

ω -Phenylalkyl-substituted zirconocene dichloride complexes as catalyst precursors for homogeneous ethylene polymerization

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Abstract

The reaction of ω -phenyl-1-bromoalkanes with cyclopentadienyl sodium, indenyl lithium or fluorenyl lithium forms ω -phenylalkyl-substituted ligand precursors in high yields. The corresponding anions react with zirconium tetrachloride to give ω -phenylalkyl-substituted zirconocene dichloride complexes. After activation with methylaluminoxane, these complexes are highly active catalysts for homogeneous ethylene polymerization. The nature of the ω -phenyl substituents determines the polymerization activities of the catalysts to a large extent. The polymerization results of 28 new complexes are compared. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Zirconium; Catalysis; Ethylene polymerization; Metallocene complexes

1. Introduction

Metallocene dichloride complexes with Group IV metals have received much attention in the past few years because they are excellent catalysts for the polymerization of α -olefins [1–24]. The number of ways in which the aromatic ligands and the bridging groups (for *ansa*-complexes) can be modified is virtually unlimited. This ability to vary the composition of the metallocene complexes allows ‘tailoring’ of the catalyst precursors. The activation of these complexes with methylaluminoxane (MAO) as a cocatalyst produces homogeneous catalysts that are well suited for the investigation of the structure–property relationships of catalysts and polymers. In this paper, we describe 28 unbridged zirconocene dichloride complexes (**27–54**) that contain one alkyl or silyl substituent with a terminal phenyl or naphthyl group on the π -ligand.

We studied to what extent type and length of these substituents determine the catalytic properties of the corresponding complexes during ethylene polymerization.

2. Results and discussion

2.1. Synthesis and characterization of substituted cyclopentadiene, indene and fluorene derivatives

2.1.1. Synthesis of the substituted cyclopentadiene derivatives **1a,b–15a,b**

Liquid ammonia is an excellent solvent for the reaction of cyclopentadienyl sodium [25] with ω -phenyl-1-bromo alkanes. Due to the low reaction temperature of -40°C , the monosubstituted product is obtained exclusively. The dimerization of the cyclopentadiene derivative is avoided. Compared with other synthesis methods [26], the yields are almost quantitative [27] because subsequent distillation steps can be avoided. The products consist of two isomers differing in the position of the double bonds in the cyclopentadienyl rings (Fig. 1).

Using this procedure, the following cyclopentadiene derivatives were synthesized (Fig. 2):

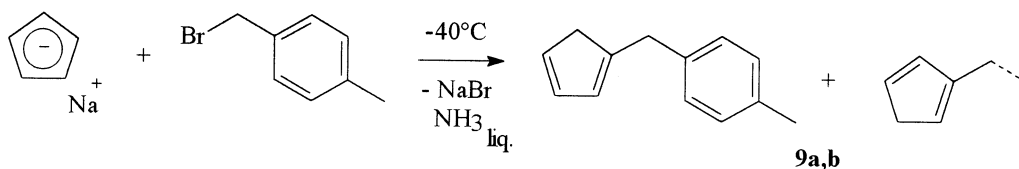
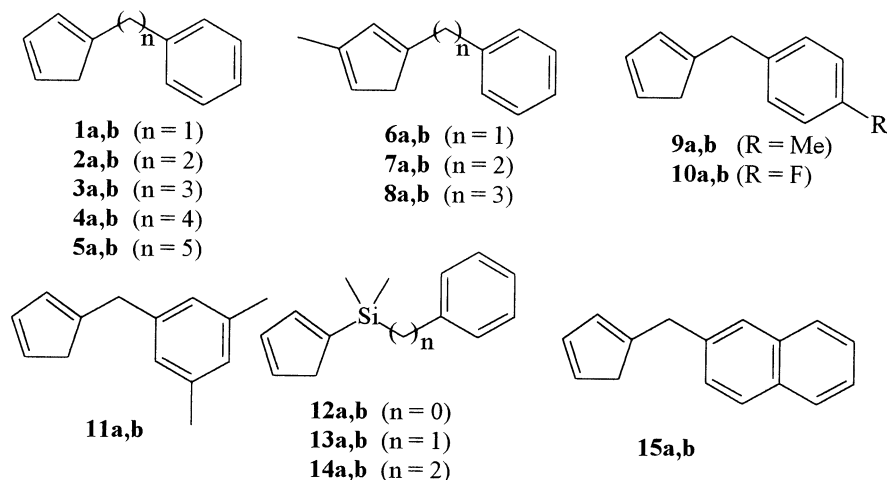
2.1.2. Synthesis of the substituted indene derivatives **16–21**

Indene derivatives substituted in position 1 are synthesized by the reaction of indenyllithium [28] with 1-haloalkanes or trialkyl chloro silanes in diethyl ether. The double bond of the resulting indene derivative is

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Fig. 1. Synthesis of 4-methylbenzyl-1,2-cyclopentadiene and isomer (**9a,b**).Fig. 2. Overview of the synthesized cyclopentadiene derivatives **1a,b–15a,b** (only one isomer is illustrated).

always in position 2. The indene derivatives shown in Fig. 3 were synthesized using this method.

Indene can also be substituted in position 2 using a multi-step synthesis [29]. The starting compound 2-indanone [30] is reacted with ω -phenylalkyl magnesium bromide in diethyl ether. The product is hydrolyzed and subsequently water is removed by addition of *p*-toluenesulfonic acid to produce the 2-(ω -phenylalkyl) indenenes **22** and **23** (Fig. 4).

2.1.3. Synthesis of the fluorene derivatives **24–26** (substituted in position 9)

The fluorene derivatives **24–26**, substituted in position 9, were synthesized analogously to the synthesis method mentioned in Section 2.1.2. Fluorenyl lithium was reacted with 1-bromoalkane in diethyl ether (Fig. 5).

2.1.4. Spectroscopic characterization of compounds **1a,b–26**

Compounds **1a,b–26** were characterized by ^1H -, ^{13}C - and ^{29}Si -NMR spectroscopy. The spectroscopic data are listed in the Section 3.

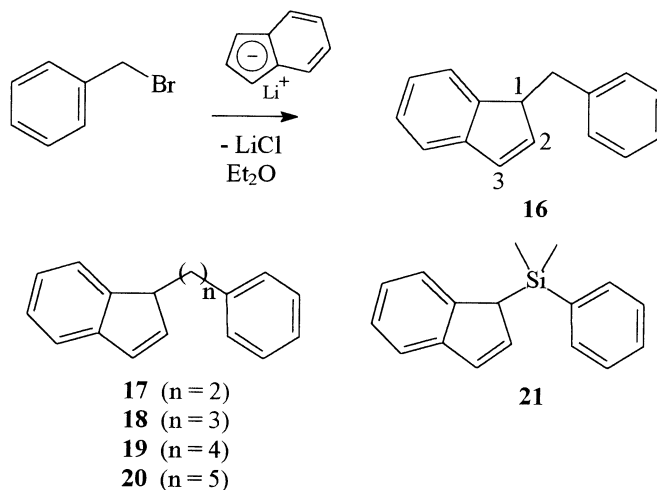
2.2. Synthesis of metallocene dichloride complexes

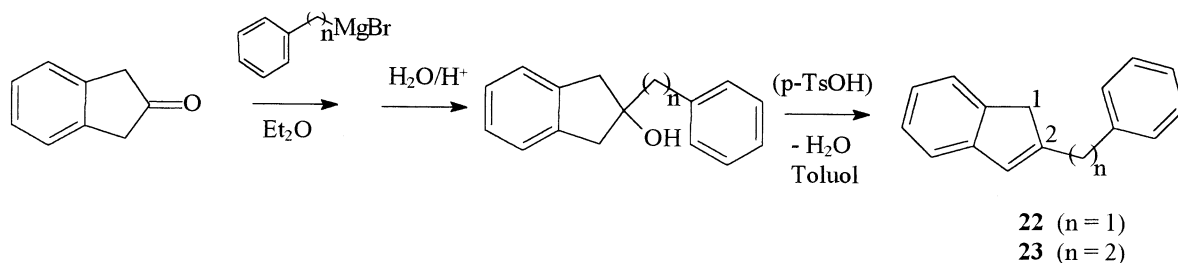
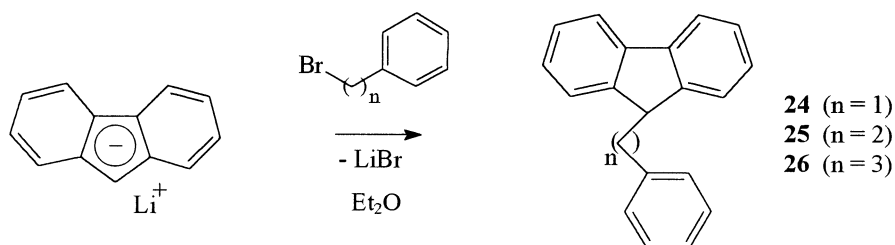
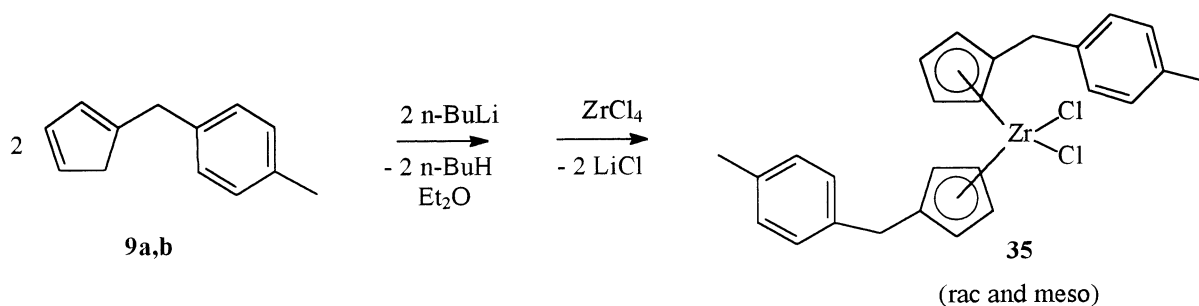
Unbridged, symmetrically substituted metallocene dichloride complexes with cyclopentadienyl, indenyl and fluorenyl ligands have been synthesized in large

numbers in recent years [31–36]. They are accessible by the reaction of cyclopentadienyl, indenyl or fluorenyl alkali metal salts with the metal tetrachlorides of titanium, zirconium or hafnium in diethyl ether (Fig. 6).

The unbridged metallocene dichloride complexes shown in Fig. 7 were synthesized using this method.

As long as there is only one substituent on the cyclopentadienyl ligand, only *rac* and *meso* isomers must be considered due to the hindered rotation of the

Fig. 3. Overview of the synthesized indene derivatives **16–21**.

Fig. 4. Synthesis of 2-(ω -phenylalkyl)indene compounds **22** and **23**.Fig. 5. Synthesis of the substituted fluorene derivatives **24–26**.Fig. 6. Synthesis of the unbridged, symmetrically substituted bis[4-methylbenzyl-(η^5 -cyclopentadienyl)] zirconium dichloride complex **35**.

π -ligands around their metal bond axis. An additional substituent in position 3 of the cyclopentadienyl ligand induces chirality upon complexation because the two prochiral ligands can coordinate in three different ways (a,a/b,b/a,b) (Fig. 8). An analogous situation can be expected for indenyl derivatives with a substituent in position 1 (**46**).

The 1-phenyl-1-methylethyl-substituted metallocene dichloride complexes **52–54** were synthesized using a ‘one-pot’ reaction. Phenyl lithium was reacted with 6,6-dimethylfulvene in diethyl ether and the resulting salt was reacted with half an equivalent of metal tetrachloride (Fig. 9).

2.3. Spectroscopic characterization of metallocene dichloride complexes

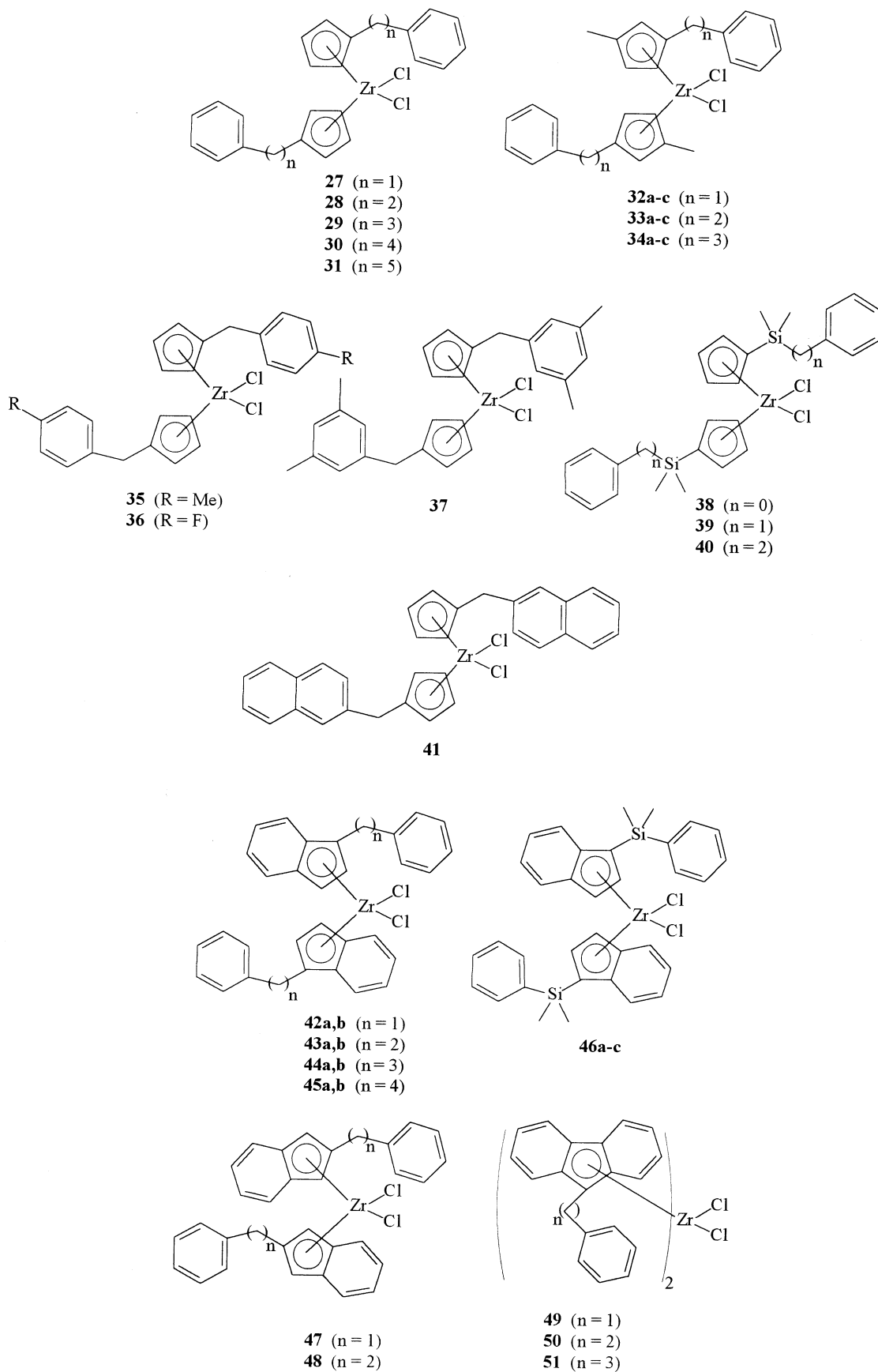
The metallocene complexes **27–54** were characterized by ^1H -, ^{13}C - and ^{29}Si -NMR spectroscopy. Complexes **32–34** with two different substituents on the cyclopentadienyl ligand or one substituent in position 1 of an

indenyl ligand (**46**) can exist as various isomers (see Fig. 8). In these cases a differentiation of the signals is not always possible. The data are listed in Section 3.

2.4. Polymerization of ethylene

The synthesized metallocene complexes are suitable precursors for catalytic olefin polymerization and were used for the homogeneous polymerization of ethylene. The complexes were activated by adding a 3000-fold molar excess of MAO. In this way, an active catalyst system was formed as indicated by a color change.

In the following discussion, the polymerization results of only some complex types are discussed in order to capture the large volume of data and to interpret clearly the important information. The polymerization activities of the activated metallocene complexes, the viscosity average molecular weights $\bar{M}_\eta$, the fusion enthalpies ΔH_m , the melting temperatures T_m and the degrees of crystallinity α of the resulting polymers are listed in Table 1.

Fig. 7. Overview of the synthesized metallocene dichloride complexes **27**–**51**.

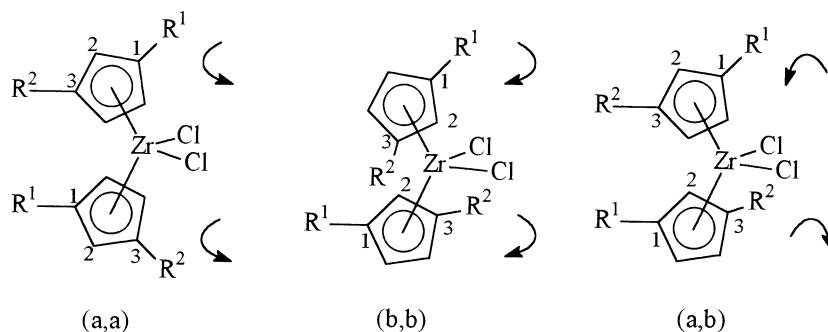


Fig. 8. Possible isomers of disubstituted bis(cyclopentadienyl) complexes (only the *rac* forms are illustrated).

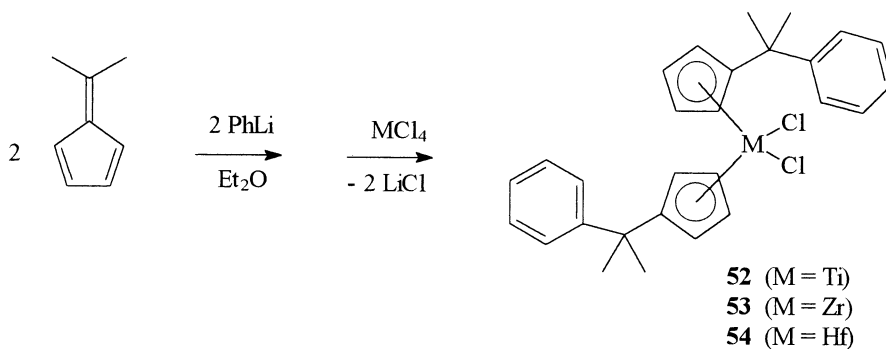


Fig. 9. Synthesis of the bis[(1-phenyl)1-methylethyl(η⁵-cyclopentadienyl)] metal dichloride complexes **52–54**.

Table 1
Overview of the ethylene polymerization experiments ^a and polymer analytic results

Catalyst precursor	Activity (kg PE g ⁻¹ Zr h ⁻¹)	$\bar{M}_n$ (kg mol ⁻¹)	DSC		
			T_m (°C)	ΔH_m (J g ⁻¹)	α (%) ^b
27	140.2	340	126.7	180.4	62.2
28	336.7	350	129.8	161.9	55.8
30	1506.0	390	136.8	155.1	53.5
31	4970.0	270	140.0	152.0	52.4
32a–c	881.0	320	125.6	177.8	61.3
33a–c	359.3	620	139.9	143.1	49.4
34a–c	582.3	570	136.0	149.0	51.4
35	1880.9	310	133.1	150.6	52.0
36	1784.0	340	134.1	152.3	52.5
37	1120.4	590	130.0	168.8	58.2
38	129.0	420	140.7	144.6	49.9
39	529.0	260	139.0	154.8	53.4
40	23.3	1050	135.1	120.2	41.5
41	1020.1	490	130.4	133.0	45.9
43a–c	868.0	370	124.8	203.7	70.3
44a–c	780.0	370	133.9	153.5	52.8
45a–c	987.1	380	136.7	152.4	52.6
46a–c	183.0	480	128.3	157.8	54.4
49	56.3	360	133.2	132.1	45.6
50	17.0	90	144.6	125.9	43.4
51	24.0	75	137.6	159.5	55.0
52 (M = Ti)	7.6	130			Not determined
53 (M = Zr)	5.8	300			Not determined

^a Homogeneous polymerization; MAO as cocatalyst (Zr:Al = 1: 3000); in *n*-pentane at 60°C.

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

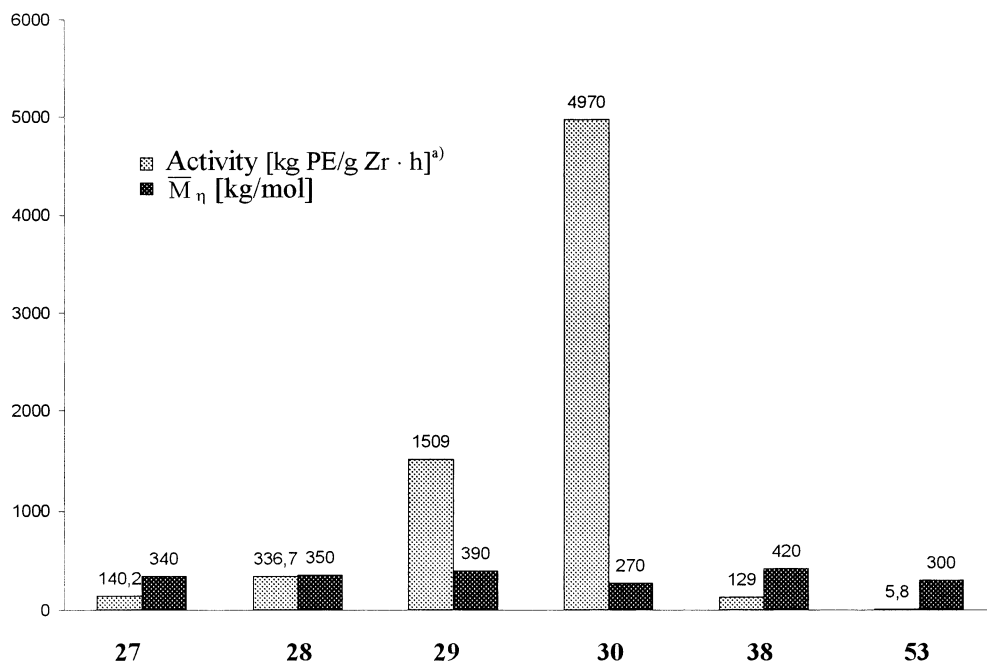


Fig. 10. Comparison of the polymerization activities of the metallocene dichloride complexes **27–30**, **38**, **53**/MAO and the molecular weights of the obtained polyethylenes. Homogeneous polymerization of ethylene after the activation with MAO (Zr:Al = 1:3000), in *n*-pentane, at 60°C.

2.4.1. Influence of the spacer chain length on the polymerization behavior of the symmetrically substituted metallocene dichloride complexes **27–30**

The chain length of the alkyl or silyl substituent has a strong impact on the polymerization behavior of the metallocene complexes synthesized. Fig. 10 shows a comparison of the polymerization activities for homogeneous polymerizations of the ω -phenylalkyl substituted bis(cyclopentadienyl) zirconium dichloride complexes **27–30**.

The polymerization activity of the metallocene dichloride complexes increases with increasing chain length of the alkylidene spacer located between the cyclopentadienyl ligand and the bulky phenyl group. The decreasing steric shielding of the catalytic center by the phenyl group and the improved separation of the MAO counterion from the active, cationic catalyst center may both be reasons for the observed improvement in activities due to increasing spacer chain length [37].

2.4.2. Influence of the spacer type on the polymerization behavior

The type and the substitution of the spacer atom in the α -position to the π -ligand have the most influence on the polymerization activities of the metallocene catalysts studied. The reason for this behavior could be steric hindrance of the active center (Fig. 11). The metallocene complexes with isopropylidene spacer groups **53** exhibit the lowest polymerization activity. Both methyl groups and the phenyl group are rigidly linked to the carbon in the α -position. This structural element seems to partially block the free coordination site (Fig. 11).

Substitution of the carbon spacer atom **53** with a silicon atom significantly increases the polymerization activity of the corresponding metallocene complex **38**. The reason for this might be the increased bond length of C–Si compared to C–C [38], but it could also be caused by the Lewis-acidic character of the heteroatom (Fig. 10).

A significant increase in polymerization activity can also be observed if both methyl groups of the isopropylidene spacer are substituted with hydrogen atoms (e.g. metallocene complex **27**). The polymerization activities of the metallocene complexes **27** and **38** indicate that the methylene spacer **27** has a similar steric effect on the active cationic catalyst center to the dimethylsilylene spacer. In contrast, the molecular weights of the synthesized polymers do not exhibit any general trends for these three metallocene complexes.

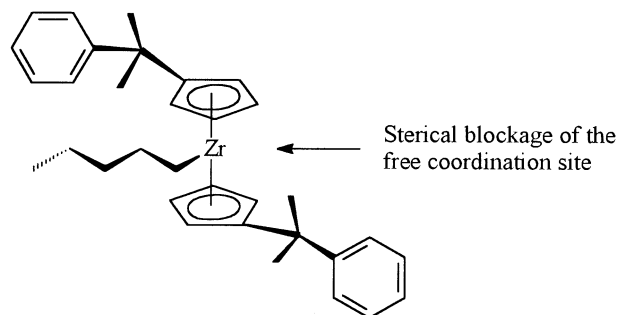


Fig. 11. Steric influence of the bulky phenyl isopropylidene group on the active catalyst center (MAO counterion not illustrated).

The unsubstituted parent compounds Cp_2ZrCl_2 and $\text{Ind}_2\text{ZrCl}_2$, when activated with MAO under the same reaction conditions, show activities of 1490 and 3200 kg PE g^{-1} Zr h^{-1} . This is considerably lower than the activity of **30**/MAO (4970 kg PE g^{-1} Zr h^{-1}).

3. Experimental

3.1. NMR spectroscopy

Bruker ARX 250, AC 300 and DRX 500 spectrometers were available for recording NMR spectra. The organometallic samples were transferred into the NMR tubes under argon and measured at 25°C. The chemical shifts in the ^1H -NMR spectra are referenced to the residual proton signal of the solvent ($\delta = 7.24$ ppm for chloroform, $\delta = 7.15$ ppm for benzene) and in ^{13}C -NMR spectra to the solvent signal ($\delta = 77.0$ ppm for chloroform- d_1 , $\delta = 128.0$ ppm for benzene- d_6).

3.2. Mass spectroscopy

Routine measurements were performed on a Varian MAT CH7 instrument (direct inlet, electron impact ionization 70 eV) in the Central Analytical Department at the University of Bayreuth. 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 using a Carlo–Erba HRGC gas chromatograph with flame ionization detector. The J&W fused silica column was 30 m long and 0.32 mm in diameter with a film thickness of 0.25 μm . Helium served as a carrier gas. The following temperature program was used:

- starting phase: 3 min at 50°C;
- heating phase: 5°C min^{-1} (15 min);
- plateau phase: 310°C (15 min).

3.4. General synthesis procedure for the cyclopentadiene derivatives **1a,b–15**

Cyclopentadiene or methylcyclopentadiene, 160.0 mmol, was placed in a reaction flask, and 100 ml ammonia were condensed into it at -78°C . Within 1 h, 100.0 mmol of the corresponding α -phenylethylbromide or chlorosilane dissolved in 100 ml *n*-pentane were added dropwise to the dark brown solution at -78°C . The reaction mixture was stirred for 2 h at -78°C and then slowly warmed up to room temperature (r.t.) where the ammonia evaporated. The residue was mixed with 200 ml *n*-pentane, the solution filtered

over sodium sulfate–silica gel and the solvent evaporated in vacuo. The products were obtained as colorless to light yellow oils in 80–90% yields and were characterized in Table 2.

3.5. General synthesis procedure for the indene derivatives **16–21**

Indene, 4.5 ml (33.0 mmol), was dissolved in 100 ml diethyl ether and mixed with 20.6 ml (33.0 mmol) *n*-butyllithium (1.6 M in *n*-hexane) at -78°C . The reaction mixture was stirred for 4 h at r.t. At -78°C , 33.0 mmol of the corresponding α -phenylalkyl bromide or dimethylphenylchloro silane were added and the reaction mixture was stirred for 3 h at r.t. Subsequently, the mixture was hydrolyzed with 50 ml of water and the organic phase dried over sodium sulfate. The solvent was evaporated in vacuo, the residue dissolved in *n*-pentane and the solution filtered over silica gel. After the solvent was evaporated, the products were obtained as colorless oils in 80–90% yields.

3.6. General synthesis procedure for the indene derivatives **22 and 23**

Over 2 h, a solution of 20.0 g (157.6 mmol) 2-indanone in 200 ml diethyl ether was added dropwise to a solution of 3.83 g (157.6 mmol) magnesium and 157.6 mmol of the corresponding α -phenylalkyl bromide in 200 ml diethyl ether. The reaction mixture was stirred overnight at r.t. and subsequently hydrolyzed with diluted hydrochloric acid at 0°C . The organic phase was then washed with 100 ml saturated sodium bicarbonate solution and dried over sodium sulfate. Next the solvent was evaporated in vacuo, and the corresponding 2-indanol derivative was obtained in 85–90% yield. This product was dissolved in 150 ml toluene, mixed with 3.0 g (16.1 mmol) *p*-toluenesulfonic acid and heated under reflux with a water separator until no further water was separated. The dark-brown suspension was successively washed with 100 ml of saturated sodium bisulfate solution and 100 ml of water. The organic phase was dried over sodium sulfate. The colorless solution was evaporated in vacuo, the residue dissolved in *n*-pentane and the products crystallized at -20°C . The indene derivatives precipitated as colorless, crystalline solids in 60–70% yields and are characterized in Table 2.

3.7. General synthesis procedure for the phenylalkylidene fluorene derivatives **24–26**

Fluorene, 6.0 g (36.1 mmol), was dissolved in 150 ml diethyl ether and slowly mixed with 22.6 ml (36.1 mmol) *n*-butyllithium (1.6 M in *n*-hexane) at r.t. The reaction mixture was stirred for 4 h at r.t. An equiva-

Table 2

Characterization of compounds **1a,b–26**

Compound	¹ H-NMR ^a (<i>J</i> _(H,H) in Hz)	¹³ C-NMR ^b	GC (s)	M ⁺ [<i>m/e</i>]
1a,b	7.50–7.15 (m, 10H), 6.60–6.72, 6.42–6.35, 6.29–6.24, 6.21–6.03 (4m, 6H), 3.83, 3.81 (2s, 4H), 3.07, 2.95 (2m, 4H)	(C _q): 148.1, 144.8, 139.8 (CH): 134.5, 133.9, 132.3, 131.3, 129.0, 128.4, 128.3, 126.9, 125.8 (CH ₂): 43.0, 41.5, 37.7, 36.3	942	156
2a,b	7.52–7.23 (m 10H), 6.66–6.54, 6.47–6.39, 6.39–6.32, 6.25–6.17 (4m, 6H), 3.44–2.94 (m, 8H), 2.94–2.75 (m, 4H)	(C _q): 148.9, 146.4, 142.1 (CH): 134.5, 133.6, 132.3, 130.5, 128.3, 128.2, 126.7, 126.1, 125.7, 125.6 (CH ₂): 43.3, 41.2, 36.0 35.2, 32.5, 32.0	1254	170
3a,b	7.42–7.18 (m, 10H), 6.58–6.48, 6.47–6.24, 6.17–6.10 (4m, 6H), 3.05–3.00 (m, 2H), 3.00–2.95 (m, 2H), 2.81–2.63 (m, 4H), 2.60–2.43 (m, 4H), 2.08–1.89 (m, 4H)	(C _q): 148.6, 146.2, 142.4 (CH): 134.6, 133.7, 132.4, 130.4, 128.4, 128.2, 126.5, 126.0, 125.6, 125.2 (CH ₂): 43.2, 41.2, 35.6, 35.5, 31.4, 30.4, 30.2, 29.3	1324	184
4a,b	7.41–7.16 (m, 10H), 6.57–6.48, 6.43–6.22, 6.15–6.09 (4m, 6H), 3.07–3.02 (m, 2H), 3.00–2.93 (m, 2H), 2.80–2.65 (m, 4H), 2.58–2.41 (m, 6H), 2.00–1.83 (m, 6H)	(C _q): 148.5, 146.2, 142.2 (CH): 134.4, 133.5, 132.6, 130.2, 128.5, 128.2, 126.3, 125.8, 125.4, 125.0 (CH ₂): 43.0, 41.1, 35.2, 35.3, 31.3, 30.2, 30.1, 29.0, 28.8, 28.5	1439	198
5a,b	7.45–7.19 (m, 10H), 6.56–6.49, 6.46–6.24, 6.17–6.10 (4m, 6H), 3.04–3.01 (m, 2H), 3.00–2.94 (m, 2H), 2.80–2.61 (m, 4H), 2.57–2.35 (m, 8H), 2.07–1.80 (m, 8H)	(C _q): 148.5, 146.3, 142.1 (CH): 134.5, 133.7, 132.5, 130.3, 128.4–128.3, 126.4, 126.2, 125.4, 125.2 (CH ₂): 43.2, 41.0, 35.0, 35.4, 31.3, 30.2, 30.0, 29.1, 28.9, 28.8, 28.3, 28.1	1513	212
6a,b	7.73–7.42 (m, 10H), 6.67 (m, 1H), 6.57 (m, 1H), 6.42 (m, 1H), 6.21 (m, 1H), 4.01 (m, 4H), 3.21 (m, 2H), 2.23 (m, 2H), 1.50 (m, 6H)	(C _q): 139.9, 139.0, 137.9 (CH): 128.6, 128.3, 128.0, 126.9, 126.2 (CH ₂): 41.7, 37.4, 34.8 (CH ₃): 13.8, 13.7	1004	170
7a,b	7.50–7.37 (m, 10H), 6.28 (m, 3H), 6.03 (m, 1H), 3.07–2.97 (m, 8H), 2.18 (m, 4H), 1.43 (s, 6H)	(C _q): 142.9, 142.3, 138.9 (CH): 128.5, 128.4, 128.0, 126.2 (CH ₂): 38.2, 33.8, 33.3, 31.1, 29.3 (CH ₃): 13.8, 13.5	1147	184
8a,b	7.51–7.37 (m, 10H), 6.27 (m, 3H), 6.02 (m, 1H), 3.07–2.78 (m, 10H), 2.18 (m, 6H), 1.42 (s, 6H)	(C _q): 142.8, 142.1, 138.6 (CH): 128.6, 128.4, 128.1, 126.3 (CH ₂): 38.2, 37.2, 35.6, 35.5, 31.4, 30.4, 30.2, 29.3 (CH ₃): 13.8, 13.6	1278	198
12a,b ^c	7.82–7.58 (m, 10H), 6.92–6.64 (m, 6H), 1.63–1.57 (m, 4H), 0.62–0.41 (m, 12H)	(C _q): 147.0, 138.7 (CH): 133.7, 133.4, 132.9, 130.8, 130.5, 128.8, 127.7, 126.7, 124.7, 123.0, 121.1, 51.4 (CH ₂): 34.7, 29.7 (CH ₃): 0.8, –2.1, –4.5	1139	200
13a,b ^d	7.42–7.19 (m, 10H), 6.84–6.66 (m, 6), 2.42–2.25 (m, 4H), 0.42–0.05 (m, 12)	(C _q): 147.0, 139.6 (CH): 142.7, 138.2, 132.9, 130.6, 128.4, 128.3, 128.2, 124.4, 124.2, 124.1 (CH ₂): 26.8, 25.9 (CH ₃): –2.7, –4.3	1814	214
14a,b ^e	7.40–7.20 (m, 16H), 2.81–2.78 (m, 2H), 1.10–1.03 (m, 2H) 0.27–0.17 (m, 12H)	(C _q): 147.0, 145.0 (CH): 128.3, 128.2, 127.91, 127.7, 127.3, 127.1, 125.5, 125.4, 124.5, 124.3, 31.23, 30.9 (CH ₂): 29.4, 29.2, 20.3, 19.6 (CH ₃): 14.4, 14.1, 0.1, –0.3, –2.4	2110	228
16	7.54–7.36 (m, 9H), 6.96 (m, 1H), 6.62 (m, 1H), 3.85 (m, 1H), 3.23 (m, 1H), 2.87 (m, 1H)	(C _q): 147.2, 144.8, 141.0 (CH): 139.1, 131.2, 129.2, 128.5, 126.9, 126.5, 124.9, 123.4, 121.4, 52.0 (CH ₂): 38.2	1723	206
17	8.01–7.48 (m, 9H), 7.16–7.14 (m, 1H), 6.82–6.78 (m, 1H), 3.51–3.28 (m, 1H), 2.84–2.79 (m, 2H), 2.53–2.42 (m, 2H)	(C _q): 147.2, 144.8, 141.0 (CH): 139.6, 132.2, 129.31, 127.5, 126.8, 125.8, 123.8, 122.1, 121.3, 50.9 (CH ₂): 34.6, 34.1	1807	220
18	7.55–7.49 (m, 9H), 7.17–7.15 (m, 1H), 6.84–6.78 (m, 1H), 3.53–3.28 (m, 1H), 2.84–2.75 (m, 2H), 2.53 (m, 2H)	(C _q): 147.2, 144.8, 141.0 (CH): 139.8, 132.2, 129.3, 128.5, 126.5, 124.9, 125.8, 123.8, 122.0, 121.3, 51.9 (CH ₂): 36.2, 34.5, 34.1	2050	234

Compound	$^1\text{H-NMR}^a$ ($J_{\text{(H,H)}}$ in Hz)	$^{13}\text{C-NMR}^b$	GC (s)	$\text{M}^+ [m/e]$
19	7.90–7.66 (m, 9H), 7.66–7.33 (m, 1H), 7.03–7.00 (m, 1H), 3.94–3.92 (m, 1H), 3.13–3.05 (t, 2H) [7.5], 2.41–1.96 (m, 6H).	(C_q): 147.6, 144.1, 142.2 (CH): 138.9, 130.7, 128.1, 128.0, 125.7, 124.5, 2091 122.6, 120.8, 118.8, 50.1 (CH_2): 35.6, 31.9, 31.2, 27.2		248
20	7.55–7.29 (m, 9H), 6.93–6.92 (m, 2H), 6.68–6.66 (m, 2H), 3.63–3.56 (m, 1H), 2.76–2.70 (m, 2H), 2.04–1.49 (m, 8H).	(C_q): 147.8, 144.2, 142.6 (CH): 139.3, 130.7, 128.3, 128.2, 126.1, 125.5, 2193 124.6, 122.7, 120.9, 50.4.5 (CH_2): 35.9, 31.3, 31.2, 29.5, 27		262
21^f	7.41–7.01 (m, 9H), 6.82 (d, 1H) [5.0], 6.51–6.48 (m, 1H), 3.63–3.61 (m, 1H), 0.82 (s, 3H), 0.03 (s, 3H).	(C_q): 144.6, 144.1, 137.3 (CH): 135.2, 133.6, 129.2, 129.2, 127.6, 124.9, 1814 123.6, 122.8, 120.9, 45.5 (CH_3): –0.5, –0.6		250
22	7.39 (m, 9H), 6.54 (s, 1H), 3.84 (s, 2H), 3.30 (s, 2H)	(C_q): 149.2, 141.6, 139.9 (CH): 128.8, 128.4, 128.3, 128.1, 127.7, 126.5, 1765 126.2, 123.8, 123.4, 120.0 (CH_2): 40.8, 37.9		206
23	7.36–7.10 (m, 9H), 6.54 (s, 1H), 3.32 (s, 2H), 2.85 (m, 4H)	(C_q): 147.1, 142.5, 140.3 (CH): 128.9, 128.5, 128.3, 128.0, 127.8, 126.8, 1875 126.4, 126.2, 124.0, 123.6, 121.3, 121.0, 120.2 (CH_2): 47.3, 46.5, 39.1		220
24	7.80 (d, 2H), 7.45–7.20 (m, 11H), 4.29 (t, 1H) [7.6], 3.17 (d, 2H) [7.6]	(C_q): 146.8, 140.8, 139.8 (CH): 129.5, 128.2, 127.1, 126.6, 124.8, 48.6 (CH_2): 40.0	1647	206
25	7.92 (d, 2H), [7.5], 7.69 (d, 2H) [7.5], 7.54–7.27 (m, 9H), 4.19 (t, 1H), [5.0], 2.64–2.48 (m, 4H)	(C_q): 145.9, 142.3, 141.2 (CH): 128.2, 128.2, 126.9, 126.9, 125.7, 124.2, 1838 119.8, 47.1 (CH_2): 34.7, 31.5		220
26	7.69 (d, 2H), [7.5], 7.42 (d, 2H) [7.5], 7.34–7.02 (m, 9H), 3.93 (t, 1H) [7.5], 2.51 (t, 2H) [7.5], 2.05–1.96 (m, 2H), 1.52–1.42 (m, 2H)	(C_q): 146.9, 142.3, 141.2 (CH): 128.2, 128.2, 126.9, 126.9, 125.7, 124.2, 1970 119.8, 47.1 (CH_2): 35.9, 31.7, 25.0		234

^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 δ (^{29}Si) = –2.9 ppm.

^d δ (^{29}Si) = 3.0 ppm.

^e δ (^{29}Si) = 17.6/15.3 ppm.

^f δ (^{29}Si) = –1.7 ppm.

lent amount of the respective ω -phenylalkylbromide derivative was added at –78°C. Subsequently, the reaction mixture was stirred overnight at r.t. and hydrolyzed with 50 ml water. The organic phase was dried over sodium sulfate and the solvent evaporated in vacuo. The residue was dissolved in *n*-pentane, the solution filtered over silica gel and the solvent evaporated in vacuo. The respective ω -phenylalkyl-substituted fluorene derivatives were obtained as colorless, crystalline solids. The yields were 85–95%.

3.8. General synthesis procedure for the metallocene dichloride complexes **27–41**

The ligand precursor (10.0 mmol) was dissolved in 100 ml diethyl ether and at –78°C mixed with 6.3 ml (10.0 mmol) *n*-butyllithium (1.6 M in *n*-hexane). Then 1.2 g (5.0 mmol) zirconium tetrachloride was added at –78°C and the reaction mixture was stirred overnight at r.t.

(a) Ether-insoluble metallocene dichloride complexes: the solvent was evaporated in vacuo and the residue washed twice with 50 ml *n*-pentane. The residue was extracted with dichloromethane, the solution was filtered over sodium sulfate and the solvent was evaporated in vacuo. The yields were 70–80%.

(b) Ether-soluble metallocene dichloride complexes: the suspension was filtered over sodium sulfate and the solution evaporated. The residue was washed twice with *n*-pentane and freed from solvent residues in vacuo. The yields were 70–90%. The complexes are characterized in Table 3.

3.9. General synthesis procedure for the bis[(1-phenyl-1-methylethyl)- η^5 -cyclopentadienyl] metal dichloride complexes **52–54**

6,6-Dimethylfulvene (2.4 ml, 20.0 mmol) was dissolved in 150 ml diethyl ether and mixed with 10.0 ml (20.0 mmol) phenyl lithium (2 M solution in 70:30

Table 3

¹H-, ¹³C- and ²⁹Si-NMR data for the metallocene dichloride complexes **27–54**

Complex	¹ H-NMR ^a (<i>J</i> _(H,H) in Hz)	¹³ C-NMR ^b	[M ⁺] (<i>m/e</i>)
27	7.46–7.12 (m, 10H), 6.39–6.32 (m, 4H), 6.28–6.16 (m, 4H), 3.98 (s, 4H)	(C _q): 141.1, 134.2 (CH): 128.6, 128.2, 128.3, 116.8, 112.4 (CH ₂): 35.7	473
28	7.47–7.14 (m, 10H), 6.39–6.29 (m, 4H), 6.26–6.16 (m, 4H), 3.14–2.90 (m, 8H)	(C _q): 141.0, 133.9 (CH): 128.5, 128.3, 128.2, 116.6, 112.1 (CH ₂): 36.6, 32.0	501
29	7.36–6.52 (m, 10H), 6.05–5.60 (m, 8H), 2.86–2.27 (m, 8H), 2.95–2.57 (m, 4H)	(C _q): 143.0, 136.0 (CH): 128.7, 126.1, 116.6, 112.0 (CH ₂): 35.8, 32.8, 30.0	529
30	7.39–7.17 (m, 10H), 6.29 (m, 4H), 6.21 (m, 4H), 2.68 (m, 8H), 1.67 (m, 8H)	(C _q): 142.3, 134.6 (CH): 128.3, 128.2, 125.6, 116.6, 112.1 (CH ₂): 35.5, 30.9, 30.1, 29.9	557
31	7.39–7.24 (m, 10H), 6.34 (m, 4H), 6.25 (m, 4H), 2.71 (m, 4H), 1.78–1.42 (m, 32H)	(C _q): 142.5, 134.8 (CH): 128.3, 128.1, 128.0, 116.6, 112.1 (CH ₂): 35.7, 31.1, 30.4, 29.9, 28.8	585
32a–c	7.31–7.15 (m, 20H), 6.11–5.95 (m, 12H), 3.96 (m, 8H), 2.23 (s, 6H), 2.05 (s, 6H)	(C _q): 148.5, 148.3, 132.9, 132.4, 132.3 (CH): 128.6, 128.5, 126.2, 125.6, 125.4, 118.7, 118.2, 116.3, 116.1, 115.5, 114.6, 113.6, 112.0, 107.0, 106.7, 106.2 (CH ₂): 35.8, 35.3 (CH ₃): 16.0, 13.1	501
33a–c	7.32–7.14 (m, 20H), 6.10–5.95 (m, 12H), 2.88 (m, 16H), 2.22 (s, 6H), 2.05 (s, 6H)	(C _q): 148.6, 148.3, 132.8, 132.5, 132.2 (CH): 128.7, 128.5, 126.3, 125.7, 125.5, 118.8, 118.2, 116.4, 116.1, 115.7, 114.5, 113.4, 112.1, 107.2, 106.8, 106.0 (CH ₂): 37.0, 35.8, 32.6, 30.2 (CH ₃): 16.1, 13.3	529
34a–c	7.34–7.17 (m, 20H), 6.12–6.06 (m, 12H), 2.74–2.56 (m, 16H), 2.20 (s, 6H), 2.13 (s, 6H), 1.86 (m, 8H)	(C _q): 148.6, 148.3, 132.8, 132.2 (CH): 128.3, 128.0, 125.7, 118.4, 116.2, 116.1, 114.1, 113.7, 106.7, 106.3 (CH ₂): 35.6, 35.4, 32.4, 31.2, 30.1, 27.8 (CH ₃): 16.0, 13.5	557
35	7.12 (m, 8H), 6.22 (m, 8H), 3.99 (s, 4H), 2.35 (s, 6H)	(C _q): 136.4, 135.9, 133.8 (CH): 129.1, 128.6, 116.8, 112.4 (CH ₂): 35.7 (CH ₃): 21.0	501
36	7.18–7.12 (m, 4H), 7.11–6.93 (m, 4H), 6.23 (m, 4H), 6.16 (m, 4H), 3.98 (s, 4H)	(C _q): 163.5, 135.3, 133.6 (CH): 130.4, 117.1, 115.5, 115.2, 112.4 (CH ₂): 35.3	513
37	7.01 (m, 6H), 6.42 (m, 8H), 4.11 (m, 4H), 2.47 (m, 12H)	(C _q): 139.7, 138.0, 133.6 (CH): 128.0, 126.6, 116.9, 112.8 (CH ₂): 36.0 (CH ₃): 21.2	529
38^c	7.56–7.39 (m, 10H), 6.63–6.61 (m, 4H), 6.32–6.30 (m, 4H), 0.64 (s, 12H)	(C _q): 137.9, 123.7 (CH): 134.1, 134.0, 133.9, 129.3, 129.2, 127.8, 127.7, 127.6, 126.0, 117.0 (CH ₂): –1.8	560
39^d	7.23–6.84 (m, 10H), 6.52–6.50 (m, 4H), 6.45–6.42 (m, 4H), 2.25 (s, 4H), 0.27 (s, 12H)	(C _q): 139.2, 125.0 (CH): 128.2, 128.2, 128.1, 125.7, 124.1, 115.7 (CH ₂): 27.2, 27.0 (CH ₃): –2.6	588
40^e	7.40–7.29 (m, 18H), 2.85–2.78 (m, 4H), 1.01–1.03 (m, 4H), 0.25 (s, 12H)	(C _q): 144.9, 144.1 (CH): 128.3, 128.1, 127.84, 127.7, 127.5, 127.4, 127.2, 126.9, 126.4, 125.7, 125.5, 125.4, 124.9, 124.3 (CH ₂): 29.3, 28.5, 19.5, 13.5 (CH ₃): –0.5, –1.5	616
41	7.80–7.74 (m, 6H), 7.6 (m, 2H), 7.48–7.41 (m, 4H), 7.34 (m, 1H), 7.31 (m, 1H), 6.22 (m, 8H), 4.17 (s, 4H)	(C _q): 137.3, 133.6, 133.5, 132.2 (CH): 128.2, 127.6, 127.5, 127.4, 127.1, 126.1, 125.6, 117.0, 112.7 (CH ₂): 36.3	411

Table 3 (Continued)

Complex	$^1\text{H-NMR}^a$ ($J_{\text{H,H}}$ in Hz)	$^{13}\text{C-NMR}^b$	$[\text{M}^+]$ (m/e)
42a–c	7.63–7.54 (m, 8H), 7.37–7.11 (m, 28H), 6.28 (d, 2H) [3.1], 6.04 (d, 2H) [3.1], 5.82 (d, 2H) [3.1], 5.29 (d, 2H) [3.1], 4.41–4.01 (m, 8H)	(C _q): 139.7, 139.5, 127.5, 121.8, 121.7 (CH): 128.9, 128.8, 128.7, 128.5, 128.4, 126.5, 126.4, 126.3, 126.2, 125.8, 125.6, 123.8, 122.1, 120.8, 99.2, 99.1 (CH ₂): 34.1, 33.9	573
43a–c	7.65–7.13 (m, 36 H), 6.21 (d, 2H) [3.1], 5.92 (d, 2H) [3.1], 5.84 (d, 2H) [3.1], 5.60 (d, 2H) [3.1], 3.41–2.77 (m, 16H)	(C _q): 141.2, 127.3, 122.3 (CH): 128.5, 128.3, 128.2, 127.3, 127.0, 126.3, 126.0, 125.9, 125.8, 125.7, 125.5, 125.4, 125.3, 125.0, 123.7, 123.6, 120.3, 99.1, 98.9 (CH ₂): 36.0, 35.9, 30.2, 29.9	601
44a–c	7.42–7.15 (m, 36H), 6.3(d, 2H) [3.2], 6.04 (d, 2H) [3.2], 5.83 (d, 2H), 3.2], 5.65 (d, 2H) [3.2], 3.01–2.58 (m, 16H), 1.94–1.60 (m, 8H)	(C _q): 141.8, 127.2, 126.0, 126.0, 122.9, 122.8 (CH): 128.3, 126.1, 125.8, 125.7, 125.7, 125.6, 125.4, 125.3, 123.7, 123.7, 121.8, 120.3, 99.2, 99.2 (CH ₂): 35.6, 35.5, 31.5, 27.7, 27.4	629
45a–c	7.43–7.23 (m, 36H), 6.42 (d, 2H) [2.8], 6.16 (d, 2H) [2.8], 5.97 (d, 2H) [2.8], 5.76 (d, 2H), [2.8], 2.99–2.59 (m, 12H), 1.66–1.53 (m, 20H)	(C _q): 150.8, 148.2, 145.7, 144.6, 144.3, 143.9, 142.6, 141.8, 125.7, 124.0, 123.6 (CH): 142.0, 139.2, 130.4, 128.2, 128.1, 126.0, 125.6, 125.5, 125.5, 124.1, 124.0, 124.0, 123.6, 123.6, 121.7, 120.1, 118.3, 117.5, 99.9 (CH ₂): 35.0, 33.7, 33.0, 23.3, 23.2	657
46a–c^f	7.61–7.18 (m, 36H), 4.49–4.47 (m, 2H), 6.41–6.40 (m, 3H), 6.06–6.04 (m, 2H), 5.70–5.68 (m, 2H), 0.73–0.64 (24H)	(C _q): 144.3, 144.1, 137.2, 134.1, 129.4 (CH): 134.1, 129.3, 127.9, 127.1, 127.0, 127.0, 126.9, 126.4, 126.2, 126.1, 125.5, 121.0, 114.1, 113.5, 106.1, 105.2 (CH ₃): –0.6, –0.7, –1.2, –1.3	717
47	7.67–7.64 (m, 4H), 7.25–7.18 (m, 10H), 7.01 (m, 4H), 5.85 (s, 4H), 3.70 (s, 4H)	(C _q): 132.8, 128.9, 126.7 (CH): 129.1, 129.0, 126.5, 126.0, 125.9, 106.3 (CH ₂): 38.0	573
48	7.66–7.62 (m, 4H), 7.25–7.19 (m, 10H), 7.04 (m, 4H), 5.74 (s, 4H), 2.70–2.60 (m, 8H)	(C _q): 133.2, 131.4, 126.8 (CH): 128.9, 128.8, 126.6, 125.9, 125.7, 105.7 (CH ₂): 36.9, 33.7	601
49	7.93–7.79 (m, 8H), 7.46–6.48 (m, 1 8H), 4.17 (s, 4H)	(C _q): 140.8, 130.9, 118.1, 105.0 (CH): 128.3, 128.2, 127.8, 126.9, 126.7, 126.3, 125.9, 124.6, 124.4, 122.5, 119.9 (CH ₂): 30.8	673
50	7.84–7.79 (m, 8H), 7.43–6.94 (m, 18H), 3.13 (t, 4H) [7.5], 2.69 (t, 4H) [7.5]	C _q : 141.6, 128.5, 119.9, 105.8 (CH): 128.4, 128.3, 128.3, 127.0, 126.5, 125.8, 124.1, 124.0, 123.9, 123.4, 119.9 (CH ₂): 36.2, 27.6	701
51	7.77–7.73 (m, 8H), 7.37–7.10 (m, 18H), 2.85–2.79 (m, 4H), 2.61–2.55 (m, 4H), 1.76–1.70 (m, 4H)	(C _q): 142.0, 130.3, 118.5, 104.6 (CH): 128.4, 128.3, 126.9 126.8, 126.6, 125.8, 124.3, 124.2, 123.9, 123.4, 119.8 (CH ₂): 34.0, 29.8, 23.2	729
52	7.31–7.17 (m, 10H), 6.49 (m, 4H), 6.11 (m, 4H), 1.79 (s, 12H)	(C _q): 149.3, 146.6, 41.2 (CH): 128.2, 126.3, 126.2, 121.2, 118.1 (CH ₃): 29.0	485
53	7.35–7.17 (m, 10H), 6.40 (m, 4H), 6.05 (m, 4H), 1.83 (s, 12H)	(C _q): 149.8, 143.1, 40.4 (CH): 128.1, 126.1, 126.0, 117.2, 113.0 (CH ₃): 29.3	529
54	7.36–7.16 (m, 10H), 6.38 (m, 4H), 6.05 (m, 4H), 1.82 (s, 12H)	(C _q): 149.7 143.7 40.3 (CH): 128.1, 126.2 126.1 116.5, 112.0 (CH ₃): 29.3	616

^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 δ (^{29}Si) = –10.8 ppm.^d δ (^{29}Si) = –5.2 ppm.^e δ (^{29}Si) = –1.3 ppm.^f δ (^{29}Si) = –10.3/–10.4 ppm.

(wt%) cyclohexane–diethyl ether at –78°C. The white suspension was stirred for 4 h at r.t. Then 10.0 mmol of the corresponding metal tetrachloride were added at

–78°C and the reaction mixture was stirred overnight at r.t. The solvent was evaporated and the residue was washed twice with 50 ml *n*-pentane. The residue was

extracted with dichloromethane, the solution was filtered over sodium sulfate and the solvent evaporated. The yields were 80–90%. MS. **52**: $m/e = 485$ [M^+]. **53**: $m/e = 529$ [M^+]. **54**: $m/e = 616$ [M^+].

3.10. Activation of the metallocene complexes with methylaluminoxane (MAO)

The corresponding metallocene complex (10–15 mg) was activated with MAO (30% in toluene) (metal:Al = 1:3000). The catalyst solution, containing 0.5–1.5 mg metallocene complex, was used within 1 h for homopolymerization.

3.11. Homopolymerization of ethylene

A volume of *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 bar was applied after an inside temperature of 50°C was reached (sometimes the polymerization reactions were highly exothermic). The mixture was stirred for 1 h at 60°C ($\pm 2^\circ\text{C}$) and the reaction terminated by releasing the pressure in the reactor. The polymer obtained was dried in vacuo.

3.12. Characterization of the polyethylene samples

3.12.1. Differential scanning calorimetry (DSC)

Phase transitions on the polymer samples were measured using DSC techniques (Pyris DSC 7 instrument). For the measurements, 5–12 mg dried polymer were fused into standard aluminum pans ($\varnothing$ 7 mm) and measured under nitrogen cooling, using the following temperature program:

First heating phase: from 25–200°C (heating rate 40°C min⁻¹).

Isothermal phase: 3 min.

Cooling phase: from 200 to –40°C (cooling rate 20°C min⁻¹).

Second heating phase: from –40 to 200°C (heating rate 20°C min⁻¹).

Melting points and fusion enthalpies were taken from the second heating course. The temperature was linearly corrected relative to indium (m.p. 429.78 K). The fusion enthalpy of indium ($H_m = 28.45$ J g⁻¹) was used for calibration.

3.12.2. Viscosimetry

The viscosity average molecular-weight determinations of the polyethylene samples were performed on an Ubbelohde precision capillary viscometer in *cis/trans*-decalin at $135 \pm 0.1^\circ\text{C}$. For the measurements, 50 mg polymer were completely dissolved in 45.0 ml decalin at 130°C within 3–4 h and insoluble ingredients filtered

over glass wool. $\bar{M}_\eta$ was determined using a calibration curve that was available for the selected concentration.

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References

- [1] W. Kaminsky, J. Chem. Soc. Dalton Trans. (1998) 1413.
- [2] M. Bochmann, J. Chem. Soc. Dalton Trans. (1996) 255.
- [3] H.-H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. Waymouth, Angew. Chem. 107 (1995) 1255; Angew. Chem. Int. Ed. Engl. 34 (1995) 1143.
- [4] M. Kaulbach, F. Küber, Chem. Unserer Zeit 28 (1994) 197.
- [5] R. Choukroun, F. Dahan, Organometallics 13 (1994) 2097.
- [6] H. Sitzmann, P. Zhou, G. Wolmershäuser, Chem. Ber. 127 (1994) 3.
- [7] P.C. Möhring, N.J. Coville, J. Mol. Catal. 96 (1995) 181.
- [8] P.C. Möhring, N. Vlachakis, N.E. Grimmer, N.J. Coville, J. Organomet. Chem. 483 (1994) 159.
- [9] R.D. Rogers, M.M. Benning, L.K. Kurihara, K.J. Moriarty, M.D. Rausch, J. Organomet. Chem. 293 (1985) 51.
- [10] J.A. Ewen, R.L. Jones, A. Razavi, J. Ferrara, J. Am. Chem. Soc. 110 (1988) 6255.
- [11] J.A. Ewen, A. Razavi, Eur. Pat. Appl. EP 351 392 (17 January 1990); Chem. Abstr. 112 (1990) 199346.
- [12] A. Razavi, J.L. Atwood, A. Razavi, J. Ferrara, J. Organomet. Chem. 459 (1993) 117.
- [13] G. Schmid, U. Thewalt, M. Polasek, K. Mach, P. Sedmera, J. Organomet. Chem. 482 (1994) 231.
- [14] M.A. Schmid, H.G. Alt, W. Milius, J. Organomet. Chem. 501 (1995) 101.
- [15] A. Razavi, J. Ferrara, J. Organomet. Chem. 435 (1992) 299.
- [16] W. Kaminsky, O. Rabe, A.-M. Schauwienold, G.U. Schupfer, J. Hanss, J. Kopf, J. Organomet. Chem. 497 (1995) 181.
- [17] J.A. Ewen, Macromol. Symp. 89 (1995) 181.
- [18] Y.-X. Chen, M.D. Rausch, J.C.W. Chien, J. Organomet. Chem. 497 (1995) 1.
- [19] G.S. Herrmann, H.G. Alt, M.D. Rausch, J. Organomet. Chem. 401 (1991) C5.
- [20] K. Patsidis, H.G. Alt, J. Organomet. Chem. 501 (1995) 31.
- [21] H.G. Alt, R. Zenk, J. Organomet. Chem. 512 (1996) 51.
- [22] H.G. Alt, R. Zenk, W. Milius, J. Organomet. Chem. 514 (1996) 257.
- [23] H.G. Alt, J. Chem. Soc. Dalton Trans. (1999) 1703.
- [24] R. Fierro, Z. Yu, M.D. Rausch, S. Dong, D. Alvares, J.C.W. Chien, J. Polym. Sci. A 32 (1994) 661.
- [25] K. Ziegler, H. Froitzheim-Kühlhorn, K. Hafner, Chem. Ber. 89 (1956) 434.
- [26] G. Erker, R. Aul, Chem. Ber. 124 (1991) 1301.
- [27] B. Peifer, Dissertation, University of Bayreuth, 1995.
- [28] O. Meth-Cohn, S. Gronowitz, J. Chem. Soc. Chem. Commun. 16 (1966) 81.
- [29] R. Schmidt, Dissertation, University of Bayreuth, 1999.
- [30] J.E. Horan, R.W. Schiessler, Org. Synth. 41 (1961) 647.

- [31] K.C. Ott, E.M.J. DeBoer, R.H. Grubbs, *Organometallics* 3 (1984) 223.
- [32] P.T. Wolczanski, J.E. Bercaw, *Organometallics* 1 (1982) 793.
- [33] R.D. Rogers, M.M. Benning, L.K. Kurihara, K.J. Moriarty, M.D. Rausch, *J. Organomet. Chem.* 293 (1985) 51.
- [34] W.C. Finch, E.V. Anslyn, R.H. Grubbs, *J. Am. Chem. Soc.* 110 (1988) 2406.
- [35] P. Courtot, R. Pichon, J.Y. Salaun, L. Toupet, *Can. J. Chem.* 69 (1991) 661.
- [36] U. Thewalt, G. Schmid, *J. Organomet. Chem.* 412 (1991) 343.
- [37] P. Schertl, Dissertation, University of Bayreuth, 1996.
- [38] A. Streitwieser, C.H. Heathcock, E.M. Kosower, *Organische Chemie*, second ed., VCH, Weinheim, New York, 1994, p. 851.