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# Synthesis and characterization of bis(cyclopentadienyl)zirconium dichloride complexes with ω-fluorenylalkyl or silyl substituents and their application in catalytic ethylene polymerization

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**Abstract**

Eight zirconocene dichloride complexes are described that contain an alkyl or silylalkyl substituent with a fluorenyl end group on the cyclopentadienyl ring. Also, a bridged cyclopentadienyl indenyl metallocene complex with a fluorenyl terminated alkyl substituent is reported. These complexes were activated with methyl aluminoxane (MAO) and used for catalytic ethylene polymerization. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Zirconium; Catalysis; Ethylene polymerization; Metallocene complexes; Substituents

## 1. Introduction

Metallocene complexes, activated with methyl aluminoxane (MAO), are attractive catalysts for olefin polymerization. The variation of the aromatic ligands with substituents can significantly impact the resulting polymer properties [1–26]. We were interested in zirconocene complexes with one alkyl or silyl substituent on the cyclopentadienyl ligand, the substituents terminated with a fluorenyl end group. The following questions were of interest: How strongly do the bulky fluorenyl groups influence olefin polymerization? If the five-membered ring of the fluorenyl group can be aromatized to form a mono anion, can it compete effectively with other π-ligands for coordination to the metal center?

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## 2. Results and discussion

### *2.1. Synthesis and characterization of substituted fluorene derivatives*

#### *2.1.1. Synthesis of the α-(9-fluorenyl)-ω-bromoalkane derivatives* **1**–***3***

The stoichiometric reaction of α,ω-dibromoalkanes with fluorenyllithium [27] leads to α-(9-fluorenyl)-ω-bromoalkane derivatives [28–30]. Solvent selection is critical for the single substitution reaction because even weakly polar solvents, e.g. diethylether, increase the amount of doubly fluorenyl substituted reaction products. When doubly substituted products are present, purification of the product results in major yield reductions. Therefore, the synthesis of the α-(9-fluorenyl)-ω-bromoalkane derivatives **1**–**3** is conducted in *n*-pentane suspension (Fig. 1).

#### *2.1.2. Synthesis of the α-(9-fluorenyl)-ω-alkene derivatives* **4**–***6***

The corresponding α-bromo-ω-alkene derivatives can be directly reacted with fluorenyllithium [27] in

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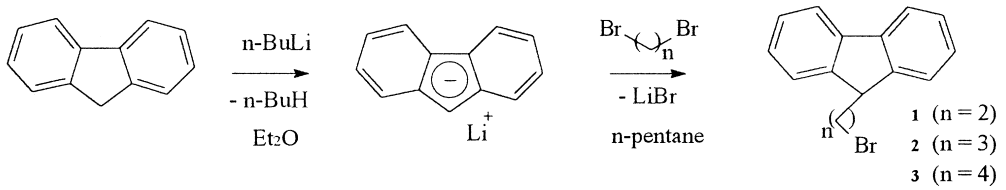



Fig. 1. Synthesis of the α-(9-fluorenyl)-ω-bromoalkane derivatives **1**–**3**.

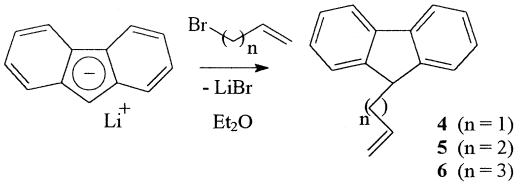



Fig. 2. Synthesis of the α-(9-fluorenyl)-ω-alkene derivatives **4**–**6**.

diethylether without changing the solvent, to synthesize the α-(9-fluorenyl)-ω-alkene derivatives **4**–**6** (Fig. 2).

### *2.1.3. Synthesis of the α-(9-fluorenyl)-ω-(dimethylchlorosilyl)alkane derivatives* **7**–***9***

The α-(9-fluorenyl)-ω-(dimethylchlorosilyl) derivatives **7**–**9** are synthesized by hydrosilylation of the α-(9-fluorenyl)-ω-alkene derivatives **4**–**6** with dimethylchlorosilane [31]. Hexachloroplatinic acid serves as catalyst for the hydrosilylation reaction. The amount of hexachloroplatinic acid used should be limited (≈6 vol.%) to control the highly exothermic reaction. Excess dimethylchlorosilane, which also serves as the solvent, is used (Fig. 3).

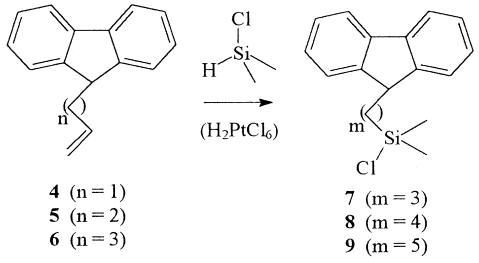



Fig. 3. Synthesis of the α-(9-fluorenyl)-ω-(dimethylchlorosilyl) derivatives **7**–**9**.

### *2.1.4. Synthesis of the α-(9-fluorenyl)-ω-(cyclopentadienyl)alkane derivatives* **10*a*,*b*–12*a*,*b***

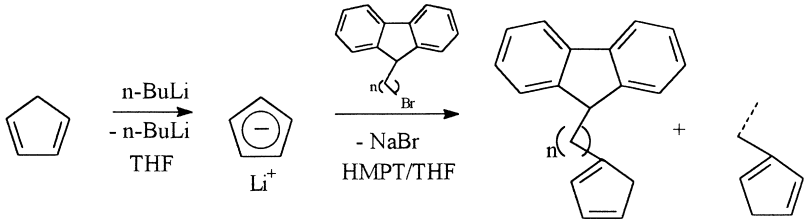
The α-(9-fluorenyl)-ω-(cyclopentadienyl)alkane derivatives **10a**,**b**–**12a**,**b** are synthesized by reacting the corresponding α-(9-fluorenyl)-ω-bromoalkane derivatives **1**–**3** with cyclopentadienyl lithium [28]. Cyclopentadiene is first deprotonated in tetrahydrofuran with *n*-butyllithium. After the formation of the anion, hexamethylphosphoric triamide and the desired α-(9-fluorenyl)-ω-bromoalkane derivatives (**1**–**3**) are added to the reaction solution. Hexamethylphosphoric triamide complexes the lithium cation and inhibits the formation of a spiro by-product (spiro[cycloalkane-1,9′-fluorene]) that results when cyclopentadienyl lithium reacts with the proton in position 9 of the fluorenyl group (Fig. 4).

### *2.1.5. Synthesis of the 1-fluorenyl-ω-(dimethylcyclopentadienylsilyl)alkane derivatives* **13*a*,*b*–15*a*,*b***

Cyclopentadiene is deprotonated with *n*-butyllithium in diethylether and then reacted with the desired chlorosilane (**7**–**9**) to give the α-(9-fluorenyl)-ω-(dimethyl-cyclopentadienylsilyl)alkane derivatives **13a**,**b**–**15a**,**b**. Two isomers, differing in the position of the double bonds in the cyclopentadienyl ring, are formed during the reaction. In solution, the isomers are in equilibrium due to metallotropic 1,2-shifts [32] (Fig. 5).

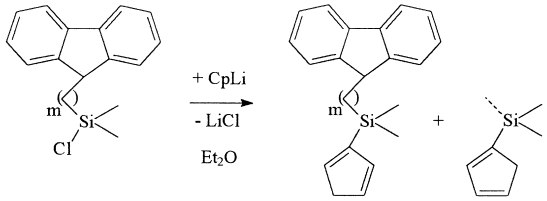
### *2.1.6. Synthesis of 1-((9-fluorenyl)isopropylidene)-3-((1-cyclopentadienyl)isopropylidene)indene (**16**)*

Fulvenes can be synthesized by base catalyzed condensation of cyclopentadiene or indene with ketones or aldehydes in methanol [33,34]. These fulvenes can be reacted with the appropriate metal salt to produce $C_1$-bridged ligand precursors [35–37]. In this reaction, the fluorenyl or indenyl anion reacts with the exocyclic double bonds of pentafulvenes to form




**10a,b** (n = 2)
**11a,b** (n = 3)
**12a,b** (n = 4)

Fig. 4. Synthesis of the α-(9-fluorenyl)-ω-(cyclopentadienyl)alkane derivatives **10a**,**b**–**12a**,**b**.




**7** (m = 3)
**8** (m = 4)
**9** (m = 5)

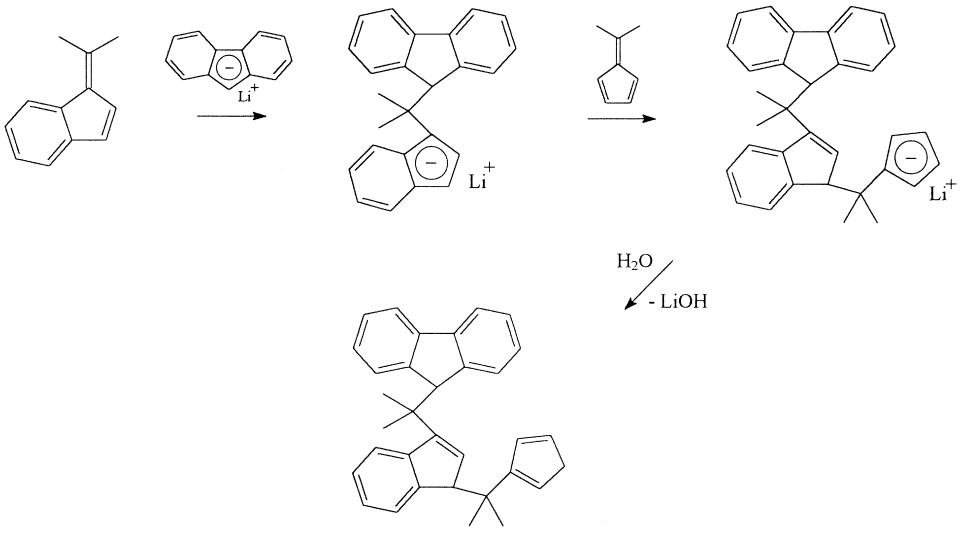
**13a,b** (m = 3)
**14a,b** (m = 4)
**15a,b** (m = 5)

Fig. 5. Synthesis of the α-(9-fluorenyl)-ω-(dimethylcyclopentadienylsilyl)alkane derivatives **13a**,**b**–**15a**,**b**.

the desired anion. Ligand precursor **16** was synthesized via a double fulvene reaction. A substituted indenyl anion is formed by reaction of fluorenyllithium with 6,6-dimethylbenzofulvene [38]. This then reacts further with 6,6-dimethylfulvene [39,40] in a one-pot reaction to form ligand precursor **16** (Fig. 6).

### *2.2. Spectroscopic characterization of compounds* **1**–***16***

Compounds **1**–**16** were characterized by $^{1}H$, $^{13}C$ and $^{29}Si$ NMR spectroscopy. Spectroscopic data are listed in Table 1. The mass spectroscopy data are found in Section 3.




**16**

Fig. 6. Synthesis of the ligand precursor **16**.

Table 1
$^{1}H$, $^{13}C$ and $^{29}Si$ NMR data for the substituted fluorene and cyclopentadiene derivatives and their precursors (**1**–**16**) (only one isomer is illustrated)

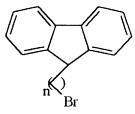
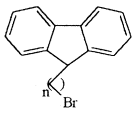
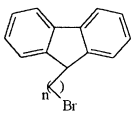
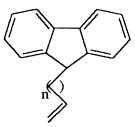
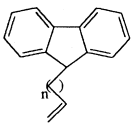
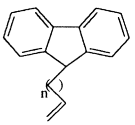
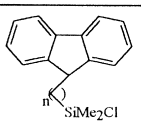
| | $^{1}H$ NMR[a] [J(H,H) in Hz] | $^{13}C$ NMR[b] | $^{29}Si$ NMR[c] |
|---|---|---|---|
|  **1** (n = 2) | 7.82 (d, 2H) [7.4], 7.58 (d 2H) [7.4], 7.45 (t, 2H) [7.4], 7,38 (t, 2H) [7.4], 4.21 (t, 1H) [6.1], 3.37 (t, 2H) [7.0], 2.53 (m, 2H) | ($C_q$): 146.2, 141.4 (CH): 127.7, 127.5, 124.6, 120.2, 46.7 ($CH_2$): 37.0, 31.0 | |
|  **2** (n = 3) | 7.80 (d, 2H) [7.4], 7.56 (d 2H) [7.4], 7.40 (t, 2H) [7.4], 7,35 (t, 2H) [7.4], 4.08 (t, 1H) [7.4], 3.29 (t, 2H) [7.0], 2.24 (m, 2H), 1.56 (m, 2H) | ($C_q$): 147.1, 141.5 (CH): 127.5, 127.4, 124.6, 120.2, 47.0 ($CH_2$): 34.6, 31.4, 28.7 | |
|  **3** (n = 4) | 7.81 (d, 2H) [7.4], 7.55 (d 2H) [7.4], 7.38 (t, 2H) [7.4], 7,35 (t, 2H) [7.4], 4.06 (t, 1H) [7.3], 3.22 (t, 2H) [7.0], 2.21 (m, 2H), 1.49 (m, 4H) | ($C_q$): 147.0, 141.6 (CH): 127.4, 127.4, 124.5, 120.2, 47.1 ($CH_2$): 34.6, 31.2, 26.7, 25.8 | |
|  **4** (n = 1) | 7.81 (d, 2H) [6.6], 7.60 (d, 2H) [6.4], 7.43-7.36 (m, 4H), 5.80 (m, 1H), 5.07 (m, 1H), 4.06 (t, 1H) [6.3], 2.78 (m, 2H) | ($C_q$): 146.8, 140.9 (CH): 135.5, 127.0, 126.6, 124.5, 119.8, 46,8 ($CH_2$): 32.6 | |
|  **5** (n = 2) | 7.91 (d, 2H) [6.6], 7.66 (d, 2H) [7.4], 7.52-7.42 (m, 4H), 5.92 (m, 1H), 5.12 (m, 1H), 4.16 (t, 1H) [5.5], 2.28 (m, 2H), 2.10 (m, 2H) | ($C_q$): 147.0, 141.0, (CH): 138.4, 126.8, 126.7, 124.2, 119.7, 46.8 ($CH_2$): 32.2, 29.6 | |
|  **6** (n = 3) | 7.91 (d, 2H) [6.6], 7.66 (d, 2H) [7.1, 7.53-7.42 (m, 4H), 5.88 (m, 1H), 5.12 (m, 1H), 4.14 (t, 1H) [5.7], 2.21 (m, 4H), 1.44 (m, 2H) | ($C_q$): 147.3, 141.0 (CH): 138.4, 126.8, 126.7, 124.2, 119.7, 47.2 ($CH_2$): 33.9, 32.4, 24.7 | |
|  **7** (n = 3) | 7.94-7.91 (m, 2H), 7.68-7.55 (m, 2H), 7.54-7.46 (m, 4H), 4.14 (t, 1H) [5.0], 2.25-2.16 (m, 2H), 1.68-1.62 (m, 2H),1.05-0.98 (m, 2H), 0.56 (s, 6H) | ($C_q$): 147.1, 140.6, (CH): 126.8, 126.7, 124.2, 119.7, 47.0 ($CH_2$): 36.3, 19.5, 18.9 ($CH_3$): 1.5 | 32.0 |

Table 1 (*Continued*)

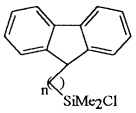
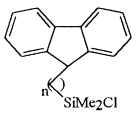
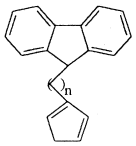
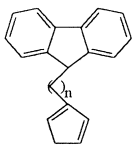
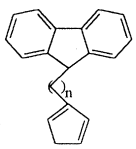
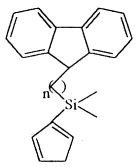
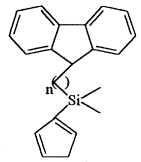
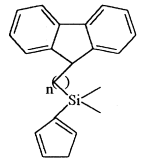
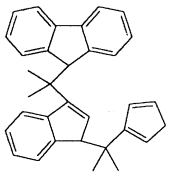
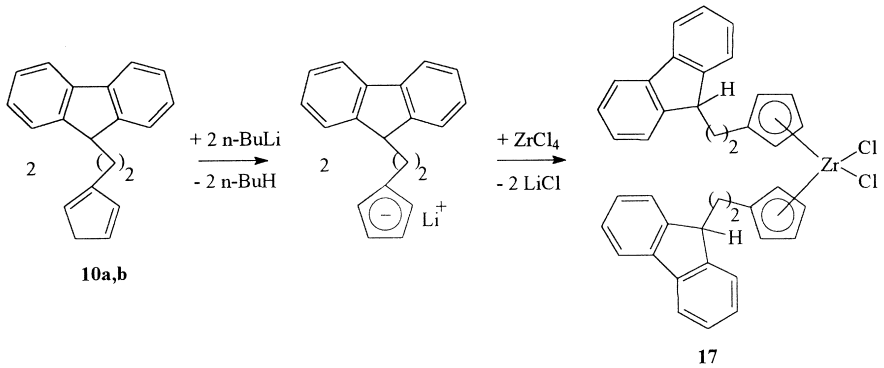
| | | | |
|---|---|---|---|
|  **8** (n = 4) | 7.67-7.64 (m, 2H), 7.42-7.40 (m, 2H), 7.29-7.18 (m,4 H), 3.88 (t, 1H) [5.0], 1.95-1.90 (m, 2H), 1.27-1.12 (m, 4H), 0.66-0.60 (m, 2H), 0,25 (s, 6H) | ($C_q$): 147.3, 141.1, (CH): 126.8, 126.7, 124.3, 119.7, 47.3 ($CH_2$): 32.7, 29.3, 23.5, 18.7 ($CH_3$): 1.5 | 35.8 |
|  **9** (n = 5) | 7.97-7.95 (m, 2H), 7.71-7.58 (m, 2H), 7.56-7.52 (m, 4H), 4.18 (t, 1H) [5.0] , 2.25-2.31 (m, 2H), 1.56-1.46 (m, 6H), 0.98-0.92 (m, 2H), 0.55 (s, 6H) | ($C_q$): 147.3, 141.0, (CH): 127.3, 126.7, 124.8, 119.7, 41.3 ($CH_2$): 36.7, 33.1, 32.7, 24.9, 22.6, 18.7 ($CH_3$): 1.5 | 32.2 |
|  **10a,b** (n = 2) | 7.85 (d, 4H) [7.4], 7.58 (d, 4H) [7.4], 7.43 (m, 4H), 7.38 (m, 8H), 6.43 (m, 3H), 6.29 (m, 1H), 6.17 (m, 1H), 6.01 (m, 1H), 4.11 (m, 2H), 3.05 (m, 2H), 2.83 (m, 2H), 2.59 (m, 2H), 2.34 (m, 2H), 1.98 (m, 2H) | (Cq): 149.1, 147.2, 147.4, 146.5, 141.1 (CH): 134.5, 133.3, 132.5, 130.6, 126.6, 126.6, 126.1, 124.0, 119.6, 47.3 ($CH_2$): 41.3, 43.5, 32.6, 32.9, 30.9, 31.1, | |
|  **11a,b** (n = 3) | 7.83 (d, 4H) [7.4], 7.57 (d, 4H) [7.4], 7.41 (m, 4H), 7.39 (m, 8H), 6.43 (m, 3H), 6.29 (m, 1H), 6.17 (m, 1H), 6.01 (m, 1H), 4.06 (m, 2H), 2.99 (m, 2H), 2.83 (m, 2H), 2.42 (m, 4H), 2.12 (m, 4H), 1.50 (m, 4H) | (Cq): 149.3, 147.3, 147.2, 146.6, 141.0 (CH): 134.6, 133.6, 132.3, 130.5, 126.7, 126.6, 126.0, 124.2, 119.7, 47.2 ($CH_2$): 41.1, 43.0, 32.6, 32.5, 30.7, 29.9, 25.3, 24.6 | |
|  **12a,b** (n = 4) | 7.78 (m, 2H), 7.53 (m, 2H), 7.33 (m,4H), 6.42 (m, 3H), 6.26 (m, 1H), 6.12 (m, 1H), 5.98 (m, 1H), 4.01 (m, 2H), 2.95 (m, 2H), 2.84 (m, 2H), 2.33 (m, 4H), 2.06 , 4H), 1.55 (m, 4H), 1.20 (m, 4H) | (Cq): 147.5, 141.1, 43.2, 41.2 (CH): 134.7, 133.6, 132.4, 130.4, 126.8, 126.2, 125.8, 124.3, 119.8, 47.4 ($CH_2$): 32.9, 30.5, 30.1, 29.6, 29.1, 25.5 | |
|  **13a,b** (n = 3) | 7.94-7.91 (m, 2H), 7.69-7.66 (m, 2H), 7.57-7.46 (m, 4H), 6.79-6.67 (m, 5H), 4.11 (m, 1H), 2.21-2.12 (m, 2H), 1.57-1.48 (m, 2H), 0.74-0.68 (m, 2H), 0.08 (s, 3H) | ($C_q$): 147.5, 140.9. (CH): 141.8, 137.7, 132.8, 123.0, 126.8, 126.7, 124.7, 122.0, 119.7, 47.2 ($CH_2$): 36.8, 20.6, 15.6 ($CH_3$): -4.0 | 7.1 |

Table 1 (*Continued*)

| | | | |
|---|---|---|---|
|  **14a,b** (n = 4) | 7.67-7.63 (m, 2H), 7.43-7.40 (m,2H), 7.29-7.21 (m, 4H), 6.56 (m, 5H), 3.90-3.86 (m,1H), 1.97-1.92 (m, 2H), 1.16-1.14 (m, 4H), 0.51-0.32 (m, 2H), 0.13 (s, 6H) | ($C_q$): 147.5, 141.1<br>(CH): 141.7, 137.6, 132.8, 129.9,126.8, 126.7, 124.2, 122.7, 119.7, 47.3<br>($CH_2$): 32.6, 29.3, 27.6, 15.9<br>($CH_3$): -4.1 | 3.7 |
|  **15a,b** (n = 5) | 7.87 (m, 2H), 7.64 (m, 2H), 7.51-7.44 (m, 4H), 7.43-6.72 (m, 5H), 4.05-3.55 (m, 1H), 2.11-1.93 (m, 2H), 1.39-1.33 (m, 6H), 0.06-0.03 (m, 2H), 0.01 (s, 6H). | ($C_q$): 147.4, 141.0<br>(CH): 141.7, 137.5, 132.8, 129.9, 126.9, 126.9, 124.4, 122.2, 119.8, 47.6,<br>($CH_2$): 33.9, 33.0, 25.3, 23.9, 15.6<br>($CH_3$): -4.2 | 3.9 |
|  **16** | 8.23 (d, 1H) [7.5], 7.99 (t, 2H) [7.6], 7.62-7.11 (m, 10H), 6.83 (m, 1H), 6.35 (m, 2H), 5.11 (s, 1H), 4.02 (s, 1H), 3.32 (m, 2H), 1.61 (s, 6H), 1.38 (s, 6H) | ($C_q$): 155.3, 151.5, 147.0, 145.2, 145.1, 144.2, 142.0, 141.8, 40.2, 38.3<br>(CH): 134.0, 132.8, 132.0, 127.0, 126.8, 126.4, 126.1, 125.9, 125.7, 124.9, 124.4, 124.2, 124.1, 121.9, 119.4, 119.2, 56.4, 53.2<br>($CH_2$): 40.9<br>($CH_3$): 27.7, 22.7 | |

[a] 25°C, in chloroform-$d_1$ $\delta$ [ppm] rel. chloroform (7.24).
[b] 25°C, in chloroform-$d_1$ $\delta$ [ppm] rel. chloroform-$d_1$ (77.0).
[c] 25°C, in chloroform-$d_1$ $\delta$ [ppm] rel. $TMS_{ext.}$ (0.0).




**10a,b** **17**

Fig. 7. Synthesis of the bis[2-(9-fluorenyl)ethylidene-1-($\eta^5$-cyclopentadienyl)] zirconium dichloride complex **17**.

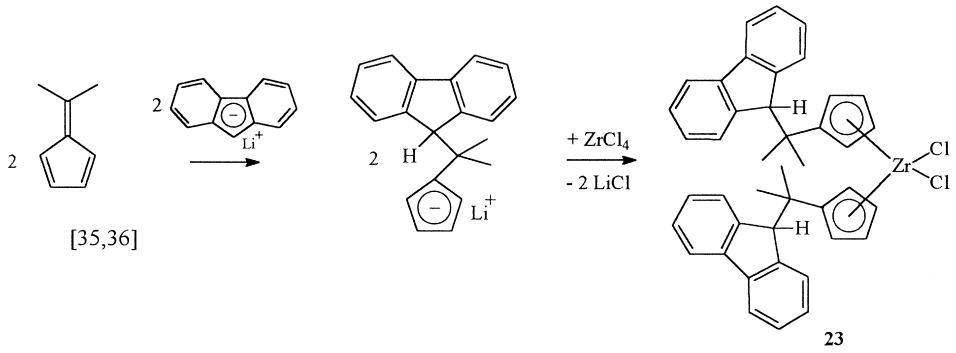



Fig. 8. Synthesis of the bis[1-(9-fluorenyl)-1-methylethylidene-1-($\eta^5$-cyclopentadienyl)] zirconium dichloride complex **23**.

### *2.3. Synthesis of the metallocene dichloride complexes* **17**–**25** *with ω-fluorenylalkyl or silyl substituents*

The ligand precursors **10a**,**b**–**15a**,**b** are lithiated to monoanions by reacting them with one equivalent of *n*-butyllithium. The *n*-butyllithium must be added dropwise to the ligand precursor in diethylether to achieve selective deprotonation of the stronger acidic CH bonds ($pK_a$ values [41–44]: cyclopentadiene 15, indene 18, fluorene 21). The corresponding unbridged metallocene dichloride complexes (**17**–**22**) are obtained by the reaction of two equivalents of the monolithiated ligand with one equivalent of zirconium tetrachloride. A very similar titanium complex has been published recently [45] (Fig. 7).

The fulvene method [35–37] can also be used to synthesize unbridged metallocene dichloride complexes containing CH-acidic substituents directly without isolating the ligand. For example, complexes **23** and **24** are formed by first quantitatively reacting fluorenyllithium with 6.6-dimethylfulvene [39,40] to give the substituted cyclopentadienyl anion and then by further reacting the anion with half an equivalent of zirconium tetrachloride or one equivalent of cyclopentadienyl zirconium trichloride [46] (Fig. 8).

Fig. 9 shows the unbridged zirconocene dichloride complexes containing CH-acidic substituents that were synthesized using one of the two synthesis methods described.

The bridged metallocene dichloride complex **25** was synthesized analogous to the unbridged metallocene complexes. The bridged ligand precursor **16** was reacted with two equivalents of *n*-butyllithium and subsequently with one equivalent of zirconium tetrachloride (Fig. 10).

The reaction of ligand precursor **16** with three equivalents of *n*-butyllithium and subsequently with one equivalent of zirconium tetrachloride led to a mixture of products that could not be isolated. Obviously, the coordination of all three π-ligands to zirconium was not achieved. Presumably, sterical factors prohibit the coordination of the fluorenyl group. Metallocene

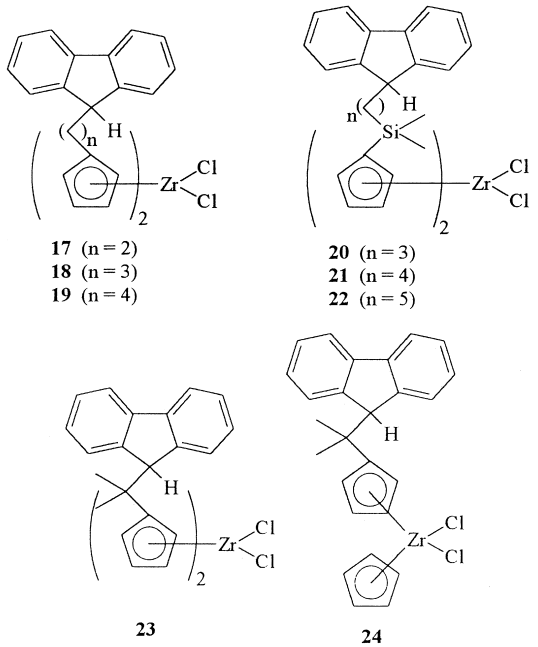
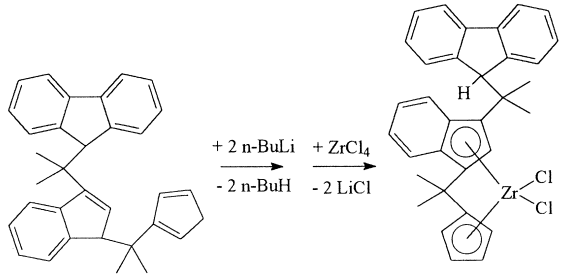



Fig. 9. Overview of the synthesized, unbridged zirconocene dichloride complexes **17**–**24**.




16 25

Fig. 10. Synthesis of the bridged zirconocene dichloride complex **25**.

complexes with one or even two σ-bonded fluorenyl ligands are known [47]. Such complexes, however, are unbridged metallocene derivatives.

### *2.4. Spectroscopic characterization of metallocene dichloride complexes* **17–25**

The metallocene dichloride complexes **17–25** were characterized by $^{1}$H, $^{13}$C and $^{29}$Si NMR spectroscopy. The spectroscopic data are listed in Table 2. The mass spectral data are found in Section 3.

### *2.5. Polymerization of ethylene*

The synthesized metallocene complexes, activated with MAO, were used for homogeneous ethylene polymerization. The complexes were activated by adding a 3000-fold molar excess of MAO. The formation of an active catalyst system was indicated by a color change. In the following paragraphs, the polymerization results for metallocene dichloride complexes **20–22** are discussed as representative examples of the catalysts formed from all the substituted zirconocene complexes presented in this paper. The polymerization activities of the activated metallocene complexes, the molecular weights $\bar{M}_\eta$, the fusion enthalpies $\Delta H_m$, the melting temperatures $T_m$ and the degrees of crystallinity, $\alpha$, of the resulting polymers are listed in Table 3.

For the metallocene dichloride complexes **20–22**, no correlation was found between ethylene polymerization activity and the length of the silylenalkylidene bridge (spacer) (Fig. 11).

The steric influence of the bulky fluorenyl group is apparently not the only way in which the fluorenyl group interacts with the catalytically active metal center. In a similar manner also terminal phenyl groups in allyl substituents of bis(cyclopentadienyl)zirconium dichloride complexes can cause such an effect [48]. The acidic character of the hydrogen in position 9 of the terminal fluorenyl group may also contribute to the observed polymerization results. The acidic hydrogen can be abstracted not only with *n*-butyllithium (see complex synthesis) but also with MAO. Depending on the spacer chain length, the formed fluorenyl anion possibly interacts intramolecularly or intermolecularly with a zirconium center. This could have great impact on the polymerization behavior of the respective catalyst and would explain the singular polymerization activities of the metallocene complexes **20–22** and molecular weights of the produced polyethylenes (700 g/mol for **20** and **21**; 260 g/mol for **22**).

## 3. Experimental

### *3.1. NMR spectroscopy*

The Bruker NMR instruments ARX 250, AC 300 and DRX 500 were available for recording of the NMR spectra. The organometallic samples were placed in the NMR tubes under argon and measured at 25°C. The chemical shifts in $^{1}$H NMR spectra were referred 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 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 with flame ionization detector. The J&W fused silica column was 30 m long,

Table 2
$^{1}H$, $^{13}C$ and $^{29}Si$ NMR data of the metallocene dichloride complexes **17–25** containing CH-acidic substituents

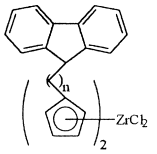
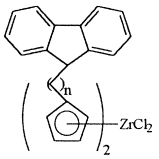
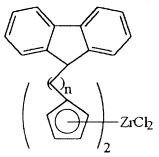
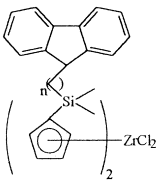
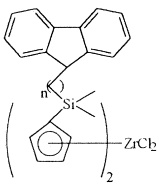
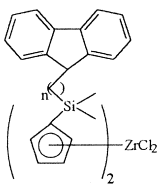
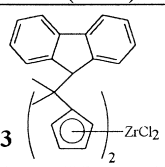
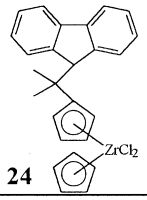
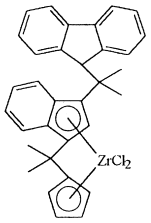
| | $^{1}H$ NMR[a] [J(H,H) in Hz] | $^{13}C$ NMR[b] | $^{29}Si$ NMR[c] |
|---|---|---|---|
|  **17** (n = 2) | 7.67 (d, 4H) [6.9], 7.42 (d, 4H) [6.9], 7.29 (m, 8H), 6.03 (m, 4H), 5.94 (m, 4H), 3.95 (t, 2H) [6.1], 2.40 (m, 4H), 2.19 (m, 4H) | ($C_q$): 146.6, 141.1, 134.2 (CH):127.1, 126.9, 124.4, 119.8, 116.1, 112.1, 47.0 ($CH_2$): 32.6, 25.9 | |
|  **18** (n = 3) | 7.65 (d, 4H)[7.7], 7.39 (d, 4H) [7.5], 7.30-7.16 (m, 8H), 6.04 (m, 4H), 5.92 (m, 4H), 3.92 (m, 2H), 2.47-2.40 (m,4H), 2.03-1.96 (m, 4H), 1.22-1.16 (m, 4H) | ($C_q$): 147.0, 141.1, 134.3 (CH):126.9, 126.9, 124.3, 119.8, 116.5, 112.4, 47.1 ($CH_2$): 32.4, 30.3, 26.3 | |
|  **19** (n = 4) | 7.74-7.71 (d, 4H) [7.5] 7.47-7.45 (m, 4H), 7.39-7.22 (m, 8H), 6.19-5.96 (m, 8H), 3.97-3.95 (m, 2H), 2.11-2.05 (m, 4H), 1.49-1.42 (m, 4H), 1. 24-1.18 (m, 8H) | ($C_q$): 147.3, 141.1, 134.2 (CH): 126.8, 126.0, 124.3, 119.8, 116.5, 112.2, 47.3 ($CH_2$): 32.6, 30.8, 29.8, 25.2 | |
|  **20** (n = 3) | 7.75 (d, 4H), [7.17], 7.4 (m, 4H), 7.34-7.27 (m, 8H), 6.57-6.44 (m, 8H), 3.95 (t, 2H), [5.0], 2.00-1.91 (m, 4H), 1.30-0.71 (m, 8H), 0.26 (s, 6H) | ($C_q$):147.6, 141.0, 134.4 (CH):126.8, 126.7, 125.8, 124.4, 119.8, 115.9, 47.3 ($CH_2$): 37.0, 20.5, 16.9 ($CH_3$): -2.1 | -4.8 |
|  **21** (n = 4) | 7.69(d, 4H) [6,5], 7.42 (m, 4H), 7.30-7.21 (m, 8H), 6.50-6.36 (m, 8H), 3.92-3.88 (m, 2H), 1.95-1.89 (m, 4H), 1.21-1.11(m, 12H), -0.21 (s, 6H) | ($C_q$): 147.5, 141.1, 134.4 (CH): 126.9, 126.8, 125.7, 124.3, 119.7, 115.8, 47.3, ($CH_2$): 32.6, 29.4, 24.3, 16.2 ($CH_3$): -0.1, -2.6 | -4.9 |
|  **22** (n = 5) | 7.77 (d, 4H) [6.7], 7.53 (d, 4H), [7.5], 7.38-7.32 (m, 8H), 6.61-6.43 (m, 8H), 4.00-3.91 (m, 2H), 2.01-1.97(m, 4H), 1.35-1.21(m, 4H), 0,28 (s, 3H), 0.12-0.03 (m, 4H) | ($C_q$): 147.5, 141.0, 134.5 (CH): 126.8, 126.7, 125.7, 124.3, 119.7, 115.8, 47.4 ($CH_2$): 33.7, 32.9, 25.4, 23.4, 16.6 ($CH_3$): -2.2 | -4.6 |
|  **23** | 7.59 (d, 4H) [7.4], 7.28 (m, 4H), 7.10 (m, 4H), 6.90 (d, 4H) [7.4], 6.23 (s, 8H), 3.89 (s, 2H), 1.42 (s, 12H) | ($C_q$): 144.7, 142.1, 140.9, 40.8 (CH): 127.3, 126.4, 125.9, 119.3, 118.8, 110.0, 61.3 ($CH_3$): 25.0 | |

Table 2 (*Continued*)

| | | | |
|---|---|---|---|
|  24 | 7.63 (d, 2H) [7.4], 7.36 (m, 2H), 7.16 (m, 2H), 6.95 (d, 2H) [7.4], 6.94 (m, 2H),6.30 (m, 2H), 6.28 (s, 5H), 3.94 (s, 1H), 1.46 (s, 6H) | ($C_q$): 144.7, 142.1, 140.9, 40.8<br>(CH): 127.3, 126.7, 126.3, 120.4, 119.4, 118.7, 118.0, 111.8, 111.0, 61.2<br>($CH_3$): 25.0 | |
|  25 | 8.16 (d, 1H) [4.5], 7.87 (d, 1H) [4.5], 7.64 (d, 1H) [4.5], 7.56 (d, 1H) [4.5], 7.49 (d, 1H) [4.5], 7.28 (t, 1H) [4.5], 7.23 (t, 1H) [4.5], 7.16 (t, 1H) [4.5], 7.09 (d, 1H) [4.5], 6.96 (t, 1H) [4.5], 6.72 (t, 1H) [4.5], 6.33 (m, 2H), 5.78 (m, 1H), 5.51 (s, 1H), 5.44 (m, 1H), 5.13 (d, 1H) [4.5], 2.21 (s, 3H), 2.14 (s, 3H), 1.67 (s, 3H), 0.57 (s, 3H) | ($C_q$): 144.8, 144.3, 142.3, 141.9, 132.8, 130.3, 119.9, 118.3, 98.6, 41.1, 38.6<br>(CH): 127.2, 127.0, 126.5, 126.2, 126.0, 125.9, 125.8, 125.2, 124.3, 121.4, 120.9, 119.5, 118.9, 114.1, 107.5, 102.3, 57.9<br>($CH_3$): 27.5, 26.6, 26.0, 19.3 | |

[a] 25°C, in chloroform-$d_1$ $\delta$ [ppm] rel. chloroform (7.24).
[b] 25°C, in chloroform-$d_1$ $\delta$ [ppm] rel. chloroform-$d_1$ (77.0).
[c] 25°C, in chloroform-$d_1$ $\delta$ [ppm] rel. $TMS_{ext.}$ (0.0).

had a diameter of 0.32 mm and had 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)
Plateau phase: 310°C (15 min)

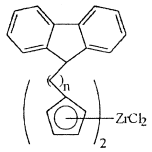
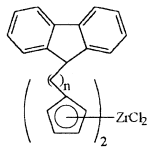
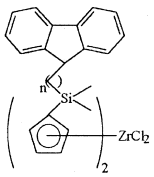
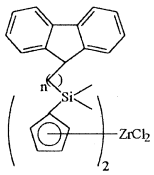
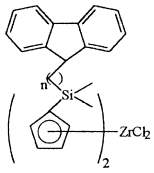
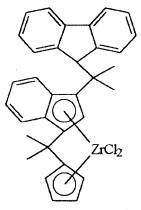
### *3.4. General synthesis procedure for the 1-bromo-ω-(9-fluorenyl)alkanes* **1–3**

Fluorenyllithium, 10.4 g (60.2 mmol), was added in portions to 100.0 mmol of the corresponding α,ω-dibromoalkane in 200 ml *n*-pentane, and the reaction mixture was stirred for 24 h at room temperature. Subsequently, the reaction mixture was filtered over sodium sulfate and crystallized at −20°C. The products precipitated as colorless, crystalline solids in 40–50% yields. MS: **1**: m/e=272 ($M^+$), **2**: m/e=286 ($M^+$), **3**: m/e=301 ($M^+$); GC: **1**: 1880 s, **2**: 2100 s, **3**: 2214 s.

### *3.5. General synthesis procedure for the ω-alkenylfluorene derivatives* **4–6**

Fluorene, 6.0 g (36.1 mmol), was dissolved in 150 ml diethylether and slowly mixed with 22.6 ml (36.1 mmol) *n*-butyllithium (1.6 M in *n*-hexane) at room temperature. The reaction mixture was stirred for 4 h at room temperature. An equivalent amount of the respective ω-alkenyl bromide derivative was added at −78°C. Subsequently, the reaction mixture was stirred overnight at room temperature 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. The respective ω-alkenyl substituted fluorene derivatives were obtained as colorless oils. The yields were 85–95%. MS: **4**: m/e=206 ($M^+$), **5**: m/e=220 ($M^+$), **6**: m/e=234 ($M^+$); GC: **4**: 1647 s, **5**: 1838 s, **6**: 1970 s.

Table 3
Overview of the polymerization experiments[a] and polymer analytic results

| | Activity[b] kg PE/g Zr·h | $\bar{M}_\eta$[c] [kg/mol] | DSC $T_m$ [°C] $\Delta H_m$ [J/g] $\alpha$[%][d] |
|---|---|---|---|
|  **18** (n= 3) | 162.0 | 540 | 138.3<br>122.0<br>42.1 |
|  **19** (n = 4) | 213.0 | 290 | 142.5<br>146.1<br>50.4 |
|  **20** (n = 3) | 208.0 | 700 | 139.1<br>146.0<br>50.3 |
|  **21** (n = 4) | 50.1 | 700 | 134.8<br>141.3<br>48.7 |
|  **22** (n = 5) | 768.2 | 260 | 137.1<br>143.9<br>49.6 |
|  **25** | 20.1 | not determined | not determined |

[a] $T_p$=60°C; solvent: 500 ml *n*-pentane; 10 bar ethylene pressure.
[b] [M]/[Al]=1:300.
[c] Intrinsic viscosity.
[d] Degree of crystallinity relative to the melting enthalpy of 100% crystalline polyethylene.

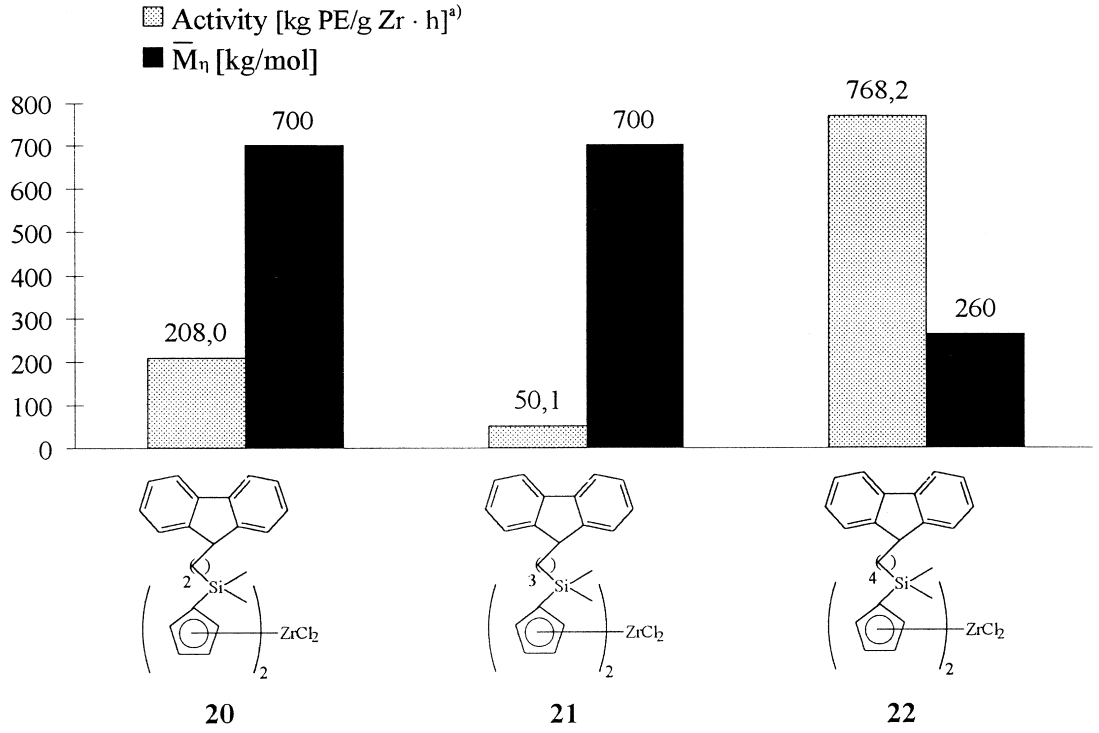



Fig. 11. Comparison of the polymerization activities for the metallocene dichloride complexes **20**–**22** and the molecular weights of the obtained polyethylenes. (a) Homogeneous ethylene polymerization after the activation with MAO (Zr:Al=1:3000), in *n*-pentane, at 60°C.

### *3.6. General synthesis procedure for the 1-fluorenyl-ω-(dimethylchlorosilyl)alkanes* **7**–***9***

20.0 mmol of the corresponding ω-alkenyl fluorene was dissolved in 15.00 ml (139.5 mmol) chlorodimethylsilane at room temperature and mixed with approx. 1 ml hexachloroplatinic acid. The reaction mixture was stirred overnight at room temperature and the solvent evaporated in vacuo. The 1-fluorenyl-ω-(dimethylchlorosilyl)alkanes **7**–**9** were formed quantitatively as colorless, crystalline solids. MS: **7**: m/e=250 ($M^+$), **8**: m/e=264 ($M^+$), **9**: m/e=278 ($M^+$).

### *3.7. General synthesis procedure for the 1-fluorenyl-ω-cyclopentadienyl alkanes* **10*a*,*b*–12*a*,*b***

Cyclopentadiene, 1.7 ml (33.0 mmol), was dissolved in 100 ml tetrahydrofuran 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 room temperature and mixed with 20 ml hexamethyl phosphoric triamide. At −78°C, 33.0 mmol of the corresponding 1-bromo-ω-fluorenyl alkane was added in small portions and stirred for additional 3 h at room temperature. The reaction mixture was hydrolyzed with a 5% ammonium chloride solution, extracted with diethylether 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. The products crystallized at −20°C as colorless crystals in 70–80% yields. MS: **10a**,**b**: m/e=242 ($M^+$), **11a**,**b**: m/e=256 ($M^+$), **12a**,**b**: m/e=270 ($M^+$); GC: **10a**,**b**: 2196 s, **11a**,**b**: 2331 s, **12a**,**b**: 2393 s.

### *3.8. General synthesis procedure for the 1-fluorenyl-ω-(dimethylcyclopentadienylsilyl)alkanes* **13*a*,*b*–15*a*,*b***

Cyclopentadiene, 1.7 ml (33.0 mmol), was dissolved in 100 ml diethylether at −78°C, mixed

with 20.6 ml (33.0 mmol) *n*-butyllithium (1.6 M in *n*-hexane) and the reaction mixture stirred for 4 h at room temperature. At −78°C, 33.0 mmol of the corresponding 1-fluorenyl-ω-(dimethylchlorosilyl)alkane was added and the reaction mixture stirred for 3 h at room temperature. Subsequently, the mixture was hydrolyzed with 50 ml 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. The products were obtained as colorless oils in 85–95% yields. MS: **13a**,**b**: m/e=304 ($M^+$), **14a**,**b**: m/e=318 ($M^+$), **15a**,**b**: m/e=332 ($M^+$); GC: **13a**,**b**: 2531 s, **14a**,**b**: 2632 s, **15a**,**b**: 2730 s.

### *3.9. 1-((9-fluorenyl)isopropylidene)-3-((1-cyclopentadienyl)isopropylidene)indene (**16**)*

Fluorene, 3.3 g (20.0 mmol), was dissolved in 100 ml diethylether and mixed with 12.5 ml (20.0 mmol) *n*-butyllithium (1.6 M in *n*-hexane) at room temperature. The reaction mixture was stirred for 6 h, then 3.1 g (20.0 mmol) 6,6-dimethylbenzofulvene was added at −78°C and the mixture was stirred for 8 h at room temperature. Then, 2.4 ml (20.0 mmol) 6,6-dimethylfulvene was added at −78°C, the reaction mixture was stirred for 4 h at room temperature and then 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, filtered over silica gel and crystallized at −20°C. The yields were 60%. GC: 3320 s; MS: m/e=429 ($M^+$).

### *3.10. General synthesis procedure for the unbridged metallocene dichloride complexes* **17**–***22***

The corresponding cyclopentadiene derivative, 10.0 mmol, was dissolved in 100 ml diethylether and a solution of 6.3 ml (10.0 mmol) *n*-butyllithium (1.6 M in *n*-hexane) in 100 ml diethylether was added dropwise at 0°C. After the *n*-butyllithium addition was completed, the mixture was stirred for 2 h. Then, 1.2 g (5.0 mmol) zirconium tetrachloride was added to the reaction mixture at −78°C, and it was stirred overnight at room temperature. The solvent was evaporated in vacuo, and the residue washed twice with 50 ml *n*-pentane. The colorless-to-yellow solids were extracted with dichloromethane. The solution was filtered over sodium sulfate and the solvent evaporated. The yields were 70–80%. MS: **17**: m/e=676 ($M^+$), **18**: m/e=704 ($M^+$), **19**: m/e=734 ($M^+$), **20**: m/e=820 ($M^+$), **21**: m/e=848, **22**: m/e=876 ($M^+$).

### *3.11. General synthesis procedure for the unbridged metallocene dichloride complexes* **23** *and* ***24***

Fluorene, 1.7 g (10.0 mmol), was dissolved in 100 ml diethylether and mixed with 6.3 ml (10.0 mmol) *n*-butyllithium (1.6 M in *n*-hexane) at room temperature (indene at −78°C). The reaction mixture was stirred for 6 h. Then, 1.2 ml (10.0 mmol) 6,6-dimethylfulvene was added at −78°C, and the reaction mixture was stirred for 4 h at room temperature. At −78°C, 1.2 g (5.0 mmol) zirconium tetrachloride or 2.3 g (10.0 mmol) cyclopentadienyl zirconium trichloride was added to the reaction mixture, and it was stirred overnight at room temperature. The solvent was evaporated in vacuo and the residue washed twice with 50 ml *n*-pentane. The colorless solid was extracted with dichloromethane, the solution filtered over sodium sulfate and the solvent evaporated. The yields were 70–80%. MS: **23**: m/e=732 ($M^+$); **24**: m/e=499 ($M^+$).

### *3.12. Synthesis of the bridged metallocene dichloride complex* ***25***

Ligand precursor **16**, 10.0 mmol, was dissolved in 150 ml diethylether, and a solution of 12.5 ml (20.0 mmol) *n*-butyllithium (1.6 M in *n*-hexane) in 150 ml diethylether was added dropwise at 0°C. After the *n*-butyllithium addition was completed, the mixture was stirred for 2 h. Then, 2.3 g (10.0 mmol) zirconium tetrachloride was added to the reaction mixture 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 colorless residue was extracted with dichloromethane, the solution filtered over sodium sulfate and the solvent evaporated. The yields were approx. 80%. MS: **25**: m/e=565 ($M^+$).

### *3.13. Activation of the metallocene complexes with MAO*

The metallocene complex, 10–15 mg, was activated with MAO (30% in toluene) (metal/Al=1:3000). A

catalyst solution that contained 0.5–1.5 mg metallocene complex was used within 1 h for homopolymerization.

### 3.14. Homopolymerization of ethylene

500 ml *n*-pentane 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 (to compensate in part the highly exothermic polymerization reaction). The mixture was stirred for 1 h at 60(±2)°C and the reaction terminated by releasing the pressure in the reactor. The obtained polymer was dried in vacuo.

### 3.15. Characterization of the polyethylene samples

#### 3.15.1. 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 was fused into standard aluminum pans (∅ 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. 429.78 K). The fusion enthalpy of indium ($H_m$=28.45 J/g) was used for calibration.

#### 3.15.2. Viscosimetry

The viscosity average molecular weight of the polyethylene samples was determined using an Ubbelohde precision capillary viscometer in *cis*/*trans* decalin at 135±0.1°C. For the measurements, 50 mg polymer was 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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