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Unbridged metallocene dichloride complexes with mono-substituted indenyl ligands and their application for the polymerization of propene

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Dedicated to Professor Henri Brunner on the occasion of his 65th birthday

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Abstract

The synthesis of unbridged metallocene dichloride complexes of the type Ind'_2ZrCl_2 (Ind′ = 2-alkyl- or arylalkyl-substituted indenyl) is described. The complexes are characterized by ^1H- and ^{13}C-NMR spectroscopy and mass spectrometry. After activation with methylalumoxane these complexes can be used for propene polymerization; they produce block copolymers consisting of alternating isotactic and atactic blocks. The polymerization results and the polymer properties are presented. The influence of the catalyst structure on the polymerization behaviour is discussed. © 2001 Elsevier Science B.V. All rights reserved.

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

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1. Introduction

After activation with methylalumoxane (MAO) [1–3] the metallocene complexes with Group 4 metals have great potential for the polymerization of olefins. The properties of the resulting polymers depend very much on the structure of the metallocene complex (see Refs. [4–24] and references cited therein).

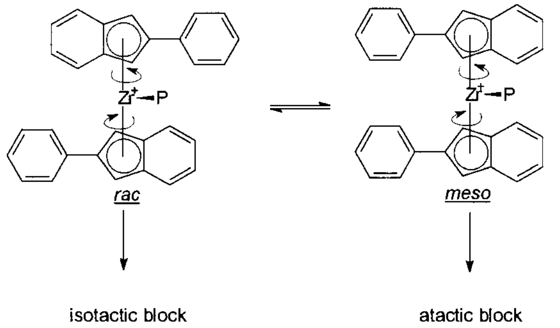

Fig. 1. Possible symmetries (rac and meso) of the model complex bis(2-phenylindenyl)zirconium dichloride.

Unbridged, symmetrically substituted bis(indenyl) complexes are able to produce block copolymers consisting of atactic and isotactic blocks (‘oscillating catalysts’) [9–22]. Depending on the substituent in position 2 of the indenyl ligand, two different symmetries (rac or meso) can be formed (Fig. 1).

The meso form produces atactic polypropene, and the rac form isotactic polypropene. The ratio of these blocks and their block lengths can be controlled by the temperature to a certain extent. Differently substituted indenyl ligands can also have a considerable influence on these parameters. Up to now, no systematic investigations have been performed with alkyl and aryl substituents in position 2 of unbridged indenyl ligands to study the effect on catalytic propene polymerization.

Here, we describe the synthesis and polymerization behaviour of unbridged metallocene complexes with mono-substituted indenyl ligands for the polymerization of propene.

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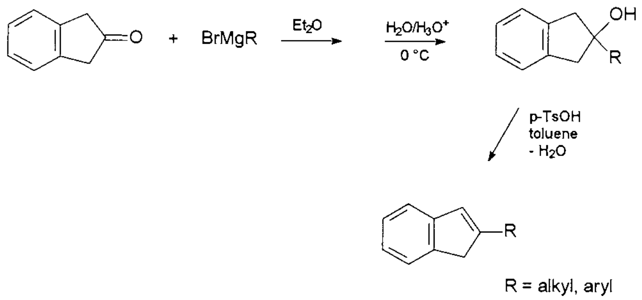


Scheme 1. Preparation of indene derivatives with a substituent in position 2.

2. Results and discussion

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

The preparation of various indene derivatives with an arylalkyl or alkyl substituent in position 2 was accomplished according to Scheme 1.

2.2. Synthesis of complexes **1**–**7**

The preparation of unbridged bis(indenyl) complexes can be achieved in the manner shown in Scheme 2.

2.3. Polymerization results

The metallocene complexes **1**–**7** were activated with an excess of MAO (Al:Zr = 3000:1). The polymerization of propene was conducted as a bulk polymerization in 500 ml of liquid propene at 0, 30 and 60°C. The tacticities of the polypropenes obtained were determined by ^{13}C-NMR spectroscopy at 90°C in 1,2,4-trichlorobenzene. The data obtained are shown in Table 1.

2.3.1. Influence of the polymerization temperature on productivity

With increasing reaction temperature the productivity is expected to increase. In most cases investigated we found a decrease with rising polymerization temperature, except for catalysts **4** [9] and **5**, which showed their top productivities at 30°C. This behaviour could be rather due to the partial decomposition of the catalysts at elevated temperatures and not to different kinetics.

All other catalysts show their highest productivities at a polymerization temperature of 0°C. Complexes with an alkyl group as substituent in position 2 of the indenyl ligand (**1**–**3**) are more active than complexes with an alkylaryl substituent in the same position (**4**, **5**, **7**) except catalyst **6**. This complex with two methylene spacer groups shows the highest productivity (273.900 g h^{-1} of polypropene per gram of Zr) (Fig. 2).

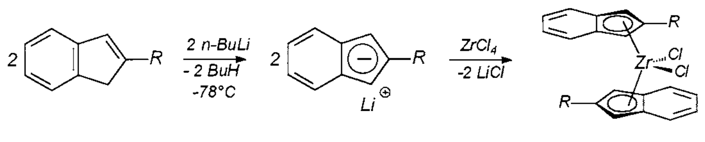
A direct comparison of the alkyl chain length shows a decrease in productivity with growing alkyl chains independent of the polymerization temperature. This trend cannot be found for catalysts with alkylaryl groups.

2.3.2. Molar masses and polydispersities of the polypropenes obtained

The molar mass averages $\bar{M}_n$ and $\bar{M}_w$ show the expected trend. The higher the polymerization temperature the lower $\bar{M}_n$ and $\bar{M}_w$. The reason could be an accelerated β-H-elimination reaction at higher temperatures. Only those polypropenes that show a significant difference in their molar mass averages were produced at 0°C.

At higher polymerization temperatures the observed molar masses reach a similar level. The length of the alkyl chain has no decisive influence on these polymer data. Among the catalysts with alkylaryl groups on the indenyl ligand no uniform trend is observed.

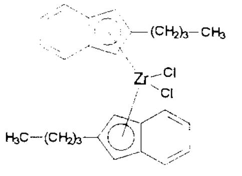
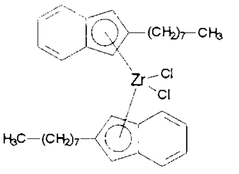
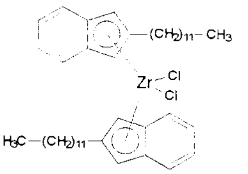
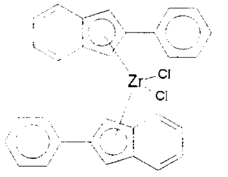
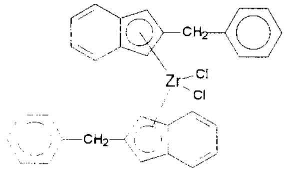
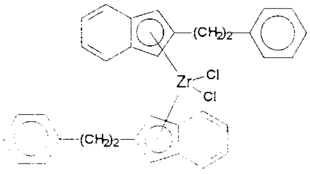
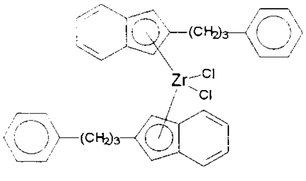
Metallocene catalysts produce polymers with polydispersities about the factor two ('single-site catalysts') [25]. At a polymerization temperature of 0°C all polypropenes obtained behave similarly. With increasing temperature the polydispersity increases. Here, a dependence on the length of the alkyl chain can be observed: the longer the alkyl chain the higher the polydispersity.



1 (R = butyl)
2 (R = octyl)
3 (R = dodecyl)
4 (R = phenyl)
5 (R = benzyl)
6 (R = phenylethyl)
7 (R = phenylpropyl)

Scheme 2. Synthesis of the bis(indenyl) complexes **1**–**7**.

Table 1
Polymerization and polymer data[a]

Catalyst precursor	productivity in g(PP)/g(Zr)*h^{-1} a) 0°C b) 30°C c) 60°C	isotacticity[b)] in % a) 0°C b) 30°C c) 60°C	$\overline{M}_w$ in g/mol a) 0°C b) 30°C c) 60°C	polydispersity a) 0°C b) 30°C c) 60°C
 1	a) 87.500 b) 20.300 c) 17.000	a) 14.6 b) 13.1 c) 11.4	a) 511.450 b) 88.780 c) 21.800	a) 2.83 b) 6.48 c) 8.04
 2	a) 57.700 b) 31.400 c) 20.800	a) 17.0 b) 12.9 c) 8.4	a) 575.670 b) 97.070 c) 41.200	a) 2.01 b) 4.93 c) 9.05
 3	a) 50.400 b) 27.800 c) 13.200	a) 15.7 b) 15.3 c) 8.1	a) 656.140 b) 71.490 c) 39.350	a) 2.31 b) 3.99 c) 13.77
 4	a) 14.300 b) 32.200 c) 23.300	a) 26.0 b) 19.6 c) 12.2	a) 851.200 b) 231.650 c) 25.880	a) 1.83 b) 3.34 c) 4.24
 5	a) 26.200 b) 45.200 c) 32.800	a) 37.4 b) 29.6 c) 18.4	a) 212.240 b) 56.920 c) 25.090	a) 2.39 b) 2.43 c) 4.99
 6	a) 273.900 b) 53.200 c) 48.500	a) 14.1 b) 10.3 c) 8.8	a) 1.047.130 b) 69.640 c) 89.000	a) 2.67 b) 14.31 c) 51.17
 7	a) 48.800 b) 20.500 c) 14.000	a) 14.0 b) 12.0 c) 7.2	a) 963.170 b) 79.620 c) 25.300	a) 3.59 b) 3.55 c) 6.11

[a)] Polymerization conditions: A1:Zr = 3.000 : 1 ; 60 minutes.

[b)] The degree of isotacticity is reflected by the amount of mmmm pentades

2.3.3. *Influence of polymerization temperature and catalyst structure on tacticity*

Complexes **1**–**7** activated with MAO produce a block copolymer consisting of alternating atactic and isotactic blocks [9,26]. The isotacticity [27–29] of the polypropenes obtained is reduced with increasing polymerization temperature. At higher temperatures the speed of the ligand oscillation is higher, and thus the atactic ratio of the polymer increases.

An alkyl chain at the indenyl ligand of the metallocene catalyst causes polypropenes with a lower isotacticity than complexes **4** and **5** with no or one methylene spacer group. Both polypropenes of catalysts **4** and **5** show a high degree of isotacticity at polymerization temperatures of 0°C and 30°C (**4**: 26.0%, 19.6%; **5**: 37.4%, 29.6%). Complexes **6** and **7** are comparable to the alkyl-substituted ones in relation to the tacticities.

It should be noted that a butyl-substituted indenyl complex produces a polypropene with only small changes in the isotacticity at different temperatures. The oscillation speed seems to be almost independent of the polymerization temperature. The steric hindrance must be low, and so is the influence on the polymer produced.

3. Experimental

All experiments were performed under inert gas atmosphere using standard Schlenk technique. The inert gas used was purified and dried argon (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.

NMR spectra were recorded in $CDCl_3$ at 25°C on a Bruker ARX 250 instrument. The chemical shifts in the ^1H-NMR spectra were referenced to the residual proton signal of the solvent ($\delta = 7.24$ ppm for $CHCl_3$); the carbon resonances in the ^{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).

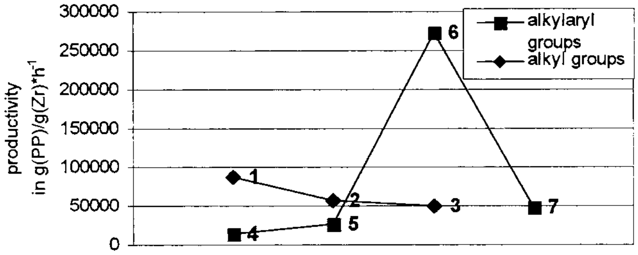


Fig. 2. Catalyst productivities at 0°C depending on the various substituents at the indenyl ligand (in position 2).

Polymerizations were conducted in a 1 l Büchi steel reactor equipped with a mechanical stirrer. Propene was polymerized in bulk at different temperatures: 0, 30, and 60°C. MAO was used as a 30% solution in toluene from Witco, Germany. The polymerizations were stopped by venting excess propene. The polymer obtained was washed with HCl–methanol and dried in vacuo.

Polymer data were recorded on a Millipore Waters GPC 150C instrument. For the separation, four successively connected polystyrene columns were used. The pore diameters of the single columns were 500, 1000, 10 000 and 100 000 Å. For the refractometric detection an RI Waters 401 refractometer was used. Degassed chloroform (flow rate 1 ml min^{-1}) was used as eluent. Polymer samples were dissolved in boiling chloroform and hot filtered. The GPC was calibrated with polystyrene standards.

3.1. *General synthesis procedure for 2-arylalkyl- or alkyl-substituted indene derivatives*

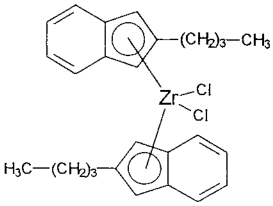
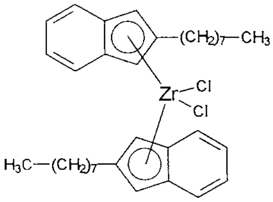
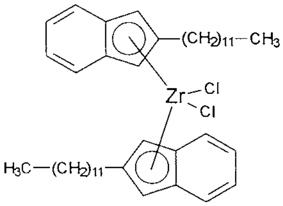
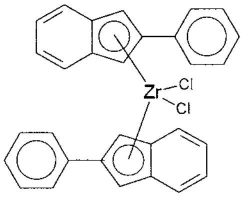
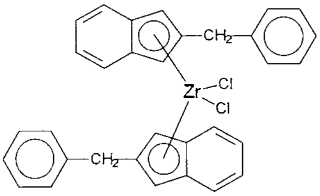
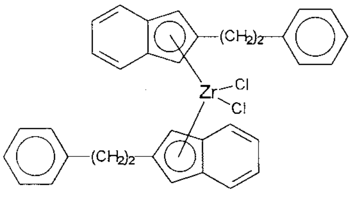
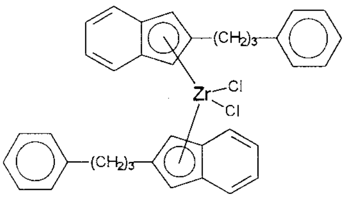
To a suspension of 2.24 g (92.5 mmol) magnesium shavings in 100 ml of diethyl ether 10 mmol of the corresponding alkylaryl bromide (or alkyl bromide) were added. After 10 min, 82.5 mmol of the alkylaryl bromide, dissolved in 50 ml of diethyl ether, were added dropwise followed by a stirring period of about 2 h. 8.0 g (61.5 mmol) of 2-indanone [30], dissolved in 100 ml diethyl ether, were added slowly. The stirring was continued overnight and subsequently the mixture was hydrolysed with a diluted HCl solution at 0°C. The organic layer was washed twice with an $NaHCO_3$ solution and dried over Na_2SO_4. The solvent was removed. The yield of the corresponding alcoholic compounds was between 75 and 90%.

The alcoholic product was dissolved in 150 ml of toluene and 8.3 mmol of *p*-toluene sulfonic acid were added. The mixture was refluxed until all water formed was separated via a Dean–Stark apparatus. After cooling to room temperature the mixture was washed with an $NaHCO_3$ solution. The organic layer was dried over Na_2SO_4 and the solvent was removed in vacuo. The residue was dissolved in *n*-pentane and filtered over silica. After evaporation of the solvent, the desired indene derivatives were obtained in an overall yield of 45–75%.

3.2. *General procedure for the synthesis of unbridged metallocene dichloride complexes*

20 mmol of the substituted indene were dissolved in diethyl ether and cooled to − 78°C. 13 ml (20.8 mmol) of *n*-butyllithium (1.6 M in *n*-hexane) were added slowly. At room temperature the mixture was stirred until gas evolution had stopped. Subsequently, 10 mmol

Table 2
NMR and mass spectroscopic data of complexes **1**–**7**

No.	Complex	^{1}H NMR [a]	^{13}C NMR [b]	M$^+$ [m/e]
1		7.66-7.62 (m, 4H), 7.25-7.21 (m, 4H), 5.82 (s, 4H), 2.38-2.32 (t, 4H), 1.35-1.19 (m, 8H), 0.92-0.80 (t, 6H)	143.2 (C_q), 128.4 (C_q), 126.3 (C_q), 125.3 (CH), 125.1 (CH), 105.2 (CH), 40.8 (CH_2), 32.9 (CH_2), 31.1 (CH_2), 22.3 (CH_2), 13.3 (CH_3)	505
2		7.66-7.62 (m, 4H), 7.25-7.21 (m, 4H), 5.83 (s, 4H), 2.37-2.31 (t, 4H), 1.32-1.20 (m, 24H), 0.88-0.83 (t, 6H)	143.2 (C_q), 126.2 (C_q), 126.1 (C_q), 125.3 (CH), 125.0 (CH), 105.2 (CH), 41.0 (CH_2), 31.9-29.3 (12x CH_2), 22.6 (CH_2), 14.1 (CH_3)	617
3		7.66-7.62 (m, 4H), 7.25-7.21 (m, 4H), 5.83 (s, 4H), 2.37-2.32 (t, 4H), 1.33-1.21 (m, 40H), 0.90-0.85 (t, 6H)	143.2 (C_q), 128.3 (C_q), 126.0 (C_q), 125.3 (CH), 125.0 (CH), 105.2 (CH), 40.1 (CH_2), 31.9-29.3 (20x CH_2), 22.6 (CH_2), 14.1 (CH_3)	725
4		7.66-7.64 (m, 4H), 7.25-7.16 (m, 10H), 7.02-6.99 (m, 4H), 5.82 (s, 4H)	134.8 (C_q), 133.3 (C_q), 129.0 (CH), 128.7 (CH), 126.8 (C_q), 126.7 (CH), 126.4 (CH), 125.1 (CH), 126.4 (CH), 125.1 (CH), 100.9 (CH)	545
5		7.67-7.64 (m, 4H), 7.25-7.18 (m, 10H), 7.02-7.01 (m, 4H), 5.85 (s, 4H), 3.70 (s, 4H)	132.8 (C_q), 129.1 (CH), 129.0 (CH), 128.9 (C_q), 126.7 (C_q), 126.5 (CH), 126.0 (CH), 125.9 (CH), 106.3 (CH), 38.0 (CH_2)	573
6		7.66-7.62 (m, 4H), 7.25-7.19 (m, 10H), 7.05-7.02 (m, 4H), 5.74 (s, 4H), 2.70-2.60 (m, 8H)	133.2 (C_q), 131.4 (C_q), 128.9 (CH), 128.8 (CH), 126.8 (C_q), 126.6 (CH), 125.9 (CH), 125.7 (CH), 105.7 (CH), 36.9 (CH_2), 33.7 (CH_2)	601
7		7.61-7.53 (m, 4H), 7.25-7.07 (m, 14H), 5.81 (s, 4H), 2.57-2.47 (m, 8H), 2.41-2.34 (m, 4H)	133.0 (C_q), 131.8 (C_q), 129.0 (CH), 128.8 (CH), 127.0 (C_q), 126.8 (CH), 125.9 (CH), 125.7 (CH), 106.0 (CH), 38.2 (CH_2), 37.8 (CH_2), 33.2 (CH_2)	629

[a] 25 °C, in chloroform-d, δ [ppm] rel. cloroform (7.24); [b] 25 °C, in chlorform-d, δ [ppm] rel. chloroform-d, (77.0)

of $ZrCl_4$ were added and the mixture was stirred overnight. After filtration over Na_2SO_4 the solvent was evaporated. After washing twice with *n*-pentane, yellowish bis(indenyl) complexes could be obtained. Yield: 65–90%.

3.3. Spectroscopic characterization

Complexes **1**–**7** were characterized by ^1H- and ^{13}C-NMR spectroscopy. In addition, mass spectra with the molecular mass peaks were obtained. NMR data are shown in Table 2.

Acknowledgements

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