Synthesis and characterization of unbridged metallocene dichloride complexes with two differently mono-substituted indenyl ligands and their application as catalysts for the polymerization of ethene and propene

Roland Schmidt, Matthias Deppner, Helmut G. Alt*

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

Abstract

The synthesis of unbridged metallocene dichloride complexes of the type $Ind^{\#}Ind'ZrCl_2$ ($Ind^{\#}$ = 2-arylalkyl-substituted indenyl, Ind' = 1-ω-alkenyl-substituted or 2-alkyl-substituted indenyl) is described. The complexes are characterized by ^1H and ^{13}C NMR spectroscopy and mass spectrometry and tested for the catalytic polymerization of ethene and propene. The polymerization results and the polymer properties indicate a considerable influence of the catalyst structure on the polymerization behavior. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Unbridged metallocene complexes; Catalysis; Olefin polymerization; Polymer properties

1. Introduction

Metallocene complexes with group 4 metals offer a great potential to produce polyolefins with new properties ([1–14], and references therein). In combination with cocatalysts like methylalumoxane (MAO) [15–18] many of them can be applied as excellent polymerization catalysts with high productivities.

Since the discovery that symmetrically substituted indenyl complexes of zirconium [19–35] are able to produce polypropenes with elastomeric properties, there is still room [36] to develop this class of metallocene complexes to a further extent.

In this work, new unbridged zirconocene complexes are presented containing two differently mono-substituted indenyl ligands. They are either substituted with an ω-alkenyl substituent in position 1, a butyl substituent in position 1 or an alkyl substituent in position 2. The second indenyl ligand is substituted in position 2 with an arylalkyl group. These complexes were activated with MAO and used for the catalytic polymerization of ethene and propene.

2. Results and discussion

2.1. Synthesis of indene derivatives with an arylalkyl or alkyl substituent in position 2

The preparation of indene derivatives with an arylalkyl or alkyl substituent in position 2 proceeds from

---

* Corresponding author. Tel.: +49-921552555;
fax: +49-921552157.
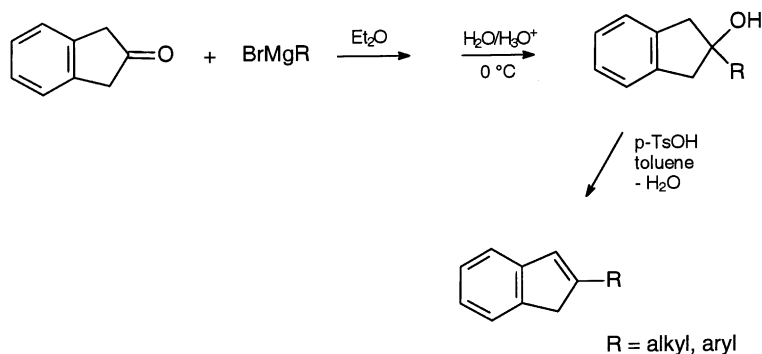*E-mail address:* helmut.alt@uni-bayreuth.de (H.G. Alt).

Fig. 1. Synthesis of indene derivatives with a substituent in position 2.

a Grignard reagent of a suitable arylalkyl bromide or an alkyl bromide and 2-indanone [37] according to the following reaction scheme (Fig. 1).

2.2. Synthesis of indene derivatives with an ω-alkenyl substitutent in position 1

Indene is reacted with one equivalent of n-butyllithium to form the corresponding lithium salt [38,39]. Then a suitable ω-alkenyl bromide [40] is added according to the following reaction scheme (Fig. 2).

2.3. Synthesis of substituted indenylzirconiumtrichloride complexes

The preparation of mixed metallocene dichloride complexes with two different indenyl ligands via reacting one equivalent of zirconiumtetrachloride with one equivalent of the corresponding alkali indenyl is not possible. Only the bis-complexes and unreacted $ZrCl_4$ are formed. In order to obtain the desired complexes, new methods were applied [41] consisting in the preparation of the corresponding half-sandwich complex as the first step (Fig. 3).
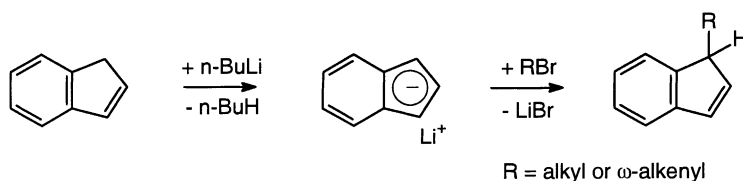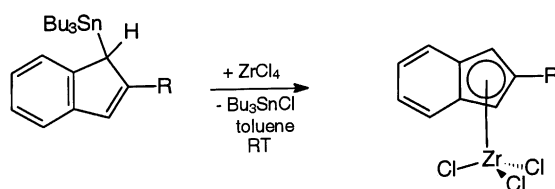

Fig. 3. Synthesis of substituted indenylzirconiumtrichloride complexes.

2.4. Synthesis of the metallocene dichloride complexes 1–25

The metallocene dichloride complexes 1–25 can be prepared from the reaction of a substituted indenylzirconiumtrichloride complex and the lithium salt of the desired ω-alkenyl-substituted indene (Fig. 4). The prepared complexes are listed in Fig. 5.

2.5. Polymerization results

2.5.1. Polymerization of ethene

The synthesized metallocene complexes 1–25 were activated with an excess of MAO (Al:Zr = 3.000:1).

Fig. 2. Preparation of indene derivatives with a substitutent in position 1.

R^1 = alkyl, ω-alkenyl, H
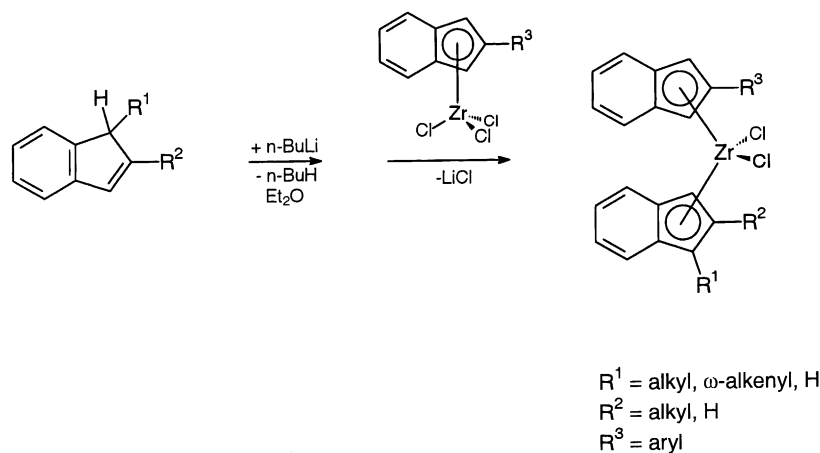R^2 = alkyl, H
R^3 = aryl

Fig. 4. Synthesis of unsymmetric unbridged bis(indenyl) complexes of zirconium.

Ethene was applied into the reactor with a pressure of 10 bar. The slurry polymerization in 500 ml *n*-pentane was carried out at 60°C. The polymerization results are shown in Table 1.

Complexes **1–16** differ in the number *k* of spacer methylene groups between the indenyl and the phenyl substituent. The other indenyl ligand is substituted with an ω-alkenyl group with different numbers of carbon atoms *n*. The productivities range from 40.000 to 250.000 g(PE)/g(Zr) h^{-1} (see Table 1). This is considerably less than the activity of the unsubstituted bis(indenyl) complex (Ind)$_2$ZrCl$_2$ (3.200.000 g(PE)/

1 (n = 1, k = 0)	**9** (n = 1, k = 2)
2 (n = 2, k = 0)	**10** (n = 2, k = 2)
3 (n = 3, k = 0)	**11** (n = 3, k = 2)
4 (n = 4, k = 0)	**12** (n = 4, k = 2)
5 (n = 1, k = 1)	**13** (n = 1, k = 3)
6 (n = 2, k = 1)	**14** (n = 2, k = 3)
7 (n = 3, k = 1)	**15** (n = 3, k = 3)
8 (n = 4, k = 1)	**16** (n = 4, k = 3)

1-16

17 (n = 2, k = 1)
18 (n = 3, k = 1)
19 (n = 4, k = 1)
20 (n = 5, k = 1)
21 (n = 2, k = 2)
22 (n = 3, k = 2)
23 (n = 4, k = 2)
24 (n = 5, k = 2)

17 - 24

25
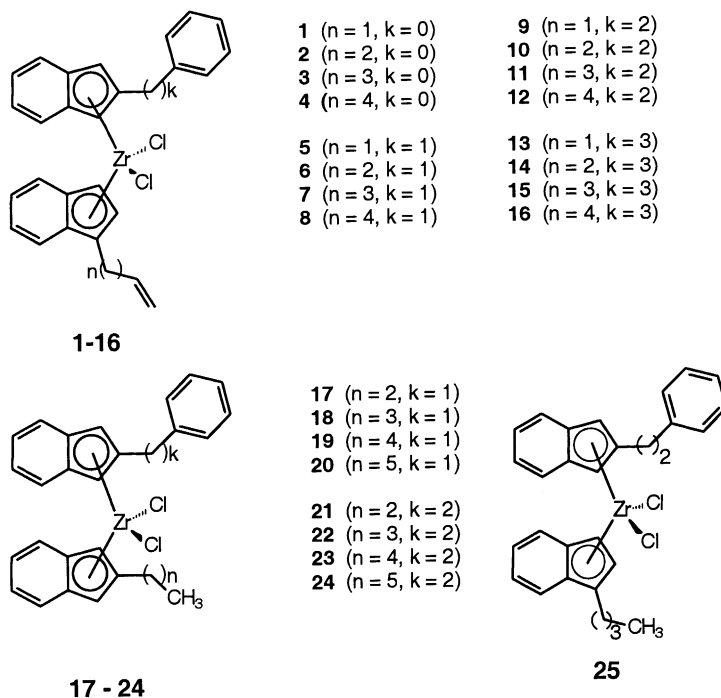
Fig. 5. Synthesized mixed unbridged complexes **1–25**.

Table 1
Polymerization results of homogeneous ethene polymerization with complexes **1–25**/MAO [a]
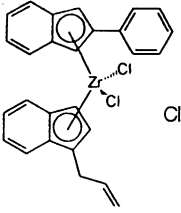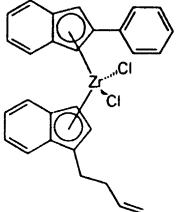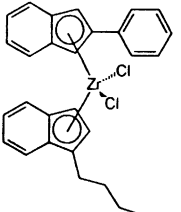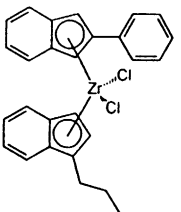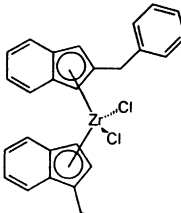
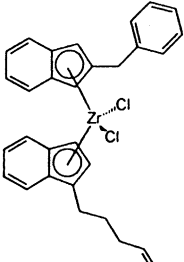| Catalyst precursor	Productivity (g(PE)/g(Zr) h^{-1})	$\bar{M}_n$ (g/mol)	Polydispersity [$\bar{M}_w/\bar{M}_n$]
1	118.200	223.700	4.76
2	70.000	172.000	5.14
3	193.100	279.900	3.73
4	59.400	249.200	3.27
5	40.000	45.400	10.12

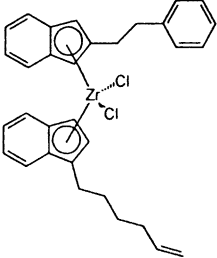Table 1 (*Continued*)
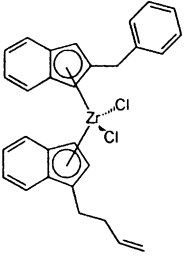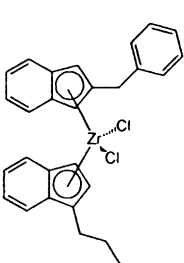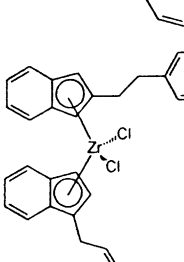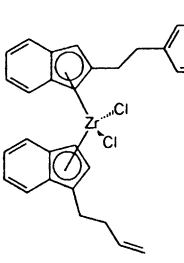
Catalyst precursor	Productivity (g(PE)/g(Zr) h^{-1})	$\bar{M}_n$ (g/mol)	Polydispersity [$\bar{M}_w/\bar{M}_n$]
6	151.000	246.200	4.55
7	198.300	144.500	5.78
8	191.000	119.100	7.41
9	123.900	179.900	5.83
10	200.800	256.900	4.22

Table 1 (*Continued*)
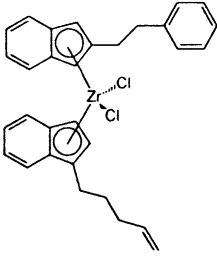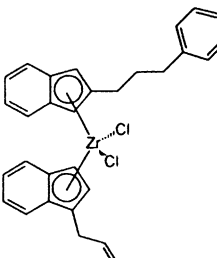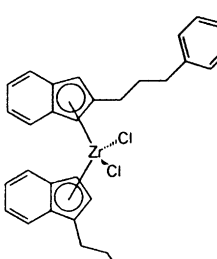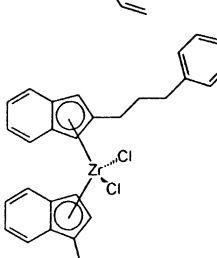
Catalyst precursor	Productivity (g(PE)/g(Zr) h^{-1})	$\bar{M}_n$ (g/mol)	Polydispersity [$\bar{M}_w/\bar{M}_n$]
11	249.400	124.000	8.64
12	151.000	239.500	4.13
13	150.600	121.300	9.23
14	112.000	150.300	6.80
15	156.300	319.300	3.94

Table 1 (*Continued*)

Catalyst precursor	Productivity (g(PE)/g(Zr) h^{-1})	$\bar{M}_n$ (g/mol)	Polydispersity [$\bar{M}_w/\bar{M}_n$]
16	180.100	124.500	9.12
17	40.200	141.100	3.70
18	89.600	47.800	19.86
19	136.800	339.800	4.98
20	85.400	41.300	23.33
21	115.900	200.000	6.01

Table 1 (*Continued*)

Catalyst precursor	Productivity (g(PE)/g(Zr) h^{-1})	$\bar{M}_n$ (g/mol)	Polydispersity [$\bar{M}_w/\bar{M}_n$]
22	115.400	223.000	5.27
23	75.800	44.800	2.76
24	105.400	175.300	5.50
25	176.000	112.300	5.94

^a Polymerization parameters: polymerization in *n*-pentane; at 60°C; 60 min; Al:Zr ratio = 3.000:1.

[a] Polymerization parameters: polymerization in *n*-pentane; at 60°C; 60 min; Al:Zr ratio = 3.000:1.

g(Zr) h^{-1}) [42]. One reason for this behavior could be the negative steric effect of indenyl substituents on the growth of the polymer chain during the polymerization process.

Independent from the number k of CH$_2$-spacer groups (Fig. 4), the highest productivities (200.000–250.000 g(PE)/g(Zr) h^{-1}) were found for complexes with an ω-pentenyl group (**3**: $k = 0$; **7**: $k = 1$; **11**: $k = 2$; **15**: $k = 3$).

The influence of structural ligand parameters on the productivity becomes obvious in complexes **10**, **25** and **22** (Fig. 6) when the change from an ω-alkenyl group in position 1 of the indenyl ligand to an alkyl group of the same number of carbon atoms triggers a loss in productivity. An additional change of this substituent from position 1 to position 2 of the indenyl ligand causes a further loss of activity.

The molecular weights (Table 1) of the produced polyethylenes do not indicate a uniform trend. In most cases, they are slightly lower than the molecular weight of the polyethylene obtained with (Ind)$_2$ZrCl$_2$/MAO under identical reaction conditions $\bar{M}_n$ = 470.000 g/mol. It is surprising that the molecular mass number averages ($\bar{M}_n$) of polyethenes produced with complexes **18** and **20** (even number of carbon atoms in the alkyl group) are reduced drastically in comparison to complexes **17** and **19** with an odd number of carbon atoms (Fig. 7). The polydispersities
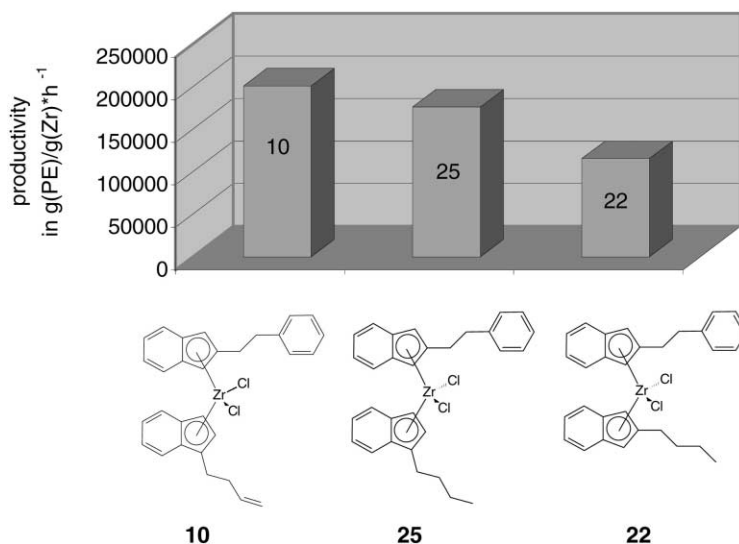
Fig. 6. Influence of different substitution patterns at the indenyl ligand on polyethene productivity.

ranges from 3.7 to 10. Normally, single site metallocene catalysts produce lower polydispersities (≈ 2). We explain our results with the formation of multi-site catalysts that are generated by the rotation of the substituted π-ligands.

2.5.2. Polymerization of propene

The polymerization of propene was conducted as a bulk polymerization in 500 ml liquid propene at 0°C (all data in Table 2).

Complexes **17**–**24** of the type Ind#Ind′ZrCl$_2$ (Ind# = 2-arylalkyl-substituted indenyl, Ind′ = 2-alkyl-substituted indenyl) show productivities up to 64.000 g(PP)/g(Zr) h^{-1}. Complex **22** exceeds the productivity of bis(2-phenylindenyl)zirconiumdichloride, the classical complex of Coates and Waymouth [19] by a factor of 3.5 (Fig. 8).

A reduction of the productivity can be observed when the alkyl substituent changes its position from 2 to 1 at the indenyl ligand (**25**). The substitution of this alkyl group with an ω-alkenyl group (complex **10**) reduces the productivity by 90% (Fig. 9).

The molecular weights $\bar{M}_n$ of the polypropenes produced with complexes **17**–**24** ranges from 60.000 to 95.000 g/mol. An exception are the data of those polypropenes produced with complexes **19** and **20** which show a much higher $\bar{M}_n$ (275.000 and 189.000 g/mol). Obviously, the longer alkyl chains (five or six carbon atoms per chain) are responsible for this effect because they block the β–H-elimination
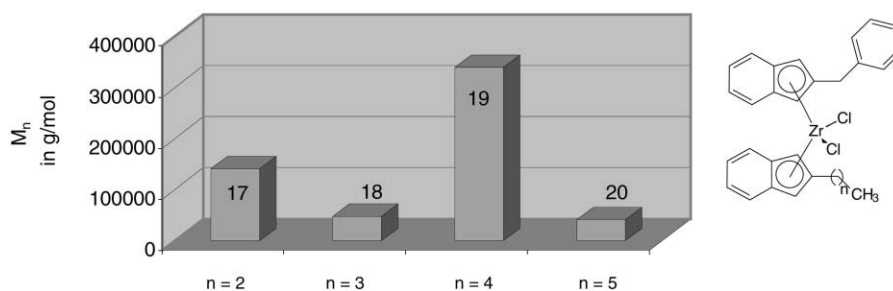

Fig. 7. Change of the $\bar{M}_n$ of polyethenes produced with complexes **17**–**20**.

Table 2
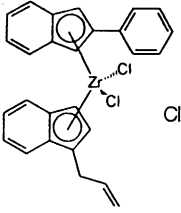Polymerization results of propene polymerization[a]
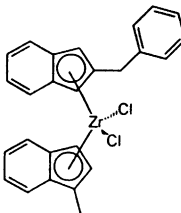
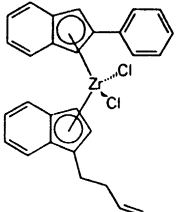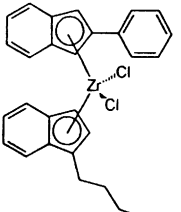| Catalyst precursor	Productivity (g(PP)/g(Zr) h^{-1})	$\bar{M}_n$ (g/mol)	Polydispersity [$\bar{M}_w / \bar{M}_n$]
1	1.600	83.200	27.38
2	1.400	72.600	34.16 (bimodal)
3	2.500	105.100	2.67
4	3.100	90.700	3.1
5	2.900	81.200	8.2

Table 2 (*Continued*)

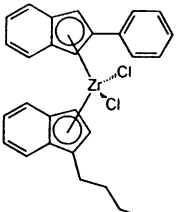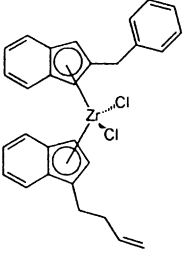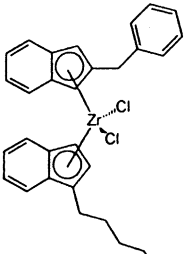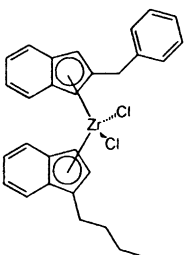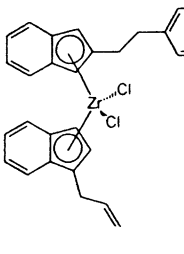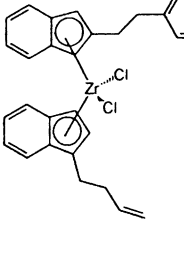| Catalyst precursor	Productivity (g(PP)/g(Zr) h^{-1})	$\bar{M}_n$ (g/mol)	Polydispersity [$\bar{M}_w/\bar{M}_n$]
6	5.000	71.200	2.49
7	8.000	142.500	4.61
8	6.400	61.800	2.24
9	4.800	88.500	5.4
10	1.200	59.500	8.98 (bimodal)

Table 2 (*Continued*)
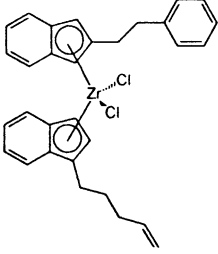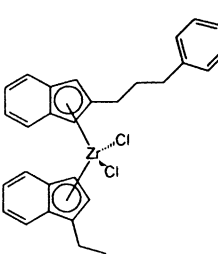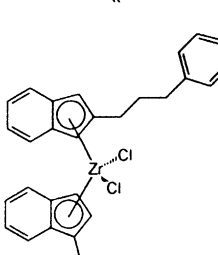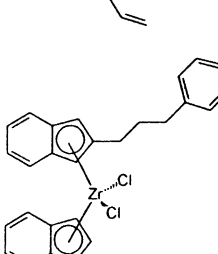
Catalyst precursor	Productivity (g(PP)/g(Zr) h^{-1})	$\bar{M}_n$ (g/mol)	Polydispersity [$\bar{M}_w/\bar{M}_n$]
11	3.000	96.800	3.47
12	3.100	73.500	4.66
13	3.400	194.000	4.99
14	2.400	20.900	10.91
15	4.900	51.800	9.83 (bimodal)

Table 2 (*Continued*)
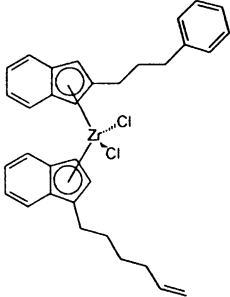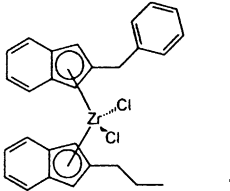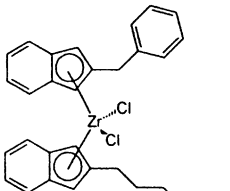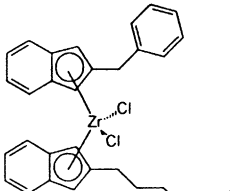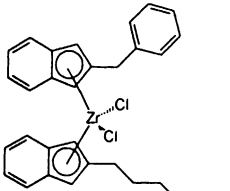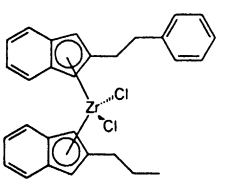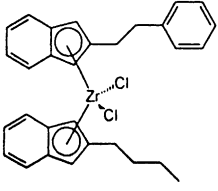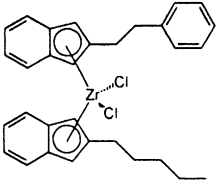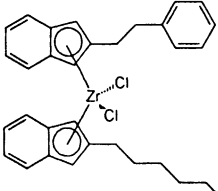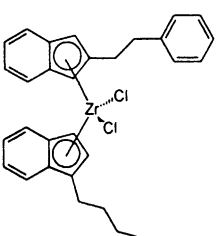
Catalyst precursor	Productivity (g(PP)/g(Zr) h^{-1})	$\bar{M}_n$ (g/mol)	Polydispersity [$\bar{M}_w/\bar{M}_n$]
16	3.700	121.500	3.87 (bimodal)
17	18.800	93.300	6.04
18	41.100	60.000	6.17
19	36.400	276.800	2.66
20	31.600	163.600	3.59
21	62.800	6.400	142.5 (bimodal)

Table 2 (*Continued*)

Catalyst precursor	Productivity (g(PP)/g(Zr) h^{-1})	$\bar{M}_n$ (g/mol)	Polydispersity [$\bar{M}_w/\bar{M}_n$]
22	64.000	57.200	9.55
23	60.100	46.600	81.62 (bimodal)
24	57.400	84.700	12.92
25	13.000	96.700	5.56

[a] Polymerization parameters: bulk polymerization in 500 ml liquid propene at 0°C; Al:Zr ratio = 3.000:1.

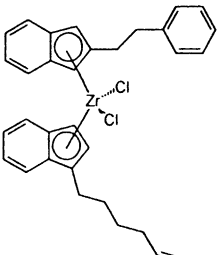process as terminating step during the polymerization. Polydispersities are between 2.6 and 13. Some polypropenes show a bimodal polymer weight distribution (**21** and **23**) (see Fig. 10) and much higher polydispersities. The explanation for this effect could be a change of the nature of the active sites in the polymerization process as a consequence of intramolecular ligand rotation.

This behavior is only observed at polypropenes that were produced with a catalyst with a –C$_2$H$_4$-spacer group between the indenyl and the phenyl ring and additionally an alkyl side chain with an odd number of carbon atoms at the second indenyl ligand. The change

from position 2 to 1 of the alkyl group (**25**) has no influence on the polymer properties (Table 3).

The produced polypropenes are supposed to consist of atactic and isotactic blocks [19]. The tacticities were measured. The pentad distribution was determined with established methods [45–48]. The average isotacticity of all polypropenes is about 15 % as confirmed by ^{13}C NMR spectroscopy (see Fig. 11).

However, it is not clear at this point whether the polypropenes produced by the asymmetric catalysts consist of only one sort of alternating isotactic or atactic blocks or not. According to Fig. 12, there should exist two different rac isomers to produce two different
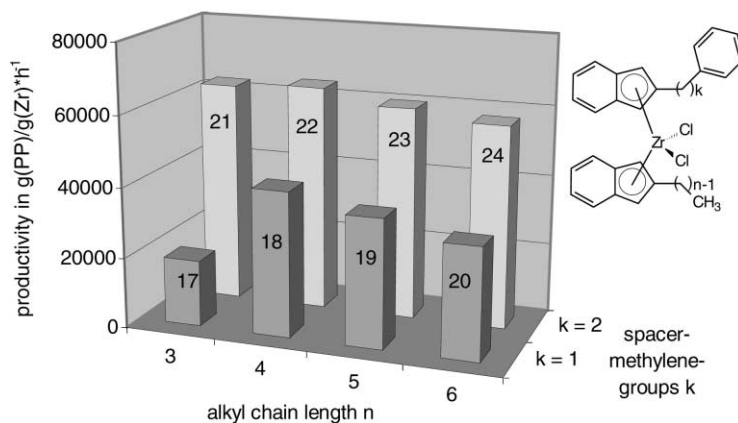
Fig. 8. Polypropene productivity dependence on the molecular structure of the metallocene complex.

isotactic polypropene blocks and two different meso isomers to produce two different atactic polypropene blocks.

Different from ansa-metallocene complexes with ω-alkenyl substituents the unbridged metallocene complexes **1–16** do not undergo self-immobilization [43,44]. The rotation of the aromatic ligand around the indenyl-metal-bond axis could be so fast that the olefin function of the substituent hardly has no chance to copolymerize.

3. Experimental

All preparations were performed under inert gas atmosphere using standard Schlenk technique in order to avoid air and moisture. As inert gas purified and dried argon was used (BTS catalyst, molecular sieves). All solvents were purchased in technical grade and purified by distillation over Na/K alloy. All other chemicals were commercially available or were synthesized according to literature procedures.
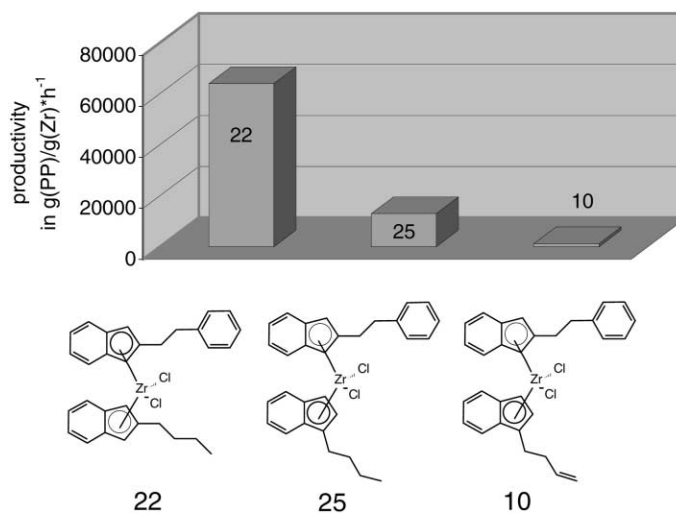
Fig. 9. Influence of structural parameters of the complexes on polypropene productivities.

W(log M)

Molar mass
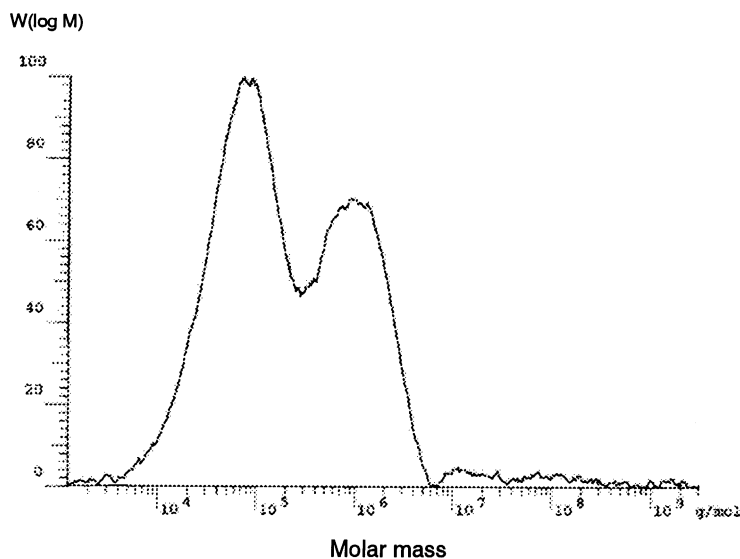
Fig. 10. HT-GPC of the polypropenes produced with complex **23**. Bulk polymerization (500 ml propene) at 0°C; Al:Zr = 3.000:1.

NMR spectra were recorded in CDCl$_3$ at 25°C on a Bruker ARX 250 instrument. The chemical shifts in the ^{1}H NMR spectra were referenced to the residual proton signal of the solvent ($\delta = 7.24$ ppm for CHCl$_3$); the carbon resonances in ^{13}C NMR spectra were also referenced to the solvent signal ($\delta = 77.0$ ppm for CDCl$_3$).

Mass spectra were recorded on a Varian MAT CH7 instrument (direct inlet system, electron impact ionization 70 eV).

Polymerizations were conducted in a 1 l Büchi steel reactor equipped with a mechanical stirrer. Ethene was polymerized at 60°C and 10 bar ethene pressure for 1 h in *n*-pentane. Propene was polymerized in bulk at 0°C. MAO was used as a 30% solution in toluene from Witco, Germany. The Al:Zr ratio was 3000:1. The polymerization reactions were stopped by venting excess ethene and propene. The obtained polymer was washed with HCl/methanol and dried in vacuo.

Polymer data were recorded on a Waters HT-GPC 150C instrument. For the separation four successively connected polystyrene columns were used. The pore diameters of the single columns were 500, 1.000, 10.000 and 100.000 Å. For the refractometric detection, a refractometer RI Waters 401 was used with degassed 1,2,4-trichlorobenzene (flow rate of 1 ml/min) as a solvent. Polymer samples were dissolved in

boiling 1,2,4-trichlorobenzene. Measurements were performed at 150°C. The HT-GPC was calibrated with polystyrene standards.

3.1. General procedure for the synthesis of 2-arylalkyl-substituted indene derivatives

To a suspension of 3.37 g (139.0 mmol) magnesium chips in 150 ml of diethylether 14.0 mmol of a suitable alkylaryl bromide were added. After 10 min 125.0 mmol of the alkylaryl bromide dissolved in 100 ml of diethylether were added dropwise followed by a stirring period of about 2 h. Then 16.5 g 2-indanone, dissolved in 150 ml diethylether, were slowly added. The stirring was continued over night. Then the mixture was hydrolyzed with a 5 mol HCl solution at 0°C. The organic layer was washed twice with a NaHCO$_3$ solution and dried over Na$_2$SO$_4$. The solvent was removed. The yields of the corresponding alcoholic compounds were between 75 and 90%.

The alcoholic compound was dissolved in 250 ml toluene and 10.0 mmol of *p*-toluene sulfonic acid were added. The mixture was refluxed until the formed water had separated in a Dean–Stark apparatus. After cooling to room temperature, the mixture was washed with a NaHCO$_3$ solution. The organic layer was dried over Na$_2$SO$_4$ and the solvent was removed in vacuo.

Table 3
NMR data of complexes **1–25**

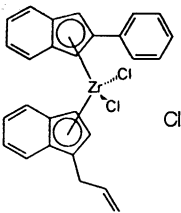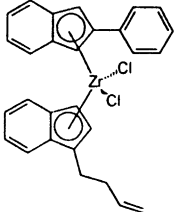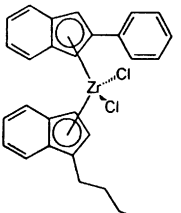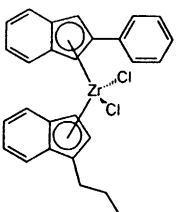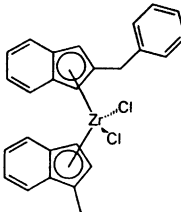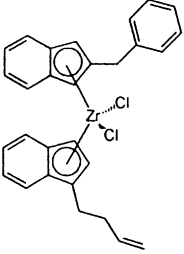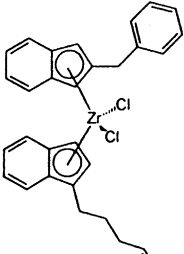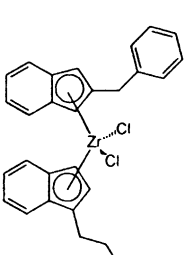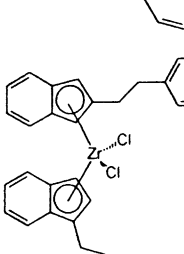| Complex	^{1}H NMR^a	^{13}C NMR^b
1	7.73–7.60 (m, 3H), 7.54–7.24 (m, 8H), 6.84–6.79 (m, 2H), 6.48 (m, 1H), 6.15 (m, 1H), 6.03–5.88 (m, 1H), 5.98 (m, 1H), 5.75 (m, 1H), 5.20–5.05 (m, 2H), 3.82–3.65 (m, 2H)	(C$_q$): 146.4, 143.2, 133.9, 133.3, 127.8, 127.1, 122.0 (CH): 135.9, 128.9, 128.1, 126.3, 126.2, 125.6, 125.5, 125.2, 123.7, 122.1, 120.4, 103.2, 100.0, 99.1 (CH$_2$): 116.6, 32.3
2	7.74–7.60 (m, 3H), 7.52–7.22 (m, 8H), 6.81–6.77 (m, 2H), 6.09 (d, $^3J(^1\mathrm{H}, ^1\mathrm{H})$ 3.1 Hz, 1H), 6.03 (d, $^3J(^1\mathrm{H}, ^1\mathrm{H})$ 3.1 Hz, 1H), 6.00–5.78 (m, 2H), 5.62 (m, 1H), 5.02–4.94 (m, 2H), 3.56–3.50 (m, 2H), 2.98–2.76 (m, 2H)	(C$_q$): 144.9, 142.5, 135.8, 133.2, 132.3, 124.9, 121.8 (CH): 137.3, 128.5, 128.3, 127.5, 126.3, 126.2, 126.1, 125.2, 124.3, 120.6, 103.2, 99.7, 99.5 (CH$_2$): 114.8, 38.6, 33.6
3	7.74–7.54 (m, 3H), 7.52–7.22 (m, 8H), 6.81–6.77 (m, 2H), 6.10 (d, $^3J(^1\mathrm{H}, ^1\mathrm{H})$ 3.2 Hz, 1H), 6.01 (d, $^3J(^1\mathrm{H}, ^1\mathrm{H})$ 3.2 Hz, 1H), 5.97–5.74 (m, 1H), 5.84 (d, $^3J(^1\mathrm{H}, ^1\mathrm{H})$ 3.2 Hz, 1H), 5.61 (d, $^3J(^1\mathrm{H}, ^1\mathrm{H})$ 3.1 Hz, 1H), 5.09–4.94 (m, 2H), 3.51 (m, 2H), 3.01–2.90 (m, 2H), 2.82–2.70 (m, 2H)	(C$_q$): 133.4, 133.0, 127.2, 126.2, 124.4 (CH): 138.2, 128.9, 128.7, 127.5, 126.7, 126.5, 125.7, 125.5, 125.4, 120.2, 103.2, 99.9, 99.0 (CH$_2$):114.7, 33.3, 29.0, 27.4
4	7.74–7.53 (m, 3H), 7.52–7.20 (m, 8H), 6.83–6.79 (m, 2H), 6.09 (d, $^3J(^1\mathrm{H}, ^1\mathrm{H})$ 3.2 Hz, 1H), 6.01 (d, $^3J(^1\mathrm{H}, ^1\mathrm{H})$ 3.2 Hz, 1H), 5.88–5.75 (m, 1H), 5.84 (d, $^3J(^1\mathrm{H}, ^1\mathrm{H})$ 3.2 Hz, 1H), 5.63 (d, $^3J(^1\mathrm{H}, ^1\mathrm{H})$ 3.1 Hz, 1H), 5.06–4.95 (m, 2H), 3.37 (m, 2H), 3.02–2.74 (m, 2H), 2.73–2.58 (m, 2H), 2.15–2.05 (m, 2H)	(C$_q$): 133.6, 133.3, 127.5, 126.9, 126.4, 124.8 (CH): 138.7, 128.9, 128.7, 128.5, 127.7, 127.2, 126.7, 126.2, 125.2, 120.8, 119.1, 118.9, 103.3, 99.9, 99.3 (CH$_2$): 114.5, 39.0, 33.5, 29.5, 28.7
5	7.71–7.58 (m, 3H), 7.44–7.38 (m, 1H), 7.33–7.20 (m, 7H), 7.15–7.11 (m, 2H), 6.29 (d, 1H), 6.11 (d, 1H), 5.94–5.87 (m, 2H), 5.22 (d, $^3J(^1\mathrm{H}, ^1\mathrm{H})$ 3.1 Hz, 1H), 5.12–5.04 (m, 2H), 3.95–3.89 (m, 2H), 3.74–3.58 (m, 2H)	(C$_q$): 141.8, 139.8, 127.3, 126.3, 125.3, 122.2 (CH): 135.7, 128.8, 128.5, 126.7, 126.4, 125.7, 125.6, 125.5, 125.4, 123.6, 119.3, 104.6, 104.0, 99.9 (CH$_2$): 116.6, 37.8, 32.4

Table 3 (*Continued*)
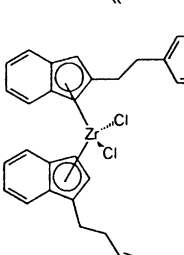
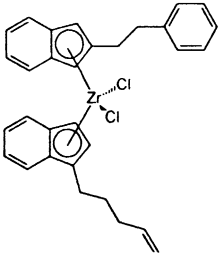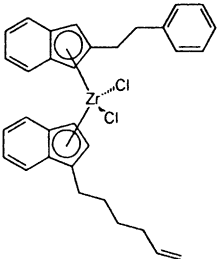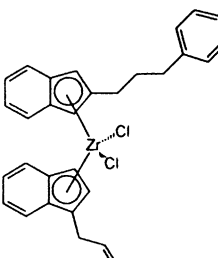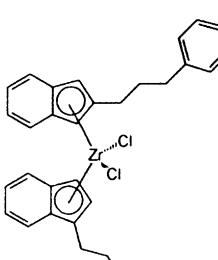| Complex	^{1}H NMR^a	^{13}C NMR^b
6	7.74–7.62 (m, 3H), 7.51–7.47 (m, 1H), 7.34–7.22 (m, 7H), 7.16–7.13 (m, 2H), 6.31 (d, 1H), 6.07 (d, 1H), 5.93–5.86 (m, 2H), 5.29 (d, $^3J(^1H, ^1H)$ 3.1 Hz, 1H), 5.09–5.00 (m, 2H), 3.94–3.87 (m, 2H), 3.11–3.04 (m, 2H), 2.90–2.80 (m, 2H)	(C_q): 141.3, 139.4, 127.5, 126.9, 124.8, 123.5, (CH): 137.3, 128.4, 128.1, 126.1, 125.9, 125.2, 125.1, 125.0, 124.9, 123.1, 119.0, 104.1, 103.8, 99.4 (CH_2): 115.0, 37.4, 33.6, 27.2
7	7.73–7.64 (m, 3H), 7.52–7.48 (m, 1H), 7.35–7.24 (m, 7H), 7.18–7.15 (m, 2H), 6.31 (d, 1H), 6.08 (d, 1H), 5.93–5.82 (m, 2H), 5.30 (d, $^3J(^1H, ^1H)$ 3.1 Hz, 1H), 5.12–5.03 (m, 2H), 3.97–3.87 (m, 2H), 3.03–2.97 (m, 2H), 2.78–2.72 (m, 2H), 2.18–2.10 (m, 2H)	(C_q): 141.7, 139.8, 128.1, 127.3, 126.2, 125.2, 124.8 (CH): 138.3, 128.8, 128.5, 126.6, 126.5, 125.7, 125.6, 125.5, 125.4, 123.8, 119.3, 104.5, 104.2, 99.8 (CH_2): 115.0, 37.8, 33.5, 29.2, 27.6
8	7.72–7.62 (m, 3H), 7.51–7.46 (m, 1H), 7.35–7.19 (m, 7H), 7.17–7.14 (m, 2H), 6.31 (d, $^3J(^1H, ^1H)$ 2.2 Hz, 1H), 6.09 (d, $^3J(^1H, ^1H)$ 2.2 Hz, 1H), 5.90–5.83 (m, 2H), 5.28 (d, $^3J(^1H, ^1H)$ 3.1 Hz, 1H), 5.09–4.99 (m, 2H), 3.97–3.86 (m, 2H), 3.03–2.98 (m, 2H), 2.77–2.72 (m, 2H), 2.17–2.09 (m, 4H)	(C_q): 141.7, 141.3, 128.1, 127.2, 126.2, 125.2, 125.0 (CH): 138.7, 128.9, 128.5, 126.6, 126.4, 125.7, 125.6, 125.4, 123.7, 119.2, 104.3, 104.2, 99.8 (CH_2): 114.5, 37.8, 33.6, 29.9, 28.9, 28.1
9	7.76–7.59 (m, 3H), 7.44–7.39 (m, 1H), 7.36–7.19 (m, 7H), 7.15–7.11 (m, 2H), 6.20 (d, $^3J(^1H, ^1H)$ 2.2 Hz, 1H), 6.04 (d, $^3J(^1H, ^1H)$ 2.2 Hz, 1H), 5.98–5.82 (m, 1H), 5.89 (d, $^3J(^1H, ^1H)$ 3.1 Hz, 1H), 5.22 (d, $^3J(^1H, ^1H)$ 3.2 Hz, 1H), 5.12–5.06 (m, 2H), 3.71–3.53 (m, 2H), 2.97–2.88 (m, 2H), 2.84–2.78 (m, 2H)	(C_q): 142.8, 141.1, 127.1, 126.0, 125.0, 122.1 (CH): 135.7, 128.5, 128.3, 126.7, 126.1, 125.6, 125.5, 125.3, 123.6, 119.3, 104.3, 103.5, 99.9 (CH_2): 116.6, 36.4, 33.6, 32.4
10	7.70–7.22 (m, 11H), 6.95–6.89 (m, 2H), 6.10 (d, $^3J(^1H, ^1H)$ 3.2 Hz, 1H), 6.04 (d, $^3J(^1H, ^1H)$ 3.2 Hz, 1H), 5.88–5.70 (m, 1H), 5.63 (m, 1H), 5.12–4.94 (m, 3H), 3.83 (m, 2H), 3.05–2.89 (m, 2H), 2.87–2.66 (m, 2H), 2.55–2.25 (m, 2H)	(C_q): 145.0, 133.3, 133.1, 127.0, 125.8, 123.8, 122.4 (CH): 137.7, 128.9, 128.7, 128.2, 127.5, 126.7, 125.6, 124.7, 123.8, 121.0, 103.6, 100.1, 99.9 (CH_2): 115.5, 39.0, 34.0, 27.5, 27.4

Table 3 (*Continued*)
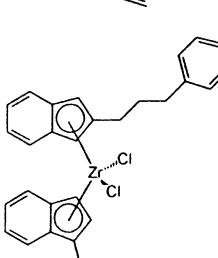
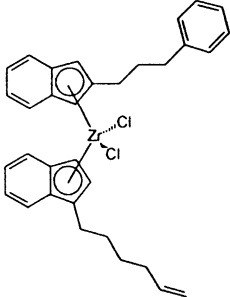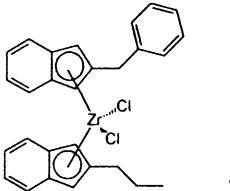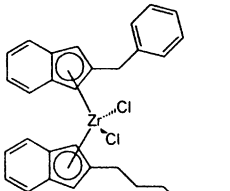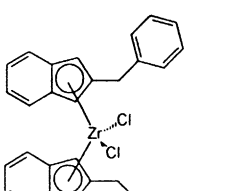| Complex	^{1}H NMR^a	^{13}C NMR^b
11	7.71–7.22 (m, 11H), 6.82–6.78 (m, 2H), 6.11 (d, $^3J(^1$H, ^{1}H) 3.2 Hz, 1H), 6.03 (d, $^3J(^1$H, ^{1}H) 3.2 Hz, 1H), 5.90–5.72 (m, 1H), 5.64 (d, $^3J(^1$H, ^{1}H) 3.2 Hz, 1H), 5.08–4.97 (m, 3H), 3.83 (m, 2H), 3.04–2.79 (m, 4H), 2.75–2.52 (m, 2H), 2.25–2.01 (m, 2H)	(C$_q$): 133.6, 133.3, 127.4, 127.0, 126.2, 124.5, 123.0 (CH): 138.3, 128.9, 128.7, 126.7, 126.5, 125.7, 125.3, 123.8, 121.0, 120.0, 103.5, 100.2, 99.9 (CH$_2$): 114.9, 39.0, 33.4, 29.2, 27.5, 27.3
12	7.73–7.20 (m, 11H), 6.82–6.79 (m, 2H), 6.12 (d, $^3J(^1$H, ^{1}H) 3.2 Hz, 1H), 6.01 (d, $^3J(^1$H, ^{1}H) 3.1 Hz, 1H), 5.91–5.69 (m, 1H), 5.62 (d, $^3J(^1$H, ^{1}H) 3.1 Hz, 1H), 5.08–4.92 (m, 3H), 3.83 (m, 2H), 3.36 (m, 2H), 3.02–2.77 (m, 2H), 2.74–2.53 (m, 2H), 2.22–2.01 (m, 4H)	(C$_q$): 133.6, 133.3, 127.5, 127.1, 126.2, 125.0, 123.5 (CH): 138.7, 128.8, 127.5, 126.7, 126.5, 125.5, 124.9, 123.8, 120.9, 119.3, 103.5, 99.9, 99.2 (CH$_2$): 39.0, 37.7, 33.5, 29.5, 28.7, 27.9, 27.8
13	7.76–7.58 (m, 3H), 7.55–7.15 (m, 10H), 6.27 (m, 1H), 6.11 (m, 1H), 6.08–5.83 (m, 2H), 5.28 (m, 1H), 5.20–5.01 (m, 2H), 3.76–3.49 (m, 2H), 3.37 (m, 2H), 2.80–2.56 (m, 4H)	(C$_q$): 150.3, 143.4, 142.2, 127.2, 126.1, 125.2, 122.0 (CH): 135.8, 128.5, 128.4, 126.3, 125.9, 125.8, 125.7, 123.6, 123.4, 119.9, 103.7, 99.1, 99.0 (CH$_2$): 115.6, 41.0, 35.6, 31.3, 28.9
14	7.76–7.58 (m, 3H), 7.57–7.16 (m, 10H), 6.29 (m, 1H), 6.09 (m, 1H), 6.03–5.85 (m, 2H), 5.30 (m, 1H), 5.19–5.00 (m, 2H), 3.40 (m, 2H), 3.25–2.57 (m, 6H), 2.52–2.27 (m, 2H)	(C$_q$): 149.9, 142.8, 141.8, 127.4, 126.8, 125.8, 122.1 (CH): 137.4, 128.0, 127.9, 126.1, 125.9, 125.4, 124.9, 123.3, 119.6, 103.8, 103.5, 99.3, 98.8 (CH$_2$): 115.0, 40.7, 35.1, 33.5, 31.8, 30.2
15	7.76–7.58 (m, 3H), 7.55–7.16 (m, 10H), 6.30 (m, 1H), 6.14 (m, 1H), 6.03–5.80 (m, 1H), 5.75 (m, 1H), 5.32 (m, 1H), 5.19–5.00 (m, 2H), 3.37 (m, 2H), 3.20–2.60 (m, 6H), 2.30–2.00 (m, 4H)	(C$_q$): 149.9, 142.8, 141.8, 141.5, 126.9, 125.8, 124.3 (CH): 137.9, 128.1, 128.0, 126.0, 125.8, 125.5, 125.0, 123.3, 119.6, 103.8, 103.5, 99.3, 98.9 (CH$_2$): 114.5, 40.7, 35.1, 33.3, 31.5, 30.4, 28.9

Table 3 (*Continued*)
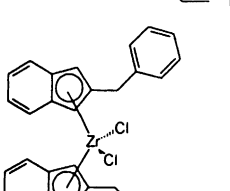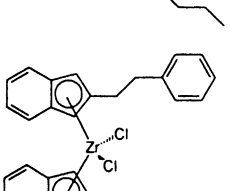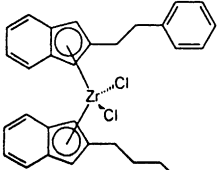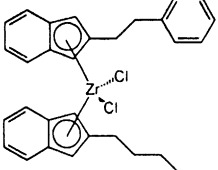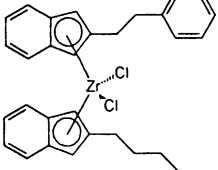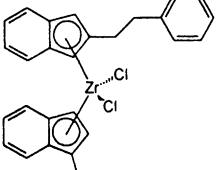
Complex	^{1}H NMR[a]	^{13}C NMR[b]
16	7.76–7.57 (m, 3H), 7.55–7.14 (m, 10H), 6.25 (m, 1H), 6.09 (m, 1H), 5.88–5.77 (m, 1H), 5.73 (m, 1H), 5.32 (m, 1H), 5.07–4.96 (m, 2H), 3.36 (m, 2H), 3.02–2.60 (m, 6H), 2.20–1.98 (m, 6H)	(C$_q$): 150.3, 143.1, 142.3, 141.9, 128.0, 127.3, 124.7 (CH): 138.7, 128.7, 128.5, 128.3, 126.3, 125.8, 125.5, 123.4, 120.0, 104.2, 103.9, 99.6, 99.2 (CH$_2$): 114.6, 41.1, 35.6, 33.6, 30.7, 30.6, 31.3, 28.7
17	7.72–7.68 (m, 4H), 7.34–7.10 (m, 7H), 7.10–7.07 (m, 2H), 5.93–5.90 (m, 4H), 3.77 (s, 2H), 2.40 (t, $^3J(^1$H, ^{1}H) 7.8 Hz, 2H), 1.75–1.70 (m, 2H), 1.06–1.00 (m, 3H)	(C$_q$): 142.7, 142.5, 140.7, 139.5, 125.7 (CH): 128.5, 128.0, 125.9, 125.0, 124.9, 124.8, 124.7, 124.6, 123.0, 119.4, 105.1, 104.9 (CH$_2$): 37.0, 32.0, 23.5 (CH$_3$): 13.5
18	7.68–7.64 (m, 4H), 7.28–7.03 (m, 7H), 7.02–6.96 (m, 2H), 5.88–5.84 (m, 4H), 3.72 (s, 2H), 2.38 (t, $^3J(^1$H, ^{1}H) 7.8 Hz, 2H), 1.68–1.62 (m, 2H), 1.34–1.25 (m, 2H), 0.98–0.93 (m, 3H)	(C$_q$): 142.9, 142.8, 140.7, 139.5, 125.9 (CH): 128.2, 128.0, 126.5, 125.0, 124.9, 124.8, 124.7, 124.6, 124.5, 123.1, 123.0, 119.4, 105.1, 105.0, 104.8 (CH$_2$): 37.0, 32.5, 30.7, 22.1 (CH$_3$): 13.4
19	7.74–7.69 (m, 4H), 7.33–7.09 (m, 7H), 7.08–7.04 (m, 2H), 5.93–5.89 (m, 4H), 3.77 (s, 2H), 2.42 (t, $^3J(^1$H, ^{1}H) 7.2 Hz, 2H), 1.71–1.67 (m, 2H), 1.46–1.28 (m, 4H), 0.99–0.93 (m, 3H)	(C$_q$): 142.9, 142.7, 140.8, 139.3, 125.7 (CH): 128.3, 128.1, 125.9, 125.2, 125.1, 125.0, 124.9, 124.8, 124.7, 123.1, 123.0, 119.4, 105.1, 105.0, 104.8 (CH$_2$): 37.0, 31.0, 30.9, 30.0, 22.0 (CH$_3$): 13.6
20	7.72–7.68 (m, 4H), 7.33–7.09 (m, 7H), 7.08–7.05 (m, 2H), 5.92–5.88 (m, 4H), 3.76 (s, 2H), 2.41 (t, $^3J(^1$H, ^{1}H) 7.8 Hz, 2H), 1.71–1.67 (m, 2H), 1.46–1.26 (m, 6H), 1.00–0.91 (m, 3H)	(C$_q$): 143.0, 142.8, 140.7, 139.5, 125.6 (CH): 128.2, 128.0, 125.9, 125.2, 125.1, 125.0, 124.9, 124.8, 124.7, 123.1, 123.0, 119.4, 105.1, 105.0, 104.8 (CH$_2$): 37.0, 31.1, 31.0, 30.3, 28.6, 22.0 (CH$_3$): 13.6
21	7.72–7.67 (m, 4H), 7.33–7.23 (m, 7H), 7.14–7.09 (m, 2H), 5.92–5.82 (m, 4H), 2.75–2.71 (m, 4H), 2.41–2.34 (m, 4H), 1.05–1.00 (m, 3H)	(C$_q$): 142.7, 142.5, 141.6, 140.7, 125.6 (CH): 128.0, 127.9, 125.8, 125.5, 125.0, 124.7, 123.1, 123.0, 119.4, 105.0, 104.9, 104.7 (CH$_2$): 36.0, 32.9, 32.7, 23.6 (CH$_3$): 13.4

Table 3 (*Continued*)

Complex	^{1}H NMR[a]	^{13}C NMR[b]
22	7.72–7.67 (m, 4H), 7.33–7.23 (m, 7H), 7.14–7.09 (m, 2H), 5.89–5.79 (m, 4H), 2.72 (m, 4H), 2.43–2.37 (m, 4H), 1.41–1.33 (m, 2H), 1.02–0.96 (m, 3H)	(C_q): 142.9, 142.8, 141.6, 140.7, 125.6 (CH): 128.0, 127.9, 125.8, 125.5, 125.1, 124.7, 123.3, 123.1, 123.0, 119.4, 104.9, 104.8, 104.6 (CH_2): 36.0, 32.6, 32.4, 30.7, 22.1 (CH_3): 13.4
23	7.72–7.68 (m, 4H), 7.33–7.24 (m, 7H), 7.14–7.09 (m, 2H), 5.91–5.81 (m, 4H), 2.74–2.71 (m, 4H), 2.43–2.37 (m, 4H), 1.42–1.29 (m, 4H), 1.00–0.94 (m, 3H)	(C_q): 143.0, 142.8, 141.6, 140.7, 125.6 (CH): 128.0, 127.8, 125.6, 125.3, 125.2, 123.1, 123.0, 119.4, 104.8, 104.7, 104.6 (CH_2): 36.0, 32.7, 31.1, 31.0, 30.0, 22.0 (CH_3): 13.5
24	7.72–7.67 (m, 4H), 7.33–7.24 (m, 7H), 7.14–7.09 (m, 2H), 5.90–5.80 (m, 4H), 2.73 (m, 4H), 2.43–2.37 (m, 4H), 1.39–1.27 (m, 6H), 1.01–0.94 (m, 3H)	(C_q): 143.0, 142.8, 141.6, 140.7, 125.6 (CH): 128.0, 127.9, 125.5, 125.0, 124.7, 123.1, 123.0, 119.4, 104.9, 104.8, 104.7 (CH_2): 36.0, 32.8, 31.1, 31.0, 30.3, 28.6, 22.1 (CH_3): 13.7
25	7.74–7.13 (m, 13H), 6.23 (m, 1H), 6.02 (m, 1H), 5.87 (m, 2H), 5.28 (m, 2H), 3.01–2.81 (m, 4H), 1.60–1.34 (m, 4H), 1.06–0.98 (m, 3H)	(C_q): 142.4, 141.2, 141.0, 127.0 (CH): 128.1, 128.0, 126.1, 125.9, 125.2, 125.0, 124.0, 123.3, 121.6, 118.8, 118.6, 103.5, 99.3, 98.7 (CH_2): 36.0, 33.2, 31.8, 27.5, 22.2 (CH_3): 13.5

[a] 25°C, in chloroform-d_1, δ (ppm) rel. chloroform (7.24).
[b] 25°C, in chloroform-d_1, δ (ppm) rel. chloroform-d_1 (77.0).

The residue was dissolved in *n*-pentane and filtered over silica. After crystallization at −25 or −78°C, the desired indene derivatives were obtained in an overall yield of 40–75%.

3.2. General procedure for the synthesis of 1-ω-alkenyl-substituted indene derivatives and 1-butylindene

To 10.0 ml (85.1 mmol) indene, dissolved in 150 ml diethylether and 15 ml tetrahydrofuran, 53.2 ml (85.1 mmol) *n*-butyllithium (1.6 M in *n*-hexane) were added dropwise at −78°C. After stirring at room temperature for 5 h, the solution was cooled to −78°C and an equimolar amount of an ω-alkenyl bromide or butylbromide was added. The mixture was hydrolyzed with 80 ml of water and stirred over night at room temperature. The organic layer was separated and dried over Na_2SO_4. The solvent was evaporated and the residue was distilled in vacuo. Yield: 80–90%.

3.3. General procedure for the synthesis of substituted 1-(tributylstannyl)indene derivatives

12.0 mmol of the corresponding indene derivative were dissolved in 150 ml of diethylether and
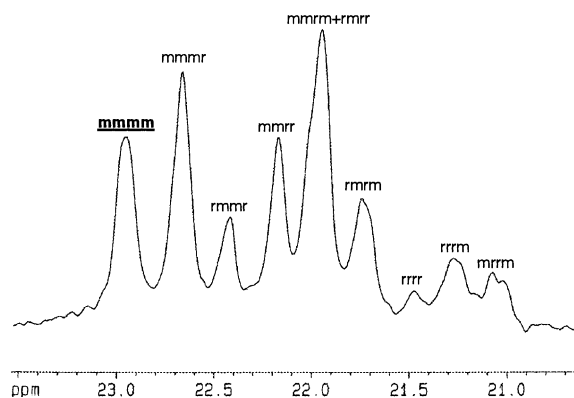
Fig. 11. Section of the ^{13}C NMR spectrum (measured at 90°C) of the polypropene produced with complex **23**/MAO (peak of isotactic rate underlined (mmmm)).

an equimolar amount of *n*-butyllithium (1.6 M in *n*-hexane) was added dropwise at −78°C. After stirring at room temperature for several hours and recooling to −78°C, tributyltinchloride was added. Stirring was continued overnight at room temperature. The solvent was evaporated and the residue was suspended in *n*-pentane. The suspension was filtered through Na$_2$SO$_4$ and the filtrate was evaporated. Yield: quantitatively.

3.4. General procedure for the synthesis of substituted indenylzirconiumtrichloride complexes

To a suspension of 5.17 g (22.0 mmol) zirconiumtetrachloride in 150 ml of toluene a solution of an equimolar amount of a 1-(tributylstannyl)indene derivative, dissolved in 80 ml of toluene, was added. The mixture was stirred overnight. After filtration and washing with *n*-pentane the solvent was evaporated in vacuo. Yield: 70–95%.

3.5. General procedure for the synthesis of the unbridged metallocene dichloride complexes **1–25**

To a solution of 4.1 mmol of the alkyl or ω-alkenyl-substituted indene derivative, dissolved in 150 ml of diethylether, 2.6 ml (4.1 mmol) *n*-butyllithium (1.6 M in *n*-hexane) were added dropwise at −78°C. After completion of the deprotonation, the mixture was cooled again to −78°C. The desired half-sandwich complex was added equimolarly. After stirring overnight and evaporation of the solvent the residue was extracted with methylenedichloride. The suspension was filtered over Na$_2$SO$_4$. The filtrate was evaporated. The precipitating complex was recrystallized from toluene at −78°C. Yield: 60–90%.

3.6. Spectroscopic characterization

Complexes **1–25** were characterized by ^{1}H and ^{13}C NMR spectroscopy (Table 3). In addition, mass spectrometry confirmed the composition of the complexes.
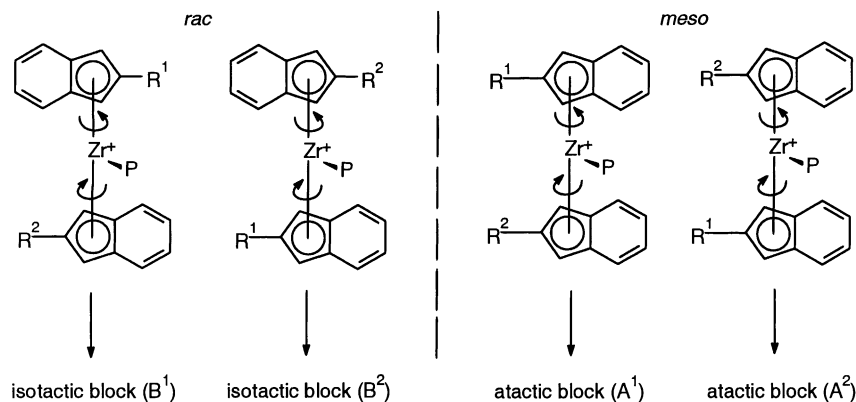
Fig. 12. Potential catalyst isomers.

References

[1] W. Kaminsky, J. Chem. Soc., Dalton Trans. (1998) 1413.

[2] H.-H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. Waymouth, Angew. Chem. Int. Ed. Engl. 34 (1995) 1143.

[3] H.G. Alt, J. Chem. Soc., Dalton Trans. (1999) 1703.

[4] M. Aulbach, F. Küber, Chemie Unserer Zeit 26 (1994) 197.

[5] G.M. Benedikt, B.L. Goodall, Metallocene Catalyzed Polymers, Plastics Design Library, Norich, NY, 1998.

[6] W.A. Herrmann, J. Rohrmann, E. Herdtweck, W. Spaleck, A. Winter, Angew. Chem. 101 (1989) 1536.

[7] W.A. Herrmann, J. Rohrmann, E. Herdtweck, W. Spaleck, A. Winter, Angew. Chem. Int. Ed. Engl. 28 (1989) 1511.

[8] H.G. Alt, E. Samuel, Chem. Soc. Rev. 27 (1998) 323.

[9] C. Janiak, in: A. Togni, R.L. Haltermann (Eds.), Metallocenes, Vol. II, Wiley-VCH, Weinheim, New York, Basel, Cambridge, Tokyo, 1998, p. 547.

[10] M. Bochmann, J. Chem. Soc., Dalton Trans. (1996) 255.

[11] P.C. Möhring, N.J. Coville, J. Organomet. Chem. 479 (1994) 1.

[12] W. Kaminsky, M. Arndt, Adv. Polym. Sci. 127 (1997) 143.

[13] W. Kaminsky, M. Arndt, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, VCH, Weinheim, New York, Basel, Cambridge, Tokyo, Vol. I, p. 220 and Vol. II, p. 664 and p. 1187.

[14] P.C. Möhring, N.J. Coville, J. Organomet. Chem. 479 (1994) 1.

[15] A. Andresen, H.-G. Cordes, J. Herwig, W. Kaminsky, A. Merck, R. Mottweiler, J. Pein, H. Sinn, H.-J. Vollmer, Angew. Chem. 88 (1976) 689.

[16] A. Andresen, H.-G. Cordes, J. Herwig, W. Kaminsky, A. Merck, R. Mottweiler, J. Pein, H. Sinn, H.-J. Vollmer, Angew. Chem. Int. Ed. Engl. 15 (1976) 630.

[17] H. Sinn, W. Kaminsky, Adv. Organomet. Chem. 18 (1980) 99.

[18] H. Sinn, W. Kaminsky, H.-J. Vollmer, R. Woldt, BASF AG, U.S. Patent 4,404,344 (1983).

[19] G.W. Coates, R.M. Waymouth, Science 267 (1995) 217.

[20] K.B. Wagener, Science 267 (1995) 191.

[21] E. Hauptman, R.M. Waymouth, J. Am. Chem. Soc. 117 (1995) 11586.

[22] R. Kravchenko, A. Masood, R.M. Waymouth, Organometallics 16 (1997) 3635.

[23] J.L. Maciejewski Petoff, M.D. Bruce, R.M. Waymouth, A. Masood, T.K. Lal, R.W. Quan, S.J. Behrend, Organometallics 16 (1997) 5909.

[24] M.D. Bruce, G.W. Coates, E. Hauptman, R.M. Waymouth, J.W. Ziller, J. Am. Chem. Soc. 119 (1997) 11174.

[25] R. Kravchenko, R.M. Waymouth, Macromolecules 31 (1998) 1.

[26] R. Kravchenko, A. Masood, R.M. Waymouth, C.L. Myens, J. Am. Chem. Soc. 120 (1998) 2039.

[27] M.D. Bruce, R.M. Waymouth, Macromolecules 31 (1998) 2707.

[28] Y. Hu, M.T. Krejchi, C.D. Shah, C.L. Myers, R.M. Waymouth, Macromolecules 31 (1998) 6908.

[29] J.L. Maciejewski Petoff, T. Agoston, T.K. Lal, R.M. Waymouth, J. Am. Chem. Soc. 120 (1998) 11316.

[30] S. Lin, E. Hauptman, T.K. Lal, R.M. Waymouth, R.W. Quan, A.B. Ernst, J. Mol. Catal. 136 (1998) 23.

[31] Y. Hu, E.D. Carlson, G.G. Fuller, R.M. Waymouth, Macromolecules 32 (1999) 3334.

[32] P. Witte, T.K. Lal, R.M. Waymouth, Organometallics 18 (1999) 4147.

[33] C.D. Tagge, R.L. Kravchenko, T.L. Lal, R.M. Waymouth, Organometallics 18 (1999) 380.

[34] S. Lin, R.M. Waymouth, Macromolecules 32 (1999) 8283.

[35] J.L. Maciejewski Petoff, C.L. Myers, R.M. Waymouth, Macromolecules 32 (1999) 7984.

[36] H. Schumann, D.F. Karasiak, S.H. Mühle, R.L. Halterman, W. Kaminsky, U. Weingarten, J. Organomet. Chem. 579 (1999) 356.

[37] J.E. Horan, R.W. Schiessler, Org. Synth. 41 (1961) 647.

[38] W.S. Murphy, C.R. Hauser, J. Org. Chem. 31 (1966) 85.

[39] O. Meth-Cohn, S. Gronowitz, J. Chem. Soc., Chem. Commun. (1966) 81.

[40] G.A. Kraus, K. Landgrebe, Synthesis 10 (1984) 885.

[41] C. Schmid, Dissertation, University of Bayreuth, Postfach, 1996.

[42] H.G. Alt, A. Köppl, Chem. Rev. 100 (2000) 1205.

[43] B. Peifer, W. Milius, H.G. Alt, J. Organomet. Chem. 562 (1998) 153.

[44] H.G. Alt, J. Chem. Soc., Dalton Trans. (1999) 1703, and references therein.

[45] A. Zambelli, P. Locatelli, G. Bajo, F.A. Bovey, Macromolecules 8 (1975) 687.

[46] F.A. Bovey, High Resolution NMR of Macromolecules, Academic Press, New York, 1972.

[47] J.C. Randall, Polymer Sequence Determination by the ^{13}C NMR Method, Academic Press, New York, 1977.

[48] J.L. Koenig, Spectoscopy of Polymers, American Chemical Society, Washington, 1991.