

Mixed substituted zirconocene dichloride complexes as catalyst precursors for homogeneous ethylene polymerization[☆]

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Abstract

The synthesis and characterization of 15 new, unbridged metallocene dichloride complexes of the type (L)(Ind)ZrCl₂ (L = ω-phenylalkyl substituted cyclopentadienyl or 1-phenylsilyl substituted indenyl; Ind = indenyl) and (L')(Flu)ZrCl₂ (L' = 1-benzyl substituted indenyl or 2-benzyl substituted indenyl; Flu = fluorenyl) are reported. After activation with methyl aluminoxane (MAO), these complexes are highly active catalysts for homogeneous ethylene polymerization. The influence of various substituents on the catalyst activities and the polymer properties are discussed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Zirconium; Catalysis; Ethylene polymerization; Metallocene complexes; Substituent effect

1. Introduction

Zirconocene dichloride complexes in combination with methyl aluminoxane (MAO) are highly active catalysts for the homogeneous polymerization of α-olefins [1–4]. In recent years, a large number of unbridged and bridged zirconocene dichloride complexes has been synthesized as catalyst precursors, activated with a co-catalyst and used for homogeneous olefin

polymerization [5–24]. These complexes offer an immense array of possibilities for varying the ligand sphere and thus, allow specific changes in catalytic and subsequent resin properties. Therefore, metallocene catalysts are well suited for studying the catalyst/polymer relationship. The steric environment of the catalytically active metallocene monoalkyl cation has a significant influence on the observed polymerization behavior.

Recently, we reported on the influence of alkyl and silyl substituents, containing a terminal phenyl group, on the polymerization behavior of symmetric zirconocene complexes [25]. The following question of interest remained: if only one of the two π-ligands contained a substituent, how would the length and type of this substituent influence the polymerization be-

[☆] Dedicated to Professor Herbert Schumann on the occasion of his 65th birthday (August 06, 2000).

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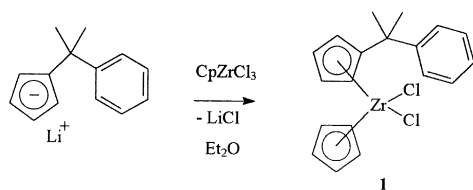


Fig. 1. Synthesis of the unbridged, mixed substituted [1-phenyl-1-methylethyl(η^5 -cyclopentadienyl)](η^5 -cyclopentadienyl) zirconium dichloride complex **1**.

havior of the resulting catalyst and the properties of the resin produced?

2. Results and discussion

2.1. Synthesis of the metallocene dichloride complexes 1–15

Mixed substituted metallocene dichloride complexes can be synthesized by the reaction of unsubstituted half-sandwich complexes with the corresponding substituted cyclopentadienyl,

indenyl or fluorenyl anions [26] as shown in Fig. 1.

Cyclopentadienylzirconium trichloride [27], indenylzirconium trichloride [28] and substituted indenylzirconium trichloride [29] half-sandwich complexes are well suited for the type of reaction shown in Fig. 1. The metallocene dichloride complexes **1–15** were synthesized by the reaction of phenyllithium with 6,6-dimethylfulvene [30] or by the lithiation of ω -phenylalkyl substituted ligand precursors [25] followed by the reaction with the appropriate half-sandwich complex.

2.2. Spectroscopic characterization of the metallocene dichloride complexes 1–15 (Fig. 2)

The metallocene dichloride complexes were characterized by ^1H , ^{13}C , and ^{29}Si NMR spectroscopy. The spectroscopic data are listed in Table 1. The mass spectroscopy data are found in the experimental section.

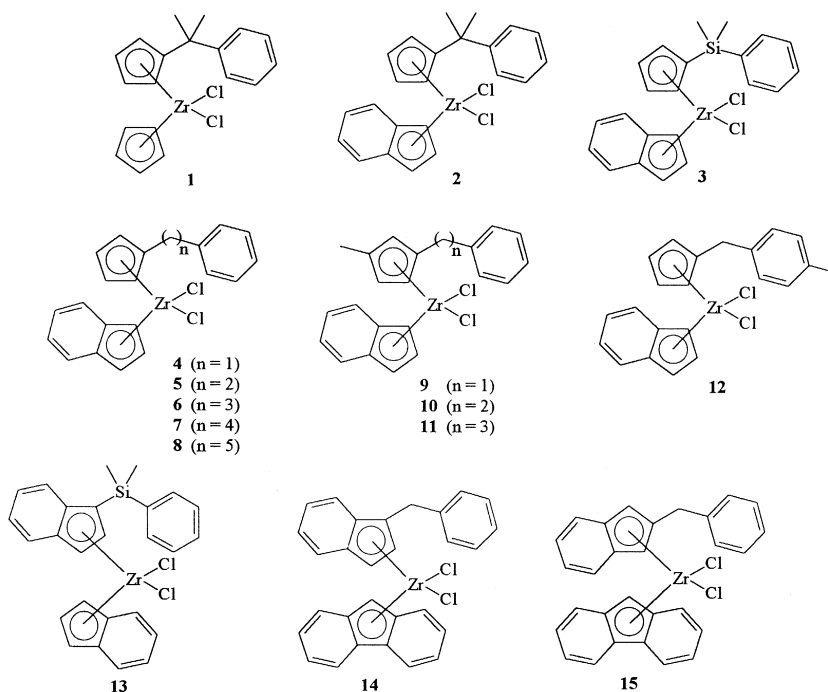


Fig. 2. Overview of the synthesized metallocene dichloride complexes **1–15**.

Table 1
 ^1H , ^{13}C , and ^{29}Si NMR data of the zirconocene dichloride complexes 1–15

	^1H NMR ^{a)} [J(H,H) in Hz]	^{13}C NMR ^{b)}	^{29}Si NMR ^{c)}
	7.34-7.22 (m, 5H), 6.45 (s, 5H), 6.39 (m, 2H), 6.27 (m, 2H), 4.04 (s, 2H)	(C _q): 139.6, 133.8 (CH): 128.9, 128.6, 126.5, 117.0, 115.7, 113.0 (CH ₂): 36.1	
	7.61 (m, 2H), 7.31-7.18 (m, 7H), 6.74 (m, 1H), 6.31 (m, 2H), 6.23 (m, 2H), 5.27 (m, 2H), 1.74 (s, 6H)	(C _q): 149.6, 142.7, 126.5 (CH): 128.2, 126.2, 126.1, 124.0, 116.2, 115.1, 103.2 (CH ₃): 29.3	
	7.57 (m, 2H), 7.53 (m, 2H), 7.41-7.38 (m, 3H), 7.28-7.26 (m, 2H), 6.67 (t, 1H) [5.0], 6.58-6.56 (m, 2H), 6.25 (m, 2H), 6.10-6.07 (m, 2H), 0.06 (s, 6H)	(C _q): 148.2, 137.9, 126.8, 122.0 (CH): 134.0, 129.4, 127.9, 126.8, 126.5, 126.2, 125.3, 124.6, 122.6, 116.5, 104.8, 103.0 (CH ₃): -1.9	-10.7
	7.66 (m, 2H), 7.31-7.14 (m, 7H), 6.88 (m, 1H), 6.44 (m, 2H), 6.01 (m, 2H), 5.88 (m, 2H), 3.91 (s, 2H)	(C _q): 139.6, 133.7 (CH): 128.8, 128.4, 126.4, 126.2, 125.4, 123.9, 117.4, 114.1, 102.8 (CH ₂): 35.9	
	7.65 (m, 2H), 7.31-7.13 (m, 7H), 6.90 (m, 1H), 6.50 (m, 2H), 5.86 (m, 4H), 2.91-2.75 (m, 4H)	(C _q): 141.0, 140.9, 134.5 (CH): 128.4, 128.2, 126.5, 126.1, 125.4, 123.9, 117.2, 113.5, 102.7 (CH ₂): 36.3, 31.8	
	7.65 (m, 2H), 7.30-7.13 (m, 7H), 6.90 (m, 1H), 6.50 (m, 2H), 5.96 (m, 2H), 5.87 (m, 2H), 2.62-2.55 (m, 4H), 1.81 (m, 2H)	(C _q): 141.8, 135.2 (CH): 128.3, 126.1, 125.8, 125.4, 124.0, 117.3, 113.6, 102.7 (CH ₂): 35.4, 31.9, 29.5	
	7.67 (m, 2H), 7.29-7.13 (m, 7H), 6.91 (m, 1H), 6.50 (m, 2H), 5.95 (m, 2H), 5.85 (m, 2H), 2.62-2.53 (m, 4H), 1.67-1.43 (m, 4H)	(C _q): 142.3, 135.4 (CH): 128.3, 128.2, 126.0, 125.6, 125.4, 124.0, 117.3, 113.6, 102.7 (CH ₂): 35.5, 30.9, 29.9, 29.8	

(continued on next page)

Table 1 (continued)

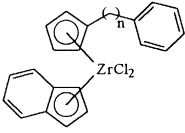
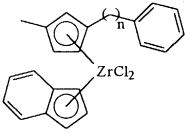
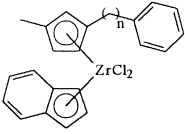
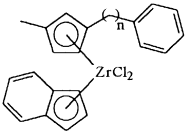
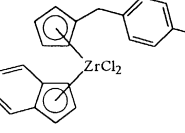
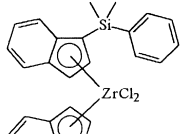
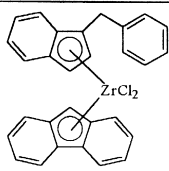
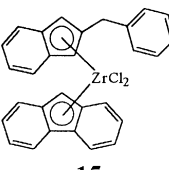
 <p>8 (n = 5)</p>	7.67 (m, 2H), 7.29-7.13 (m, 7H), 6.91 (m, 1H), 6.50 (m, 2H), 5.94 (m, 2H), 5.86 (m, 2H), 2.62-2.53 (m, 4H), 1.69-1.41 (m, 6H)	(C _q): 142.2, 135.5, (CH): 128.3, 128.1, 126.0, 125.6, 125.4, 124.0, 117.3, 113.6, 102.7 (CH ₂): 35.6, 30.4, 30.2, 29.7, 29.6	
 <p>9a, b (n = 1)</p>	7.65 (m, 2H), 7.32-7.24 (m, 5H), 7.11 (m, 2H), 6.91 (m, 1H), 6.47 (m, 1H), 6.39 (m, 1H), 5.89 (m, 1H), 5.67 (m, 1H), 5.45 (m, 1H), 5.07 (m, 1H)	(C _q): 139.6, 132.6 (CH): 128.7, 128.4, 126.3, 125.9, 125.2, 124.0, 119.0, 115.3, 112.3, 108.7, 102.9, 102.2 (CH ₂): 34.0 (CH ₃): 13.5	
 <p>10a,b (n = 2)</p>	7.65 (m, 4H), 7.33-7.20 (m, 14H), 6.92 (t, 1H) [3.4], 6.83 (t, 1H) [3.4], 6.50 (m, 4H), 5.94 (m, 1H), 5.82 (m, 1H), 5.70 (m, 1H), 5.59 (m, 1H), 5.53 (m, 2H), 2.76 (m, 8H), 2.13 (s, 3H), 1.92 (s, 3H)	(C _q): 141.0, 134.4, 133.4, 130.5 (CH): 128.7, 128.4, 125.9, 125.8, 125.4, 125.2, 124.0, 122.7, 119.4, 117.5, 115.1, 112.7, 111.8, 108.6, 102.7, 102.5, 102.0 (CH ₂): 36.6, 35.5, 32.3, 29.9 (CH ₃): 15.9, 13.1	
 <p>11a,b (n = 3)</p>	7.67 (m, 4H), 7.31-7.17 (m, 14H), 6.94 (m, 1H), 6.82 (m, 1H), 6.49 (m, 4H), 5.93 (m, 1H), 5.85 (m, 1H), 5.76 (m, 1H), 5.63 (m, 1H), 5.55 (m, 1H), 2.71-2.47 (m, 8H), 2.15 (s, 1H), 2.04 (s, 3H), 1.77 (m, 4H)	(C _q): 141.8, 134.8, 134.1, 130.4 (CH): 128.2, 125.9, 125.8, 125.7, 125.3, 125.2, 122.6, 119.4, 117.6, 115.0, 112.9, 112.0, 108.6, 102.6, 102.5, 102.3, 102.0 (CH ₂): 35.5, 35.3, 32.1, 30.9, 29.9, 27.6 (CH ₃): 15.9, 13.3	
 <p>12</p>	7.67 (m, 2H), 7.29 (m, 2H), 7.07 (m, 4H), 6.88 (t, 1H) [3.4], 6.44 (d, 2H) [3.4], 6.00 (m, 2H), 5.87 (m, 2H), 3.86 (s, 2H), 2.33 (s, 3H)	(C _q): 136.5, 135.9, 134.1 (CH): 129.1, 129.0, 128.7, 126.5, 125.4, 124.0, 117.3, 114.2, 102.8 (CH ₂): 35.6 (CH ₃): 21.0	
 <p>13a,b</p>	7.65-7.24 (m, 13H), 6.89 (d, 1H) [2.5], 6.47 (d, 1H) [2.5], 5.92 (d, 2H) [5], 5.69 (m, 1H), 0.82 (s, 3H), 0.76 (s, 3H)	(C _q): 137.8, 132.4, 128.3, 127.8, 127.5, 110.2 (CH): 134.0, 130.5, 129.4, 127.9, 127.7, 126.7, 126.6, 126.5, 126.4, 125.2, 126.9, 125.8, 125.3, 125.1, 124.9, 119.5, 110.3, 105.5, 104.1 (CH ₃): -1.2, -1.3	-10.5

Table 1 (continued)

 <p style="text-align: center;">14a, b</p>	8.02, (d, 2H) [8.4], 7.74 (m, 2H), 7.50–7.00 (m, 13H), 5.93 (d, 1H) [3.4], 5.81 (s, 1H), 5.68 (d, 1H) [3.4], 4.09 (d, 1H) [15.9], 3.91 (d, 1H) [15.9]	(C _q): 137.9, 132.2, 128.1, 127.7, 127.6 (CH): 128.7, 128.5, 128.3, 127.0, 126.6, 126.3, 125.8, 125.3, 125.2, 100.5, 87.6 (CH ₂): 34.1	
 <p style="text-align: center;">15</p>	8.02, (d, 2H) [8.4], 7.74 (m, 2H), 7.50 (t, 2H) [8.4], 7.39–7.30 (m, 10H), 7.07 (m, 1H), 6.16 (s, 2H), 5.38 (s, 1H), 3.75 (s, 2H)	(C _q): 140.1, 138.9, 126.4, 125.3 (CH): 128.6, 128.3, 126.2, 125.8, 125.7, 125.6, 124.5, 124.4, 124.2, 104.3, 87.7 (CH ₂): 37.4	

^a 25°C, in chloroform-*d*₁ δ [ppm] rel. chloroform (7.24).

^b 25°C, in chloroform-*d*₁ δ [ppm] rel. chloroform-*d*₁ (77.0).

^c 25°C, in chloroform-*d*₁ δ [ppm] rel. TMS_{ext.} (0.0).

Complexes with doubly substituted cyclopentadienyl ligands (**9–11**) or mono substituted indenyl ligands (substituted in position 1: **13, 14**) can appear as isomers (**a, b**) because of the prochirality of these ligands. In addition, the indenyl derivatives can form *rac* and *meso* isomers. As a consequence, the ¹H and ¹³C NMR spectra of these complexes can show more than the expected number of signals.

2.3. Polymerization of ethylene

The synthesized metallocene complexes, activated with MAO, were used for the homogeneous polymerization of ethylene. The complexes were activated by adding a 3000-fold molar excess of MAO to the toluene solution of the corresponding complex. The formation of an active catalyst system was indicated by a color change.

In the following paragraphs, the experimental polymerization results of one complex type or family are discussed. The polymerization activities of the activated metallocene complexes, the viscosity average molecular weights, \overline{M}_η , the

fusion enthalpies, ΔH_m , the melting temperatures, T_m and the degrees of crystallinity, α , of the resulting polymers are listed in Table 2.

2.4. Discussion of the polymerization results: effect of the catalyst structure on the catalyst properties

Principally, it is difficult to predict precise catalyst features for different metallocene catalysts. Too many parameters can determine the activity of the catalysts and the properties of the polymers, such as the nature of the organic ligands (cyclopentadienyl, indenyl, fluorenyl), the influence of ligand substituents (alkyl or aryl groups, with or without hetero atoms), the metal (Ti, Zr, Hf), the co-catalysts (MAO, PHT [31], boranes, borates, etc.), the solvent a.o. Some parameters can be contra-productive and a compromise has to be found for the best catalyst performance. In this investigation, we made an empiric approach and compared the activities of various unbridged metallocene catalysts for ethylene polymerization (Table 2). All

Table 2
Overview of the polymerization experiments^a and polymer analytic results

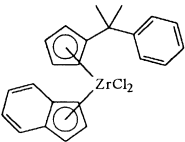
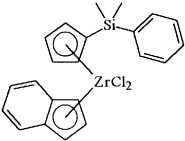
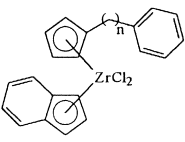
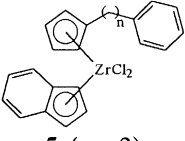
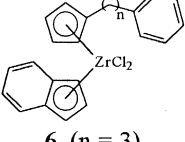
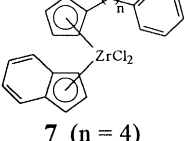
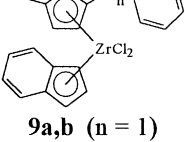
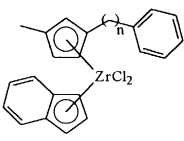
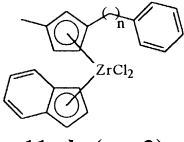
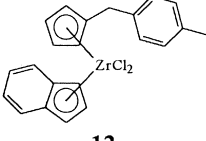
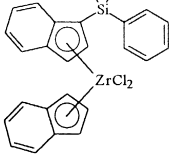
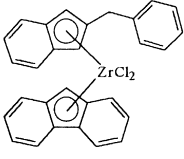
	Activity ^{b)} [$\frac{\text{kg PE}}{\text{g Zr}\cdot\text{h}}$]	\overline{M}_η ^{c)} [kg/mol]	DSC T _m [°C] ΔH _m [J/g] α[%] ^{d)}
 2	15.2	450	139.1 102.1 35.2
 3	289	450	130.5 167.3 57.7
 4 (n = 1)	2887.8	500	127.0 170.3 58.7
 5 (n = 2)	1899.2	640	139.7 152.6 52.6
 6 (n = 3)	3534.0	630	138.4 140.0 48.3
 7 (n = 4)	4508.7	610	132.5 148.1 51.1
 9a,b (n = 1)	2986.0	560	137.8 152.5 52.6

Table 2 (continued)

 <p>10a,b (n = 2)</p>	2676.0	600	136.5 138.5 47.8
 <p>11a,b (n = 3)</p>	3579.0	420	139.7 137.4 47.4
 <p>12</p>	979.0	620	137.0 141.6 48.9
 <p>13a,b</p>	300	390	134.9 185.0 63.8
 <p>15</p>	85.4	360	139.1 137.3 47.3
Cp₂ZrCl₂	1490	290	

^a $T_p = 60^\circ\text{C}$; solvent: 500-ml *n*-pentane; 10 bar ethylene pressure.

^b $[\text{M}]/[\text{Al}] = 1:3000$.

^cIntrinsic viscosity.

^dDegree of crystallinity relative to the fusion enthalpy of 100% crystalline polyethylene.

parameters were kept constant except the structure of the catalyst precursors **1–15**.

Catalyst precursors **4–7** possess an alkyl substituent of a variable chain length and a terminal phenyl group.

Fig. 3 shows the drastic increase of activity when the length of such an alkylidene spacer $(-\text{CH}_2-)_n$ increases from $n = 2$ to $n = 4$.

The activities of the corresponding catalysts **4–7**/MAO are, in all cases, higher than the activity of the parent catalyst Cp_2ZrCl_2 /MAO (1490 kg PE/g(Zr) h) under the same reaction conditions. An explanation for this behavior could be a better separation of the contact ion pair in the activated form of the catalyst (metallocene monomethyl cation/MAO anion [31,32])

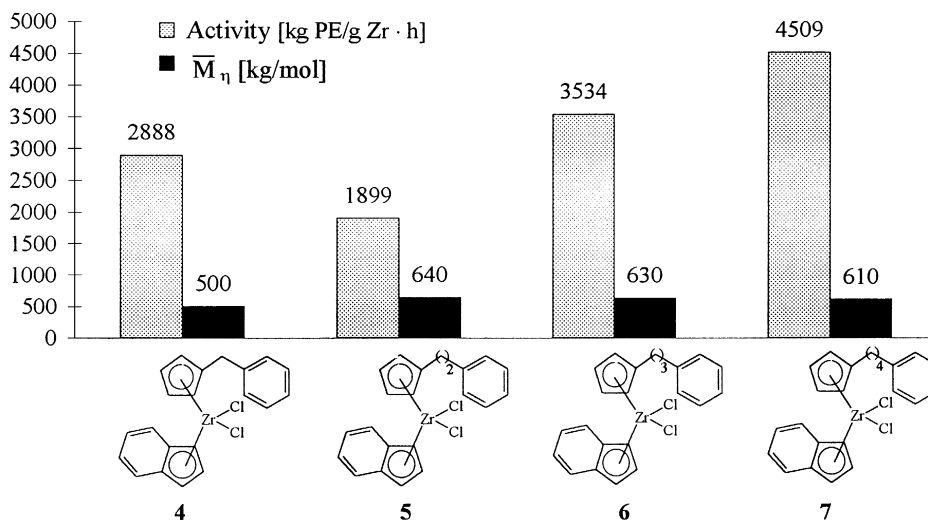


Fig. 3. Comparison of the polymerization activities for the metallocene complexes **4–7** and molecular weights of the produced polyethylenes.

induced by an increased spacer effect of the bulkier alkyl substituent. Zirconocene dichloride complexes with two ω -phenylalkylcyclopentadienyl ligands do not show such a strong trend with increasing spacer chain length [25]. This positive effect on the activity becomes negative as soon as methyl substituents are fixed on a C_1 -spacer (2887.8 kg PE/g(Zr) h in **4**/MAO vs. 15.2 kg PE/g(Zr) h in **2**/MAO). There is no obvious explanation for such a drastic drop in activity except when it is assumed that the terminal phenyl group can undergo a better interaction with the metal center and thus, compete with the coordination of the ethylene in the first polymerization step. A similar explanation can be given for the drop of activity of **12**/MAO due to the electron pushing effect of the methyl substituent in the para position of the phenyl ring that enhances the interaction of the aromatic ring system with the Lewis acidic center at the metal. Such an intramolecular interaction of a phenyl group with the metal center is known from similar complexes [33–35].

This interpretation would also explain the remarkable improvement of activity when the C_1 -spacer of **2** is substituted by a Si_1 -spacer to give **3** (15.2 kg PE/g(Zr) h in **2**/MAO vs. 289 kg PE/g(Zr) h in **3**/MAO).

The activity of catalysts **4–7**/MAO only slightly improves when an additional methyl substituent is fixed in position 3 of the cyclopentadienyl ligand to give the diastereomers **9a,b–11a,b**. This effect could be due to an even better separation of the corresponding catalyst cation and MAO anion compared with the parent complexes.

The substitution of the silyl substituted cyclopentadienyl ligand of **3** for an indenyl ligand to give the diastereomers **13a,b** has only a small positive influence on the catalyst activity (289 kg PE/g(Zr) h in **3**/MAO vs. 300 kg PE/g(Zr) h in **13a,b**/MAO) and is, by far, lower than the activity of the parent catalyst Ind_2ZrCl_2 /MAO (3200 kg PE/g(Zr) h) under identical reaction conditions.

The low activity of **15**/MAO (85.4 kg PE/g(Zr) h) clearly results from the thermal instability of the unbridged fluorenyl complex **15**. It is known that fluorenyl complexes readily undergo ring slippage reactions [36] from $\eta^5 \rightarrow \eta^3 \rightarrow \eta^1$ bonding modes and then lose the ligand in the final step. For this reason, unbridged fluorenyl ligands are not attractive for catalyst molecules.

The viscosity average molecular weights of the polyethylenes produced with the metal-

locene complexes **4–7** are in the range 500–640 kg/mol. For the metallocene complexes **5–7**, they are in a very narrow region (610–640). Obviously, the spacer chain length has only little influence on the chain termination rates, except in the case of the C₁-spacer.

3. Experimental part

3.1. NMR spectroscopy

The Bruker spectrometers ARX 250, AC 300, and DRX 500 were available for recording the NMR spectra. The organometallic samples were placed into the NMR tubes under argon and measured at 25°C. The ¹H NMR spectral chemical shifts are referred to the residual proton signal of the solvent ($\delta = 7.24$ ppm for chloroform) and in ¹³C NMR spectra to the solvent signal ($\delta = 77.0$ ppm for chloroform-*d*₁).

3.2. Mass spectroscopy

Routine measurements were performed using a VARIAN MAT CH7 instrument (direct inlet, electron impact ionization 70 eV). GC/MS spectra were recorded using a VARIAN 3700 gas chromatograph in combination with a VARIAN MAT 312 mass spectrometer.

3.3. Gas chromatography

Organic compounds were analyzed with a Carlo-Erba HRGC gas chromatograph equipped with a flame ionization detector. The J&W fused silica column was 30 m long, had a diameter of 0.32 mm, and a film thickness of 0.25 μm . Helium served as carrier gas. The following temperature program was used:

starting phase: 3 min at 50°C;
heating phase: 5°C/min (15 min); and
plateau phase: 310°C (15 min).

3.4. General synthesis procedure for the metallocene dichloride complexes **1** and **2**

6,6-Dimethylfulvene, 1.2 ml (10.0 mmol), was dissolved in 150 ml diethylether at -78°C and mixed with 5.0 ml (10.0 mmol) phenyllithium (2 M solution in cyclohexane/diethylether 70%/30%). The white suspension was stirred for 4 h at room temperature. Then, the reaction mixture was mixed with 10.0 mmol of the corresponding half-sandwich complex at -78°C and stirred overnight at room temperature. The solvent was evaporated in vacuo, and the residue washed twice with 50-ml *n*-pentane. The residue was extracted with dichloromethane, the solution filtered over sodium sulfate and the solvent evaporated. The yields were 80–90%. **1**: MS: $m/e = 410$ (M^+); **2**: MS: $m/e = 461$ (M^+).

3.5. General synthesis procedure for the metallocene dichloride complexes **3–15**

The selected ligand precursor, 10.0 mmol, was dissolved in 150 ml diethylether at -78°C and mixed with 6.3 ml (10.0 mmol) *n*-butyllithium (1.6 M solution in *n*-hexane). The reaction mixture was then stirred for 6 h at room temperature. Then, 10.0 mmol of the corresponding half-sandwich complex were added at -78°C , and the reaction mixture was stirred overnight at room temperature. The solvent was evaporated in vacuo, and the residue washed twice with 50-ml *n*-pentane. The residue was extracted with dichloromethane, the solution filtered over sodium sulfate and the solvent evaporated in vacuo. The yields were 80–90% (Table 3).

3.6. Activation of the metallocene complexes with MAO

The selected metallocene complex, 10–15 mg, was activated with MAO (10% in toluene) (Zr:Al = 1:3000). A volume of the catalyst solution, containing 0.5–1.5 mg metallocene com-

Table 3
MS data of the compounds 3–15

Compound	M ⁺ [m/e]
3	526
4	270
5	284
6	298
7	312
8	326
9a,b	284
10a,b	498
11a,b	312
12	284
13a,b	393
14	533
15	533

plex, was used within 1 h for homopolymerization.

3.7. Homopolymerization of ethylene

n-Pentane, 500 ml, was placed in a 1 l Büchi laboratory autoclave, mixed with the catalyst solution and the autoclave thermostated at 60°C. An ethylene pressure (99.98% ethylene) of 10 bars was applied after an inside temperature of 50°C was reached. The mixture was stirred for 1 h at 60(±2)°C, and subsequently, the reaction was terminated by releasing the pressure in the reactor. The obtained polymer was dried in vacuo.

3.8. Characterization of the polyethylene samples

3.8.1. Differential scanning calorimetry (DSC)

The polymer samples were investigated for phase transitions with DSC using a Pyris DSC 7 instrument. For the measurements, 5–12 mg dried polymer were fused into standard aluminum pans (0.7 mm) and measured under nitrogen using the following temperature program: first heating phase: from 25°C to 200°C (heating rate 40 K/min), isothermal phase (3 min), cooling phase from 200°C to –40°C (cooling rate 20°C/min), second heating phase

from –40°C to 200°C (heating rate 20°C/min). Melting points and fusion enthalpies were taken from the second heating phase. The temperature was linearly corrected relative to indium (Mp. 429.79 K). The fusion enthalpy of indium ($H_m = 28.45$ J/g) was used for calibration.

3.8.2. Viscosimetry

The viscosity average molecular weight determination of the polyethylene samples was performed using an Ubbelohde precision capillary viscometer in *cis/trans* decalin at 135 ± 0.1°C. For the measurements, 50 mg polymer were completely dissolved in 45.0 ml decalin at 130°C within 3–4 h and insoluble ingredients were filtered over glass wool. \bar{M}_η was determined using a calibration curve that was available for the selected concentration.

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