could have sufficiently different propagation and chain termination rates to be considered as individual active sites. A similar explanation was suggested recently by Waymouth and coworkers for MWD-broadening obtained with the unbridged bis(1-methyl-2-phenylindenyl)zirconocene/MAO catalyst systems [20].

As shown previously [21], the MWD of a polyolefin produced with a Ziegler–Natta catalyst system can be described as a superposition of narrower distributions assigned to each individual site of the catalyst. Preliminary deconvolution studies of the polyethylene MWDs obtained with 4/MAO indicate the presence of three different kinds of active sites producing Flory molecular weight distributions (Fig. 5). This results in residual R^2 values ranging from 99.7–99.9%, whereas modeling with two Flory curves yields R^2 values 95.5–98.1% [22]. The polypropylene MWDs can be modeled satisfacto-

rily with two separate Flory curves yielding R^2 values 99.1–99.9% (Fig. 6). Modeling with a single curve gives R^2 values 71.4–92.7%, except for the polypropylene sample obtained at [Al]:[Zr] = 10000:1 for which $R^2 = 99.3%$, suggesting that propylene is predominantly polymerized by two types of active sites and, that for 4/MAO, the number of polymerizing active sites could be monomer dependent. A third ‘eclipsed’ conformation can be envisioned between the limiting Y and Π indenyl conformers. These three conformational isomers may have different receptibilities toward agostic interactions [23] and produce polymers of different chain lengths. Steric hindrance toward propylene coordination in e.g. the indenyl-forward conformer of 4/MAO could explain the narrower MWDs of the polypropylenes. Ethylene is a smaller monomer, and the polymerization behavior of 4/MAO toward ethylene should thus reflect more the electronic than the steric properties of the catalyst. Consequently, ethylene would be polymerized by all of the catalyst conformations.

Other potential sources for MWD broadening include temperature changes and mass transfer limita-

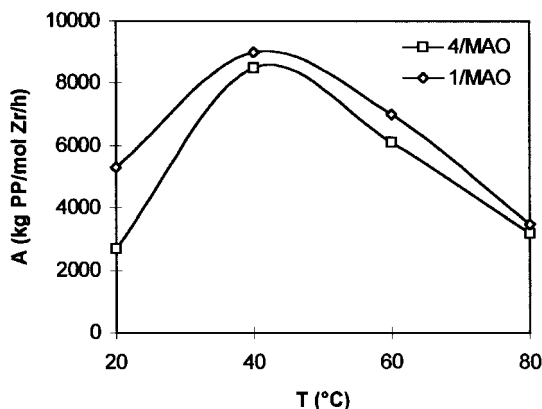


Fig. 2. Propylene polymerization activities of 4/MAO and 1/MAO ([3]b) vs T_p .

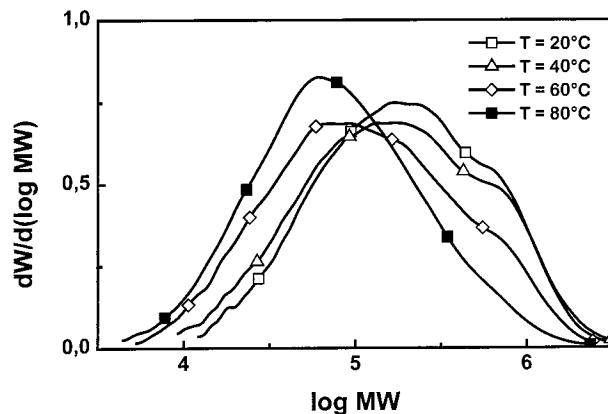


Fig. 3. Molecular weight distributions of the polyethylenes obtained with 4/MAO vs T_p .

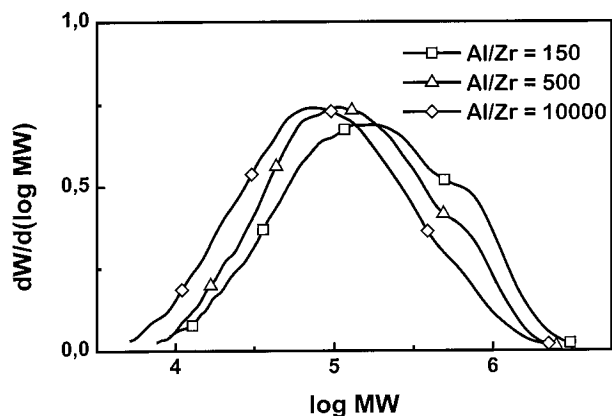


Fig. 4. Molecular weight distributions of the polyethylenes obtained with **4**/MAO vs [Al]:[Zr] ratio.

tions in the polymerization system, dynamical dissociation/association of MAO, and changes in its state of coordination. The polyethylene formed with **4**/MAO was insoluble at temperatures below 80°C, which implies mass transfer limitations. The ethylene consumption curves show that the monomer transfer to catalyst was a strongly limiting factor at $T_p = 40\text{--}60^\circ\text{C}$. At $T_p = 20^\circ\text{C}$, the decrease in ethylene consumption was

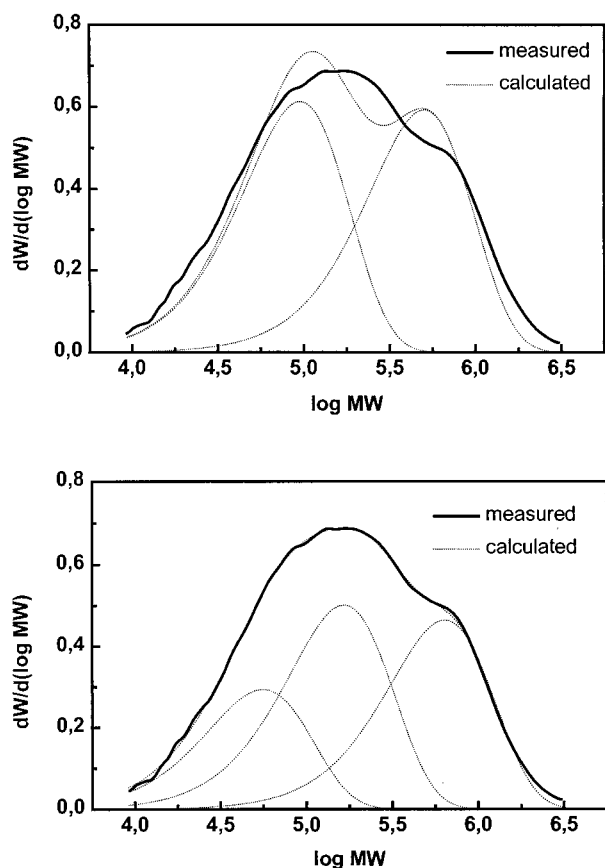


Fig. 5. Modeling of a PE-MWD obtained with **4**/MAO with two (top) and three (bottom) Flory distributions ($T_p = 40^\circ\text{C}$; [Al]:[Zr] = 150:1).

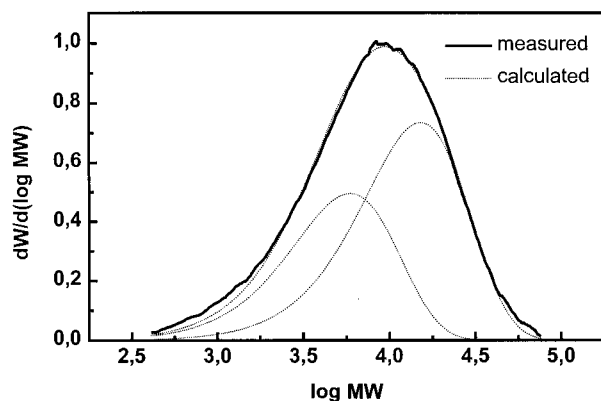
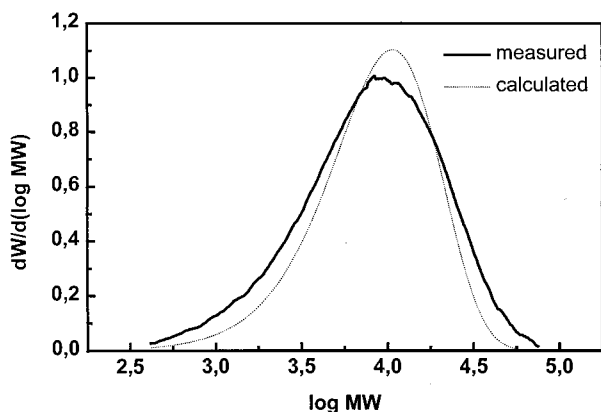


Fig. 6. Modeling of a PP-MWD obtained with **4**/MAO with one (top) and two (bottom) Flory distributions ($T_p = 40^\circ\text{C}$; [Al]:[Zr] = 250:1).

present but less pronounced. At different [Al]:[Zr] ratios, the ethylene consumption curves were nearly identical in shape, indicating similar mass transfer conditions. Thus, the observed broadening of the MWDs can not be explained by mass transfer limitations alone. The high stereospecificity of **4**/MAO in propylene polymerization at 20°C and the observed 'monomer dependence' of the MWD broadening are inconsistent with decomposition of the metallocene to multiple active species. Also, the monomer consumption remains high during the whole polymerization reaction. Further studies, such as quantum mechanics calculations of the cationic complexes and dynamic NMR measurements should provide more information on the origin of the observed effects.

2.3. Summary and conclusions

rac-[Ethylenebis(2-(thexyldimethylsiloxy)indenyl)]zirconium dichloride (**4**) has been prepared and its molecular structure determined. Structural variations in the siloxy groups alter the catalytic behavior of the corresponding *ansa*-metallocene catalysts. Increase in the size of the siloxy substituent from *tert*-butyl to hexyl decreases the molecular weight of the produced

polyethylene and isotactic polypropylene. The effect on catalytic activity was less pronounced under the employed polymerization conditions. Deconvolution studies of the polymer MWDs obtained with 4/MAO suggest that a temperature dependent fluctuation of the indenyl-ligands may hinder the coordination of propylene at higher polymerization temperatures.

3. Experimental section

3.1. General comments

All operations were carried out in an argon or nitrogen atmosphere using standard Schlenk, vacuum, or glovebox techniques. Solvents were dried and distilled under argon prior to use. 2-Indanone (Acros Chimica) and thexyldimethylchlorosilane (ABCR GmbH) were used without further purification. The ^1H - and ^{13}C -NMR spectra were recorded in CDCl_3 or CD_2Cl_2 solutions using a JEOL JNM-LA400 or JEOL JNM-A500 NMR spectrometer and referenced against tetramethylsilane or the residual protons of the deuterated solvents. Direct inlet electron ionization mass spectra (EIMS) were obtained on a Varian VG-7070E or a Varian-8000 mass spectrometer. The propylene and ethylene polymerization procedures and details of the polymer analysis have been described previously ([3]a, b).

3.2. 2-(Thexyldimethylsiloxy)indene (2)

To a solution of thexyldimethylchlorosilane (100.0 g, 559.3 mmol) and imidazole (38.08 g, 559.3 mmol) in DMF (350 ml) was added in one portion 2-indanone (67.40 g, 510.0 mmol). The reaction mixture was stirred for 2 days at room temperature, treated with water (300 ml), and extracted with Et_2O (3×200 ml). The combined organic phases were washed with water (2×200 ml) and dried over sodium sulfate. Evaporation of the solvents left a red oil. Distillation under reduced pressure gave 116.89 g (83.5%) of **2** as a yellow oil (b.p. 128–130°C/0.4 mbar). $^1\text{H-NMR}$ (CDCl_3 , δ): 7.24–7.10 (m, 3H); 7.00 (td, $^3J = 7.3$ Hz, $^4J = 1.3$ Hz, 1H); 5.74 (d, $^4J = 0.6$ Hz, 1H); 3.28 (s, 2H); 1.70 (sept, $^3J = 6.8$ Hz, 1H); 0.93 (s, 6H); 0.92 (d, $^3J = 6.8$ Hz, 6H); 0.29 (s, 6H). $^{13}\text{C-NMR}$ (CDCl_3 , δ): 162.82; 145.71; 137.03; 126.86; 123.45; 122.73; 119.29; 106.92; 40.00; 34.49; 25.51; 20.51; 18.89; –2.26.

3.3. Bis(2-(thexyldimethylsiloxy)indenyl)ethane (3)

To a solution of **2** (68.62 g, 250.0 mmol) in THF (250 ml) at 0°C was added dropwise *n*-BuLi (100.0 ml of a 2.5 M solution in hexane, 250.0 mmol), and the reaction mixture was stirred overnight at room tempera-

ture. The resulting solution was then cooled to –80°C and treated dropwise with a solution of dibromoethane (23.48 g, 125.0 mmol) in THF (100 ml). After completed addition the reaction mixture was stirred overnight at room temperature and washed with saturated ammonium chloride solution (350 ml). Solvents from the organic phase were evaporated, and the product was dissolved in Et_2O (350 ml), washed with water (2×300 ml) and dried over sodium sulfate. Repeated crystallizations at –15°C afforded 37.48 g (52.2%) of **3** as off-white crystals. The first crystalline fraction consisted of diastereomerically pure material that was used for spectral characterization. EIMS (calcd/found): m/e 574.3662/574.3659. $^1\text{H-NMR}$ (CDCl_3 , δ): 7.22–7.07 (m, 6H); 6.97 (td, $^3J = 7.4$ Hz, $^4J = 1.2$ Hz, 2H); 5.65 (s, 2H); 3.15 (m, 2H); 1.91–1.84 (m, AA', 2H); 1.67 (sept, $^3J = 6.8$ Hz, 2H); 1.57–1.50 (m, BB', 2H); 0.89 (m, 24H); 0.27 (s, 6H); 0.24 (s, 6H). $^{13}\text{C-NMR}$ (CDCl_3 , δ): 164.75; 144.45; 140.58; 126.46; 122.60; 122.33; 118.68; 104.96; 49.24; 33.93; 25.03; 24.32; 20.14; 20.02; 18.51; 18.47; –2.66; –2.95.

3.4. rac-[Ethylenebis(2-(thexyldimethyl-siloxy)indenyl)]-zirconium dichloride (4)

To an ice-cooled solution of **3** (11.50 g, 20.0 mmol) in THF (100 ml) was added dropwise *n*-BuLi (16.0 ml of a 2.5 M solution in hexane, 40.0 mmol) and the reaction mixture was stirred overnight at room temperature. The resultant off-yellow suspension was then added via cannula to a suspension of ZrCl_4 (4.66 g, 20.0 mmol) in THF (25 ml) at –80°C. The reaction mixture was gradually warmed to room temperature and stirred overnight. Evaporation of the solvents left a yellow solid that was extracted with CH_2Cl_2 (150 ml) and filtrated through Celite to remove lithium chloride. Concentration and cooling to –30°C gave 3.25 g (22.1%) of **4** as a yellow microcrystalline solid. In the EIMS mass spectrum of **4**, parent ions of composition $\text{C}_{36}\text{H}_{52}\text{Si}_2\text{O}_2\text{ZrCl}_2^+$ were observed at $m/e = 732$ –740 in the appropriate isotope ratios. $^1\text{H-NMR}$ (CD_2Cl_2 , δ): 7.66 (dq, $J = 8.6$ Hz, 1.8 Hz, 1.0 Hz, 2H); 7.35–7.29 (m, 4H); 7.08–7.04 (m, 2H); 5.95 (d, $^4J = 0.6$ Hz, 2H); 4.04–3.94 (m, AA', 2H); 3.56–3.46 (m, BB', 2H); 1.74 (sept, $^3J = 6.8$ Hz, 2H); 0.99 (s, 6H); 0.97 (s, 6H); 0.95 (d, $^3J = 6.8$ Hz, 6H); 0.94 (d, $^3J = 6.8$ Hz, 6H); 0.26 (s, 6H); 0.25 (s, 6H). $^{13}\text{C-NMR}$ (CD_2Cl_2 , δ): 150.48; 126.13; 125.18; 125.10; 124.85; 123.32; 116.94; 108.45; 98.53; 34.22; 26.41; 25.84; 20.35; 20.14; 18.80; 18.64; –1.62; –2.01.

3.5. X-ray structure determination

Single crystals for the X-ray structure determination were obtained by slowly cooling a hot saturated toluene

Table 4
Crystal data and structure refinement for **4**

Formula	C ₃₆ H ₅₂ Cl ₂ O ₂ Si ₂ Zr
Formula weight	735.10
Crystal size (mm)	0.30 × 0.25 × 0.30
Crystal system	Triclinic
Space group	P ₁
Unit cell dimensions	
<i>a</i> (Å)	12.9072(9)
<i>b</i> (Å)	15.345(1)
<i>c</i> (Å)	10.7896(9)
α (°)	104.684(6)
β (°)	107.514(6)
γ (°)	103.270(6)
<i>V</i> (Å ³)	1859.9(3)
<i>Z</i>	2.00
<i>D</i> _{calc} (g cm ⁻³)	1.313
<i>F</i> (000)	772
Mo–K α (cm ⁻¹)	5.26
Temperature (K)	294
Measured reflections	6550
Max and min transmission	1.00 and 0.97
Number of observations [<i>I</i> > 3.00(<i>I</i>)]	5215
Number of variables	430
Reflection/parameter ratio	12.13
Residuals <i>R</i> and <i>R</i> _w	0.034 and 0.032
Goodness-of-fit indicator	2.01
Max, min $\Delta\rho$ (e Å ⁻³)	0.66 and -0.38

solution of **4** to room temperature. Crystallographic data and parameters for **4** are presented in Table 4. The data set was collected on a Rigaku AFC5S diffractometer using Mo–K α radiation ($\lambda = 0.71069$ Å) at 293 K. Experimental absorption correction (ψ -scan) was carried out. Heavy atoms were refined with anisotropic and hydrogen atoms with isotropic displacement parameters except methyl hydrogen atoms, which were included in calculated positions with fixed displacement parameters (1.2 × that of the host atom). All refinements were performed using TEXSAN-TEXRAY software [24]. Figures were plotted on ORTEPII [25]. The atomic coordinates of **4** are collected in Table 5. Additional data including front and top views of **4** and complete listings of the interatomic distances and angles are recorded as supplementary material and can be obtained from the authors upon request.

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Table 5
Atomic coordinates and isotropic displacement parameters (Å²) for **4**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso}
Zr	0.30473(3)	0.36165(2)	0.64622(3)	2.55(1)
Cl(1)	0.22860(8)	0.48952(6)	0.71363(8)	4.04(3)
Cl(2)	0.50294(7)	0.46015(6)	0.71398(8)	3.96(3)
Si(1)	0.48353(8)	0.24095(6)	0.3337(1)	3.32(3)
Si(2)	0.02451(8)	0.31723(7)	0.8553(1)	3.63(3)
O(1)	0.3863(2)	0.2224(1)	0.4082(2)	3.38(7)
O(2)	0.0943(2)	0.2778(1)	0.7577(2)	3.69(8)
C(1)	0.2042(3)	0.2186(2)	0.4313(3)	2.9(1)
C(2)	0.3042(3)	0.2634(2)	0.4120(3)	2.9(1)
C(3)	0.3042(3)	0.3541(2)	0.4049(3)	3.1(1)
C(4)	0.1955(3)	0.3619(2)	0.4005(3)	3.1(1)
C(5)	0.1420(3)	0.4308(2)	0.3777(3)	3.7(1)
C(6)	0.0339(3)	0.4170(3)	0.3755(4)	4.5(1)
C(7)	-0.0263(3)	0.3367(3)	0.3977(4)	4.5(1)
C(8)	0.0218(3)	0.2691(3)	0.4205(4)	3.9(1)
C(9)	0.1340(3)	0.2790(2)	0.4199(3)	3.1(1)
C(10)	0.1713(3)	0.1211(2)	0.4422(3)	3.4(1)
C(11)	0.2341(3)	0.2146(2)	0.6946(3)	2.9(1)
C(12)	0.2053(3)	0.2833(2)	0.7818(3)	3.0(1)
C(13)	0.3059(3)	0.3559(2)	0.8821(3)	3.1(1)
C(14)	0.4011(3)	0.3275(2)	0.8706(3)	2.9(1)
C(15)	0.5200(3)	0.3663(2)	0.9533(3)	3.6(1)
C(16)	0.5917(3)	0.3212(3)	0.9193(4)	4.4(1)
C(17)	0.5498(3)	0.2374(3)	0.8021(4)	4.6(1)
C(18)	0.4362(3)	0.1974(2)	0.7195(4)	3.8(1)
C(19)	0.3576(3)	0.2412(2)	0.7533(3)	2.9(1)
C(20)	0.1508(3)	0.1255(2)	0.5767(4)	3.5(1)
C(21)	0.4111(4)	0.2573(3)	0.1693(4)	6.3(2)
C(22)	0.6067(3)	0.3487(3)	0.4548(4)	5.6(2)
C(23)	0.5250(3)	0.1293(2)	0.3104(4)	4.2(1)
C(24)	0.5473(5)	0.1091(4)	0.4459(5)	8.9(3)
C(25)	0.4250(4)	0.0457(3)	0.1965(6)	9.4(2)
C(26)	0.6380(4)	0.1429(3)	0.2817(5)	6.2(2)
C(27)	0.6398(4)	0.1780(4)	0.1652(5)	8.3(2)
C(28)	0.6801(5)	0.0572(4)	0.2690(6)	9.9(3)
C(29)	0.1218(4)	0.4184(3)	1.0166(4)	6.5(2)
C(30)	-0.0770(4)	0.3570(3)	0.7385(5)	7.7(2)
C(31)	-0.0567(3)	0.2159(3)	0.8928(4)	5.5(1)
C(32)	-0.1394(4)	0.2606(4)	0.9654(6)	9.3(3)
C(33)	-0.1350(4)	0.1346(3)	0.7569(3)	7.1(2)
C(34)	0.0100(5)	0.1865(4)	1.0007(6)	10.2(3)
C(35)	0.0941(5)	0.1452(5)	0.9460(8)	12.8(4)
C(36)	-0.0603(5)	0.1161(4)	1.0494(5)	10.6(3)

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