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C_1-Bridged fluorenylidene cyclopentadienylidene complexes of the type $(C_{13}H_8{-}CR^1R^2{-}C_5H_3R)ZrCl_2$ (R^1, R^2 = alkyl, phenyl, alkenyl; R = H, alkyl, alkenyl, substituted silyl) as catalyst precursors for the polymerization of ethylene and propylene

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Abstract

The synthesis and characterization of 14 new C_1-bridged fluorenylidene cyclopentadienylidene complexes of zirconium is described. After activation with methylaluminoxane (MAO), these metallocene complexes can be used for the polymerization of ethylene and propylene. Various substituents in the bridge and in position 3 of the cyclopentadienylidene ligand have a strong influence on the activity of the corresponding catalysts and the molecular weights of the formed polyolefins. The bulkiness of the substituents in position 3 of the cyclopentadienylidene ring determines the extent of the stereospecific polymerization of propylene. Substituents can be selected that produce hemitactic, syndiotactic or isotactic polypropylenes and/or the corresponding block copolymers. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Catalysis; Polymerization; Metallocene complexes; Zirconium; Polyethylene; Polypropylene

1. Introduction

The C_1-bridged fluorenylidene cyclopentadienylidene complex $(C_{13}H_8{-}CMe_2{-}C_5H_4)ZrCl_2$ is regarded as the classical metallocene catalyst precursor for the synthesis of syndiotactic polypropylene [1–4]. Recently we showed that substitutions on the fluorenylidene ligand [5–7] or on the bridging carbon atom [6,8] strongly influence the catalyst activity as well as the molecular weight of the produced syndiotactic polypropylene. Substituents in position 3 of the cyclopentadienylidene ligand of these complexes play key roles in determining the stereoselectivity of polypropylenes produced with the respective catalysts [9–12]. In this paper we report the synthesis and the characterization of new C_1-bridged fluorenylidene cyclopentadienylidene complexes. We have investigated the influence of various substituents in the bridge and substituents in position 3 of the cyclopentadienylidene moiety on the polymerization of ethylene and propylene.

2. Results and discussion

2.1. Synthesis of C_1-bridged ligand precursors of the type $C_{13}H_9{-}CR^1R^2{-}C_5H_4R$ (R^1, R^2 = alkyl, phenyl, alkenyl; R = H, alkyl, alkenyl, substituted silyl)

The synthesis of C_1-bridged ligand precursors was performed with the 'fulvene method' [13,14]. According to this method, the lithium salts of fluorene, substituted fluorenes, indene or substituted indenes are reacted with a fulvene or a substituted fulvene. The anion adds nucleophilic to the exocyclic double bond of the fulvene to yield anion **A**. After hydrolysis, the corresponding neutral ligand precursor **B** is obtained. This method has

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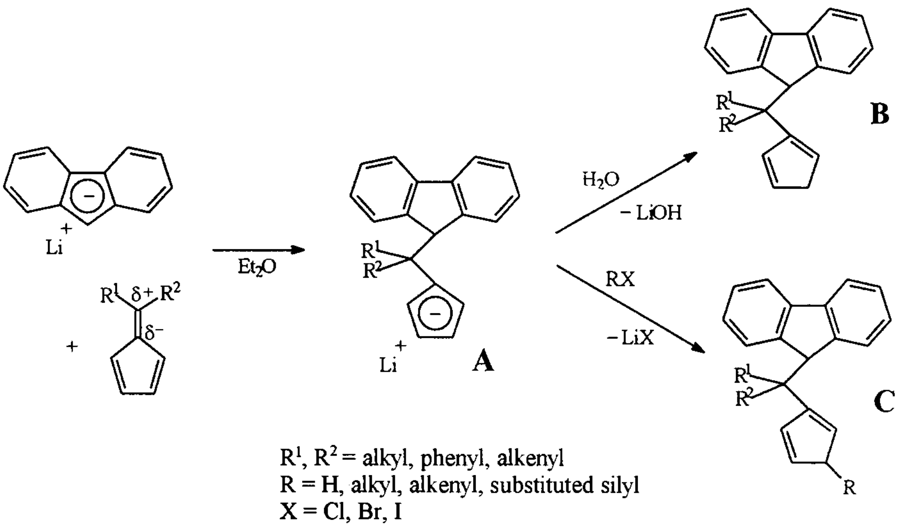


Scheme 1. General synthesis of the ligand precursors of the type $C_{13}H_9$–CR^1R^2–C_5H_4R (R^1, R^2 = alkyl, phenyl; R = H, alkyl, alkenyl, substituted silyl).

unlimited application, if the acidity of the cyclopentadiene derivative and the fulvene are higher than that of the anion used ($pK_{a_{FluH}}$ ca. 22, $pK_{a_{IndH}}$ ca. 19, $pK_{a_{CpH}}$ ca. 15).

Reactive halocarbons and trialkylchlorosilanes can be reacted with the cyclopentadienyl anion **A**. This high yield one-pot synthesis route allows the substitution of position 3 of the cyclopentadienyl ring to yield the neutral ligand precursor **C** (Scheme 1).

The substituted C_1-bridged ligand precursors **1/1*–13/13*** were obtained by reacting fluorenyllithium with 6,6-dimethylfulvene, 3-(3-butenyl)-6,6-dimethylfulvene, 6-(3-butenyl)-6-methylfulvene, 6,6-tetramethylene fulvene, 6,6-pentamethylene fulvene, 6,6-hexamethylene fulvene, or 6,6-heptamethylene fulvene and reacting this product with water, methyliodide, trimethylchlorosilane or allyldimethylchlorosilane (Fig. 1).

The large rings of 6,6-undecamethylene fulvene and 6,6-tetradecamethylene fulvene prevent the reaction of these compounds with fluorenyllithium. Even the addition of hexamethylphosphoric triamide (HMPA) to the reaction mixtures did not give the desired products. The sterical demand of these large rings completely inhibits the nucleophilic addition of the fluorenyl anion (Table 1).

2.2. Synthesis of the C_1-bridged ansa-metallocene dichloride complexes ($C_{13}H_8$–CR^1R^2–C_5H_3R)$ZrCl_2$ (R^1, R^2 = alkyl, phenyl, alkenyl; R = H, alkyl, alkenyl, substituted silyl) (**14–26/26***)

Bridged metallocene dichloride complexes were synthesized according to known procedures [15,16]. The selected ligand precursor is reacted with two equivalents *n*-butyllithium in diethyl ether to form the dianion. In a second step, the dianion is reacted with $ZrCl_4$ to form the ansa-metallocene dichloride complex (Scheme 2) [17,19,20].

Starting with the appropriate ligand precursors, the ansa-metallocene dichloride complexes listed in Fig. 2 and Table 2 were synthesized. The complexes indicated with a star (*) are diastereomers.

We have recently demonstrated [22] that the fluorenylidene ligand in C_1-bridged metallocene complexes is η^3 bonded in solution. The ^{13}C-NMR chemical shift of the quaternary carbon 9 of the fluorenylidene ligand is indicative of the bonding mode. The ^{13}C-NMR shifts for these carbon atoms in the C_1-bridged metallocene complexes reported here are around $\delta = 78$ ppm while the corresponding shifts of C_1-bridged η^5-bonded fluorenylidene complexes are found between $\delta = 105$–115 ppm [18]. In the ^{1}H-NMR spectrum of **23** (Fig. 3a), the individual signal groups are separated. The trimethylsilyl group shows a signal at $\delta = 0.10$ ppm. The signals for the 12 protons of the six methylene groups of the cycloheptylidene ring are found at $\delta = 3.41$ (2H), 2.36 (2H), 2.04 (4H) and 1.77 ppm (4H).

The three protons of the cyclopentadienylidene ligand ($\delta = 6.34$, 5.98 and 5.67 ppm) appear as virtual triplets. The ^{1}H-NMR signals for the fluorenylidene hydrogen atoms are found in the region of $\delta = 7.20$–8.10 ppm. The distance of the two non-equivalent benzo rings of the fluorenylidene ligand from the center of asymmetry of the molecule results in similar chemical shifts. Therefore, four signal groups are found, and two of these signal groups overlap (Fig. 3a, Fig. 3b).

The *J*-modulated ^{13}C-NMR spectrum of **23** (Fig. 3b) displays the expected signals for the nine quaternary, 11 tertiary and the six methylene carbon atoms, as well as the signal for the trimethylsilyl group ($\delta = -1.0$ ppm). Due to the asymmetry of the complex, a separate signal

Table 1
NMR data of the C_1-bridged ligand precursors **1/1*–13/13***

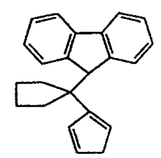
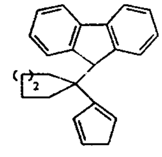
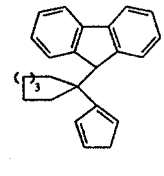
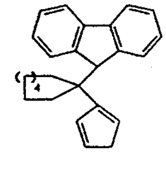
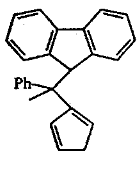
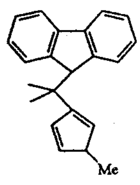
	^{1}H-NMR$^{a)}$	^{13}C-NMR$^{a)}$
 **1/1***	7.81 (d, $^{3}J(^{1}H,^{1}H)$ 7.5 Hz, 2H), 7.60-7.57 (2H)$^{b)}$, 7.47-7.20 (4H)$^{b)}$, 6.24-6.20 (m, 1H, CH_{cp}), 6.09-6.06 (m, 1H, CH_{cp}), 5.78 (m, 1H, CH_{cp}), 3.93 (s, 1H, CH_{flu}), 2.81 (d, $^{3}J(^{1}H,^{1}H)$ 1.4 Hz, 1H), 2.70 (s, 1H), 2.20 (m, 2H, CH_2),1.99-1.54 (6H, CH_2)$^{b)}$	151.5, 150.1, 146.1, 146.0, 141.9, 141.7 (C_q), 133.2, 132.6, 131.4, 130.9, 127.9, 126.9, 126.9, 126.8, 126.1, 126.0, 125.9, 125.8, 119.4, 119.3 (CH), 58.1, 56.1 ($CH_{flu\text{-}9}$), 41.5, 40.7 (C_q), 38.2, 37.0, 36.1, 23.4, 23.3 (CH_2)
 **2/2***	7.64 (d, $^{3}J(^{1}H,^{1}H)$ 7.5 Hz, 2H, CH_{flu}), 7.33-7.11 (6H, CH_{flu})$^{b)}$, 6.49-6.28 (2H, CH_{cp})$^{b)}$, 5.87-5.82 (m, 1H, CH_{cp}), 3.95 (s, 1H, CH_{flu}), 2.98 (d, $^{3}J(^{1}H,^{1}H)$ 1.4 Hz, 1H), 2.71 (s, 1H), 1.92-1,87 (m, 2H, CH_2), 1.70-1.27 (8H, CH_2)$^{b)}$	151.2, 149.3, 145.2, 145.1, 142.2 (C_q), 133.5, 132.8, 131.7, 130.9, 130.4, 129.4, 126.9, 126.8, 126.7, 126.6, 125.6, 125.5, 119.2, 119.1 (CH), 58.9, 57.4 ($CH_{flu\text{-}9}$), 44.2 (CH_2), 41.0, 40.8 (C_q), 33.7, 32.5, 26.2, 26.1, 22.4, 22.3 (CH_2)
 **3/3***	7.78 (d, $^{3}J(^{1}H,^{1}H)$ 7.2 Hz, 2H), 7.33-7.27 (2H)$^{b)}$, 7.23-7.08 (4H)$^{b)}$, 6.79 (m), 6.58 (m), 6.48 (m), 6.42 (m), 6.08 (s), 5.93 (s), 4.02 (m, 1H, CH_{flu}), 3.08 (s, 1H), 3.03 (s, 1H), 1.83-1.77 (m, 2H, CH_2), 1.64-1.57 (m, 2H, CH_2), 1.45-1.31 (8H, CH_2)$^{b)}$	151.2, 149.3, 145.2, 145.1, 142.2 (C_q), 133.7, 133.6, 131.8, 130.9, 129.5, 127.7, 126.8, 126.8, 126.5, 126.4, 125.7, 125.6, 119.1, 119.0 (CH), 59.6, 57.6 ($CH_{flu\text{-}9}$), 40.7 (C_q), 34.1, 28.2, 28.1, 23.1, 22.8 (CH_2)
 **4/4***	7.81 (d, $^{3}J(^{1}H,^{1}H)$ 7.0 Hz, 2H), 7.66 (d, $^{3}J(^{1}H,^{1}H)$ 7.6 Hz, 1H), 7.56 (d, $^{3}J(^{1}H,^{1}H)$ 7.4 Hz, 2H), 7.39-7.13 (3H)$^{b)}$, 6.71 (m), 6.54 (m), 5.88 (m), 4.05 (s, 1H), 3.91 (s, 1H), 3.04 (d, $^{4}J(^{1}H,^{1}H)$ 1.4 Hz, 1H), 1.91-1.88 (4H)$^{d)}$, 1.44-1.29 (10H)$^{b)}$	151.3, 145.5, 143.1, 142.1, 141.6 (C_q), 133.6, 133.4, 128.1, 126.8, 126.7, 126.6, 126.5, 126.4, 125.6, 125.0, 119.8, 119.2 (CH), 57.2, 54.9 ($CH_{flu\text{-}9}$), 40.8 (C_q), 36.9, 31.0, 28.6, 25.0, 23.2 (CH_2)
 **5/5***	7.74-7.70 (4H)$^{b)}$, 7.64-7.60 (4H)$^{b)}$, 7.42-7.27 (10H)$^{b)}$, 7.19-7.07 (4H)$^{b)}$, 6.96-6.83 (4H)$^{b)}$, 6.56 (2H)$^{b)}$, 6.50 (m), 6.22-6.06 (m), 4.98 (s, 2H), 3.10-3.03 (4H)$^{b)}$, 1.10 (s, 3H), 1.03 (s, 3H)	155.5, 153.3, 147.4, 146.7, 145.2, 142.2, 142.2 (C_q), 134.0, 133.9, 131.9, 131.9, 128.2, 128.0, 127.5, 127.4, 127.1, 127.0, 127.0, 126.6, 126.3, 126.3, 126.3, 126.2, 126.1, 126.1, 126.0, 125.8, 119.3, 119.2, 119.2 (CH), 56.2, 54.9 ($CH_{flu\text{-}9}$), 47.7, 46.5, 41.9, 40.8 (C_q), 18.7, 18.4 (CH_3)
 **6/6***	7.69 (d, $^{3}J(^{1}H,^{1}H)$ 7.7 Hz, 2H), 7.33-7.27 (2H)$^{b)}$, 7.22-7.10 (4H)$^{b)}$, 6.52 (m, 1H), 6.08 (m), 5.94 (m), 5.89 (m), 5.65 (m, 1H), 4.11 (s, 1H), 3.05 (s, 1H), 2.94 (s, 1H), 2.17 (d, $^{3}J(^{1}H,^{1}H)$ 1.5 Hz, 3H, CH_3), 0.99 (s, 6H, CH_3)	145.3, 143.5, 141.9 (C_q), 128.0, 126.8, 126.2, 125.8, 122.2, 119.2 (CH), 55.4 ($CH_{flu\text{-}9}$), 44.0, 39.8 (C_q), 24.2, 16.5 (CH_3)$^{c)}$

Table 1 (Continued)

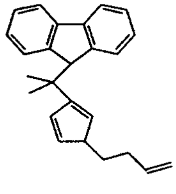
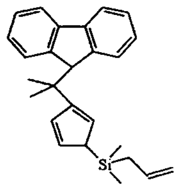
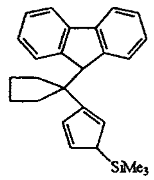
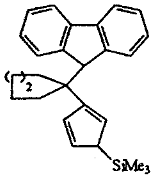
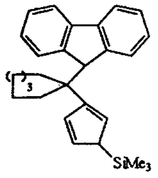
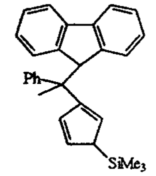
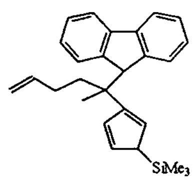
	^{1}H-NMR[a]	^{13}C-NMR[a]
 **7/7***	7.84 (d, $^3J(^1H,^1H)$ 7.5 Hz, 2H), 7.49-7.42 (3H)[b], 7.36-7.28 (3H)[b], 6.70 (m), 6.16 (m), 6.07 (m, 1H, $=C\mathbf{H}$), 5.85 (m), 5.30-5.16 (m, 2H, $=C\mathbf{H}_2$), 4.26, 4.19, 3.97 (3s, 1H), 3.25, 3.18, 3.11 (3s, 1H), 2.79-2.48 (4H)[b], 1.20 (s, 3H, $C\mathbf{H}_3$), 1.19 (s, 3H, $C\mathbf{H}_3$)	158.0, 155.3, 154.8, 150.0, 146.6, 146.3, 145.5, 145.4, 142.1, 142.1 ($\mathbf{C}_q$), 138.6, 138.5 ($=CH$), 129.1, 127.6, 127.2, 127.1, 127.0, 126.8, 126.8, 126.5, 126.4, 126.1, 126.1, 126.0, 125.1, 124.9, 124.4, 123.9, 122.5, 122.2, 119.9, 119.4, 119.4 (CH), 114.9, 114.8 ($=\mathbf{C}H_2$), 57.9, 55.7 ($\mathbf{C}H_{flu\text{-}9}$), 42.5. 42.4, 40.5, 40.5, 40.3, 39.5, 37.0, 34.1, 34.0, 33.2. 32.7, 30.6. 30.4, 29.7 ($\mathbf{C}H_2$ and $\mathbf{C}_q$), 25.7, 24.4 (CH_3)
 **8/8***[d]	7.61-7.54 (m, 2H), 7.44 (d, $^3J(^1H,^1H)$ 7.5 Hz, 1H), 7.26-7.09 (3H)[b], 7.04-7.01 (m, 1H), 6.94-6.88 (m, 1H), 6.79 (m, 1H), 6.69 (m, 1H), 6.51 (m, 1H), 5.88 (m, 1H), 5.70 (m, 1H, $=C\mathbf{H}$), 4.82-4.72 (m, 2H, $=CH_2$), 4.10 (s. 1H), 3.31 (s, 1H), 1.44 (d, $^3J(^1H,^1H)$ 8.1 Hz, 2H). 1.31 (s, 3H, $C\mathbf{H}_3$), 0.57 (s, 3H, $C\mathbf{H}_3$), -0.16 (s, 6H, $C\mathbf{H}_3$)	154.2, 145.6, 145.5, 142.2, 139.8 ($\mathbf{C}_q$), 134.6 ($=\mathbf{C}H$), 133.9, 130.8, 126.9, 126.7, 126.4, 126.1, 126.0, 125.9, 125.8, 125.7, 119.4, 119.3, 119.2. 119.0 ($\mathbf{C}H$), 113.4 ($=\mathbf{C}H_2$), 56.1, 55.9 ($\mathbf{C}H_{flu\text{-}9}$), 39.5 ($\mathbf{C}_q$), 28.9 ($\mathbf{C}H_3$), 23.4 ($\mathbf{C}H_2$), 22.0, -4.3, -4.4 ($\mathbf{C}H_3$)
 **9/9***[e]	7.78-7.74 (2H)[b], 7.67-7.45 (3H)[b], 7.37-7.24 (3H)[b], 6.14 (m, 1H), 6.03 (m, 1H), 5.87 (m, 1H), 4.13 (s, 1H), 3.90 (s, 1H), 2.47-2.35 (m, 2H, $C\mathbf{H}_2$), 2.25-2.09 (m, 2H, $C\mathbf{H}_2$), 1.80-1.55 (4H, $C\mathbf{H}_2$)[b], 0.07, -0.22 (s, 9H, $C\mathbf{H}_3$)	146.3, 145.9, 143.1, 141.6 ($\mathbf{C}_q$), 134.6. 132.6, 130.8, 129.0, 128.3, 126.7, 126.6, 126.6, 126.1, 125.9, 125.5, 125.1, 124.9, 124.7, 124.4, 124.3, 123.9, 120.2, 119.8, 119.3 ($\mathbf{C}H$), 57.3, 54.2. ($\mathbf{C}H_{flu\text{-}9}$), 49.8 ($\mathbf{C}H$), 38.6, 36.8, 36.4, 23.3, 23.1 ($\mathbf{C}H_2$). -2.1, -2.8 ($\mathbf{C}H_3$)
 **10/10***[f]	7.67-7.57 (2H)[b], 7.32-7.05 (4H)[b], 7.05 (t, $^3J(^1H,^1H)$ 7.5 Hz, 1H), 6.79 (d, $^3J(^1H,^1H)$ 7.5 Hz, 1H), 6.50-6.46 (2H)[b], 5.91 (d, $^3J(^1H,^1H)$ 1.7 Hz, 1H), 4.00 (s, 1H), 3.21 (d, $^3J(^1H,^1H)$ 1.2 Hz, 1H), 2.30-2.20 (m, 1H), 2.12-2.06 (m, 1H), 1.61-1.33 (6H, $C\mathbf{H}_2$)[b], 1.18-1.10 (m, 2H, $C\mathbf{H}_2$), -0.02 (s, 9H, $C\mathbf{H}_3$)	147.9, 145.3 ($\mathbf{C}_q$), 133.3, 131.1, 130.8, 127.0, 126.7, 126.6, 126.5, 125.5, 125.3, 119.2, 118.8 ($\mathbf{C}H$), 57.8, 54.2 ($\mathbf{C}H_{flu\text{-}9}$), 50.2 ($\mathbf{C}H$), 44.3 ($\mathbf{C}_q$), 35.7. 30.2, 26.2, 22.7, 21.9 ($\mathbf{C}H_2$), -1.7 ($\mathbf{C}H_3$)
 **11/11***[g]	7.81 (d, $^3J(^1H,^1H)$ 7.1 Hz, 1H), 7.73-7.64 (3H)[b], 7.56 (d, $^3J(^1H,^1H)$ 7.3 Hz, 1H), 7.47-7.24 (3H)[b], 7.04 (d, $^3J(^1H,^1H)$ 7.5 Hz, 1H), 6.78 (m, 1H), 6.63 (m, 1H), 6.03 (m, 1H), 4.10 (s, 1H), 3.92 (s, 1H), 3.33 (s, 1H), 2.40 (m, 1H), 2.17 (m, 1H), 1.51-0.96 (10H, $C\mathbf{H}_2$)[b], 0.06 (s, 9H, $C\mathbf{H}_3$)	151.2, 145.8, 145.4, 143.3, 142.8, 141.9. 141.8 ($\mathbf{C}_q$), 134.1, 131.3, 129.1, 129.1, 127.0, 126.9, 126.7, 126.7, 126.5, 125.7, 125.5, 125.0, 119.9, 119.3, 118.9 ($\mathbf{C}H$), 58.4, 54.0 ($\mathbf{C}H_{flu\text{-}9}$), 50.0 ($\mathbf{C}H$), 47.5 ($\mathbf{C}_q$), 37.5, 36.9, 32.6, 28.9, 28.6, 23.6. 23.3 ($\mathbf{C}H_2$), -1.6 ($\mathbf{C}H_3$)
 **12/12***[h]	7.71-7.68 (2H)[b], 7.57 (m, 1H), 7.49 (m, 1H), 7.36-7.20 (5H)[b], 7.04-7.01 (2H)[b], 6.96-6.86 (2H)[b], 6.89 (m), 6.60 (m), 6.46 (m), 6.28 (m), 6.08 (m), 5.03 (s), 4.96 (s, 1H). 3.32 (s), 3.29 (s, 1H), 1.20 (s), 1.11 (s, 3H, $C\mathbf{H}_3$), -0.02 (s), -0.21 (s, 9H, $C\mathbf{H}_3$)	151.7, 147.9, 145.4, 145.0, 142.0 ($\mathbf{C}_q$). 134.7, 134.1, 133.8, 131.7, 128.1, 128.7, 128.3, 128.0, 127.6, 127.4, 126.9, 126.6, 126.3, 126.2, 126.1, 126.0, 125.9, 125.2, 124.3, 124.0, 120.3, 119.1 ($\mathbf{C}H$), 56.2, 55.0, 50.6 ($\mathbf{C}H$), 46.8 ($\mathbf{C}_q$), 20.6, 19.0. -1.5, -2.0 ($\mathbf{C}H_3$)

Table 1 (Continued)

	^{1}H-NMR[a]	^{13}C-NMR[a]
 **13/13***[i]	7.79-7.64 (3H)[b], 7.39-7.24 (3H)[b], 7.16 (m, 1H), 7.00 (m, 1H), 6.72 (m, 1H), 6.57 (m, 1H), 6.11 (m, 1H), 5.88 (m, 1H, =CH), 5.07-4.85 (m, 2H, =CH_2), 4.28, 4.21, 4.18 (3s, 1H), 3.90 (s, 1H), 3.34 (d, $^3J(^1H,^1H)$ 1.2 Hz), 3.10 (m, 1H), 2.24-1.92 (4H, CH_2)[b], 1.12 (s), 0.54 (s, 3H, CH_3), 0.22 (s), 0.06 (s, 9H, CH_3)	151.2, 145.4, 145.2, 142.5, 141.9 (C_q). 139.4 (=CH). 134.8, 134.2, 130.9, 129.0, 128.0, 127.0, 126.8. 126.7, 126.2, 126.1, 126.0, 125.9, 125.8, 125.0. 119.9, 119.5, 119.3, 119.1, 118.9 (CH). 114.0, 113.8 (=CH_2), 56.6, 56.2 (CH_{flu-9}), 50.2 (CH), 43.3, 40.4, 36.9, 29.7 (CH_2), 17.7 (CH_3), -0.6, -1.6 (CH_3)

[a] $CDCl_3$ (saturated solution) at 25°C; [b] indicated as a shift range due to signal overlap; [c] further signals could not be recorded. [d] δ (^{29}Si) = 2.7ppm; [e] δ (^{29}Si) = 5.5, 2.7 ppm; [f] δ (^{29}Si) = 3.2 ppm; [g] δ (^{29}Si) = 3.6 ppm; h) δ (^{29}Si) = 4.2, 1.1 ppm; [i] δ (^{29}Si) = 3.8, 3.7 ppm.

appears for every carbon atom. The C and CH_2 carbon atoms (negative signals) are in anti phase to the CH and CH_3 carbon atoms (positive signals). The signals at $\delta = 129.0$, 128.7, 126.6, 125.0, 124.8, 124.7, 124.5 and 123.7 ppm correspond to the tertiary carbon atoms, and the resonances at $\delta = 123.5$, 123.5, 122.7, 121.7 and 79.5 ppm to the quaternary carbon atoms of the fluorenylidene ligand. The signal at $\delta = 79.5$ ppm for the quaternary carbon atom 9 is typical and indicative for all C_1-bridged trihapto bonded fluorenylidene metallocene complexes. The signals at $\delta = 123.4$, 107.0 and 106.8 ppm and at $\delta = 128.9$ and 117.7 ppm derive from the tertiary and quaternary carbon atoms of the cyclopentadienylidene ligand. The signals for the methylene groups of the cycloheptylidene bridge appear at $\delta = 39.1$, 38.8, 27.5, 27.4, 23.9 and 23.5 ppm.

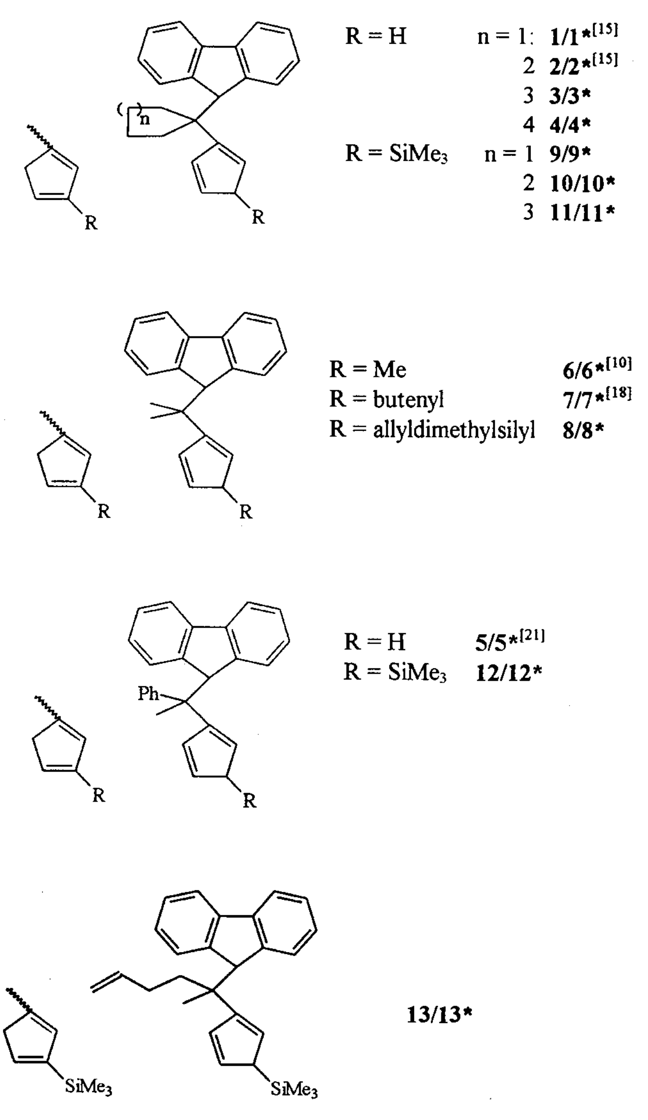


Fig. 1. Overview of the synthesized ligand precursors **1/1***–**13/13***.

2.3. Polymerization of ethylene

All synthesized metallocene complexes reported here polymerize ethylene after activation with methylalumi-noxane (MAO). The metallocene catalyst precursors **15**, **16** and **26/26***, which contain an ω-alkenyl substituent, are able to copolymerize themselves during the polymerization of α-olefins. In this way, the homogeneous metallocene catalysts are self-immobilizing and catalyze the further polymerization heterogeneously [18]; the formed polymer serves as organic support.

In Fig. 4 and Fig. 5, the intrinsic viscosity molecular weights of the polyethylenes that were produced with the C_1-bridged fluorenylidene cyclopentadienylidene complexes **14–27** are compared. Until now, these catalysts have primarily been tested for propylene polymerization [5–8,11,21,23]. In Fig. 4, the molecular weights of the polyethylenes that were produced with complexes **17–20** and **24** are given (unsubstituted cyclopentadienylidene ligands), and in Fig. 5, those that were produced with complexes **14–16** and **21–27** (substituent in position 3 of the cyclopentadienylidene ligand). Complexes **17–20** each contain a ring system of different size in the bridge. The size of the ring has an influence on the molecular weight. The polyethylene prepared with the cyclohexylidene bridged complex **18** has the lowest molecular weight ($M_\eta = 140 \times 10^3$ g mol^{-1}). The complexes with smaller or larger bridging rings produce

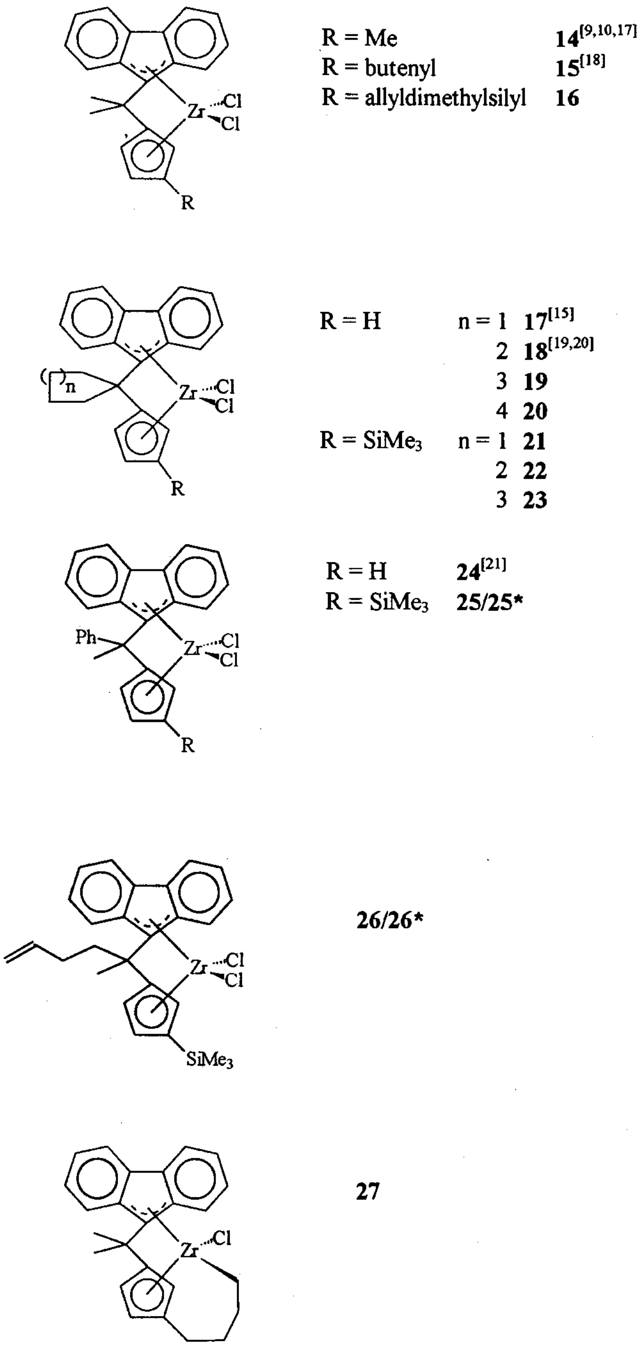


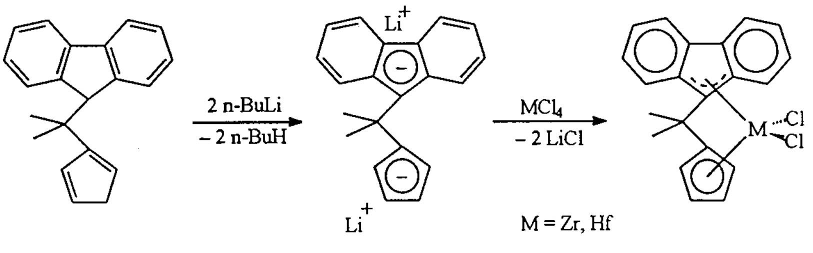
Fig. 2. Overview of the synthesized metallocene complexes **14**–**27**.

higher molecular weights. The methyl phenyl methylene bridged complex **24** performs the highest molecular weight ($M_\eta = 280\ 10^3$ g mol $-$ ^{1} [21]) after its activation with MAO (Fig. 4).

The melting points of polyethylenes made with complexes **17**–**20** and **24** are in the range of 136 ± 1.5°C (Table 3). The corresponding enthalpy values of 80–115 J g^{-1} indicate crystallinity degrees of 28–40%, which are unusually low values for polyethylenes. The polymer obtained with **18** has the lowest molecular weight and the highest enthalpy value.

Fig. 5 displays the molecular weights of the polyethylenes synthesized with the fluorenylidene cyclopentadienylidene complexes **14**–**16** and **21**–**27**, all substituted in position 3 of the cyclopentadienylidene moiety (continuous line). The molecular weights range from 125×10^3–175×10^3 g mol^{-1} except for complex **27** which produces polyethylene with an inherent molecular weight of $M_\eta = 330 \times 103$ g mol^{-1}. Complex **27** is a metallacycle derived from complex **15** and it produces a molecular weight that has doubled compared with that of **15**. The cyclohexylidene bridged complex **21** produces the lowest molecular weight ($M_\eta = 125 \times 10^3$ g mol^{-1}). For comparison, the molecular weights of the polyethylenes that were obtained with the corresponding unsubstituted complexes **17**–**20** and **24**, are also shown (dotted line) in Fig. 5. The unsubstituted complexes produce higher molecular weights than their substituted homologues. Obviously a substituent in position 3 of the cyclopentadienylidene ligand favors termination over propagation.

The melting points of the polyethylenes made with complexes **14**–**16** and **21**–**27** are in the range of 134.0–138.0°C (Table 3). Most of these polymers have melting points around 137 ± 1°C. The corresponding fusion enthalpies range from 140 to 160 J g^{-1} (ca. crystallinity degrees of 48–55%) and are significantly higher than those for the unsubstituted complexes. Substitution of the cyclopentadienylidene ligand increases the crystallinity of the polyethylene by an average of 18%. Whether the substituent is a trimethylsilyl group, a methyl group or a butenyl group is insignificant.



Scheme 2. Synthesis of the metallocene complexes.

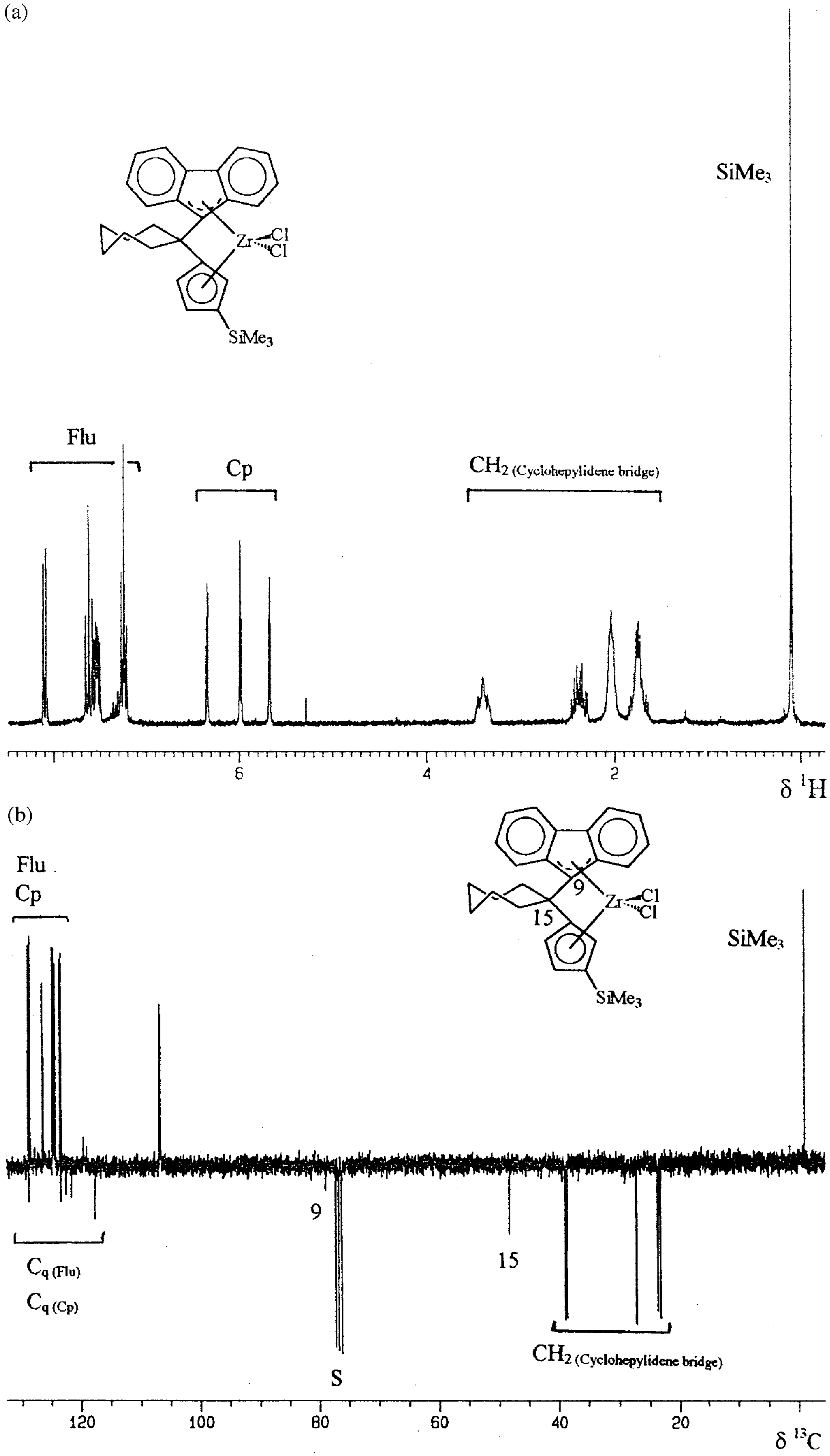


Fig. 3. (a) 250.13 MHz ^{1}H-NMR spectrum of **23** ($CDCl_3$, 25°C). (b) 62.9 MHz *J*-modulated $^{13}C\{^1H\}$-NMR spectrum of **23** ($CDCl_3$, 25°C). Quarternary and CH_2 carbon atoms (negative signals) as well as CH and CH_3 carbon atoms (positive signals) are in phase; S = $CDCl_3$.

Table 2
NMR data of the C_1-bridged metallocene complexes **14–27**

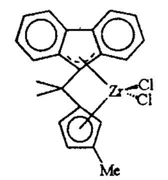
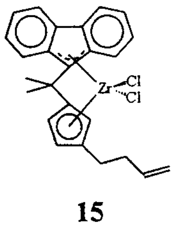
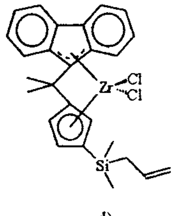
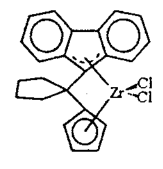
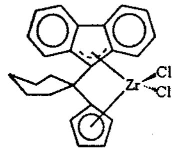
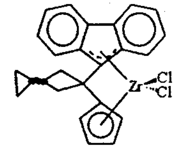
	^{1}H-NMR$^{a)}$	^{13}C-NMR$^{a)}$
 **14**	8.03-7.93 (2H)$^{b)}$, 7.71-7.57 (2H)$^{b)}$, 7.47-7.35 (2H)$^{b)}$, 7.14-7.08 (2H)$^{b)}$, 5.83 (s, 1H, C**H**$_{Cp}$), 5.50 (m, 1H, C**H**$_{Cp}$), 5.27 (m, 1H, C**H**$_{Cp}$), 2.21 (s, 3H, C**H**$_3$), 2.19 (s, 3H, C**H**$_3$), 1.91 (s, 3H, C**H**$_3$)	142.0, 131.5 (C$_q$), 128.9, 128.8, 124.9, 124.8, 124.7, 124.7, 123.3 (CH), 123.2 (C$_q$), 123.2 (CH), 123.1, 122.7, 122.6 (C$_q$), 118.0 (CH), 113.9 (C$_q$), 103.9, 103.0 (CH), 79.5 (C$_{q\text{-flu}}$), 40.4 (C$_q$, CMe$_2$), 28.7, 28.6, 15.2 (CH$_3$)
 **15**	8.12 (dd, ^3J(^{1}H,^{1}H) 8.3 Hz, ^4J(^{1}H,^{1}H) 1.6 Hz, 2H), 7.84-7.75 (m, 2H), 7.56-7.49 (m, 2H), 7.27-7.21 (m, 2H), 6.01 (m, 1H, C**H**$_{cp}$), 5.78 (m, 1H, =C**H**), 5.68 (m, 1H, C**H**$_{Cp}$), 5.43 (m, 1H, C**H**$_{Cp}$), 4.99-4.89 (m, 2H, =C**H**$_2$), 2.52 (m, 2H, C**H**$_2$), 2.35 (s, 3H, C**H**$_3$), 2.32 (s, 3H, C**H**$_3$), 2.20 (m, 2H, C**H**$_2$)	137.8 (=CH), 135.3 (C$_q$), 129.2, 129.2, 125.2, 125.1, 125.1, 125.1, 123.7 (CH), 123.6 (C$_q$), 123.5 (CH), 123.4, 123.2, 123.1 (C$_q$), 117.5 (CH), 115.2 (=CH$_2$), 113.8 (C$_q$), 103.3, 103.2 (CH), 80.1 (C$_{q\text{-flu}}$), 40.7 (C$_q$, CMe$_2$), 34.2, 29.4 (CH$_2$), 29.0 (CH$_3$)
 **16$^{d)}$**	8.08 (d, ^3J(^{1}H,^{1}H) 8.4 Hz, 2H), 7.83-7.76 (m, 2H), 7.57-7.49 (m, 2H), 7.26-7.20 (m, 2H), 6.37 (m, 1H, C**H**$_{Cp}$), 5.97 (m, 1H, C**H**$_{Cp}$), 7.57-5.58 (m, 1H, =C**H**), 5.67 (m, 1H, C**H**$_{Cp}$), 4.80-4.73 (m, 2H, =C**H**$_2$), 2.38 (s, 3H, C**H**$_3$), 2.37 (s, 3H, C**H**$_3$), 1.60 (**AB**M, 2H, C**H**$_2$), 0.14 (s, 3H, C**H**$_3$), 0.11 (s, 3H, C**H**$_3$)	134.5 (=CH), 129.0, 128.7 (CH), 127.2 (C$_q$), 127.0, 125.1, 125.0, 124.9, 124.6 (CH), 123.7, 123.6 (C$_q$), 123.5, 123.2 (CH), 123.0, 122.0, 117.5 (C$_q$), 113.4 (=CH$_2$), 106.9 (CH)$^{c)}$, 79.6 (C$_{q\text{-flu}}$), 40.5 (C$_q$, CMe$_2$), 29.1, 28.6 (CH$_3$), 24.1 (CH$_2$), -3.3, -3.5 (CH$_3$)
 **17**	8.11 (d, ^3J(^{1}H,^{1}H) 7.5 Hz, 1H), 7.77 (d, ^3J(^{1}H,^{1}H) 7.0 Hz, 1H), 7.71 (d, ^3J(^{1}H,^{1}H) 8.8 Hz, 1H), 7.56-7.51 (2H)$^{b)}$, 7.39-7.22 (3H)$^{b)}$, 6.29 (m, 2H, C**H**$_{Cp}$), 5.70 (m, 2H, C**H**$_{Cp}$), 3.20 (m, 2H, C**H**$_2$), 2.73 (m, 2H, C**H**$_2$), 2.10-1.95 (m, 4H, C**H**$_2$)	129.0, 126.7, 125.2, 125.0, 122.8, 119.8, 119.3, 102.3, 101.9 (CH), 54.0 (C$_q$, CMe$_2$), 37.8, 29.9, 29.8, 23.4 (CH$_2$)$^{e)}$
 **18**	8.15-8.10 (m, 2H), 7.75 (d, ^3J(^{1}H,^{1}H) 9.0 Hz, 2H), 7.58-7.51 (2H)$^{b)}$, 7.30-7.23 (2H)$^{b)}$, 6.30 (m, 2H, C**H**$_{Cp}$), 5.73 (m, 2H, C**H**$_{Cp}$), 3.35-3.23 (m, 2H, C**H**$_2$), 2.41-2.27 (m, 2H, C**H**$_2$), 1.97-1.90 (m, 6H, C**H**$_2$)	129.3, 125.0, 124.8 (CH), 123.6 (C$_q$), 123.4 (CH), 123.1 (C$_q$), 119.1 (CH), 114.8 (C$_q$), 101.9 (CH), 46.8 (C$_q$, CMe$_2$), 35.9, 25.9, 21.7 (CH$_2$)$^{e)}$
 **19**	8.12 (d, ^3J(^{1}H,^{1}H) 8.3 Hz, 1H), 7.65-7.47 (3H)$^{b)}$, 7.35-7.10 (4H)$^{b)}$, 6.30 (m, 1H, C**H**$_{Cp}$), 5.75 (m, 1H, C**H**$_{Cp}$), 5.36 (m, 1H, C**H**$_{Cp}$), 5.18 (m, 1H, C**H**$_{Cp}$), 2.57-2.49 (m, 2H, C**H**$_2$), 2.41-2.29 (m, 2H, C**H**$_2$), 2.08-2.01 (m, 4H, C**H**$_2$), 1.83-1.70 (m, 4H, C**H**$_2$)	145.0, 142.2, 135.3 (C$_q$), 127.0, 126.3, 125.7 (CH), 123.7, 122.8 (C$_q$), 119.0 (CH), 115.6 (C$_q$), 109.4, 102.4 (CH), 48.1 (C$_q$, CMe$_2$), 36.1, 29.2, 23.2 (CH$_2$)$^{e)}$

Table 2 (Continued)

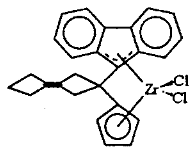
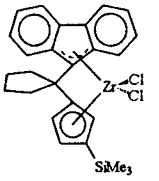
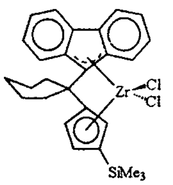
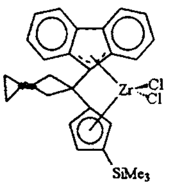
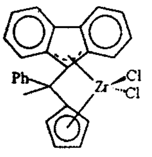
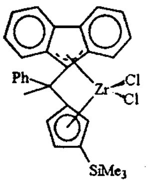
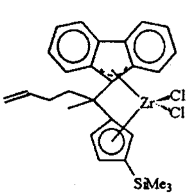
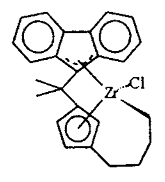
	^{1}H-NMR$^{a)}$	^{13}C-NMR$^{a)}$
 **20**	8.07 (d, $^3J(^1H,^1H)$ 8.3 Hz, 1H), 7.82-7.70 (2H)$^{b)}$, 7.62-7.46 (2H)$^{b)}$, 7.42-7.18 (3H)$^{b)}$, 6.32 (m, 2H, CH_{Cp}), 5.75 (m, 2H, CH_{Cp}), 2.72-2.63 (m, 2H, CH_2), 2.50-1.61 (m, 12H, CH_2)	129.3, 126.7, 126.7, 125.0, 124.8, 124.0 (CH), 123.6, 123.1 (C_q), 119.8, 119.4, (CH), 115.9 (C_q), 102.5 (CH), 79.5 ($C_{q\text{-}Flu}$), 49.1 (C_q, CMe_2), 36.9, 33.7, 29.7, 28.3, 22.1 (CH_2)$^{f)}$
 **21$^{d)}$**	8.07 (d, $^3J(^1H,^1H)$ 8.1 Hz, 2H), 7.68 (t, $^3J(^1H,^1H)$ 8.5 Hz, 2H), 7.57-7.52 (2H)$^{b)}$, 7.26-7.19 (2H)$^{b)}$, 6.33 (m, 1H, CH_{Cp}), 5.92 (m, 1H, CH_{Cp}), 5.60 (m, 1H, CH_{Cp}), 3.20 (m, 2H, CH_2), 2.75 (m, 2H, CH_2), 2.06 (4H, CH_2)$^{b)}$, 0.19 (s, 9H, CH_3)	129.2 (C_q), 128.8, 128.6, 126.6, 125.1, 125.0, 124.9, 124.7 (CH), 123.4, 123.1 (C_q), 123.0, 122.7 (CH), 121.8 (C_q), 117.1 (C_q), 107.2, 106.6 (CH), 79.7 ($C_{q\text{-}Flu}$), 50.9 (C_q, CMe_2), 38.3, 37.7, 23.6, 23.5 (CH_2), -0.8 (CH_3)
 **22$^{d)}$**	8.10 (dt, $^3J(^1H,^1H)$ 8.4 Hz, $^4J(^1H,^1H)$ 1.0 Hz, 2H), 7.72 (td, $^3J(^1H,^1H)$ 9.1 Hz, $^4J(^1H,^1H)$ 0.7 Hz, 2H), 7.57-7.49 (2H)$^{b)}$, 7.28-7.20 (2H)$^{b)}$, 6.35 (m, 1H, CH_{cp}), 5.97 (t, $^3J(^1H,^1H)$ 2.9 Hz, 1H, CH_{cp}), 5.66 (t, $^3J(^1H,^1H)$ 2.3 Hz, 1H, CH_{cp}), 3.34-3.29 (m, 2H, CH_2), 2.38-2.27 (m, 2H, CH_2), 1.99-1.80 (6H, CH_2)$^{b)}$, 0.11 (s, 9H, CH_3)	129.3, 129.2 (CH), 128.9 (C_q), 126.5, 124.9, 124.9, 124.7, 124.6 (CH), 123.8 (C_q), 123.4, 123.3 (CH), 122.3, 117.2 (C_q), 106.6, 106.5 (CH), 77.5 ($C_{q\text{-}Flu}$), 46.7 (C_q, CMe_2), 36.4, 35.7, 25.9, 21.9, 21.8 (CH_2), -0.9 (CH_3)
 **23$^{d)}$**	8.09 (d, $^3J(^1H,^1H)$ 8.0 Hz, 2H), 7.66-7.51 (m, 4H), 7.28-7.20 (2H)$^{b)}$, 6.34 (m, 1H, CH_{Cp}), 5.98 (m, 1H, CH_{Cp}), 5.67 (m, 1H, CH_{Cp}), 3.46-3.35 (m, 2H, CH_2), 2.43-2.28 (m, 2H, CH_2), 2.06-1.98 (4H, CH_2), 1.79-1.66 (4H, CH_2), 0.10 (s, 9H, CH_3)	129.0 (CH), 128.9 (C_q), 128.7, 126.6, 124.9, 124.8, 124.7, 124.5, 123.7 (CH), 123.6, 123.5 (C_q), 123.5 (CH), 122.8, 121.7, 117.8 (C_q), 107.0, 106.8 (CH), 79.0 ($C_{q\text{-}Flu}$), 48.5 (C_q, CMe_2), 39.1, 38.8, 27.5, 27.4, 23.9, 23.5 (CH_2), -1.0 (CH_3)
 **24**	8.18-8.09 (m, 2H), 7.92-7.84 (m, 2H), 7.65-7.33 (7H)$^{b)}$, 6.92-6.88 (2H)$^{b)}$, 6.40 (m, 1H, CH_{Cp}), 6.30 (m, 1H, CH_{Cp}), 6.20 (d, $^3J(^1H,^1H)$ 8.8 Hz, 1H, CH_{Flu}), 5.88 (m, 1H, CH_{Cp}), 5.72 (m, 1H, CH_{Cp}), 2.52 (s, 3H, CH_3)	146.3 (C_q), 129.6, 129.2, 129.1, 128.6, 127.7, 127.3, 125.2, 125.1, 125.1, 124.4 (CH), 124.1 (C_q), 123.8 (CH), 123.7 (C_q), 123.0 (CH), 122.6, 121.0 (C_q), 120.3, 117.7 (CH), 112.4 (C_q), 104.0, 102.6 (CH), 79.2 ($C_{q\text{-}Flu}$), 49.8 (C_q, CMe_2), 31.1 (CH_3)
 **25/25*$^{d,g)}$**	8.12-8.05 (2H)$^{b)}$, 7.94-7.85 (2H)$^{b)}$, 7.75-7.72 (4H)$^{b)}$, 7.52-7.10 (14H)$^{b)}$, 6.76-6.65 (4H)$^{b)}$, 6.32 (m, 1H, CH_{Cp}), 6.18 (m, 1H, Ch_{Cp}), 6.04 (d, $^3J(^1H,^1H)$ 8.8 Hz, 1H, CH_{Flu}), 5.99 (d, $^3J(^1H,^1H)$ 8.8 Hz, 1H, CH_{Flu}), 5.94 (m, 1H, CH_{Cp}), 5.79 (m, 1H, CH_{Cp}) 5.65 (m, 1H, CH_{Cp}), 5.48 (m, 1H, CH_{Cp}), 2.39 (s, 6H, CH_3), 0.03 (s, 9H, CH_3), -0.06 (s, 9H, CH_3)	129.4, 129.1, 128.5, 127.4, 127.2, 125.1, 124.9, 119.2, 108.6 (CH), 30.9 (CH_3), -0.8, - 1.1 (CH_3)$^{e)}$
 **26/26*$^{d,g)}$**	8.09 (m, 1H), 7.79 (m, 1H), 7.59-7.50 (3H)$^{b)}$, 7.29-7.21 (3H)$^{b)}$, 6.36 (m, 1H, CH_{Cp}), 6.07 (m, 1H, =CH), 5.97 (m, 1H, CH_{Cp}), 5.69 (m, 1H, CH_{Cp}), 5.21-5.10 (m, 2H, =CH_2), 3.20 (m, 1H), 2.57 (m, 1H), 2.40 (s, 3H, CH_3), 2.28 (m, 1H), 1.82 (m, 1H), 0.11 (s, 9H, CH_3)	137.7 (=CH), 129.7 (C_q), 129.3, 128.8, 126.1, 125.1, 125.0, 124.9, 124.7 (CH), 123.7, 123.5 (C_q), 123.4, 122.8 (CH), 122.2, 117.4 (C_q)$^{h)}$, 115.4 (=CH_2), 107.3, 106.0 (CH), 78.3 ($C_{q\text{-}Flu}$), 44.1 (C_q, CMe_2), 39.4, 27.9 (CH_2), 26.9, -0.9 (CH_3)

Table 2 (Continued)

	^{1}H-NMR$^{a)}$	^{13}C-NMR$^{a)}$
 **27**	8.22 (d, $^3J(^1H,^1H)$ 8.5 Hz, 1H), 8.03 (d, $^3J(^1H,^1H)$ 8.5 Hz, 1H), 7.76 (d, $^3J(^1H,^1H)$ 8.7 Hz, 1H), 7.68 (d, $^3J(^1H,^1H)$ 8.7 Hz, 1H), 7.49-7.41 (m, 2H), 7.28-7.09 (m, 2H), 5.68 (m, 2H, CH_{Cp}), 5.32 (m, 1H, CH_{Cp}), 2.85 (dt, $^3J(^1H,^1H)$ 14.2 Hz, 1H, CH_2), 2.23 (m, 1H, CH_2), 2.20 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 1.83-1.62 (2H, CH_2)$^{b)}$, 1.14 (m, 1H, CH_2), 0.84 (m, 1H, CH_2), 0.07 (m, 1H, CH_2), -2.17 (m, 1H, CH_2)	128.5 (CH), 127.9 (C_q), 127.1, 124.8. 124.5 (CH), 124.2 (C_q), 123.8, 123.5 (CH). 122.7 (C_q), 122.6 (CH), 122.1 (C_q), 121.6 (CH), 120.0 (C_q), 114.1 (CH), 112.7 (C_q), 100.2, 99.4 (CH). 78.4 ($C_{q\text{-}Flu}$), 64.9 (CH_2), 40.4 (C_q, CMe_2), 28.9 (CH_2). 28.9 (CH_3), 28.8 (CH_2), 28.4 (CH_3), 27.6 (CH_2)

[a] In $CDCl_3$ (saturated solution) at 25°C; [b] indicated as a shift range because of resonance overlap; [c] ^{13}C-NMR signals not completely separated because of overlap; [d] δ (^{29}Si) (**16**) = 2.8; δ (^{29}Si) (**21**) = −5.5, δ (^{29}Si) (**22**) = −5.5, δ (^{29}Si) (**23**) = −5.5; δ (^{29}Si) (**25/25***) = −5.3; δ (^{29}Si) (**26/26***) = −5.4 ppm; [e] complex less soluble in chloroform. not all resonances observed; [f] decomposition during measurement; [g] the complete spectroscopic characterization of the isomers was not carried out; [h] no further C_q found.

2.4. Polymerization of propylene

2.4.1. Molecular weights of the produced polypropylenes

All C_1-bridged fluorenylidene cyclopentadienylidene complexes were activated with MAO and successfully tested for propylene polymerization. The molecular weights of the polypropylenes are dependent on the size of the bridging cycloalkylidene ring in the catalyst molecule (Fig. 6). The molecular weights of the polypropylenes synthesized with complexes **17–20** vary from 54000 (**18**) to 110000 g mol^{-1} (**19**), and the resin made with complex **24** reaches 160000 g mol^{-1}.

Substituents in position 3 of the cyclopentadienylidene moiety have little effect on the molecular weights (Fig. 7) of the produced polypropylenes (48000 (**25/25***, **26/26***, **14**, **16**)–63000 g mol^{-1} (**21**, **27**)). For comparison, the molecular weights of polypropylenes made with the homologous unsubstituted complexes are included in Fig. 7 (dotted line).

The molecular weights of the polypropylene samples were also measured using gel permeation chromatography (GPC). The GPC equipment available could only be operated with chloroform as a solvent at room temperature (r.t.). Therefore, large portions of the respective samples remained insoluble and were not available for measurements. The polymer samples made with complexes **14**, **15**, **23**, **25/25*** and **27** were sufficiently soluble to perform the GPC experiment (Table 3). The remaining samples were too insoluble for measurements.

2.4.2. Configuration of the polypropylene chains

The polypropylene samples were also studied by NMR spectroscopy to determine their stereospecifity. The pentad distribution of the methyl groups in the ^{13}C-NMR spectrum gives information about the structure of the polymers [24–27]. The methyl groups can be arranged in two ways in the polymer: two neighboring

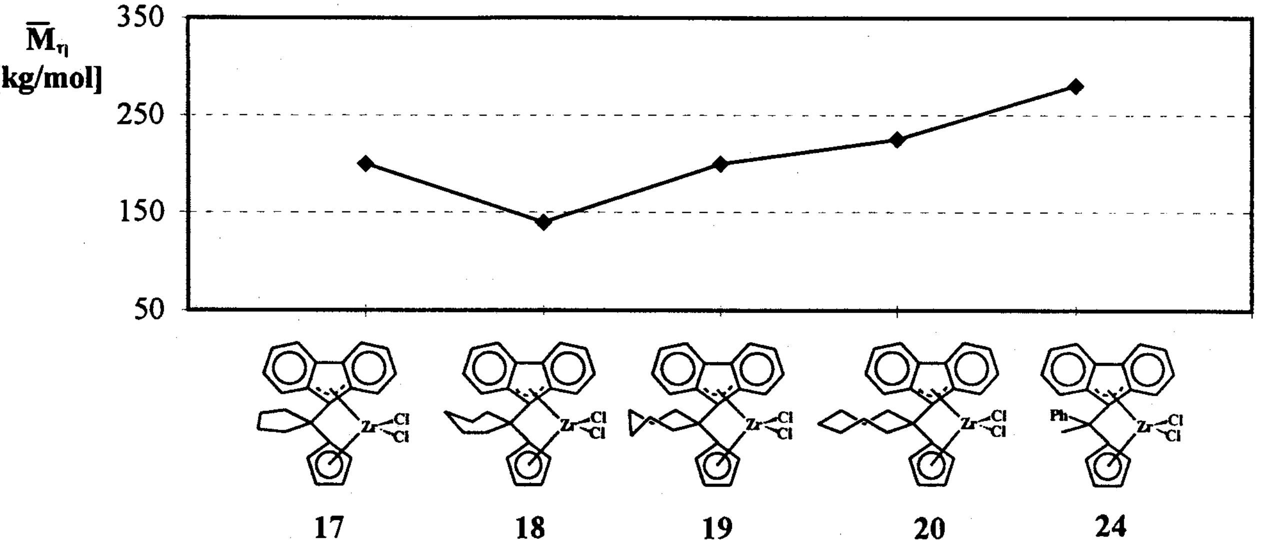


Fig. 4. Mean intrinsic viscosity $\overline{M}_\eta$ of the polyethylenes synthesized with the complex type $(C_{13}H_8\text{–}CR^1R^2\text{–}C_5H_4)ZrCl_2$/MAO.

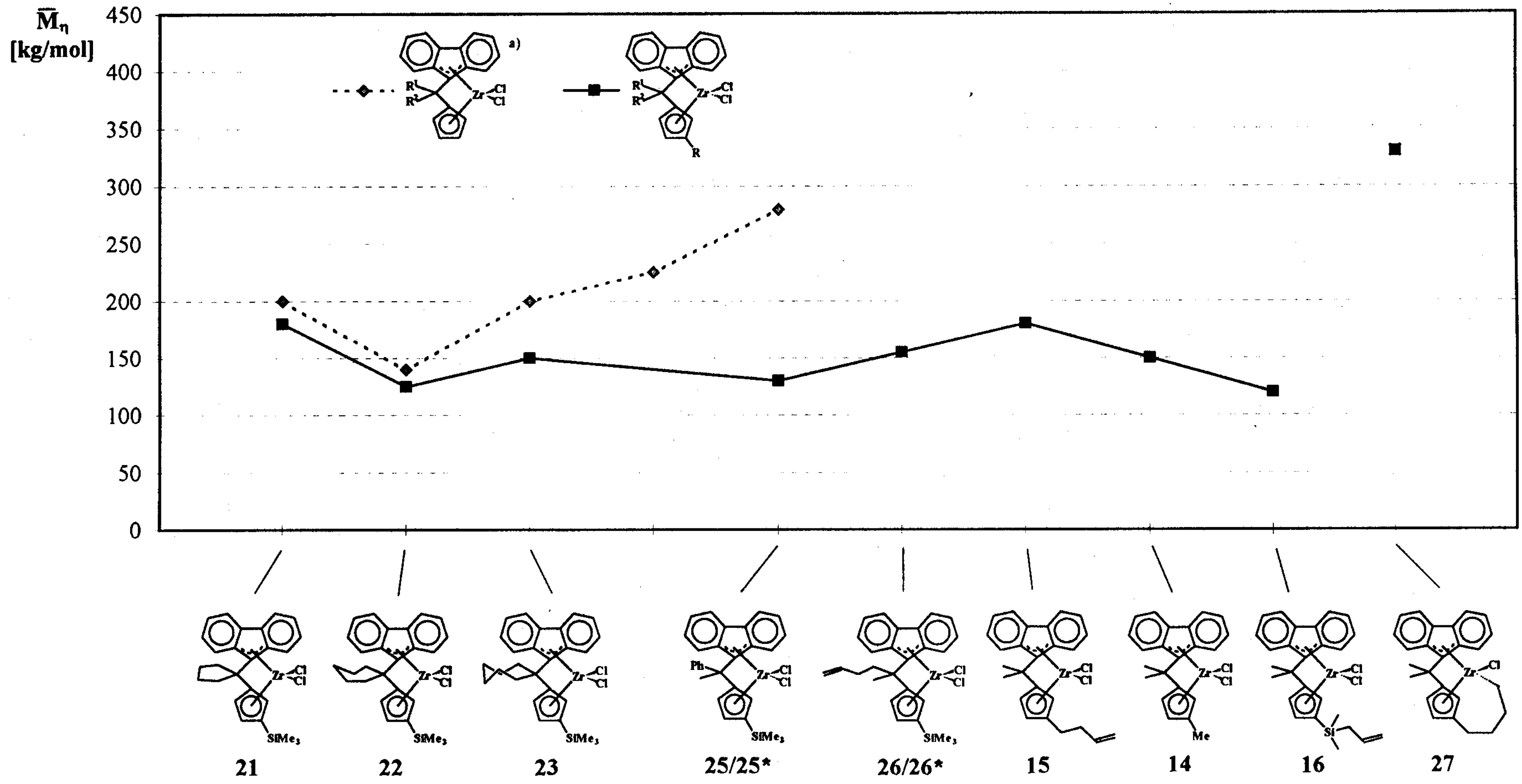
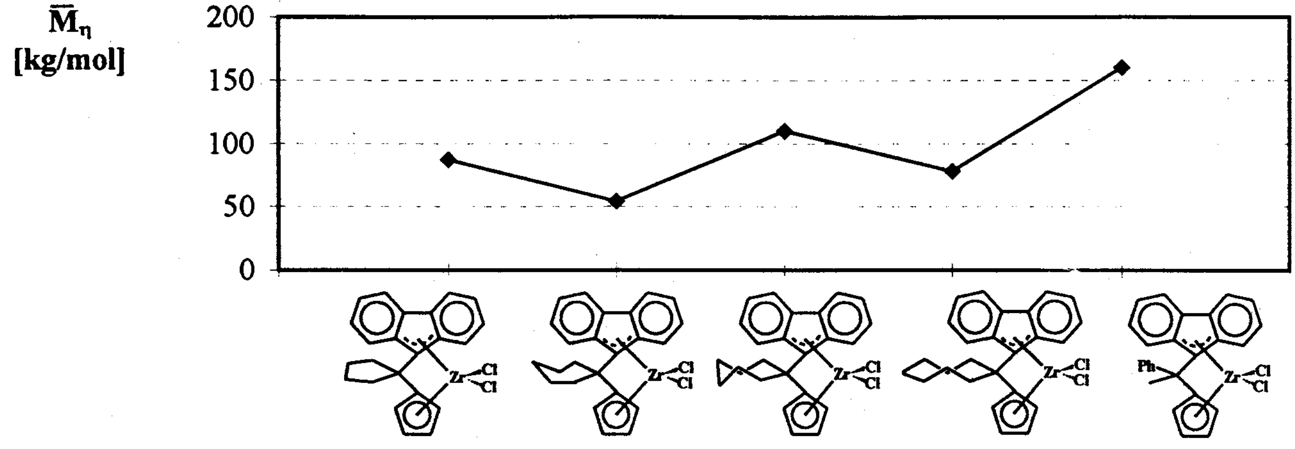


Fig. 5. $\overline{M}_\eta$ of the polypropylenes synthesized with the complex type ($C_{13}H_8$–CR^1R^2–C_5H_3R)$ZrCl_2$/MAO. [a] For comparison of the molecular weights of the polyethylenes synthesized with the corresponding unsubstituted metallocene complexes (dotted line, Fig. 4) and metallocene **27** (■) are included.



17 18 19 20 24

Fig. 6. M_η of the polypropylenes synthesized with the complex type $(C_{13}H_8{-}CR^1R^2{-}C_5H_4)ZrCl_2$/MAO.

methyl groups of the same configuration (*meso* (*m*) or isotactic), two neighboring methyl groups of the opposite configuration (racemic (*r*) or syndiotactic). One pentad consists of four diades. There are ten possible combinations of diades in one pentad. The total r and *m* portion of a polypropylene sample was calculated according to: $\Sigma\ r\ [\%] = \frac{1}{2}$ mr + rr; mr = mmrm + mmrr + rmrm + rmrr; rr = mrrm + mrrr + rrrr. $\Sigma\ m\ [\%] = \frac{1}{2}$ mr + mm; mr = mmrm + mmrr + rmrm + rmrr; mm = mmmm + mmmr + rmmr. The ^{13}C-NMR spectrum of polypropylene produced with **19** is illustrated in Fig. 8 as an example. The unsubstituted cyclopentadienylidene complexes produce polypropylenes which are almost exclusively racemic, e.g. syndiotactic polypropylenes [1,13,15]. The remaining signals derive from mistakes in the polymer structure.

If a hydrogen in position 3 of the cyclopentadienylidene ligand is exchanged for a methyl group (**14**), this catalyst produces a block copolymer with small iso- and syndiotactic polypropylene units [10,11]. In this hemiisotactic polypropylene [11,23,28–30] every other methyl substituted carbon atom has the same configuration and all other methyl substituted carbon atoms have a statistic configuration. The methyl group of the cyclopentadienylidene ligand can influence the coordination sphere of the metal and, therefore, it has a significant impact on the structure of the polymer [11]. The polypropylene produced with **14** has an mmmm pentad content of 9.7% and an rrrr pentad content of 41.0%. The total *r* diade content is 65.6%, and the total *m* diade content is 34.4%. Thus the highly syndiotactic nature of polymers made with the unsubstituted species is lost by a methyl substituent at the cyclopentadienylidine ring. Fig. 9 contains the ^{13}C-NMR spectrum of polypropylene made with **14** (compare to [10,11]).

The analysis of the polypropylene obtained with complex **15** shows that it is similarly high in mmmm (17.1%) pentads and rrrr pentads (19.5%); this is the same behavior as seen for the corresponding polypropylene produced with complex **27**. Small iso- and syndiotactic alternating blocks are found in this polypropylene (stereoblock polymer). This polymer is almost identical in structure to that produced with complex **14**. The ^{13}C-NMR spectrum of the polypropylene synthesized with complex **15** is shown in Fig. 10.

A *tert*-butyl group in position 3 of the cyclopentadienylidene ligand leads to highly isotactic polypropylene [11,12]. The *tert*-butyl group sterically blocks one side of the complex. The growing polymer chain cannot move to the side of the metal atom where the *tert*-butyl group is located. This fixes the chain and the propylene insertion occurs from one side (chain stationary insertion). As a consequence polypropylene with an isotactic configuration is formed.

The isotactic content decreases to approximately 80–85% [11] if a trimethylsilyl or an allyldimethylsilyl group is located in position 3 instead of a *tert*-butyl group. In this case, 15–20% of the polymer consists of syndiotactic blocks. Fig. 11 shows the ^{13}C-NMR spectrum of the polypropylene synthesized with complex **16**.

Fig. 12 summarizes the results of the pentad analyses for all the polypropylenes synthesized. The exact pentad distribution is listed in Table 6.

Fig. 13 shows the amount of racemic and isotactic diades found in polymers made from complexes with selected structures. The tacticities of the various polypropylenes are compared. It is obvious that the size of the α group of the substituent in position 3 of the cyclopentadienylidene ligand is decisive in determining the resulting tacticity of the polypropylene chain.

An allyldimethylsilyl group on the cyclopentadienylidene ligand (**16**) has the same effect on tacticity as a trimethylsilyl group [11], and a butenyl group (**15**) has the same effect as a methyl group (**14**). Therefore, one

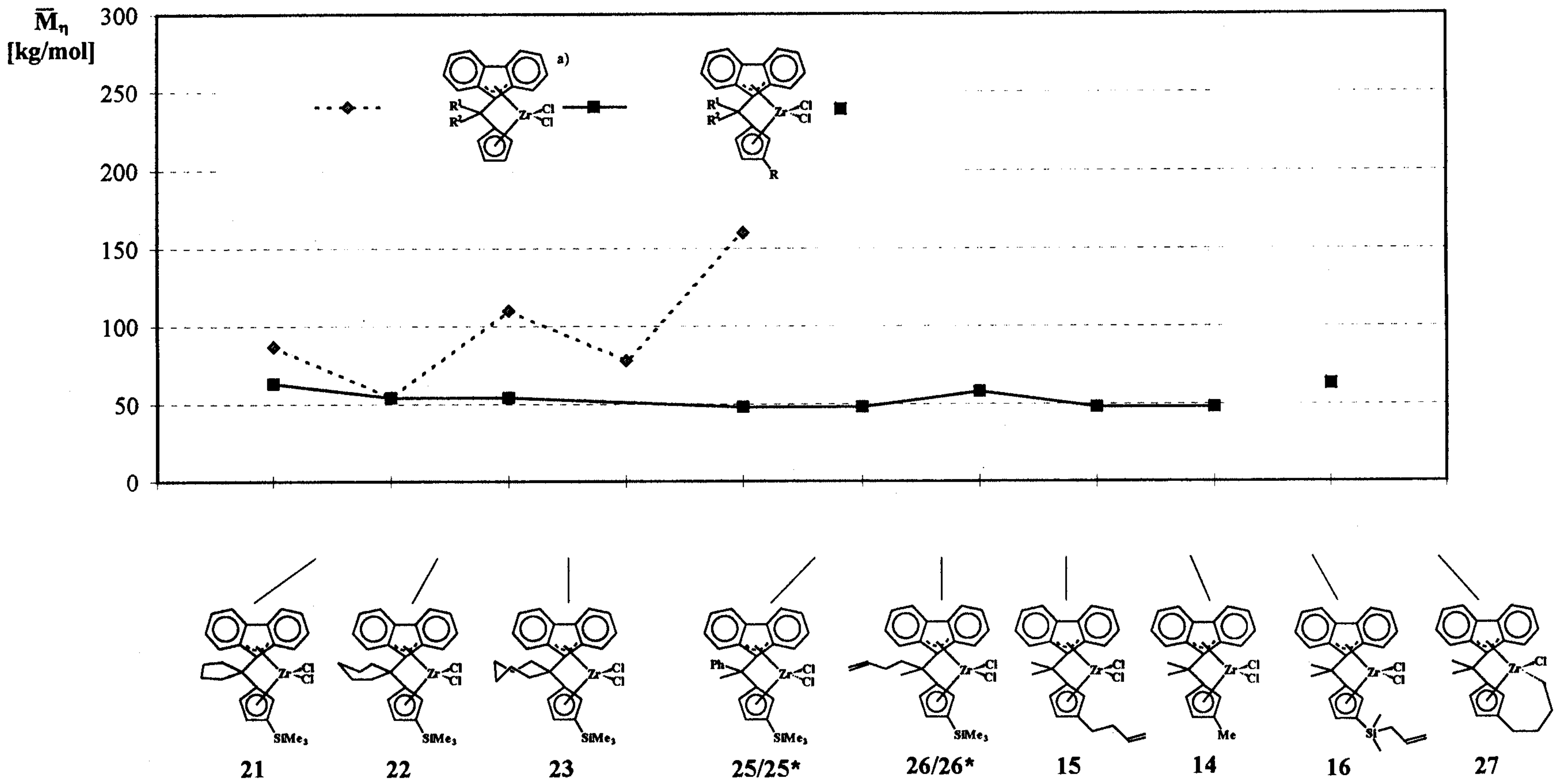


Fig. 7. $\overline{M}_\eta$ of the polypropylenes synthesized with the complex type $(C_{13}H_8–CR^1R^2–C_5H_3R)ZrCl_2$/MAO. [a] For comparison of the mean intrinsic viscosity of the polypropylenes synthesized with the corresponding unsubstituted metallocene complexes (dotted line, Fig. 6) and with the metallocene 27 (■) are included.

Table 3
Overview of the polymerization experiments with ethylene and polymer analysis

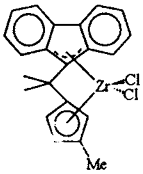
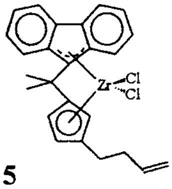
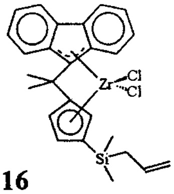
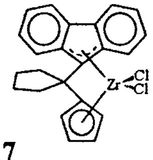
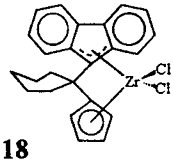
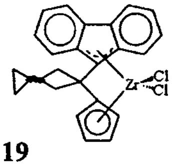
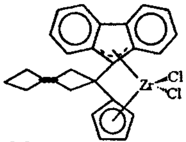
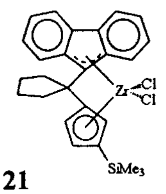
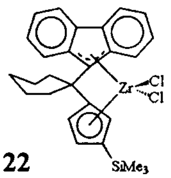
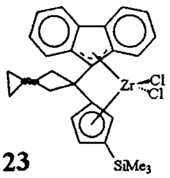
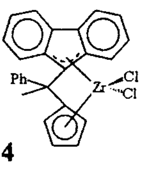
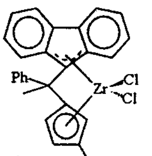
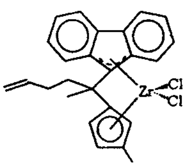
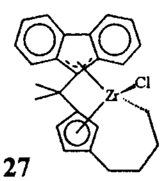
Complex	$\overline{M}_\eta$ [g/mol]	**Activity**$^{a)}$ $\frac{[g]\ PE}{[mmol]\ Zr\ h}$ $(T_{i,max})[°C]^{b)}$	$\Delta H_m{}^{c)}$ [J/g]	$\alpha^{d)}$ [%]	$T_m{}^{e)}$ [°C]	**Co-p.**$^{f)}$
 **14**	150 000	17 800 (60.1)	142.69	49	135.60	–
 **15**	180 000	19 500 (64.6)	143.19	49	134.02	++
 **16**	120 000	95 500$^{g)}$ (95.0)	157.61	54	137.91	++
 **17**	198 000	7 800 (60.3)	80.08	28	137.52	–
 **18**	120 000	13 700 (60.4)	115.71	40	137.97	–
 **19**	215 000	4 500$^{h)}$ (59.9)	89.06	31	138.66	–
 **20**	225 000	17 000$^{i)}$ (70.3)	102.03	35	134.30	–

Table 3 (Continued)

 **21**	180 000	71 600[j)] (85.3)	149.70	52	137.05	–
 **22**	125 000	24 000 (?)	146.21	50	136.30	–
 **23**	150 000	152 000[k)] (85.3)	144.53	50	136.50	–
 **24**	280 000	8 300 (62.7)	114.57	40	136.60	–
 **25/25***	130 000	73 700[i)] (80.2)	147.64	51	137.24	–
 **26/26***	155 000	35 900[i)] (76.5)	139.06	48	134.84	+
 **27**	330 000	15 700 (71.6)	135.14	47	133.57	++

[a)] [Zr]:[Al] = 1:17000; [b)] $T_{i,max}$ = maximum inside temperature of the reactor, during polymerisation; [c)] the values of the second heating course of the DSC were indicated as fusion enthalpies ΔH_m; [d)] see [31]; [e)] the maximum of the melting peak of the second heating course of the DSC was selected as melting point; [f)] ability of the catalyst to copolymerize: + + = very good, + = good, 0 = sufficient, – = none; [g)] Polymerization time 15 min; [h)] Polymerization time 80 min; [i)] Polymerization time 30 min; [j)] Polymerization time 25 min; [k)] Polymerization time 10 min.

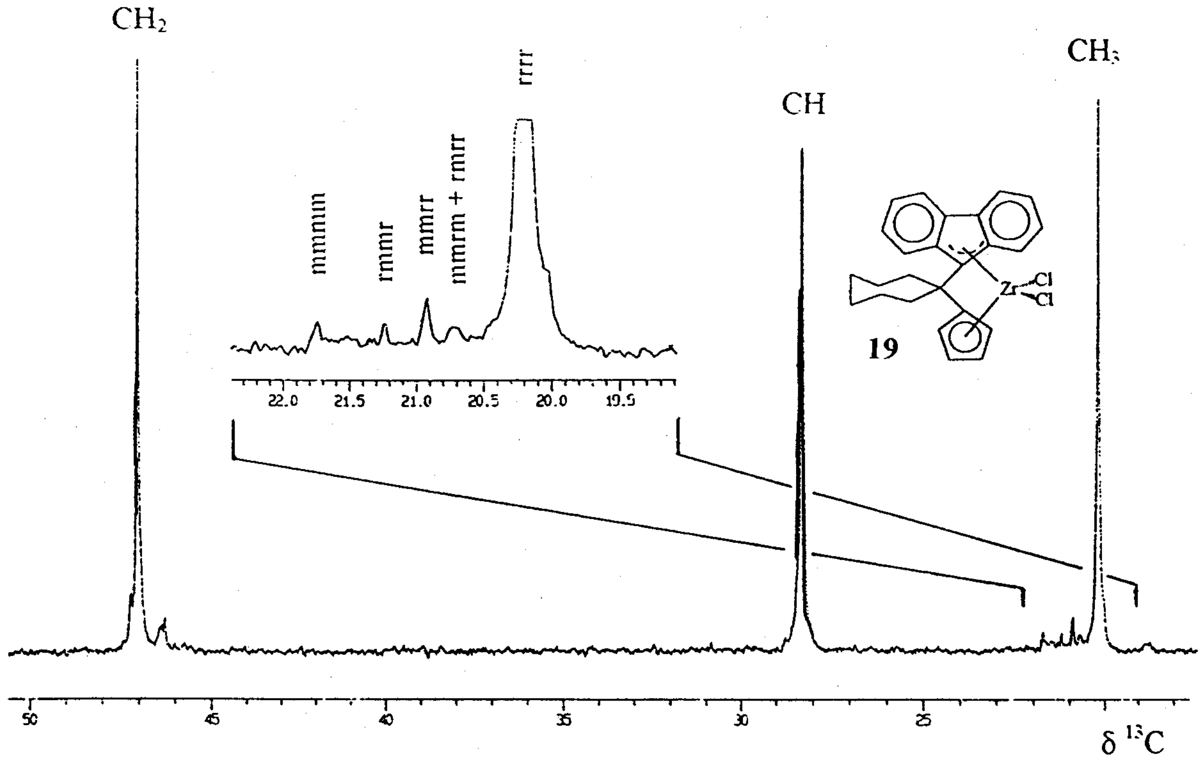


Fig. 8. 67.8 MHz $^{13}C\{^1H\}$-NMR spectrum of polypropylene synthesized with complex **19**/MAO; in $C_2D_2Cl_4/C_6H_3Cl_3$ (1/2; v/v) at 120°C (55306 scans; total measuring time 12.5 h.

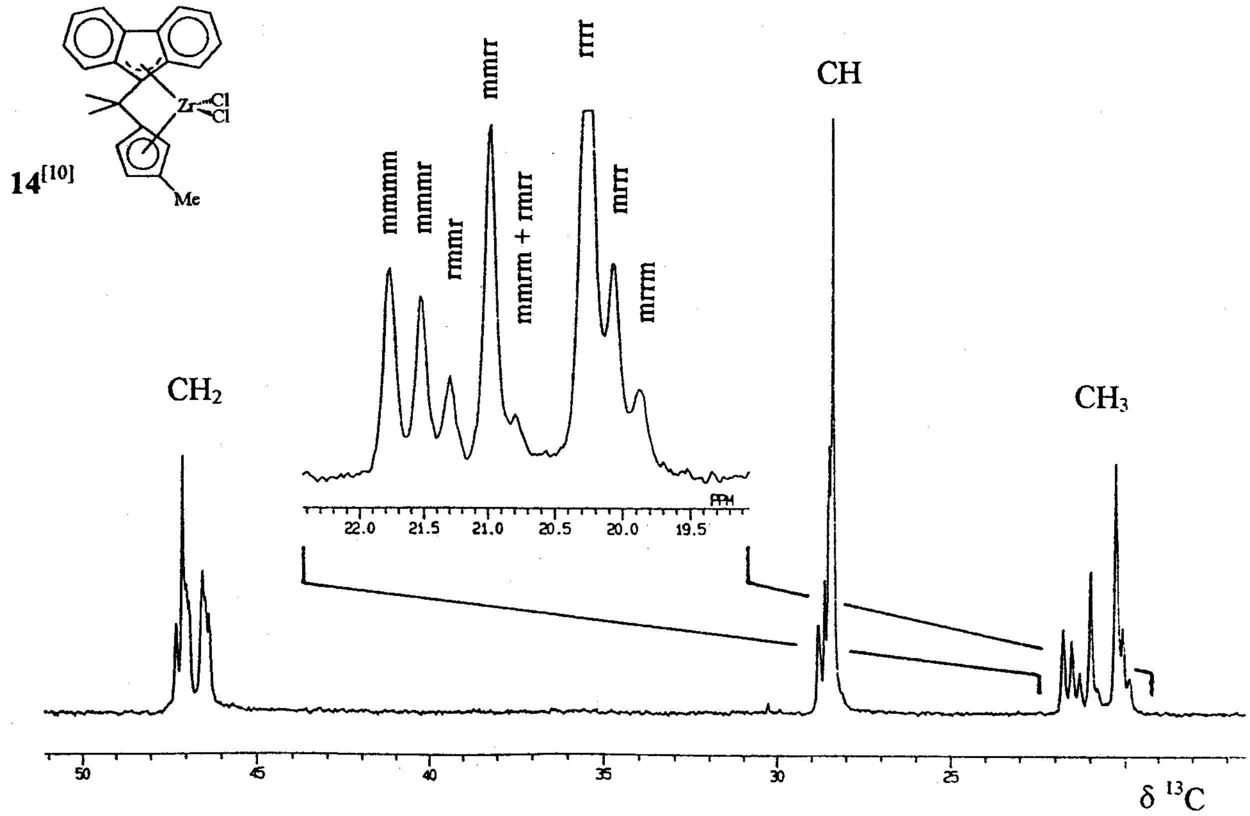


Fig. 9. 67.8 MHz $^{13}C\{^1H\}$-NMR spectrum of polypropylene synthesized with complex **14**/MAO; in $C_2D_2Cl_4/C_6H_3Cl_3$ (1/2; v/v) at 120°C (43172 scans; total measuring time 9 h 50 min.

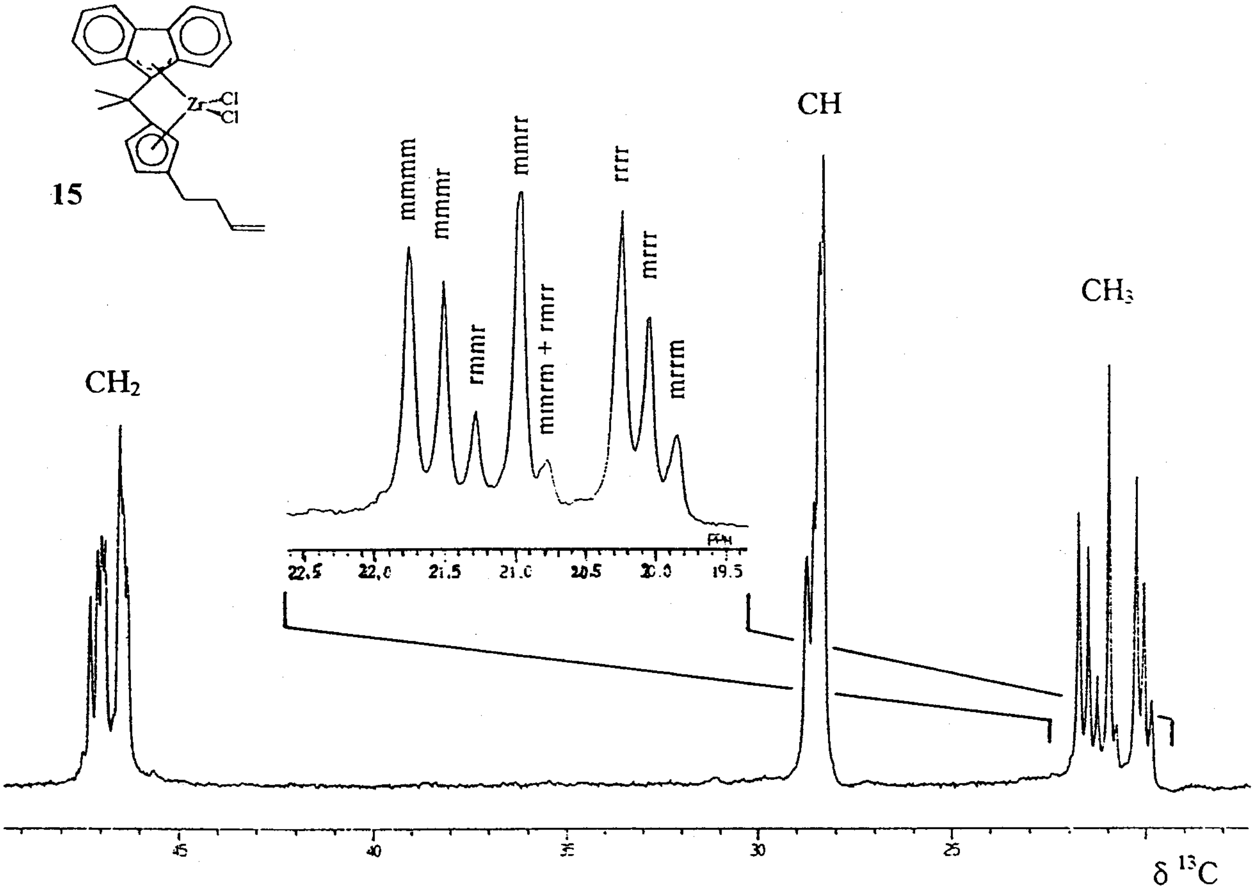


Fig. 10. 67.8 MHz $^{13}C\{^1H\}$-NMR spectrum of polypropylene synthesized with complex **15**/MAO; in $C_2D_2Cl_4/C_6H_3Cl_3$ (1/2; v/v) at 120°C (100000 scans; total measuring time 22 h 45 min.

can control the tacticity of the polypropylene chains made with C_1-bridged fluorenylidene cyclopentadienylidene complexes by the choice of the substituent in position 3 of the cyclopentadienylidene ring. At the same time the metallocene catalyst becomes self-immobilizing because of the *ω*-alkenyl substituent (Tables 3–6).

2.4.3. Fusion enthalpies of the polypropylenes

The fusion enthalpies, ΔH_m, of the polypropylenes vary from 6.4 to 37.5 J g^{-1} (see Table 6). The polypropylene produced with complex **14** has a fusion enthalpy of only 6.4 J g^{-1}. This indicates a highly disordered and amorphous structure. Accordingly, the polymer has a high glass transition enthalpy of 0.40 J g^{-1}. The DSC fusion enthalpies were not obtained for polymer samples produced with complexes **15** and **27**. The glass transition enthalpies of 0.42 (**15**) and 0.46 J g^{-1} (**27**) indicate a fusion enthalpy as low as that for the polypropylene made with complex **14**. The syndiotactic polypropylenes made with complexes **17–20** and **24** have fusion enthalpies of 20.8–29.0 J g^{-1} and low glass transition enthalpies of 0.06–0.21 J g^{-1}. The trimethylsilyl substituted complexes **17–19**, **25/25***, **26/26*** and **16**, with an allyldimethylsilyl substituent, yield isotactic polypropylenes with syndiotactic blocks. The fusion enthalpies of these polymers vary over a wide range (14.6–37.5 J g^{-1}) and approach the high enthalpies found for syndiotactic polypropylenes (Fig. 14).

2.4.4. Comparison of the polymerization activities

Unsubstituted C_1-bridged fluorenylidene cyclopentadienylidene complexes **17–20** and **24** have higher polymerization activities for propylene than for ethylene (**14**). This is unusual and cannot be explained satisfactorily except when electronic parameters determine the kinetics of the polymerization.

The trimethylsilyl substituted complexes **21–23**, **25/25***, **26/26*** and **16** exhibit considerably higher polymerization activities for ethylene than for propylene. When the substituent is a sterically smaller group like alkenyl (**15**), alkyl (**27**) or methyl (**14**), the activities for ethylene and propylene are both low. Smaller groups have no influence on the polymerization activity of ethylene, larger groups do. Unfortunately, the most active propylene catalysts tended to begin polymerizing in the burette as soon as they were charged to the reactor filled with propylene. This sometimes blocked some of the catalyst from reaching the reactor and resulted in low activity

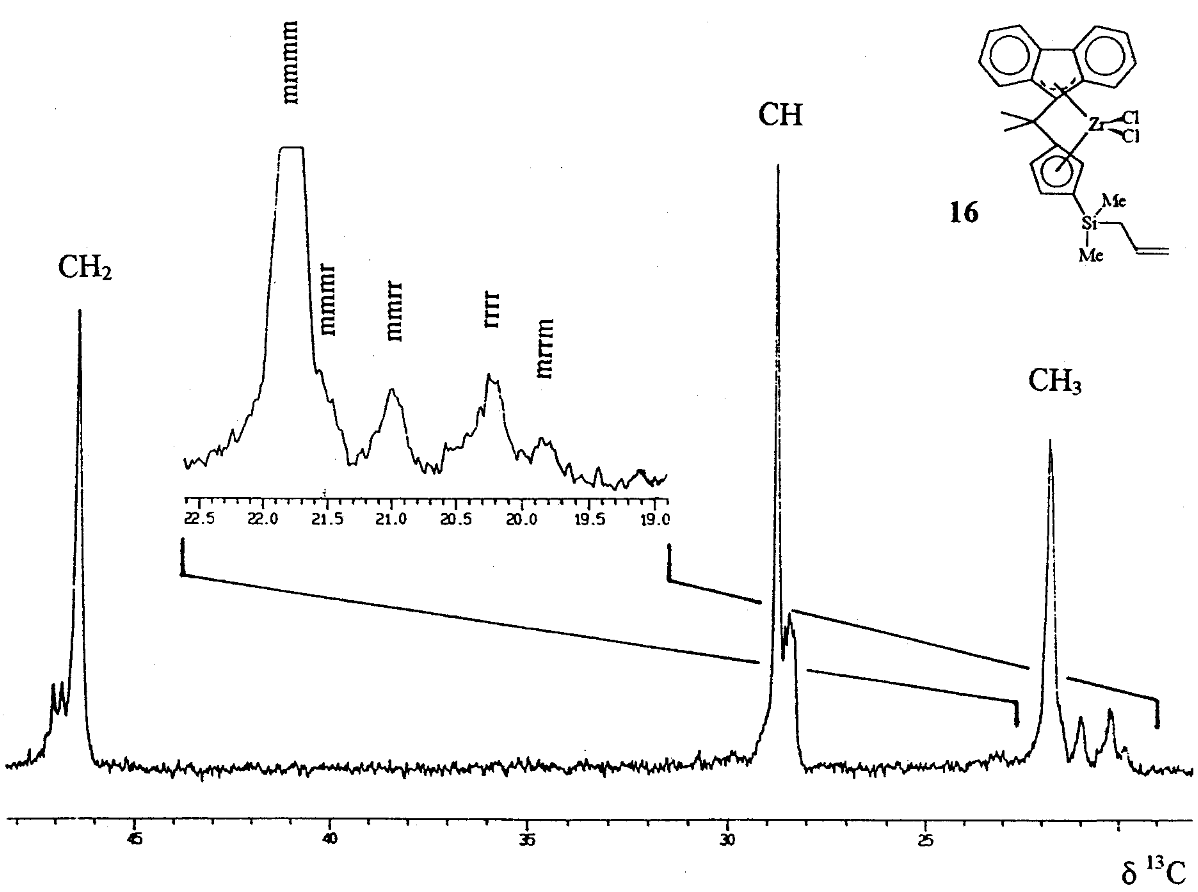


Fig. 11. 67.8 MHz $^{13}C\{^1H\}$-NMR spectrum of polypropylene synthesized with complex **16**/MAO; in $C_2D_2Cl_4/C_6H_3Cl_3$ (1/2; v/v) at 120°C (40176 scans; total measuring time 9 h 10 min.

numbers. Therefore, it is possible that some of the measured activities are too low.

3. Experimental

3.1. NMR spectroscopy

The instruments Jeol JNM-EX 270 E, Bruker ARX 250 and Bruker DRX 500 were available to record the NMR spectra. The samples were filled under argon and routinely measured in $CDCl_3$ at 25°C. The chemical shifts in the ^1H-NMR spectra are referred to the residual proton signal of the solvent ($\delta = 7.24$ for $CHCl_3$), in the ^{13}C-NMR spectra to the solvent signal ($\delta = 77.0$ for $CDCl_3$) and in the ^{29}Si-NMR spectra to the resonance of external TMS ($\delta = 0.0$) [32].

3.2. Mass spectroscopy

Routine measurements were conducted with a VARIAN MAT CH7 instrument (direct inlet system, 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

A Carlo Erba HRGC gas chromatograph with flame ionization detector was used to analyze organic compounds. The gas chromatograph was equipped with a 30 m long J&W fused silica column (DB1, film thickness 0.25 μm). Helium served as carrier gas; the flow through the column was 3.8 ml min^{-1}, split 1:30, septum flushing 1.3 ml min^{-1}. The following temperature program was routinely used: 3 min at 50°C (starting phase), 5 K min^{-1} (heating phase), 15 min at 310°C (plateau phase). The retention time was indicated in seconds.

3.4. General synthesis procedure for the C_1-bridged ligand precursors of the type $C_{13}H_9$–CR^1R^2–C_5H_5 (R^1, R^2 = Me, cycloalkylidene, phenyl) (**1/1*–5/15***)

A total of 6.0 g (36 mmol) fluorene was dissolved in 100 ml diethyl ether and slowly mixed with 22.5 ml (36 mmol) *n*-butyllithium (1.6 M in hexane) at r.t. The

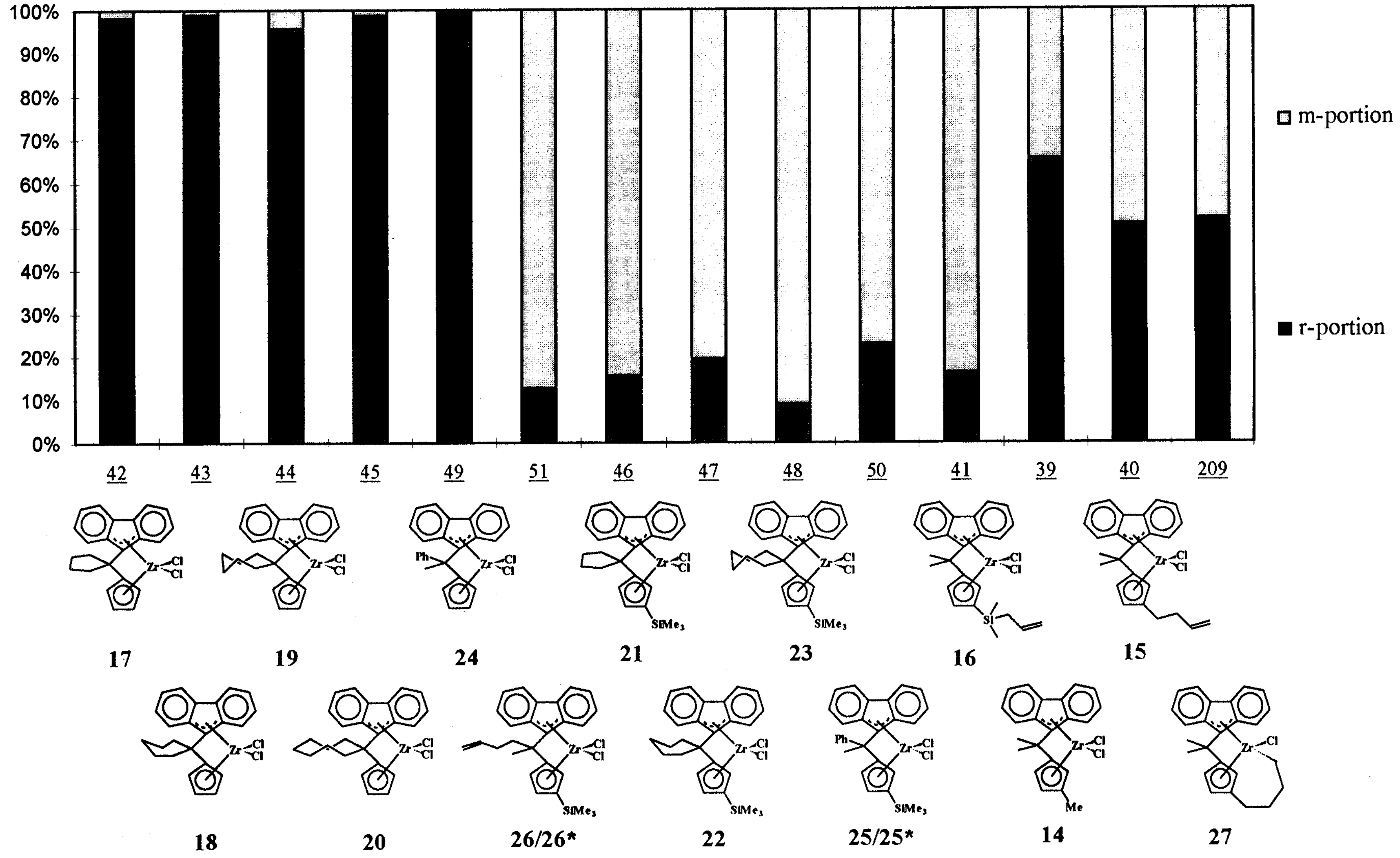


Fig. 12. Pentad analysis of the polypropylenes: r- and $m^{a)}$-portions of the polypropylenes are related to the corresponding catalyst system. $^{a)}$ $\Sigma\ r\ [\%] = \frac{1}{2}$ mr + rr; mr = mmrm + mmrr + rmrm + rmmr; rr = mrrm + mrrr + rrrr; $\Sigma\ m\ [\%] = \frac{1}{2}$ mr + mm; mm = mmmm + mmmr + rmmr, the r portion corresponds to syndiotactic polypropylene, the m portion to isotactic polypropylene.

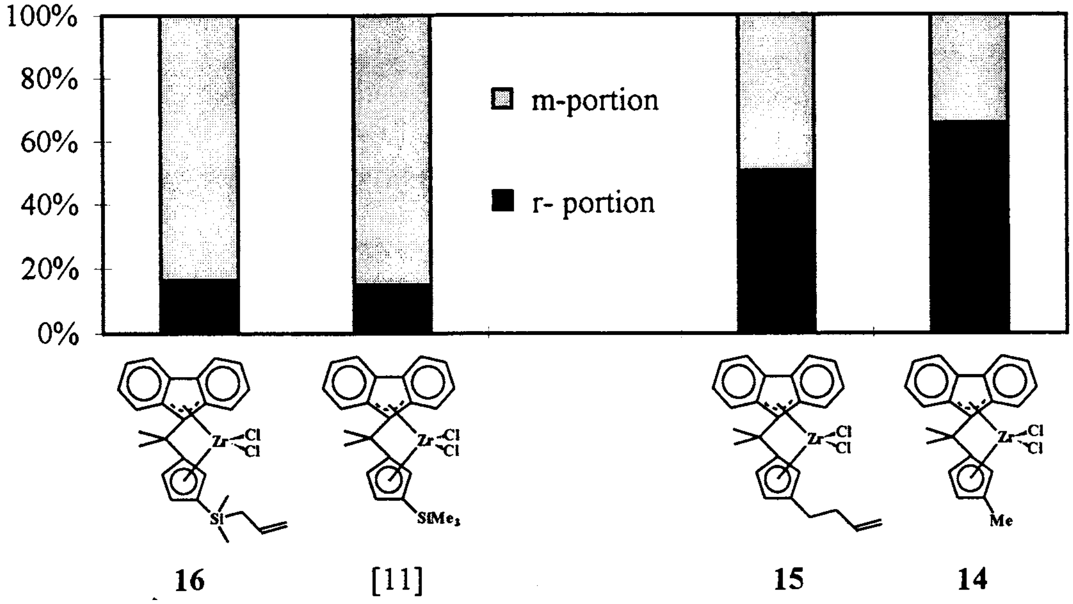


Fig. 13. Comparison of the tacticities of the polypropylenes synthesized with substituted fluorenylidene cyclopentadienylidene complexes/MAO.

reaction mixture was stirred for at least 6 h. An equimolar amount of the corresponding fulvene derivative was added and stirred overnight. Then a 0.1 equivalent butyllithium was added to convert the excess fulvene into a more soluble compound. The mixture was stirred for another 30 min and hydrolyzed with 50 ml water. The organic phase was dried over sodium sulfate, and the solvent evaporated in vacuo. For purification, the residue was dissolved in pentane, the solution was filtered over silica and the compound was crystallized at − 18°C. The yields were 70–90%.

1-(9-Fluorenyl)-1-[1-(1,3-cyclopentadienyl)]cyclopentane and isomer (**1/1***): GC: 2436 s. MS: *m*/*e* 298 (M^+). 1-(9-Fluorenyl)-1-[1-(1,3-cyclopentadienyl)]cyclohexane and isomer (**2/2***): GC: 2540 s, 2555 s. MS: *m*/*e* 312 (M^+). 1-(9-Fluorenyl)-1-[1-(1,3-cyclopentadienyl)]cycloheptane and isomer (**3/3***): GC: 2804 s, 2811 s. MS:

Table 4
Pentad analysis of the polypropylenes produced with the catalysts **14**–**27**/MAO

	Isotactic portion			mr			Syndiotactic portion			$\Sigma r^{a,b}$	$\Sigma m^{a,b}$
	mmmm (%)	mmmr (%)	rmmr (%)	mmrr (%)	mmrm + rmrr (%)	rmrm (%)	rrrr (%)	mrrr (%)	mrrm (%)		
δ ^{13}C	21.83	21.59	21.37	21.05	20.85	20.60	20.31	20.10	19.95		
14	9.7	9.5	4.2	20.8	1.1		41.0	9.8	3.8	65.6	34.4
15	17.1	11.4	7.8	26.0			19.5	12.8	5.3	50.6	49.4
16	80.1[c]	80.1[c]		7.2			10.1		2.6	16.3	83.7
17			0.8	1.5	0.5		92.4[d]	4.9		98.2	1.8
18				2.2			97.8			98.9	1.1
19	1.4		1.0	2.4	1.4		93.2			95.1	4.3
20				2.3			97.7			98.8	1.2
21	72.1	8.0		8.5			8.9		2.4	15.6	84.4
22	75.9			4.7	4.7		7.4	7.4		19.5	80.6
23	78.6	7.0		10.9					3.5	9.0	91.0
24							99.0			99.0	
25/25*	52.4	13.4	2.0	16.3	2.4		9.3	2.1	2.2	22.9	77.1
26/26*	74.4	8.3		9.3			5.8		2.2	12.7	87.3
27	17.8	7.8	3.0	39.4			20.3	9.0	3.0	51.9	48.3

[a] Σr (%) = 0.5mr + rr; mr = mmrm + mmrr + rmrm + rmrr; rr = mrrm + mrrr + rrrr; Σm (%) = 0.5mr + mm; mm = mmmm + mmmr + rmmr.
[b] ^{13}C-NMR data of the polypropylenes: spectra recorded in 1,2,4-trichlorobenzene/1,1,2,2-tetrachlorodeuteroethane (3:1 v/v) at 120°C.
[c] No signal resolution.
[d] Error ± 1.5%.

Table 5
Molecular weight determinations for the polypropylene samples produced with **14**, **15**, **23**, **25/25***, **27**/MAO using gel permeation chromatography

Complex	$\bar{M}_n^a$ (g mol^{-1})	$\bar{M}_w^b$ (g mol^{-1})	$\bar{M}_z^c$ (g mol^{-1})	Dispersity ($\bar{M}_w/\bar{M}_n$)	$\bar{M}_\eta^d$ (g mol^{-1})
14	20 382	44 403	71 643	2.18	48 000
15	27 654	68 507	124 984	2.47	58 000
23	25 595	64 353	119 057	2.51	54 000
25/25*	13 716	41 479	74 187	3.02	48 000
27	31 333	73 106	132 120	2.33	63 000

[a] $\bar{M}_n$, number average molecular weight. [b] $\bar{M}_w$, weight average molecular weight. [c] $\bar{M}_z$, z-average molecular weight. [d] For comparison, the mean intrinsic viscosity $\bar{M}_\eta$ is included.

m/e 327 (M^+). 1-(9-Fluorenyl)-1-[1-(1,3-cyclopentadienyl)]cyclooctane and isomer(**4/4***): GC: 2878 s, 2891 s. 1-(9-Fluorenyl)-1-[1-(1,3-cyclopentadienyl)]-1-phenylethane and isomer (**5/5***): GC: 2832 s, 2850 s. MS: *m/e* 334 (M^+).

*3.5. General synthesis procedure for C_1-bridged ligand precursors of the type $C_{13}H_9$–CR^1R^2–C_5H_4R; (R^1, R^2, R = alkyl, alkenyl, phenyl, substituted silyl) (**6/6*–13/13***)*

A total of 6.0 g (36 mmol) fluorene was dissolved in 100 ml diethyl ether and slowly mixed with 22.5 ml (36 mmol) *n*-butyllithium (1.6 M in hexane) at r.t. The reaction mixture was stirred for at least 6 h. An equimolar amount of the corresponding fulvene derivative was added, and the mixture was stirred overnight. At −78°C, an equimolar amount of methyl iodide, allyldimethylsilyl chloride or trimethylsilyl chloride was added to the reaction mixture, and the mixture was stirred overnight. For processing, the mixture was hydrolyzed with 50 ml water, the organic phase was dried over sodium sulfate, and the solvent evaporated in vacuo. For purification, the residue was dissolved in

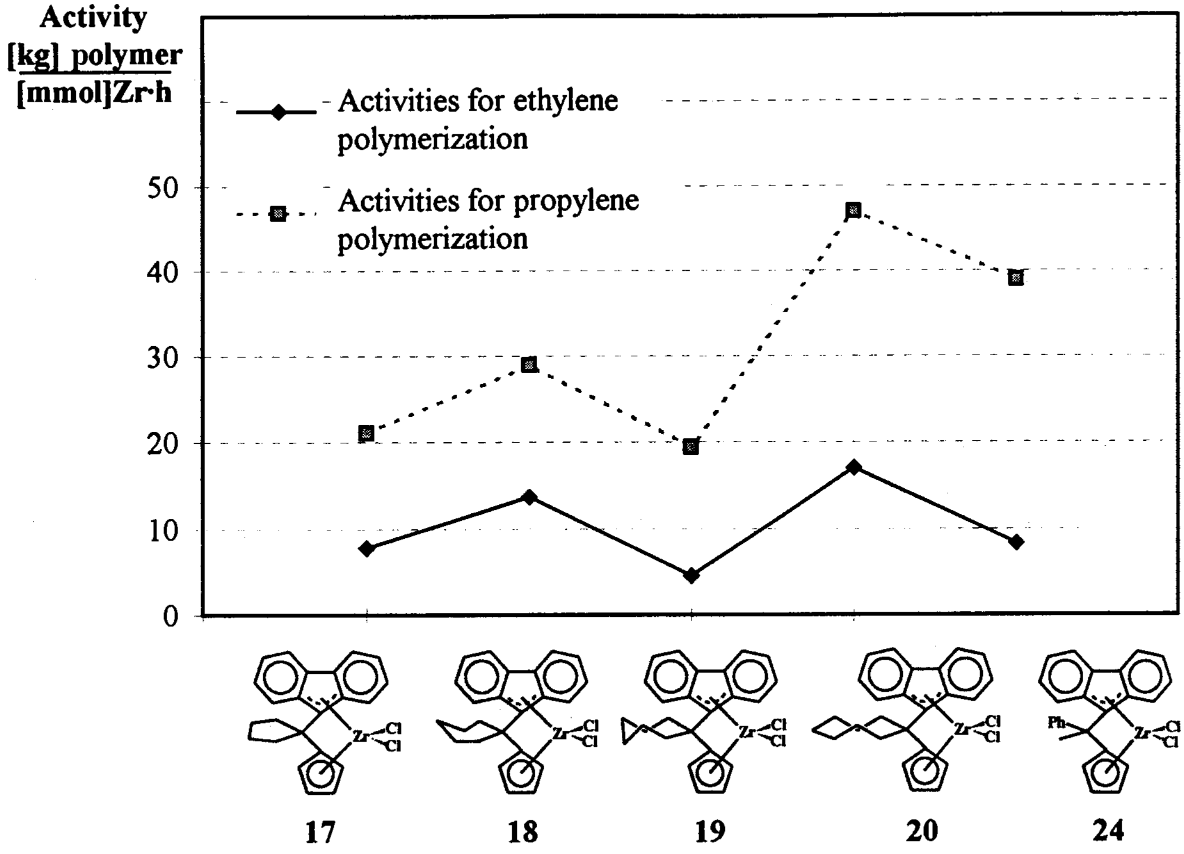


Fig. 14. Polymerization activities for substituted metallocene complexes of the type ($C_{13}H_8$–CR^1R^2–C_5H_4)$ZrCl_2$/MAO: ethylene compared with propylene.

Table 6
Overview of the polymerization experiments with propylene and polymer analysis

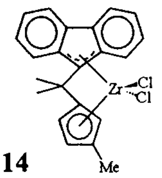
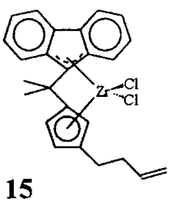
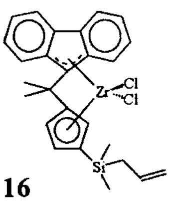
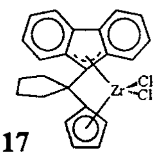
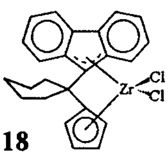
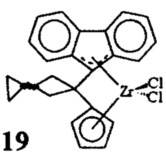
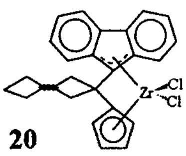
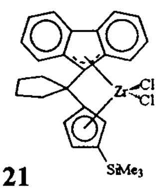
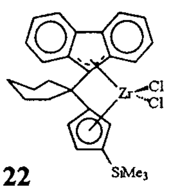
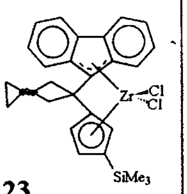
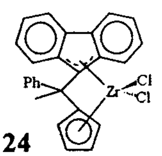
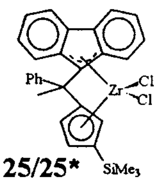
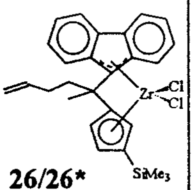
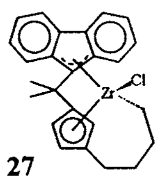
Complex	$\overline{M}_\eta$ [g/mol]	**Activity**[a] $\frac{[g]\ PE}{[mmol]\ Zr\ h}$ ($T_{i,max}$)[°C][b]	ΔH_m[c] [J/g]	T_m[d] [°C]	T_g[e] [°C] $\Delta c_p(T_g)$[f] [J/g]	^{13}C-NMR[g] Σ m [%] Σ r [%]
 **14**	48 000	28 700 (60.7)	-6.38	78.01	-5.73 0.402	34.4 65.6
 **15**	58 000	not determined (58.3)	n.v.	n.v.	-6.69 0.421	49.4 50.6
 **16**	48 000	10 600 (59.4)	-28.14	80.71	-5.73 0.071	83.7 16.3
 **17**	87 000	21 200 (60.6)	-29.02	76.34	0.85 0.095	1.8 98.2
 **18**	54 000	28 900 (82.7)	-22.13	70.07	-4.69 0.206	1.1 98.9
 **19**	110 000	19 400 (61.3)	-26.97	71.28	2.00 0.056	4.3 95.1
 **20**	78 000	47 000 (62.0)	20.79	134.96[h]	6.12 0.103	1.2 98.8

Table 6 (Continued)

 **21**	63 000	21 700 (61.3)	-31.88	68.18	3.35 0.122	84.4 15.6
 **22**	54 000	20 300 (60.2)	-37.54	64.39	4.10 0.086	80.6 19.5
 **23**	54 000	20 000 (60.0)	-26.33	78.13	-2.47 0.086	91.0 9.0
 **24**	160 000	39 200 (66.1)	-25.53	85.68	4.08 0.140	- 99.0
 **25/25***	48 000	11 300 (59.2)	-14.64	83.16	-4.51 0.317	77.1 22.9
 **26/26***	48 000	27 000 (60.6)	-23.70	75.50	-10.43 0.071	87.3 12.7
 **27**	63 000	not determined (58.4)	n.v.	n.v.	-4.38 0.463	48.3 51.9

[a] [Zr]:[AI] = 1:17000; [b] $T_{i,max}$ = maximum inside temperature of the reactor during polymerisation; [c] ΔH_m, describes the cristallization enthalpy for the second cooling phase of the DSC: [d] the minimum of the crystallization peak of the second cooling phase was selected as melting point; [e] the changing point of the glass transition of the DSC was selected as glass temperature; [f] glass transition enthalpies; g)Σ r [%] = $\frac{1}{2}$ rr, mr = mmrm + mmrr + rmrm + rmrr, rr = mrrm + mrrr + rrr, Σ m [%] = $\frac{1}{2}$ mr + mm, mm = mmmm + mmmr + rmmr; [h] Melting temperature of the second heating course due to missing crystallization peak.

pentane, the solution was filtered over silica, and the compound crystallized at − 18°C. The yields were 70–90%.

2-(9-Fluorenyl)-2-[1-(3-methyl)-1,3-cyclopentadienyl]-propane and isomer (**6/6***): GC: 2273 s. MS: *m/e* 286 (M$^+$). 2-(9-Fluorenyl)-2-{1-[3-(3-butenyl)]-1,3-cyclopentadienyl}propane and isomer (**7/7***): GC: 2665 s, 2680 s. 2-(9-Fluorenyl)-2-{1-[3-(allyl-dimethylsilyl)]-1,3-cyclopentadienyl}propane and isomer (**8/8***): GC: 2666 s. MS: *m/e* 370 (M$^+$). 1-(9-Fluorenyl)-l-[l-(3-trimethylsilyl)-1,3-cyclopentadienyl]cyclopentane and isomer (**9/9***): GC: 2650 s. 1-(9-Fluorenyl)-1-[1-(3trimethylsilyl)-1,3-cyclopentadienyl]cyclohexane and isomer (**10/10***): GC: 2766 s, 1-(9-Fluorenyl)-l-[l-(3-trimethylsilyl)-l,3-cyclopentadienyl]cycloheptane and isomer (**11/11***): GC: 3119 s. MS: *m/e* 398(M$^+$). 1-(9-Fluorenyl)-1-[1-(3-trimethylsilyl)-1,3-cyclopentadienyl]-1-phenylethane and isomer (**12/12***): GC: 3360 s. MS: **m/e** 406 (M$^+$). 5-(9-Fluorenyl)-5-[1-(3-trimethylsilyl)-1,3-cyclopentadienyl]-1-hexene and isomer (**13/13***): GC: 2824 s, MS: **m/e** 384 (M$^+$).

3.6. General synthesis procedure for the bridged metallocene complexes ***14–26/26****

A total of 1.0 g of the corresponding ligand precursor was dissolved in 40 ml diethyl ether and stirred with exactly two equivalents of *n*-butyllithium (1.6 M in hexane) for at least 8 h at r.t. Then one equivalent zirconium tetrachloride or hafnium tetrachloride was added, and the mixture stirred overnight. Further processing was conducted based on the solubility of the product: for ether soluble complexes, the mixture was filtered directly from the lithium chloride by-product; for the less soluble complexes, either the solvent was evaporated and the residue extracted with methylene chloride, or the complex solution was filtered over sodium sulfate, and the product extracted with methylene chloride or toluene from the frit. The solvent was then evaporated in vacuo.

2-η^3-(9-Fluorenylidene)-2-η^5-[1-(3-methyl)cyclopentadienylidene]propane zirconium dichloride (**14**): red crystals. MS: *m/e* 446 (M$^+$). 2-η^3-(9-Fluorenylidene)-2-η^5-{1-[3-(3-butenyl)lcyclopentadienylidene}propane zircorium dichloride (**15**): red crystals. 2-η^3-(9-Fluorenylidene)-2-η^5-{1-[3-(allyldimethylsilyl)]cyclopentadienylidene}propane zirconium dichloride (**16**): red crystals, elemental analysis, found: C 50.97, H 4.97. $C_{26}H_{28}SiZrCl_2 \cdot 1.3\ CH_2Cl_2$ calc.: C 51.14, H 4.81. MS: *m/e* 530 (M$^+$). 1-η^3-(9-Fluorenylidene)-l-η^5-(l-cyclopentadienylidene)cyclopentane zirconium dichloride (**17**): red crystals. MS: *m/e* 458 (M$^+$). 1-η^3-(9-Fluorenylidene)-1-η^5-(l-cyclopentadienylidene)cyclohexane zirconium dichloride (**18**): red crystals. 1-η^3-(9-Fluorenylidene)-1-η^5-(l-cyclopentadienylidene)cycloheptane zirconium dichloride (**19**): red crystals. MS: *m/e* 486 (M$^+$). 1-η^3-(9-Fluorenylidene)-1-η^5-(l-cyclopentadienylidene)cyclooctane zirconium dichloride (**20**): orange crystals. MS: *m/e* 500 (M$^+$). 1-η^3-(9-Fluorenylidene)-1-η^5-[1-(3-trimethylsilyl)cyclopentadienylidene]cyclopentane zirconium dichloride (**21**): red crystals. MS: *m/e* 530 (M$^+$). 1-η^3-(9-Fluorenylidene)-1-η^5-[1-(3-trimethylsilyl)cyclopentadienylidene]cyclohexane zirconium dichloride (**22**): red crystals. MS: *m/e* 544 (M$^+$). 1-η^3-(9-Fluorenylidene)-l-η^5-[1-(3-trimethylsilyl)cyclopentadienylidene]cycloheptane zirconium dichloride (**23**): red crystals. MS: *m/e* 559 (M$^+$). 1-η^3-(9-Fluorenylidene)-l-η^5-(l-cyclopentadienylidene)-l-phenylethane zirconium dichloride (**24**): red crystals. MS: *m/e* 494 (M$^+$). 1-η^3-(9-Fluorenylidene)-l-η^5-[1-(3-trimethylsilyl)cyclopentadienylidene]-l-phenylethane zirconium dichloride and isomer (**25/25***): red crystals. MS: *m/e* 566 (M$^+$). 5-η^3-(9-Fluoorenylidene)-5-η^5-[1-(3-trimethylsilyl)cyclopentadienylidene]-1-hexene zirconium dichloride and isomer (**26/26***): red crystals. MS: *m/e* 544 (M$^+$).

3.7. Synthesis procedure for metallocene complex **27**

A total of 3.0 mmol of the metallocene dichloride complex **15** and 0.79 g (3.11 mmol) lithium aluminum-tri-*tert*-butoxy hydride was dissolved in 50 ml THF, and the mixture was stirred at least overnight at r.t. The solvent was evaporated in vacuo, and the residue was extracted with toluene. Complex **27** forms orange crystals at − 25°C when hexane is added. Yield: 40%.

3.8. Self-immobilization

Investigations on self-immobilization were conducted in Schlenk tubes. Approximately 10 mg of the corresponding metallocene complex were activated with 10 ml MAO (30% solution in toluene), diluted with 40 ml toluene and then exposed to an ethylene pressure of 0.4–0.6 bar. The incorporation of the ω-alkenyl substituted metallocene complexes into the polymer chains was indicated by the characteristic color of the formed polymer precipitate.

3.9. Polymerization experiments

3.9.1. Activation of the catalyst precursors

The respective metallocene complex was weighed under inert gas (ca. 8–12 ± 0.1 mg) and activated with MAO (1 ml MAO (30% in toluene) per mg metallocene dichloride complex. The solution was diluted with toluene in a way that ca. 0.2–0.5 mg of the metallocene complex were dissolved in 1 ml of toluene. From this solution, an aliquot containing ca. 1 mg catalyst was removed and used for polymerization. These solutions were used for polymerization within 60 min after preparation.

3.9.2. Polymerization of ethylene

A 1 l Büchi laboratory autoclave BEP 280 was filled with 500 ml pentane, 7 ml MAO (30% in toluene) and the corresponding amount of catalyst solution ([Zr]:[Al] 1:17000). The reactor was thermostated at 60°C, and a constant ethylene pressure of 10 bar was applied. The polymerization was terminated after 1 h by venting the ethylene.

3.9.3. Polymerization of propylene

A total of 500 ml propylene ('polymerization grade') was condensed into the reactor, stirred for 20 min with 5 ml MAO (30% in toluene) at 20°C and then cooled to −5°C. The prepared catalyst solution (toluene/MAO = 10:1) was pressed into the cooled stirring vessel with 6.5 bar argon pressure from a burette. The reactor temperature was increased to 60°C within 15 min. Then the polymerization was conducted at ca. 25 bar propylene pressure and terminated after 1 h by releasing the unreacted propylene.

3.10. Characterization of the polymer samples

3.10.1. Differential scanning calorimetry

A Perkin Elmer calorimeter DSC-7 was available to measure the thermal properties of the polymer samples. Prior to the measurements, the polymer samples were dried in vacuo. To determine the fusion enthalpies of the polyethylenes and polypropylenes, 3–5 mg of each of the polymers were fused into standard aluminum pans and measured using the following temperature program: first heating phase (20 K min^{-1}) from 50 to 200°C, cooling phase (−20 K min^{-1}) to 50°C, second heating phase (20 K min^{-1}) from 50 to 200°C, secondly the cooling phase (−20 K min^{-1}) to 50°C. The temperature was linearly corrected relative to indium (m.p. 156.6°C); the fusion enthalpy of indium ($\Delta H_m = 28.45$ J g^{-1}) was used for calibration. The maximum of the melting temperatures during the second heating run was selected for the polyethylenes; for the polypropylenes, the minimum of the crystallization peak during the second cooling phase.

To determine the glass transition enthalpies of the polypropylene samples, 30–50 mg of the polymer were fused into standard aluminum pans and measured using the following temperature program: first heating phase (20 K min^{-1}) from −40 to 40°C, cooling phase (−20 K min^{-1}) to −40°C, second heating phase (20 K min^{-1}) from −40 to 40°C, 2nd cooling phase to −40°C.

To determine the crystallinity degree, α, the relationship $\alpha = \Delta H_m/\Delta H_m^\circ$ was selected. ΔH_m is derived from the data of the second heating course of the DSC. The fusion enthalpy for 100% crystalline polyethylene was assumed as 290 J g^{-1} [31].

3.10.2. Viscosimetry

The intrinsic viscosity was determined using an Ubbelohde precision capillary viscometer in *cis/trans* decalin at 135 ± 0.1°C. Prior to the measurements, the samples were weighed into sealable small flasks and dissolved in an exactly measured amount of decalin at 140–150°C over a period of 3–4 h. Calibration curves were available for the determination of M_η. Every polymer sample was weighed and measured twice to reduce the error.

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