Group 4 metallocene complexes with annulated twelve-membered ring cyclopentadienyl ligands: their synthesis, characterization and catalytic behavior in olefin polymerization

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Abstract

The synthesis, characterization and olefin polymerization properties of Group 4 compounds $\{1,2\text{-}(CH_2)_{10}(C_5H_3)\}_2MCl_2$ (M = Ti 5, Zr 6, Hf 7) containing annulated twelve-membered ring cyclopentadienyl ligands are reported. The reactions of lithiated annulated cyclopentadiene ($Li[1,2\text{-}(CH_2)_{10}C_5H_3]$) with $MCl_4(THF)_2$ (M = Ti, Zr) or $HfCl_4$ in tetrahydrofuran gave new metallocene products in reasonable yields. 6 and 7 have been characterized by single crystal X-ray diffraction studies. The compound 6 [7] crystallizes in the orthorhombic space group $P2_12_12_1[P2_12_12_1]$, with $a = 8.188(1)$ [8.190(5)] Å, $b = 11.371(1)$ [11.352(5)] Å, $c = 30.253(1)$ [30.177(8)] Å, $Z = 4$ [4] and $V = 2816.6(4)$ [2805.7] Å^3. Both compounds are isostructural and adopt a distorted tetrahedron around the metal center. The steric crowding of the annulated twelve-membered ring in 6 and 7 is greater than that of the seven-membered ring in $(2\text{-Me-4,5-}(CH_2)_3Cp)_2ZrCl_2$. The catalytic behavior of the new metallocenes in propylene and ethylene polymerization has been studied in the presence of excess amount of methylaluminoxane.

Keywords: Group 4; Catalysts; Metallocene complexes; Annulated cyclopentadienyl; Olefin polymerization; Structures

1. Introduction

The Group 4 metallocene compounds have become an important class of catalysts for the synthesis of organic molecules [1] and polymers [2]. The known organometallic chemistry of the Group 4 metals Ti, Zr and Hf has largely been developed by the use of cyclopentadienyl and substituted cyclopentadienyl ligands [3]. The broader, tunable features of electronic and steric factors in the cyclopentadienyl type ligands allow greater versatility in the design of catalytic systems, able to specifically change the catalytic activity and product properties [4–7]. At present, many research groups are involved in ligand modification to introduce novel features into the catalytic behavior, reactivity and stability of the resulting complexes, and in finding an explicit relationship between ligand properties of the catalysts and polymer structures [8–16]. It is known that the chemical and physical properties of Group 4 bent metallocenes can be varied over a wide range by modifying the substituents on the cyclopentadienyl ring.

Particularly in comparison with olefin polymerization studies of a series of $(CpR_n)_2MCl_2$ complexes [3b], only a few studies have been carried out with annulated cyclopentadienyl ring complexes. The complex A, which leads to highly isotactic polypropylene in the presence of methylaluminoxane (MAO) as a cocatalyst [8], is easily accessible through simple hydrogenation of the indenyl precursor compound. Herrmann et al. [17] have also prepared zirconium complexes B ($n = 5$, 6) with a larger fused-ring cyclopentadienyl ligand than the tetra-

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hydroindenyl ligand, but their catalytic behavior in olefin polymerization has not been reported.

A

B

C
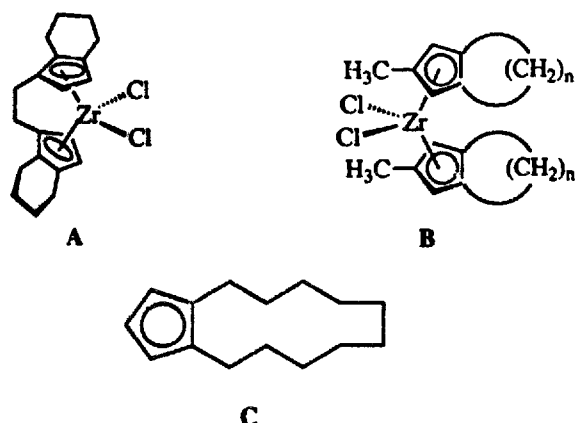
We thought it would be interesting to prepare Group 4 bent metallocenes containing much larger annulated ring systems, and to evaluate the increased annulated ring size effect on the catalytic behavior and stability of the complexes. As part of our efforts in developing new non-bridged metallocene catalyst systems, we have explored the reactions of Group 4 metals with a fused-ring cyclopentadienyl ligand (C) containing a ten-membered alkylidene group, =$(CH_2)_{10}$=, in 1,2-positions. Reported herein are accounts of the synthesis, structural
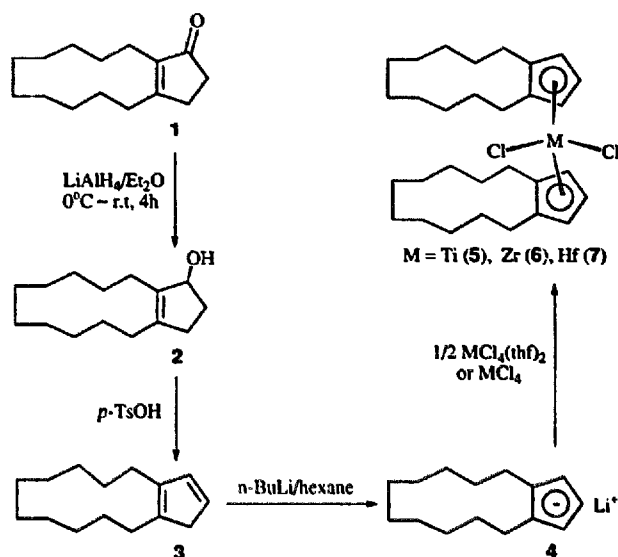
Scheme 1.

characterization and catalytic activity of the new Group 4 metal complexes with annulated twelve-membered ring cyclopentadienyl ligand (C).

2. Results and discussion

A synthetic approach to the new Group 4 metallocenes is outlined in Scheme 1. Reduction of

Table 1
Analytical and spectroscopic data [a]

Compound	Analysis		^{1}H NMR	$^{13}C(^1H)$ NMR
	C	H		
5	68.05 (68.61)	9.18 (8.83)	6.29 [2H, d(J_{H1-H2} = 3), H_2]	138.0 [2C, C_1]
			6.19 [1H, t(J_{H1-H2} = 3), H_1]	119.9 [2C, C_2]
			2.70 [2H, m, H_{aa}]	110.0 [1C, C_1]
			2.39 [2H, m, H_{ab}]	29.3 [2C, C_a]
			1.74-1.23 [16H, m(br), H_5-H_8]	26.1 [2C, C_5]
				25.8 [2C, C_6]
				25.0 [2C, C_7]
				22.8 [2C, C_8]
6	63.24 (63.38)	7.84 (8.16)	6.12 [3H, s, H_1 and H_2]	133.4 [2C, C_1]
			2.59 [2H, m, H_{aa}]	114.6 [2C, C_2]
			2.39 [2H, m, H_{ab}]	107.7 [1C, C_1]
			1.73-1.15 [16H, m(br), H_5-H_8]	29.7 [2C, C_a]
				25.7 [2C, C_5]
				25.2 [2C, C_6]
				25.1 [2C, C_7]
				22.8 [2C, C_8]
7	55.26 (54.95)	7.94 (7.07)	6.02 [3H, s, H_1 and H_2]	131.2 [2C, C_1]
			2.57 [2H, m, H_{aa}]	113.4 [2C, C_2]
			2.41 [2H, m, H_{ab}]	106.1 [1C, C_1]
			1.65-1.19 [16H, m(br), H_5-H_8]	29.9 [2C, C_a]
				25.7 [2C, C_5]
				25.1 [4C, C_6 and C_7]
				22.8 [2C, C_8]

[a] Analytical data are given as observed (calculated) in per cent. The NMR spectra were recorded in $CDCl_3$. Data given as: chemical shift (δ) [relative intensity, multiplicity (J in hertz) for ^{1}H NMR, assignment]. Key labelling used for the assignment:
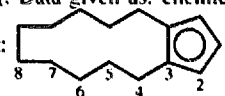
bicyclo[10,3,0]pentadec-12(1)-en-13-one **1**, which is commercially available, with LiAlH$_4$ in diethyl ether, followed by acidic work-up and dehydration with p-toluenesulfonic acid, gave the new ligand precursor fused-ring cyclopentadiene **3** via **2** as a pale yellow oil in ca. 60% overall yield. The ^{1}H NMR spectrum of the product revealed the presence of a mixture of isomers, as expected. Treatment of crude **3** in hexane solution with a slight excess of n-butyllithium gave fine white precipitates; after filtration and thorough washing with pentane, extremely moisture sensitive Li[1,2-(CH$_2$)$_{10}$(C$_5$H$_3$)] **4** was obtained in ca. 92% yield. This can be stored in a glovebox at room temperature for an extended period.

Straightforward treatment of the lithium salt **4** with MCl$_4$(THF)$_2$ (M = Ti, Zr) or HfCl$_4$ in 2:1 molar ratio under the conditions usually applied for metallocene formation (see Experimental section) resulted in the formation of the new metallocene derivatives {1,2-(CH$_2$)$_{10}$(C$_5$H$_3$)}$_2$MCl$_2$ (M = Ti **5**, Zr **6**, Hf **7**) in yields of 32–46%.

The analytical and spectroscopic data for the metallocene compounds **5–7** are summarized in Table 1. The titanium compound **5** gives a pseudo-doublet and a triplet signals for Cp-ring protons ($J_{H-H} = 3$ Hz), while the zirconium and hafnium compounds show only one singlet Cp-ring proton signal. The ^{1}H and ^{13}C{^{1}H} resonances of the Cp-ring for the metallocenes **5–7** tend to appear upfield for the heavier congener analogue. A similar trend, which is the consequence of the different
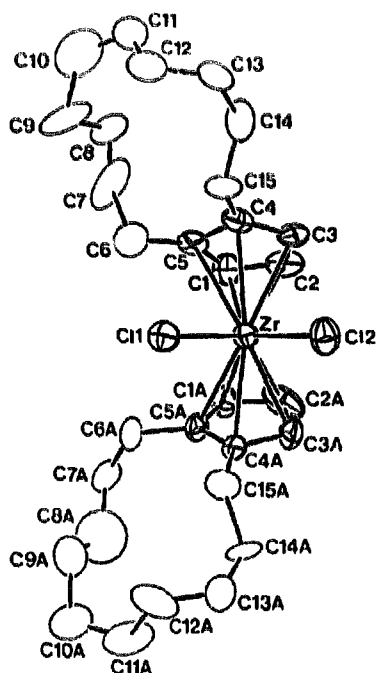

Fig. 1. ORTEP drawing of the molecular structure of **6** showing the atomic numbering scheme. Atoms are drawn with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 2
Selected bond distances and angles for **6** and **7** [a]

	6	7
Bond distances (Å)		
M–C11	2.451(1)	2.424(4)
M–C12	2.444(1)	2.420(3)
M–C1	2.460(11)	2.42(2)
M–C2	2.477(09)	2.45(2)
M–C3	2.542(11)	2.51(3)
M–C4	2.592(12)	2.56(3)
M–C5	2.554(10)	2.51(3)
M–C1A	2.461(12)	2.47(3)
M–C2A	2.428(13)	2.48(2)
M–C3A	2.500(12)	2.54(2)
M–C4A	2.547(10)	2.57(3)
M–C5A	2.527(11)	2.55(3)
M–Cp1	2.2186	2.1839
M–Cp2	2.1946	2.2037
Bond angles (deg)		
Cp1–M–Cp2	129.9	130.1
Cp1–M–C11	106.4	104.5
Cp1–M–C12	106.7	107.5
Cp2–M–C11	107.9	110.4
Cp2–M–C12	106.2	104.7
C11–M–C12	94.2(1)	93.7(1)
Cp1–Cp2 (dihedral)	54.9(3)	54.0(7)

[a] Cp1 is the centroid of C1–C2–C3–C4–C5. Cp2 is the centroid of C1A–C2A–C3A–C4A–C5A.

electronegativities of the metals, has been observed previously [18]. The extent of magnetic inequivalency of the allylic CH$_2$ can be measured as the chemical shift difference between two allylic CH$_2$ protons, which tends to decrease from titanium (0.31 ppm) to zirconium (0.20 ppm) to hafnium (0.16 ppm) derivatives. In the ^{13}C{^{1}H} NMR spectra, the appearance of only three signals for Cp-ring carbons and five signals for ten annulated ring carbons for **5, 6** and **7** indicates that rotation of Cp-rings about the metal–Cp-ring vector is almost unhindered in solution.

2.1. X-ray analysis

In order to ascertain the conformation of these metallocene complexes in the solid state, the X-ray crystal structures of **6** and **7** have been determined. The molecular structure of {1,2-(CH$_2$)$_{10}$Cp}$_2$MCl$_2$ (**6**) is shown in Fig. 1. No ORTEP drawing of the hafnium complex is displayed since **6** and **7** are isostructural. The atomic numbering scheme used for both molecules is the same. Selected interatomic bond distances and angles are given in Table 2.

As expected, in both molecules the geometry about the metal atom is a distorted tetrahedron, each annulated cyclopentadienyl ligand occupying a single coordination position. The Cp-rings of the annulated cyclopentadienyl ligand are approximately planar, and the dihedral
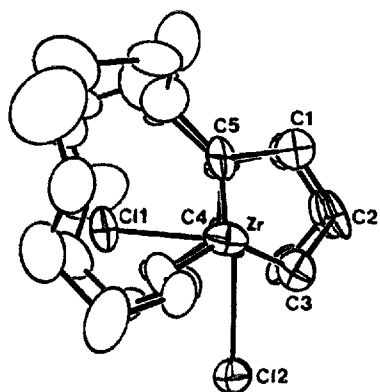
Fig. 2. Alternative view of 6. This view is a projection of the annulated Cp ligands onto the ZrCl$_2$ plane.

angle between the least-squares planes through these rings is larger for zirconium 6 (54.9°) than for hafnium 7 (54.0°). These values are larger than that found (52.1°) for the similar zirconocene compound {2-Me-4,5-(CH$_2$)$_5$C$_5$H$_2$}$_2$ZrCl$_2$ (8) [17], and consequently the Cl–M–Cl angles of 94.2(1)° in 6 and 93.7(1)° in 7 are smaller than that (97.74°) in 8.

In contrast to the structure of 8 which contains two-fold rotational symmetry, a projection of the annulated Cp ligands onto the MCl$_2$ plane, displayed in Fig. 2, shows that in 6 and 7 the Cp-rings are almost eclipsed and the bulky twelve-membered rings lie on the same side, folded away from the center of the molecule. Thus, one of the chlorine atoms is situated in the space between the annulated twelve-membered rings of the molecule.

The metal–halogen bond distances are in the typical range at Zr–Cl = 2.448 Å (av.) and Hf–Cl = 2.422 Å (av.). The M=Cp-ring centroid distance of 2.207 Å (av.) in 6 is similar to that (2.194 Å (av.)) in 7. The Cp-ring centroid=M=Cp-ring centroid angles for 6 and 7 are 129.9° and 130.1° respectively, both of which fall within the normal range for these types of complex [18].

The metal–Cp-ring carbon bond distances indicate that the metal–Cp-ring interaction is asymmetric. These distances are in the ranges 2.460–2.592 and 2.428–2.547 Å for the zirconium compound and 2.42–2.56 and 2.47–2.57 Å for the hafnium compound. As noted for the other (η^5-RCp)$_2$MCl$_2$ structures, the metal–Cp-ring

carbon bond distance is longest for the carbon atom bonded to the substituent group [19]. In fact, the bridgehead carbon atoms C4, C5, C4A and C5A for 6 and 7 form longer distances with the metal atom than the other Cp-ring carbon atoms (see Table 2).

2.2. Polymerization

The newly synthesized metallocenes 5–7 described above were used for generating homogeneous Ziegler-type α-olefin polymerization catalysts in order to investigate the effects of the elongated annulation on the catalytic properties of these compounds. The non-bridged bent metallocene compounds were dissolved in toluene and activated in the presence of excess olefin by treating with a large excess of methylaluminoxane. The polymerization of propylene was carried out at two temperatures (−30 and 25°C). The results of the propylene polymerization are given in Table 3. As can be seen from the table, the polymerization activities of zirconocene 6/MAO catalyst systems are significantly higher than those of titanocene 5 systems, and this may be due to the larger size of the zirconium atom. Increasing the temperature of these homogeneous catalyst systems from −30 to 25°C under otherwise analogous conditions resulted in about a double increase in polymerization activity. However, the viscosity average molecular weight $\bar{M}_\eta$ of the polypropylene products, which was calculated by the Mark–Houwink equation [20a] [η] = 1.0 × 10^{-4} $M_\eta^{0.80}$, decreased with an increase of the polymerization temperature. An interesting observation is that the molecular weight of polypropylene produced by using the zirconocene catalyst at −30°C is higher than those of polypropylene by using the titanocene and hafnocene catalysts, whereas at 25°C a hafnocene 7/MAO system produces the highest molecular weight polypropylene. These results differ in some important aspects from those previously reported for general Group 4 metallocene catalysts, in which a hafnocene system produces the highest molecular weight polymer at any temperature. Although the polymerization activities of our systems cannot be exactly compared with those of related metallocene catalyst systems because the polymerization reactions were conducted

Table 3
Results of the polymerization of propylene with compounds 5, 6 and 7 [a]

Catalyst	[M] (μmol)	[Al] (mmol) [b]	T_p (°C)	t_p (h)	Yield (g)	Activity [c]	$\bar{M}_\eta$ [d] × 10^5
5	15	75	−30	6	1.2	11.0	1.44
5	15	75	25	12	3.0	28.0	—
6	15	75	−30	6	22.6	210	3.15
6	7.5	37.5	25	2	7.24	400	0.57
7	32	80	−30	6	1.25	5.4	1.48
7	15	30	25	3	0.6	11.1	0.95

[a] Conditions: 250 ml of toluene, 1.2 atm of C$_3$H$_6$. [b] Al content in MAO. [c] Units of Kg PP/(mol M) atm h.
[d] Viscosity average molecular weight calculated by Mark–Houwink equation [20a]. [η] = 1.0 × 10^{-4} $M_\eta^{0.80}$.

under different conditions, the polymerization activity of the 6/MAO system at −30°C is similar to that (400 kg PP/(mol Zr) atm h) of the Cp_2ZrCl_2/MAO system [21], and about six times higher than that (32.8 kg PP/(mol Zr) h) of the non-bridged bis(neoisomenthyl-tetrahydroindenyl) zirconium dichloride/MAO system [15b].

The $^{13}C\{^1H\}$ NMR spectra of the methyl triad region of the polypropylenes obtained using 5, 6 and 7 with MAO at −30°C reveal a similar pattern to typical atactic polypropylene with 1:2.3:1.5, 2.1:2.2:1 and 1.8:2.5:1 ratios of mm:mr:rr respectively, and the decreased tacticity can be ascribed to the rotation of the Cp-ring about the metal–Cp-ring center vector in solution state.

The new metallocenes, $\{1,2-(CH_2)_{10}Cp\}_2MCl_2$ (M = Ti 5, Zr 6, Hf 7), have also been tested as catalysts for the polymerization of ethylene, which is a smaller monomer than propylene and lacks prochirality. The polymerization behavior of metallocene catalysts toward ethylene is thus believed to reflect more the electronic rather than the steric properties of the metallocene structure [7d,22]. The results are summarized in Table 4. The ethylene polymerization activity is also highest in the zirconium complex 6 system, as for propylene polymerization. The viscosity average molecular weights $\overline{M}_\eta$ of the polyethylenes produced were calculated by the Mark–Houwink equation [20b] $[\eta] = 2.3 \times 10^{-4}M_\eta^{0.82}$. The viscosity molecular weights of polyethylene products produced by the catalyst systems 6 and 7 are similar, but a significantly lower molecular weight polymer was obtained for the catalyst 5. The melting points of the polyethylenes obtained for 5, 6 and 7/MAO catalyst systems at 40°C were measured as 128.7, 137.0 and 133.0°C respectively.

3. Experimental section

3.1. General procedures

Manipulations of organic compounds were performed in air. Reactions with organometallic reagents were carried out under a pure dinitrogen atmosphere using standard Schlenk or glovebox techniques. Organic solvents were carefully dried by distillation from suit-

3.2. Annulated twelve-membered ring cyclopentadiene (3)

To a suspension of $LiAlH_4$ (800 mg, 20 mmol) in 100 ml of diethyl ether at 0°C a solution of bicyclo[10,3,0]pentadec-12(1)-en-13-one (4.4 g, 20 mmol) in 100 ml of diethyl ether was added dropwise over a period of 30 min using a cannula. The reaction mixture was allowed to warm slowly in the cold bath to room temperature over a 4 h period, and then hydrolyzed carefully with water until hydrogen evolution ceased. The ether layer was separated from the mixture and the solvent was removed on a rotary evaporator giving a colorless oil (2). The oil product was dissolved in 50 ml of methylene chloride and p-toluenesulfonic acid hydrate (ca. 1 g) was added with stirring. The extended stirring (4 h) of the resulting reaction mixture gave a green solution which was washed with aqueous Na_2CO_3 (1.0 g, 100 ml) and H_2O (2 × 100 ml). The aqueous layer was extracted with methylene chloride (2 × 20 ml), and the combined portion of organic layers

Table 4
Results of the polymerization of ethylene with compounds 5, 6 and 7 [a]

Catalyst	[M] (μmol)	[Al] (mmol) [b]	t_p (h)	Yield (g)	Activity [c]	$\overline{M}_\eta$ [d] × 10⁻⁵	M.p.
5	8	40	3	0.61	21.2	0.21	128.7
6	1.2	6	6	4.70	6580	1.12	137.0
7	4.8	24	6	2.20	380	1.58	133.0

[a] Conditions: 250 ml of toluene, 1.2 atm of C_2H_4, $T_p = 40°C$. [b] Al content in MAO. [c] Units of kg PE/(mol M) atm h. [d] Viscosity average molecular weight calculated by Mark–Houwink equation [20b], $[\eta] = 2.3 \times 10^{-4}M_\eta^{0.82}$.

was dried (MgSO₄) and concentrated in vacuo to give a yellow oil. The yellow oil was chromatographed on SiO₂ (hexane) to give a light yellow oil. Yield 50–60%. MS (EI): m/e 204 (M⁺). ¹H NMR (200 MHz, CDCl₃, 298 K): δ 6.37–6.00 (m, 2H), 2.70 (m, 2H), 2.34 (m, 4H), 1.64–1.20 (br, 16H). ¹³C{¹H} NMR (50 MHz, CDCl₃, 298 K): δ 141.1, 139.6, 134.7, 129.9, 42.9, 27.9, 26.6, 24.5, 23.6, 22.3, 22.2.

3.3. Li[1,2-(CH₂)₁₀(C₅H₃)] (4)

The compound 3 (2 g, 10 mmol) was dissolved in 100 ml of hexane. At −78°C, 8 ml (12.8 mmol) of butyllithium (1.6 M hexane solution) was added dropwise over 20 min. The reaction mixture was warmed slowly to room temperature. From the pale yellow solution a white precipitate was formed. After 12 h of stirring, the cyclopentadienyllithium salt 4 was collected by filtration, washed twice with hexane (50 ml each) and dried in vacuo. Yield 82% (1.7 g).

3.4. [1,2-(CH₂)₁₀(C₅H₃)]₂TiCl₂ (5)

A solution of lithium salt 4 (210 mg, 1 mmol) in 20 ml of tetrahydrofuran was added dropwise at −78°C to a precooled solution of TiCl₄(THF)₂ (166 mg, 0.5 mmol) in 20 ml of tetrahydrofuran. The reaction mixture was allowed to warm slowly in the cold bath to room temperature during 6 h and then stirred for an additional 18 h. After removal of volatiles, the residue was extracted with 50 ml of methylene chloride, and removal of solvent in vacuo resulted in a greenish powder which was collected and extracted with 100 ml of toluene. Treatment of the filtered toluene extract with an excess amount of hexane gave a red crystalline solid. Recrystallization of this product from toluene/hexane afforded an analytically pure product in a yield of 37% (97 mg). Anal. Found: C, 68.05; H, 9.18, C₃₀H₄₆Cl₂Ti Calc.: C, 68.61; H, 8.83%. ¹H NMR (200 MHz, CDCl₃, 298 K): δ 6.29 (d, $J = 3$ Hz, 4H), 6.19 (t, $J = 3$ Hz, 2H), 2.70 (m, 4H), 2.39 (m, 4H), 1.74–1.23 (br, 32H). ¹³C{¹H} NMR (50 MHz, CDCl₃, 298 K): δ 138.0, 119.9, 110.0, 29.3, 26.1, 25.8, 25.0, 22.8.

3.5. [1,2-(CH₂)₁₀(C₅H₃)]₂ZrCl₂ (6)

To a suspension of lithium salt 4 (210 mg, 1 mmol) and ZrCl₄(THF)₂ (188 mg, 0.5 mmol) in 10 ml of hexane was added 20 ml of tetrahydrofuran at −78°C. The reaction mixture was allowed to warm slowly in the cold bath to room temperature during 6 h and then stirred for an additional 18 h. Solvent was removed in vacuo and the remaining solid was extracted with 100 ml of methylene chloride. A precipitate was filtered off and the clear filtrate was concentrated in vacuo to a final volume of 10 ml, addition of ca. 50 ml of hexane

followed. The resulting greenish solid was collected and recrystallized from toluene/hexane, affording analytically pure product 6 in 32% yield (90 mg) as a colorless crystalline solid. Anal. Found: C, 63.24; H, 7.84. C₃₀H₄₆Cl₂Zr Calc.: C, 63.38; H, 8.15%. ¹H NMR (200 MHz, CDCl₃, 298 K): δ 6.12 (s, 6H), 2.59 (m, 4H), 2.39 (m, 4H), 1.73–1.15 (br, 32H). ¹³C{¹H} NMR (50 MHz, CDCl₃, 298 K): δ 133.4, 114.6, 107.7, 29.7, 25.7, 25.2, 25.1, 22.8.

3.6. [1,2-(CH₂)₁₀(C₅H₃)]₂HfCl₂ (7)

By adopting a similar procedure described for the compound 6, the hafnium compound 7 was obtained from 210 mg (1 mmol) of lithium salt 4 and 160 mg (0.5 mmol) of HfCl₄ in 46% yield (150 mg) as a colorless crystalline solid. Anal. Found: C, 55.26; H, 7.94. C₃₀H₄₆Cl₂Hf Calc.: C, 54.95; H, 7.07%. ¹H NMR (200 MHz, CDCl₃, 298 K): δ 6.02 (s, 6H), 2.57 (m, 4H), 2.41 (m, 4H), 1.65–1.19 (br, 32H). ¹³C{¹H} NMR (50 MHz, CDCl₃, 298 K): δ 131.2, 113.4, 106.1, 29.9, 25.7, 25.1, 22.8.

3.7. X-ray structural determinations

Diffraction-quality crystals were obtained by diffusion of hexane at −10°C into solutions of the compounds (6 and 7) in CH₂Cl₂ as colorless rectangular blocks. All crystals were mounted on glass fibers and diffraction data were collected on an Enraf-Nonius CAD4 diffractometer equipped with graphite monochromated Mo Kα radiation (0.71073 Å) operating at ca. 293 K. Accurate unit cell parameters and an orientation matrix were determined from the least-squares fits of accurately centered reflections (6, 24 reflections with 19° ≤ 2θ ≤ 28°; 7, 21 reflections with 12° ≤ 2θ ≤ 22°). Intensity data were collected in the ω–2θ scan mode for 6 and 7 to a maximum 2θ of 50° and 46° respectively. The intensities of three standard reflections were monitored every 7200 s of exposure, and no significant decay was observed over the course of the data collection. Two standard reflections checked every 200 reflections were used to check the orientation changes of the crystal. All data sets were corrected for Lorentz and polarization effects, and empirical absorption corrections were applied using azimuthal Ψ-scan data. Systematic absences uniquely defined the space groups of both compounds.

Heavy atoms were located by use of the Patterson method (SHELXS 86) [24]. Atoms not located from the initial structure solution were found by successive difference Fourier maps with iterative cycles of least-squares refinement (SHELXL 93) [25] on an IBM RS/6000 workstation. All non-hydrogen atoms except carbon atoms in 7 were anisotropically treated. Full-matrix least-squares refinements were used in all cases. In

Table 5
Details of crystallographic data [a] for 6 and 7

Compound	6	7
Formula	$C_{30}H_{46}Cl_2Zr$	$C_{30}H_{46}Cl_2Hf$
FW	568.79	656.06
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)
a (Å)	8.188(1)	8.190(5)
b (Å)	11.371(1)	11.352(5)
c (Å)	30.253(1)	30.177(8)
Z	4	4
Cell volume (Å³)	2816.6(4)	2805.6(22)
d_{calc} (g cm⁻³)	1.341	1.553
μ (mm⁻¹)	0.596	3.925
$F(000)$	1200	1328
No. of independent reflections	1816	2046
No. of observed reflections	1617 ($I \geq 2\sigma(I)$)	1873 ($I \geq 2\sigma(I)$)
R_1 [b]; wR_2 [c] (%)	2.26; 5.55	5.36; 13.37
GOOF (= S) (obs.)	1.136	3.191
a [c]	0.0293	0.0293
b [c]	1.2111	1.2111

[a] All data collected with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K.
[b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = (F_o^2 + 2F_c^2)/3$.

Table 6
Positional and equivalent isotropic thermal parameters [a] for non-hydrogen atoms of 6

Atom	x	y	z	U_{eq} [b] (Å²)
Zr	0.82260(4)	0.90785(3)	0.75011(5)	0.03114(13)
Cl1	1.11788(12)	0.94312(9)	0.7506(2)	0.0530(3)
Cl2	0.75258(13)	1.11684(8)	0.7502(2)	0.0469(3)
C1	0.6471(17)	0.7941(11)	0.6998(4)	0.052(4)
C2	0.7991(17)	0.7455(8)	0.6959(3)	0.044(3)
C3	0.9036(15)	0.8233(12)	0.6755(3)	0.042(3)
C4	0.8153(13)	0.9250(11)	0.6647(4)	0.042(3)
C5	0.6454(14)	0.9128(11)	0.6807(3)	0.039(3)
C6	0.5025(16)	0.9874(14)	0.6781(5)	0.069(5)
C7	0.3946(16)	0.9566(11)	0.6354(5)	0.106(6)
C8	0.4325(9)	0.9947(9)	0.5951(3)	0.059(3)
C9	0.4211(19)	1.1263(15)	0.5895(5)	0.096(6)
C10	0.5048(22)	1.1564(17)	0.5435(6)	0.145(8)
C11	0.6687(16)	1.1400(8)	0.5309(4)	0.065(3)
C12	0.7874(18)	1.1981(11)	0.5581(4)	0.068(4)
C13	0.9409(18)	1.1216(12)	0.5653(4)	0.073(4)
C14	0.9131(16)	1.0112(11)	0.5944(5)	0.062(4)
C15	0.8733(14)	1.0302(10)	0.6423(3)	0.044(3)
C1A	0.8926(15)	0.8265(13)	0.8231(4)	0.051(4)
C2A	0.7912(19)	0.7447(11)	0.8012(4)	0.067(4)
C3A	0.6359(15)	0.7970(11)	0.8005(4)	0.047(3)
C4A	0.6453(11)	0.9046(12)	0.8193(4)	0.037(3)
C5A	0.8019(13)	0.9285(8)	0.8331(4)	0.030(2)
C6A	0.8713(13)	1.0369(11)	0.8583(4)	0.049(3)
C7A	0.9085(15)	1.0049(11)	0.9069(3)	0.051(4)
C8A	0.9388(14)	1.1151(14)	0.9335(4)	0.072(4)
C9A	0.7956(20)	1.1937(12)	0.9392(4)	0.076(4)
C10A	0.6453(21)	1.1402(17)	0.9688(4)	0.139(7)
C11A	0.4767(15)	1.1716(12)	0.9587(4)	0.075(4)
C12A	0.4358(14)	1.1338(11)	0.9125(5)	0.065(4)
C13A	0.4085(21)	1.0081(15)	0.9013(4)	0.154(7)
C14A	0.3757(10)	0.9593(12)	0.8567(4)	0.063(3)
C15A	0.4995(11)	0.9910(11)	0.8236(4)	0.046(4)

[a] Units of each e.s.d. in parentheses are those of the least significant digit of the corresponding parameters. [b] The isotropic equivalent thermal parameter is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

the final stages of refinement, hydrogen atoms were placed at the calculated positions of 0.93 Å (aromatic) and 0.97 Å (methylene) from their parent carbon atoms for 6, with isotropic thermal parameters the distances were 1.2 times these. Final difference Fourier maps showed insignificant residual electron density for 6 and four residual electron densities of 1.98, 1.78, 1.73 and 1.69 e Å^{-3} only near the hafnium atom for 7. The floating origin restraint was applied automatically for both non-centrosymmetric systems by the use of SHELXL 93. Attempts to confirm the correct absolute structures were made by evaluating the Flack absolute structure X-parameters of $-0.01(14)$ for 6 and $0.12(6)$ for 7. A summary of the crystal and other data is given in Table 5. Final atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms are listed in Tables 6 and 7.

3.8. Polymerizations and polymer analysis

Solution polymerizations in toluene were carried out using a Teflon magnetic spinbar for agitation at a total pressure of 1.2 atm in a 500 ml glass reactor. Toluene (200 ml) was introduced into the reactor, the temperature was increased to polymerization temperature, and then the toluene was saturated with monomer. A prescribed amount of MAO and a given metallocene dissolved in toluene were injected into the reactor by a tuberculin syringe. After the polymerization was stopped by removing monomer and injecting ethanol, the polymer produced was quenched by an excess of acidified methanol (ca. five times the amount of toluene used). The precipitated polymer was collected by filtration, washed with fresh ethanol and dried in vacuo. The appearance of the resulting polypropylenes is resinous.

The intrinsic viscosity [η] of the polymers obtained was determined using a modified Ubbelohde viscometer at 135°C by one-point intrinsic viscosity. The viscosity average molecular weights $\overline{M}_\eta$ of the polypropylene and polyethylene were calculated from a Mark–Houwink equation [25]. The melting point of the polyethylenes was determined from the peaks of the DSC curves obtained with a Du Pont Analyst 2000

Table 7
Positional and equivalent isotropic thermal parameters [a] for non-hydrogen atoms of 7

Atom	x	y	z	U_{eq} [b] (Å^2)
Hf	0.17816(4)	0.09362(3)	0.24998(4)	0.0309(3)
C11	0.2453(4)	−0.1137(2)	0.2503(2)	0.0439(6)
C12	−0.1146(3)	0.0585(2)	0.2498(3)	0.0508(7)
C1	0.3484(16)	0.2058(11)	0.2004(4)	0.042(5)
C2	0.1952(16)	0.2538(9)	0.1967(4)	0.043(5)
C3	0.0975(16)	0.1740(9)	0.1751(4)	0.048(6)
C4	0.1904(17)	0.0767(10)	0.1654(5)	0.048(6)
C5	0.3454(14)	0.0963(11)	0.1811(5)	0.038(4)
C6	0.4988(26)	0.0189(18)	0.1786(6)	0.049(6)
C7	0.6124(37)	0.0350(21)	0.1378(9)	0.107(12)
C8	0.5917(44)	−0.0085(27)	0.0973(8)	0.127(16)
C9	0.5700(25)	−0.1356(24)	0.0909(7)	0.061(7)
C10	0.4978(52)	−0.1605(31)	0.0441(12)	0.135(21)
C11	0.3259(40)	−0.1490(29)	0.0320(9)	0.093(10)
C12	0.1969(40)	−0.1920(22)	0.0576(10)	0.088(10)
C13	0.0562(24)	−0.1192(18)	0.0664(7)	0.054(6)
C14	0.1023(19)	−0.0031(15)	0.0928(6)	0.028(4)
C15	0.1206(28)	−0.0247(18)	0.1406(7)	0.053(6)
C1A	0.3789(16)	0.2013(11)	0.3005(5)	0.045(5)
C2A	0.2225(20)	0.2586(10)	0.3030(4)	0.071(7)
C3A	0.1090(16)	0.1777(12)	0.3229(4)	0.054(7)
C4A	0.1953(14)	0.0705(10)	0.3328(5)	0.038(5)
C5A	0.3621(14)	0.0851(10)	0.3189(5)	0.033(4)
C6A	0.4993(27)	0.0007(20)	0.3230(8)	0.057(6)
C7A	0.6216(22)	0.0451(21)	0.3569(7)	0.065(7)
C8A	0.5634(23)	0.0059(18)	0.4028(7)	0.061(7)
C9A	0.5617(43)	−0.1283(27)	0.4144(9)	0.092(10)
C10A	0.5221(34)	−0.1729(21)	0.4573(8)	0.064(7)
C11A	0.3576(43)	−0.1324(23)	0.4700(6)	0.081(9)
C12A	0.2166(33)	−0.2004(19)	0.4396(5)	0.055(6)
C13A	0.0672(40)	−0.1193(23)	0.4351(8)	0.095(12)
C14A	0.0637(27)	−0.0152(23)	0.4052(9)	0.058(7)
C15A	0.1308(29)	−0.0384(13)	0.3565(5)	0.036(5)

[a] Units of each e.s.d. in parentheses are those of the least significant digit of the corresponding parameters. [b] The isotropic equivalent thermal parameter is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

differential scanning calorimeter at a heating rate of $20°C \ min^{-1}$.

Acknowledgements

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