

# New bridged zirconocenes for olefin polymerization: Binuclear and hybrid structures <sup>1</sup>

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## Abstract

Four newly synthesized bridged bisindenyl zirconocenes which are derivatives of known structures have been tested in polymerizations of liquid propylene with methylaluminumoxane as cocatalyst. They include two asymmetric and two binuclear systems which are suitable for isotactic polymerization. Surprising differences from the behavior of similar systems (regiospecificity, chain termination) are found and discussed. © 1998 Published by Elsevier Science B.V.

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## 1. Introduction

Highly active soluble zirconocene-methylaluminumoxane catalysts for olefin polymerization are known since nearly twenty years. Since publication of the first system [1], a large variety of different structures has been synthesized and tested. These efforts have brought forth industrially applicable metallocene catalysts for the production of various polyolefins including completely new polymers and also much insight into details of the polymerization mechanisms [2,3].

One of our contributions to this field was the step-by-step-development of zirconocene structures highly effective in isospecific propylene

polymerization. We found, and so did other groups parallel to us, that certain structural increments of the zirconocene molecule are responsible for certain aspects of the polymerization behavior of the catalyst [4–6]. Bridged chiral bis(2-alkyl-4-aryindenyl) zirconocenes in combination with methylaluminumoxane turned out to be highly efficient catalysts for isotactic propylene polymerization. They combine an unprecedented high activity with high stereospecificity and high molecular weight of the polymer [4].

In the work described here we used a typical indenyl ligand of these high-efficiency systems, 2-methyl-4-aryindenyl, as a structural increment in 2 new ‘hybrid’ and 2 new binuclear metallocenes, which were tested in the polymerization of liquid propylene. Comparison of the results with previous data might give some more insight into structure–performance-rela-

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<sup>1</sup> Dedicated to Professor Dr. Gottfried Huttner on the occasion of his 60th birthday.

tionships and, thus, contribute to the discussion about modified or new mechanistical hypotheses which has evolved recently [2,3,7].

## 2. Results

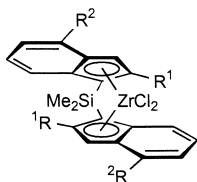
### 2.1. General approach

#### 2.1.1. 'Hybrid' systems

The bridged bisindenyl zirconocenes of our previous work all had  $C_2$ -symmetry, i.e., the respective ligand system consisted of two identical indenyl moieties connected by a  $C_s$ -symmetrical bridge (Fig. 1). We now synthesized and tested two 'hybrid' structures, consisting each of two different indenyl moieties combined in one complex. The performance effect of each of these indenyl moieties in a  $C_2$ -symmetric system is already known. The hybrid systems should show whether this performance effect needs  $C_2$ -symmetry as a necessary condition or not. We managed to synthesize systems with the ligand combinations indenyl/2-methyl-4-phenylindenyl and 2-methylindenyl/2-methyl-4-phenylindenyl, both with dimethylsilyl bridges (Fig. 2).

#### 2.1.2. Binuclear systems

Within the discussions on polymerization mechanisms also reactions between two active zirconocene species have been discussed, either



1a:  $R^1 = R^2 = H$

1b:  $R^1 = Me, R^2 = H$

1c:  $R^1 = H, R^2 = Ph$

1d:  $R^1 = Me, R^2 = Ph$

Fig. 1. Bridged  $C_2$ -symmetric bisindenyl zirconocenes previously described.

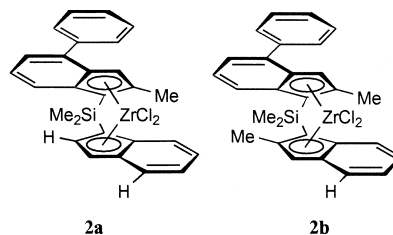


Fig. 2. New bridged dissymmetric bisindenyl zirconocenes.

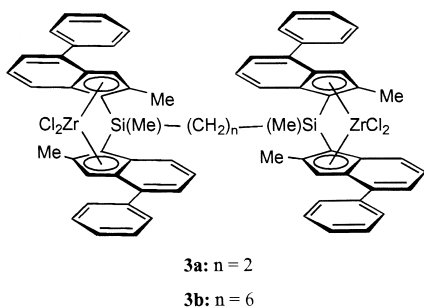
contributing to deactivation [8] or influencing polymerization by exchange of polymer chains from one active center to another one [7]. Two active species brought into close vicinity by a structural bridge might thus have an interesting polymerization behaviour. We managed to synthesize two binuclear species derived from the previously described dimethylsilylbis(2-methyl-4-phenylindenyl)zirconium dichloride (**1d**) which differ from each other in the length of the structural bridge (Fig. 3). They are the first known examples of isospecific binuclear zirconocenes.

### 2.2. Preparation of zirconocenes 2a, 2b, 3a, 3b

The preparations basically followed the well-known sequence [4] of first synthesizing the appropriate indenyl structures, form their lithium salts by reaction with butyllithium, introduce the silicon bridge by reaction of the lithium salt with the appropriate alkylsilicon chloride and forming the complex by reaction of the lithiated ligand system with zirconium tetrachloride.

In case of systems **2a** and **2b** (with two different indenyls within the complex, see Fig. 2) introduction of the bridge is a two-step-operation, first reacting the bridging reagent with one indenyl moiety and the product of this with the other. In the end, the desired complexes **2a** and **2b** (see Fig. 2) can be isolated pure and in good yield.

In case of binuclear systems **3a** and **3b** (see Fig. 3) the dimeric ligand system is synthesized in one step by reaction of 4 moles of the

Fig. 3. New dimeric bisindenyl zirconocenes (*rac-rac* isomers).

substituted indene lithium salt with one mole of the appropriate 1,*n*-bis(methyldichlorosilyl)alkane. The complex formation results, as to be expected, in an isomer mixture. This mixture should contain three different isomers: *rac-rac*, *rac-meso*, and *meso-meso*, *rac* and *meso* meaning the chiral *rac*-complex **1d** (Fig. 1) and its achiral *meso* stereoisomer. In both cases, **3a** and **3b**, the mixture could not be resolved. NMR and mass spectra of the purified mixture are in agreement with the expected structures, but do not give information about the isomers' ratios. Taking into account that formation of complex mono-**1d** yields *rac* and *meso* isomers in equal amount, the ratio *rac-rac*:*rac-meso*:*meso-meso* 1:2:1 should be expected. This is only in rough agreement with the polymerization results (v.i. and Table 1): The polypropylene product contains only 2.4% (**3a**), respectively, 6.1% (**3b**) of atactic polypropylene (aPP) formed by the achiral *meso* active centers. Under comparable polymerization conditions a 1:1 mixture of chiral **1d** and its *meso* stereoisomer

Table 2

Melting point and  $^{13}\text{C}$ -NMR data of polypropylene homopolymers: Products by metallocenes described, and by conventional  $\text{TiCl}_3$  catalyst, for comparison

| Catalyst        | m.p. (°C) | mm (%) | mr (%) | rr (%) | 2,1-i (%) |
|-----------------|-----------|--------|--------|--------|-----------|
| $\text{TiCl}_3$ | 163       | 93.6   | 3.4    | 3.0    | n.d.      |
| <b>1a</b>       | 136       | 90.1   | 6.2    | 2.7    | 0.6+0.4   |
| <b>1b</b>       | 145       | 92.6   | 4.8    | 2.1    | 0.5       |
| <b>1c</b>       | 148       | 93.5   | 3.6    | 1.2    | 1.7       |
| <b>1d</b>       | 159       | 98.9   | 0.6    | 0.2    | 0.3       |
| <b>2a</b>       | 151       | 95.8   | 2.6    | 0.2    | 0.7       |
| <b>2b</b>       | 155       | 96.0   | 3.2    | 0.4    | 0.4       |
| <b>3a</b>       | 153       | 96.2   | 1.8    | 0.5    | 1.5       |
| <b>3b</b>       | 154       | 96.4   | 2.1    | 0.4    | 1.1       |

All samples were purified from atactic material (see Table 1) by shear crystallization prior to spectroscopy.

NMR signal integrations are depicted as percentage of total integration of methyl region.

Regioirregular 2,1-units detected were exclusively *meso*-configured in all cases except with catalyst **1a** (*meso*: 0.6; *rac*: 0.4); that sample was also the only one with traces of 1,3-insertion (< 0.05%).

gives product with 8% aPP-content, i.e., the *meso* centers in the binuclear species are either less active than in the mononuclear analogue or have a share of less than 50% of all centers.

### 2.3. Polymerization results

The newly synthesized metallocenes **2a**, **2b** and **3a**, **3b** were tested with methylaluminoxane as cocatalyst in polymerizations of liquid propylene at 70°C. The metallocenes were prereacted with the cocatalyst prior to polymerization. A high Al:Zr ratio (12000:1) was applied to demonstrate performance under optimum condi-

Table 1

Polymerization of liquid propylene with previously described and new zirconocene/methylaluminoxane catalysts (70°C, Zr:Al = 1:12000)

| Metallocene | Productivity (kg PP / mmol Zr h) | $M_w$ ( $10^3$ g/mol) | $M_w/M_n$ | aPP (wt%) | m.p. (°C) |
|-------------|----------------------------------|-----------------------|-----------|-----------|-----------|
| <b>1a</b>   | 190                              | 35                    | 2.5       | < 0.2     | 136       |
| <b>1b</b>   | 102                              | 190                   | 2.6       | < 0.2     | 145       |
| <b>1c</b>   | 55                               | 42                    | 2.3       | < 0.2     | 148       |
| <b>1d</b>   | 765                              | 740                   | 2.7       | < 0.2     | 159       |
| <b>2a</b>   | 503                              | 128                   | 2.6       | < 0.2     | 151       |
| <b>2b</b>   | 446                              | 530                   | 2.7       | < 0.2     | 155       |
| <b>3a</b>   | 50                               | 620                   | 4.7       | 6.1       | 153       |
| <b>3b</b>   | 93                               | 780                   | 2.7       | 2.4       | 154       |

Table 3

Polymerization of liquid propylene with zirconocenes **2a** and **2b** and methylaluminumoxane as cocatalyst: Experimental values and comparisons with 'average performance' of incremental precursors

|                                | <b>2a</b> , experimental | Comparison: '( <b>1a</b> + <b>1d</b> )/2' | <b>2b</b> , experimental | Comparison: '( <b>1b</b> + <b>1d</b> )/2' |
|--------------------------------|--------------------------|---|--------------------------|---|
| Productivity (kg PP/mmol Zr h) | 503                      | 477                                       | 446                      | 433                                       |
| $M_w$ ( $10^3$ g/mol)          | 128                      | 388                                       | 530                      | 465                                       |
| m.p. (°C)                      | 151                      | 148                                       | 155                      | 152                                       |
| mm (%)                         | 95.8                     | 94.5                                      | 96.0                     | 95.8                                      |
| mr (%)                         | 2.6                      | 3.4                                       | 3.2                      | 2.7                                       |
| rr (%)                         | 0.9                      | 1.45                                      | 0.4                      | 1.2                                       |
| 2,1-i (%)                      | m-0.7                    | m-0.5 + r-0.2                             | m-0.4                    | m-0.4                                     |

Comparison values were calculated as arithmetic average of experimental values of incremental precursors (**1a–1d**, see Tables 1 and 2), i.e., (**1a** + **1d**)/2 in case of **2a** and (**1b** + **1d**)/2 in case of **2b**.

tions. The results are summarized in Tables 1 and 2 together with the data of suitable systems previously described ([4], see Fig. 1). The 'hybrid' structures **2a** and **2b** combine the indenyl moieties of  $C_2$ -symmetric zirconocenes **1a** and **1d** in case of **2a**, respectively, **1b** and **1d** in case of **2b** within one structure (**1a**, **1b**, **1d** see Fig. 1). Thus, it is interesting to compare the polymerization performance data of **2a** and **2b** with the arithmetic averages of the polymerization performance data of their incremental precursor structures **1a** and **1d**, and **1b** and **1d**, respectively. The comparison is shown in Table 3. Productivity numbers are in the range of the arithmetic averages defined above, stereospecificities (according to polymer melting point and NMR triad distributions) are high despite dissymmetry of structure (v.s., and cp. [9]) and tend to be slightly better than the average values. Polymer molecular weight is about 60% below the average value of the incremental precursors' performance in case of **2a**, which can be regarded as a marked deviation. The mononuclear precursor structure of binuclear zirconocenes **3a** and **3b** is species **1d** (see Fig. 1). Productivities of **3a** and **3b** are in the range of 10% of the mononuclear precursor structure activity, molecular weights are roughly the same as with **1d**, and melting points of polymer are reduced by 5–6°C. Comparing the NMR-data (Table 2) the reduction of regiospecificity (1.1,

respectively, 1.5% 2,1-insertions instead of 0.3% with **1d**) is the most remarkable observation<sup>2</sup>.

### 3. Discussion

It is generally accepted that isotactic propylene polymerisation with zirconocene/methylaluminumoxane catalysts takes place by a regioselective 1,2-insertion of the propylene monomer into the metal carbon bond between the zirconium central atom and the first carbon atom of the polymerizing chain. The active species is believed to be a cationic 14-electron complex of type  $(Cp_2Zr-alkyl)^+$ , stabilised by a voluminous aluminumoxane counterion which is just weakly coordinating, thus allowing olefin molecules to enter the inner coordination sphere for insertion. Fig. 4 shows a simplified picture of the cationic complex of **1d** (counterion and dimethylsilyl bridge are omitted) with the two prochiral positions of the monomer leading to 1,2-insertion. Due to repulsive interactions between the ligand frame, the polymer chain and the coordinated monomer the position with the

<sup>2</sup> In contrast to systems earlier described reduced regiospecificity of **3b** is not accompanied by reduction of polymer molecular weight which is a valuable property for purposes of industrial use. A likewise new and valuable combination of performance data is high m.p. and low  $M_w$  with **2a**.

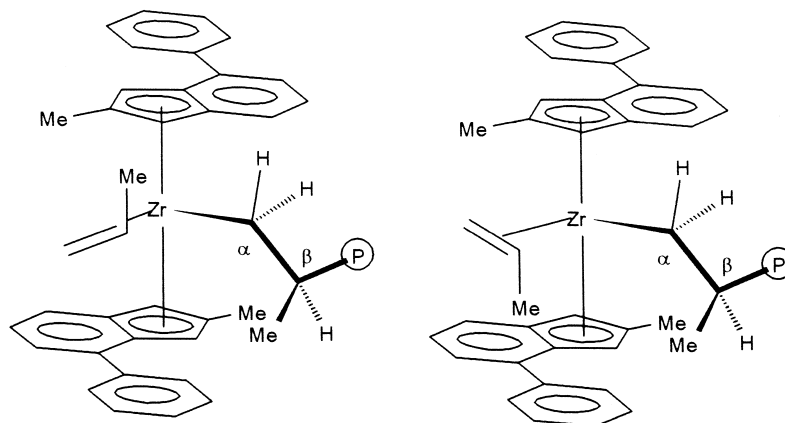


Fig. 4. Coordination positions of propylene for 1,2-insertion.

methyl group of propylene in trans-position to the  $\beta$ -carbon of the chain is energetically favored, which effect results in stereospecific polymerization [10]. Regioirregular (2,1) coordination and insertion is energetically disfavoured, but does occur as minor side reaction. Consecutive insertions might follow a ‘flip-flop-mechanism’, i.e., during insertion the chain migrates to the coordination position of the just inserted monomer, leaving the position just left for the next coordination. Such chain migration with or without insertion is well proven in case of metallocene catalysts of the bridged fluorenyl-cyclopentadienyl-type [11]. On the other hand in previously described bridged bisindenyl systems both coordination positions of the zirconium center are equivalent, due to the molecule’s  $C_2$ -symmetry, so that stationary or migratory chain mechanisms give identical polymerization results.

The following discussion of polymerization experiments with new metallocenes **2a**, **2b**, **3a**, **3b** will focus on a few instructive points, as the different influence factors on activity, chain termination (i.e., molecular weight of polymer) and stereospecificity have recently been reviewed [2,3,7] in a very competent and detailed manner.

According to our earlier investigations [4] the productivity differences between catalysts **1a**, **1b**, and **1d**, the incremental precursors of ‘hybrids’ **2a** and **2b**, can be satisfactorily inter-

preted by the mere electronic influence of their ligands. In line with this reasoning the productivity numbers of the ‘hybrid’ metallocenes **2a** and **2b** are about the arithmetic average productivities of **1a** + **1d**, and **1b** + **1d**, respectively (Table 3). On the other hand, molecular weights and melting points of polymer, which mainly follow sterical influences, deviate from such average values. This might be direct evidence of chain migration without insertion. In contrast to  $C_2$ -symmetric bisindenyl systems, the two possible coordination positions in systems **2a** and **2b** are sterically and, thus, energetically non-equivalent. Thus migration of the chain to energetically favoured position without insertion becomes a relevant pathway, and within the overall polymerization result, the influence of the sterical nature of one of the inequivalent positions must prevail. Fitting to the explanation, the largest deviation from ‘average’ values is  $M_w$  with system **2a**, the system with the larger differences between its two indenyl moieties.

In contrast to **2a** and **2b**, the productivity difference between binuclear zirconocenes **3a** and **3b** and their parent structure **1d** (a factor of 10–15, see Table 1) cannot be explained by electronic factors which influence chain propagation rate.

As the active zirconium is encountered with the (nearly, v.i.) same ligand surrounding in both **3a/3b** and **1d**, the chain termination rate

should stay the same. Massive reduction of chain propagation rate would then result in strong increase of polymer molecular weight which is not observed. Thus the reason of lower activity must be lower number of active centers. Several influence factors can be discussed:

- 50% or even some more of the zirconium centers are within meso-indenyl moieties and practically do not contribute to productivity (v.s.)

- poor solubility of the binuclear species in liquid propylene due to their high molecular weight

- enhanced rate of bimolecular deactivations [8]

- simultaneous polymerization activity of both zirconium centers in one binuclear species does not occur due to sterical reasons [12]

- high concentration of ‘dormant’ centres due to enhanced rate of 2,1-misinsertions (v.i.) [13].

As just mentioned, ‘dimerization’ of structure **1d** to binuclear species **3a** and **3b** reduces regioselectivity of the polymerization centers (2,1-irregularities 1.1–1.5% instead of 0.3% with **1d**, see Table 2). Reduction of polymer melting point is the macroscopic consequence<sup>3</sup>. The marked loss in regioselectivity is accompanied by a comparably small reduction in stereospecificity. Among previously described systems **1a–1d**, only 4,4′-bis-phenyl-substituted bisindenyl system **1c** shows a regioselectivity even poorer than that of **3a** and **3b**: Lack of substitution in 2,2′-position as in **1a** and unlike **1b**, gives space for 2,1-monomer coordination [14] and may also modify the effect of 4,4′-phenyl-groups on the position of the chain in a way contrary of their effect in **1d**, i.e., making re-

gioirregular insertion easier. Within **3a** and **3b**, similar slight distortions of the complex geometry, compared with **1d**, might be due to replacement of methyl groups on the bridge silicons by methylene groups or, at least in **3a**, merely by sterical interference of the two neighbored complex moieties. Other effects may contribute, e.g., reduction of regio- and stereospecificity by chain exchange between active centers, as recently proposed by Chien [7].

## 4. Experimental

All chemicals were reagent grade and purified as required. Hexane, tetrahydrofuran, toluene and diethylether used in metallorganic reactions were all dried and deoxygenated by distillation from sodium–potassium alloy under argon. Dichloromethane was dried and deoxygenated by distillation from calcium hydride under argon. NMR Spectra were obtained on a 100 MHz Bruker AM 100. Mass spectra were measured on a Finnigan MAT 95 Q, EI(70 eV), CI (*iso*-butane).

### 4.1. Preparation of metallocenes

#### 4.1.1. Dimethylsilanediyl(1-indenyl)(2-methyl-4-phenyl-1-indenyl)zirconium dichloride (**2a**)

35 ml of a 2.5 M solution of butyllithium in hexane were added dropwise at room temperature to a solution of 18 g (88 mmol) of 2-methyl-7-phenylindene [4] in 180 ml of toluene and 9 ml of diethyl ether. The mixture was subsequently stirred for a further 2 h at 40°C. The suspension was subsequently added dropwise at room temperature to a solution of 42.4 ml (348 mmol) dimethyldichlorosilane in 120 ml of toluene and the mixture was stirred for a further 3 h at room temperature. The solvent was removed in vacuo and the residue was dried in vacuo and subsequently taken up in 240 ml of toluene. To this solution there was added dropwise at room temperature a suspension of

<sup>3</sup> 2,1-regio-misinsertions are more effective in reducing polymer crystallinity and, thus, melting point than 1,2-stereo-misinsertions as shown in Table 2: Polypropylene made by a conventional TiCl<sub>3</sub> catalyst has a melting point 10°C higher than polypropylene made by e.g. metallocene **3a**, the former is less stereotactic according to isotactic triads mm, but essentially free of regioirregularities.

indenyllithium (prepared by reaction of 10.1 g (87 mmol) of indene (90% pure) in 100 ml of toluene and 5 ml of THF at room temperature with 35 ml of a 2.5 M solution of butyllithium in hexane and stirring for a further 1 h at 40°C) over a period of 50 min and the mixture was subsequently stirred for a further 2 h at room temperature. After aqueous work up the residue was purified by chromatography on 400 g of silica gel (hexane/CH<sub>2</sub>Cl<sub>2</sub> 9:1). 18.8 g (56%) of the ligand system of **2a** were obtained as a colorless solid. <sup>1</sup>H-NMR (100 MHz, CDCl<sub>3</sub>): 7.8–7.1 (m, 12 H, arom.); 6.9 (s, 1H, olef. inden.); 6.8 (m, 1 H, olef. inden.); 6.65 (m, 1 H, olef. inden.); 3.8 (s, 1 H, CH–Si); 2.3 (s, 3 H, CH<sub>3</sub>); 0.0 (s, 6 H, (CH<sub>3</sub>)<sub>2</sub>–Si). 19.7 ml (52.8 mmol) of a 20% solution of butyllithium in toluene were added dropwise at 50°C to a solution of 10.0 g (26.4 mmol) of the ligand system in 80 ml of toluene. The mixture was subsequently stirred for a further 2 h at 100°C. The mixture was cooled to –40°C and admixed with 6.15 g (25.4 mmol) of ZrCl<sub>4</sub> and stirred for a further 1 h at room temperature. After filtration through a G3 Schlenk frit the filtrate was evaporated to half its volume and left to crystallize at –30°C. This gave 3.9 g (26%) of **2a** as a colorless solid. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 6.9 to 7.7 (m, 14 H, arom. H and β-H), 6.2 (d, 1H, α-IndH), 2.3 (s, 3H, CH<sub>3</sub>), 1.3 (2 s, 6 H, CH<sub>3</sub>Si). Mass spectrum: 538 M<sup>+</sup>, correct disintegration pattern.

#### 4.1.2. Dimethylsilanediyl(2-methyl-1-indenyl)(2-methyl-4-phenyl-1-indenyl)zirconium dichloride (**2b**)

Following the procedure described for **2a** the bridged ligand system was prepared from 2-methylindenyllithium (prepared by reaction of 9.5 g (73 mmol) of 2-methylindene [15], 60 ml toluene, 6 ml of THF, 29 ml of a 2.5 M solution of butyllithium in hexane) added at room temperature to a solution of 21.9 g (73 mmol) of dimethyl(2-methyl-4-phenylindene)chlorosilane (v.s.) in 170 ml of toluene/10 ml THF. This gave 16.1 g (61%) of the ligand system of **2b** as

a colorless solid. <sup>1</sup>H-NMR (100 MHz, CDCl<sub>3</sub>): 7.8–7.1 (m, 12 H, arom.); 6.8 (s, 1 H, olef. inden.); 6.6 (s, 1 H, olef. inden.); 3.8 (s, 1 H, CH–Si); 3.7 (s, 1 H, CH–Si); 2.3 (s, 1 H, CH<sub>3</sub>), 2.25 (s, 3 H, CH<sub>3</sub>), –0.2 (s, 6 H, (CH<sub>3</sub>)<sub>2</sub>–Si). **2b** was prepared accordingly to **2a** (15.2 ml (40.8 mmol) 20% butyllithium in toluene, 8.0 g (20.4 mmol) ligand system in 50 ml toluene, 4.75 g (20.4 mmol) ZrCl<sub>4</sub>). 3.4 g (30%) of **2b** was obtained after crystallization at –30°C as a yellow solid. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 6.9 to 7.8 (m, 14 H, arom. H and β-H), 2.1 (2s, 6 H, CH<sub>3</sub>), 1.2 (2 s, 6 H, CH<sub>3</sub>Si). Mass spectrum: 550 M<sup>+</sup>, correct disintegration pattern.

#### 4.1.3. 1,2-Bis[methylsilyl-bis(2-methyl-4-phenylindenyl)zirconium dichloride]ethane (**3a**)

36.1 ml (97 mmol) of a 20% solution of butyllithium in toluene were added at room temperature over a period of 30 minutes to a solution of 20 g (97 mmol) of 2-methyl-7-phenylindene in 200 ml of toluene and 10 ml of THF. The mixture was heated for a further 2 h at 80°C. Subsequently, 6.2 g (24.2 mmol) of 1,2-bis(methyldichlorosilyl)ethane in 10 ml of toluene were added at 0°C and the mixture was stirred for further 1.5 h at room temperature. After aqueous workup and filtration through 200 g of silica gel (hexane/CH<sub>2</sub>Cl<sub>2</sub> 5:1), 11.8 g (52%) of the ligand system was obtained as a viscous oil. <sup>1</sup>H-NMR (100 MHz, CDCl<sub>3</sub>): 7.0 to 7.7 (m, 32 H, arom.); 6.6 to 6.9 (m, 4 H, H–C(3)); 3.4 to 3.7 (m, 4 H, H–C(1)), 1.9 to 2.2 (m, 12 H, CH<sub>3</sub>-indene); –0.3 to 1.1 (m, 10 H, CH<sub>2</sub>–Si and CH<sub>3</sub>Si). 21.5 ml (57.6 mmol) of a 20% solution of butyllithium in toluene were added dropwise at room temperature over a period of 30 min to a solution of 10.8 g (11 mmol) of ligand in 150 ml diethyl ether. After addition was complete, the mixture was heated under reflux for a further 2 h, the solvent was removed in vacuo and the residue was filtered using hexane through a G3 Schlenk frit. After drying the tetralithium salt was subsequently added at –78°C to a suspension of 5.4 g (23 mmol) of zirconium tetrachloride in 200 ml

$\text{CH}_2\text{Cl}_2$ . After warm up to room temperature the reaction mixture was filtered through a G3 Schlenk frit, the filtrate was freed of solvent in vacuo and the residue was washed a number of times with hexane. Subsequently, it was recrystallized from toluene at  $-30^\circ\text{C}$ . This gave 5.6 g (39%) of **3a** as isomer mixture in the form of a yellow amorphous solid.  $^1\text{H-NMR}$  (100 MHz),  $\text{CDCl}_3$ ): 6.8 to 7.8 (m, 36 H, arom. H and  $\beta$ -H-indene); 2.1 and 2.3 (2 m, 12 H,  $\text{CH}_3$ -indene); 1.2 to 2.0 (m, 10 H,  $\text{CH}_2\text{Si}$  and  $\text{CH}_3\text{Si}$ ). Mass spectrum:  $1250 \text{ M}^+$ , correct desintegration pattern.

#### 4.1.4. 1,6-Bis[methylsilyl-bis(2-methyl-4-phenyl-indenyl)]zirconium dichloride]hexane (**3b**)

Following the procedure described for **3a** (36.1 ml (97 mmol) 20% solution of butyllithium in toluene, 20 g (97 mmol) 2-methyl-7-phenylindene, 200 ml toluene, 10 ml THF, 7.6 g (24.3 mmol) 1,2-bis (methyl dichloro silyl) hexane) 11.7 g (48%) of the ligand system were obtained after chromatography ( $\text{SiO}_2$ , hexane/ $\text{CH}_2\text{Cl}_2$  5:1) as a viscous oil.  $^1\text{H-NMR}$  (100 MHz,  $\text{CDCl}_3$ ): 7.1 to 7.7 (m, 32 H, arom.); 6.7 to 6.9 (m, 4 H, H-C(3)); 3.6 to 3.8 (m, 4 H, H-C(1)); 2.1 to 2.3 (m, 12 H,  $\text{CH}_3$ -indene);  $-0.1$  to 1.3 (m, 18 H, 4  $\text{CH}_2$ ,  $\text{CH}_2$ -Si and  $\text{CH}_3\text{Si}$ ) The complex **3b** was obtained (22 ml (59 mmol) 20% solution of butyllithium in toluene, 11.7 g (12 mmol) ligand in 150 ml diethyl ether, 5.5 g (24 mmol) zirconium tetrachloride, 200 ml  $\text{CH}_2\text{Cl}_2$ ,  $-78^\circ\text{C}$  to room temperature) after recrystallization from toluene at  $-30^\circ\text{C}$ . This gave 7.3 g (47%) of **3b** as isomer mixture in the form of a yellow amorphous solid.  $^1\text{H-NMR}$  (100 MHz),  $\text{CDCl}_3$ ): 6.9 to 7.8 (m, 36 H, arom. H and  $\beta$ -H-indene); 2.3 and 2.5 (2 m, 12 H,  $\text{CH}_3$ -indene); 1.2 to 1.7 (m, 18 H, 4  $\text{CH}_2$ ,  $\text{CH}_2\text{Si}$  and  $\text{CH}_3\text{Si}$ ). Mass spectrum:  $1250 \text{ M}^+$ , correct desintegration pattern.

#### 4.2. Polymerizations

Polymerization grade propylene was further purified by passage through columns of 10 A

molecular sieves prior to polymerization. A solution of methylaluminumoxane in toluene (10 wt% MAO, cryoscopic  $M_w = 950 \text{ g/mol}$ ) purchased from Witco GmbH was directly applied. Polymerizations were conducted according the following procedure: A dry 16-l, thermostatable steel reactor was charged with nitrogen and 10 l of liquid propylene at  $30^\circ\text{C}$ . Then 30 ml of the solution of methylaluminumoxane in toluene (v.s., 45 mmol Al) was added to the stirred reactor. Simultaneously, the calculated amount of metallocene (6.3  $\mu\text{mol}$ ; Zr:Al = 1:12000) was dissolved in an identical solution of methylaluminumoxane in toluene (20 ml, 30 mmol) and allowed to react for 15 min at  $25^\circ\text{C}$ . The coloured solution was then added to the reactor. The reactor was heated to  $70^\circ\text{C}$  within 3 min and kept at this temperature for 1 h. The reaction was stopped by the addition of isopropanol (10 ml), cooled, the pressure released, the product taken out and dried in vacuum. The yield was determined by weighing.

#### 4.3. Polymer analyses

Molecular masses were determined by gel permeation chromatography on a Waters 150 C instrument (solutions in 1,2-dichlorobenzene at  $135^\circ\text{C}$ ). Melting points were determined with a Perkin Elmer DSC-4 system at a heating rate of  $20^\circ\text{C}/\text{min}$ .  $^{13}\text{C-NMR}$  measurements were performed on a Bruker WP 300 instrument at  $110^\circ\text{C}$ , (the polymer dissolved in hexachlorobutadiene/ $\text{CDCl}_2\text{CDCl}_2$ ). Spectra were evaluated according to the literature [16,17].

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