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Synthesis, characterization and catalytic properties of metallacyclic zirconocene complexes

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Abstract

A series of 22 metallacyclic zirconocene complexes has been synthesized by the reaction of ω-phenyl-substituted zirconocene dichloride complexes with two equivalents of *n*-butyllithium via CH bond-activation reactions on the phenyl ring. After activation with methyl aluminoxane, these metallacycles are up to five times more active ethylene polymerization catalysts than the original metallocene dichloride complexes similarly activated. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Metallacycles; Zirconocene complexes; CH activation; Catalysis; Ethylene polymerization

1. Introduction

Metallocene catalysts, used for polymerizing α-olefins, have been either unbridged or bridged metallocene dichloride complexes in combination with methylaluminoxane (MAO) [1–24]. In the work described here, a new class of metallocene complexes, metallacycles, is described for the polymerization of α-olefins.

After the activation with MAO, metallacyclic zirconocene complexes, containing a substituent directly linked to the center metal, are well suited for catalytic olefin polymerization [25,26]. Prior to this work, an efficient method of synthesizing these metallocycles was not available [25–30]. Here, we present a general, easy and efficient synthetic method for the preparation of metallacyclic zirconocene complexes. These metallacycles were then studied to determine the effects of cyclometallation on α-olefin polymerization reactions.

2. Results and discussion

2.1. Synthesis of metallacyclic zirconocene complexes using CH bond activation reactions

Metallacycles in this paper are defined as metallocene complexes with a substituent on at least one of the π-ligands forming a σ-bond or a π-bond to the central transition-metal atom.

The newly developed synthesis method for the formation of these metallacycles consists of reacting ω-phenylalkyl-substituted zirconocene dichloride complexes with two equivalents of *n*-butyllithium. The key reaction step for this method is CH bond activation that leads to cyclometallation. The reaction is presumed to proceed as shown below.

During this reaction a zirconocene dibutyl complex [31], which is stable for some minutes in solution at low temperatures (−40°C), is formed as an intermediate. The unsubstituted parent compound of this complex was characterized using spectroscopy [32]. Subsequently, the dibutyl complex eliminates *n*-butane [33,34] via a β-H transfer reaction. This results in the formation of a reactive (η^2-butene) complex. $Cp_2ZrC_4H_8$, formed as an intermediate during the reaction of Cp_2ZrCl_2 with two equivalents of *n*-butyllithium, can be trapped, using trimethylphosphine, and

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characterized [35–37] (see Section 2.4). The ω-phenylalkyl group of the (η^2-butene) metallocene complex, shown in Fig. 1, then further reacts to yield the corresponding metallacycle via a CH bond activation reaction.

A large number of metallocene dichloride complexes with a variety of π-ligands and substituents were reacted with *n*-butyllithium to study the influence of steric factors on the course of the cyclometallation reaction. The metallacycles are numbered **1**, **2**, etc. and the respective metallocene dichloride precursors **1c**, **2c**, etc.

2.2. Synthesis of metallacyclic complexes

Metallocene dichloride complexes containing ω-phenylalkyl-substituted cyclopentadienyl ligands Cp′ of the type $(Cp')_2ZrCl_2$ [38] or $(Cp')(Ind)ZrCl_2$ [39] are well suited as starting materials for the synthesis of metallacyclic complexes. Only a single reaction product is obtained when the metallocene dichloride complexes with a C_1, C_2 or C_3 carbon chain between the π-ligand and the phenyl group (C_1-, C_2- or C_3-spacer) are reacted with *n*-butyllithium. The NMR spectroscopic investigation (see Section 2.3) confirms that the formed metallacycles contain a carbon zirconium σ-bond (**1** and **2**). No carbon zirconium σ-bond was found for the metallacycles containing a C_3-spacer (**3**). In the latter case, the phenyl substituent is fixed at the metal via an agostic hydrogen atom in the *ortho* position. Such a coordination mode has also been observed very recently by Green and coworkers [40]. If metallocene dichloride complexes with C_4- or C_5-spacers are used, intramolecular interactions between the phenyl group and the center metal atom are much more difficult and, as a result, product mixtures are obtained that have not yet been identified (Fig. 2).

Similar intramolecular activation reactions of the aromatic CH-bond are also observed when substituted benzyl derivatives (4-methyl, 3,5-dimethyl, 4-fluoro and benzo anellated) are used. Metallacycles are produced in 80–90% yields when metallocene dichloride complexes with ω-phenylalkyl-substituted cyclopentadienyl ligands carrying one methyl group in position 2 are reacted with *n*-butyllithium. Replacement of a C_1-spacer with a *Si*-spacer leads to very high yields of metallacycles. The metallacycles and metallocene complexes shown in Fig. 3 were synthesized starting with the corresponding metallocene dichloride complexes.

The mono-substituted zirconocene dichloride complex **16c** reacts with *n*-butyllithium to give metallacycle **16** (Fig. 4). The CH-activation and cyclometallation reaction yields are not quantitative in this example due to low steric shielding of the metal from only one sterically demanding substituent. Metallacycle **16** is produced in only 60% yield.

Metallocene dichloride complexes with ω-phenylalkyl-substituted indenyl ligands are also suitable starting compounds for cyclometallation reactions. They react with two equivalents of *n*-butyllithium as shown in the reaction scheme in Fig. 4. The products formed are metallacycles or metallocene butene complexes (see Section 2.4 for structural discussions).

The metallacycles and metallocene butene complexes shown in Fig. 5 were synthesized using this method.

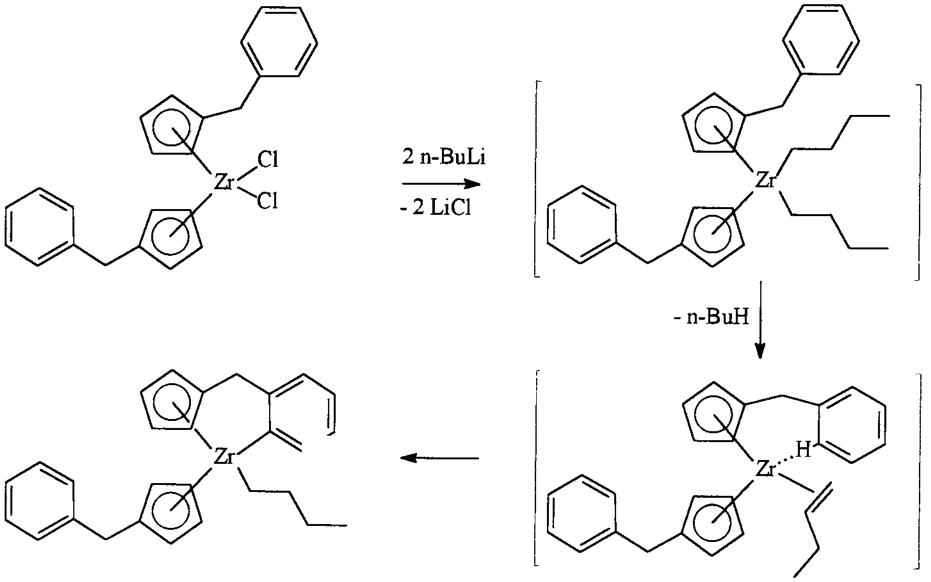

Fig. 1. Proposed reaction scheme for synthesizing a metallacycle from a metallocene dichloride complex.

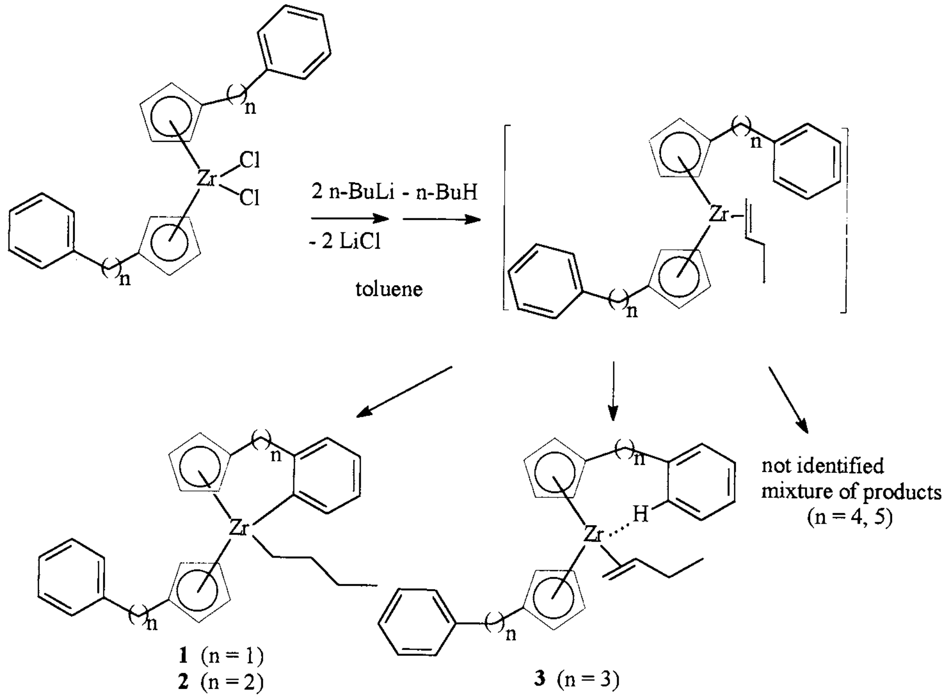

Fig. 2. Reaction of ω-phenylalkyl-substituted zirconocene dichloride complexes with two equivalents of *n*-butyllithium.

2.3. Spectroscopic characterization of the metallocene complexes

Metallocene complexes **1**–**22a**,**b** were characterized using ^{1}H-, ^{13}C- and ^{29}Si-NMR spectroscopy. Spectral results are listed in Table 2. The ^{1}H- and ^{13}C-NMR spectra of metallocene complex **1** are discussed below as an example.

Fig. 6 shows the ^{1}H-NMR spectrum of **1**. Eight different resonance signals at $\delta = 6.56$, 6.12, 5.98, 5.89, 5.85, 5.68, 5.49 and 5.08 ppm are assigned to the eight cyclopentadienyl protons. This indicates a chiral metallocene complex structure caused by the Zr–C σ-bond (Zr–C(12)) to the central metal atom. The resonance signals for the protons of the butyl group are found as multiplets at $\delta = 1.67$ (β-CH$_2$) and 1.35 ppm (γ-CH$_2$), as a triplet at $\delta = 1.02$ ppm (CH$_3$; $^3J(^1\mathrm{H}^1\mathrm{H}) = 7.3$ Hz) and as multiplets at $\delta = 0.90$ and 0.52 ppm (α-CH$_2$). The different chemical shifts for both protons of the methylene group in the α-position and the higher spin order of its splitting pattern are remarkable and correspond to an α-agostic interaction with the central metal. The signals for both phenyl groups appear at $\delta = 7.51$ ppm (H(11)) and in the region of $\delta = 7.25$–6.85 ppm (8H). Due to cyclization, the protons of the C_1-spacer (H(18a,b)) form two doublets at $\delta = 4.03$ and 3.90 ppm ($^2J(^1\mathrm{H}^1\mathrm{H}) = 16.7$ Hz), while the protons of the C_1-spacer (H(18)) of the free benzyl substituent appear as singlet at $\delta = 3.53$ ppm.

Fig. 7 represents the ^{13}C-NMR spectrum of metallacycle **1**. The eight different tertiary carbon resonance signals (C(1–4) and C(13–16)) for both cyclopentadienyl ligands in the region of $\delta = 120$–130 ppm are significant for metallacycle **1** (chiral metallocene complex). Due to this interaction, two different resonance signals in the region of $\delta = 28$–40 ppm are found for the C_1-spacer groups (C(6) and C(18)). In a similar way, a larger number of resonance signals are observed for the carbon atoms of both phenyl groups (C(7–12) and C(19–24)) compared with the non-bonded phenyl groups of the corresponding metallocene dichloride complexes (three resonance signals). A typical shift to lower field for the zirconium-bonded quaternary carbon C(12) of the phenyl group is observed at $\delta = 186.0$ ppm. The shift differs significantly from carbon-bonded quaternary phenyl carbon atoms ($\delta = 120$–150 ppm). Due to the deshielding of the central metal, the carbon atom C(7) of the phenyl group is significantly shifted to lower field at $\delta = 166.3$ ppm.

The resonance signal for the methylene group in the α-position to zirconium of the butyl group (C(25)) is found at $\delta = 58.8$ ppm. Due to the direct bond to the metal, the signal is shifted significantly to lower field compared with the remaining carbon resonance signals of the butyl group (C(26–28): $\delta = 35.1$, 29.7 and 14.1 ppm.

2.4. Discussion of the tendency to form metallacyclic metallocene complexes

The metallacycles that contain a zirconium–carbon σ-bond are formed only from the complexes with a C_1-,

C_2- or *Si*-spacer moiety between the π-ligand and the aromatic group (phenyl, fluorenyl and indenyl). Presumably, an interaction between the π-electrons of the aromatic group and the free orbitals (LUMO) of the d^2-configurated zirconium with subsequent hydrogen transfer onto the η^2-butenyl ligand is only possible for these spacers (Fig. 8).

In the case of a C_3-spacer, an interaction of an agostic hydrogen atom in the *ortho* position of the phenyl group and a free orbital of zirconium is favored. Presumably, a hydrogen transfer reaction to the η^2-butene ligand does not occur in this case for steric reasons. Therefore, the typical resonance signals of a η^2-bonded butene ligand are found in the ^{13}C-NMR spectrum of metallacycle **3** at $\delta = 74.1$ (CH), 60.9 and 45.6 (CH_2) and $\delta = 14.2$ ppm (CH_3) (see Table 2).

The π-coordinated metallocene complex **3** is stable in solution and at higher temperatures (60°C). This stability is analogous to that observed for the trimethylphosphine stabilized (η^2-butene)(trimethylphosphine) zirconocene complex and is presumably due to the strong interaction of the $1a_1$-orbital of zirconium with the π*-orbital of the olefin [41] (Fig. 9).

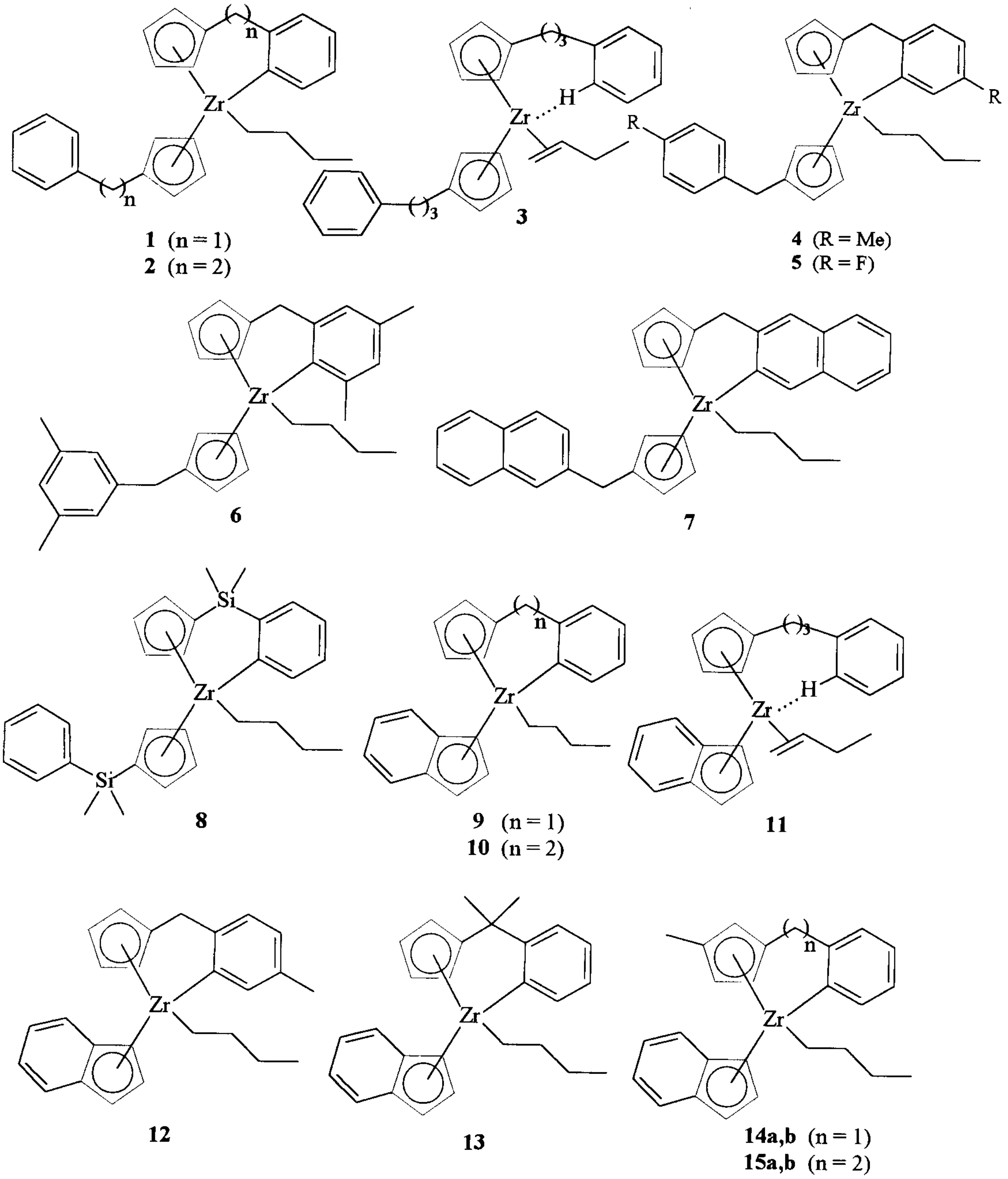

Fig. 3. Overview of synthesized metallacycles **1**–**15a**,**b** (only one isomer is illustrated for **14a**,**b** and **15a**,**b**).

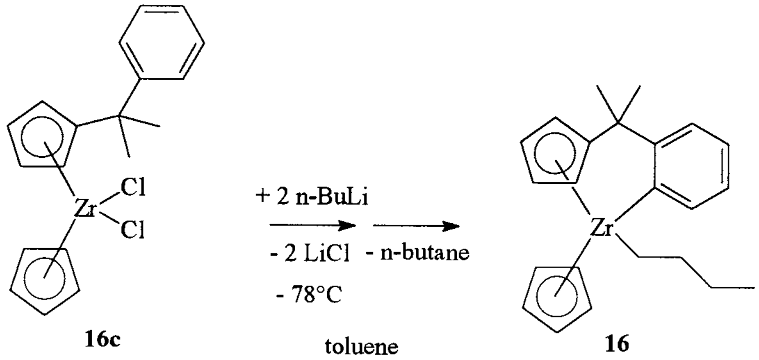

Fig. 4. Synthesis of metallacycle **16**.

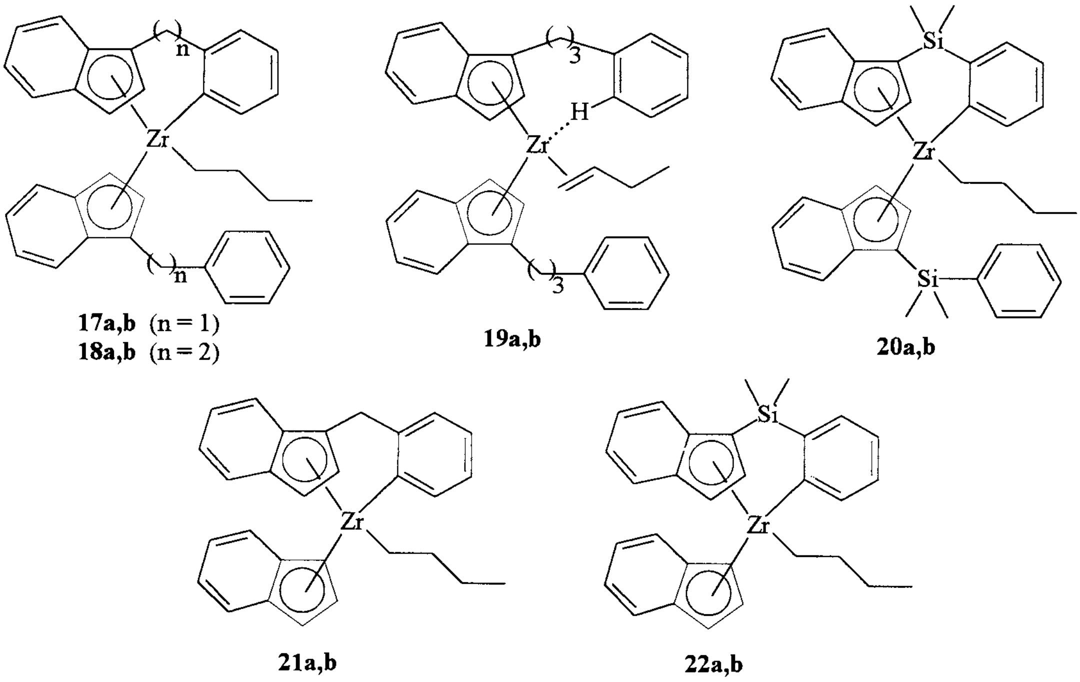

Fig. 5. Overview of synthesized metallacycles **17a**,**b**–**22a**,**b** (only one isomer illustrated).

If spacer groups longer than C_3 are present, the spatial time-average proximity of the phenyl group to the central metal is greatly reduced. Therefore, mixtures of products, due to intra- and intermolecular reactions, are likely to be formed.

The insertion of one methyl group in position 3 of the ω-phenylalkyl-substituted cyclopentadienyl ligand suppresses the cyclometallation reaction. Approximately 80% cyclometallation reaction occurs with C_1- and C_2-spacers (metallacycles **14a**,**b** and **15a**,**b**). A mixture of products is produced with C_3-spacers.

The metallacycle synthesis is obviously limited by various structural parameters. However, a wide range of metallacycles can be synthesized, using CH-activation and subsequent cyclometallation, from the wide variety of available zirconium dichloride complexes.

2.5. Ethylene polymerization

The resultant metallacycles are suitable precursors for homogeneous ethylene polymerization. The complexes are activated by adding a 3000-fold molar excess of MAO. The formation of an active catalyst system is indicated by a color change.

To keep the length of the paper manageable, only selected metallocene polymerization experimental data are presented and compared with the results of the corresponding metallocene dichloride complexes [25,26]. The polymerization activities of the activated metallacycles, the viscosity average molecular weights, $\bar{M}_\eta$, the fusion enthalpies, ΔH_m, the melting temperatures, T_m and the degree of crystallinity, α, of resulting polyethylenes are listed in Table 1.

*2.5.1. Influence of the spacer chain length on the polymerization behavior of symmetrically substituted metallocene dichloride complexes **1c**–**4c** and derived metallacycles **1**–**3***

The chain length of the spacer has a strong impact on the polymerization behavior of the synthesized metallocene complexes. Fig. 10 exhibits a comparison of the homogeneous polymerization activities for the ω-phenylalkyl-substituted bis(cyclopentadienyl) zirconium dichloride complexes **1c**–**4c** and the analogous metallacycles **1**–**3**. Compared with the respective metallocene dichloride complexes, the metallacyclic complexes have, after activation with MAO, three to five times higher polymerization activity. Reacting metallocene dichloride complex **4c** with *n*-butyllithium does not form a metallacycle due to its long spacer chain length (C_4) (see Section 2.4). After activation with MAO, the unidentified product mixture **4*** has very high polymerization activity. However, the polymerization activity is lower than that of the uncyclized dichloride complex **4c**. These results demonstrate that the formation of metallacycles from substituted bis(cyclopentadienyl) complexes enhances their polymerization activity. The polymerization activity, however, decreases if the metallacycle cannot be formed and the chloro ligands are only exchanged for alkyl ligands.

The polymerization activity increases considerably for the metallocene dichloride complexes **1c**–**4c** as well as for the metallacycles **1**–**3** with increasing chain length of the carbon spacer between the cyclopentadienyl ligand and the bulky phenyl group. The reason for this behavior may be the decreasing steric shielding of the catalytic center by the phenyl group, due to longer spacer chains, better separation of the MAO counter ion from the active center of the cationic species or a combination of these effects [42].

Fig. 11 exhibits the melting temperatures (T_m) of the polymers synthesized with the metallocene dichloride

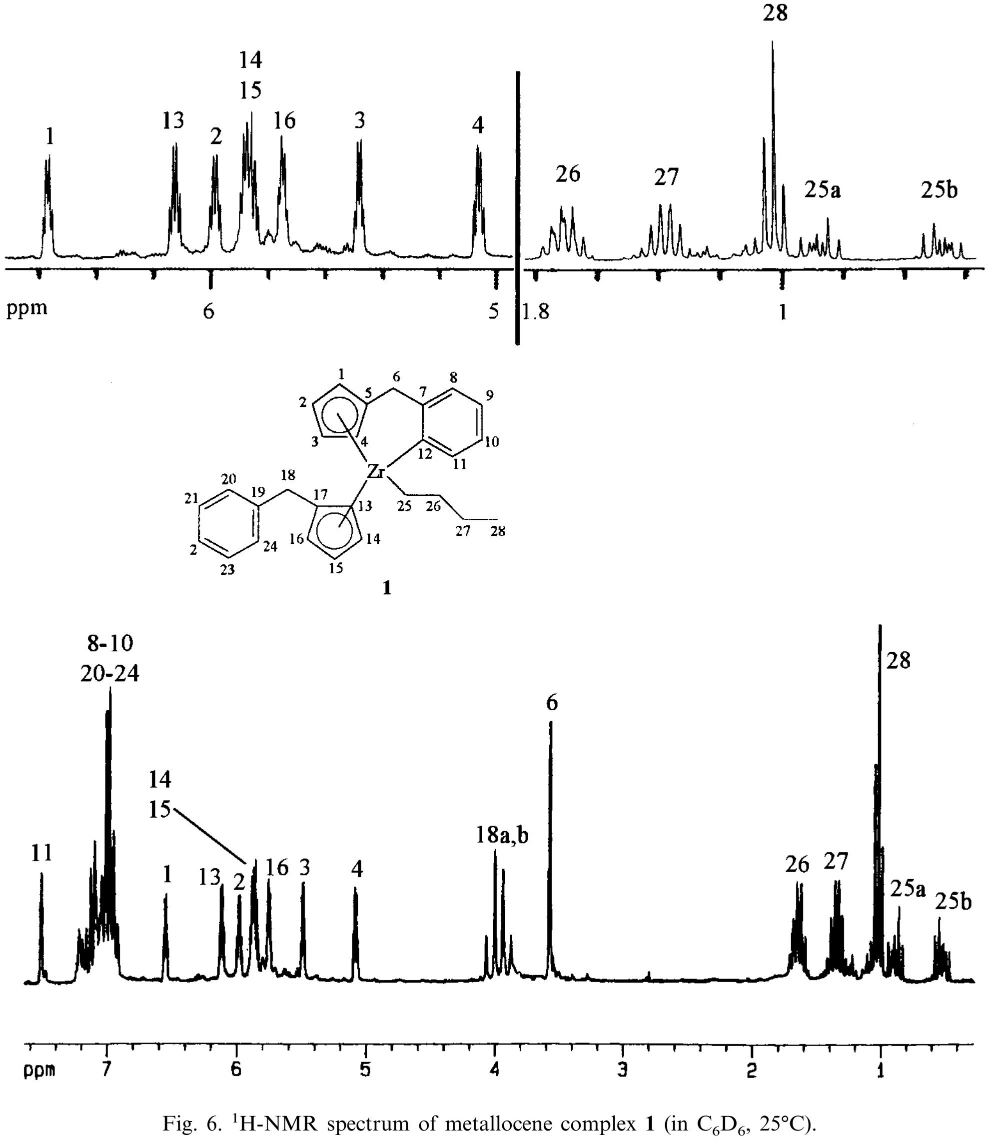

Fig. 6. ^{1}H-NMR spectrum of metallocene complex **1** (in C_6D_6, 25°C).

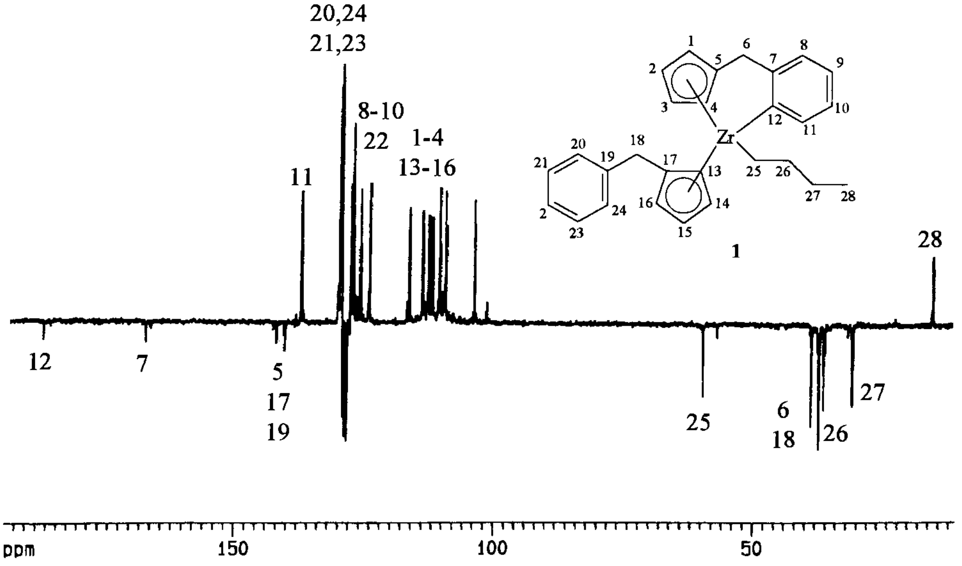

Fig. 7. *J*-mod. $^{13}C\{H\}$-NMR spectrum of metallocene complex **1** (in C_6D_6, 25°C).

complexes **1c**–**4c**, the metallacycles **1**–**3** and the unknown complex **4***. The T_m of the polyethylenes increases with increasing chain length of the spacers between the cyclopentadienyl ligand and bulky phenyl group for the metallocene dichloride complexes **1c**–**4c** and the metallacycle derivatives **1**–**3**. The melting temperatures of the polymers produced with the complexes **1**–**3** are in all cases higher than those of the respective noncyclic precursors **1c**–**3c**.

2.5.2. *Influence of the spacer chain length on the polymerization behavior of the mixed substituted metallocene dichloride complexes **9c**–**11c** and the metallacycle derivatives **9**–**11***

The activity of the mixed substituted metallocene dichloride complexes **9c**–**12c** and of the analogous metallacycles **9**–**11** increases as the chain length of the ω-phenylalkyl group increases (Fig. 10). In comparison with the symmetrically substituted metallocene dichloride complexes **1c**–**4c** and metallacycles **1**–**3**, the activity of the mixed substituted metallocene complexes increases only modestly with increasing spacer chain length. The reason for such a modest increase could be the fact that the coordination sphere of the active catalyst center is only influenced by one ω-phenylalkyl group. In contrast to the symmetrical metallocene complexes, the polymerization activities of metallocene complexes **9c** and **9**, containing a C_1-spacer, are higher than those for the metallocene complexes **10c** and **10** containing a C_2-spacer. This indicates a complex relationship between the steric influence on the catalytic center by the substituent and the separation of the contact ion pair metallocene monoalkyl cation–MAO anion [42].

The molecular weights of the polyethylenes produced with the metallocene complexes **9c**–**12c** and **9**–**11** are compared in Fig. 12. They are significantly higher (450–640 kg mol^{-1}) than the molecular weights of the polyethylenes obtained with symmetrically substituted bis(cyclopentadienyl) metal complexes (290–360 kg mol^{-1}). The exchange of one ω-phenylalkyl-substituted cyclopentadienyl ligand by one non-substituted indenyl ligand seems to reduce the chain termination rate independent of the polymerization activity and therefore leads to higher polyethylene molecular weights.

2.5.3. *Influence of substituents on the ω-phenyl group on the polymerization behavior*

The largest activity increase on going from the dichloride complex to the metallacycle is found for complexes **1c** and **1**, containing an unsubstituted benzyl group

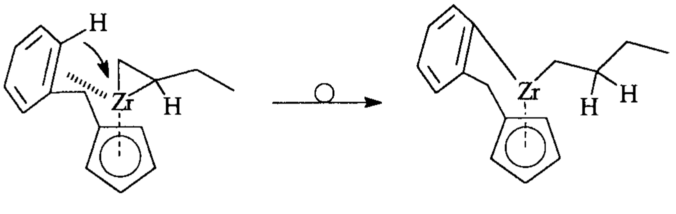

Fig. 8. Scheme for the intramolecular CH-activation with subsequent cyclometallation reaction. (To keep the overall view, the second π-ligand (beneath the paper plane) is not shown.)

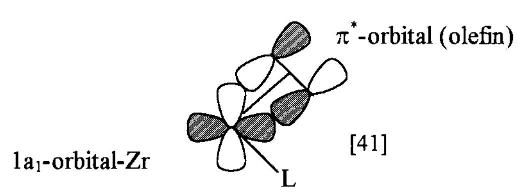

Fig. 9. Stabilizing interaction of the $1a_1$-orbital of zirconium with the π*-orbital of the olefin [41].

Table 1
Overview of the polymerization experiments [a] and polymer analytic results

Complex (catalyst precursor)	Activity [b]	$\bar{M}_\eta$ [c] (kg mol^{-1})	DSC		
			T_m (°C)	ΔH_m (J g^{-1})	α (%) [d]
1	790.4	360	133.1	188.2	64.9
2	1810.7	290	142.2	212.2	73.2
3	5577.0	350	137.2	137.9	47.6
4	1231.6	330	135.7	147.5	50.9
5	1040.0	510	136.4	154.1	53.1
6	1413.7	520	124.8	170.1	58.7
8	164.5	650	142.0	131.9	45.5
9	2850.0	450	141.1	144.5	49.8
10	2460.0	610	134.0	156.0	53.8
11	4560.0	450	136.1	152.6	52.6
13	100.7	590	138.9	137.0	47.3
14a,**b**	1325.0	770	139.6	137.5	47.4
19a,**b**	1509.0	360	138.2	142.6	49.2
20a,**b**	131.6	500	136.0	153.8	53.0
21a,**b**	2222.9	620	135.3	148.7	51.3
22a,**b**	878	580	131.4	148.1	51.1

[a] $T_p = 60$°C; solvent: 500 ml pentane; 10 bar ethylene pressure.
[b] [M]/[Al] = 1:3000.
[c] Intrinsic viscosity.
[d] Degree of crystallinity relative to the fusion enthalpy of 100% crystalline polyethylene.

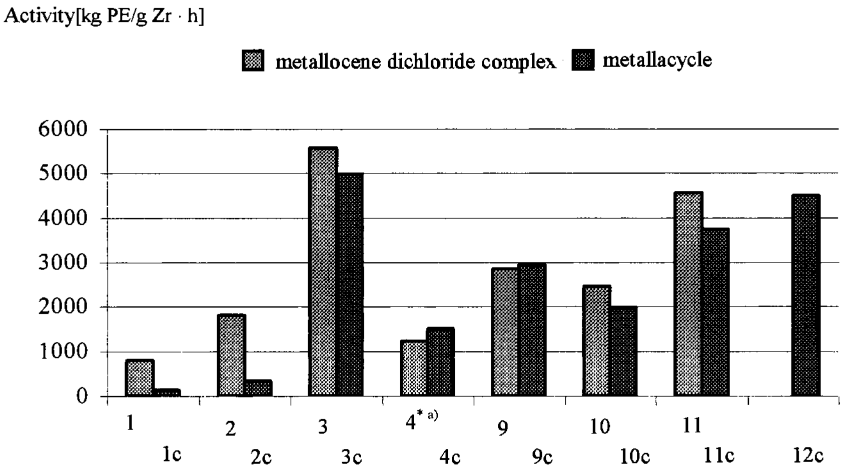

Fig. 10. Comparison of the polymerization activities for the metallocene dichloride complexes **1c**–**4c** and **9c**–**12c** and the metallacycles **1**–**4** and **9**–**11**. Reaction of **4c** with two equivalents of *n*-butyllithium leads to an unidentified mixture of products **4***.

(Fig. 13). In contrast, a negative cyclization effect (transition from the metallocene dichloride complex to the metallacycle) is observed for the 4-methylbenzyl-substituted metallocene complexes **4c** and **4**. The reason for these behavioral differences seems to be the methyl group in position 4. The additional methyl group in position 4 of the phenyl group has no steric influence on the active catalyst center. However, it can increase the distance to the MAO counter ion [42]. For metallacycles **1** and **4**, one benzyl or one 4-methylbenzyl substituent is removed from the coordination sphere of the center metal by incorporation into a polymer chain. Therefore, there is less steric hindrance. Simultaneously, the metallocene monoalkyl cation–MAO anion contact ion pair is less effectively separated. The combination of these two effects has the most influence on the metallacycle containing a 4-methylbenzyl substituent.

The 3,5-dimethyl-substituted and the benzoanellated benzyl substituents of metallocene complexes **6c** and **6** or **7c** and **7** have steric influence on the active catalyst center as well as on the extent of separation of the MAO counter ion. Both dichloride complexes **6c** and **7c** that possess comparable activities are lower in activity than the 4-methyl-substituted complex **4c**. A slightly positive (naphthyl group) or a slightly negative cyclization effect is observed for the polymerization activities of the analogous metallacycles.

Fig. 14 exhibits the molecular weights for the polyethylenes obtained with the benzyl-substituted metallocene complexes. The molecular weights for the polymers synthesized with the benzyl- and the 4-methylbenzyl-substituted metallocene complexes **1c** and **1** or **4c** and **4** are 310–360 kg mol^{-1}. The metallocene complexes **7c** and **7** or **6c** and **6** containing sterically more demanding 3,5-dimethylbenzyl and naphthyl-2-methyl substituents produce polymers with significantly higher molecular weights in the range 490–590 kg mol^{-1}. Presumably, a reduction in the β-H-elimination reaction during polymerization is the cause of the higher molecular weights for the sterically burdened metallocene complexes.

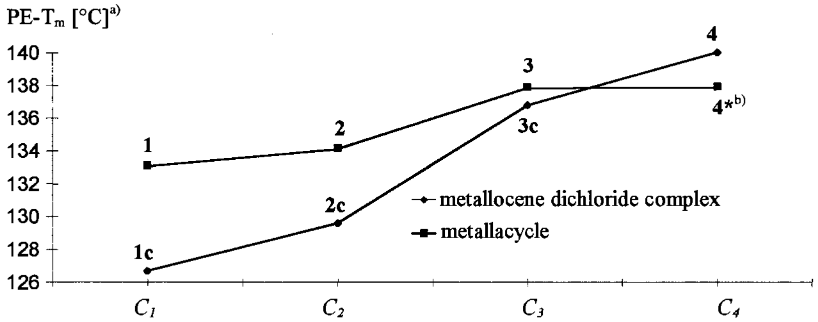

Fig. 11. Melting temperatures $T_m^{a)}$ of the polymers synthesized with the metallocene dichloride complexes **1c**–**4c** and the metallocene complexes **1**–**3** and **4***. (a) The values are taken from the second heating course of DSC. (b) Reaction of **4c** with two equivalents of *n*-butyllithium leads to an unidentified mixture of products **4***.

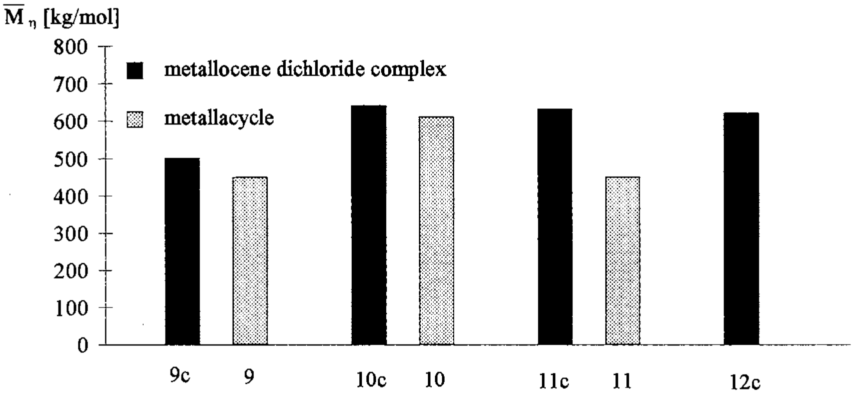

Fig. 12. Comparison of the molecular weights of the polyethylenes synthesized by mixed substituted metallocene complexes and the corresponding metallacycles.

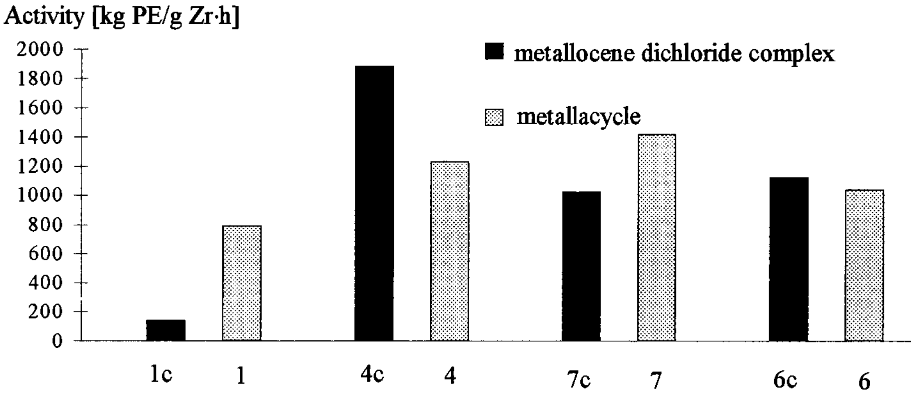

Fig. 13. Dependency of the polymerization activity on the substituents on the phenyl group for the corresponding metallocene complexes.

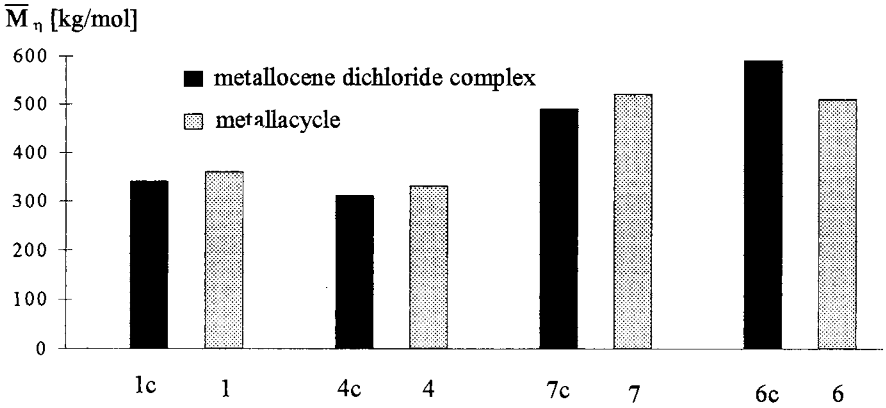

Fig. 14. Dependency of the molecular weights of the obtained polyethylenes on the substituents of the phenyl group of the corresponding metallocene complexes.

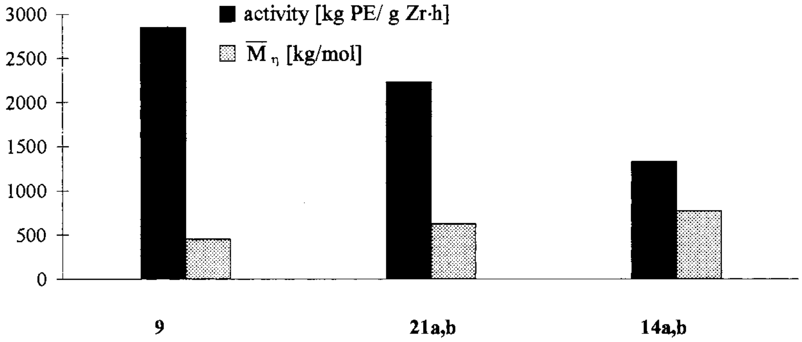

Fig. 15. Influence of the substitution of one ligand on the polymerization activity of the metallocene complexes **9**, **21a**,**b** and **14a**,**b** and the molecular weights of the obtained polymers.

2.5.4. *Influence of the substituents on the cyclopentadienyl ligand on the polymerization behavior*

Substitution of the cyclopentadienyl ligand has great impact on the polymerization activity of the corresponding metallocene complex and on the molecular weight of the obtained polyethylene. The polymerization activity decreases when the cyclopentadienyl ligand (**9**) is substituted, by an indenyl ligand (**21a**,**b**) or a 3-methyl-substituted cyclopentadienyl ligand (**14a**,**b**) (Fig. 15). The opposite effect is observed for the molecular weights of the obtained polyethylenes: the growing polymer chain is obviously kept away from the coordination center by the steric demand of the benzene ring or the methyl group. Therefore, a chain termination reaction by β-H-elimination could be inhibited.

3. Experimental

3.1. *NMR spectroscopy*

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

3.2. *Mass spectroscopy*

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

3.3. *Gas chromatography*

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

Starting phase: 3 min at 50°C

Table 2
^{1}H-[a], ^{13}C-[b] and ^{29}Si-[c] NMR data of the metallocene complexes **1**–**22a**,**b**

Complex	^{1}H-NMR [a] (J(H,H) in Hz)	^{13}C-NMR [b]
1	7.51 (m, 1H),7.25–6.85 (m, 8H), 6.56 (m, 1H), 6.12 (m, 1H), 5.98 (m, 1H), 5.89 (m, 2H), 5.85 (m, 1H), 5.49 (m, 1H), 5.08 (m, 1H), 4.03 (d, 1H) [16.7], 3.90 (d, 1H) [16.7], 3.53 (s, 2H), 1.67 (m, 2H), 1.35 (m, 2H), 1.02 (t, 3H) [7.3], 0.90 (m, 1H), 0.52 (m, 1H)	(C$_q$): 186.0, 166.3, 141.2, 139.6; (CH): 136.4, 128.9, 128.6, 128.4, 126.8, 126.4, 125.0, 123.2, 115.7, 113.1, 111.9, 111.2, 109.8, 108.7, 103.1; (CH$_2$): 58.8, 38.2, 38.2, 36.3, 35.1; (CH$_3$): 14.1
2	7.23–7.00 (m, 9H), 6.26 (m, 1H), 5.71 (m, 3H), 5.43 (m, 2H), 5.26 (m, 1H), 4.96 (m, 1H), 2.83–2.65 (m, 4H), 2.44 (m, 2H), 2.18 (m, 1H), 1.84 (m, 1H), 1.56 (m, 2H), 1.46 (m, 2H), 1.09 (m, 4H), 0.69 (m, 1H)	(C$_q$): 188.9, 147.7, 141.9, 130.5; (CH): 128.8, 128.7, 128.6, 128.5, 127.3, 126.8, 126.4, 126.3, 123.6, 115.3, 114.5, 112.1, 109.3, 109.1, 106.9, 103.7, 103.4; (CH$_2$): 55.0, 43.8, 38.7, 38.0, 35.3, 32.6, 32.2, 30.0, 29.9; (CH$_3$): 14.2
3	7.27–6.82 (m, 10H), 6.52 (m, 1H), 5.59 (m, 3H), 5.44 (m, 2H), 5.26 (m, 1H), 4.84 (m, 1H), 2.80–1.04 (m, 15H), 0.74 (m, 1H), 0.23 (m, 1H)	(C$_q$): 151.8, 142.2, 141.4; (CH): 128.7, 128.6, 128.5, 128.3, 127.0, 126.1, 114.8, 112.9, 112.1, 111.0, 110.0, 109.8, 107.5, 102.9, 74.1; (CH$_2$): 60.9, 45.6, 35.6, 35.4, 33.8, 29.9, 29.3, 29.0; (CH$_3$): 14.2
4	7.51 (m, 1H),7.24–6.85 (m, 6H), 6.56 (m, 1H), 6.13 (m, 1H), 5.98 (m, 1H), 5.88 (m, 2H), 5.84 (m, 1H), 5.48 (m, 1H), 5.08 (m, 1H), 4.02 (d, 1H) [16.7], 3.90 (d, 1H) [16.7], 3.53 (s, 2H), 2.29 (s, 3H), 2.18 (s, 3H), 1.67 (m, 2H), 1.35 (m, 2H), 1.02 (t, 3H) [7.3], 0.90 (m, 1H), 0.52 (m, 1H)	(C$_q$): 186.1, 163.3, 139.8, 138.2, 135.6, 131.5; (CH): 137.0, 129.3, 128.9, 127.7, 124.8, 115.6, 113.1, 111.8, 111.2, 109.9, 109.8, 103.1; (CH$_2$): 58.7, 37.4, 36.0, 35.5, 29.7; (CH$_3$): 21.1, 21.0, 14.1
5	7.51 (m, 1H),7.23–6.72 (m, 6H), 6.50 (m, 1H), 6.13 (m, 1H), 5.98 (m, 1H), 5.92 (m, 1H), 5.70 (m, 1H), 5.69 (m, 1H), 5.40 (m, 1H), 5.03 (m, 1H), 3.93 (d, 1H) [16.7], 3.75 (d, 1H) [16.7], 3.31 (s, 2H), 1.57 (m, 2H), 1.37 (m, 2H), 1.05 (t, 3H) [7.3], 0.99 (m, 1H), 0.44 (m, 1H)	(C$_q$): 186.8, 163.8, 161.8, 159.9, 157.8, 140.0, 137.1; (CH$_2$): 130.3, 130.2, 115.7, 115.4, 115.1, 113.4, 112.1, 111.2, 109.9, 109.8, 108.7, 103.2; (CH$_2$): 60.6, 36.9, 34.9, 29.7; (CH$_3$): 14.0
6	7.24–6.66 (m, 5H), 6.46 (m, 1H), 5.92 (m, 3H), 5.83 (m, 2H), 5.45 (m, 1H), 5.11 (m, 1H), 3.95 (d, 1H) [16.6], 3.74 (d, 1H) [16.6], 3.52 (d, 1H) [16.6], 3.39 (d, 1H) [16.6], 2.37–2.20 (m, 12H), 1.72 (m, 2H), 1.42 (m, 2H), 1.07 (m, 4H), 0.32 (m, 1H)	(C$_q$): 180.8, 160.4, 142.8, 140.9, 138.0, 137.8, 136.4, 136.0; (CH): 128.5, 127.1, 127.0, 126.9, 126.7, 123.4, 117.9, 112.8, 110.3, 110.2, 110.1, 110.0, 101.9; (CH$_2$): 56.9, 37.8, 35.9, 33.4, 29.8; (CH$_3$): 25.9, 21.4, 21.3
	8.13 (2, 1H),7.95–7.03 (m, 12H), 6.50 (m, 1H), 6.18 (m, 1H), 6.07 (m, 1H), 5.92 (m, 1H), 5.80 (m, 1H), 5.72 (m, 1H), 5.45 (m, 1H), 5.03 (m, 1H), 4.17 (d, 1H) [16.7], 4.05 (d, 1H) [16.7], 3.70 (s, 2H), 1.68 (m, 2H), 1.36 (m, 2H), 1.04 (t, 3H) [7.3], 0.92 (m, 1H), 0.63 (m, 1H)	(C$_q$): 185.8, 162.7, 140.3, 138.6, 134.1, 133.3, 132.8, 131.0; (CH): 135.2, 128.8, 128.3, 128.2, 128.1, 128.0, 127.7, 127.6, 126.3, 125.9, 125.7, 125.0, 121.7, 115.2, 114.3, 112.3, 112.0, 109.7, 109.5, 109.0, 102.8; (CH$_2$): 58.6, 37.8, 36.6, 35.6, 29.7; (CH$_3$): 14.2
8 [d]	7.52–7.09 (m, 8H), 6.72 (m, 1H), 6.55 (m, 1H), 56.47 (m, 1H), 6.42 (m, 1H), 5.98 (m, 1H), 5.80 (m, 1H), 5.72 (m, 1H), 5.44 (m, 1H), 1.65 (m, 2H), 1.36 (m, 2H), 1.03 (t, 3H) [7.3], 0.70 (m, 1H), 0.57 (s, 3H), 0.45 (s, 3H), 0.43 (s, 3H), 0.36 (m, 1H), 0.35 (s, 3H),	(C$_q$): 194.3, 158.5, 139.0, 117.1; (CH): 134.8, 134.2, 132.6, 129.5, 128.1, 126.4, 125.4, 120.8, 120.4, 120.2, 120.1, 114.2, 113.9, 113.4, 108.1; (CH$_2$): 58.9, 35.6, 29.6; (CH$_3$): 14.0, −0.4, −0.9, −1.6, −1.7
9	7.77 (m, 1H), 7.51 (d, 1H) [7.9], 7.20–6.75 (m, 6H), 6.47 (m, 1H), 6.33 (m, 2H), 5.95 (m, 1H), 5.79 (m, 1H), 5,20 (m, 1H), 4.95 (m, 1H), 3.97 (d, 1H) [16.6], 3.77 (d, 1H) [16.6], 1.48 (m, 2H), 1.29 (m, 2H), 1.04 (t, 3H) [7.2], 0.14 (m, 1H), −0.20 (m, 1H)	(C$_q$): 185.8, 165.4, 138.9; (CH): 135.8, 126.8, 125.2, 125.1, 124.4, 124.3, 123.6, 123.0, 117.0, 115.6, 112.9, 110.7, 105.3, 102.3, 97.6; (CH$_2$): 62.1, 37.6, 35.4, 29.8; (CH$_3$): 14.1
10	7.31–6.78 (m, 8H), 6.18 (m, 1H), 5.99 (m, 1H), 5.92 (m, 1H), 5.83 (m, 1H), 5,53 (m, 1H), 5.13 (m, 1H), 4.75 (m, 1H) 2.70 (m, 4H), 1.57 (m, 2H), 1.29 (m, 2H), 1.04 (t, 3H) [7.2], 0.20 (m, 1H), −0.07 (m, 1H)	(C$_q$): 188.4, 147.4, 130.7; (CH): 131.2, 128.6, 127.0, 126.8, 125.2, 124.8, 124.2, 124.1, 117.6, 115.6, 114.2, 113.6, 105.1, 100.7, 97.3; (CH$_2$): 59.3, 43.6, 37.6, 30.1, 29.3; (CH$_3$): 14.1
11	7.31–6.73 (m, 7H), 6.40 (m, 2H), 6.02 (m, 1H), 5.84 (m, 1H), 5.54 (m, 1H), 5,48 (m, 1H), 4.94 (m, 1H), 4.84 (m, 1H) 2.76–0.76 (m 12H), −0.51(m, 1H), −0.65 (m, 1H)	(C$_q$): 151.8, 140.5, 124.6; (CH): 129.3, 128.7, 128.6, 128.4, 127.5, 124.3, 124.2, 122.0, 114.8, 114.4, 110.4, 108.1, 104.4, 104.3, 96.3, 74.8; (CH$_2$): 65.0, 46.1, 36.0, 30.5, 29.0; (CH$_3$): 14.1

Table 2 (Continued)

Complex	^{1}H-NMR [a] (J(H,H) in Hz)	^{13}C-NMR [b]
12	7.68 (m, 1H), 7.53 (d, 1H) [7.9], 7.20–6.79 (m, 5H), 6.48 (m, 1H), 6.39 (m, 2H), 6.02 (m, 1H), 5.82 (m, 1H), 5,20 (m, 1H), 4.95 (m, 1H), 3.90 (d, 1H) [16.6], 3.78 (d, 1H) [16.6], 2.35 (s, 3H), 1.48 (m, 2H), 1.27 (m, 2H), 1.00 (t, 3H) [7.1], 0.22 (m, 1H), −0.08 (m, 1H)	(C_q): 186.0, 162.4, 139.2, 131.3; (CH): 136.4, 127.7, 125.1, 124.8, 124.4, 124.2, 123.7, 117.2, 115.6, 112.9, 110.8, 105.3, 102.2, 97.9; (CH_2): 61.9, 37.2, 35.5, 29.8; (CH_3): 21.5, 14.0
13	7.65 (m, 1H), 7.45 (d, 1H) [7.9], 7.23–6.72 (m, 6H), 6.38 (m, 2H), 6.31 (m, 1H), 6.04 (m, 1H), 5.96 (m, 1H), 5,25 (m, 1H), 4.87 (m, 1H), 1.78–1.19 (m, 10H), 0.97 (t, 3H) [7.1], 0.21 (m, 1H), 0.00 (m, 1H)	(C_q): 183.9, 172.6, 149.7, 43.8 (CH): 134.3, 129.3, 127.9, 125.3, 124.5, 124.1, 123.8, 123.5, 117.7, 116.1, 113.8, 103.7, 101.7, 98.3 (CH_2): 60.9, 54.1, 35.5, 29.8 (CH_3): 31.7, 30.5, 14.0
14a,**b**	7.71 (m, 1H), 7.46 (d, 1H) [7.9], 7.25–6.75 (m, 6H), 6.52 (m, 1H), 6.38 (m, 1H), 6.14 (m, 1H), 5.85 (m, 1H), 5,20 (m, 1H), 4.98 (m, 1H), 4.77 (m, 1H),3.92 (m, 2H), 1.93 (s, 3H), 1.67 (m, 2H), 1.29 (m, 2H), 1.05 (t, 3H) [7.2], 0.49 (m, 1H), −0.13 (m, 1H)	(C_q): 184.2, 164.8, 137.1, 125.7; (CH): 136.3, 127.2, 125.7, 125.5, 124.4, 124.0, 123.5, 123.1, 118.5, 115.5, 111.6, 103.1, 101.0, 99.2; (CH_2): 58.7, 36.3, 34.9, 30.0; (CH_3): 14.0, 13.9
15a,**b**	7.48–6.75 (m, 16H), 6.19–5.83 (m, 6H), 5.74–5.39 (m, 4H), 5.05 (m, 1H), 4.75 (m, 1H), 2.71 (m, 4H), 2.24–0.97 (m, 24H), 0.28 (m, 1H), 0.05 (m, 1H), −0.12 (m, 1H), −0.28 (m, 1H)	(C_q): 189.7, 188.1, 147.8, 147.1, 146.9, 130.7; (CH): 132.2, 130.1, 128.8, 128.7, 126.9, 126.7, 125.0, 125.0, 124.9, 124.7, 124.2, 123.7, 123.3, 122.2, 116.0, 115.9, 114.0, 112.6, 112.1, 106.7, 105.6, 105.2, 102.7, 100.2, 96.9, 95.2; (CH_2): 59.6, 57.5, 43.7, 42.8, 36.2, 30.6, 30.5, 26.9; (CH_3):14.1, 14.0
16	7.51 (m, 1H), 7.21–7.08 (m, 3H), 6.37 (m, 1H), 6.08 (m, 1H), 6.00 (s, 5H), 5.63 (m, 1H), 5.12 (m, 1H), 1.82–1.24 (m, 10 H), 0.99 (t, 3H) [7.3], 0.54 (m, 2H)	(C_q): 183.2, 172.1, 150.7, 138.2, 43.1; (CH):135.2, 128.3, 126.7, 126.5, 123.7, 114.2, 113.6, 110.5, 105.5, 100.8; (CH_2): 59.3, 37.7, 29.8; (CH_3): 32.0, 30.4, 14.1
17a,**b**	7.63 (d, 1H) [7.9], 7.31–6.71 (m, 38 H), 6.48 (m, 1H), 5.73 (m, 1H), 5.12 (m, 1H), 4.39–3.62 (m, 8H), 1.45–0.81 (m, 14H), −0.28 (m, 1H), −0.84 (m, 1H), −1.20 (m, 1H), −0.41 (m, 1H)	(C_q): 184.8, 184.5, 165.6, 165.4, 142.2, 141.1, 121.6, 120.4, 112.8, 111.1; (CH): 136.8, 136.3, 129.2, 128.9, 128.8, 128.6, 128.5, 126.7, 126.5, 126.4, 126.0, 125.6 125.5, 125.4, 125.0, 124.8, 124.7, 124.6, 124.4, 124.1, 124.0, 123.9, 123.6, 123.5, 123.4, 123.3, 123.2, 123.1, 120.9, 120.8, 103.5, 101.9, 96.2, 93.8; (CH_2): 64.9, 62.5, 38.1, 36.7, 36.4, 34.7, 33.8, 33.7, 30.8, 30.4; (CH_3): 14.0, 13.9
18a,**b**	7.53–6.55 (m, 40 H),), 5.73 (m, 1H), 5.12 (m, 1H), 2.93–1.52 (m, 16H), 1.47–0.79 (m, 14H), −0,13 (m, 1H), −0.73 (m, 1H), −1.11 (m, 1H), −0.62 (m, 1H)	Not determined
19a,**b**	7.43–6.91 (m, 36H), 6.51 (m, 2H), 6.01–5.91 (m, 4H), 5.67 (d, 1H) [3.2], 5.50 (d, 1H) [3.2], 2.89–2.45 (m, 12H), 1.96–0.88 (m, 20H), 0.36 (m, 2H), −0.97 (m, 2H)	(C_q): 141.9, 141.8, 141.6, 116.3, 116.1, 115.9, 103.9; (CH): 128.9, 128.7, 128.6, 126.3, 126.2, 126.1, 126.0, 125.0, 124.9, 124.8, 124. 7, 124.3, 124.2, 124.0, 123.9, 123.8, 98.7, 98.5, 49.7, 47.5, 46.8; (CH_2): 63.1, 58.8, 54.0, 36.4, 35.8, 34.6, 33.2, 31.2, 30.0, 28.5, 27.4, 27.1; (CH_3): 10.3, 10.1
20a,**b** [e]	7.23–6.51 (m, 36H), 6.36 (m, 1H), 6.23 (m, 2H), 5.63 (m, 1H), 5.59 (m, 2H), 1.33–0.34 (m, 38 H), −0.96 (m, 1H), −1.27 (m, 1H), 1.31 (m, 1H), −1.98 (m, 1H)	(C_q): −194.6, 192.8, 161.1, 155.8, 139.7, 138.4, 136.7, 133.9, 131.5, 131.1, 130.3, 130.0, 114.4, 104.9; (CH): 134.9, 134.2, 134.1, 134.0, 129.3−120.6 (m), 119.7, 114.2, 111.0, 10.6, 101.2, 91.5; (CH_2): 69.2, 66.3, 40.8, 36.9, 35.7, 31.9, 30.1, 26.6; (CH_3): 13.7, 13.5, 10.7, 10.6, 2.2, −0.4, −0.5, −0.6
21a,**b**	7.34–6.95 (m, 15 H), 6.32 (d, 1H) [6.4], 4.,78 (d, 1H) [11.5], 4.20 (d, 1H) [16.8], 3.91 (d, 1H) [16.8], 1.51–0.90 (m, 7H), −0.63 (m, 1H), −1.53 (m, 1H)	(C_q): 184.4, 165.6, [d]; (CH): 136.9, 128.8, 128.6, 126.7, 125.6, 125.4, 125.3, 124.9, 124.8, 124.5, 124.0, 123.3, 123.2, 120.3, 119.1; (CH_2): 63.9, 36.5, 36.4, 30.6; (CH_3): 14.0
22a,**b** [e]	7.41–6.32 (m, 14H), 6.66 (m, 1H), 5.16 (d, 1H) [3.0], 5.01 (d, 1H) [2.4], 1.58–0.95 (m, 7H), 0.75 (s, 3H), 0.45 (s, 3H), −0.19 (m, 1H), −1.60 (m, 1H)	(C_q): 193.3, 158.3, 131.9, 129.9, 114.2; (CH): 136.2, 134.5, 132.4, 128.2, 126.9, 126.5, 125.7, 125.6, 125.3, 125.0, 124.7, 120.4, 102.9, 102.6, 100.1; (CH_2): 65.5, 37.5, 31.1; (CH_3): 14.0, −0.7, −0.9

[a] 25°C, in benzene-d_6 δ [ppm] rel. benzene (7.24).

[b] 25°C, in benzene-d_6 δ [ppm] rel. benzene-d_6 (77.0).

[c] 25°C, in benzene-d_6 δ [ppm] rel. $TMS_{ext.}$ (0.0).

[d] δ (Si) = −9.9, 11.6 ppm.

[e] δ (Si) = −10.5 ppm.

Heating phase: 5°C min^{-1} (15 min)

Plateau phase: 310°C (15 min)

3.4. General synthesis procedure for the metallocene complexes ***1–22a,b***

The metallocene dichloride complex, 3.00 mmol, was dissolved in 50 ml toluene and at −78°C mixed with 3.8 ml (6.0 mmol) *n*-butyllithium. The reaction mixture was warmed to room temperature over 6 h and stirred overnight. The reaction mixture was filtered over sodium sulfate, and the solvent evaporated in vacuo. The metallocene complexes were obtained as yellow oils or solids in 60–98% yields and were characterized by NMR spectroscopy (Table 2).

3.5. Activation of the metallocene complexes with MAO

The desired metallocene complex, 10–15 mg, was activated with MAO (30% in toluene) (Zr:Al = 1:3000). A volume of the catalyst solution contained 0.5–1.5 mg metallocene complex and was used within 1 h for homopolymerization.

3.6. Homopolymerization of ethylene

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

3.7. Characterization of the polyethylene samples

3.7.1. Differential scanning calorimetry (DSC)

The polymer samples were investigated for phase transitions by DSC using a Pyris DSC 7 instrument. For the measurements, 5–12 mg dried polymer were fused into standard aluminum pans (∅ 7 mm) and measured under nitrogen cooling using the following temperature program:

First heating phase: from 25 to 200°C (heating rate 40 K min^{-1}).

Isothermal phase (3 min).

Cooling phase from 200 to −40°C (cooling rate 20 K min^{-1}).

Second heating phase from −40 to 200°C (heating rate 20 K min^{-1}).

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

3.7.2. Viscosimetry

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

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