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Journal of Molecular Catalysis A: Chemical 195 (2003) 11–27

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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Dinuclear ansa zirconocene complexes as dual-site catalysts for the polymerization of ethylene

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Received 8 July 2002; accepted 16 September 2002

Abstract

A series of 21 dissymmetric dinuclear ansa zirconocene complexes and their ligand precursors have been synthesized and characterized. After activation with methylalumoxane (MAO), these catalysts polymerize ethylene with different productivities and polydispersities in homogeneous and heterogeneous media. The tendencies of these series are shown.

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

1. Introduction

Specially designed mononuclear metallocene complexes have proven to be excellent single-site catalysts for the polymerization of ethylene [1–5]. The resulting polyolefins can be produced with a very high catalyst productivity and the polymer has a typical narrow molecular weight distribution. This fact can be disadvantageous in industrial processing. Catalyst mixtures were used to obtain broader molecular weight distributions but sometimes with the negative side-effect of a loss of productivity. It was the intention to design dissymmetric dinuclear metallocene complexes with the potential of dual-site catalysts in order to solve this problem. The known dinuclear metallocene complexes do not unify two different catalytic centers [6–13].

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2. Results and discussion

2.1. Synthesis of the dichlorosilane and tetrachlorodisilane precursors

The dichlorosilanes and tetrachlorodisilanes **1**–**19** were synthesized according to Schemes 1–3.

The hexenyl derivative **5** was formed by a catalytic hydrosilation reaction [14,15].

The resulting ω-alkenyl substituted methyldichlorosilane derivatives were treated with an alkyl (i.e. methyl, ethyl or isopropyl) derivative of dichlorosilane in a catalytic hydrosilation reaction.

2.2. Synthesis of the ligand precursors

The tetrachlorodisilane derivatives were treated with four equivalents of sodium cyclopentadienide. The ligand precursors were formed by salt elimination reactions according to Scheme 4 [16–20].

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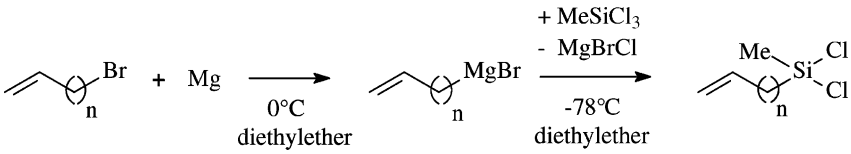
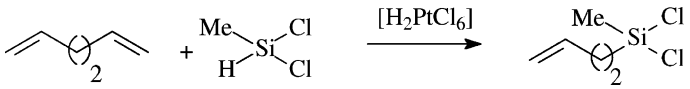
PII: S1381-1169(02)00534-4



1 (n = 0)
2 (n = 1)
3 (n = 2)
4 (n = 3)

Scheme 1. Synthesis of ω-alkenyl substituted methyldichlorosilane derivatives by Grignard reactions.



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Scheme 2. Synthesis of ω-hexenyl methyldichlorosilane (**5**) by a hydrosilation reaction.

The indenyl and fluorenyl derivatives **34**–**40** were prepared in the same manner (Scheme 5).

The ligand precursors of the mononuclear derivatives **L1**–**L3** were synthesized by a similar salt elimination reaction (Scheme 6).

2.3. Preparation of the complexes

The dinuclear *ansa* zirconocene complexes **41**–**54** were prepared according to Scheme 7 [21,22].

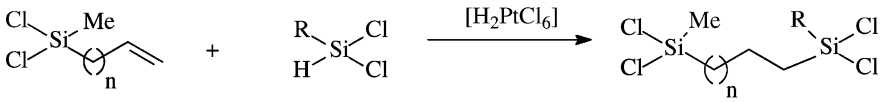
The indenyl and fluorenyl complexes **55**–**61** were synthesized in an analogous manner (Scheme 8).

The complexes **R1**–**R3** were synthesized for comparison purposes (Scheme 9) [17,20].

2.4. ^{13}C NMR spectra of *42* and *47*

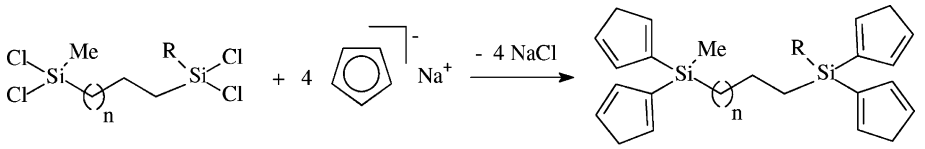
The J modulated ^{13}C NMR spectrum of the symmetrical complex **42** shows four resonance signals at $\delta = 129.3$ and 113.8 ppm for the tertiary carbon atoms of the cyclopentadienyl rings and one resonance signal at $\delta = 108.1$ ppm for the corresponding quaternary carbon atoms, as well as signals at $\delta = 16.7$ and 15.5 ppm for the $(CH_2)_3$ bridge and at $\delta = -7.0$ ppm for the silicon-bound methyl groups (Scheme 10).

The ^{13}C NMR spectrum of **47** shows resonance signals at $\delta = 129.3$, 128.7, 128.6, 128.0, 115.1, 114.8, and 113.7 ppm for the aromatic CH groups of the



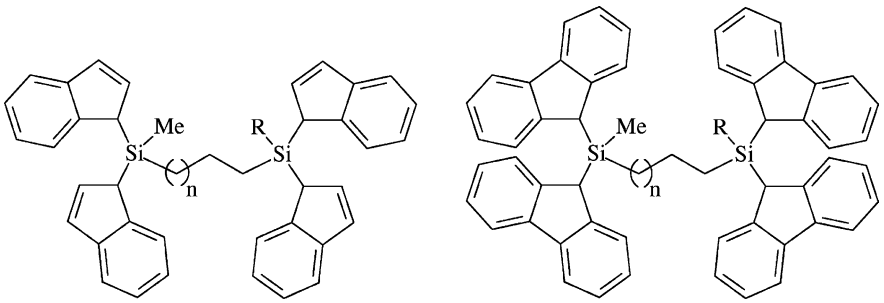
R = methyl		R = ethyl		R = iso-propyl	
6	**(n = 0)**	11	**(n = 0)**	16	**(n = 0)**
7	**(n = 1)**	12	**(n = 1)**	17	**(n = 1)**
8	**(n = 2)**	13	**(n = 2)**	18	**(n = 3)**
9	**(n = 3)**	14	**(n = 3)**	19	**(n = 4)**
10	**(n = 4)**	15	**(n = 4)**		

Scheme 3. Formation of the tetrachlorodisilane derivatives **6**–**19** by hydrosilation reactions [14,15].



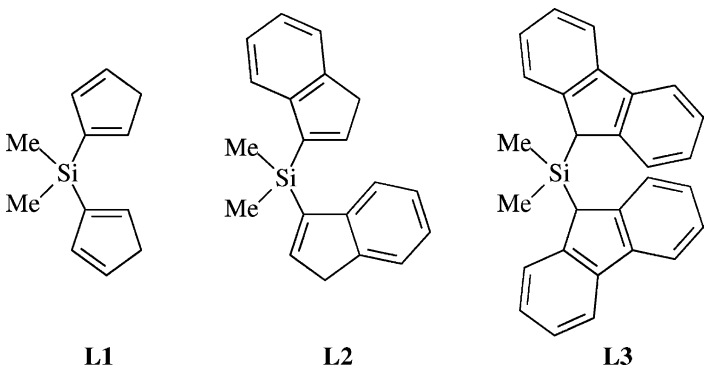
R = methyl		R = ethyl		R = iso-propyl	
20	(n = 0)	**25**	(n = 0)	**30**	(n = 0)
21	(n = 1)	**26**	(n = 1)	**31**	(n = 1)
22	(n = 2)	**27**	(n = 2)	**32**	(n = 3)
23	(n = 3)	**28**	(n = 3)	**33**	(n = 4)
24	(n = 4)	**29**	(n = 4)		

Scheme 4. Synthesis of the cyclopentadienyl substituted ligand precursors **20**–**33**.



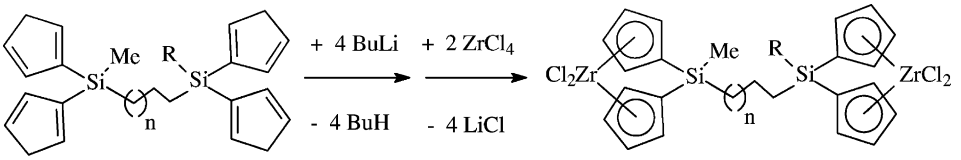
R = ethyl		R = iso-propyl		R = iso-propyl	
34	(n = 4)	**35**	(n = 0)	**38**	(n = 0)
		36	(n = 1)	**39**	(n = 1)
		37	(n = 4)	**40**	(n = 4)

Scheme 5. Indenyl and fluorenyl ligand precursors **34**–**40**.



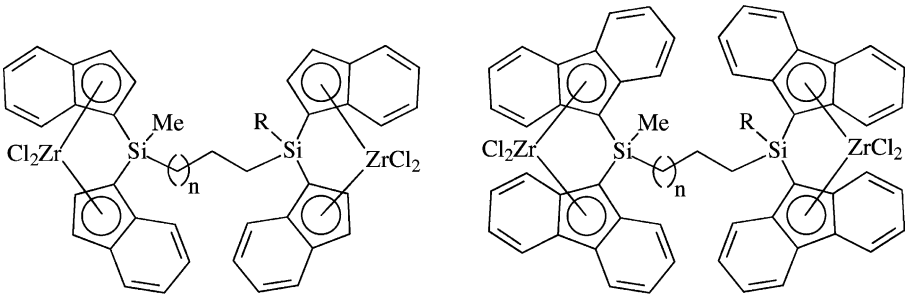
L1 **L2** **L3**

Scheme 6. Reference ligand precursors **L1**–**L3**.



R = methyl		R = ethyl		R = iso-propyl	
41	(n = 0)	**46**	(n = 0)	**51**	(n = 0)
42	(n = 1)	**47**	(n = 1)	**52**	(n = 1)
43	(n = 2)	**48**	(n = 2)	**53**	(n = 3)
44	(n = 3)	**49**	(n = 3)	**54**	(n = 4)
45	(n = 4)	**50**	(n = 4)		

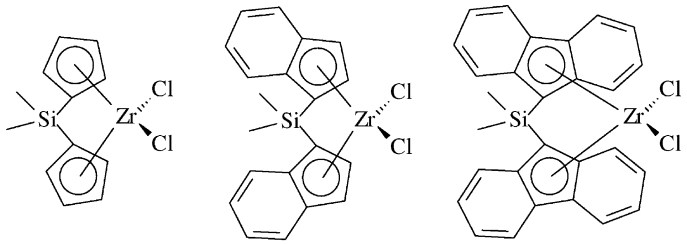
Scheme 7. Synthesis of the *ansa* zirconocene complexes **41**–**54** with cyclopentadienyl ligands.



R = ethyl		R = iso-propyl		R = iso-propyl	
55	(n = 4)	**56**	(n = 0)	**59**	(n = 0)
		57	(n = 1)	**60**	(n = 1)
		58	(n = 4)	**61**	(n = 4)

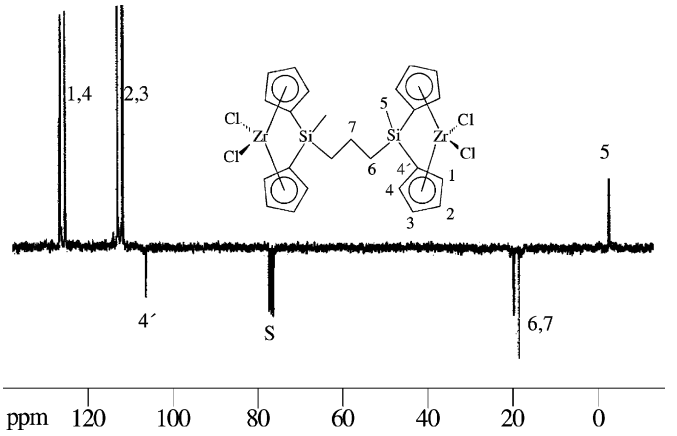
Scheme 8. Fluorenyl and indenyl substituted *ansa* zirconocene complexes **55**–**61**.

cyclopentadienyl rings. The quaternary carbon atoms appear at $\delta = 108.0$ and 107.5 ppm. The resonance signals for the propylidene bridge are observed at $\delta = 16.9$, 15.7, and at 11.2 ppm, and those for the ethyl substituent occur at $\delta = 6.7$ ppm (CH_3) and 1.7 ppm (CH_2). The highest field signal at $\delta = -6.9$ ppm is assigned to the methyl substituent (Scheme 11).



R1 **R2** **R3**

Scheme 9. Reference catalyst precursors **R1**–**R3**.



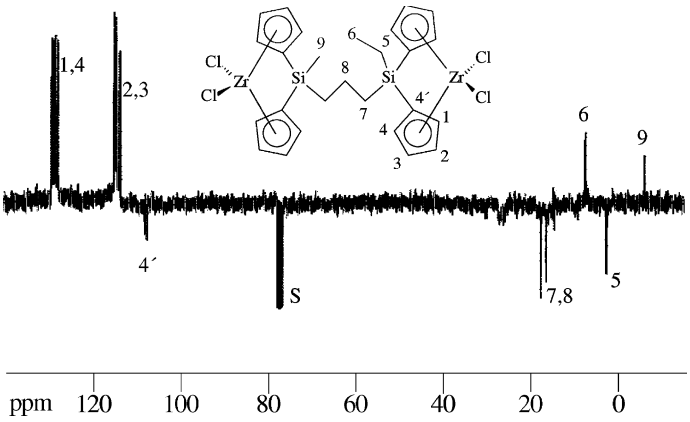
Scheme 10. ^{13}C NMR spectrum of **42** (S = $CDCl_3$).

2.5. Polymerization results

The dinuclear complexes **41**–**61** and the reference compounds **R1**–**R3** were activated with methylalumoxane (MAO) in toluene solution. The homogeneous catalyst solution was used for ethylene polymerization. For the heterogeneous polymerization, the activated catalyst solutions were treated with silica gel (1 g SiO_2/μmol(Zr)). Then the solid and dried catalyst was used for polymerization. The polymerization results are given in Table 1.

The most surprising result is that in almost all cases the catalyst productivity in the heterogeneous run is higher than under homogeneous conditions. Scheme 12 gives an overview. This result is in contrast to previous observations [15,17,21,22]. This behavior could be due to the fact that polar oxygen atoms on the surface of silica can no longer interact with the catalytic metal center and reduce the catalyst's activity. It is even likely that the dinuclear complexes form more efficiently cationic species on the surface of silica than in homogeneous solution. Due to the fact that the MAO counteranion does also occupy a large area close to the catalytic centers of the activated complexes, the polymerization may be hindered sterically.

Another tendency is obvious from Scheme 12: The longer the spacer between the two catalyst centers the higher the productivity. A bigger spacer means less



Scheme 11. ^{13}C NMR spectrum of **47** (S = $CDCl_3$).

Table 1
Polymerization data of the catalyst precursors **41**–**61**, of the reference catalyst precursors **R1**–**R3** in homogeneous and heterogeneous ethylene polymerization

Complex	Activity (g(PE)/g(Zr)h) (homogeneous conditions)	Activity (g(PE)/g(Zr)h) (heterogeneous conditions)
41	122.200	109.000
42	104.400	158.000
43	120.000	180.000
44	133.100	187.700
45	134.400	201.000
46	42.200	60.800
47	50.300	75.300
48	76.400	162.000
49	82.600	165.200
50	142.500	188.600
51	48.000	66.000
52	64.400	72.200
53	80.000	79.100
54	89.900	98.500
55	172.200	313.000
56	126.000	144.800
57	126.100	151.000
58	201.700	321.000
59	152.000	239.500
60	161.300	260.000
61	184.000	295.600
R1	109.000	102.000
R2	250.000	190.000
R3	320.000	260.000

sterical stress in the molecule or in the catalyst ion pair with MAO. Scheme 13 shows this effect explicitly.

The series of complexes **46**–**50** with methyl and ethyl silyl groups shows the growing spacer length and the comparison with the supported catalysts and the reference. While in homogeneous polymerizations, only the counterions have to arrange sterically, the situation in the supported catalyst can be different. The distance between the cation and the anion in the ion pair of the catalyst could be increased because of the interaction with the support. The consequence would be a higher activity of the catalyst (see [23]).

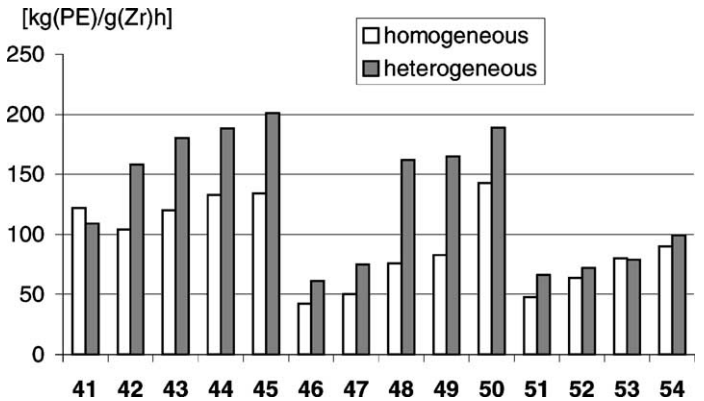
An increase in activity can also be observed when the cyclopentadienyl ligand is substituted with an indenyl or fluorenyl group (Scheme 14). This fact is known from former results [1,4,15,17,22].

Besides increasing activity because of a larger ligand sphere, Scheme 14 shows another detail: The single-site catalysts show generally higher activities under homogeneous conditions, while the supported dinuclear catalysts range on the same level as the supported mononuclear catalysts.

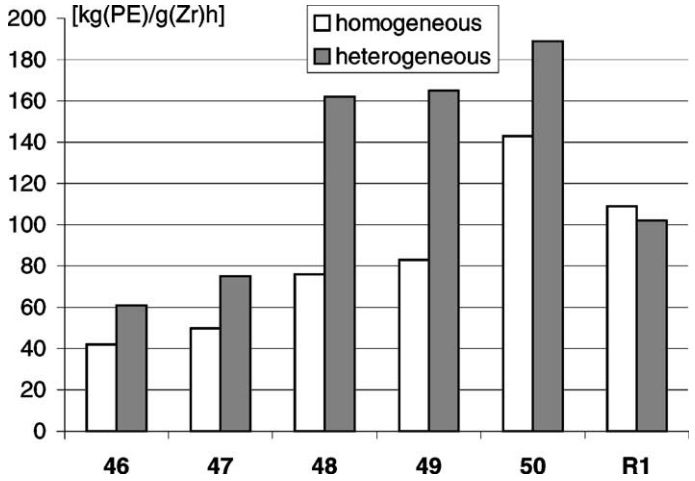
The impacts on the catalyst's behavior are obviously greater in case of dinuclear catalysts because the number of parameters that can influence the polymerization kinetics is higher in the case of mononuclear complexes.

The molecular weight distributions of the polyethylenes produced with the dinuclear catalysts indicate bimodal resins. The dissymmetric catalysts **47/MAO** and **50/MAO** clearly show two different molecular weights (Schemes 15 and 16).

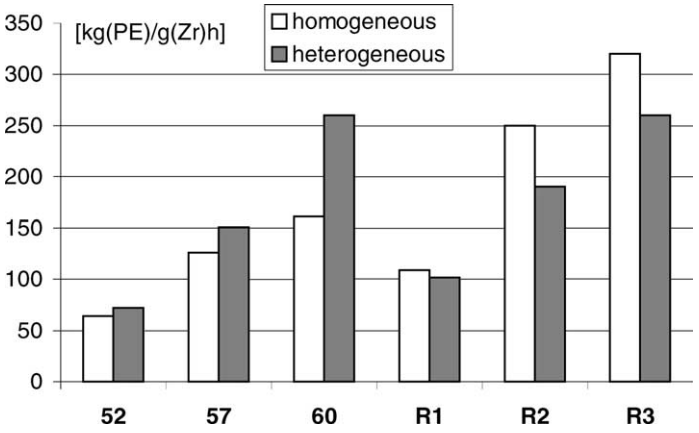
The fact that also the symmetric catalyst **41/MAO** can produce a bimodal resin (Scheme 17) leads to the conclusion that the MAO counteranion induces the necessary dissymmetry of the active sites in the activation process.



Scheme 12. Comparison of the catalyst productivities of cyclopentadienyl substituted catalysts **41**–**54/MAO**.



Scheme 13. Catalyst productivities of **46**–**50**/**MAO** with methyl and ethyl silyl groups.



Scheme 14. Comparison of catalyst productivities of dinuclear with mononuclear catalysts.

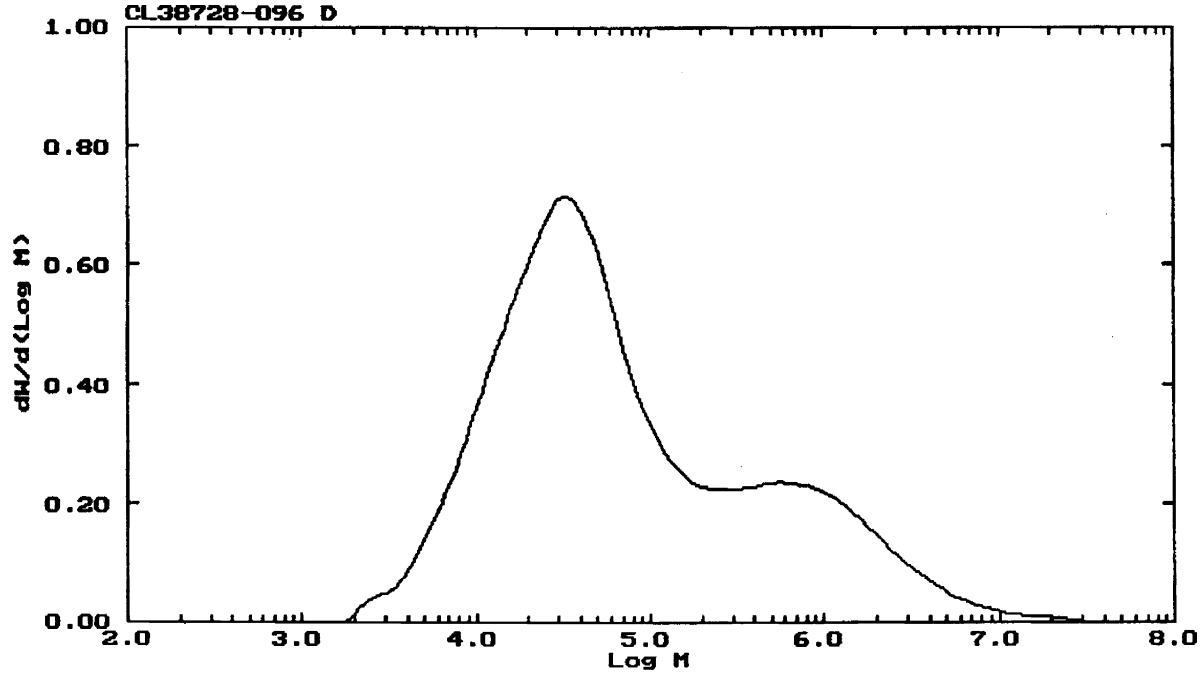
3. Experimental

All experimental work was routinely carried out using Schlenk technique. Dried and purified argon was used as inert gas. Toluene, pentane, diethyl ether and tetrahydrofuran were purified by distillation over Na/K alloy. Ether was additionally distilled over lithium aluminum hydride. Methylene chloride was dried with CaH_2. Deuterated solvents such as chloroform-d_1 and benzene-d_6 were dried over molecular sieves (300 ppm), degassed and stored under inert gas atmosphere.

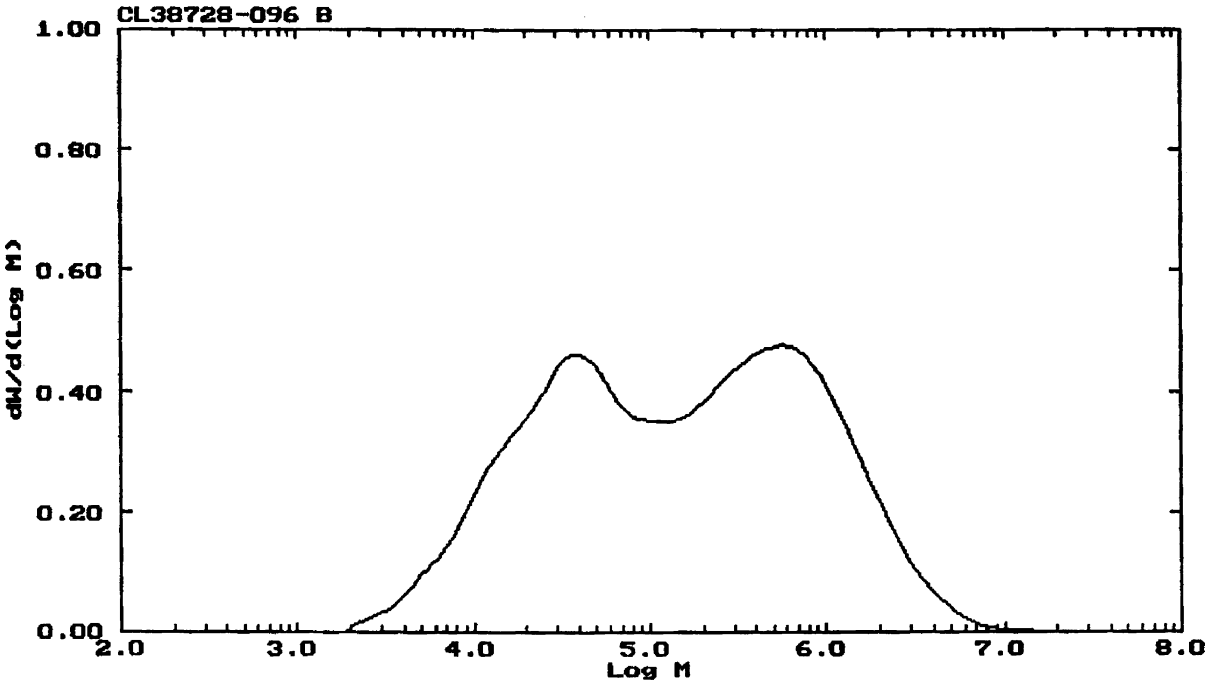
Commercially available indene was distilled and stored at $-28\,^{\circ}C$. Cyclopentadiene was freshly distilled from the dimer. Methylalumoxane (30% in toluene) was supplied by Witco Company, Bergkamen. All the other starting materials were commercially available and were used without further purification.

3.1. NMR spectroscopy

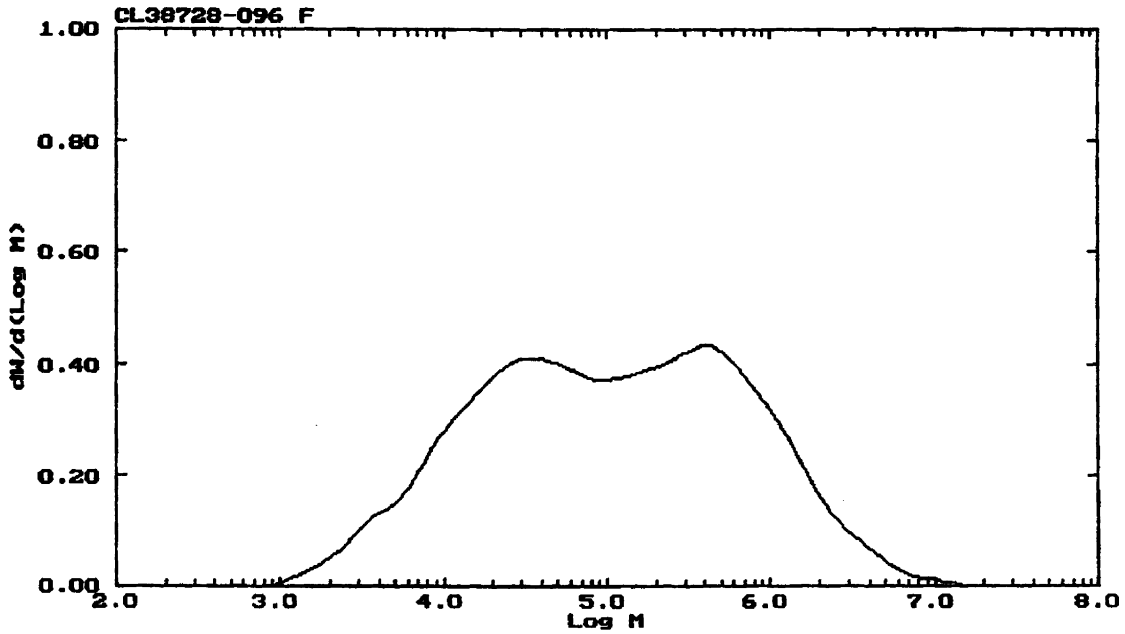
The spectrometer Bruker ARX 250 was available for the recording of the NMR spectra. The organometallic compounds were prepared under inert



Scheme 15. Bimodal molecular weight distribution of polyethylene produced with **47/MAO** as catalyst.



Scheme 16. Bimodal molecular weight distribution of polyethylene produced with **50/MAO** as catalyst.



Scheme 17. Bimodal molecular weight distribution of polyethylene produced with **41/MAO** as catalyst.

gas atmosphere (argon). The spectra were recorded at 25 °C. The chemical shifts in the ^{1}H NMR spectra are referred to the residual proton signal of the solvent ($\delta = 7.24$ ppm for chloroform, $\delta = 7.15$ ppm for benzene) and in the ^{13}C NMR spectra to the solvent signal ($\delta = 77.0$ ppm for chloroform-d_1, $\delta = 128.0$ ppm for benzene-d_6). Tetramethylsilane ($\delta = 0.0$ ppm) was used as external calibration for ^{29}Si NMR spectra.

3.2. GC/MS 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 °C (starting phase); 20 °C/min (heating phase); variable time at 210 °C (final phase).

3.3. Mass spectroscopy

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.

3.4. Preparation of ω-bromo-1-alkenes by elimination reaction

An amount of 440 mmol of α,ω-dibromoalkane was heated to 200 °C and 240 mmol of hexamethylphosphoric acid triamide (HMPT) was added slowly. The resulting ω-bromo-1-alkene was distilled off the reaction mixture and purified by another distillation at normal pressure. Yields: 40–60%.

3.5. Preparation of the alkyl or ω-alkenyl substituted dichlorosilane derivatives ***1–4*** by Grignard reaction

An amount of 6.1 g (250 mmol) of magnesium suspended in 100 ml of diethyl ether was placed in a three-necked flask with dropping funnel and reflux cooling system at 0 °C. The magnesium was activated by addition of 0.1 g I_2. An amount of 240 mmol of an alkyl, aryl or ω-alkenyl bromide in 100 ml of ether was added slowly during 1 h. After addition of the

bromide, the mixture was stirred for another hour at room temperature.

An amount of 70 ml (450 mmol) of a trichlorosilane derivative in 100 ml of diethyl ether was placed in a Schlenk vessel. The Grignard product was added slowly to this mixture at −78 °C within 1 h and brought to room temperature within 3 h. The solvent and the excess trichlorosilane were distilled off the mixture. The residue was suspended in pentane, filtered over Na_2SO_4 and the crude product was distilled. Yields: 50–80%. The products were characterized by NMR spectroscopy (Table 2).

3.6. Preparation of 5-hexen-1-yl-methyl-dichlorosilane (**5**) by hydrosilation reaction

An amount of 150 mmol of 1,5-hexadiene was dissolved in 5 ml of pentane and treated with 30–50 mg hexachloroplatinic acid hydrate. An amount of 50 mmol of dichloromethylsilane was added and the mixture was stirred for 40 h. After filtration over Na_2SO_4, the solvent and the excess 1,5-hexadiene were removed in vacuo. The crude product was distilled in vacuo. Yield: 80%.

3.7. Preparation of ligand precursor ***L1***

An amount of 4.5 g (51.1 mmol) of sodium cyclopentadienide in 50 ml of tetrahydrofurane was placed in a Schlenk vessel. An amount of 4.32 g (25.6 mmol) of dichlorodimethylsilane was added and the mixture was stirred for 15 h at room temperature. The solvent was removed in vacuo and the residue was suspended in diethyl ether. The suspension was filtered over Na_2SO_4/SiO_2 and the solvent was removed in vacuo. Yield: 80%.

3.8. Preparation of indenyl or fluorenyl substituted ligand precursors ***L2–L3***

An amount of 52 mmol of indenyl lithium or fluorenyl lithium in 100 ml of diethyl ether was placed in a Schlenk vessel. An amount of 26 mmol of dimethyldichlorosilane dissolved in 10 ml of diethyl ether was added and the mixture was stirred for 8 h at room temperature. The suspension was filtered over Na_2SO_4/SiO_2 and the solvent was removed in vacuo. Yields: 60–70%.

3.9. Preparation of tetrachlorodisilane derivatives ***6–19*** by hydrosilation reaction

An amount of 19.4 mmol of an ω-alkenyl-dichloromethylsilane derivative and 19.4 mmol of an alkyl substituted dichlorosilane derivative was dissolved in 5 ml of pentane. An amount of 30–50 mg of hexachloroplatinic acid was added. The mixture was stirred for 40 h at room temperature, then filtered over Na_2SO_4 and the solvent was removed in vacuo. The products were white, crystalline solids or slightly yellow highly viscous oils. Yields: 90–95%. The products were characterized by NMR spectroscopy (Table 2) and GS/MS (Table 3).

3.10. Preparation of the cyclopentadienyl substituted ligand precursors ***20–33***

An amount of 6 mmol of 1,1,*n*,*n*-tetrachloro-1-alkyl-1,*n*-disila-alkane in 100 ml of diethyl ether was placed in a Schlenk vessel and 2.1 g (24 mmol) of cyclopentadienyl sodium (dissolved in 10 ml of THF) was added. The mixture was stirred for 6 h at room temperature. The solvent was removed in vacuo, the residue was suspended in diethyl ether and filtered over Na_2SO_4/SiO_2. The solvent was removed in vacuo again. Yields: 90–95%. The products were characterized by NMR spectroscopy (Table 2) and GC/MS (Table 3).

3.11. Preparation of the indenyl and fluorenyl substituted ligand precursors ***34–40***

An amount of 24 mmol fluorenyl lithium/indenyl lithium was dissolved in 100 ml of diethyl ether at room temperature and 6 mmol of a 1,1,3,3-tetrachloro-1-alkyl-1,3-disila-butane dissolved in 10 ml of diethyl ether was added. The reaction mixture was stirred for 4 h, then filtered over Na_2SO_4/SiO_2 and the solvent was removed in vacuo. The crude product was dissolved in pentane and crystallized at −28 °C. The products were slightly yellow powders (fluorenyl derivatives) or yellow, very viscous liquids (indenyl derivatives. Yields: 80–90%. The products were

Table 2
NMR data of compounds **1**–**44**

Compound	^{1}H NMR	^{13}C NMR	^{29}Si NMR
1	n.d.	n.d.	n.d.
2	5.87–5.58 (m, 1H, vinyl-CH), 5.11–5.05 (m, 2H, vinyl-CH_2), 2.12–2.05 (d, 2H, allyl-CH_2), 0.76 (s, 3H, Si–CH_3)	129.6 (vinyl-CH), 118.9 (vinyl-CH_2), 28.4 (CH_2, allyl substituent), 4.4 (Si–CH_3)	28.1
3	5.79–5.68 (m, 1H, vinyl-CH), 5.09–4.92 (m, 2H, vinyl-CH_2), 2.11–2.07, 1.35–0.89 (m, 4H, butenyl-CH_2), 0.45 (s, 3H, Si–CH_3)	138.9 (vinyl-CH), 114.5 (vinyl-CH_2), 33.9, 21.7 (CH_2, butenyl substituent), 5.0 (Si–CH_3)	32.8
4	5.67–5.54 (m, 1H, vinyl-CH), 4.89–4.77 (m, 2H, vinyl-CH_2), 2.08–1.92, 1.47–1.40, 0.97–0.91 (m, 6H, pentenyl-CH_2), 0.57 (s, 3H, Si–CH_3)	139.3 (vinyl-CH), 115.8 (vinyl-CH_2), 36.4, 29.1, 22.0 (CH_2, pentenyl substituent), 5.4 (Si–CH_3)	33.0
5	n.d.	n.d.	32.7
6	1.29 (s, 4H, bridge), 0.89 (s, 6H, Si–CH_3)	13.3 (CH_2, bridge), 4.6 (Si–CH_3)	33.1
7	1.87–1.79, 1.35–1.28 (m, 6H, bridge), 0.86 (s, 6H, Si–CH_3)	24.6, 16.2 (CH_2, bridge), 5.4 (Si–CH_3)	31.8
8	1.74–1.12 (m, 8H, bridge), 0.81 (s, 6H, Si–CH_3)	29.0, 22.5 (CH_2, bridge), 5.3 (Si–CH_3)	33.0
9	1.64–1.54, 1.22–1.15 (m, 10H, bridge), 0.84 (s, 3H, Si–CH_3)	35.1, 29.5, 22.1 (CH_2, bridge), 5.3 (Si–CH_3)	33.0
10	1.56–1.45, 1.19–1.12 (m, 12H, bridge), 0.80 (s, 6H, Si–CH_3)	31.9, 22.3, 21.6 (CH_2, bridge), 5.3 (Si–CH_3)	33.1
11	1.26–1.22 (m, 4H, bridge), 1.19–1.13 (m, 5H, Et–CH_3, Et–CH_2), 0.85 (s, 3H, Si–CH_3)	13.7, 12.7 (CH_2, bridge), 11.8 (Et–CH_2), 6.1 (Et–CH_3), 4.0 (Si–CH_3)	34.9 (Et–Si), 33.0 (Me–Si)
12	1.86–1.75, 1.37–1.23 (m, 6H, bridge), 1.17–1.13 (m, 5H, Et–CH_3, Et–CH_2), 0.82 (s, 3H, Si–CH_3)	24.6, 22.8, 16.1 (CH_2, bridge), 12.7 (Et–CH_2), 6.2 (Et–CH_3), 5.7 (Si–CH_3)	33.7 (Et–Si), 31.8 (Me–Si)
13	1.68–1.54, 1.37–1.04 (m, 8H, bridge), 1.19–1.06 (m, 5H, Et–CH_3, Et–CH_2), 0.79 (s, 3H, Si–CH_3)	n.d.	34.6 (Et–Si), 32.8 (Me–Si)
14	1.72–1.55, 1.38–0.99 (m, 10H, bridge), 1.23–0.97 (m, 5H, Et–CH_3, Et–CH_2), 0.57 (s, 3H, Si–CH_3)	n.d.	33.9 (Et–Si), 33.0 (Me–Si)
15	1.57–1.40, 1.18–1.10 (m, 12H, bridge), 1.15–1.11 (m, 5H, Et–CH_3, Et–CH_2), 0.80 (s, 3H, Si–CH_3)	32.0, 31.9, 22.3, 22.2, 21.6, 19.9 (CH_2, bridge), 12.7 (Et–CH_2), 5.9 (Et–CH_3), 4.6 (Si–CH_3)	35.1 (Et–Si), 33.1 (Me–Si)
16	1.49–1.33 (m, 1H, ^{i}Pr–CH), 1.21–1.17 (m, 4H, bridge), 1.15–1.10 (m, 6H, ^{i}Pr–CH_3), 0.80 (s, 3H, Si–CH_3)	19.0 (^{i}Pr–CH), 16.9 (^{i}Pr–CH_3), 13.2, 9.8 (CH_2, bridge), 4.9 (Si–CH_3)	35.9 (^{i}Pr–Si), 33.0 (Me–Si)
17	1.84–1.69 (m, 1H, ^{i}Pr–CH), 1.33–1.06 (m, 6H, bridge), 1.16–1.11 (m, 6H, ^{i}Pr–CH_3), 0.77 (s, 3H, Si–CH_3)	24.4, 20.9, 16.4 (CH_2, bridge), 18.5 (^{i}Pr–CH), 15.9 (^{i}Pr–CH_3), 5.2 (Si–CH_3)	34.5 (^{i}Pr–Si), 32.1 (Me–Si)
18	1.72–1.40, 1.18–1.05 (m, 10H, bridge), 1.62–1.46 (m, 1H, ^{i}Pr–CH), 1.18–1.08 (m, 6H, ^{i}Pr–CH_3), 0.79 (s, 3H, Si–CH_3)	35.2, 22.5, 22.1, 21.5, 18.1 (CH_2, bridge), 18.9 (^{i}Pr–CH), 16.4 (^{i}Pr–CH_3), 5.8 (Si–CH_3)	35.5 (^{i}Pr–Si), 33.0 (Me–Si)
19	2.19–2.06 (m, 1H, ^{i}Pr–CH), 1.72–1.40, 1.21–1.09 (m, 12H, bridge), 1.18–1.13 (m, 6H, ^{i}Pr–CH_3), 0.77 (s, 3H, Si–CH_3)	32.0, 31.9, 22.2, 22.1, 21.5, 18.2 (CH_2, bridge), 18.5 (^{i}Pr–CH), 16.8 (^{i}Pr–CH_3), 5.4 (Si–CH_3)	35.9 (^{i}Pr–Si), 33.0 (Me–Si)
20	6.89–6.36 (m, 16H, ar H, Cp), 3.06–1.98 (m, 8H, al H, Cp), 1.51–0.22 (m, 4H, bridge), 0.02, −0.26 (s, 6H, Si–CH_3)	141.9, 138.7, 133.3, 130.4 (CH, ar, Cp), 129.4, 122.5 (C_q, Cp), 45.6 (CH_2, al, Cp), 19.8, 18.4 (CH_2, bridge), −6.8, −7.1 (Si–CH_3)	5.8, −4.9

Table 2 (*Continued*)

Compound	^{1}H NMR	^{13}C NMR	^{29}Si NMR
21	6.56–6.45 (m, 16H, ar H, Cp), 2.99–2.94 (m, 8H, al H, Cp), 0.58–0.26 (m, 6H, bridge), −0.24, −0.01, −0.28 (s, 6H, Si–CH_3)	143.4, 138.2, 132.7, 132.6, 132.3, 130.6, 130.4, 129.6 (CH, ar, Cp), 45.9, 43.7, 43.1 (CH_2, al, Cp), 26.3, 6.3, 6.6, 6.3, 6.1 (CH_2, bridge), −6.9, −7.3, −7.4 (Si–CH_3)	6.0, −5.0
22	6.93–6.43 (m, 16H, ar H, Cp), 2.96–1.99 (m, 8H, al H, Cp), 1.51–0.22 (m, 8H, bridge), −0.06, −0.32 (s, 6H, Si–CH_3)	142.0, 140.1, 133.3, 130.4 (CH, ar, Cp), 129.1 (C_q, Cp), 44.9 (CH_2, al, Cp), 26.5, 22.9, 19.8, 18.4 (CH_2, bridge), −5.9, −6.5 (Si–CH_3)	6.0, −4.9
23	6.82–6.43 (m, 16H, ar H, Cp), 3.00–2.94 (m, 8H, al H, Cp), 1.21–1.14, 0.58–0.07 (m, 10H, bridge), −0.03, −0.27 (s, 6H, Si–CH_3)	143.0, 138.1, 138.0, 132.7, 132.6, 130.7, 130.5, 130.0 (CH, Cp), 120.9, 120.7 (C_q, Cp), 51.0, 49.6 (CH, al, Cp), 45.9 (CH_2, al, Cp), 37.2, 29.5, 23.7, 22.9, 22.8, 14.6, 13.0 (CH_2, bridge), −6.7, −6.9 (Si–CH_3)	4.1, −7.4
24	6.79–6.34 (m, 16H, ar H, Cp), 3.17–2.94 (m, 8H, al H, Cp), 1.21–1.14, 0.58–0.07 (m, 12H, bridge), −0.03, −0.27 (s, 6H, Si–CH_3)	144.1, 138.4, 136.9, 132.2, 132.0, 130.9, 130.3, 129.7 (CH, Cp), 122.0, 120.4 (C_q, Cp), 50.2, 46.9 (CH, al, Cp), 43.9 (CH_2, al, Cp), 36.2, 30.9, 26.7, 24.9, 22.8, 14.4, 13.5 (CH_2, bridge), −6.9, −7.2 (Si–CH_3)	4.2, −6.2
25	6.91–6.50, 5.54–5.19 (m, 16H, ar H, Cp), 3.39–2.65 (m, 8H, al H, Cp), 1.98–0.45, −0.07–0.30 (m, 12H, bridge, Et substituent, Si–CH_3)	141.2, 140.0, 138.0 (C_q, Cp), 133.4, 133.1, 132.2, 131.0, 129.2, 128.0 (CH, ar, Cp), 49.6, 48.3 (CH, al, Cp), 46.8 (CH_2, al, Cp), 27.0, 15.2 (CH_2, bridge), 18.5 (CH_3, Et), 14.0 (CH_2, Et), −6.2 (Si–CH_3)	5.8 (Et–Si), 4.9 (Me–Si) −4.5
26	6.75–6.12, 5.42–4.99 (m, 16H, ar H, Cp), 3.66–3.02 (m, 8H, al H, Cp), 1.69–0.50, 0.11–0.23 (m, 14H, bridge, Et substituent, Si–CH_3)	139.9, 138.4, 138.0 (C_q, Cp), 133.0, 132.1, 132.0, 131.4, 130.2, 130.0 (CH, ar, Cp), 50.7, 50.3 (CH, al, Cp), 47.2 (CH_2, al, Cp), 27.6, 18.8, 16.3 (CH_2, bridge), 17.5 (CH_3, Et), 13.2 (CH_2, Et), −6.7 (Si–CH_3)	6.0 (Et–Si), 5.2 (Me–Si) −4.6
27	6.81–6.64, 5.53–5.08 (m, 16H, ar H, Cp), 3.50–2.91 (m, 8H, al H, Cp), 1.67–0.13 (m, 16H, bridge, Et substituent, Si–CH_3)	n.d.	5.7 (Et–Si), 4.6 (Me–Si) −5.0
28	6.66–6.23, 5.64–5.35 (m, 16H, ar H, Cp), 3.71–3.09 (m, 8H, al H, Cp), 1.77–0.53, 0.21–0.30 (m, 18H, bridge, Et substituent, Si–CH_3)	138.3, 137.2, 137.0 (C_q, Cp), 133.9, 132.8, 132.0, 131.1, 130.7, 129.7 (CH, ar, Cp), 51.0, 50.4 (CH, al, Cp), 46.0 (CH_2, al, Cp), 27.6, 23.1, 17.4, 13.3 (CH_2, bridge), 18.2 (CH_3, Et), 12.9 (CH_2, Et), −5.9 (Si–CH_3)	5.4 (Et–Si), 4.3 (Me–Si) −4.7
29	6.89–6.53, 5.44–5.29 (m, 16H, ar H, Cp), 3.56–2.84 (m, 8H, al H, Cp), 2.07–0.33, 0.01–0.03, −0.25 to 0.30 (m, 20H, bridge, Et substituent, Si–CH_3)	139.6, 138.3 (C_q, Cp), 134.2, 133.6, 133.2, 132.4, 131.2, 130.6 (CH, ar, Cp), 49.4 (CH, al, Cp), 46.1 (CH_2, al, Cp), 27.6, 25.3, 18.3, 16.8, 13.7 (CH_2, bridge), 16.9 (CH_3, Et), 13.2 (CH_2, Et), −6.6 (Si–CH_3)	4.6 (Et–Si), 3.6 (Me–Si) −7.6
30	6.75–6.40 (m, 16H, ar H, Cp), 3.79–3.42 (m, 8H, al H, Cp), 1.26–0.90 (m, 10H, bridge, ^{i}Pr–CH_3), 0.72–0.50 (m, 1H, ^{i}Pr–CH), −0.18 (s, 3H, Si–CH_3)	140.0, 139.5, 138.2 (C_q, Cp), 133.4, 133.0, 132.8, 132.5, 132.0, 130.7, 129.8 (CH, ar, Cp), 51.1, 49.7 (CH, al, Cp), 45.9 (CH_2, al, Cp), 25.7, 15.1 (CH_2, bridge), 17.6, 17.5 (CH_3, ^{i}Pr), 15.0 (CH, ^{i}Pr), −5.8 (Si–CH_3)	6.3 (^{i}Pr–Si) 4.8 (Me–Si) −5.8

Table 2 (*Continued*)

Compound	^{1}H NMR	^{13}C NMR	^{29}Si NMR
31	6.87–6.39 (m, 16H, ar H, Cp), 3.70–3.28 (m, 8H, al H, Cp), 1.46–1.01 (m, 12H, bridge, ^{i}Pr–CH_3), 0.67–0.51 (m, 1H, ^{i}Pr–CH), −0.21 (s, 3H, Si–CH_3)	139.9, 138.9, 138.7 (C_q, Cp), 133.2, 132.9, 132.8, 131.0, 130.9, 130.8 (CH, ar, Cp), 50.8, 50.6 (CH, al, Cp), 47.0 (CH_2, al, Cp), 27.6, 18.8, 16.3 (CH_2, bridge), 17.5, 17.4 (CH_3, ^{i}Pr), 14.2 (CH, ^{i}Pr), −6.5 (Si–CH_3)	
32	6.98–6.58 (m, 16H, ar H, Cp), 3.70–3.28 (m, 8H, al H, Cp), 1.69–0.87 (m, 16H, bridge, ^{i}Pr–CH_3), 0.62–0.41 (m, 1H, ^{i}Pr–CH), −0.18 (s, 3H, Si–CH_3)	142.0, 140.9, 139.8 (C_q, Cp), 133.7, 133.0, 132.3, 131.0, 130.5, 130.2 (CH, ar, Cp), 50.1, 48.9 (CH, al, Cp), 46.4 (CH_2, al, Cp), 28.3, 26.0, 23.6, 18.8, 15.2 (CH_2, bridge), 17.6, 17.5 (CH_3, ^{i}Pr), 13.8 (CH, ^{i}Pr), −6.3 (Si–CH_3)	5.9 (^{i}Pr–Si) 4.7 (Me–Si) −5.8
33	6.81–6.29 (m, 16H, ar H, Cp), 3.73–3.41 (m, 8H, al H, Cp), 2.16–1.97, 1.46–0.87 (m, 18H, bridge, ^{i}Pr–CH_3), 0.64–0.49 (m, 1H, ^{i}Pr–CH), −0.19 (s, 3H, Si–CH_3)	140.0, 139.4, 138.0 (C_q, Cp), 135.2, 134.7, 133.2, 131.9, 130.1, 129.8 (CH, ar, Cp), 51.0, 50.1 (CH, al, Cp), 46.3 (CH_2, al, Cp), 29.8, 28.4, 27.6, 18.5, 16.1, 13.2 (CH_2, bridge), 17.4, 17.3 (CH_3, ^{i}Pr), 14.2 (CH, ^{i}Pr), −6.7 (Si–CH_3)	6.2 (^{i}Pr–Si) 4.8 (Me–Si)
34	7.43–7.10, 6.71–6.22 (m, 24H, ar H, Ind), 3.92–3.02 (m, 8H, al H, Ind), 2.19–2.13, 1.59–0.13 (m, 15H, bridge, Et–CH_3), −0.11–0.53 (m, 5H, Et–CH_2, Si–CH_3)	143.6, 143.5, 138.2, 138.0 (C_q, Ind), 133.2, 133.1, 132.9, 130.0, 128.4, 128.3, 128.2, 128.0, 126.9, 126.7, 126.4, 126.1 (CH, ar, Ind), 46.4, 46.1, 44.0 (CH_2, al, Ind), 33.6, 33.5, 30.9, 24.6, 15.0, 13.5 (CH_2, bridge), 8.3 (CH_3, Et substituent), 5.2 (CH_2, Et substituent), −6.7 (Si–CH_3)	5.3 (Et–Si), 4.9 (Me–Si) −5.8
35	7.76–7.29, 6.82–6.56 (m, 24H, ar H, Ind), 4.02–3.42 (m, 8H, al H, Ind), 2.19–2.13, 1.59–0.13 (m, 10H, bridge, ^{i}Pr–CH_3), 0.14–0.42 (m, 4H, ^{i}Pr–CH, Si–CH_3)	144.8, 144.5, 144.0 (C_q, Ind), 134.6, 134.2, 133.1, 132.3, 131.0, 130.0, 127.3, 126.8, 125.7, 124.5, 123.1, 121.3, 119.8 (CH, Ind), 47.1, 46.0, 44.1 (CH, al, Ind), 40.0 (CH_2, al, Ind), 35.2, 32.9, 26.3, 10.9 (CH_2, bridge), 18.1, 17.4, 17.0, 16.0, 11.1 (CH_3, CH, ^{i}Pr substituent), −4.9, −6.0 (Si–CH_3)	6.5 (^{i}Pr–Si) 5.0 (Me–Si) −6.1
36	7.73–6.72 (m, 24H, ar H, Ind), 3.98–3.32 (m, 8H, al H, Ind), 2.31–2.02, 1.62–0.83, 0.47–0.10 (m, 15H, bridge, ^{i}Pr–CH_3), −0.11 to 0.35 (m, 4H, ^{i}Pr–CH, Si–CH_3)	145.1, 144.3, 144.0 (C_q, Ind), 135.7, 134.2, 133.3, 131.2, 126.3, 125.8, 125.1, 124.0, 123.0, 122.1, 121.0, 119.4 (CH, Ind), 47.6, 44.3, 43.6 (CH, al, Ind), 39.5 (CH_2, al, Ind), 35.1, 32.9, 26.0, 9.9, 8.6 (CH_2, bridge), 18.0, 17.0, 15.6, 14.1 (CH_3, CH, ^{i}Pr substituent), −5.1, −6.3 (Si–CH_3)	4.1 (^{i}Pr–Si) 1.8 (Me–Si) −7.2
37	7.90–7.37, 6.99–6.62 (m, 24H, ar H, Ind), 3.88–3.42 (m, 8H, al H, Ind), 2.31–2.02, 1.42–0.63, 0.47–0.21 (m, 18H, bridge, ^{i}Pr–CH_3), −0.12 to 0.31 (m, 4H, ^{i}Pr–CH, Si–CH_3)	145.0, 144.9, 144.4 (C_q, Ind), 135.3, 134.5, 134.2, 133.3, 132.2, 131.1, 129.7, 126.3, 125.8, 125.2, 124.6, 124.0, 123.1, 121.0, 120.1 (CH, Ind), 47.3, 45.2, 44.5, 44.1 (CH, al, Ind), 39.8 (CH_2, al, Ind), 35.2, 35.1, 33.1, 32.9, 32.8, 26.4, 26.2, 9.9, 8.6 (CH_2, bridge), 18.0, 17.3, 17.1, 15.9, 14.3 (CH_3, CH, ^{i}Pr substituent), −5.7, −5.9 (Si–CH_3)	4.3 (^{i}Pr–Si) 4.8 (Me–Si) −5.8

Table 2 (*Continued*)

Compound	^{1}H NMR	^{13}C NMR	^{29}Si NMR
38	7.38–6.41 (m, 32H, ar H, Flu), 4.53, 4.39 (s, 4H, al H, Flu), 1.99–1.75 (m, 6H, ^{i}Pr–CH_3), 0.79–0.27 (m, 5H, bridge, ^{i}Pr–CH), −0.23, −0.38 (s, 3H, Si–CH_3)	145.7, 141.2, 140.8 (C_q, Flu), 134.4, 128.6, 127.7, 126.2, 125.9, 125.8, 125.2, 124.2, 124.0 (CH, ar, Flu), 40.8, 39.7 (CH, al H, Flu), 28.4, 14.7 (CH_2, bridge), 17.4, 17.3, 9.9 (CH_3, CH, ^{i}Pr substituent), −5.2, −7.1 (Si–CH_3)	3.3 (^{i}Pr–Si) 1.8 (Me–Si) −7.8
39	7.47–6.69 (m, 32H, ar H, Flu), 4.31, 4.19 (s, 4H, al H, Flu), 2.11–1.82 (m, 6H, ^{i}Pr–CH_3), 0.81–0.20 (m, 7H, bridge, ^{i}Pr–CH), −0.09, −0.27 (s, 3H, Si–CH_3)	144.9, 144.1, 140.8 (C_q, Flu), 134.4, 131.8, 128.4, 127.3, 126.7, 126.0, 124.8, 124.52, 124.2, 123.8 (CH, ar, Flu), 41.0, 39.3 (CH, al H, Flu), 28.4, 21.6, 13.5 (CH_2, bridge), 17.6, 17.5, 10.1 (CH_3, CH, ^{i}Pr substituent), −5.2, −7.1 (Si–CH_3)	2.3 (^{i}Pr–Si) −0.5 (Me–Si) −7.9
40	7.59–6.72 (m, 32H, ar H, Flu), 4.47, 4.30 (s, 4H, al H, Flu), 2.06–1.75 (m, 6H, ^{i}Pr–CH_3), 1.89–1.34, 0.83–0.31 (m, 13H, bridge, ^{i}Pr–CH), −0.03, −0.18 (s, 3H, Si–CH_3)	n.d.	2.3 (^{i}Pr–Si) −0.4 (Me–Si) −8.8
41	6.78–6.66, 5.62–5.50 (m, 16H, ar H, Cp), 1.24–1.09, 0.79–0.64 (m, 4H, bridge), 0.30 (s, 6H, CH_3)	129.0, 127.8, 114.7, 113.9 (CH, Cp), 108.2 (C_q, Cp), 12.0 (CH_2, bridge), −7.0 (Si–CH_3)	−11.4
42	6.80–5.79 (m, 16H, Cp), 2.11–1.37 (m, 6H, bridge), 0.72 (s, 6H, Si–CH_3)	129.3, 128.0, 115.1, 114.1 (CH, Cp), 108.1 (C_q, Cp), 16.7, 15.5 (CH_2, bridge), −7.0 (Si–CH_3)	−12.9
43	7.12–5.87 (m, 16H, Cp), 1.93–1.20 (m, 8H, bridge), 0.74 (s, 6H, Si–CH_3)	129.2, 128.0, 114.9, 113.8 (CH, Cp), 108.4 (C_q, Cp), 22.7, 11.1 (CH_2, bridge), −7.1 (Si–CH_3)	−12.2
44	6.87–6.84, 5.67–5.61 (m, 16H, Cp), 1.51–0.83 (m, 10H, bridge), 0.26 (s, 6H, Si–CH_3)	129.0, 127.4, 114.8, 113.8 (CH, Cp), 108.4 (C_q, Cp), 36.8, 22.8, 10.9 (CH_2, bridge), −7.5 (Si–CH_3)	−12.8
45	6.97–6.79, 6.19–5.88 (m, 16H, Cp), 1.72–0.98 (m, 12H, bridge), 0.71 (s, 6H, Si–CH_3)	129.6, 127.6, 115.2, 114.1 (CH, Cp), 108.2 (C_q, Cp), 35.7, 34.8, 24.6, 22.7, 11.1, 10.2 (CH_2, bridge), −6.9 (Si–CH_3)	−12.2
46	7.20–5.96 (m, 16H, Cp), 1.37–0.68 (m, 9H, Et substituent, bridge), 0.10 (s, 3H, Si–CH_3)	129.5, 128.1, 117.8, 116.7 (CH, Cp), 108.2, 107.3 (C_q, Cp), 11.0, 9.7 (CH_2, bridge), 6.2 (CH_3, Et substituent), 1.1 (CH_2, Et substituent), −6.9 (Si–CH_3)	−10.8 (Et–Si), −11.3 (Me–Si)
47	7.03–6.87, 6.09–5.87 (m, 16H, Cp), 2.07–0.61 (m, 11H, bridge, Et substituent), 0.75 (s, 3H, Si–CH_3)	129.3, 128.7, 128.6, 128.0, 115.1, 114.8, 113.7 (CH, Cp), 108.0, 107.5 (C_q, Cp), 16.9, 15.7, 11.2 (CH_2, bridge), 6.7 (CH_3, Et substituent), 1.7 (CH_2, Et substituent), −6.9 (s, 3H, Si–CH_3)	−12.9 (Et–Si), −13.0 (Me–Si)
48	7.01–6.89, 6.07–5.90 (m, 16H, Cp), 1.89–0.57 (m, 13H, bridge, Et substituent), 0.71 (s, 3H, Si–CH_3)	128.9, 128.7, 128.0, 117.8, 117.3, 116.7 (CH, Cp), 108.5, 108.0 (C_q, Cp), 26.9, 11.1, 9.4 (CH_2, bridge), 6.2 (CH_3, Et substituent), 1.8 (CH_2, Et substituent), −7.3 (Si–CH_3)	−11.0 (Et–Si), −12.2 (Me–Si)
49	6.94–6.69, 5.95–5.80 (m, 16H, Cp), 1.49–0.52 (m, 15H, Et substituent, bridge), 0.48 (s, 3H, Si–CH_3)	129.1, 128.5, 128.1, 114.9, 114.1, 113.9 (CH, Cp), 37.1, 22.7, 12.0, 9.3, 6.6 (CH_2, bridge), 6.3 (CH_3, Et substituent), 1.7 (CH_2, Et substituent), −6.7 (Si–CH_3)	−10.9 (Et–Si),−11.4 (Me–Si)
50	6.93–6.67, 6.12–5.88 (m, 16H, Cp), 2.95–2.41, 2.07–1.68, 1.13–0.61 (m, 17H, bridge, Et substituent), 0.23 (s, 3H, Si–CH_3)	n.d.	−11.1 (Et–Si),−11.6 (Me–Si)

Table 2 (*Continued*)

Compound	^{1}H NMR	^{13}C NMR	^{29}Si NMR
51	6.86–6.71, 5.85–5.43 (m, 16H, Cp), 1.74–1.30, 0.92–0.79 (m, 11H, bridge, ^{i}Pr substituent), 0.11 (s, 3H, Si–CH_3)	129.4, 216.5, 119.8, 119.0 (CH, Cp), 125.1, 123.0 (C_q, Cp), 26.5, 25.6 (CH_2, bridge), 20.0 (CH_3, ^{i}Pr substituent), 16.5 (CH, ^{i}Pr substituent), −6.4 (Si–CH_3)	−9.8(^{i}Pr–Si) −10.9 (Me–Si)
52	6.98–6.80, 5.67–5.49 (m, 16H, Cp), 1.98–1.38, 0.79–0.39 (m, 13H, bridge, ^{i}Pr substituent), 0.09 (s, 3H, Si–CH_3)	n.d.	−9.9 (^{i}Pr–Si) −11.1 (Me–Si)
53	6.96–6.87, 5.76–5.68 (m, 16H, Cp), 1.82–0.79 (m, 17H, bridge, ^{i}Pr substituent), 0.35 (s, 3H, Si–CH_3)	129.4, 216.5, 119.8, 119.0 (CH, Cp), 125.1, 123.0 (C_q, Cp), 26.5, 25.6 (CH_2, bridge), 20.0 (CH_3, ^{i}Pr substituent), 16.5 (CH, ^{i}Pr substituent), −6.4 (Si–CH_3)	−9.7 (^{i}Pr–Si) −11.0 (Me–Si)
54	6.76–5.28 (m, 16H, Cp), 2.08–0.41 (m, 19H, bridge, ^{i}Pr substituent), 0.17 (s, 3H, Si–CH_3)	129.1, 128.0, 115.0, 114.0 (CH, Cp), 35.9, 30.0, 26.9, 22.7, 11.1, 10.5 (CH_2, bridge), 18.0, 16.8 (CH_3, ^{i}Pr substituent), 21.9 (CH, ^{i}Pr substituent), −7.1 (Si–CH_3)	−10.0 (^{i}Pr–Si) −12.0 (Me–Si)
55	7.71–6.60, 6.10–6.06, 5.80–5.77 (m, 24H, Ind), 2.10–0.53 (m, 20H, bridge, Et substituent, Si–CH_3)	144.8, 144.4, 142.6, 140.9 (C_q, Ind), 129.8, 129.5, 128.6, 128.4, 128.1, 127.5, 126.4, 126.3, 125.7, 125.4, 124.1, 119.4, 104.0 (CH, Ind), 33.6, 27.2, 26.6, 24.4, 10.7, 8.9 (CH_2, bridge), 14.1 (CH_3, Et substituent), 1.6 (CH_2, Et substituent), −6.3 (Si–CH_3)	−11.6 (Et–Si), −12.4 (Me–Si)
56	7.69–7.13, 6.48–6.42, 6.18–6.10 (m, 24H, Ind), 1.56–0.81 (m, 11H, bridge, ^{i}Pr substituent), 0.09 (s, 3H, Si–CH_3)	n.d.	−10.3 (^{i}Pr–Si) −12.9 (Me–Si)
57	7.76–6.90 (m, 24H, Ind) 2.09–1.89, 1.81–0.46 (m, 13H, bridge, ^{i}Pr substituent), −0.25 (s, 3H, Si–CH_3)	144.4, 144.0, 139.8 (C_q, Ind), 127.4, 127.2, 126.0, 125.5, 123.5, 123.1, 122.3, 122.0, 120.8, 120.5, 120.0 (CH, Ind), 26.8, 10.1, 9.8 (CH_2, bridge), 18.3 (CH_3, ^{i}Pr substituent), 13.8 (CH, ^{i}Pr substituent), −6.1 (Si–CH_3)	−9.8 (^{i}Pr–Si) −10.8 (Me–Si)
58	7–91–6.87, 6.39–6.33, 6.20–6.15 (m, 24H, Ind), 2.15–0.64 (m, 19H, ^{i}Pr substituent, bridge), 0.37 (s, 3H, Si–CH_3)	140.7, 140.4, 139.9 (C_q, Ind), 132.0, 130.8, 127.5, 126.8, 126.2, 126.0, 125.4, 125.0, 124.7, 123.4, 122.3, 121.0, 104.2 (CH, Ind), 36.4, 33.7, 29.7, 27.0, 26.6, 25.4, 14.6, 9.2, 8.6 (CH_2, bridge), 18.3, 15.1, 13.8 (CH_3, CH, ^{i}Pr substituent), −7.0 (Si–CH_3)	−10.7 (^{i}Pr–Si) −12.1 (Me–Si)
59	7.90–7.76, 7.39–7.06 (m, 32H, Flu), 1.32–0.91 (m, 6H, ^{i}Pr–CH_3), 0.46–0.37 (m, 1H, ^{i}Pr–CH), −0.36 (s, 3H, Si–CH_3)	147.6, 147.1, 141.5 (C_q, Flu), 126.1, 125.8, 125.6, 125.1, 124.2, 120.1 (CH, Flu), 27.5, 26.4 (CH_2, bridge), 17.9, 17.8 (CH_3, ^{i}Pr substituent), 10.9 (CH, ^{i}Pr substituent), −7.9 (Si–CH_3)	−10.2 (^{i}Pr) −12.8 (Me–Si)
60	7.88–7.64, 7.34–7.01 (m, 32H, Flu), 2.27–1.96, 1.41–0.96 (m, 12H, bridge, ^{i}Pr–CH_3), 0.46–0.37 (m, 1H, ^{i}Pr–CH), −0.14 (s, 3H, Si–CH_3)	n.d.	−10.8 (^{i}Pr–Si) −12.4 (Me–Si)
61	7.86–6.79 (m, 32H, Flu), 1.65–0.22 (m, 19H, bridge, ^{i}Pr substituent), −0.37 (s, 3H, Si–CH_3)	146.4, 145.6, 141.3 (C_q, Flu), 130.0, 128.5, 126.5, 126.0, 124.7, 124.0, 123.4, 121.6, 121.2, 120.7, 120.2, 119.8, 119.4, 117.9 (CH, Flu), 33.7, 33.3, 27.2, 26.5, 11.7, 10.8 (CH_2, bridge), 18.3 (CH_3, ^{i}Pr substituent), 8.3 (CH, ^{i}Pr substituent), −7.2 (Si–CH_3)	−11.0 (^{i}Pr–Si) −12.9 (Me–Si)

n.d.: not determined.

Table 3
GC/MS data of the ligand precursors

Compound number	*m/z*	Compound number	*m/z*	Compound number	*m/z*
6	256	**25**	389	**44**	737
7	270	**26**	403	**45**	751
8	284	**27**	417	**46**	709
9	298	**28**	431	**47**	723
10	312	**29**	445	**48**	737
11	270	**30**	403	**49**	751
12	284	**31**	417	**50**	765
13	298	**32**	445	**51**	723
14	312	**33**	459	**52**	737
15	326	**34**	n.d.	**53**	765
16	284	**35**	n.d.	**54**	779
17	298	**36**	n.d.	**55**	765
18	326	**37**	n.d.	**56**	n.d.
19	340	**38**	n.d.	**57**	n.d.
20	375	**39**	n.d.	**58**	n.d.
21	389	**40**	n.d.	**59**	n.d.
22	403	**41**	695	**60**	n.d.
23	417	**42**	709	**61**	n.d.
24	431	**43**	723		

n.d.: not determined due to decomposition.

characterized by NMR spectroscopy (Table 2) and GC/MS (Table 3).

3.12. Preparation of the dinuclear metallocene complexes ***41–61***

3.12.1. General procedure

An amount of 5 mmol of the ligand precursor was dissolved in 400 ml of diethyl ether and 12.5 ml of a butyl lithium solution (1.6 M in hexane; 20 mmol) was added at room temperature. The reaction mixture was stirred for 8 h. Subsequently, the solution was cooled to −78 °C, an equimolar amount of $ZrCl_4$ was added and then the suspension was brought to room temperature slowly within 6 h and was stirred for another 6 h. The solvent was removed in vacuo, the residue was suspended in methylene chloride and the suspension was filtered over Na_2SO_4. The solvent was removed in vacuo to almost dryness, pentane was added until precipitation started and the crude product was crystallized at −28 or −78 °C. Yields: 40–80%. The complexes were characterized by NMR spectroscopy (Table 2) and GC/MS (Table 3).

The synthesis of the reference complexes **R1**–**R3** was performed in the same manner. The stoichiometry of the addition of butyl lithium and zirconium tetrachloride is corresponding to the acid protons of the mononuclear ligand precursors.

3.13. Polymerization reactions

An amount of 20–25 mg of the corresponding complex was dissolved in 50 ml of toluene. A volume of the solution containing 1–2 mg of the complex was activated with MAO (30% in toluene; Al:Zr = 2500:1).

For heterogeneous polymerization reactions, silica gel was added (1 g SiO_2/μmol(Zr)) to this solution and stirred for 3 min. Both for homogeneous and heterogeneous polymerizations, the catalyst suspension was charged to 250 ml of pentane and transferred to a 1 l Büchi laboratory autoclave and thermostated at 60 °C. An ethylene pressure of 10 bar was applied to the reactor and the catalyst was polymerized for 30 min at 60 ± 3 °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 Phillips Petroleum Company (Bartlesville, OK, USA) and the Deutsche Forschungsgemeinschaft (DFG) for the financial support and Witco company (Bergkamen) for the donation of methylalumoxane.

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