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C_2-bridged metallocene dichloride complexes of the types $(C_{13}H_8–CH_2CHR–C_9H_{6-n}R'_n)ZrCl_2$ and $(C_{13}H_8–CH_2CHR–C_{13}H_8)MCl_2$ ($n = 0, 1$; R = H, alkenyl; R′ = alkenyl, benzyl; M = Zr, Hf) as self-immobilizing catalyst precursors for ethylene polymerization[1]

Helmut G. Alt *, Michael Jung

Laboratorium für Anorganische Chemie der Universität Bayreuth, Postfach 10 12 51, D-95440 Bayreuth, Germany

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Abstract

A total of 15 C_2-bridged fluorenylidene indenylidene and bis(fluorenylidene) metal dichloride complexes (metal = Zr, Hf) and the corresponding ligand precursors have been prepared and characterized. ω-Alkenyl substituents with various chain lengths in the C_2-bridge or in position 3 of the indenylidene moiety have an impact on the polymerization activity of the catalysts and the molecular weights of the produced polyethylenes. These ω-alkenyl substituents cause 'self-immobilization' due to their incorporation into the backbone of a growing polymer chain providing heterogeneous catalyst systems. © 1999 Published by Elsevier Science S.A. All rights reserved.

Keywords: Catalysis; Polymerization; Zirconium; Metallocene complexes

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1. Introduction

In the past 15 years metallocene complexes with group 4 metals became established catalysts for the polymerization of α-olefins [1–7]. *ansa*-Metallocene complexes with a C_2-bridge show very high catalytic olefin polymerization activities [8,9]. The C_2-bridge causes a favorable dihedral angle between both aromatic ligands and it allows their sufficient mobility that is advantageous for the kinetics of the olefin polymerization. We synthesized C_2-bridged fluorenylidene indenylidene and bis(fluorenylidene) metal dichloride complexes (metal = Zr, Hf) with one ω-alkenyl substituent in the bridge or in position 3 of the indenylidene ligand to investigate and compare their catalytic ethylene polymerization activities. We were especially interested in the influence of the position of the ω-alkenyl substituent on the polymerization properties of the catalysts and the molecular weights of the produced polyethylenes.

2. Results and discussion

2.1. Synthesis of the ω-alkenyl oxiranes **1–3**

No suitable synthesis was yet available for the substitution of an ethylene bridge in *ansa*-metallocene complexes with an alkenyl group. The synthetic route described here offers a new method for the substitution of a C_2-bridge with an ω-alkenyl substituent. The first step is the one-sided epoxidation of a diene to form an optically active alkenyl oxirane [10]. The respective

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* Corresponding author. Fax: +49 921 552157.

[1] Dedicated to Professor Dr. Günter Marx on the occasion of his 60th birthday (23.11.98).

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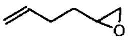
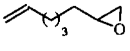
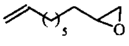
Table 1
NMR data of the alkenyl oxiranes **1**–**3** (250.13 MHz (^{1}H), 69.2 MHz (^{13}C))

	^{1}H-NMR$^{a)}$	^{13}C-NMR$^{a)}$
 **1**	5.68 (m, 1H,=**CH**), 4.83 (m, 1H,=**CH$_2$**), 4.83 (m, 1H,=**CH$_2$**), 2.73 (ABMX$_2$, 1H, **CH**), 2.54 (ABM, 1H, **CH$_2$**), 2.27 (ABM, 1H, **CH$_2$**), 2.05 (m, 2H, **CH$_2$**), 1.45 (m, 2H, **CH$_2$**)	137.6 (=**CH**), 115.1 (=**CH$_2$**), 51.8 (**CH**), 47.1 (**CH$_2$**), 31.8, 30.1 (**CH$_2$**)
 **2**	5.66 (m, 1H,=**CH**), 4.81 (m, 1H,=**CH$_2$**), 4.81 (m, 1H,=**CH$_2$**), 2.77 ABMX$_2$, 1H, **CH**), 2.60 (ABM, 1H, **CH$_2$**), 2.32 (ABM, 1H, **CH$_2$**), 1.94 (m, 2H, **CH$_2$**), 1.43–1.31 (6H, **CH$_2$**)^b	138.3 (=**CH**), 114.2 (=**CH$_2$**), 51.9 (**CH**), 46.6 (**CH$_2$**), 33.4, 32.1, 28.4, 25.2 (**CH$_2$**)
 **3**	5.73 (m, 1H,=**CH**), 4.86 (m, 1H,=**CH$_2$**), 4.86 (m, 1H,=**CH$_2$**), 2.80 (ABMX$_2$, 1H, **CH**), 2.67 ABM, 1H, **CH$_2$**), 2.40–2.36 (ABM, 1H, **CH$_2$**), 1.95 (m, 2H, **CH$_2$**), 1.45–1.27 (10H, **CH$_2$**)^b	138.8 (=**CH**), 114.1 (=**CH$_2$**), 52.1 (**CH**), 46.8 (**CH$_2$**), 33.6, 32.3, 29.1, 28.8, 28.7, 25.7 (**CH$_2$**)

$^{a)}$in $CDCl_3$ (saturated solution) at 25°C; $^{b)}$indicated as a shift range due to resonance overlap.

dienes are reacted with an equimolar amount of *m*-chloroperbenzoic acid in methylene chloride to give the 1,2-epoxy alk-ω-ene compounds **1**–**3**. The NMR spectroscopic data of the epoxy alkenes **1**–**3** are listed in Table 1 (Fig. 1).

2.2. Synthesis of C_2-bridged ligand precursors of the types $C_{13}H_8$–CH_2CHR–C_9H_7 and $C_{13}H_8$–CH_2CHR–$C_{13}H_8$ (R = H, alkenyl)

The 1,2-epoxy alkenes **1**–**3** react quantitatively with fluorenyllithium by ring opening to form the corresponding alcoholates or, after hydrolysis, to give the corresponding alcohols **4**/**4***–**6**/**6*** [11–13]. The subsequent mesylation [14] of the alcohol with mesyl chloride in dichloromethane in the presence of triethylamine produces compounds **7**/**7***–**9**/**9***. The compounds are a mixture of isomers formed by addition of the fluorenyllithium to the two methylene carbon atoms of the oxirane. The isomer mixture is used for the further reactions (Fig. 2). The NMR spectroscopic data of compounds **4**/**4***–**9**/**9*** are given in Table 2.

The mesylates react with fluorenyllithium or indenyllithium in a nucleophilic substitution to form the corresponding C_2-bridged ligand precursors **10**/**10***–**15**/**15***. These reactions are relatively slow. Therefore, to achieve high yields, the reaction mixtures are stirred for 4–5 days at room temperature. The isomers **10**/**10***–**12**/**12*** could not be separated and were used without separation for the subsequent complexation reactions (Fig. 3).

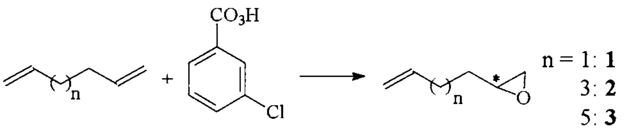


Fig. 1. One-sided epoxidation of α, ω-dienes.

2.3. Synthesis of C_2-bridged ligand precursors of the type $C_{13}H_9$–C_2H_4–C_9H_6R (R = alkyl, alkenyl)

A ligand precursor with an unsubstituted ethylene bridge is obtained by the reaction of 2-(9-fluorenyl)-1-bromoethane and indenyllithium or substituted indenyllithium compounds. HMPT (hexamethylphosphoric triamide) has to be added to avoid the formation of 4,5,6,7-dibenzospiro[2,4]heptane [15]. Using this reaction pathway, several 1-indenes (i.e. allyl-1-indene, 3-butenyl-1-indene, 4-pentenyl-1-indene, 5-hexenyl-1-indene, benzyl-1-indene and 5-hexenyldimethylsilyl-1-indene) were reacted to prepare $C_{13}H_9$–C_2H_4–C_9H_6R ligand precursors according to known procedures [16] (Scheme 1).

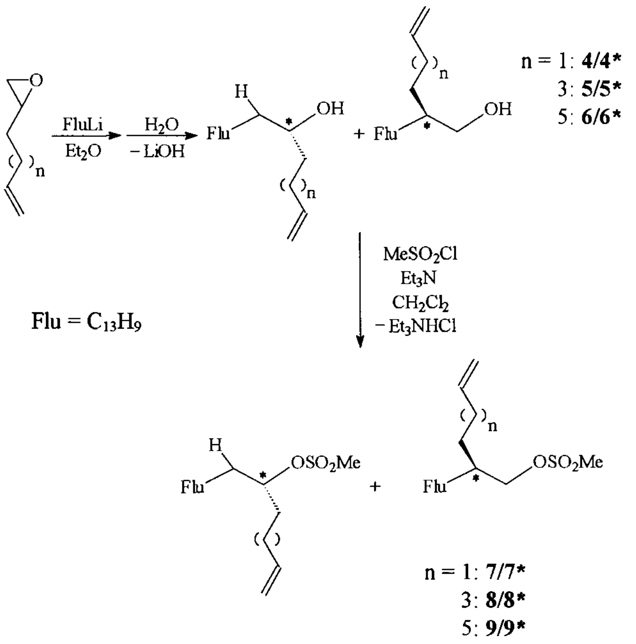
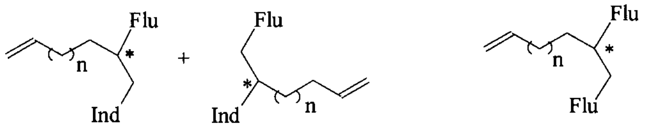


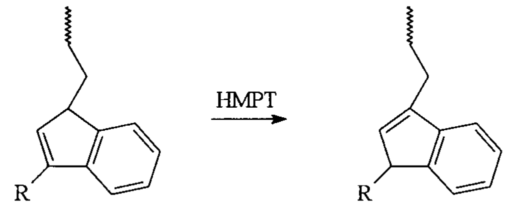
Fig. 2. Reaction pathway for the isomer mixtures **7**/**7***–**9**/**9***.



n = 1: **10/10***
3: **11/11***
5: **12/12***

n = 1: **13**
3: **14**
5: **15**

Fig. 3. Ligand precursors **10/10***–**15/15***.



Scheme 2. Isomerization of the double bond by addition of HMPT.

The increase of the solvent polarity, due to the addition of HMPT, causes an isomerization of the double bond in the five-membered indenyl ring (Scheme 2). 2-(9-Fluorenyl)-1-bromoethane [15] reacts with the corresponding substituted and lithiated indenyl derivatives to form the ethylene bridged ligand precursors **16/16***–**21/21***. The NMR spectroscopic data of compounds **10/10***–**21/21*** are listed in Table 3 (Figs. 3 and 4).

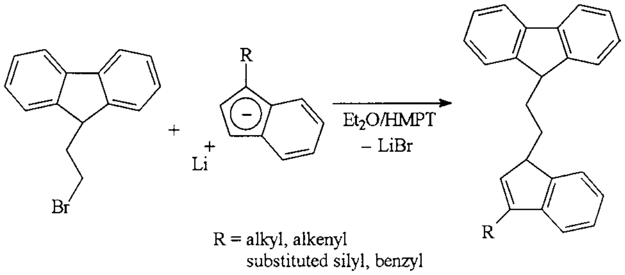
2.4. Synthesis of the metallocene dichloride complexes

The bridged metallocene complexes **22/22***–**35** were synthesized in diethyl ether using standard procedures [8,17]. The ligand precursor was mixed with *n*-butyllithium, and the dianion formed was reacted with solid zirconium tetrachloride or hafnium tetrachloride (Scheme 3).

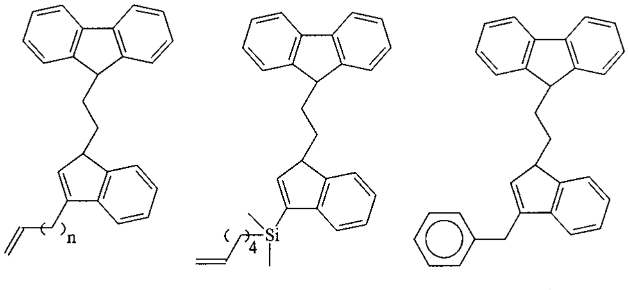
The ethylene bridged bis(fluorenylidene) complexes are fairly air stable. Fig. 5 provides an overview of the metallocene complexes synthesized. Compounds **22/22***–**24/24*** exist as a mixture of various isomers (Fig. 6). Therefore, no clear interpretation of the NMR-spectra of these complexes was possible. The bis(fluorenylidene) complexes **25**–**29** possess higher symmetry than the mixed fluorenyl indenyl derivatives due to the two identical π-ligands and exist as enantiomeric pairs (Fig. 7). Fig. 8(a) shows the ^{1}H-NMR spectrum of **25**. The assignment of the signals in the ^{1}H- and ^{13}C-NMR spectra was confirmed by a 250.13 MHz 2D-^{1}H, ^{1}H-Cosy 45 experiment and a 62.9 MHz 2D-^{1}H, ^{13}C heteronuclear shift correlation experiment (Table 4). The ^{1}H-NMR spectrum shows doublets in the aromatic region at $\delta = 8.10$, 8.02, 7.81, 7.79, 7.70, 7.69, 7.51 and 4.47 ppm, as well as triplets at $\delta = 7.36$, 7.25, 7.22, 7.21, 7.20, 7.08 and 7.06 ppm. These are attributed to the aromatic protons of both fluorenylidene ligands. The vinyl group signals appear as three multiplets at $\delta = 5.86$, 5.05 and 5.00 ppm. The protons of the ethylene bridge form an AMX spin system whereby the proton of the alkenyl group bonding carbon atom (= X part) couples additionally with the neighboring methylene group. The multiplet appears at $\delta = 5.16$ ppm; the AM-part forms a doublet of a doublet, each at $\delta = 4.65$ and 4.24 ppm. The multiplets at $\delta = 2.42$ and 2.09 ppm are attributed to the two methylene groups of the alkenyl chain.

The J-modulated ^{13}C-NMR spectrum of **25** (Fig. 8(b)) shows ten signals for the quaternary carbon atoms at $\delta = 129.3$, 128.4, 125.5, 124.4, 123.7, 123.6, 120.4, 120.1, 107.6 and 101.7 ppm and 16 signals for the tertiary carbon atoms of both fluorenylidene ligands at $\delta = 128.3$, 128.2, 128.0, 127.7, 125.6, 125.4, 125.2, 125.2, 125.1, 124.8, 124.5, 124.3, 123.1, 123.0, 122.9 and 121.9 ppm. The signals at $\delta = 42.5$ ppm (tertiary carbon atom) and $\delta = 35.5$ ppm (secondary carbon atom) are attributed to the ethylene bridge. The signals at $\delta = 34.8$ and 32.3 ppm correspond to the two methylene groups of the butenyl chain.

The quaternary carbon atoms 9 and 9′ are located at $\delta = 107.1$ and 101.7 ppm in the region of a η^5-bonded fluorenylidene ligand [18–20]. In contrast, the signal of the quaternary carbon atom in C$_1$-bridged fluorenylidene complexes appears at $\delta = 80$ ppm corresponding to a η^3 bonding mode of the ligand. For the recently



Scheme 1. Synthesis of C$_2$-bridged ligand precursors.



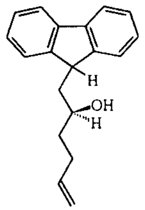
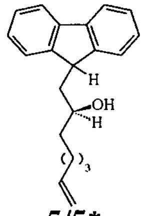
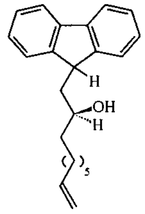
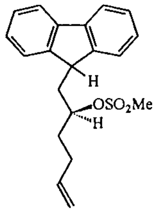
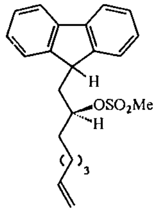
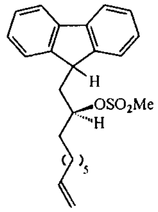
n = 1: **16/16***
2: **17/17***
3: **18/18***
4: **19/19***

20/20*

21/21*

Fig. 4. Ligand precursors **16/16***–**21/21***.

Table 2
NMR data of compounds **4**/**4***–**9**/**9*** (250.13 MHz (^{1}H), 69.2 MHz (^{13}C))

	^{1}H-NMR[a]	^{13}C-NMR[a]
 **4/4***	7.83–7.79 (m, 2H), 7.67 (m, 1H), 7.55 (m, 1H), 7.45–7.35 (4H)[b], 5.83 (m, 1H, =**CH**), 5.07 (m, 1H, =**CH**$_2$) 5.07 (m, 1H, =**CH**$_2$), 4.23 (m, 1H, **CH**), 3.95 (m, 1H, **CH**), 2.31–2.10 (m, 4H, **CH**$_2$), 1.93–1.83 (m, 1H, **CH**), 1.63–1.58 (m, 2H, **CH**$_2$)	147.6, 147.1, 140.9, 140.8 (**C**$_q$), 138.3 (=**CH**), 127.1, 127.0, 127.0, 126.8, 125.1, 124.3, 120.0, 119.8 (**CH**), 114.7 (=**CH**$_2$), 69.2 (**CHOH**), 44.5 (**CH**$_{Flu}$), 41.2, 37.2, 29.9 (**CH**$_2$)
 **5/5***	7.83–7.79 (m, 2H),7.67 (m, 1H), 7.53 (m, 1H), 7.40–7.30 (4H)[b], 5.83 (m, 1H, =**CH**), 5.07 (m, 1H, **CH**$_2$), 5.07 (m, 1H, =**CH**$_2$), 4.23 (m, 1H, **CH**), 3.96 (m, 1H, **CH**), 2.31–2.10 (m, 2H, **CH**$_2$), 2.07–1.97 (m, 2H,**CH**$_2$), 1.93–1.83 (m, 1H, **CH**), 1.63–1.58 (6H)[b]	147.6, 147.1, 140.9, 140 8 (**C**$_q$), 138.3 (=**CH**), 127.1, 127.0, 127.0, 126.8, 125.1, 124.3, 120.0, 119.8 (**CH**), 114.7 (=**CH**$_2$), 69.2 (**CHOH**), 44.5 (**CH**$_{Flu}$), 41.0, 37.9, 33.5, 28.1 (**CH**$_2$)[c]
 **6/6***	7.76 (d, ^3J(^{1}H, ^{1}H) 5.6 Hz, 2H), 7.62 (d, ^3J(^{1}H, ^{1}H)7.0 Hz, 1H), 7.50–7.47 (d, ^3J(^{1}H, ^{1}H) 7.0 Hz, 1H), 7.37–7.30 (4H)[b], 5.80 (m, 1H, =**CH**), 4.97 (m, 1H, =**CH**$_2$), 4.97 (m, 1H, =**CH**$_2$), 4.18 (m, 1H, **CH**), 3.75 (m. 1H, **CH**), 2.23 (m, 1H), 1.99 (m, 2H), 1.88 (m, 1H), 1.45–1.25 (12H)[b]	147.4, 147.0, 140.9, 140 7 (**C**$_q$), 139.0 (=**CH**), 127.1, 127.0. 127.0, 126.8, 125.0, 124.2, 120.0, 119.8 (**CH**), 114.1 (=**CH**$_2$), 69.7 (**CHOH**), 44.6 (**CH**$_{Flu}$), 41.0, 38.2, 33.7, 29.4, 28.9, 28.7, 25.4 (**CH**$_2$)
 **7/7***	7.78–7.75 (m, 2H), 7.67 (m, 1H), 7.48 (m, 1H), 7.38–7.28 (4H)[b], 5.72 (m, 1H, =**CH**), 4.94 (m, 1H, =**CH**$_2$), 4.94 (m, 1H, =**CH**$_2$), 4.89 (m, 1H, **CH**), 4.11 (m, 1H, **CH**), 2.74 (s, 3H, **CH**$_3$), 2.64–2.55(m, 2H, **CH**$_2$), 2.20–2.08 (m, 2H, **CH**$_2$), 1.79–1.71 (m, 2H, **CH**$_2$)	146.1, 146.0, 140.9, 140 7 (**C**$_q$), 136.7 (=**CH**), 127.4, 127.3, 127.1, 126.9, 126.8, 124.9, 124.7, 119.9 (**CH**), 115.5 (=**CH**$_2$), 80.8 (**CHOR**), 43.9 (**CH**$_{Flu}$), 38.3 (**CH**$_3$), 37.6, 34.5, 29.8 (**CH**$_2$)
 **8/8***	7.78–7.33 (8H)[b], 5.76 (m, 1H, =**CH**), 4.97 (m, 1H, **CH**$_2$), 4.97 (m, 1H, **CH**$_2$), 4.83 (m, 1H, **CH**), 4.10 (m, 1H, **CH**), 2.70(s, 3H, **CH**$_3$), 2.58–2.48 (m, 2H, **CH**$_2$), 2.15–1.98 (m, 2H, **CH**$_2$), 1.64–1.47 (m, 2H, **CH**$_2$), 1.38–1.29 (4H, **CH**$_2$)[b]	146.4, 146.1, 139.9, 139 7 (**C**$_q$), 138.2 (=**CH**), 127.24, 127.22, 127.18, 127.15, 124.7, 124.6, 123.9, 119.8 (**CH**), 114.4 (=**CH**$_2$), 81.3 (**CHOR**), 43.8 (**CH**$_{Flu}$), 38.1 (**CH**$_3$), 37.3, 35.0, 32.1, 28.1 (**CH**$_2$)
 **9/9***	7.77–7.66 (m, 2H), 7.49–7.30 (6H)[b], 5.78 (m, 1H, =**CH**), 4.98 (m, 1H, =**CH**$_2$), 4.98 (m, 1H, =**CH**$_2$), 4.85 (m, 1H, **CH**), 4.10 (m, 1H, **CH**), 2.72 (s, 3H, **CH**$_3$), 2.08–1.97 (m, 2H,**CH**$_2$), 1.64–1.60 (m, 2H, **CH**$_2$), 1.31–1.22 (m, 10H, **CH**$_2$)	146.2, 146.1, 140.9, 140.8 (**C**$_q$), 138.9 (=**CH**), 127.4, 127.3, 127.1, 124.9, 124.1, 120.0 (**CH**)[c], 114.2 (=**CH**$_2$), 81.6(**CHOR**), 44.0 (**CH**$_{Flu}$), 38.3 (**CH**$_3$), 37.6, 35.4, 33.6, 29.0, 28.7, 28.7, 24.3 (**CH**$_2$)

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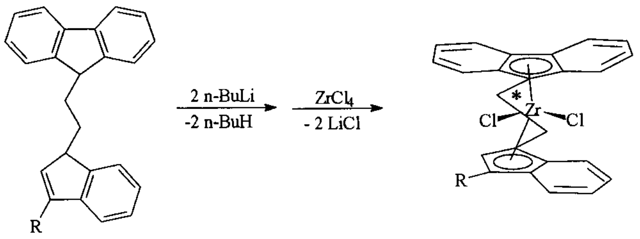
[a] in CDCl$_3$ (saturated solution) at 25°C; [b] indicated as a shift range due to signal overlap; [c] ^{13}C-NMR signals not completely separated due to signal overlap.



Scheme 3. Synthesis of the metallocene dichloride complexes.

synthesized C$_1$-bridged bis(fluorenylidene) complexes $(C_{13}H_8-CHBu-C_{13}H_8)MCl_2$ (M = Zr, Hf) [14], the signals of carbon 9 of the fluorenylidene moiety appear at $\delta = 71.9$ (Zr) and 72.9 ppm (Hf). In these cases, a η^1 bonding mode of the fluorenylidene ligand has to be assumed.

2.5. Polymerization of ethylene

All metallocene complexes, synthesized in this study, polymerize ethylene after activation with methylaluminoxane (MAO) [15–18]. One remarkable characteristic of metallocene complexes with an ω-alkenyl substituent is their ability to incorporate themselves into the growing polymer chain as a comonomer during the polymerization of α-olefins. In this way, these homogeneous metallocene catalysts become self-immobilizing. The further formation of polyolefin is catalyzed heterogeneously [21,22]. The polymer chain serves as an organic support. Table 5 lists the self-immobilizing potential of the individual complexes.

Fig. 9 presents the molecular weights of the polyethylenes obtained with the three different types of C$_2$-bridged complexes. In comparison, resins prepared with the fluorenylidene indenylidene complexes **22**/**22***–**24**/**24***/MAO (ω-alkenyl substituent in the bridge) have lower molecular weights ($270-330 \times 10^3$ g mol^{-1}) than those produced with the bis(fluorenylidene) complexes **25**–**27**/MAO ($380-430 \times 10^3$ g mol^{-1}). The C$_2$-bridged complexes **30**–**35**/MAO, with the substituent in position 3 of the indenylidene ligand, produce polyethylenes with molecular weights of $130-170 \times 10^3$ g mol^{-1}. Since the molecular weights of the polymers are mainly determined by the β-H-elimination rate during the catalytic process it becomes obvious that the length and the position of the substituents R can have a considerable influence on this chain terminating step.

The melting temperatures of the polyethylenes are between 131.7 and 140.0°C, with most melting points in the area of 136.0 ± 1.5°C (Fig. 10, Table 5). The fusion enthalpies show remarkable differences. Polyethylenes produced with the C$_2$-bridged complexes **30**–**35**/MAO (substituents on the indenylidene ligand) have the highest fusion enthalpies of 160 ± 5 J g^{-1}. This corresponds to a degree of crystallinity between 53 and 57% [23] which falls between those of conventional PE-LD ($\alpha = 40-50\%$) and PE-HD ($\alpha = 60-80\%$). The bis(fluorenylidene) complexes **25**–**27**/MAO produce resins with fusion enthalpies of 135 ± 5 J g^{-1} indicating a degree of crystallinity between 45 and 48%. The ethylene bridged fluorenylidene indenylidene complexes **22**/**22***–**24**/**24***/MAO (substituted in the bridge) synthesize polyethylenes with enthalpies of 120 ± 5 J g^{-1} ($\alpha = 40-43\%$) that are comparable with those for C, and Si bridged complexes [16].

2.6. The influence of the position of ω-alkenyl substituents on the polymerization properties and on the molecular weights of the polymers

The fluorenylidene indenylidene complexes **22**/**22***–**24**/**24*** contain one ω-alkenyl substituent in the C$_2$-

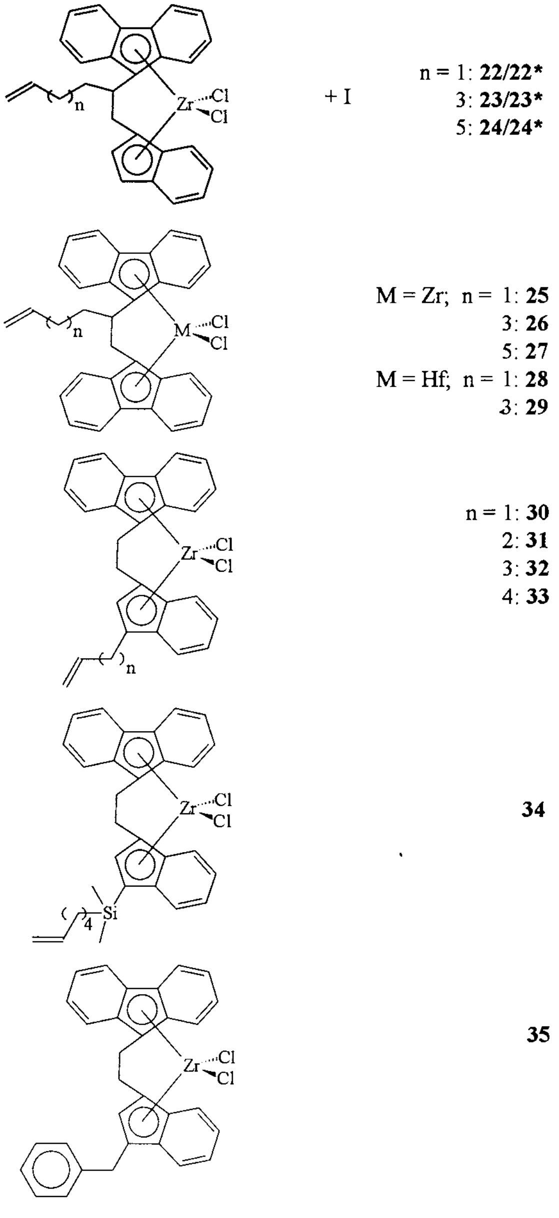


Fig. 5. Overview of the synthesized metallocene dichloride complexes.

Table 3
NMR data of the ligand precursors **10**/**10***–**21**/**21*** (250.13 MHz (^{1}H), 69.2 MHz (^{13}C))

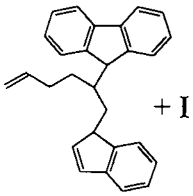
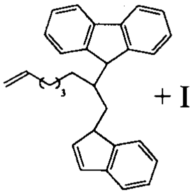
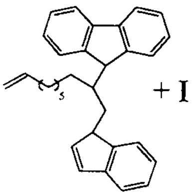
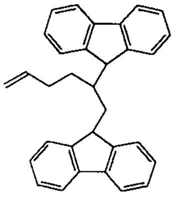
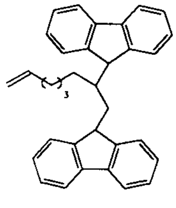
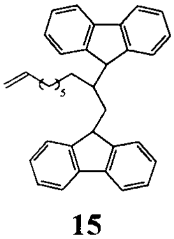
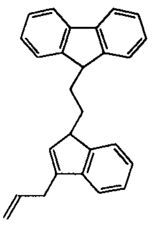
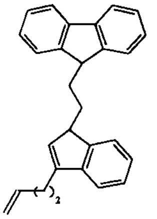
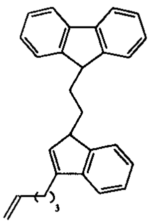
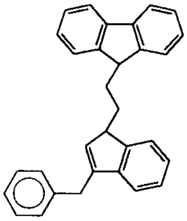
	^{1}H-NMR$^{a)}$	^{13}C-NMR$^{a)}$
 + I **10/10***$^{d)}$	7.71-7.23 (12H)$^{b)}$, 6.95 (m, 1H), 6.55 (m, 1H), 5.65 (m, 1H, =**CH**), 4.90 (m, 1H, =**CH$_2$**), 4.90 (m, 1H, =**CH$_2$**), 4.18 (m), 3.95 (m), 3.80 (m, 1H, **CH**), 3.68 (s), 3.56 (s), 3.33 (s, 1H, **CH**), 2.44 (m, 1H, **CH**), 2.13 (m, 2H, **CH$_2$**), 1.85 (m, 2H, **CH$_2$**), 1.51 (m, 2H, **CH$_2$**)	$^{c)}$ 147.8, 147.8, 147.7, 147.7, 146.8, 145.0, 141.1, 141.1, 141.1 (**C$_q$**), 138.5, 138.3, 136.5, 136.4, 132.2, 132.0, 127.1, 127.0, 126.9, 126.8, 126.7, 126.6, 126.5, 126.4, 124.6, 124.6, 124.5, 124.5, 123.2, 122.8, 121.0, 120.0, 119.9, 119.8, 119.7 (**CH**), 114.5, 114.4 (=**CH$_2$**), 53.2, 53.0, 45.7, 45.6, 36.5, 36.4 (**CH**), 33.8, 32.5, 31.8, 31.7, 30.1 (**CH$_2$**)
 + I **11/11***$^{d)}$ 0.6 / 0.4	7.83-7.64 (2H)$^{b)}$, 7.46-7.13 (10H)$^{b)}$, 6.90 (m, 1H, **CH$_{ind}$**), 6.56 (m, 1H, **CH$_{ind}$**), 5.75 (m, 1H, =**CH**), 4.96 (m, 1H, **CH$_2$**), 4.96 (m, 1H, **CH$_2$**), 4.17 (t, $^3J(^1H,^1H)$ 6.4 Hz), 3.80 (t, $^3J(^1H,^1H)$ 6.1 Hz, 1H, **CH**), 3.67 (s), 3,56 (s, 1H, **CH**), 2.39 (m, 1H, **CH**), 2.03 (m, 2H, **CH$_2$**), 1.87 (m, 1H, **CH$_2$**), 1.67 (m, 1H, **CH$_2$**), 1.54-1.30 (6H, **CH$_2$**)	147.8, 147.6, 147.5, 147.3, 146.6, 146.5, 145.0, 141.0, 140.9, 140.8, 140.7 (**C$_q$**), 138.8, 136.9, 136.6, 132.1, 131.8, 127.0, 127.0, 126.8, 126.8, 126.8, 126.7, 126.6, 126.4, 126.4, 124.6, 124.5, 124.5, 124.5, 123.1, 122.8, 120.9, 120.0, 119.9, 119.7, 119.6 (**CH**), 114.3, 114.1 (=**CH$_2$**), 53.3, 53.2, 45.8, 45.7, 37.1, 37.0 (**CH**), 36.4, 33.7, 33.5, 33.4, 33.3 (**CH$_2$**), 30.8 (**CH**), 30.7, 28.8, 27.0, 27.0 (**CH$_2$**)
 + I **12/12***$^{d)}$	7.83-7.64 (2H)$^{b)}$, 7.46-7.13 (10H)$^{b)}$, 6.98 (m, 1H, **CH$_{ind}$**), 6.62 (m, 1H, **CH$_{ind}$**), 5.90 (m, 1H, =**CH**), 5.07 (m, 1H, =**CH$_2$**), 5.07 (m, 1H, =**CH$_2$**), 4.22 (t, $^3J(^1H,^1H)$ 6.4 Hz, 4.04 (m), 3.86 (t, $^3J(^1H,^1H)$ 6.1 Hz, 1H, **CH**), 3.74 (s), 3.63 (s), 3.47 (d, $^3J(^1H,^1H)$ 1.8 Hz, 1H, **CH**), 2.42 (m, 1H), 2.21-2.03 (m, 2H, **CH$_2$**), 1.62-1.29 (10H, **CH$_2$**)$^{b)}$	$^{c)}$ 147.8, 147.6, 147.5, 146.6, 146.5, 145.0, 140.9, 140.8, 140.7 (**C$_q$**), 138.8, 136.9, 136.6, 132.1, 131.8, 127.0, 126.9, 126.8, 126.8, 126.7, 126.7, 126.6, 126.4, 126.3, 124.6, 124.5, 124.5, 124.4, 123.1, 122.7, 120.9, 119.9, 119.9, 119.8, 119.6, (**CH**), 114.1, 114.0 (=**CH$_2$**), 53.3, 53.2, 45.8, 45.7, 37.1, 37.0 (**CH**), 36.4, 33.7, 33.5, 33.4, 33.3 30.8 30.7, 28.8, 27.0, 27.0 (**CH$_2$**)
 **13**	7.88-7.76 (4H)$^{b)}$, 7.43-7.30 (12H)$^{b)}$, 5.52 (m, 1H, =**CH**), 4.84 (m, 1H, =**CH$_2$**), 4.84 (m, 1H, =**CH$_2$**), 4.11 (d, $^3J(^1H,^1H)$ 2.0 Hz, 1H, **CH**), 3.94 (t, $^3J(^1H,^1H)$ 6.0 Hz, 1H, **CH**), 2.57-2.51 (dt, (t, $^3J(^1H,^1H)$ 4.5 Hz; d, $^3J(^1H,^1H)$ 2.5 Hz) 1H, **CH**), 2.01-1.77 (4H, **CH$_2$**)$^{b)}$, 1.31-1.21 (m, 2H, **CH$_2$**)	147.6, 147.2, 146.0, 145.9, 141.5, 141.4, 140.6, 140.5 (**C$_q$**), 138.2 (=**CH**), 127.1, 126.9, 126.8, 126.7, 126.6, 124.8, 124.6, 124.5, 124.5, 124.4, 119.9, 119.7, 119.7 (**CH**)$^{e)}$, 114.6 (=**CH$_2$**), 49.5, 45.5, 38.4 (**CH**), 35.1, 31.5, 31.2 (**CH$_2$**)
 **14**	7.72 (d, $^3J(^1H,^1H)$ 6.7 Hz, 4H), 7.38-7.27 (12H)$^{b)}$, 5.65 (m, 1H, =**CH**), 4.85 (m, 1H, =**CH$_2$**), 4.85 (m, 1H, =**CH$_2$**), 4.06 (d, $^3J(^1H,^1H)$ 2.0 Hz, 1H, **CH**), 3.92 (d, $^3J(^1H,^1H)$ 6.4 Hz, 1H, **CH**), 2.43 (m, 1H, **CH**), 1.92-1.75 (4H, **CH$_2$**)$^{b)}$, 1.24-1.05 (6H, **CH$_2$**)$^{b)}$	147.5, 147.1, 146.0, 145.8, 141.4, 141.3, 140.5, 140.4 (**C$_q$**), 138.1 (=**CH**), 127.0, 126.8, 126.7, 126.7, 126.5, 124.7, 124.5, 124.4, 124.4, 124.3, 119.8, 119.6 119.6 (**CH**)$^{e)}$, 114.5 (=**CH$_2$**), 49.4, 45.4, 38.3 (**CH**), 35.0, 31.4, 31.1, 29.2, 28.6 (**CH$_2$**)
 **15**	7.77-7.73 (4H)$^{b)}$, 7.43-7.27 (12H)$^{b)}$, 5.78 (m, 1H, =**CH**), 4.97 (m, 1H, =**CH$_2$**), 4 97 (m, 1H, =**CH$_2$**), 4.10 (s, 1H, **CH**), 3.94 (t, $^3J(^1H,^1H)$ 6.3 Hz, 1H, **CH**), 2.47 (m, 1H, **CH**), 1.98-1.93 (m, 2H, **CH$_2$**), 1.91-1.75 (m, 2H, **CH$_2$**), 1.29-1.07 (10H, **CH$_2$**)$^{b)}$	147.9, 147.4, 146.3, 146.2, 141.7, 141.7, 141.0, 140.8 (**C$_q$**), 139.2 (=**CH**), 126.9, 126.8, 124.8, 124.7, 124.5, 119.8, 119.8 (**CH**)$^{e)}$, 114.1 (=**CH$_2$**), 49.8, 45.7, 39.2 (**CH**), 35.3, 33.7, 32.1, 29.2, 28.8, 27.5 (**CH$_2$**)$^{e)}$

Table 3 (Continued)

	^{1}H-NMR[a]	^{13}C-NMR[a]
 **16/16***[d]	7.74 (d, $^3J(^1H,^1H)$ 7.6 Hz, 2H), 7.48-7.15 (10H)[b], 6.14 (d, $^3J(^1H,^1H)$ 2.0 Hz, 1H, CH_{ind}), 6.10 (m, 1H, =CH), 5.15 (m, 1H, CH_2), 5.15 (m, 1H, CH_2), 3.96 (t, $^3J(^1H,^1H)$ 5.5 Hz, 1H, CH), 3.29-3.26 (m, 3H, CH, CH_2), 2.12 (m, 1H, CH_2), 1.95 (m, 1H, CH_2), 1.70 (m, 1H, CH_2), 1.38 (m, 1H, CH_2)	148.0, 147.0, 146.9, 141.5, 141.2 (C_q)[c], 135.5 (=CH), 133.7, 126.9, 126.8, 126.2, 124.7, 124.2, 122.7, 119.7, 119.7, 119.1 (CH), 116.2 (=CH_2), 48.8, 47.3 (CH), 32.2, 29.6, 26.7 (CH_2)
 **17/17***[d]	7.90-7.82 (2H)[b], 7.67 (m, 1H), 7.49-7.24 (8H)[b], 7.13 (d, $^3J(^1H,^1H)$ 6.6 Hz, 1H), 6.26 (d, $^3J(^1H,^1H)$ 1.6 Hz), 6.22 (d, $^3J(^1H,^1H)$ 1.6 Hz, 1H, CH_{ind}), 6.01 (m, 1H, =CH), 5.15 (m, 1H, =CH_2), 5.15 (m, 1H, =CH_2), 4.21 (t, $^3J(^1H,^1H)$ 5.0 Hz), 4.05 (d, $^3J(^1H,^1H)$ 5.4 Hz, 1H, CH), 3.42 (m, 1H, CH), 2.70 (m, 1H, CH_2), 2.57-2.40 (3H, CH_2), 2.20 (m, 1H, CH_2), 2.15-1.94 (m, 1H, CH_2), 1.78 (m, 1H, CH_2), 1.62 (m, 2H, CH_2)	148.5, 148.1, 147.1, 147.1, 145.1, 144.8, 143.4, 143.0, 141.4, 141.3, 141.3 (C_q), 138.7, 138.4 (=CH), 132.9, 132.7, 127.1, 127.0, 126.9, 126.8, 126.3, 126.3, 126.0, 124.8, 124.4, 124.3, 122.9, 122.8, 120.0, 120.0, 119.9, 119.8, 119.8, 119.0, 118.9, 118.6 (CH), 114.9, 114.8 (=CH_2), 48.8, 48.4, 47.4, 47.3 (CH), 32.1, 31.8, 31.3, 31.0, 29.6, 26.8 (CH_2)
 **18/18***[d]	7.94-7.85 (2H)[b], 7.67 (m, 1H), 7.53 -712 (8H)[b], 7.05 (m, 1H), 6.23 (d, $^3J(^1H,^1H)$ 1.9 Hz), 6.17 (d, $^3J(^1H,^1H)$ 1.9 Hz, 1H, CH_{ind}), 5.89 (m, 1H, =CH), 5.09 (m, 1H, =CH_2), 5.09 (m, 1H =CH_2), 4.18 (t, $^3J(^1H,^1H)$ 5.5 Hz), 4.01 (t, $^3J(^1H,^1H)$ 5.5 Hz, 1H), 3.37 (m, 1H, CH), 2.61-2.36 (3H, CH_2)[b], 2.23-2.11 (3H, CH_2)[b], 1.89-1.77 (2H, CH_2)[b], 1.57-1.34 (2H, CH_2)[b]	148.6, 148.1, 147.1, 147.0, 145.1, 144.8, 143.4, 143.1, 141.3, 141.3, 141.2 (C_q), 138.8, 138.7 (=CH), 133.0, 132.8, 132.7, 127.0, 126.9, 126.2, 124.6, 124.3, 122.8, 119.9, 119.8, 119.8, 118.9 (CH), 114.8, 114.6 (=CH_2), 48.9, 48.7, 47.5, 47.3, 47.2 (CH), 34.1, 33.6, 31.3, 27.2, 27.0, 26.9, 23.3, 18.3 (CH_2)
 **21/21***[d]	7.94-7.83 (3H)[b], 7.58-7.31 (13H)[b], 7.14 (m, 1H), 6.67 (d, $^3J(^1H,^1H)$ 5.5 Hz, 2H), 6.27 (d, $^3J(^1H,^1H)$ 5.5 Hz, 1H), 6.23 (m), 6.18 (m), 6.15 (m, 1H, CH_{ind}), 4.03 (m, 2H), 3.97 (s, 1H, CH), 3.44 (s, 1H, CH), 2.44 (2H, CH_2), 2.23 (m, 1H, CH_2), 2.05 (m, 1H, CH_2)	not determined

[a] in $CDCl_3$ (saturated solution) at 25°C; [b] indicated as a shift range because of signal overlap; [c] ^{13}C-NMR signals not completely separated because of signal overlap; [d] the complete spectroscopic determination of the ligand precursors was not carried out.

bridge. Complexes **30**–**35** have the ω-alkenyl substituent in position 3 of the indenylidene ligand. Polymer characterization results for resins made with these complexes are displayed in Figs. 11–13. They show that the substitution of the ω-alkenyl substituent in different positions of the complexes produces different polymers.

The polyethylenes produced with complexes **30**–**35**/MAO (substituents on the indenylidene ligand) possess molecular weights that are approximately 50% lower than the ones for polyethylenes produced with complexes **22**/**22***–**24**/**24***/MAO. The higher fusion enthalpies of the resins prepared with complexes **30**–**35**/MAO correspond to crystallinities of 53–57% [23]; an increase of approximately 10–18%. Complexes **30**–**35**/MAO achieve polymerization activities that are about ten times higher than those of complexes **22**/**22***–**24**/**24***/MAO (substituents in the bridge). Thus, the polymerization properties, the molecular weights and other polymer properties (e.g. crystallinity) can be controlled or influenced by a simple change of the position of the substituent.

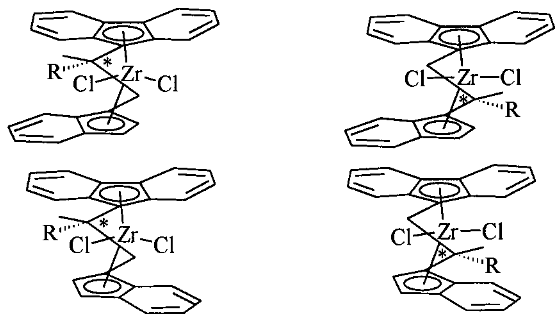


Fig. 6. Isomers of compounds **22**/**22***–**24**/**24***.

3. Experimental

3.1. NMR spectroscopy

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

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.

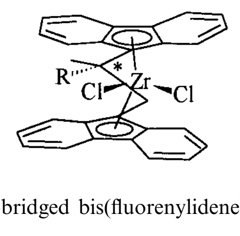


Fig. 7. C_2-bridged bis(fluorenylidene) complexes.

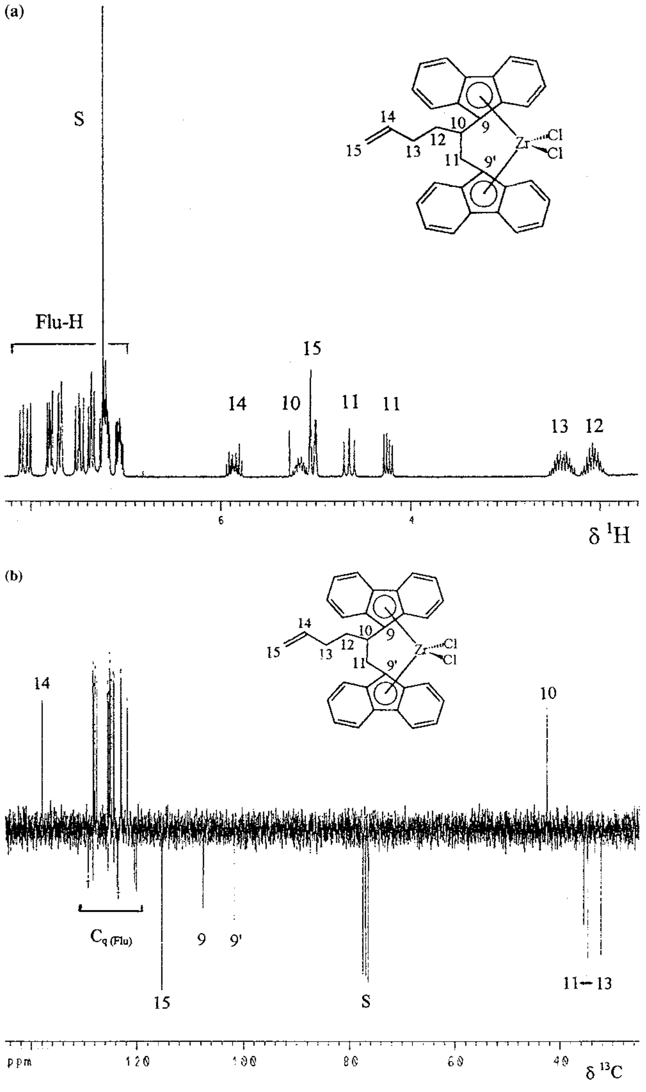


Fig. 8. (a) 250.13 MHz ^1H-NMR spectrum of **25** ($CDCl_3$, 25°C); S = $CHCl_3$. (b). 62.9 MHz J-modulated $^{13}C\{^1H\}$-NMR spectrum of **25** ($CDCl_3$, 25°C). Quaternary and CH_2 carbon atoms (negative phase), CH- and CH_3 carbon atoms (positive phase) are in phase; S = $CDCl_3$.

3.4. General synthesis procedure for the ω-alkenyl oxiranes *1–3*

A total of 13.75 g (79.6 mmol) *m*-chlorobenzoic acid in 250 ml methylene chloride were added dropwise to a solution of 9 g (110 mmol) 1,ω-alkadiene in 200 ml methylene chloride and the mixture was stirred over night. The suspension was filtered and washed with 2 M $NaHCO_3$, 2 N KOH and water. The organic phase was dried over sodium sulfate, the solvent evaporated in vacuo and the residue distilled. Yields: 60–80%.

But-3-en oxirane (**1**): colorless liquid, b.p. 119–121°C. Hex-5-en oxirane (**2**): colorless liquid, b.p. 146–150°C. Oct-7-en oxirane (**3**): colorless liquid, b.p. 75–80°C (15 Torr).

Table 4
NMR data of the metallocene complexes **25**–**35** (250.13 MHz (^{1}H), 69.2 MHz (^{13}C))

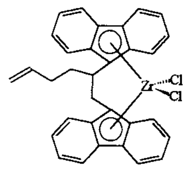
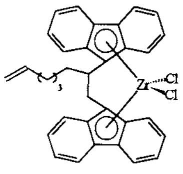
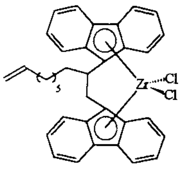
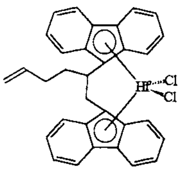
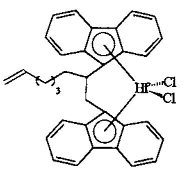
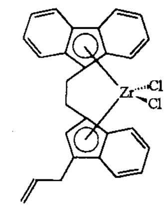
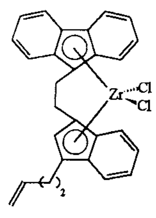
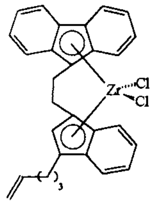
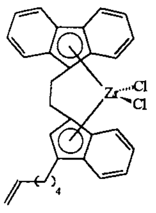
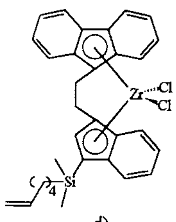
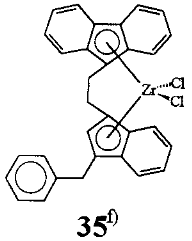
	^{1}H-NMR[a)]	^{13}C-NMR[a)]
 **25**	8.10 (d, $^{3}J(^{1}H,^{1}H)$ 8.5 Hz, 1H), 8.02 (d, $^{3}J(^{1}H,^{1}H)$ 8.5 Hz, 1H), 7.81 (d, $^{3}J(^{1}H,^{1}H)$ 5.0 Hz, 1H), 7.79 (d, $^{3}J(^{1}H,^{1}H)$ 5.0 Hz, 1H), 7.71 (t, $^{3}J(^{1}H,^{1}H)$ 1.25 Hz, 1H), 7.69 (d, $^{3}J(^{1}H,^{1}H)$ 1.25 Hz, 1H), 7.51 (d, $^{3}J(^{1}H,^{1}H)$ 8.75 Hz, 1H), 7.47 (d, $^{3}J(^{1}H,^{1}H)$ 8.75 Hz, 1H), 7.36 (t, $^{3}J(^{1}H,^{1}H)$ 6.8 Hz, 1H) 7.36 (t, $^{3}J(^{1}H,^{1}H)$ 6.8 Hz, 1H), 7.25 (m, 1H), 7.23 (m, 1H), 7.22 (m, 1H), 7.20 (m, 1H), 7.08 (m, 1H), 7.06 (m, 1H), 5.86 (m, 1H, =CH), 5.17 (m, 1H, CH), 5.05 (m, 1H, =CH_2), 5.05 (m, 1H, =CH_2), 4.65 (t, $^{3}J(^{1}H,^{1}H)$ 14.5 Hz, 1H, CH), 4.24 (dd, $^{3}J(^{1}H,^{1}H)$ 14.5 Hz, $^{3}J(^{1}H,^{1}H)$ 7.5 Hz, 1H, CH), 2.35 (m, 2H, CH_2), 2.05 (m, 2H, CH_2)	137.9 (=CH), 128.4, 128.3 (C_q), 128.2, 128.0, 127.9, 127.5, 125.6, 125.5 (CH), 125.4 (C_q), 125.2, 125.1, 125.0, 124.8, 124.5 (CH), 124.4 (C_q), 124.3 (CH), 123.7, 123.6 (C_q), 123.1, 123.0, 122.9, 121.9 (CH), 120.4, 120.1 (C_q), 115.4 (=CH_2), 107.6, 101.7 (C_q), 42.5 (CH), 35.5, 34.8, 32.3 (CH_2)
 **26**	8.09 (d, $^{3}J(^{1}H,^{1}H)$ 8.6 Hz, 1H), 8.04 (d, $^{3}J(^{1}H,^{1}H)$ 8.6 Hz, 1H), 7.82 (d, $^{3}J(^{1}H,^{1}H)$ 4.6 Hz, 1H), 7.78 (d, $^{3}J(^{1}H,^{1}H)$ 4.6 Hz, 1H), 7.71-7.67 (2H)[b)], 7.49 (m, 2H), 7.36 (t, $^{3}J(^{1}H,^{1}H)$ 7.0 Hz, 1H), 7.36 (t, $^{3}J(^{1}H,^{1}H)$ 7.0 Hz, 1H), 7.27-7.17 (4H)[b)], 7.11-7.05 (2H)[b)], 5.71 (m, 1H, =CH), 5.13 (m, 1H, CH), 4.90 (m, 1H, =CH_2), 4.90 (m, 1H, =CH_2), 4.63 (t, $^{3}J(^{1}H,^{1}H)$ 12.5 Hz, 1H), 4.23 (dd, $^{3}J(^{1}H,^{1}H)$ 12.5 Hz, $^{3}J(^{1}H,^{1}H)$ 7.5 Hz, 1H, CH), 2.34 (m, 1H, CH_2), 2.25 (m, 1H, CH_2), 2.00 (m, 2H, CH_2), 1.50-1.40 (3H, CH_2), 1.25-1.20 (m, 1H, CH_2)	138.6 (=CH), 129.4 (C_q), 128.4 (CH), 128.4 (C_q), 128.1, 128.0, 127.6 , 125.5 (CH), 125.5 (C_q), 125.4, 125.2, 125.1, 125.0, 124.8, 124.5, 124.3 (CH), 123.7, 123.6 (C_q)[c)], 123.1, 122.9, 122.8, 121.9 (CH), 120.4, 120.1 (C_q), 114.4 (=CH_2), 107.9, 101.9 (C_q), 43.5 (CH), 35.6, 33.5, 28.8, 27.8 (CH_2)
 **27**	8.09 (d, $^{3}J(^{1}H,^{1}H)$ 8.6 Hz, 1H), 8.04 (d, $^{3}J(^{1}H,^{1}H)$ 8.6 Hz, 1H), 7.83-7.78 (2H)[b)], 7.72-7.67 (2H)[b)], 7.50 (t, $^{3}J(^{1}H,^{1}H)$ 8.3 Hz, 2H), 7.39-7.33 (2H)[b)], 7.27-7.19 (4H)[b)], 7.09-7.05 (2H)[b)], 5.75 (m, 1H, =CH), 5.15-5.05 (m, 1H, CH), 4.94 (m, 1H, =CH_2), 4.94 (m, 1H, =CH_2) 4.63 (t, $^{3}J(^{1}H,^{1}H)$ 13.4 Hz, 1H, CH), 4.23 (dd, $^{3}J(^{1}H,^{1}H)$ 14.3 Hz, 7.3 Hz, 1H, CH), 2.33 (m, 1H, CH_2), 2.23 (m, 1H, CH_2), 1.98 (m, 2H, CH_2), 1.38-1.23 (8H, CH_2)[b)]	139.0 (=CH), 129.4 (C_q), 128.4, 128.1, 127.9, 127.5, 125.5, 125.4, 125.2, 125.1, 125.0, 124.8, 124.4, 124.3 (CH), 123.7, 123.5 (C_q)[c)], 123.1, 122.9, 121.9 (CH), 120.4, 120.0 (C_q), 114.2 (=CH_2), 108.1, 101.9 (C_q), 43.5 (CH), 35.8, 35.7, 33.6, 29.4, 28.9, 28.8, 28.3 (CH_2)
 **28**	8.09 (d, $^{3}J(^{1}H,^{1}H)$ 8.6 Hz, 1H), 8.04 (d, $^{3}J(^{1}H,^{1}H)$ 8.6 Hz, 1H), 7.83-7.68 (4H)[b)], 7.55-7.14 (8H)[b)], 7.02-6.98 (2H)[b)], 5.85 (m, 1H, =CH), 5.11 (m, 1H, CH), 5.07 (m, 1H, =CH_2), 5.07 (m, 1H, =CH_2), 4.62-4.40 (2H, CH)[b)], 2.40 (m, 2H, CH_2), 2.07 (m, 2H, CH_2)	138.0 (=CH), 128.7 (C_q), 128.2, 127.9, 127.8 (CH), 127.6 (C_q), 127.4, 127.2, 127.0, 126.8, 125.4, 125.3, 125.0, 124.9, 124.7, 124.5, 124.3 (CH), 123.5 (C_q)[c)], 122.8, 122.8 (CH), 122.6 (C_q), 121.7, 120.1 (CH), 119.2 , 118.9 (C_q), 115.3 (=CH_2), 103.6, 98.3 (C_q), 41.9 (CH), 35.0, 34.7, 32.4 (CH_2)
 **29**	8.09 (d, $^{3}J(^{1}H,^{1}H)$ 8.6 Hz, 1H), 8.04 (d, $^{3}J(^{1}H,^{1}H)$ 8.6 Hz, 1H), 7.83-7.78 (2H)[b)], 7.77-7.68 (2H)[b)], 7.55-7.00 (10H)[b)], 5.72 (m, 1H, =CH), 5.07 (m, 1H, CH), 4.90 (m, 1H, =CH_2), 4.90 (m, 1H, =CH_2), 4.61-4.37 (2H, CH)[b)], 2.29 (m, 1H, CH_2), 2.20 (m, 1H, CH_2), 1.97 (m, 2H, CH_2), 1.49-1.40 (4H, CH_2), 1.18 (m, 2H, CH_2)	138.7 (=CH), 128.8 (C_q), 128.2, 127.9, 127.8 (CH), 127.7 (C_q), 127.3, 126.9, 126.7, 126.6, 125.4, 125.3, 124.9, 124.9, 124.8, 124.6, 124.4, 124.3 (CH), 123.8 (C_q), 122.8, 122.6 (CH), 122.6 (C_q), 121.7, 119.8 (CH), 119.7, 118.8 (C_q), 114.4 (=CH_2), 104.0, 98.4 (C_q), 42.8 (CH), 35.8, 34.8, 33.5, 28.8, 28.0 (CH_2)

Table 4 (Continued)

	^{1}H-NMR[a]	^{13}C-NMR[a]
 **30**	7.95 (d, $^3J(^1H,^1H)$ 8.5 Hz, 1H), 7.85 (d, $^3J(^1H,^1H)$ 8.5 Hz, 1H), 7.75-7.65 (2H)[b], 7.48-7.22 (6H)[b], 7.01-6.99 (2H)[b], 5.98 (s, 1H, CH_{Ind}), 5.71 (m, 1H, =CH), 4.89 (m, 1H, =CH_2), 4.89 (m, 1H, =CH_2), 4.30 (m, 1H, CH_2), 4.16-3.99 (2H, CH_2), 3.89 (m, 1H, CH_2), 3.34 (**AB**M, 2H)	136.3 (=CH), 128.6, 128.5 (CH), 127.4, 127.3 (C_q), 126.2, 125.9 (CH), 125.6, 125.5 (C_q), 125.4, 125.3, 125.0, 124.6, 123.9 (CH), 123.4, 122.7 (C_q), 122.6, 122.4 (CH), 121.7 (C_q), 120.8 (CH), 120.1 (C_q), 115.9 (=CH_2), 113.7 (CH_{Ind}), 103.7 ($C_{q\text{-}Ind}$), 32.6, 29.7, 29.3 (CH_2)
 **31**	7.97 (dt, $^3J(^1H,^1H)$ 8.4 Hz, $^4J(^1H,^1H)$ 1.0 Hz, 1H), 7.87 (dt, $^3J(^1H,^1H)$ 7.3 Hz, $^4J(^1H,^1H)$ 1.0 Hz, 1H), 7.78-7.66 (3H)[b], 7.56 (td, $^3J(^1H,^1H)$ 6.9 Hz, $^4J(^1H,^1H)$ 1.0 Hz, 1H), 7.43-7.32 (2H)[b], 7.29-7.20 (2H)[b], 7.15-7.01 (2H)[b], 5.96 (s, 1H, CH_{Ind}), 5.70 (m, 1H, =CH), 4.91 (m, 1H, =CH_2), 4.91 (m, 1H, =CH_2), 4.30 (m, 1H, CH_2), 4.19-3.97 (2H, CH_2), 3.86 (m, 1H, CH_2), 2.79 (m, 2H, CH_2), 2.18 (m, 2H, CH_2)	137.8 (=CH), 128.5, 128.4 (CH), 127.3, 127.2 (C_q), 126.1, 125.7 (CH), 125.6, 125.3 (C_q), 125.3, 125.2, 124.9, 124.6, 123.8 (CH), 123.4, 122.6 (C_q), 122.5, 122.3 (CH), 122.2, 121.4 (C_q), 120.8 (CH), 115.1 (=CH_2), 113.4 (CH_{Ind}), 103.6 ($C_{q\text{-}Ind}$), 34.1, 29.7, 29.2, 27.6 (CH_2)
 **32**	7.94 (d, $^3J(^1H,^1H)$ 8.4 Hz, 1H), 7.85 (d, $^3J(^1H,^1H)$ 8.2 Hz, 1H), 7.76-7.64 (3H)[b], 7.54 (t, $^3J(^1H,^1H)$ 6.9 Hz, 1H), 7.41-7.23 (4H)[b], 7.11-6.99 (2H)[b], 5.95 (s, 1H, CH_{Ind}), 5.73 (m, 1H, =CH), 4.93 (m, 1H, CH_2), 4.93 (m, 1H, CH_2), 4.36 (m, 1H, CH_2), 4.19-3.97 (2H, CH_2)[b], 3.87 (m, 1H, CH_2), 2.60 (m, 2H, CH_2), 1.97 (m, 2H, CH_2), 1.50 (m, 2H, CH_2)	138.3 (=CH), 128.5, 128.4 (CH), 127.3, 127.1 (C_q), 126.0, 125.6 (CH), 125.5, 125.3 (C_q), 125.2, 125.1, 124.9, 124.5, 123.9 (CH), 123.3, 123.0, 122.6 (C_q), 122.5, 122.3 (CH), 121.4 (C_q), 120.8 (CH), 114.6 (=CH_2), 113.4 (CH_{Ind}), 103.5 ($C_{q\text{-}Ind}$), 33.4, 29.7, 29.4, 29.2, 27.5 (CH_2)
 **33**	7.93 (d, $^3J(^1H,^1H)$ 8.4 Hz, 1H), 7.84 (d, $^3J(^1H,^1H)$ 8.4 Hz, 1H), 7.73 (d, $^3J(^1H,^1H)$ 8.5 Hz, 1H), 7.67-7.63 (2H)[b], 7.53-7.20 (6H)[b], 7.12-6.98 (2H)[b], 5.94 (s, 1H, CH_{Ind}), 5.71 (m, 1H, =CH), 4.91 (m, 1H, =CH_2), 4.91 (m, 1H, =CH_2), 4.33 (m, 1H, CH_2), 4.16-4.00 (2H, CH_2), 3.87 (m, 1H, CH_2), 2.67 (m, 1H, CH_2), 2.56 (m, 1H, CH_2), 1.97 (m, 2H, CH_2), 1.44-1.22 (4H, CH_2)[b]	138.7 (=CH), 128.5, 128.4 (CH), 127.3, 127.2 (C_q), 126.1, 125.7 (CH), 125.5, 125.4 (C_q), 125.3, 125.1, 124.9, 124.6, 123.9 (CH), 123.4, 123.3, 122.6 (C_q), 122.5, 122.4 (CH), 121.4 (C_q), 120.8 (CH), 114.4 (=CH_2), 113.4 (CH_{Ind}), 103.6 ($C_{q\text{-}Ind}$), 33.5, 28.7, 29.3, 28.7, 28.0 (CH_2)
 **34**[d]	8.02-7.83 (2H)[b], 7.81-7.65 (2H)[b], 7.60-7.25 (6H)[b], 7.14-7.00 (2H)[b], 6.08 (s, 1H, CH_{Ind}), 5.70 (m, 1H, =CH), 4.88 (m, 1H, =CH_2), 4.88 (m, 1H, =CH_2), 4.57 (m, 1H, CH_2), 4.06-3.89 (m, 3H, CH_2), 1.88 (m, 2H, CH_2), 1.33-1.14 (4H, CH_2)[b], 0.66 (m, 2H, CH_2), 0.23 (s, 3H, CH_3), 0.17 (s, 3H, CH_3)	139.1 (=CH), 136.1, 128.9 (C_q), 128.7, 127.9 (CH), 127.6 (C_q), 127.3, 126.8 (CH), 126.6 (C_q), 126.2, 126.1, 125.9, 125.6 (CH), 125.6, 125.5 (C_q), 125.2, 124.9, 124.1, 123.3 (CH), 123.2 (C_q), 122.9, 122.0, 121.4, 119.9, 118.6 (CH), 114.0 (=CH_2), 112.6, 102.8 (C_q), 33.3, 32.5, 30.5, 30.1, 23.3, 18.3, 16.1 (CH_2), -2.1, -2.7 (CH_3)
 **35**[f]	7.92 (d, $^3J(^1H,^1H)$ 8.0 Hz, 1H), 7.81 (d, $^3J(^1H,^1H)$ 8.0 Hz, 1H), 7.68-7.61 (3H)[b], 7.53 (m, 1H), 7.50-6.98 (11H)[b], 5.94 (d, $^4J(^1H,^1H)$ 3.2 Hz, 1H), 4.31 (m, 1H, CH_2), 3.97 (m, 3H, CH_2), 3.92 (AB, $^3J(^1H,^1H)$ 6.8 Hz, 2H)	not determined[e]

[a] in $CDCl_3$ (saturated solution) at 25°C; [b] indicated as a shift range due to signal overlap; [c] ^{13}C NMR signals not completely separated due to signal overlap; [d] $\delta(^{29}Si)$ **34** = -45 ppm; [e] complex less soluble in chloroform; measured at 67°C in $C_2D_2Cl_4$.

*3.5. General synthesis procedure for the l-fluorenyl-ω-alkenyl-2-ols **4**/**4***–**6**/**6****

A total of 38.2 ml *n*-butyllithium was slowly added to a solution of 10.2 g (61.1 mmol) fluorene in 150 ml diethyl ether, and the mixture was stirred for 6 h at room temperature. At −78°C, 61.1 mmol of the corresponding ω-alkenyl oxirane were added to the reaction mixture. The mixture was stirred over night at room temperature, and the solution hydrolyzed with NH_4Cl/H_2O and washed. The organic phase was evaporated in vacuo. The conversion was quantitative. The crude product was used without further processing for subsequent reactions.

1-Fluorenyl-hex-5-en-2-ol (**4**/**4***): GC 2200 s. MS: *m*/*e* 264 (M^+). 1-Fluorenyl-oct-7-en-2-ol (**5**/**5***): GC 2420 s. 1-Fluorenyl-dec-9-en-2-ol (**6**/**6***): GC 2635 s. MS: *m*/*e* 320 (M^+).

*3.6. General synthesis procedure for the 1-fluorenyl-ω-alkenyl-2-mesylates (1-fluorenyl-ω-alkenyl-2-methane sulfonates) **7**/**7***–**9**/**9****

At −40 to −50°C, over a period of 15 min, 7.56 g (66 mmol) mesyl chloride were added dropwise to a solution of 61.0 mmol of the corresponding 1-fluorenyl-ω-alkenyl-2-ol and 13.91 ml (100 mmol) trimethylamine in 100 ml methylene chloride. The reaction mixture was stirred without further cooling for 15 min, then extracted with ice water, cold 10% hydrochloric acid and cold saturated sodium bicarbonate solution. The organic phase was dried over sodium sulfate and the solvent evaporated in vacuo to obtain the corresponding 1-fluorenyl-ω-alkenyl-2-mesylate.

1-Fluorenyl-hex-5-en-2-mesylate (**7**/**7***): MS: *m*/*e* 342 (M^+). 1-Fluorenyl-oct-7-en-2-mesylate (**8**/**8***): MS: *m*/*e* 370 (M^+). 1-Fluorenyl-dec-9-en-2-mesylate (**9**/**9***): MS: *m*/*e* 398 (M^+).

*3.7. General synthesis procedure for the C_2-bridged ligand precursors of the type $C_{13}H_9$–CH_2CHR–C_9H_7 and of the type $C_{13}H_9$–CH_2CHR–$C_{13}H_9$ (R = alkenyl) **10**/**10***–**15**/**15****

At −78°C, 61 mmol indenyllithium or 61 mmol fluorenyllithium in 100 ml diethyl ether were mixed with the corresponding 1-fluorenyl-ω-alkenyl-2-ol-mesitylate, stirred for at least 4 days, hydrolyzed with 50 ml water, the organic phase dried over sodium sulfate and the solvent evaporated in vacuo. The residue was dissolved in pentane and the solution filtered over silica. After crystallization in pentane at −18°C (after 2–3 weeks), the yields were 40–50%.

6-(9-Fluorenyl)-5-(1-indenyl)-1-hexene (**10**/**10***): GC 2844 s. MS: *m*/*e* 362 (M^+). 8-(9-Fluorenyl)-7-(1-indenyl)-1-octene (**11**/**11***): GC 3048 s. MS: *m*/*e* 390 (M^+). 10-(9-Fluorenyl)-9-(1-indenyl)-1-decene (**12**/**12***): GC 3233 s. MS: *m*/*e* 418 (M^+). 5,6-(9,9-Bisfluorenyl)-l-hexene (**13**/**13***): GC 3288 s. MS: *m*/*e* 412 (M^+). 7,8-(9,9-Bisfluorenyl)-l-octene (**14**/**14***): GC 3270 s. 9,10-(9,9-Bisfluorenyl)-l-decene (**15**/**15***): GC 3473 s, 3480 s. MS: *m*/*e* 468 (M^+).

*3.8. General synthesis procedure for the C_2-bridged ligand precursors of the type $C_{13}H_9$–C_2H_4–C_9H_6R (R = alkenyl, benzyl) **16**/**16***–**21**/**21****

At −78°C, 6.25 ml *n*-butyllithium (1.6 M solution in hexane) were added dropwise to a solution of 10 mmol 1-allyl-indene, 1-(3-butenyl)indene, 1-(4-pentenyl)indene, 1-(5-hexenyl)indene, 1-benzylindene or 1-(5-hexenyl-dimethylsilyl)indene [9] in 60 ml diethyl ether and 6 ml HMPT. The mixture was stirred for 5 h at room temperature. At −78°C, 2.73 g (10 mmol) 1-bromo-2-(9-fluorenyl)ethane were added to this solution and the reaction mixture was stirred for 3 days at room temperature. The mixture was hydrolyzed with 50 ml water, the organic phase dried over sodium sulfate and the solvent evaporated in vacuo. The residue was dissolved in pentane and the solution filtered over silica. After the solvent was evaporated, an oil remained that was used without further processing for the synthesis of the complexes. The yields were 65–75%.

1-(9-Fluorenyl)-2-[1-(3-allyl)indenyl]ethane (**16**/**16***): GC 2820 s. MS: *m*/*e* 348 (M^+). 1-(9-Fluorenyl)-2-[1-(3-but-3-enyl)indenyl]ethane (**17**/**17***): GC 2976 s. MS: *m*/*e* 362 (M^+). 1-(9-Fluorenyl)-2-[1-(3-pent-4-enyl)indenyl]ethane (**18**/**18***): GC 3061 s. MS: *m*/*e* 376 (M^+). 1-(9-Fluorenyl)-2-[1-(3-hex-5-enyl)indenyl]ethane (**19**/**19***): GC 3300 s. MS: *m*/*e* 390 (M^+). 1-(9-Fluorenyl)-2-[1-(3-hex-5-enyldimethylsilyl)indenyl]ethane (**20**/**20***): GC 3360 s. MS: *m*/*e* 448 (M^+). 1-(9-Fluorenyl)-2-[1-(3-benzyl)indenyl]ethane (**21**/**21***): GC 3341 s. MS: *m*/*e* 398 (M^+).

*3.9. General synthesis procedure for the bridged metallocene complexes **22**/**22***–**35***

A total of 1.0 g of the corresponding ligand precursor was dissolved in 40 ml diethyl ether and stirred with two equivalents *n*-butyllithium (1.6 M in hexane) for at least 8 h at room temperature. Then one equivalent zirconium tetrachloride or hafnium tetrachloride was added and the mixture was stirred over night. The processing was conducted according to the solubility of the product: for ether soluble complexes, the mixture was filtered directly from the produced lithium chloride. For less soluble complexes, either the solvent was evaporated and the residue extracted with methylene chloride, or the complex was filtered over sodium sulfate,

Table 5
Overview of the polymerization experiments and the polymer analysis

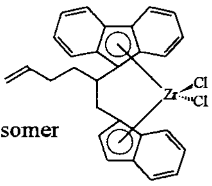
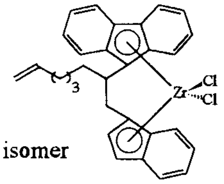
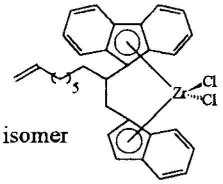
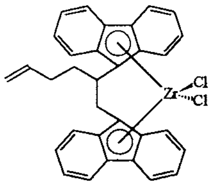
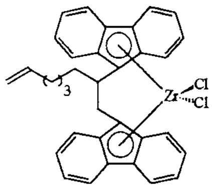
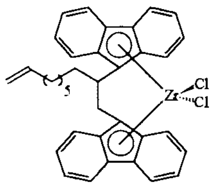
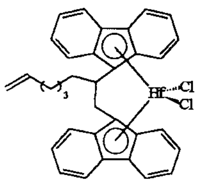
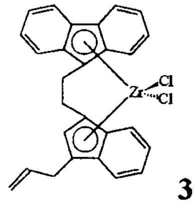
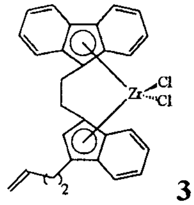
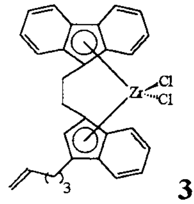
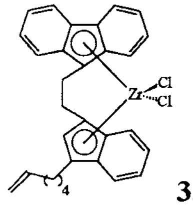
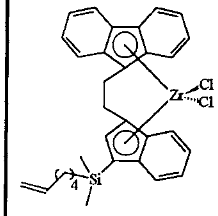
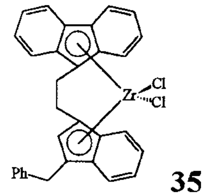
Complex	$\bar{M}_\eta$ [g/mol]	**Activity**[a)] $\frac{\text{[g] PE}}{\text{[mmol] Zr·h}}$ ($T_{i,max}$)[°C][b)]	ΔH_m[(c)] [J/g]	α[d)] [%]	T_m[e)] [°C]	**Co-p.**[f)]
 + isomer **22/22***	330 000	11 500 (61.1)	123.88	43	135.42	+
 + isomer **23/23***	270 000	9 300 (59.7)	114.42	39	131.68	+
 + isomer **24/24***	270 000	17 300 (61.7)	127.23	44	135.92	++
 **25**	420 000	148 000 (74.0)	129.29	45	135.05	+
 **26**	370 000	333 000[g)] (94.0)	140.92	49	134.27	+
 **27**	430 000	290 000[h)] (85.0)	n.b.	n. b.	136.85	++

Table 5 (Continued)

Complex	$\overline{M}_\eta$ [g/mol]	**Activity**[a)] $\frac{[g]\ PE}{[mmol]\ Zr\cdot h}$ ($T_{i,max}$)[°C][b)]	ΔH_m[(c)] [J/g]	α[d)] [%]	T_m[e)] [°C]	**Co-p.**[f)]
 **29**	1 600 000	3 000 (58.0)	30.99	11	136.11	++
 **30**	160 000	153 000 (91.4)	162.33	56	134.75	+
 **31**	125 000	198 000[h)] (88.9)	164.69	57	135.02	+
 **32**	180 000	204 000[h)] (92.8)	154.27	53	139.90	+
 **33**	155 000	198 000[g)] (77.8)	153.59	53	137.37	++
 **34**	180 000	60 800 (84.0)	155.08	53	135.94	++
 **35**	140 000	110 000[i)] (86.9)	154.00	53	139.44	–

[a)] [Zr]: [Al] = 1:17000; [b)] $T_{i,max}$ = maximum inside temperature of the polymerization reactor; [c)] the values of the second heating course of the DSC were indicated as fusion enthalpies ΔH_m; see [20]; [e)] the maximum of the melting peak of the second heating course of the DSC was selected as melting point; [f)] Ability for copolymerization; ability of the catalyst to copolymerize in the polymer chain: + + = very good + = good, 0 = sufficient,- = none; [g)] Polymerization time 30 min [h)] Polymerization time 10 min; [i)] Polymerization time 15 min.

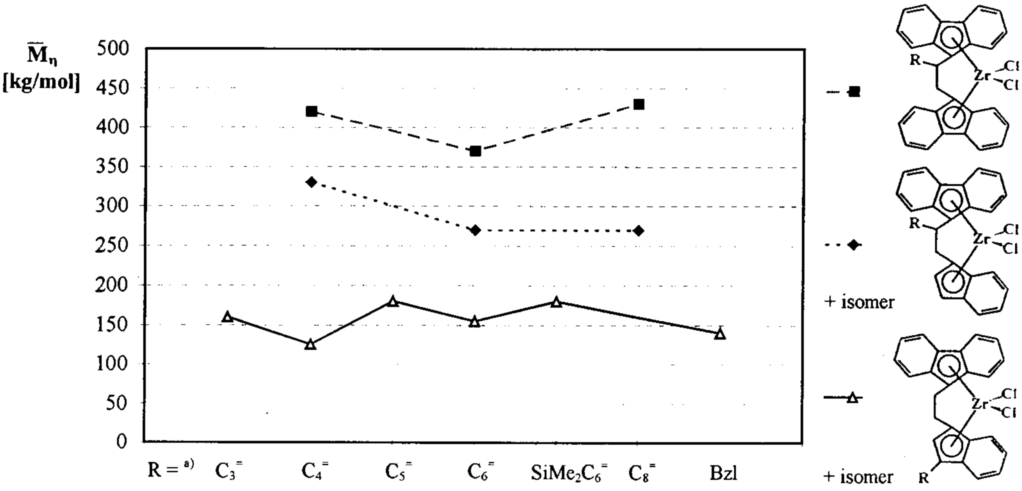


Fig. 9. Mean intrinsic viscosity of the polyethylenes synthesized with the complex types $(C_{13}H_8{-}CH_2CHR{-}C_9H_6)ZrCl_2$/MAO, $(C_{13}H_8{-}CH_2CHR{-}C_{13}H_8)ZrCl_2$/MAO and $(C_{13}H_8{-}C_2H_4{-}C_9H_5R)$ $ZrCl_2$/MAO (R = alkenyl, benzyl). ^{a} $C_n^=$:ω-Alkenyl substituent of the chain length *n*.

and the product extracted with methylene chloride or toluene from the frit. Then the solvent was evaporated in vacuo. The yields were 30–40%.

6-η^5-(9-Fluorenylidene)-5-η^5-(1-indenylidene)-1-hexene zirconium dichloride (**22**/**22***): orange crystals. MS: *m*/*e* 522 (M^+). 8-η^5-(9-Fluorenylidene)-7-η^5-(1-indenylidene)-1-octene zirconium dichloride (**23**/**23***): orange-crystals. MS: *m*/*e* 550 (M^+). 10-η^5-(9-Fluorenylidene)-9-η^5-(1-indenylidene)-1-decene zirconium dichloride (**24**/**24***): orange crystals. MS: *m*/*e* 578 (M^+). 5,6-η^5,η^5-(9,9-Bisfluorenylidene)-1-hexene zirconium dichloride (**25**): red crystals. MS: *m*/*e* 572 (M^+). 7,8-η^5,η^5-(9,9-Bisfluorenylidene)-1-octene zirconium dichloride (**26**): red crystals. MS: *m*/*e* 600 (M^+). 9,10-η^5,η^5-(9,9-Bisfluorenylidene)-1-decene zirconium dichloride (**27**): red crystals. MS: *m*/*e* 628 (M^+). 5,6-η^5,η^5-(9,9-Bisfluorenylidene)-1-hexene hafnium dichloride (**28**): orange crystals. MS: *m*/*e* 660 (M^+). 7,8-η^5,η^5-(9,9-Bisfluorenylidene)-1-octene hafnium dichloride (**29**): orange crystals. MS: *m*/*e* 688 (M^+). 1-η^5-(9-Fluorenylidene)-2-η^5-[1-(3-allyl)indenylidene] ethane zirconium dichloride (**30**): orange crystals. MS: *m*/*e* 506 (M^+). 1-η^5-(9-Fluorenylidene)-2-η^5-[1-(3-but-3-enyl)indenylidene]ethane zirconium dichloride (**31**): orange crystals. MS: *m*/*e* 522 (M^+). 1-η^5-(9-Fluorenylidene)-2-η^5-[1-(3-pent-4-enyl)indenylidene]ethane zirconium dichloride (**32**): orange crystals. MS: *m*/*e* 536 (M^+). 1-η^5-(9-Fluorenylidene)-2-η^5-[1-(3-hex-5-enyl)indenylidene]ethane zirconium dichloride (**33**): orange crystals. MS: *m*/*e* 550 (M^+). 1-η^5-(9-Fluorenylidene)-2-η^5-[1-(3-hex-5-enyldimethylsilyl)indenylidene]ethane zirconium dichloride (**34**): orange crystals. MS: *m*/*e* 608 (M^+). 1-η^5-(9-Fluorenylidene)-2-η^5-[1-(3-benzyl)indenylidene]ethane zirconium dichloride (**35**): orange crystals, elemental analysis found: C, 63.71; H, 4.37; $C_{31}H_{24}ZrCl_2 \cdot 0.5CH_2Cl_2$. Calculated: C, 62.94; H, 4.19; MS: *m*/*e* 558 (M^+).

3.10. Self-immobilization

Self-immobilization studies were conducted in Schlenk tubes. Approximately 10 mg of the respective complex were activated with 10 ml MAO (30% solution in toluene), diluted with 40 ml toluene and then an ethylene pressure of 0.4–0.6 bar was applied. The insertion of the complex into the polymer chain was indicated by the characteristic color of the produced precipitate.

3.11. Polymerization reactions

3.11.1. Activation of the catalyst precursors

The respective metallocene complex was weighed under inert gas (approximately 8–12 ± 0.1 mg) and activated with MAO (usually 1 ml MAO (30% in toluene) per mg metallocene dichloride complex). The solution was diluted with toluene to an extent that approximately 0.2–0.5 mg metallocene complex were dissolved in 1 ml toluene. Approximately 1 mg catalyst of this solution was used for polymerization. These solutions were used for polymerization within 60 min.

3.11.2. 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] = 1:17 000). The reactor was heated to 60°C and a constant ethylene pressure of 10 bar was applied. The polymerization was terminated after 1 h by releasing the ethylene.

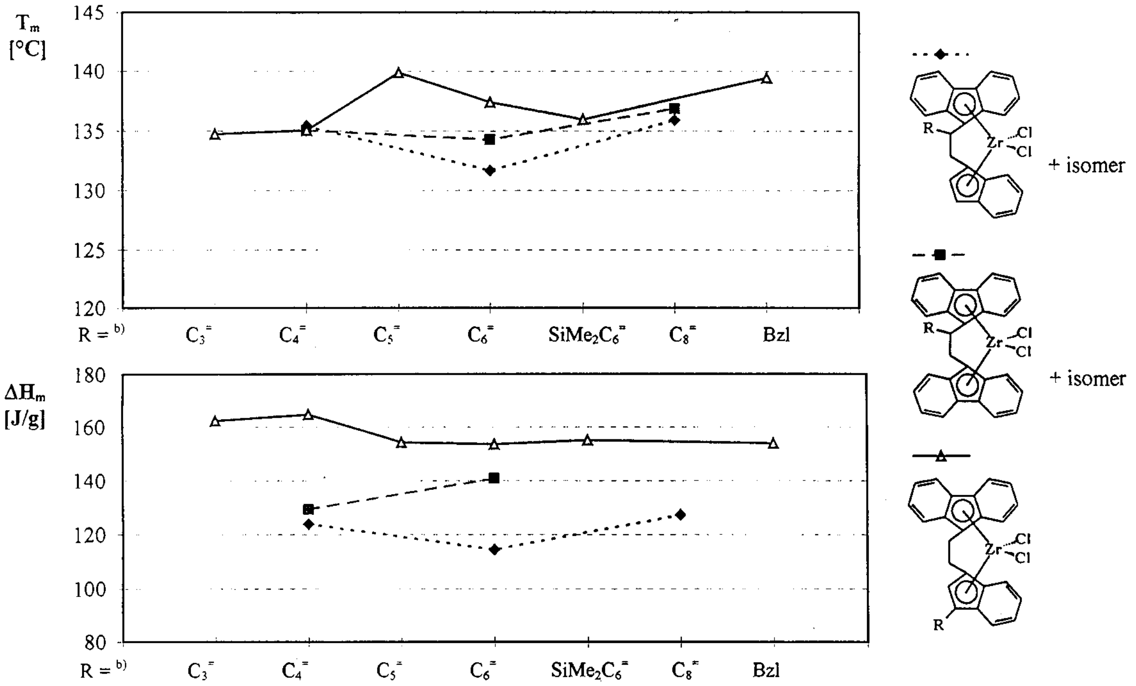


Fig. 10. Melting temperatures T_m and fusion enthalpies ΔH_m[a] for polyethylenes synthesized with the complex types ($C_{13}H_8$–CH_2CHR–C_9H_6)$ZrCl_2$/MAO, ($C_{13}H_8$–CH_2XHR–$C_{13}H_8$)$ZrCl_2$/MAO and ($C_{13}H_8$–C_2H_4–C_9H_5R)$ZrCl_2$/MAO (R = alkenyl, benzyl). [a] The values are referred to the second heating course of the DSC; [b] $C_n^=$: ω-alkenyl substituent with the chain length n.

3.12. Characterization of the polymers

3.12.1. Differential scanning calorimetry

A Perkin–Elmer DSC-7 calorimeter 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, 3–5 mg each of the polymer were fused into standard aluminum pans and measured using the following temperature program: 1st heating phase (20 K min^{-1}) from 50 to 200°C, cooling phase (−20 K min^{-1}) to 50°C; 2nd heating phase (20 K min^{-1}) from 50 to 200°C, 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. To determine the crystallinity degree α, the relationship $\alpha = \Delta H_m / \Delta H_m^0$ was selected. ΔH_m derives from the data of the second heating course of the DSC. The fusion enthalpy, 290 J g^{-1} [23], was assumed for ΔH_m^0 for 100% crystalline polyethylene.

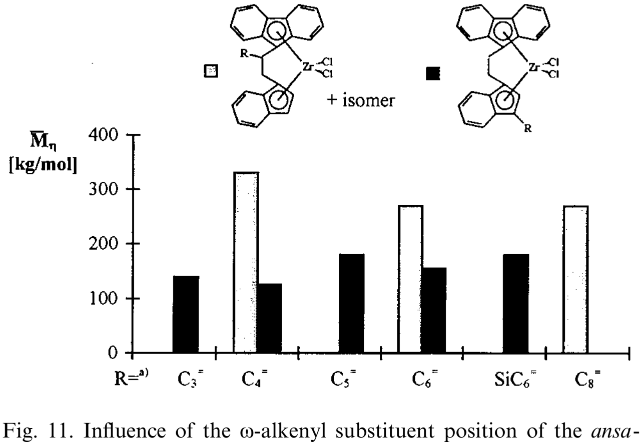


Fig. 11. Influence of the ω-alkenyl substituent position of the *ansa*-metallocene complexes on the molecular weight of the produced polyethylenes. [a] $C_n^=$: ω-alkenyl substituent with the chain length n.

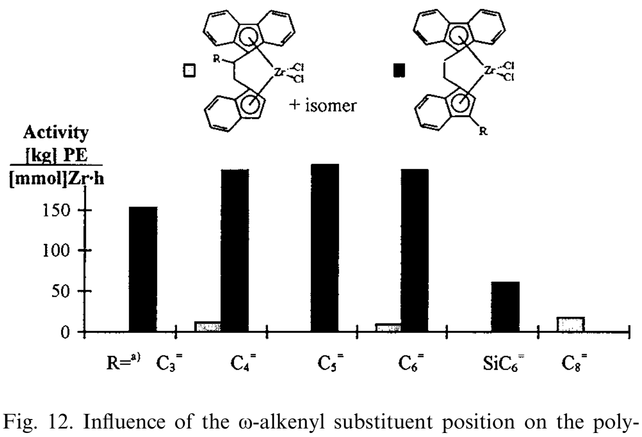


Fig. 12. Influence of the ω-alkenyl substituent position on the polymerization activities of the *ansa*-metallocenes complexes. [a] $C_n^=$: ω-alkenyl substituents with the chain length n.

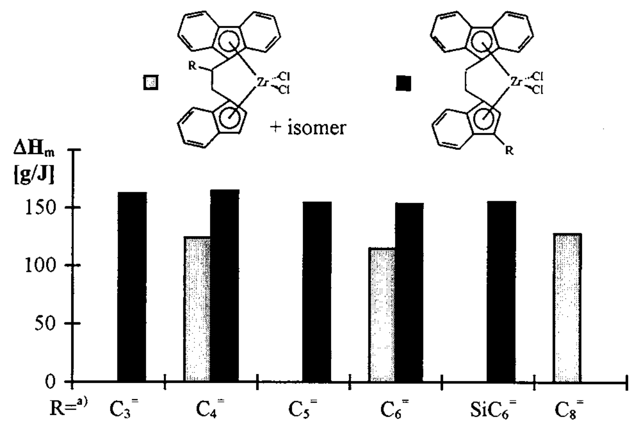


Fig. 13. Influence of the ω-alkenyl substituents positon of the ansa-metallocene complexes on the fusion enthalpies of the synthesized polyethylenes. [a] $C_n^=$:ω-alkenyl substituents with the chain length *n*.

3.12.2. Viscosimetry

The intrinsic viscosity $\bar{M}_\eta$ 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 $\bar{M}_\eta$. Every polymer sample was weighed and measured twice to reduce the error.

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