

Dinuclear ansa zirconocene complexes containing a sandwich and a half-sandwich moiety as catalysts for the polymerization of ethylene

Helmut G. Alt*, Rainer Ernst, Ingrid K. Böhmer

Laboratorium für Anorganische Chemie der Universität Bayreuth, Lehrstuhl für Anorganische Chemie II, Universität Bayreuth, Postfach 10 12 51, Universitätsstrasse 30, NW I, D-95440 Bayreuth, Germany

Received 16 May 2002; received in revised form 5 June 2002; accepted 14 June 2002

Abstract

Dinuclear ansa zirconocene complexes containing a half-sandwich and a sandwich moiety and their ligand precursors have been synthesized and characterized. After activation with methylalumoxane (MAO), these catalysts produce polyethylenes with bimodal molecular weight distributions in homogeneous and heterogeneous media. The catalyst performances and the polymer properties were compared with mono nuclear reference catalysts. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ansa zirconocene; Half-sandwich complexes; Dual site catalysts; Dinuclear complexes; Homogeneous and heterogeneous ethylene polymerization

1. Introduction

In the last decade metallocene complexes have been established as excellent catalysts for the polymerization of ethylene and propylene [1–5]. The produced polyolefins have narrow molecular weight distributions due to identical active sites of the catalyst. However, this can be disadvantageous for industrial processing. In order to obtain broader molecular weight distributions, cumbersome or costly approaches, like the blending of different resins, are necessary. On the other side, in most cases, it is not possible to obtain the desired multi modal resins by mixing individual mono nuclear catalysts (averaging effect). Therefore, it was the intention to solve this problem with dinuclear complexes as catalyst precursors. Two different active sites in one molecule should be able to produce two different polymer chains with different molecular weights. Other known dinuclear complexes do not unify two different catalytic centers

[6–13]. The model compounds presented in this paper should provide the advantages of both the half-sandwich (high molecular mass) [14,15] and the sandwich catalysts (low molecular mass) [5,16,17] and thus have the potential of dual site catalysts.

2. Results and discussion

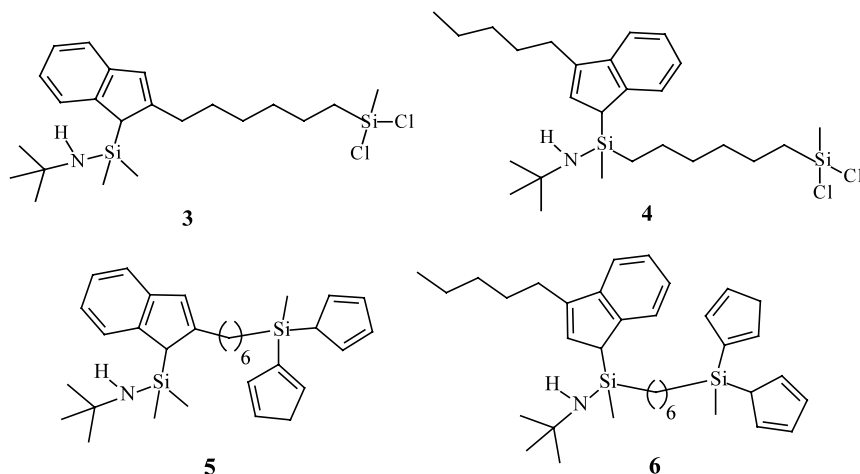
2.1. Synthesis of the ligand precursors

For the preparation of asymmetric dinuclear metallocene complexes, a ligand precursor with an ω -alkenyl functionality is reacted catalytically with dichloromethylsilane in a hydrosilylation reaction [18]. This chlorosilane intermediate then reacts in an S_N2 reaction [19–23] with two equivalents of sodium cyclopentadienide to form the ligand precursor (Scheme 1).

In the same manner, the following intermediates and ligand precursors were synthesized:

* Corresponding author. Tel.: +49-921-552555; fax: +49-921-552157

E-mail address: helmut.alt@uni-bayreuth.de (H.G. Alt).

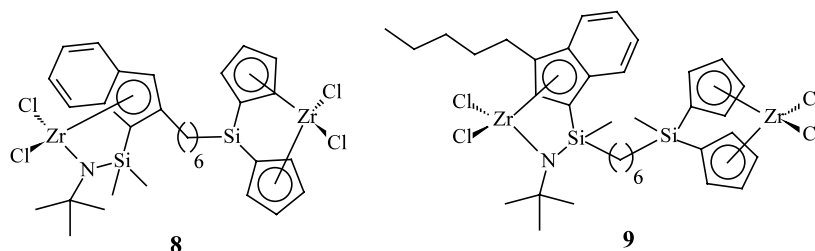


2.2. Synthesis of the dinuclear complexes 7–9

The reaction of such a ligand precursor with four equivalents of butyllithium and two equivalents of zirconium tetrachloride leads to the dinuclear complexes 7–9 (Scheme 2).

The following complexes were synthesized in the same manner:

Compounds 7–9 showed mid range activities in the homogeneous polymerization which varied around the value for reference catalyst 11/methylalumoxane (MAO). The homogeneous polymerization with 9/MAO exceeded the activity of the reference catalyst 11/MAO by ca. 50%. The activities from the heterogeneous experiments were generally lower than those from the homogeneous series. This result confirms the



For comparison purposes, the already known silyl bridged sandwich complex 10 [20,23] (Scheme 3) and the half-sandwich complex 11 [14,15] (Scheme 4) were synthesized.

2.3. Polymerization of ethylene

Half-sandwich catalysts of titanium and zirconium are known to produce polyethylenes of very high molecular masses ($> 10^6 \text{ g mol}^{-1}$) [13,14]. In contrast, silyl bridged bis(cyclopentadienyl) catalysts produce resins with a significantly lower molecular mass ($< 5 \times 10^5 \text{ g mol}^{-1}$) [20,23]. The polymerization properties of the asymmetric dinuclear complexes 7–9 meet the expectations (Table 1).

observations from other metallocene catalysts [17,20,23] where heterogenization on silica gel causes decreasing activities (Scheme 5). The lowest decrease is observed in the case of the half-sandwich reference catalyst 11/MAO.

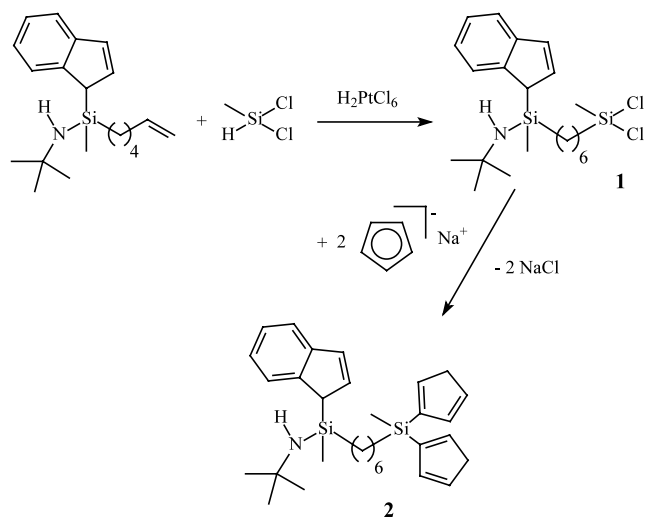
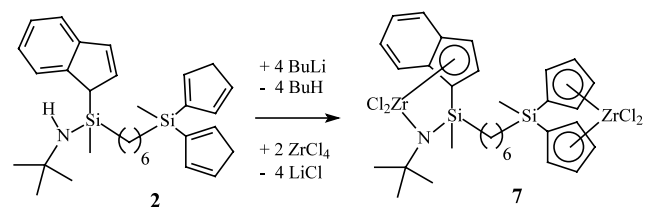
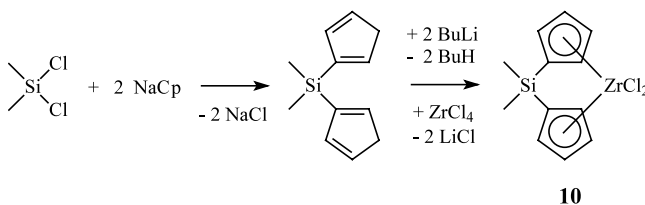
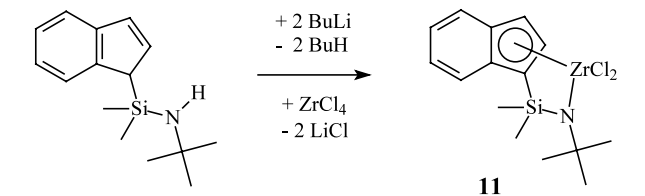
The molecular masses of these polyethylenes produced with the dinuclear catalysts 7–9/MAO are significantly higher than those of the reference catalyst 10/MAO; the trend of the molecular weights by heterogenization was not found to follow a certain rule (Scheme 6).

The polymer produced with catalyst 11/MAO shows the highest M_n of the complete series both under homo- and heterogeneous conditions. All other polymers vary around $M_n = 80 \text{ kg mol}^{-1}$ under homogeneous condi-

Table 1
Polymerization data

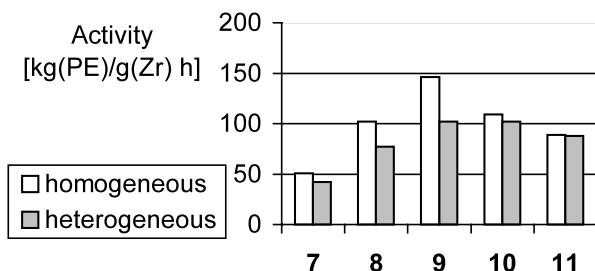
Catalyst	Activity g(PE)/g(Zr) h	M_n M_w M_n M_z Polydispersity HI	T_m ΔH_m Crystallinity α
<i>Homogeneous conditions</i>			
7	51,000	81,210	138.1
		505,500	147.3
		1,654,000	50.8
		406,400	
		6.2	
8	102,000	85,230	139.3
		614,800	145.8
		2,098,000	50.3
		498,900	
		7.5	
9	146,000	70,400	140.9
		578,600	175.6
		2,983,000	60.6
		446,100	
		8.2	
10	109,000	95,120	n.d.
		266,400	
		851,600	
		217,200	
		2.8	
11	89,000	261,500	n.d.
		737,200	
		1,981,000	
		717,200	
		2.8	
<i>Heterogeneous conditions (supported on silica gel)</i>			
7	42,000	33,400	139.3
		406,950	147.8
		1,679,990	50.9
		316,000	
		12.2	
8	77,000	91,060	140.1
		710,200	149.1
		2,417,000	51.4
		577,100	
		7.8	
9	102,000	45,140	136.5
		357,450	155.6
		1,329,840	53.7
		284,090	
		7.9	
10	102,000	104,000	n.d.
		271,200	
		1,075,000	
		258,900	
		2.6	
11	88,000	196,100	n.d.
		488,300	
		2,008,000	
		416,900	
		2.5	

n.d., not determined.

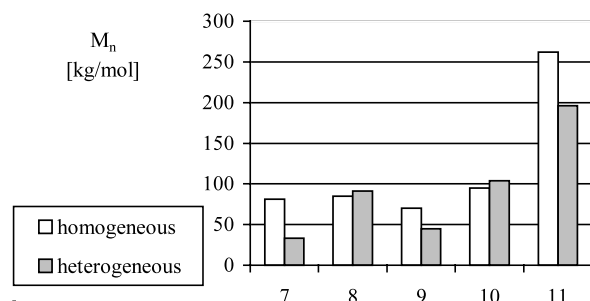
Scheme 1. Synthesis of the intermediate **1** and the ligand precursor **2**.Scheme 2. Synthesis of the dinuclear complex **7**.Scheme 3. Synthesis of the mono nuclear silyl bridged metallocene complex **10**.Scheme 4. Synthesis of the mono nuclear amido silyl half-sandwich complex **11**.

tions. Silica supported catalysts develop molecular masses that are in the range of the homogeneously produced polymers or below (Scheme 6).

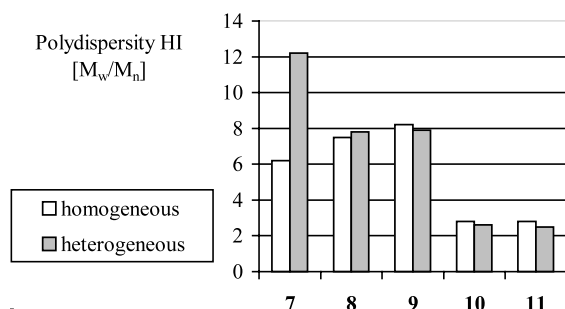
Polymerization with the dinuclear complexes/MAO gave resins with a broader molecular mass distribution width HI than with mononuclear complexes. The polydispersities observed were between HI = 6.2 and



Scheme 5. Activities of the catalysts 7–11/MAO in the homogeneous and heterogeneous polymerization reactions of ethylene.



Scheme 6. Molecular weights M_n of the polyethylenes obtained from 7–11/MAO.



Scheme 7. Polydispersities HI of the polyethylenes obtained from 7–11/MAO.

12.2 under homo- and heterogeneous conditions. They exceeded the values of the reference polymers of 10/MAO (homogeneous: HI = 2.8; heterogeneous: HI = 2.6) and 11/MAO (homogeneous: HI = 2.8; heterogeneous: HI = 2.5) by more than 100% (Scheme 7).

This width increase is especially pronounced with the polyethylene produced from 7/MAO where two relative maxima can be seen in the HT-GPC plot (Scheme 8).

It is well known from former results that half-sandwich catalysts produce polyethylenes with high molecular masses ($> 10^6$ g mol⁻¹) [13,14]. The amido silyl compounds are sterically not very demanding and the active center of the catalysts is easily accessible for the addition of the monomer. Polymer growth occurs stress free, termination reaction only starts at high molecular weight. It can be postulated that the fraction with a maximum at 700,000 g mol⁻¹ is produced by the half-sandwich component, the fraction with a maximum

at 25,000 g mol⁻¹ by the sandwich component of catalyst 7. This conclusion can be derived from the properties of the monomeric reference catalysts and the produced polymers.

The HT-GPC curve does not always show two separate maxima but a distinct broadening of the molecular mass distribution relative to the mononuclear catalysts.

Polymerization with a 1:1 mixture of 10/MAO and 11/MAO does not give the same bimodal molecular weight distribution as with 9/MAO. The 1:1 mixture of 10/MAO and 11/MAO produces a mononuclear resin with only a slightly broadened molecular weight. We assume that in the mixture, the two originally different active sites ‘communicate’ with each other, eventually via the cocatalyst MAO to give an ‘averaged’ molecular weight.

In the dinuclear catalysts, the active sites are separated from each other and cannot undergo such a reaction. This behavior is the major justification for the preparation of such dual site catalysts.

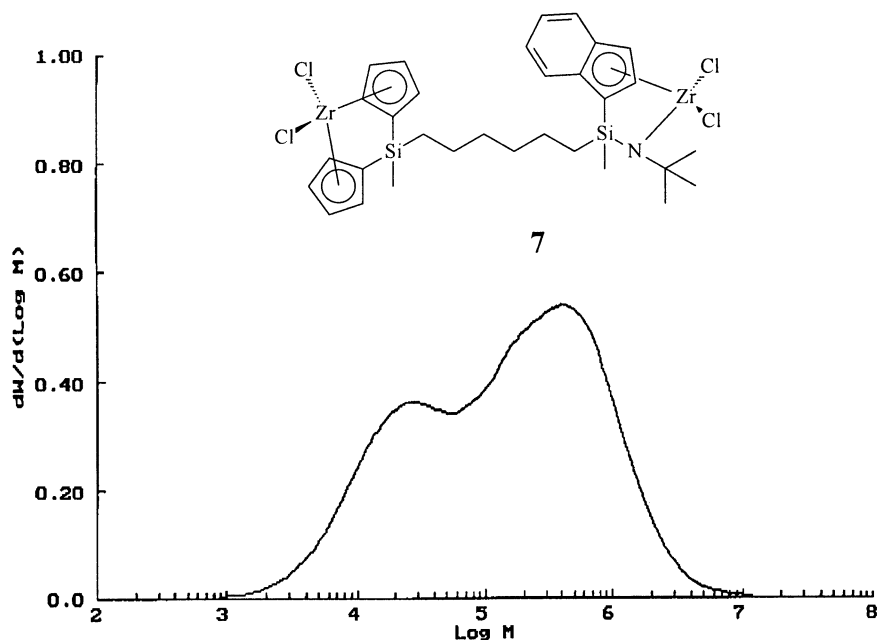
3. Experimental

All experimental work was routinely carried out using Schlenk technique. Dried and purified Ar was used as inert gas. Toluene, pentane, diethylether and tetrahydrofuran were purified by distillation over Na/K alloy. Ether was additionally distilled over LiAlH₄. Methylene chloride was dried with CaH₂. Deuterated solvents such as CHCl₃-d₁ and C₆H₆-d₆ were dried over molecular sieves (300 pm), degassed and stored under inert gas atmosphere.

Commercially available indene was distilled and stored at –28 °C. Cyclopentadiene was freshly distilled from the dimer. MAO (30% in C₆H₅CH₃) was supplied by Witco Company, Bergkamen. All the other starting materials were commercially available and were used without further purification.

3.1. NMR spectroscopy

The spectrometer Bruker ARX 250 was available for the recording of the NMR spectra. The organometallic compounds were prepared under inert gas atmosphere (Ar). The spectra were recorded at 25 °C. The chemical shifts in the ¹H-NMR spectra are referred to the residual proton signal of the solvent (δ = 7.24 ppm for CHCl₃, δ = 7.15 ppm for C₆H₆) and in the ¹³C-NMR spectra to the solvent signal (δ = 77.0 ppm for CHCl₃-d₁, δ = 128.0 ppm for C₆H₆-d₆). Tetramethylsilane (δ = 0.0 ppm) was used as external reference for ²⁹Si-NMR spectra.



Scheme 8. Molecular weight distribution of the polyethylene produced with 7/MAO under homogeneous conditions.

3.2. GC–MS and mass spectroscopy

GC–MS spectra were performed with a HP5971A mass detector in combination with a HP5890 gas chromatograph. Helium was applied as carrier gas, a 12 m J&W Fused Silica column (DB 1, film 0.25 μm) was used. The measuring program was: 3 min at 70 $^{\circ}\text{C}$ (starting phase); 20 $^{\circ}\text{C min}^{-1}$ (heating phase); variable time at 210 $^{\circ}\text{C}$ (final phase).

The mass spectra were recorded with a VARIAN MAT CH7 instrument, GC–MS with a VARIAN 3700 gas chromatograph in combination with a VARIAN MAT 312 mass spectrometer.

3.3. Gas chromatography

Gas chromatograms were recorded using a Perkin–Elmer Auto System gas chromatograph with flame ionization detector (FID) and He as carrier gas (1 ml min^{-1}).

Temperature program:

Starting phase: 3 min at 50 $^{\circ}\text{C}$
 Heating phase: 5 $^{\circ}\text{C min}^{-1}$ (15 min)
 Plateau phase: 310 $^{\circ}\text{C}$ (15 min)

3.4. High temperature gel permeation chromatography (HT-GPC)

A Waters HT-GPC 150C instrument was applied to measure the mass distributions of the polymer samples. Four columns filled with cross-linked polystyrene were used for separation of the fractions. The pore diameters

of the styragels were 500, 1000, 10,000 and 100,000 $\text{\AA}$ in the individual columns. A RI Waters 401 refractometer was used for detection. The polymer samples were dissolved in boiling 1,2,4-trichlorobenzene that was also used as eluent. The measurements were carried out at 150 $^{\circ}\text{C}$. The apparatus was calibrated with an internal polystyrene standard.

3.5. Synthesis of the chlorosilane precursors

3.5.1. General procedure

ω -Alkenyl substituted half-sandwich ligand precursor (10 mmol) in 10 ml of C_5H_{12} and ca. 50 mg of hexachloroplatinic acid hydrate were given to a Schlenk vessel at room temperature (r.t.). Methylchlorosilane (1.15 g, 10 mmol) was added and the mixture was stirred for 40 h. Then the suspension was filtered through Na_2SO_4 and the solvent was removed in vacuo. Yields: 90–95%.

3.6. Synthesis of the ligand precursors 1–6

3.6.1. General procedure

The corresponding chlorosilane precursor (5 mmol) in 100 ml of Et_2O was treated with 0.88 g (10 mmol) sodium cyclopentadienide dissolved in 10 ml of THF. The mixture was stirred for 8 h at r.t. The suspension was filtered through Na_2SO_4 and the solvent was removed in vacuo. Yields: 90–95%.

Table 2
NMR data of compounds 1–9

Compound	¹ H-NMR	¹³ C-NMR	²⁹ Si-NMR
1	7.59–7.19 (m, 5H, ar H, Ind), 6.61 (s, 1H, ar H, Ind), 3.79 (s, 1H, al H, Ind), 2.03–0.57 (m, 12H, bridge), 0.91 (s, 3H, N–Si–CH ₃), 0.78 (s, 9H, ^t Bu), 0.14 (s, 3H, Cl–Si–CH ₃)	144.7, 143.1 (C _q , Ind), 131.5, 129.9, 126.6, 124.6, 122.6 (CH, Ind), 44.9 (CH, al, Ind), 32.1, 30.0, 22.5, 21.8, 18.2, 14.2 (CH ₂ , bridge), 4.2 (CH ₃ , ^t Bu), 0.9, –0.2 (Si–CH ₃)	33.1 (Cl–Si), 4.2 (Ind–Si)
2	7.50–7.22 (m, 12H, ar H, Ind), 6.95–6.47 (m, 8H, ar H, Cp), 3.52 (s, 2H, al H, Ind), 3.06–3.00 (m, 2H, al H, Cp), 1.26–0.45 (m, 12H, bridge), 1.21 (m, 9H, ^t Bu), 0.02–0.10 (s, 6H, Si–CH ₃)	144.6, 143.9 (C _q , Ind, Cp), 138.5, 132.9, 129.6, 126.2, 124.5, 122.3 (CH, ar, Ind, Cp), 47.3 (CH, al, Ind, Cp), 33.1, 29.9, 23.9, 22.9 (CH ₂ , bridge), –3.2, –4.5 (Si–CH ₃)	5.5, –7.3
3	7.67–7.31 (m, 4H, ar H, Ind), 6.41 (s, 1H, ar H, Ind), 3.72 (s, al H, Ind), 2.76–2.71, 1.87–1.23 (m, 12H, bridge), 1.33 (s, 3H, N–Si–CH ₃), 0.84 (s, 9H, ^t Bu), 0.29 (s, 6H, Cl–Si–CH ₃)	144.8, 143.9 (C _q , Ind), 127.8, 125.8, 124.6, 123.7, 119.5 (CH, ar, Ind), 45.7 (CH, al, Ind), 33.5, 33.1 (CH ₃ , ^t Bu), 31.9, 27.5, 23.6, 19.9 (CH ₂ , bridge), 5.4, 0.3, ±0.0 (Si–CH ₃)	32.8 (Cl–Si), 7.3 (Ind–Si)
4	7.63–7.22 (m, 4H, ar H, Ind), 6.34 (s, 1H, ar H, Ind), 3.69 (s, 1H, al H, Ind), 2.68–0.54 (m, 20 H, bridge, pentyl-substituent), 0.91 (s, 3H, N–Si–CH ₃), 0.79 (s, 9H, ^t Bu), 0.18 (s, 6H, Cl–Si–CH ₃)	145.1, 144.6, 143.8 (C _q , Ind), 127.5, 125.6, 124.4, 123.6, 119.5 (CH, ar, Ind), 44.9 (CH, al, Ind), 32.5, 32.1, 28.4, 27.9, 22.7, 22.4, 21.7, 16.6 (CH ₂ , bridge, pentyl-substituent), 15.8 (CH ₃ , ^t Bu), 14.3 (CH ₃), –1.4, –1.9 (Si–CH ₃)	33.1 (Cl–Si), 5.4 (Ind–Si)
5	7.52–7.19 (m, 12H, ar H, Ind), 6.93–6.23 (m, 8H, ar H, Cp), 3.54 (s, 2H, al H, Ind), 3.02 (m, 2H, al H, Cp), 1.77–0.13 (m, 8H, bridge), 1.23 (s, 9H, ^t Bu), –0.07–0.26 (s, 9H, Si–CH ₃)	145.7, 144.8 (C _q , Ind, Cp), 132.9, 129.3, 125.1, 124.1, 123.2, 119.4 (CH, ar, Ind, Cp), 46.3 (CH, al, Cp), 32.5, 29.9, 27.6, 23.4 (CH ₂ , bridge), –4.6, –5.9 (Si–CH ₃)	–7.0
6	7.53–7.26 (m, 12H, ar H, Ind), 6.98–6.33 (m, 8H, ar H, Cp), 3.68 (s, 2H, al H, Ind), 3.01 (m, 2H, al H, Cp), 1.34–0.55 (m, 20H, bridge), 1.19–1.17 (m, 9H, ^t Bu), 0.05–0.13 (s, 6H, Si–CH ₃)	144.9, 144.3 (C _q), 137.3, 133.2, 127.8, 125.4, 124.7, 122.6 (CH, ar, Ind, Cp), 46.4 (CH, al, Cp), 35.4, 32.6, 29.6, 24.3, 23.6, 22.8 (CH ₂ , bridge), –4.2, –5.9 (Si–CH ₃)	4.9, –7.5
7	7.55–6.38 (m, 14H, ar H), 2.72–0.46 (m, 23H, bridge, pentyl-substituent), 1.33 (s, 9H, ^t Bu), –0.03, –0.15 (s, 6H, Si–CH ₃)	145.8, 145.1 (C _q , Ind, Cp), 138.3, 132.9, 130.9, 129.4, 125.1, 123.9, 119.5 (CH, Ind, Cp), 45.9 (C _q , ^t Bu), 33.2, 32.2, 29.9, 28.6, 27.6, 24.2, 24.1, 22.8, 13.4, 13.3 (CH ₂ , bridge, pentyl-substituent), 14.3 (CH ₃ , ^t Bu), 5.8, –6.7 (Si–CH ₃)	–7.5 (Cp–Si), –9.5 (Ind–Si)
8	7.64–6.61 (m, 14H, ar H), 2.30–0.41 (m, 12H, bridge), 1.41 (s, 9H, ^t Bu), 0.11–0.01 (s, 6H, Si–CH ₃)	145.6, 143.9 (C _q , Ind, Cp), 131.0, 128.3, 126.4, 123.9, 121.4 (CH, Ind, Cp), 32.2, 29.7, 27.1, 26.5, 24.3, 22.9 (CH ₂ , bridge), 4.5 (CH ₃ , ^t Bu), 1.9, –6.5 (Si–CH ₃)	–7.6 (Cp–Si), –8.1 (Ind–Si)
9	7.62–6.67 (m, 14H, ar H), 2.74–0.47 (m, 8H, bridge), 1.05 (s, 9H, ^t Bu), 0.21, 0.19, –0.01 (s, 9H, Si–CH ₃)	145.8, 144.6 (C _q , Ind, Cp), 130.7, 128.6, 127.5, 124.7, 119.8 (CH, Ind, Cp), 33.2, 32.9 (^t Bu), 30.8, 30.7, 27.4, 26.2, 19.8, 14.1 (CH ₂ , bridge), 0.3, 0.2, –6.5 (Si–CH ₃)	–7.8 (Cp–Si), –12.9 (Ind–Si)

3.7. Synthesis of the dinuclear complexes 7–9

3.7.1. General procedure

The ligand precursor (5 mmol) was dissolved in 400 ml of Et₂O and 12.5 ml (20 mmol) of *n*-butyllithium (1.6 M in C₆H₁₄) were added. The reaction mixture was stirred for a minimum of 8 h at r.t.

The solution was cooled to –78 °C. Then 2.33 g (10 mmol) of ZrCl₄ was added. The reaction mixture was brought to r.t. within 6 h and stirred for another 6 h. The solvent was removed in vacuo, the residue suspended in CH₂Cl₂ and the suspension filtered through Na₂SO₄. The CH₂Cl₂ phase was removed in vacuo, the residue washed with C₅H₁₂ and the product crystallized from CH₂Cl₂/C₅H₁₂. Yields: 60–70% (Table 2).

3.8. Synthesis of the ligand precursors for the mono nuclear complexes

3.8.1. General procedure

Dichlorodimethylsilane (2.58 g, 20 mmol) in 200 ml of Et₂O and 10 mmol of sodium cyclopentadienide (or 10 mmol of fluorenyllithium) were mixed at r.t. in a Schlenk vessel. The mixture was stirred for 8 h, then filtered through Na₂SO₄ and silica gel. The solvent was removed in vacuo. Yield: 95%.

3.9. Preparation of the indenyl chlorosilane precursor

Indene (80 mmol) in 150 ml of Et₂O was treated with 50 ml (80 mmol) of butyllithium (1.6 M solution in C₆H₁₄). The solution was stirred for 4 h at r.t. Then it was cooled to –78 °C. Dichlorodimethyl silane (80

mmol) was added, slowly warmed to r.t. and stirred for 12 h. The suspension was filtered through Na_2SO_4 and the solvent was removed in vacuo. Yield: 95%.

3.10. Preparation of the indenyl ligand precursor

The indenyl chlorosilane precursor (80 mmol) in 200 ml of CH_2Cl_2 was treated with 200 mmol of *t*-butylamine at r.t. The mixture was stirred for 12 h, then the solvent was removed in vacuo. The residue was suspended in 200 ml of C_5H_{12} and the suspension was filtered through Na_2SO_4 . The solvent was removed in vacuo. Yield: 95%.

3.11. Preparation of the mono nuclear zirconocene complex 10

The ligand precursor (10 mmol) was dissolved in 200 ml of Et_2O . Butyllithium solution (12.5 ml, 1.6 M in C_6H_{14} ; 20 mmol) was added. The mixture was stirred for at least 8 h at r.t. Then the solution was cooled to -78°C and 2.33 g (10 mmol) of ZrCl_4 was added. The mixture was brought to r.t. within 6 h and stirred for another 6 h. The solvent was removed in vacuo, the residue was suspended in CH_2Cl_2 and the suspension was filtered through Na_2SO_4 . The solvent of the CH_2Cl_2 phase was removed in vacuo, the residue was washed with C_5H_{12} and Et_2O several times, dissolved in CH_2Cl_2 and the solution was crystallized at -28°C . Yields: 50–70%.

3.12. Synthesis of the amidosilyl zirconium complex 11

The ligand precursor (20 mmol) was dissolved in 400 ml of Et_2O . Butyllithium solution (12.5 ml, 1.6 M in C_6H_{14} ; 20 mmol) was added at -78°C . The mixture was stirred for 12 h at r.t. Then the solution was cooled to -78°C again and 4.66 g (20 mmol) of ZrCl_4 was added. The mixture was brought to r.t. within 10 h and stirred for another 10 h. The solvent was removed in vacuo, the residue was suspended in C_5H_{12} and the suspension was filtered through Na_2SO_4 . The solvent was removed in vacuo, the residue was suspended in C_5H_{12} and the LiCl containing solution was filtered. The solution was stored for 24 h at -28°C . The yellowish complex precipitated. Yield: 35%.

3.13. Polymerization reactions

An amount of 20–25 mg of the corresponding complex was dissolved in 50 ml of $\text{C}_6\text{H}_5\text{CH}_3$. A volume of the solution containing 1–2 mg of complex was taken and activated with MAO (30% in $\text{C}_6\text{H}_5\text{CH}_3$; Al–Zr = 2500:1).

For heterogeneous polymerizations silica gel was added (1 g $\text{SiO}_2 \mu\text{mol}^{-1}$ (Zr)) to this solution and the

suspension was stirred for 3 min. Both for homogeneous and heterogeneous polymerizations, the catalyst suspension was diluted with 250 ml of C_5H_{12} and injected to a 1 l Büchi laboratory autoclave thermostated at $60 \pm 3^\circ\text{C}$. An ethylene pressure of 10 bar was applied to the reactor and the catalyst was polymerized for 30 min at $60 \pm 3^\circ\text{C}$. The obtained polymer was dried in air for at least 60 h. The polymerization results and the physical data of the polymers are presented in Table 1.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (DFG) and Phillips Petroleum Company (Bartlesville, OK, USA) for the financial support and Witco company (Bergkamen) for the donation of methylalumoxane.

References

- [1] (a) H.-H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. Waymouth, *Angew. Chem.* 107 (1995) 1255;
(b) H.-H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. Waymouth, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 1143.
- [2] M. Bochmann, *J. Chem. Soc. Dalton Trans.* (1996) 255.
- [3] F. Küber, *Chem. Unserer Zeit* 28 (1994) 197.
- [4] W. Kaminsky, *J. Chem. Soc. Dalton Trans.* (1998) 1413.
- [5] H.G. Alt, A. Köppl, *Chem. Rev.* 100 (2000) 1205 (and references therein).
- [6] W. Spaleck, F. Küber, B. Bachmann, C. Fritze, A. Winter, *J. Mol. Catal. A* 128 (1998) 279.
- [7] S. Ciruelos, T. Cuenca, P. Gómez-Sal, A. Manzanero, P. Royo, *Organometallics* 14 (1995) 177.
- [8] S.K. Noh, J. Kim, J. Jung, C.S. Ra, D. Lee, H.B. Lee, S.W. Lee, W.S. Huh, *J. Organomet. Chem.* 580 (1999) 90.
- [9] K.P. Reddy, J.L. Petersen, *Organometallics* 8 (1989) 2107.
- [10] H. Lang, S. Blau, A. Muth, K. Weiss, U. Neugebauer, *J. Organomet. Chem.* 490 (1995) C32.
- [11] I.E. Nifant'ev, M.V. Borzov, A.V. Churakov, S.G. Mkoyan, L.O. Atovmyan, *Organometallics* 11 (1992) 3942.
- [12] W. Abriel, G. Baum, H. Burdorf, J. Heck, *Z. Naturforsch. Teil. B* 46 (1991) 841.
- [13] M. Bochmann, S.J. Lancaster, M.B. Hursthouse, M. Mazid, *Organometallics* 12 (1993) 4718.
- [14] (a) G.J.P. Britovsek, V.C. Gibson, D.F. Wass, *Angew. Chem.* 111 (1999) 448;
(b) G.J.P. Britovsek, V.C. Gibson, D.F. Wass, *Angew. Chem. Int. Ed. Engl.* 38 (1999) 428.
- [15] H.G. Alt, *J. Mol. Catal. A: Chem.* 174 (2001) 35.
- [16] B. Peifer, W. Milius, H.G. Alt, *J. Organomet. Chem.* 553 (1998) 205.
- [17] H.G. Alt, M. Jung, *J. Organomet. Chem.* 580 (1999) 1.
- [18] J.L. Speier, *Adv. Organomet. Chem.* 17 (1979) 407.
- [19] U. Stehling, J. Diebold, R. Kirsten, W. Röhl, H.H. Brintzinger, S. Jüngling, R. Mülhaupt, F. Langhauser, *Organometallics* 13 (1994) 964.
- [20] S.J. Palackal, Dissertation, Universität Bayreuth, 1991.
- [21] N. Klouras, H. Köpf, *Monatsh. Chem.* 112 (1981) 887.
- [22] C.S. Baygur, W.R. Tikkanen, J.L. Petersen, *Inorg. Chem.* 24 (1985) 2539.
- [23] K. Patsidis, H.G. Alt, W. Milius, S.J. Palackal, *J. Organomet. Chem.* 509 (1996) 63.