

Synthesis, characterization, and catalytic properties of bis[alkylindenyl]-, bis[alkenylindenyl]- and [alkenylindenyl(cyclopentadienyl)]zirconium dichloride complexes

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Received 15 February 2001; accepted 29 March 2001

Dedicated to Professor Nefedov on the occasion of his 70th birthday

Abstract

4,7-Dimethylindenyl lithium or 2,4,7-trimethylindenyl lithium reacts with 1-bromobutane, 1-chloro-2-propene, or 1-bromo-3-methyl-2-butene to give 3-butyl-4,7-dimethyl-1*H*-indene (**1**), 3-(2-propene-1-yl)-2,4,7-trimethyl-1*H*-indene (**2**), or 3-(3-methyl-2-butene-1-yl)-2,4,7-trimethyl-1*H*-indene (**3**), respectively. Deprotonation of **1–3** with *n*-butyl lithium yields the lithium salts **1a–3a**. The reactions of **1a–3a** and of [1-(4-pentene-1-yl)indenyl]lithium (**4a**) with zirconiumtetrachloride produce the complexes bis[1-butyl-4,7-dimethylindenyl]- (**1b**), bis[1-(2-propene-1-yl)-2,4,7-trimethyl-indenyl]- (**2b**), bis[1-(3-methyl-2-butene-1-yl)-2,4,7-trimethylindenyl]- (**3b**) or bis[1-(4-pentene-1-yl)indenyl]zirconium dichloride (**4b**). The reaction of cyclopentadienylzirconium trichloride with [2-(3-butene-1-yl)-4,7-dimethylindenyl]lithium or [2-(4-pentene-1-yl)-4,7-dimethylindenyl]lithium affords the mixed complexes [2-(3-butene-1-yl)-4,7-dimethylindenyl(cyclopentadienyl)]zirconium dichloride (**5c**) or [2-(4-pentene-1-yl)-4,7-dimethylindenyl(cyclopentadienyl)]zirconium dichloride (**6c**). All new compounds were characterized by elemental analysis, ¹H- and ¹³C{¹H}-NMR spectroscopy as well as by mass spectrometry. In addition, single-crystal X-ray structural analysis was done for **3b**. The complexes **1b–4b**, **5c**, and **6c** were tested as catalysts for the homopolymerization and copolymerization of ethene and propene and the results were compared to those of analogous compounds. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Alkylindenes; Alkenylindenes; Indenyl lithium salts; Indenyl zirconium complexes; Ethene polymerization; Propene polymerization; Copolymerization

1. Introduction

Metallocenes of the Group IVB elements, especially of zirconium, play an important role in catalysis. Indenyl zirconium complexes have been studied intensively due to their ability to catalyze the stereoselective polymerization of alkenes [1]. Our work in this research area has been focused on the synthesis of alkenyl

indenes and their bis(alkenylindenyl)zirconium dichloride complexes [2]. It was of special interest to find out if there is any influence of the length and of the bonding site of the alkenyl side chain on the polymerization processes and to compare the results with those complexes obtained in which one of the alkenylindenyl ligand is substituted by a cyclopentadienyl ligand.

Here we report the synthesis, characterization and polymerization properties of new [alkylindenyl]-, [alkenylindenyl]-, and [alkenyl(cyclopentadienyl)indenyl]zirconium dichloride complexes, which enlarge the list of analogous complexes already described [2] to such an extent that comparative studies of their catalytic properties are possible.

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2. Synthesis and properties

2.1. Alkyl- and alkenylindenes

The reaction of 1-bromobutane, 1-chloro-2-propene, or 1-bromo-3-methyl-2-butene with 4,7-dimethylindenyl lithium or 2,4,7-trimethylindenyl lithium in THF at 20°C yields the alkyl- or alkenylindenes: 3-butyl-4,7-dimethyl-1*H*-indene (**1**), 3-(2-propene-1-yl)-2,4,7-trimethyl-1*H*-indene (**2**), or 3-(3-methyl-2-butene-1-yl)-2,4,7-trimethyl-1*H*-indene (**3**), respectively (Scheme 1). At reaction temperatures above 0°C the formation of the 3-positional isomer is favored to the 1-positional isomer. The indenes **1–3** can be purified by fractional vacuum distillation and were isolated as light yellow liquids with yields of 80–90%. The required distillation conditions (> 80°C/0.01 mbar) cause some self-polymerization.

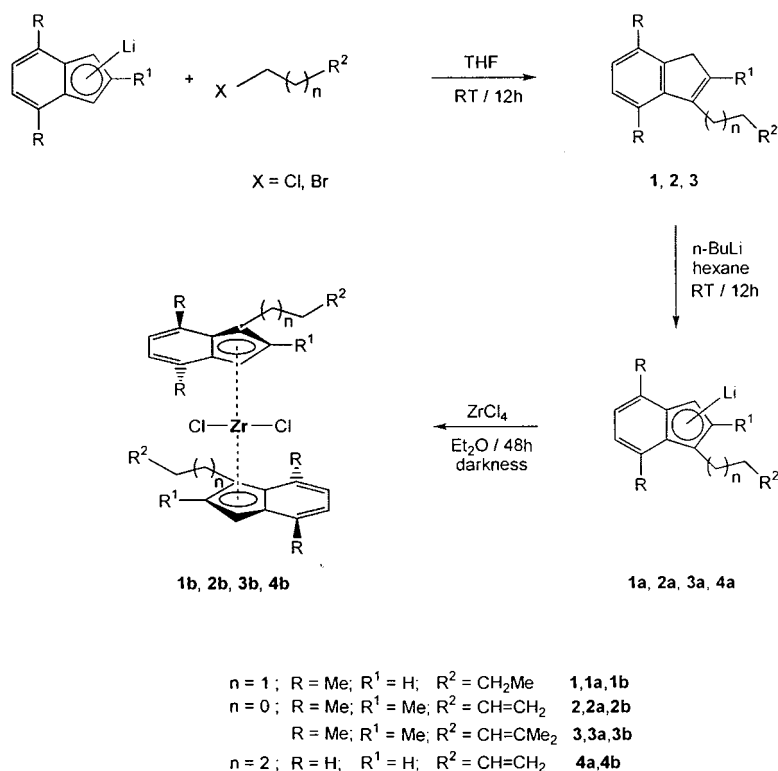
2.2. Alkylindenyl- and alkenylindenyl lithium salts

Deprotonation of the indenes **1–3** with an excess of *n*-BuLi in hexane at room temperature yields the lithium salts [1-butyl-4,7-dimethylindenyl]lithium (**1a**), [1-(2-propene-1-yl)-2,4,7-trimethylindenyl]lithium (**2a**), or [1-(3-methyl-2-butene-1-yl)-2,4,7-trimethylindenyl]lithium (**3a**) as white solids (Scheme 1). They are insoluble in hexane, but readily soluble in diethyl ether and THF, melt with decomposition in the range 170–185°C

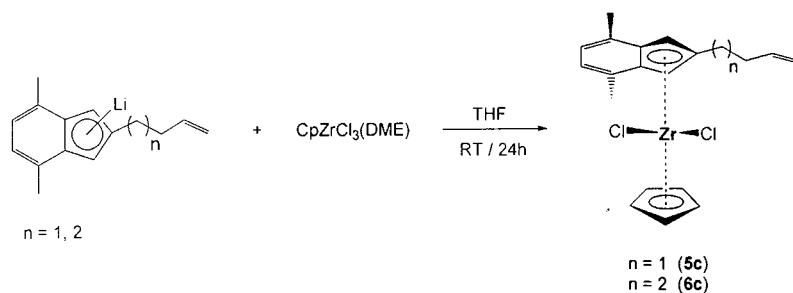
and are very sensitive towards oxygen and moisture. Their ¹H-NMR spectra show that the lithium atom is not coordinated by solvent molecules. Furthermore, a comparison of the spectrum of **2a** with those of alkenyl-cyclopentadienyl cobalt complexes in which the alkenyl double bond is coordinated to the metal center [3–5] indicates that the lithium atom is also not coordinated by the terminal propenyl double bond. In such a case, a larger splitting of the geminal *cis*- and *trans*-CH=CH₂ proton signals as well as a highfield shift of those signals of at least 3 ppm relative to their position in the spectrum of **2** should be expected.

2.3. Bis[alkylindenyl]- and bis[alkenylindenyl]zirconium dichloride complexes

Zirconium tetrachloride reacts with the twofold molar amount of the indenyl lithium salts **1a–3a** or of [1-(4-pentene-1-yl)indenyl]lithium (**4a**) [2] in ether at room temperature and in the dark with formation of the respective bis[1-alkylindenyl]- or bis[1-alkenylindenyl]zirconium dichloride complexes **1b–4b** with yields of 50–65% (Scheme 1). The yellow solids are sensitive towards air and moisture and are soluble in polar solvents and to some extent also in hexane and pentane. They can be crystallized from hexane at 0°C. The complexes melt with decomposition, the butylindenyl derivative **1b** at 218°C and the alkenylindenyl complexes **2b–4b** in the range of 89–120°C.



Scheme 1.



Scheme 2.

In the $^1\text{H-NMR}$ spectra of **1b–4b**, which show similar features like the corresponding bis[1-alkenylindenyl]zirconium dichloride complexes described in Ref. [2], the number and the splitting pattern of the CH-signals of the five-membered ring part of the indenyl ligands indicate the presence of equimolar mixtures of *rac-meso* diastereomers and, as a consequence, the restricted rotation of the two alkenylindenyl ligands. The separation of the diastereomers was not attempted.

2.4. [Alkenylindenyl(cyclopentadienyl)]zirconium dichloride complexes

[2-(3-Butene-1-yl)-4,7-dimethylindenyl(cyclopentadienyl)]zirconium dichloride (**5c**) and [2-(4-pentene-1-yl)-4,7-dimethylindenyl(cyclopentadienyl)]zirconium dichloride (**6c**) are formed in the reactions of equimolar mixtures of [cyclopentadienyl]zirconium trichloride [6] with [2-(3-butene-1-yl)-4,7-dimethylindenyl]lithium [2] or [2-(4-pentene-1-yl)-4,7-dimethylindenyl]lithium [2] in THF at 20°C (Scheme 2). The complexes are isolated from hexane at 0°C as yellow crystalline solids with yields of 60–70%. They are soluble in polar as well as in non-polar solvents and melt in the same temperature range like the bis[1-alkenylindenyl]zirconium dichloride complexes **2b–4b** ($83–85^\circ\text{C}$ (**5c**); $95–96^\circ\text{C}$ (**6c**)), but without decomposition.

The reason for the synthesis of these mixed ligand complexes was to avoid the mutual steric hindrance of the ligands as is the case in the bis[1-alkenylindenyl]zirconium complexes. The unsubstituted cyclopentadienyl ligand should give enough space for a free rotation of both ligands around the respective Zr–L bond axis. The $^1\text{H-NMR}$ spectra of **5c** and **6c** confirm this suggestion showing only singlet signals for the Cp protons, for the protons of the five-membered indenyl ring part, and for the protons of the six-membered indenyl ring part.

3. Molecular structure of **3b**

Crystals of **3b** suitable for X-ray structural analysis were obtained from hexane at 0°C . Apparently, the

flexible indenyl side chains of the new complexes described seriously interfere in the formation of well-shaped crystals. The crystallographic data and refinement parameters are listed in Table 1. The complex crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit contains two crystallographically independent molecules that differ only slightly in their

Table 1
Crystal data and details of data collection and structure refinement for **3b**

Chemical formula	$\text{C}_{34}\text{H}_{42}\text{ZrCl}_2$
Formula weight (g mol^{-1})	612.8
Crystal size (mm)	$0.11 \times 0.26 \times 0.38$
Color	Yellow
Crystal system	Triclinic
Space group	$P\bar{1}$
Z (molecules)	4
Unit cell dimensions	
<i>a</i> (\AA)	12.77140(10)
<i>b</i> (\AA)	14.8527(2)
<i>c</i> (\AA)	16.6828(3)
α ($^\circ$)	86.7460(10)
β ($^\circ$)	76.1860(10)
γ ($^\circ$)	89.2900(10)
<i>V</i> (\AA^3)	3068.07(7)
<i>D</i> _{calc} (g cm^{-3})	1.327
<i>F</i> (000)	1280
μ (Mo–K α) (mm^{-1})	0.553
Diffractometer	Siemens SMART CCD
<i>T</i> (K)	173(2)
Radiation (Mo–K α) (\AA)	0.71073
2θ Range ($^\circ$)	$3 \leq 2\theta \leq 61$
Reflections collected	28 925
Reflections unique	18 472
Absorption correction	SADABS
Max/min transmission	0.9548, 0.5628
Reflections observed, $I > 2\sigma(I)$	8331
Completeness to theta = 30.7° (%)	97.1
Data/restraints/parameters	18 472/0/687
Goodness-of-fit ^a	0.933
$R_1 I > 2\sigma(I)$ /all data ^b	0.0764/0.1946
$wR_2 I > 2\sigma(I)$ /all data ^c	0.1072/0.1391
Largest difference peak and hole (e \AA^{-3})	1.368 and -1.060

^a Goodness-of-fit = $[\sum w(|F_o| - |F_c|)^2 / (n - p)]^{1/2}$.

^b $R_1 = \sum (|F_o| - |F_c|) / \sum |F_o|$.

^c $wR_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ and $w = 1/[\sigma^2(F_o^2) + (0.005P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

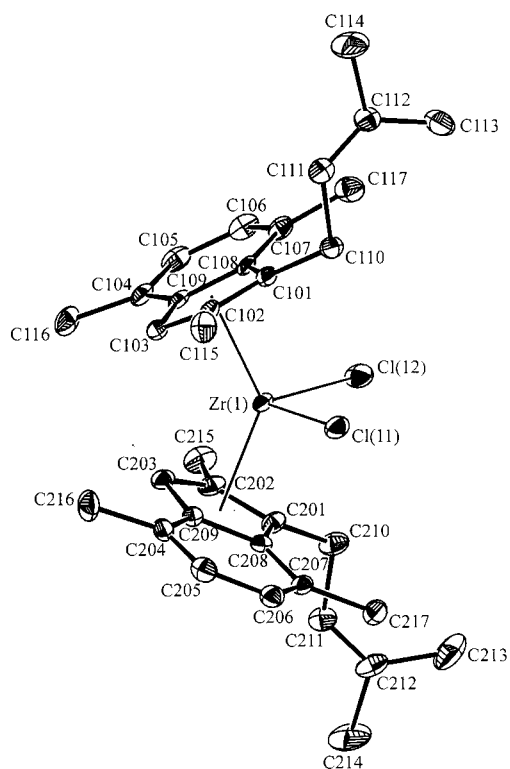


Fig. 1. ORTEP plot [8] of **3b**. Selected bond distances (Å) and angles (°), estimated standard deviations in parentheses. Cp(1) and Cp(2) defines the centroids of the indenyl ring atoms C(101)–C(103), C(108), C(109) and C(201)–C(203), C(208), C(209), respectively: Zr(1)–Cl(11), 2.4124(11); Zr(1)–Cl(12), 2.422(2); Zr(1)–Cp(1), 2.241(2); Zr(1)–Cp(2), 2.243(2); Cp(1)–Zr(1)–Cp(2), 133.52(7); Cp(1)–Zr(1)–Cl(11), 104.83(6); Cp(1)–Zr(1)–Cl(12), 105.53(6); Cp(2)–Zr(1)–Cl(11), 105.35(6); Cp(2)–Zr(1)–Cl(12), 104.91(6); Cl(11)–Zr(1)–Cl(12), 97.01(5); plane Cp(1)–Cp(2), 52.5(2).

geometrical properties. The molecular structure of one molecule is depicted in Fig. 1. It adopts C_2 -symmetry and the twofold axis lies in the plane defined by the Cl and Zr atoms. The indenyl ligand itself has two prochiral faces *si* and *re*. Conclusively, there are two almost identical *si*–*si* *rac* enantiomers and two *re*–*re* *rec* enantiomers in the unit cell. The *meso* product could not be crystallized. Complex **3b** shows a distorted tetrahedral arrangement of the coordination sphere around the zirconium atom, which is coordinated by two Cl atoms and by the η^5 -cyclopentadienyl parts of the two alkenylindenyl ligands. In agreement with our former published results [2], the double bonds of the alkenylindenyl side chains neither coordinate the zirconium atom nor do they significantly change the structural parameters of the indenyl core. The average bond distances Zr–Cl (2.418 Å) and Zr–Cp' (2.239 Å) (Cp' = centroid of the five-membered ring part of the indenyl system) and the average bond angles Cp'–Zr–Cp' (133.6°) and Cl–Zr–Cl (97.34°) are of the order estimated for other unbridged and bridged zirconocene complexes [7].

4. Catalytic activity

The complexes **1b–4b**, **5c** and **6c** were tested as catalysts for the homopolymerization or copolymerization of ethene or/and propene at 30°C and in the presence of methylaluminoxane (MAO) as a cocatalyst. The results are listed in Tables 2 and 3 along with the results already published for the bis[1-alkenylindenyl]zirconium dichloride complexes **7b–12b** [2].

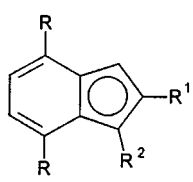
4.1. Homopolymerization

The activity data of the 2-propene substituted complexes **7b**, **9b**, and **2b** and of the 3-butene substituted complexes **8b**, **10b**, and **12b** (Table 2) indicate some general features. The data clearly demonstrate that the activity in ethene polymerization decreases going from 2-propene to the corresponding 3-butene derivative and going from the respective non-methylated via the 4,7-dimethylated to the 2,4,7-trimethylated alkenylindenyl complex. The masses of the polymers formed show the same decreasing trend when going from **9b** to **10b** or from **2b** to **12b**, but show a reverse trend to that found for the activities values when going from **7b** to **8b** and from the non-methylated via the 4,7-dimethylated to the 2,4,7-trimethylated alkenylindenyl complexes.

Concerning the polymerization of propene, the activity data of all complexes are on an essentially lower level than those obtained for the ethene polymerization. The activity also decreases going from the propenyl-substituted complex **7b** to the butenyl-substituted derivative **8b**, showing a reverse trend for the transition **9b** to **10b** and a very low but somewhat equal activity for **2b** and **12b**. In accordance with the trend in the ethene polymerization, the activities decrease going from the non-methylated via the 4,7-dimethylated to the 2,4,7-trimethylated alkenylindenyl complexes. Like the activities, the molar masses of the polymers formed in the propene polymerization are altogether much lower than those of the ethene polymers. In contrast to the results of the ethene polymerization, the masses of the polymers obtained with the catalysts **7b** and **8b** decrease in the same direction as the activity values and in the case of the low-active catalysts **2b** and **12b**, the 2-propenyl complex **2b** affords the polymer of lower mass. In accordance to the results of the ethene polymerization, the masses increase with increasing methyl substitution of the respective indenyl moiety. At this point it should be mentioned that the polypropylene formed in the presence of **2b** as a catalyst shows an isotacticity of [mmmm] 41%, a considerable high value for an unbridged bisindenyl metal system.

In conclusion, in the ethene as well as in the propene polymerization the propenyl-substituted complexes are generally more active than the butenyl-substituted com-

Table 2
 Polymerization results obtained with L_2ZrCl_2 (**1b–4b**, **7b–12b**) and $LCpZrCl_2$ (**5c** and **6c**)

No.	L	Activity ($kg_{\text{Pol}}/mol_{Zr} \cdot h \cdot mol_{\text{mon}}/l$)	M ($g \text{ mol}^{-1}$)	T_m ($^{\circ}\text{C}$)	ΔH_m ($J \text{ g}^{-1}$)	T_g ($^{\circ}\text{C}$)	[mmmm] (%)
							
<i>Ethene</i>							
R = R ¹ = H							
7b	R ² = CH ₂ CH=CH ₂	170 000	268 000	140	160	n.d.	–
8b	R ² = (CH ₂) ₂ CH=CH ₂	83 000	430 000	143	178	n.d.	–
4b	R ² = (CH ₂) ₃ CH=CH ₂ R = Me, R ¹ = H	980 000	324 000	142	187	n.d.	–
9b	R ² = CH ₂ CH=CH ₂	160 000	591 000	143	158	n.d.	–
10b	R ² = (CH ₂) ₂ CH=CH ₂	11 000	551 000	141	157	n.d.	–
11b	R ² = (CH ₂) ₃ CH=CH ₂	18 000	493 000	138	154	n.d.	–
1b	R ² = C ₄ H ₉ R = R ¹ = Me	51 000	730 000	140	151	n.d.	–
2b	R ² = CH ₂ CH=CH ₂	5800	Insoluble	142	174	n.d.	–
12b	R ² = (CH ₂) ₂ CH=CH ₂	1500	710 000	138	96	n.d.	–
3b	R ² = CH ₂ CH=CMe ₂ R = Me, R ² = H	123 000	194 000	139	169	n.d.	–
5c	R ¹ = (CH ₂) ₂ CH=CH ₂	54 800	Insoluble	141	135	n.d.	–
6c	R ¹ = (CH ₂) ₃ CH=CH ₂	169 000	52 300	141	130	n.d.	–
<i>Propene</i>							
R = R ¹ = H							
7b	R ² = CH ₂ CH=CH ₂	500	5100			n.d.	–
8b	R ² = (CH ₂) ₂ CH=CH ₂	10	1500	87	2	–40	18
4b	R ² = (CH ₂) ₃ CH=CH ₂ R = Me, R ¹ = H	< 10	1600	140	1	–43	9
9b	R ² = CH ₂ CH=CH ₂	< 10	14 000	–	–	n.d.	–
10b	R ² = (CH ₂) ₂ CH=CH ₂	10	n.d.	–	–	n.d.	–
11b	R ² = (CH ₂) ₃ CH=CH ₂	< 10	10 100	–	–	n.d.	–
1b	C ₄ H ₉ R = R ¹ = Me	< 10	4400	am.	–	–19	4
2b	R ² = CH ₂ CH=CH ₂	< 10	13 000	147	18	–21	41
12b	R ² = (CH ₂) ₂ CH=CH ₂	< 10	80 300	145	11	–31	18
3b	R ² = CH ₂ CH=CMe ₂ R = Me, R ² = H	< 10	12 700	am.	–	n.d.	7
5c	R ¹ = (CH ₂) ₂ CH=CH ₂	500	9300	am.	–	–9	11
6c	R ¹ = (CH ₂) ₃ CH=CH ₂	1250	17 400	am.	–	–4	11

n.d.: not detected; am.: amorphous.

pounds; both producing polymers whose mass increase with increasing methyl substitution of the indenyl moiety.

The activity data of the pentenyl derivatives **4b** and **11b** as well as the mass values of the polymers formed by these catalysts mostly follow their own trends. They only follow the general trend derived for the propene- and butene-substituted indenylzirconium dichloride complexes with regard to the degree of methylation of the indenyl ligand.

Compared with the butenyl complex **10b** the corresponding butyl complex **1b** shows a higher activity in ethene polymerization but a lower activity in propene

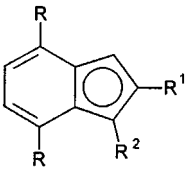
polymerization. The new mixed [2-alkenyl-4,7-dimethylindenyl(cyclopentadienyl)]zirconium dichloride complexes **5c** and **6c** show activity values in ethene polymerization which are comparable with the mean value of all tested bis[1-alkenylindenyl] complexes or with the highest value of the bis[1-propenylindenyl] complex **7b**, respectively. The activity values in propene polymerization are remarkably high compared to those of the bis[1-alkenylindenyl] complexes.

4.2. Copolymerizations

The copolymerizations of ethene and propene were

Table 3

Results of the copolymerization^a of ethene and propene obtained with L₂ZrCl₂ (**2b**, **3b**, **5b**, **6b**) and LCpZrCl₂ (**5c** and **6c**)

No.	L	Activity (kg _{Pol} /mol _{Zr} *h*mol _{mon} /l)	M (g mol ⁻¹)	T _m (°C)	ΔH _m (J g ⁻¹)	T _g (°C)	X _{propene} (%)
							
	Ethene/propene ^a R = R ¹ = Me						
2b	R ² = CH ₂ CH=CH ₂	50	150 000	117	46	n.d.	10.3
3b	R ² = CH ₂ CH=CMe ₂	50	23 700	115	4	-1	23.7
	R = Me, R ² = H						
5b	R ¹ = (CH ₂) ₂ CH=CH ₂	2600	71 100	69	21	n.d.	27.1
6b	R ¹ = (CH ₂) ₃ CH=CH ₂	18 200	46 000	68	4	n.d.	23.2
5c	R ² = (CH ₂) ₂ CH=CH ₂	227 000	Insoluble	95	33	n.d.	9.9
6c	R ¹ = (CH ₂) ₃ CH=CH ₂	169 000	Insoluble	89	37	n.d.	9.5

^a Ethene–propene ratio in the feed: 0.2/0.8.

n.d.: not detected.

carried out with the complexes **2b** and **3b**, the bis[2-(alken-1-yl)-4,7-dimethylindenyl]zirconium dichloride complexes **5b** and **6b**, and the two [2-alkenyl-4,7-dimethylindenyl(cyclopentadienyl)]zirconium dichloride complexes **5c** and **6c** as catalysts (Table 3). In all cases, propene is incorporated into the copolymer only to a relatively low extent. Accordingly, the ethene sequences are long and cause a crystalline state of all copolymers as proved by their WAXS diagrams (Fig. 2). At $2\theta = 21.6$ and 24° and at low temperatures the diagrams show the 110 and the 200 *hkl*-values of polyethylene, which decrease with increasing temperature according to the progressive approach to the melting temperatures. While the use of the bis(1-alkenylindenyl) catalyst systems leads to copolymers having a tendency to be blocky (θ values of 0.78–0.90), the 2-alkenylindenyl(cyclopentadienyl) catalyst systems produce statistical copolymers (θ values of 1.03–1.04).

5. Experimental

5.1. General comments

All operations were performed under a dry N₂ atmosphere using standard Schlenk techniques. The solvents used were dried over Na–benzophenone and distilled prior to use. The NMR spectra were recorded on a Bruker ARX 200 or a Bruker ARX 400 spectrometer. Proton and carbon assignments were generally made based on COSY and HETCOR spectra. CH analyses were performed on a Perkin–Elmer 240 C elemental analyzer. Mass spectra were determined on a Varian MAT 311 A spectrometer using electron impact (stan-

dard 70 eV, otherwise specified). Melting points were determined in sealed capillaries with a HWS-SG 2000 melting point determination apparatus and are uncorrected. The syntheses of the complexes **5b**–**12b** are described in Ref. [2].

5.2. Alkyl- and alkenylindenes and their lithium salts

5.2.1. 3-Butyl-4,7-dimethyl-1H-indene (**1**)

To a solution of 4,7-dimethylindenyllithium (3.4 g, 22.66 mmol) in THF, 1-bromobutane (3.1 g, 22.66 mmol) in THF (50 ml) was added slowly at 20°C. The mixture was stirred for 12 h. Then the solvent was removed under reduced pressure and replaced by water (20 ml). The aqueous phase was extracted several times with Et₂O and the combined Et₂O extracts were dried over MgSO₄. Fractional distillation yielded **1** as a yel-

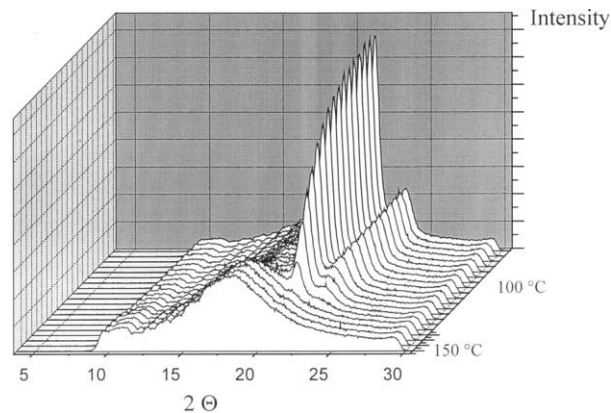


Fig. 2. WAXS diagram (DESY) of **2b**. Crystalline state during heating up from 70 to 150°C.

low liquid (3.65 g, 81%). B.p.: 96–102°C/0.01 mbar. ¹H-NMR (CDCl₃, 200 MHz): δ = 6.97 (d, *J* = 7.6 Hz, 1H, CH arom.), 6.92 (d, *J* = 7.6 Hz, 1H, CH arom.), 6.21 (m, 1H, =CH), 3.17 (m, 2H, CH₂), 2.59 (s, 3H, CH₃), 2.41 (m, 2H, CH₃), 2.34 (s, 3H, CH₃), 1.67–0.86 (m, 6H, CH₂). ¹³C{¹H}-NMR (CDCl₃, 50.32 MHz): δ = 146.7 (C), 145.4 (C), 144.1 (C), 143.1 (C), 142.6 (C), 139.0 (CH=CH₂), 129.3 (CH arom.), 128.9 (CH=), 125.6 (CH arom.), 36.3 (CH₂), 31.4 (CH₂CH₂), 30.6 (CH₂CH₂), 22.8 (CH₂CH₂), 19.8 (CH₃), 18.2 (CH₃), 14.0 (CH₃). LRMS (87°C); *m/z*: 200 (40) [M]⁺, 158 (100) [C₁₂H₁₄]⁺, 143 (32) [C₁₁H₁₁]⁺, 129 (15) [C₁₀H₉]⁺, 115 (9) [C₉H₇]⁺. C₁₅H₂₀ (200.32 g mol⁻¹): Anal. Found: C, 89.94; H, 10.06. Calc.: C, 89.67; H, 10.03%.

5.2.2. 3-(2-Propene-1-yl)-2,4,7-trimethyl-1H-indene (2)

Analogous to the preparation of **1**, 2,4,7-trimethylindenyllithium [9] (4.60 g, 28 mmol) in THF (50 ml) reacted with 3-chloropropene (2.57 g, 33.6 mmol) to give **2** as a light yellow liquid (4.87 g, 88%). B.p.: 81–82°C/0.01 mbar. ¹H-NMR (CDCl₃, 200 MHz): δ = 6.95 (d, ³*J*(H,H) = 7.6 Hz, 1H, CH), 6.81 (d, ³*J*(H,H) = 7.6 Hz, 1H, CH), 6.57 (m, 1H, CH), 5.20 (m, 1H, CH), 4.88 (m, 2H, CH₂), 3.43 (m, 1H, CH), 2.89 (m, 1H, CH₂), 2.74 (m, 1H, CH₂), 2.40 (s, 3H, CH₃), 2.36 (s, 3H, CH₃), 2.10 (s, 3H, CH₃). ¹³C{¹H}-NMR (CDCl₃, 50.32 MHz): δ = 147.7 (C), 143.9 (C), 143.7 (C), 133.8 (CH), 129.9 (C), 129.5 (CH), 126.3 (C), 125.7 (CH), 125.5 (CH), 115.9 (CH₂), 51.5 (CH), 31.7 (CH₂), 18.8 (CH₃), 18.2 (CH₃), 15.4 (CH₃). LRMS (73°C); *m/z* (%): 198 (30) [M]⁺, 157 (100) [C₁₂H₁₃]⁺, 142 (17) [C₁₁H₁₀]⁺, 115 (6) [C₉H₇]⁺. C₁₅H₁₈ (198.31 g mol⁻¹): Anal. Found: C, 90.71; H, 9.14. Calc.: C, 90.85; H, 9.15%.

5.2.3. 3-(3-Methyl-2-buten-1-yl)-2,4,7-trimethyl-1H-indene (3)

Analogous to the preparation of **1**, 2,4,7-trimethylindenyllithium [9] (4.60 g, 28 mmol) in THF (50 ml) reacted with 1-bromo-3-methyl-2-butene (5.0 g, 33.6 mmol) to yield **3** as a light yellow liquid (5.63 g, 89%). B.p.: 96–101°C/0.01 mbar. ¹H-NMR (CDCl₃, 200 MHz): δ = 6.97 (d, ³*J*(H,H) = 7.6 Hz, 1H, CH), 6.83 (d, ³*J*(H,H) = 7.6 Hz, 1H, CH), 6.58 (m, 1H, CH), 4.57 (m, 1H, CH), 3.42 (m, 1H, CH), 2.75 (m, 2H, CH₂), 2.41 (s, 3H, CH₃), 2.39 (s, 3H, CH₃), 2.08 (s, 3H, CH₃), 1.64 (s, 3H, CH₃), 1.58 (s, 3H, CH₃). ¹³C{¹H}-NMR (CDCl₃, 50.32 MHz): δ = 148.6 (C), 144.5 (C), 143.8 (C), 132.2 (C), 129.9 (C), 127.7 (CH), 126.2 (C), 125.6 (CH), 125.2 (CH), 119.8 (CH), 51.7 (CH), 26.3 (CH₂), 25.6 (CH₃), 18.7 (CH₃), 18.2 (CH₃), 18.0 (CH₃), 15.5 (CH₃). LRMS (90°C); *m/z* (%): 226 (57) [M]⁺, 157 (100) [C₁₂H₁₃]⁺, 142 (14) [C₁₁H₁₀]⁺. C₁₇H₂₂ (226.36 g mol⁻¹): Anal. Found: C, 90.10; H, 9.79. Calc.: C, 90.20; H 9.80%.

5.2.4. [1-Butyl-4,7-dimethylindenyl]lithium (1a)

To a solution of **1** (3.65 g, 18.22 mmol) in hexane (150 ml) which was cooled to 0°C a solution of *n*-BuLi (1.6 M in hexane, 12 ml, 19.19 mmol) was added slowly. The suspension was stirred for 12 h at 20°C and was then filtered. The remaining solid was washed with hexane (150 ml) and dried under reduced pressure to give **1a** as a white solid (3.33 g, 89%). M.p. (dec.): 182–185°C. ¹H-NMR (C₅D₅N, 200 MHz): δ = 7.20 (d, *J* = 3.3 Hz, 1H, CH), 6.72 (s, 2H, CH arom.), 6.66 (d, *J* = 3.3 Hz, 1H, CH), 3.50 (t, 2H, CH₂), 3.03 (s, 3H, CH₂), 2.75 (s, 3H, CH₃), 1.95 (m, 2H, CH₂), 1.61 (q, 2H, CH₂), 0.96 (t, 3H, CH₃). ¹³C{¹H}-NMR (C₅D₅N, 50.32 MHz): δ = 131.1 (C), 126.0 (C), 125.3 (C), 124.2 (C), 117.6 (CH), 113.8 (CH), 113.4 (CH), 112.3 (CH), 110.3 (C), 38.1 (CH₂), 31.3 (CH₂), 22.8 (CH₂), 22.5 (CH₃), 20.0 (CH₃), 14.2 (CH₃). LRMS (54°C); *m/z*: 206 (0) [M]⁺, 200 (31) [C₁₅H₂₀]⁺, 157 (100) [C₁₂H₁₃]⁺, 143 (42) [C₁₁H₁₁]⁺, 128 (30) [C₁₀H₉]⁺, 115 (23) [C₉H₇]⁺. C₁₅H₁₉Li (206.26 g mol⁻¹): Anal. Found: C, 87.22; H, 9.25. Calc.: C, 87.35; H, 9.28%.

5.2.5. [1-(2-Propene-1-yl)-2,4,7-trimethylindenyl]lithium (2a)

Similar to the preparation of **1a**, the indene **2** (4.87 g, 24.6 mmol) reacts with *n*-BuLi (1.6 M in hexane, 18.4 ml, 29.5 mmol) to give **2a** as a white solid (4.07 g, 81%). M.p. (dec.): 170–172°C. ¹H-NMR (C₅D₅N, 200 MHz): δ = 6.75 (s, 2H, CH), 6.57 (s, 1H, CH), 6.52 (m, 1H, CH), 5.30 (m, 1H, CH₂ trans), 5.08 (m, 1H, CH₂ cis), 4.27 (t, *J* = 1.6 Hz, 1H, CH₂), 4.24 (t, *J* = 1.6 Hz, 1H, CH₂), 3.11 (s, 3H, CH₃), 2.83 (s, 3H, CH₃), 2.82 (s, 3H, CH₃). ¹³C{¹H}-NMR (C₅D₅N, 50.32 MHz): δ = 144.2 (CH), 129.5 (C), 127.1 (C), 125.9 (C), 114.5 (CH), 112.5 (CH), 110.9 (CH₂), 103.8 (C), 92.7 (CH), 33.5 (CH₂), 22.5 (CH₃), 20.4 (CH₃), 15.5 (CH₃). LRMS (26°C); *m/z* (%): 204 (0) [M]⁺, 198 (41) [C₁₅H₁₈]⁺, 157 (100) [C₁₂H₁₃]⁺, 142 (15) [C₁₁H₁₀]⁺. C₁₅H₁₇Li (204.24 g mol⁻¹): Anal. Found: C, 87.86; H, 8.36. Calc.: C, 88.21; H, 8.39%.

5.2.6. [1-(3-Methyl-2-buten-1-yl)-2,4,7-trimethylindenyl]lithium (3a)

Similar to the preparation of **1a**, the indene **3** (5.63 g, 24.9 mmol) reacts with *n*-BuLi (1.6 M in hexane, 18.7 ml, 29.9 mmol) to give **3a** as a white solid (4.68 g, 81%). ¹H-NMR (C₅D₅N, 200 MHz): δ = 6.73 (s, 2H, CH), 6.51 (s, 1H, CH), 5.80 (m, 1H, CH), 4.19 (s, 1H, CH₂), 4.16 (s, 1H, CH₂), 3.09 (s, 3H, CH₃), 2.80 (s, 3H, CH₃), 2.79 (s, 3H, CH₃), 2.00 (s, 3H, CH₃), 1.77 (s, 3H, CH₃). ¹³C{¹H}-NMR (C₅D₅N, 50.32 MHz): δ = 131.9 (CH), 129.2 (C), 126.8 (C), 125.3 (C), 124.3 (C), 124.1 (C), 123.3 (C), 114.5 (CH), 112.5 (CH), 106.2 (C), 92.2 (CH), 27.6 (CH₂), 26.0 (CH₃), 22.5 (CH₃), 20.4 (CH₃),

18.1 (CH₃), 15.5 (CH₃). LRMS (42°C); *m/z* (%): 232 (0) [M]⁺, 226 (40) [C₁₇H₂₂]⁺, 157 (100) [C₁₂H₁₃]⁺, 142 (12) [C₁₁H₁₀]⁺. C₁₇H₂₁Li (232.29 g mol⁻¹): Anal. Found: C, 87.64; H, 9.09. Calc.: C, 87.90; H, 9.11%.

5.3. Bis[1-alkylindenyl]- and bis[1-alkenylindenyl]zirconium complexes

5.3.1. Bis[1-butylindenyl]zirconium dichloride (**1b**)

In a darkened flask, the lithium salt **1a** (0.70 g, 3.39 mmol) [2] and zirconium tetrachloride (0.79 g, 3.39 mmol) were dissolved in Et₂O (60 ml) and the mixture was stirred for 48 h at room temperature (r.t.). The mixture was filtered to separate precipitated LiCl and from the filtrate the solvent was removed under reduced pressure (10⁻² mbar). The solid residue was washed several times with hexane (50 ml) and then dried in vacuo to yield **1b** as a yellow solid which was crystallized from hexane at 0°C (0.62 g, 65%). M.p. (dec.): 215–218°C. ¹H-NMR (C₅D₅N, 200 MHz): δ = 6.91 (m, 8H, CH arom.), 6.60 (d, *J* = 3.2 Hz, 4H, CH), 6.03 (d, *J* = 3.2 Hz, 4H, CH), 3.39–3.03 (m, 8H, CH₂), 2.70 (s, 12H, CH₃), 2.31 (s, 12H, CH₃), 1.62–1.30 (m, 16H, CH₂), 0.86 (m, 12H, CH₃). ¹³C{¹H}-NMR (C₅D₅N, 50.32 MHz): δ = 133.4 (C), 132.6 (C), 131.8 (C), 127.2 (C), 126.7 (CH arom.), 126.0 (CH arom.), 124.3 (C), 118.3 (CH), 97.4 (CH), 33.3 (CH₂), 30.6 (CH₂), 22.5 (CH₂), 20.5 (CH₃), 18.4 (CH₃), 13.8 (CH₃). LRMS (144°C); *m/z*: 558 (14) [M(⁹⁰Zr, ³⁵Cl)]⁺, 359 (95) [C₁₅H₁₉ZrCl₂]⁺, 323 (28) [C₁₅H₁₈ZrCl]⁺, 281 (22) [C₁₂H₁₂ZrCl]⁺. C₃₀H₃₈ZrCl₂ (560.76 g mol⁻¹): Anal. Found: C, 64.20, H, 6.80. Calc.: C, 64.26, H, 6.83%.

5.3.2. Bis[1-(2-propene-1-yl)-2,4,7-trimethylindenyl]zirconium dichloride (**2b**)

Analogous to the preparation of **1b**, the lithium salt **2a** (0.77 g, 3.8 mmol) reacted with zirconium tetrachloride (0.44 g, 1.9 mmol) to give **2b** as a yellow solid (0.5 g, 50%). Yellow crystals of **2b** were obtained from hexane at 0°C. M.p. (dec.): 118°C. ¹H-NMR (C₅D₅N, 200 MHz): δ = 6.86 (d, *J* = 0.9 Hz, 4H, CH), 6.83 (d, *J* = 0.9 Hz, 4H, CH), 6.28 (s, 4H, CH), 5.95 (m, 4H, =CH), 5.02–6.64 (m, 8H, CH=CH₂), 4.10–3.49 (m, 8H, CH₂), 2.60 (s, 12H, CH₃), 2.30 (s, 24H, CH₃). ¹³C{¹H}-NMR (C₅D₅N, 50.32 MHz): δ = 136.97 (CH=), 133.0 (C), 131.0 (C), 130.81 (C), 127.8 (C), 127.5 (C), 126.9 (CH arom.), 125.4 (CH arom.), 121.9 (C), 114.7 (=CH₂), 98.3 (CH), 32.0 (CH₂), 20.3 (CH₃), 18.7 (CH₃), 14.7 (CH₃). LRMS (159°C); *m/z*: 554 (12) [M(⁹⁰Zr, ³⁵Cl)]⁺, 357 (100) [C₁₅H₁₇ZrCl₂]⁺, 321 (24) [C₁₅H₁₆ZrCl]⁺, 294 (17) [C₁₃H₁₃ZrCl]⁺, 198 (28) [C₁₅H₁₈]⁺, 157 (78) [C₁₂H₁₃]⁺. C₃₀H₃₄ZrCl₂ (556.73 g mol⁻¹): Anal. Found: C, 64.65; H, 6.14. Calc.: C, 64.72; H, 6.16%.

5.3.3. Bis[1-(3-methyl-2-butene-1-yl)-2,4,7-trimethylindenyl]zirconium dichloride (**3b**)

Analogous to the preparation of **1b**, the lithium salt **3a** (0.79 g, 3.4 mmol) reacted with zirconium tetrachloride (0.40 g, 1.7 mmol) yielding **3b** as a yellow solid (0.57 g, 55%). Yellow crystals were obtained from hexane at 0°C. M.p. (dec.): 120°C. ¹H-NMR (C₅D₅N, 200 MHz): δ = 6.87 (m, 8H, CH arom.), 6.59 (s, 4H, CH), 5.08 (m, 4H, =CH), 3.65–3.52 (m, 8H, CH₂), 2.71 (s, 12H, CH₃), 2.64 (s, 12H, CH₃), 1.85 (s, 12H, CH₃), 1.63 (s, 12H, CH₃), 1.59 (s, 12H, CH₃). ¹³C{¹H}-NMR (C₅D₅N, 50.32 MHz): δ = 135.5 (C), 134.6 (C), 131.8 (C), 131.5 (C), 131.3 (C), 129.8/129.7 (C), 126.8 (CH), 125.4 (CH), 123.6 (CH), 95.8 (CH), 27.7 (CH₂), 25.1 (CH₃), 20.8 (CH₃), 19.2 (CH₃), 17.7 (CH₃), 13.7 (CH₃). LRMS (165°C); *m/z*: 612 (12) [M(⁹⁰Zr, ³⁵Cl)]⁺, 385 (100) [C₁₇H₂₁ZrCl₂]⁺, 349 (18) [C₁₇H₂₀ZrCl]⁺, 331 (9) [C₁₃H₁₅ZrCl₂]⁺, 226 (28) [C₁₇H₂₁]⁺, 157 (78) [C₁₂H₁₃]⁺. C₃₄H₄₂ZrCl₂ (612.84 g mol⁻¹): Anal. Found: C, 66.53, H, 6.89. Calc.: C, 66.64, H, 6.91%.

5.3.4. Bis[1-(4-pentene-1-yl)indenyl]zirconium dichloride (**4b**)

Analogous to the preparation of **1b**, [1-(4-pentene-1-yl)indenyl]lithium (**4a**) [2] (0.70 g, 3.6 mmol) reacted with zirconium tetrachloride (0.43 g, 1.8 mmol) yielding **4b** as a yellow solid (0.56 g, 58%). Crystals of **4b** were obtained from hexane at 0°C. M.p. (dec.): 89–93°C. ¹H-NMR (C₅D₅N, 200 MHz): δ = 7.70–7.20 (m, 8H, CH arom.), 6.69 (d, *J* = 3.2 Hz, 2H, =CH), 6.32 (d, *J* = 3.2 Hz, 2H, =CH), 6.30 (d, *J* = 3.2 Hz, 2H, =CH), 6.04 (d, *J* = 3.2 Hz, 2H, =CH), 5.82 (m, 4H, CH=CH₂), 5.00 (m, 8H, =CH₂), 3.1–2.8 (m, 8H, CH₂CH₂), 2.06 (m, 8H, CH₂CH₂), 1.72 (m, 8H, CH₂CH₂). ¹³C{¹H}-NMR (C₅D₅N, 50.32 MHz): δ = 145.5 (C), 144.3 (C), 144.1 (C), 138.2/138.2 (CH=CH₂), 128.0–118.0 (CH), 114.8/114.7 (=CH₂), 99.3/99.3 (CH), 33.4/33.4 (CH₂CH₂), 29.7/29.3 (CH₂CH₂), 27.7/27.3 (CH₂CH₂). LRMS (151°C); *m/z*: 526 (10) [M(⁹⁰Zr, ³⁵Cl)]⁺, 343 (100) [C₁₄H₁₅ZrCl₂]⁺, 307 (18) [C₁₄H₁₄ZrCl]⁺, 184 (12) [C₁₄H₁₆]⁺, 128 (28) [C₁₀H₈]⁺, 115 (22) [C₉H₇]⁺. C₂₈H₃₀ZrCl₂ (528.67 g mol⁻¹): Anal. Found: C, 63.30, H, 5.70. Calc.: C, 63.61, H, 5.72%.

5.4. [2-Alkenylindenyl][cyclopentadienyl]zirconium complexes

5.4.1. [2-(3-Butene-1-yl)-4,7-dimethylindenyl][cyclopentadienyl]zirconium dichloride (**5c**)

To a stirred solution of CpZrCl₃(DME) [6] (0.71 g, 2.0 mmol) in THF (50 ml) was added [2-(3-butene-1-yl)-4,7-dimethylindenyl]lithium [2] (0.53 g, 2.0 mmol). The reaction mixture was stirred for 24 h at r.t. The suspension was filtered and the filtrate evaporated to dryness. The remaining yellow solid was washed with hexane (50 ml) and dried under reduced pressure leaving yellow

crystals of **5c** (0.56 g, 66%). M.p.: 83–85°C. ¹H-NMR (C₅D₅N, 200 MHz): δ = 6.92 (s, 2H, CH aromat.), 6.66 (s, 2H, CH), 6.29 (s, 5H, Cp), 5.92 (m, 1H, CH=), 5.05 (m, 2H, =CH₂), 2.94 (m, 2H, CH₂CH₂), 2.51 (s, 6H, CH₃ aromat.), 2.39 (m, 2H, CH₂CH₂). ¹³C{¹H}-NMR (C₅D₅N, 100.64 MHz): δ = 139.56 (C), 138.02 (CH=CH₂), 131.84 (C), 127.45 (C), 125.29 (CH), 116.48 (CH), 114.93 (=CH₂), 103.97 (CH), 33.45 (CH₂CH₂), 31.35 (CH₂CH₂), 18.86 (CH₃ aromat.). LRMS (116°C); *m/z*: 422 (69) [M(⁹⁰Zr, ³⁵Cl)]⁺, 386 (22) [C₂₀H₂₁ZrCl]⁺, 357 (100) [C₁₅H₁₇ZrCl₂]⁺, 225 (32) [C₅H₅ZrCl₂]⁺, 197 (60) [C₁₅H₁₇]⁺. C₂₀H₂₂ZrCl₂ (424.52 g mol⁻¹): Anal. Found: C, 56.52; H, 5.19. Calc.: C, 56.59; H, 5.22%.

5.4.2. [2-(4-Pentene-1-yl)-4,7-dimethylindenyl]-[cyclopentadienyl]zirconium dichloride (**6c**)

Analogous to the preparation of **5c**, CpZrCl₃(DME) [6] (0.79 g, 2.24 mmol) was treated with [2-(4-penten-1-yl)-4,7-dimethylindenyl]lithium [2] (0.49 g, 2.24 mmol) yielding **6c** which was isolated from hexane (30 ml) at 0°C as a yellow crystalline solid (0.61 g, 62%). M.p.: 95–96°C. ¹H-NMR (C₅D₅N, 200 MHz): δ = 6.92 (s, 2H, CH aromat.), 6.64 (s, 2H, CH), 6.25 (s, 5H, Cp), 5.84 (m, 1H, CH=), 5.03 (m, 2H, =CH₂), 2.84 (m, 2H, CH₂CH₂), 2.52 (s, 6H, CH₃ aromat.), 2.10 (m, 2H, CH₂CH₂), 1.71 (m, 2H, CH₂CH₂). ¹³C{¹H}-NMR (C₅D₅N, 100.64 MHz): δ = 140.30 (C), 138.18 (CH=CH₂), 131.96 (C), 127.55 (C), 125.32 (CH), 116.50 (CH), 114.91 (=CH₂), 103.93 (CH), 33.36 (CH₂CH₂), 31.19 (CH₂CH₂), 30.11 (CH₂CH₂), 18.89 (CH₃ aromat.). LRMS (126°C); *m/z*: 436 (97) [M(⁹⁰Zr, ³⁵Cl)]⁺, 381 (60) [C₁₇H₁₇ZrCl₂]⁺, 371 (82) [C₁₆H₁₉ZrCl₂]⁺, 225 (12) [C₅H₅ZrCl₂]⁺, 211 (40) [C₁₆H₁₉]⁺. C₂₁H₂₄ZrCl₂ (438.55 g mol⁻¹): Anal. Found: C, 57.45; H, 5.50. Calc.: C, 57.51; H, 5.52%.

5.5. X-ray crystallographic analysis of **3b**

Suitable crystals of **3b** were obtained from hexane at 0°C. For the crystallographic measurements a Siemens SMART CCD diffractometer equipped with a low-temperature device was used. The crystal data, data collections and refinement parameters are listed in Table 1. Intensity data were collected over a hemisphere of reciprocal space by a combination of three sets of exposures. Each set had a different 2θ angle and each exposure covered 0.3° scan in ω–2θ. Lattice parameters were derived from the setting angles of 8192 reflections [10]. Structure solution was performed by direct methods and subsequent difference Fourier synthesis (SHELXTL) [11]. Full-matrix least-squares refinement was performed on *F*². Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included by using a riding model with *d*(C–H) = 0.96 Å, *U*_{iso} = 0.08 Å². After all atoms had

been added to the model of the structure an empirical absorption correction SADABS [12] was applied: effective transmission, max, 0.9548; min, 0.5628. Geometrical calculations were performed with PLATON [13]. The ORTEP [8] illustration depicts thermal ellipsoids which are scaled to 30% probability level.

5.6. Polymerization reactions

Ethylene and propylene, purchased from Linde or Gerling, Holz & Co., respectively, were purified by passage through columns containing Cu catalysts (BASF R3-11) and through molecular sieves (10 Å). MAO was purchased from Witco. Toluene was refluxed over Na/K for several days prior to use. Polymerizations were carried out in a 1 l Büchi AG type I autoclave equipped with an additional internal cooling system and the reactions were monitored by a Büchi data system bds 488. Homopolymerizations were carried out according to the standard experiment described in Ref. [2]. For the standard copolymerization experiment, the reactor was heated to 95°C and evacuated for 1 h, then cooled down to the polymerization temperature of 30°C and charged subsequently with 500 ml of toluene and 1000 mg of MAO. Then ethene and propene were added, so that the total monomer concentration was 1 mol l⁻¹. Polymerization was started by injection of the toluenic metallocene solution. During the reaction the total pressure was kept constant by supplying ethene. The polymerization was quenched by addition of ethanol (5 ml). The polymer solution was stirred overnight with dilute hydrochloric acid followed by neutralization with NaHCO₃, washing with water, evaporation of toluene and drying for 48 h at 40°C in vacuo.

5.7. Polymer analyses

The tacticity as well as the incorporation rates were determined by ¹³C-NMR-spectroscopy at 100°C on a Bruker MSL 300 spectrometer at 75 MHz using samples prepared by dissolving the polymer (10 mass%) in a mixture of perchlorobutadiene (PCB) and 1,1,2,2-tetrachloro-1,2-dideuteroethane (TCE-*d*₂). The molar masses *M_n* were determined at 135°C with an Ubbelohde viscosimeter (capillary 0a, *K* = 0.005) using samples prepared by dissolving 50 mg of polymer in 50 ml of decahydronaphthalene (stabilized with 1 g l⁻¹ of 2,6-di-*t*-Bu-4-methylphenol). Since the Mark–Houwink constants for the EPMS are unknown, the molar masses are calculated using the values for PE, which were taken from the literature [9]. Molar mass distributions were determined by gel permeation chromatography on a Waters high temperature 150-C-ALC/GPC instrument (1,2,4-trichlorobenzene, 135°C) using a PL-EMD-960 evaporation light scattering detector. Differential scan-

ning calorimetry was performed on a Mettler-Toledo DSC 821e with samples (10 mg) which were heated to 200°C, then cooled to –100°C and again heated to 200°C with cooling–heating rates of 20°C min⁻¹. The values of each second run are reported. The temperature dependent WAXS-measurements were carried out at an A2 HASYLAB in the Deutsches Elektronen Synchrotron (DESY). The temperature profiles correspond to those of the DSC measurements considering that 30°C is the minimum temperature.

6. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 141696 for compound **3b**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Acknowledgements

This work was supported financially by the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft and the Bayer AG.

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