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Asymmetric dinuclear *ansa* zirconocene complexes with methyl and phenyl substituted bridging silicon atoms as dual site catalysts for the polymerization of ethylene

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Dedicated to Professor Pierre Braunstein

Abstract

Sixteen asymmetric dinuclear *ansa* zirconocene complexes bearing cyclopentadienyl, indenyl or fluorenyl ligands and their ligand precursors have been synthesized and characterized by NMR spectroscopy. After activation with methylalumoxane (MAO), the complexes behave like dual site catalysts and produce polyethylenes with bimodal or broad molecular weight distributions in homogeneous and heterogeneous media.

Keywords: *Ansa* zirconocene complexes; Dual site catalysts; Dinuclear asymmetric complexes; Homogeneous and heterogeneous ethylene polymerization

1. Introduction

In the past, monomeric metallocene complexes have proven excellent single site catalysts for the polymerization of ethylene and propylene [1–5]. The produced polyolefins have narrow molecular weight distributions and this can be disadvantageous for industrial processing. In order to obtain broader molecular weight distributions, it is possible to mix various catalysts or the corresponding polyolefins. Both approaches can cause additional problems and costs. Therefore, it was the intention to solve this problem with asymmetric dinuclear metallocene complexes. They should have the potential of dual site catalysts. Other known dinuclear metallocene complexes do not unify two different catalytic centers [6–13].

In this context silylene bridged metallocene moieties appeared as attractive building blocks due to the observation that $-SiR^1R^2-$ bridges give better activities than $-CR^1R^2-$ bridges [3,14–18]. Surprisingly also the substituents R^1 and R^2 have a strong influence on the activities of these catalysts and the molecular weights of the polymers formed [3,14–18].

2. Results and discussion

2.1. Synthesis of the dichlorosilane and tetrachlorodisilane precursors

Dichlorosilanes and tetrachlorodisilanes were synthesized according to Schemes 1–3:

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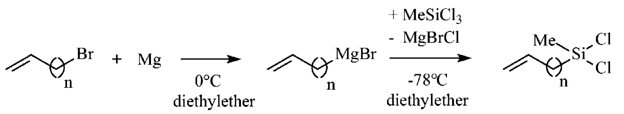
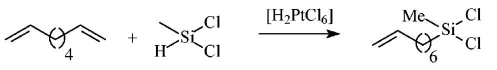


1 (n = 0)
2 (n = 1)
3 (n = 2)
4 (n = 3)
5 (n = 4)

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

The octenyl derivative **6** was formed in a catalytic hydrosilation reaction [14,15]:



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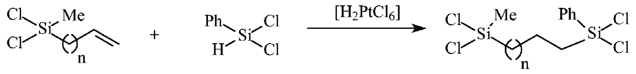
Scheme 2. Synthesis of ω-octenyl methyldichlorosilane (**6**) by hydrosilation reaction.

The resulting ω-alkenyl substituted methyldichlorosilane derivatives were treated with phenyldichlorosilane in catalytic hydrosilation reactions.

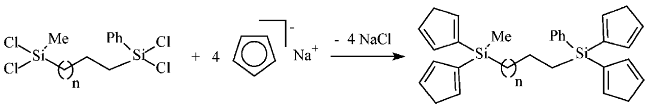


7 (n = 0) **10** (n = 3)
8 (n = 1) **11** (n = 4)
9 (n = 2) **12** (n = 6)

Scheme 3. Formation of tetrachlorodisilane derivatives by hydrosilation reactions [19,20].

2.2. Synthesis of the ligand precursors

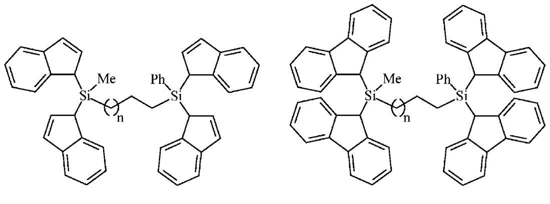
The tetrachlorodisilane derivatives were treated with 4 equiv. of sodium cyclopentadienide. The ligand precursors were formed by salt elimination reactions according to Scheme 4 [21–25]:



13 (n = 0) **16** (n = 3)
14 (n = 1) **17** (n = 4)
15 (n = 2) **18** (n = 6)

Scheme 4. Synthesis of the ligand precursors **13**–**18**.

The indenyl and fluorenyl derivatives **19**–**28** were prepared in the same manner (Scheme 5):



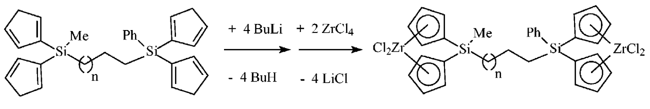
19 (n = 0) **22** (n = 4)
20 (n = 1) **23** (n = 6)
21 (n = 3)

24 (n = 0) **27** (n = 4)
25 (n = 1) **28** (n = 6)
26 (n = 3)

Scheme 5. Indenyl and fluorenyl ligand precursors **19**–**28**.

2.3. Preparation of the complexes

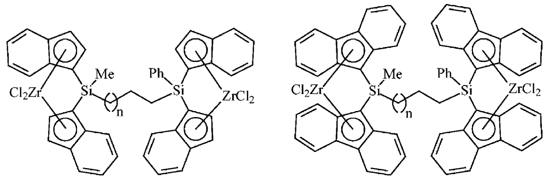
The dinuclear *ansa* zirconocene complexes were prepared according to Scheme 6 [26,27]:



29 (n = 0) **32** (n = 3)
30 (n = 1) **33** (n = 4)
31 (n = 2) **34** (n = 6)

Scheme 6. Synthesis of the *ansa* zirconocene complexes **29**–**34**.

The indenyl and fluorenyl complexes **35**–**44** were prepared in an analogous manner (Scheme 7):

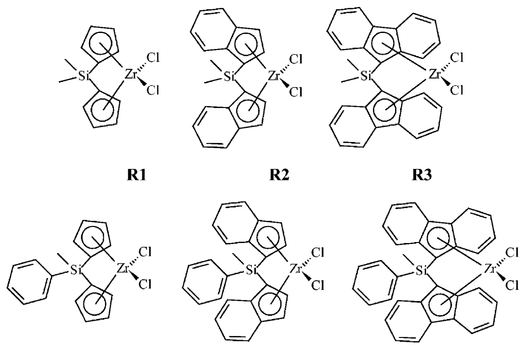


35 (n = 0) **38** (n = 4)
36 (n = 1) **39** (n = 6)
37 (n = 3)

40 (n = 0) **43** (n = 4)
41 (n = 1) **44** (n = 6)
42 (n = 3)

Scheme 7. Fluorenyl and indenyl substituted *ansa* zirconocene complexes **35**–**44**.

For comparison the following monomeric reference complexes **R1**–**R6** were synthesized [21,25] (Scheme 8):



R1 **R2** **R3**

R4 **R5** **R6**

Scheme 8. Reference catalyst precursors **R1**–**R6**.

2.4. Polymerization results

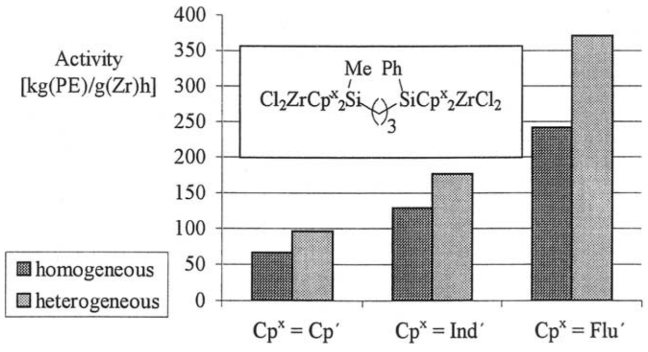
The dinuclear complexes **29**–**44** and the reference compounds **R1**–**R6** were activated with MAO in toluene solution. The homogeneous catalyst solution was used for ethylene polymerization. In a similar manner the corresponding activated catalyst solutions were treated with silica gel [1 g SiO_2/μmol(Zr)] and then used for heterogeneous ethylene polymerization. The polymerization results are given in Table 1:

A comparison of the homogeneous and the heterogeneous polymerization runs shows the surprising result that the heterogeneous catalysts in nearly all cases are more active than the homogeneous ones (Scheme 9). This result is contrary to earlier observations [20,22,26,27] and could be due to the fact that the dinuclear complexes form cationic species more efficiently on the surface of silica than in homogeneous solution. Another explanation could derive from reduced deactivation processes during the polymerization and reduced intermolecular blocking of the coordination spheres of the catalysts.

An increase of activity can also be observed when the cyclopentadienyl ligand is substituted with an indenyl or fluorenyl group. The results are summarized in Scheme 9.

The chain length of the $(CH_2)_n$ spacers has also considerable influence on the activity of the homogeneous or heterogeneous catalysts. The best results were obtained for $n = 5$. A 1,5-pentylidene spacer seems to provide the best distance between the two catalyst centers to optimize the activity (Scheme 10). A crucial factor that could determine kinetics of polymerization could be the steric requirement for the orientation of the polymer chains during the polymerization process.

Also the molecular weight goes up when polyethylene is produced with a heterogeneous catalyst instead of a homogeneous (Scheme 11). This could be indicative for a hindered β-H elimination reaction as chain terminating step [28–30].



Scheme 9. Activities of various dinuclear catalysts in homogeneous and heterogeneous polymerization reactions of ethylene. Cp′ = C_5H_4, Ind′ = C_9H_6, Flu′ = $C_{13}H_3$.

Table 1
Polymerization data of the catalyst precursors **29**–**44**, the reference catalyst precursors **R1**–**R6** and mixtures thereof in homogeneous and heterogeneous ethylene polymerization reactions

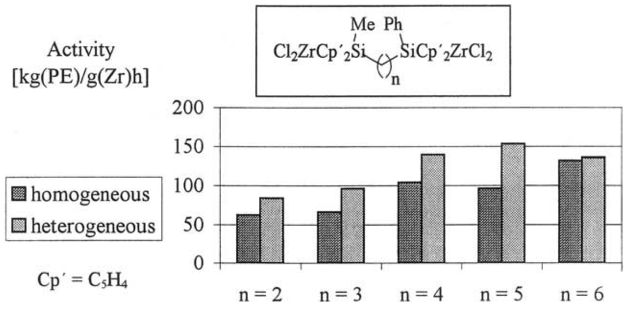
Complex	Activity [g(PE)/g(Zr)h] M_n [g mol^{-1}] HI [M_w/M_n] (homogeneous conditions)	Activity [g(PE)/g(Zr)h] M_n [g mol^{-1}] HI [M_w/M_n] (heterogeneous conditions)
29	61 600 36 140 13.1	84 000 202 400 54.4 [a]
30	66 000 22 520 11.0	96 000 425 000 18.6
31	105 000 64 420 6.2	139 000 473 000 7.7
32	96 000 54 890 9.2	153 000 n.d.
33	132 000 70 210 8.8	136 000 496 000 7.7
34	117 500 98 980 9.9	163 000 37 110 12.6
35	91 500 177 900 8.6	172 000 143 400 5.6
36	128 500 231 600 3.5	176 900 167 700 4.5
37	113 200 108 000 16.7 [a]	185 400 940 317.2
38	168 200 99 600 8.4	222 700 97 780 9.3
39	210 000 51 360 5.5	240 000 88 870 390.6 [a]
40	240 000 282 000 35.0 [a]	286 000 125 500 10.3
41	241 300 496 600 3.0	370 000 363 100 5.9
42	190 000 775 700 2.3	227 400 800 600 2.4
43	252 000 224 200 44.9 [a]	253 000 448 400 44.6 [a]
44	256 000 841 400 118.9 [a]	232 000 396 400 3.3
R1	109 000	102 000

Table 1 (*Continued*)

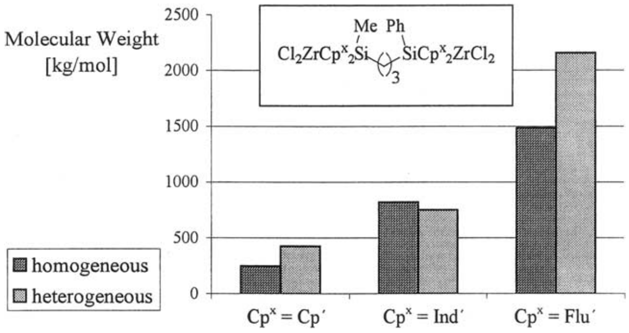
Complex	Activity [g(PE)/g(Zr)h] M_n [g mol^{-1}] HI [M_w/M_n] (homogeneous conditions)	Activity [g(PE)/g(Zr)h] M_n [g mol^{-1}] HI [M_w/M_n] (heterogeneous conditions)
	95 120 2.8	104 000 2.6
R2	250 000 135 700 2.6	190 000 149 500 2.5
R3	320 000 413 800 3.0	260 000 396 000 2.3
R4	103 000 99 310 2.8	96 000 121 500 2.4
R5	265 000 145 400 2.7	210 000 150 900 2.7
R6	330 000 486 400 2.9	270 000 417 200 2.3
R1+R4	101 000 69 640 3.2	97 000 104 700 3.4
R2+R5	241 000 195 100 4.5	193 000 184 300 8.0
R3+R6	316 000 551 900 11.1	262 000 1 282 000 7.5

n.d., not determined.

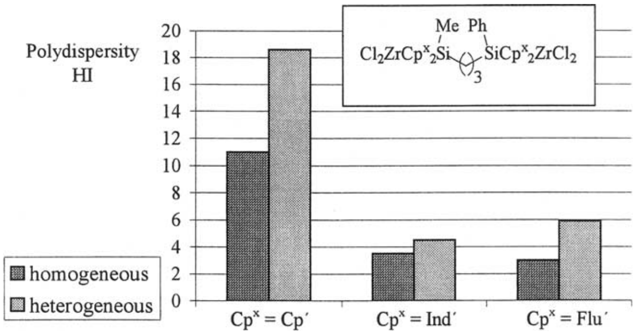
[a] Molecular masses were too high to be determined, curve was extrapolated; the measured data is not involved in the discussion of the results.



Scheme 10. Correlation between spacer length and activity of a catalyst.



Scheme 11. Molecular weights of polyethylenes from homogeneous and heterogeneous polymerization conditions.



Scheme 12. Polydispersities of polyethylenes from homogeneous and heterogeneous polymerization conditions.

The molecular weight distributions of the produced polyethylenes confirm the expectations: they are all of bimodal character (Scheme 12).

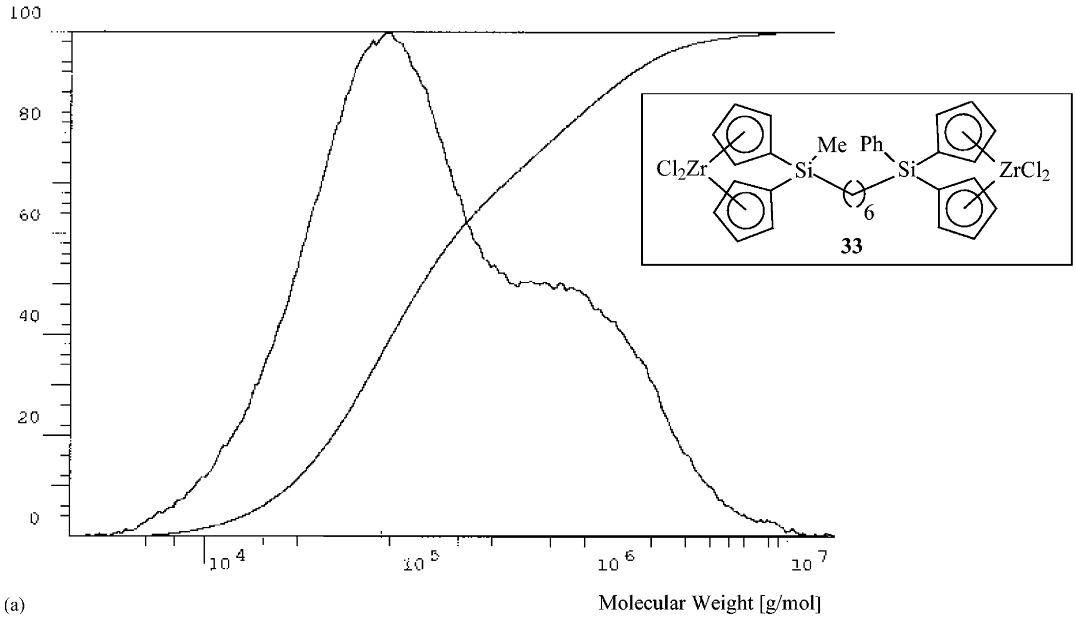
The broadest molecular weight distributions were obtained with the cyclopentadienyl complexes. In these derivatives the asymmetry of the dinuclear complex has the strongest impact (Scheme 13).It can be postulated that the low molecular mass fraction at a maximum molecular weight of 100 000 g mol^{-1} is produced by the methyl silyl catalyst moiety and the higher molecular mass fraction (at 1 000 000 g mol^{-1}) by the phenyl silyl component. It is known from single site catalyst experiments [22,25] that the molecular masses of those compounds show such characteristic distributions.

In order to investigate the question whether a similar polydispersity can be obtained by mixing the corresponding monomeric complexes the following experiments were conducted:

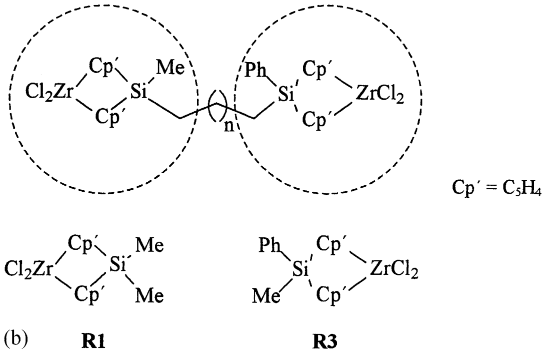
The mononuclear reference complexes **R1**–**R6** were activated with MAO and polymerized under homogeneous and heterogeneous conditions and as equimolar mixtures.

Scheme 14 shows two single site catalyst precursors that result from the ‘split’ of a dinuclear complex. The results of the ethylene polymerizations with these reference catalysts are shown in Scheme 15.

As a general observation, it was found that the catalyst activity increases from *cyclo*pentadienyl to fluorenyl substitution. The mixtures are in the same range as the single site catalysts. On the other hand, heterogenization on silica gel causes a decrease of activity. The phenyl-substituted catalysts produce higher molecular masses of the polymers and have a slightly higher productivity. The polydispersities of the poly-



Scheme 13. HT-GPC plot of polyethylene produced with **33** under heterogeneous conditions.



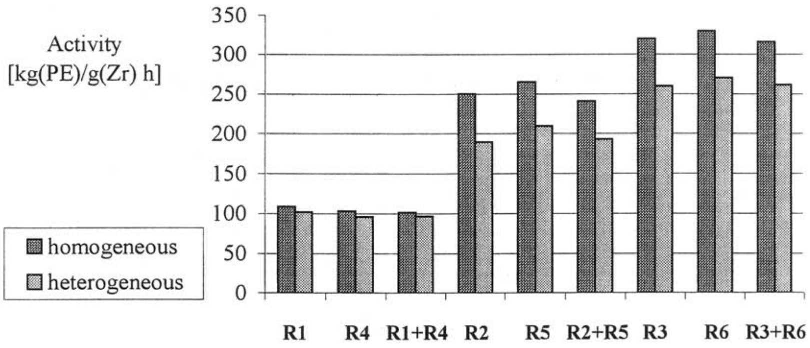
Scheme 14. Splitting of a dinuclear metallocene complex into two mononuclear complexes.

ethylenes produced with the reference catalysts are shown in Scheme 16:

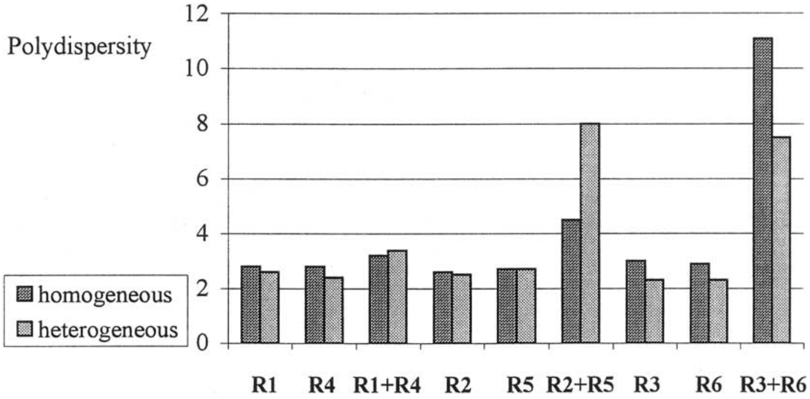
It becomes obvious that catalyst mixtures produce polymers with a higher HI than the single site catalysts. This broadening effect increases in the series cyclopentadienyl < indenyl < fluorenyl. Polymerizations of ethylene with catalyst mixtures are known and show similar results [31–36].

The difference between two dinuclear complexes is caused by the different chain lengths of the spacer units between the two metal centers. This is an indication for a cooperative effect of the two metal centers that must also be dependent from the steric conditions during the polymerization process. As a consequence, the average values of the catalyst activities and the polydispersities of the formed polymers were calculated and compared with the performance of the mixture of the mononuclear catalysts.

Scheme 17 shows the catalyst activities of the three catalyst reference mixtures and the averaged activities of the cyclopentadienyl, indenyl and fluorenyl substituted catalysts. It is obvious that the dinuclear catalysts increase their activities after heterogenization. This is rather uncommon. In case of mononuclear species, the opposite effect is observed. On the other hand, the activities of the dinuclear catalysts are generally lower



Scheme 15. Activities of the reference catalysts **R1**–**R6** and mixtures thereof.



Scheme 16. Polydispersities of the reference catalysts **R1**–**R6** and mixtures thereof.

under homogeneous conditions. The polydispersities are presented in Scheme 18.

The effects that contribute to the amount of the polydispersities are not as clear as in the case of the activities, but a good tendency can be anticipated: The average molecular mass distribution of the polymers produced with dinuclear catalysts is decreasing with growing size of the ligands from cyclopentadienyl to fluorenyl substitution. The polymers produced with catalyst mixtures show an opposite effect. The larger the ligands the higher the results of the polydispersity. It seems that a larger ligand sphere in case of mononuclear catalysts has a much stronger impact on the catalyst properties than in the case of a dinuclear catalyst.

3. Experimental

All experimental work was routinely carried out using Schlenk technique. Dried and purified Ar was used as inert gas. Toluene, C_5H_{12}, Et_2O and THF were purified by distillation over Na/K alloy. Ether was additionally distilled over $LiAlH_4$. Methylene chloride was dried with CaH_2. Deuterated solvents such as $CHCl_3$-d_1 and C_6H_6-d_6 were dried over molecular sieves (300 pm), degassed and stored under inert gas atmosphere.

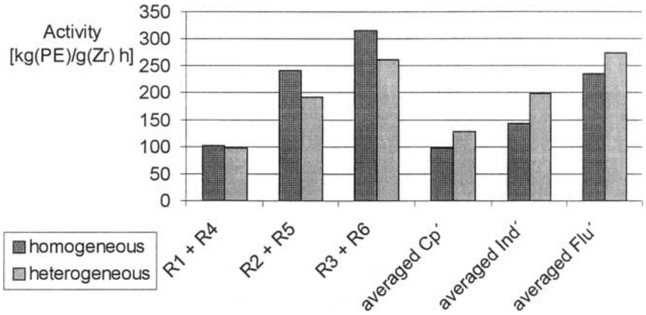
Commercially available indene was distilled and stored at −28 °C. Cyclopentadiene was freshly distilled from the dimer. Methylalumoxane (MAO; 30% in $C_6H_5CH_3$) was supplied by Witco Company, Bergkamen. All the other starting materials were commercially available and were used without further purification.

3.1. NMR spectroscopy

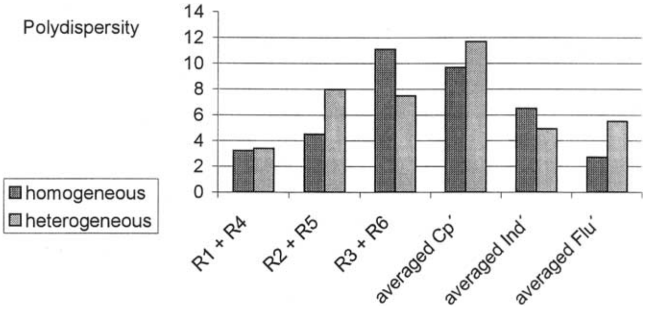
The spectrometer Bruker ARX 250 was available for the recording of the NMR spectra. The organometallic compounds were prepared under inert gas atmosphere (Ar). The spectra were recorded at 25 °C. The chemical shifts in the ^1H NMR spectra are referred to the residual proton signal of the solvent ($\delta = 7.24$ ppm for $CHCl_3$, $\delta = 7.15$ ppm for C_6H_6) and in the ^{13}C NMR spectra to the solvent signal ($\delta = 77.0$ ppm for $CHCl_3$-d_1, $\delta = 128.0$ ppm for C_6H_6-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 thickness 0.25 μm) was used. The measuring program was: 3 min at 70 °C (starting phase); 20 °C min^{-1} (heating phase); variable time at 210 °C (final phase).



Scheme 17. Comparison of catalyst activities of catalyst mixtures and dinuclear catalysts.



Scheme 18. Polydispersities of polyethylenes produced with catalyst mixtures and with dinuclear catalysts.

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. 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 °C
Heating phase: 5 °C min^{-1} (15 min)
Plateau phase: 310 °C (15 min)

3.5. 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 Å 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 °C. The apparatus was calibrated with an internal polystyrene standard.

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

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

3.7. Preparation of alkyl, aryl or ω-alkenyl substituted dichlorosilane derivatives by hydrosilation reaction

α,ω-Alkadiene (150 mmol) was dissolved in 5 ml of C_5H_{12} and treated with 30–50 mg hexachloroplatinic acid hydrate. Dichloromethylsilane (50 mmol) was added and this mixture was stirred for 40 h. After filtration (Na_2SO_4 filled filter column) the solvent and the excess amount of α,ω-alkadiene were removed in vacuo. The crude product was distilled in vacuo. Yields: 70–80%.

3.8. Preparation of ω-octenyl methyl dichlorosilane by hydrosilation reaction

1,7-Octadiene (11 g, 100 mmol), hexachloroplatinic acid hydrate (30–50 mg) and C_5H_{12} (10 ml) were given to a Schlenk vessel. Dichloromethylsilane (30 mmol) was added and this mixture was stirred for 20 h. After filtration (Na_2SO_4 filled filter column) the solvent and the excess amount of 1,7-octadiene were removed in vacuo. The crude product was distilled in vacuo. Yield: 95%.

3.9. Preparation of the alkyl, aryl or ω-alkenyl substituted dichlorosilane derivatives **1–6** by Grignard reaction

Magnesium turnings (6.1 g, 250 mmol) suspended in 100 ml of Et_2O were placed in a three necked flask with dropping funnel and reflux cooling system at 0 °C. The Mg was activated by addition of 0.1 g I_2. Alkyl, aryl or ω-alkenyl bromide (240 mmol) in 100 ml of ether were added slowly during 1 h. After addition of the bromide the mixture was stirred for another hour at room temperature (r.t.).

Trichlorosilane derivative (70 ml, 450 mmol) in 100 ml of Et_2O was placed in a Schlenk vessel. The Grignard product was added slowly to this mixture at −78 °C within 1 h and brought to r.t. within 3 h. The solvent and the excess trichlorosilane were distilled off the mixture. The residue was suspended in C_5H_{12}, the solution filtered over Na_2SO_4 and the crude product was distilled. Yields: 50–80%. The products were characterized by NMR spectroscopy (Table 2).

3.10. Preparation of cyclopentadienyl substituted ligand precursors

Sodium cyclopentadienyl (4.5 g, 51.1 mmol) in 50 ml of THF was placed in a Schlenk vessel. 2-Sila-2,2-dichloro-5-hexene (4.32 g, 25.6 mmol) was added and the mixture was stirred for 15 h at r.t. The solvent was removed in vacuo and the residue was suspended in Et_2O. The suspension was filtered over Na_2SO_4/SiO_2 and the solvent was removed in vacuo. Yields: 70–80%.

3.11. Preparation of indenyl or fluorenyl substituted ligand precursors

Indenyl lithium or fluorenyl lithium (23.4 mmol) in 100 ml of Et_2O was placed in a Schlenk vessel. 2-Sila-2,2-dichloro-ω-alkene (25.6 mmol) dissolved in 10 ml of Et_2O was added and the mixture was stirred for 8 h at r.t. The suspension was filtered over Na_2SO_4/SiO_2 and the solvent was removed in vacuo. Yields: 60–70%.

Table 2
NMR data [a] 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.	n.d.
6	n.d.	n.d.	n.d.
7	7.49–7.45, 7.24–7.20 (m, 5H, Ph), 1.24–1.17, 1.02–0.95 (m, 4H, bridge), 0.52 (s, 3H, Si–CH$_3$)	133.6, 132.2, 128.6 (CH, Ph), 130.8 (C$_q$, Ph), 13.8, 12.5 (CH$_2$, bridge), 3.9 (Si–CH$_3$)	33.1 (Me–Si) 19.3 (Ph–Si)
8	7.68–7.64, 7.18–7.08 (m, 5H, Ph), 1.75–1.69, 1.19–1.12, 0.89–0.82 (m, 6H, bridge), 0.39 (s, 3H, Si–CH$_3$)	133.4, 132.0, 128.7 (CH, Ph), 132.2 (C$_q$, Ph), 34.1, 22.4, 21.8 (CH$_2$, bridge), 4.9 (Si–CH$_3$)	31.8 (Me–Si) 18.5 (Ph–Si)
9	7.87–7.65, 7.46–7.38 (m, 5H, Ph), 1.78–1.17 (m, 8H, bridge), 0.79 (s, 3H, Si–CH$_3$)	133.4, 130.8, 129.0 (CH, Ph), 132.1 (C$_q$, Ph), 34.5, 24.1, 21.7, 14.5 (CH$_2$, bridge), 4.1 (Si–CH$_3$)	32.8 (Me–Si) 19.7 (Ph–Si)
10	7.59–7.55, 7.33–7.27 (m, 5H, Ph), 1.43–1.33, 1.21–1.15 (m, 10H, bridge), 0.59 (s, 3H, Si–CH$_3$)	133.6, 131.9, 128.6 (CH, Ph), 132.6 (C$_q$, Ph), 35.2, 22.3, 20.7 (CH$_2$, bridge), 5.5 (Si–CH$_3$)	33.0 (Me–Si) 19.2 (Ph–Si)
11	7.67–7.64, 7.18–7.10 (m, 5H, Ph), 1.89–1.03, 0.81–0.72 (m, 12H, bridge), 0.42 (s, 3H, Si–CH$_3$)	134.1, 132.0, 129.9 (CH, Ph), 133.1 (C$_q$, Ph), 33.0, 27.4, 25.6, 20.7, 18.2, 15.5 (CH$_2$, bridge), 5.0 (Si–CH$_3$)	33.1 (Me–Si) 19.4 (Ph–Si)
12	7.57–7.55, 7.30–7.27 (m, 5H, Ph), 1.22–1.07, 0.96–0.70 (m, 16H, bridge), 0.59 (s, 3H, Si–CH$_3$)	133.3, 131.5, 128.3 (CH, Ph), 132.4 (C$_q$, Ph), 32.3, 32.2, 28.8, 28.7, 22.4, 21.6, 21.5, 20.6 (CH$_2$, bridge), 5.2 (Si–CH$_3$)	33.2 (Me–Si) 19.1 (Ph–Si)
13	7.45–7.33 (m, 5H, Ph), 6.69–6.33 (m, 16H, ar H, Cp), 3.60–2.98 (m, 8H, al H, Cp), 1.25–0.30 (m, 4H, bridge), −0.01, −0.27 (s, 3H, Si–CH$_3$)	138.6, 134.5, 132.7, 131.1, 129.4, 127.6, 117.4 (CH, ar, Cp, Ph), 136.2, 128.1 (C$_q$, Cp, Ph), 46.9, 44.2 (CH$_2$, al, Cp), 21.9, 20.8 (CH$_2$, bridge), −6.5, −6.9 (Si–CH$_3$)	5.6 (Me–Si) −6.0 (Ph–Si)
14	7.68–7.21 (m, 5H, Ph), 6.98–6.92, 6.22–5.87 (m, 16H, ar H, Cp), 3.93–3.67 (m, 8H, al H, Cp), 1.32–0.52 (m, 6H, bridge), 0.12, −0.07 (s, 3H, Si–CH$_3$)	142.5, 141.9, 140.0 (C$_q$, Cp, Ph), 134.5, 133.9, 132.9, 131.1, 129.3, 127.6 (CH, Cp, Ph), 47.8 (CH$_2$, al, Cp), 26.8, 8.9, 8.6 (CH$_2$, bridge), −4.4 (Si–CH$_3$)	−2.6 (Me–Si) −13.7 (Ph–Si)
15	7.71–7.17 (m, 5H, Ph), 6.95–6.78, 6.43–5.91 (m, 16H, ar H, Cp), 3.90–3.81 (m, 8H, al H, Cp), 1.73–0.55 (m, 8H, bridge), −0.09, −0.26 (s, 3H, Si–CH$_3$)	144.4, 144.0, 140.6 (C$_q$, Cp, Ph), 134.8, 133.8, 133.4, 133.0, 131.4, 130.6, 129.8, 128.1 (CH, Cp, Ph), 46.3 (CH$_2$, al, Cp), 25.4, 23.4, 12.9, 10.8 (CH$_2$, bridge), −5.8 (Si–CH$_3$)	−2.9 (Me–Si) −13.3 (Ph–Si)
16	7.83–7.29 (m, 5H, Ph), 7.01–6.95, 6.32–5.91 (m, 16H, ar H, Cp), 3.85–3.71 (m, 8H, al H, Cp), 1.92–0.42 (m, 10H, bridge), 0.09, −0.13 (s, 3H, Si–CH$_3$)	142.4, 142.0, 140.5 (C$_q$, Cp, Ph), 133.7, 132.9, 132.2, 131.0, 130.3, 127.2 (CH, Cp, Ph), 46.4 (CH$_2$, al, Cp), 28.3, 18.8, 17.4, 9.1, 8.8 (CH$_2$, bridge), −5.2 (Si–CH$_3$)	−2.5 (Me–Si) −13.7 (Ph–Si)
17	7.65–7.34 (m, 5H, Ph), 6.78–6.43 (m, 16H, ar H, Cp), 3.82–3.03 (m, 8H, al H, Cp), 2.22–0.61 (m, 10H, bridge), 0.21, 0.06, −0.15 (s, 3H, Si–CH$_3$)	143.1, 142.7, 139.6 (C$_q$, Cp, Ph), 135.1, 134.8, 134.1, 133.2, 131.4, 130.8, 130.1, 128.2 (CH, Cp, Ph), 46.9 (CH$_2$, al, Cp), 33.4, 24.4, 23.4, 13.6, 11.5, 11.0 (CH$_2$, bridge), −0.1, −6.5 (Si–CH$_3$)	3.2 (Me–Si) −7.9 (Ph–Si)
18	7.58–7.18 (m, 5H, Ph), 6.53–6.21 (m, 16H, ar H, Cp), 3.96–2.89 (m, 8H, al H, Cp), 1.99–0.96 (m, 16H, bridge), −0.24, −0.37 (s, 3H, Si–CH$_3$)	145.2, 145.0, 144.5, 141.1, 140.8 (C$_q$, Cp, Ph), 134.5, 134.0, 129.1, 129.0, 128.0, 126.0, 125.6, 124.5, 124.0, 120.0, 119.9, 119.8, 119.7 (CH, ar, Cp, Ph), 40.4, 39.7, 38.5 (CH, al, Cp), 33.4, 33.2, 28.3, 26.6, 25.6, 23.1, 22.7, 11.6, 10.6, 10.4, 9.0 (CH$_2$, bridge), −6.3, −7.1 (Si–CH$_3$)	4.2 (Me–Si) −7.2, −7.4 (Ph–Si)
19	7.39–6.21 (m, 29H, ar Ind, Ph), 3.81, 3.76, 3.56 (m, 4H, al H, Ind), 3.02 (s, 4H, al H, Ind), 0.13, −0.16, −0.31 (s, 3H, Si–CH$_3$)	n.d.	6.1 (Me–Si) −4.9 (Ph–Si)
20	7.21–6.22 (m, 29H, ar H, Ind, Ph), 3.91–3.43, 3.03–3.00 (m, 8H, al H, Ind), 1.39–1.10, 0.90–0.81 (m, 6H, bridge), −0.14, −0.32 (s, 3H, Si–CH$_3$)	144.4, 144.0, 142.1 (C$_q$, Ind, Ph), 133.8, 129.9, 127.8, 127.4, 124.1, 123.7, 121.4 (CH, Ind, Ph), 42.6, 40.9, (CH, al, Ind), 38.8 (CH$_2$, al, Ind), 27.3, 27.1, 19.6 (CH$_2$, bridge), −1.6 (Si–CH$_3$)	4.1 (Me–Si) −4.2 (Ph–Si)

Table 2 (*Continued*)

Compound	^{1}H NMR	^{13}C NMR	^{29}Si NMR
21	7.51–7.31, 7.22–6.50 (m, 29H, ar H, Ind, Ph), 3.54–3.39 (m, 4H, al H, Ind), 1.25–0.91 (m, 10H, bridge), −0.29 (s, 3H, Si–CH$_3$)	145.2, 145.1, 144.8, 140.1 (C$_q$, Ind, Ph), 135.6, 134.4, 134.0, 131.8, 130.4, 129.6, 129.4, 128.1, 124.7, 123.4, 121.7, 121.5 (CH, ar, Ind, Ph), 47.8, 46.6, 45.6, 44.8 (CH, al, Ind), 30.0, 29.9, 24.8, 22.8, 22.7 (CH$_2$, bridge), −6.5 (Si–CH$_3$)	5.7 (Me–Si) −4.4 (Ph–Si)
22	7.44–7.12, 6.77–6.74, 6.28, 6.23 (m, 29H, ar H, Ind, Ph), 3.82–3.05 (m, 8H, al H, Cp), 2.21–0.37 (m, 12H, bridge), −0.08, −0.11, −0.30 (s, 3H, Si–CH$_3$)	145.2, 144.9, 143.9, 143.2 (C$_q$, Ind, Ph), 133.4, 132.6, 131.7, 130.8, 130.6, 129.3, 128.5, 128.4, 128.1, 127.9, 127.6, 126.2, 123.1 (CH, ar, Ind, Ph), 47.7, 44.4, 41.4, 39.1 (CH, al, Ind), 33.1, 33.0, 27.0, 26.5, 14.2, 13.6 (CH$_2$, bridge), 0.1, −5.9 (Si–CH$_3$)	6.1, 5.7 (Me–Si) −5.0, −5.3 (Ph–Si)
23	7.68–6.72 (m, 31H, Ind, Ph), 3.63, 3.51, 3.38 (s, 8H, al h, Ind), 1.35–0.51 (m, 16H, bridge), 0.07, −0.16, −0.30 (s, 3H, Si–CH$_3$)	144.4, 143.6, 142.6 (C$_q$, Ind, Ph), 135.2, 134.1, 132.0, 129.5, 129.4, 127.7, 126.8, 126.2, 124.8, 124.5, 123.6, 122.7, 121.2, 121.0, 120.9, (CH, ar, Ind, Ph), 51.8, 50.6, 44.3, 44.0 (CH, al, Ind), 39.0 (CH$_2$, al, Ind), 33.3, 33.1, 32.9, 29.7, 29.5, 29.3, 29.0, 22.9, 22.8 (CH$_2$, bridge), −6.2 (Si–CH$_3$)	5.9 (Me–Si) −4.6, −4.8 (Ph–Si)
24	7.87–6.83 (m, 37H, ar H, Flu, Ph), 4.42, 3.92 (s, 4H, al H, Flu), 3.18–3.14, 2.26–2.17 (m, 4H, bridge), −0.36, −0.38, −0.71 (s, 3H, Si–CH$_3$)	n.d.	8.2 (Me–Si) −3.8 (Ph–Si)
25	7.62–7.38 (m, 5H, Ph), 7.38–6.63 (m, 32H, Flu), 4.24, 3.52 (s, 4H, al H, Flu), 1.34–1.19 (m, 6H, bridge), 0.11 (s, 3H, Si–CH$_3$)	143.8, 142.9, 142.1, 140.1 (C$_q$, Flu, Ph), 135.3, 128.3, 127.6, 127.0, 126.2, 124.9, 120.5 (CH, Flu, Ph), 38.3, 38.1 (CH, al, Flu), 27.3, 26.8, 22.1 (CH$_2$, bridge), 0.1 (Si–CH$_3$)	0.8 (Me–Si) −8.8 (Ph–Si)
26	7.82–7.45 (m, 5H, Ph), 7.18–6.70 (m, 32H, Flu), 4.03, 3.72 (s, 4H, al H, Flu), 1.56–1.07 (m, 10H, bridge), −0.17 (s, 3H, Si–CH$_3$)	144.6, 144.1, 142.1, 140.0 (C$_q$, Flu, Ph), 135.3, 134.7, 131.0, 128.2, 127.2, 126.9, 126.3, 125.0, 123.4, 120.5 (CH, Flu, Ph), 39.9, 38.6 (CH, al, Flu), 29.6, 27.3, 26.8, 22.1, 19.4 (CH$_2$, bridge), −0.2 (Si–CH$_3$)	0.8 (Me–Si) −8.5 (Ph–Si)
27	7.78–7.44 (m, 5H, Ph), 7.05–6.57 (m, 32H, Flu), 3.81 (s, 4H, al H, Flu), 1.98–0.56 (m, 12H, bridge), −0.05 (s, 3H, Si–CH$_3$)	143.9, 143.0, 142.4, 139.7 (C$_q$, Flu, Ph), 135.3, 134.3, 131.7, 128.9, 128.1, 127.8, 126.6, 126.1, 125.0, 121.5, 120.5 (CH, Flu, Ph), 39.3 (CH, al, Flu), 32.1, 30.0, 27.3, 26.8, 22.1, 17.2 (CH$_2$, bridge), 0.0 (Si–CH$_3$)	7.9 (Me–Si) −4.0 (Ph–Si)
28	7.82–7.53 (m, 5H, Ph), 7.38–6.41 (m, 32H, ar H, Flu), 4.53, 3.99 (s, 4H, al H, Flu), 1.39–0.20 (m, 16H, bridge), −0.23, −0.52 (s, 3H, Si–CH$_3$)	145.8, 145.7, 141.2, 140.8, 131.6 (C$_q$, Flu, Ph), 134.5, 134.4, 127.6, 126.7, 126.2, 125.9, 125.8, 125.6, 125.5, 125.2, 124.6, 124.2, 124.2, 120.1, 120.0, 119.8, 119.7 (CH, ar, Flu, Ph), 40.8, 40.4, 39.7, 38.7 (CH, al H, Flu), 33.4, 33.2, 29.9, 28.4, 28.3, 26.6, 25.9, 23.6, 23.4, 22.7 (CH$_2$, bridge), −5.2, −7.1 (Si–CH$_3$)	7.1 (Me–Si) −0.1 (Ph–Si)
29	7.93–7.38 (m, 5H, Ph), 6.98–6.83, 6.38–6.27 (m, 16H, Cp), 1.57–1.31, 0.99–0.82 (m, 4H, bridge), 0.02 (s, 3H, Si–CH$_3$)	144.4, 143.3, 139.9, (C$_q$, Cp, Ph), 135.1, 129.8, 129.6, 129.0, 128.6, 127.6, 115.5, 114.9, 113.2 (CH, Cp, Ph), 12.1, 11.4 (CH$_2$, bridge), −5.9 (Si–CH$_3$)	−11.6 (Me–Si) −22.1 (Ph–Si)
30	7.62–7.54, 7.30–7.23, 6.87–6.83 (m, 21H, Cp, Ph), 1.52–0.81 (m, 6H, bridge), 0.17 (s, 3H, Si–CH$_3$)	145.2, 141.6, 140.6 (C$_q$, Cp, Ph), 135.1, 131.4, 130.7, 130.0, 129.0, 126.9, 116.3, 114.6, 113.9 (CH, Cp, Ph), 27.1, 16.6, 14.0 (CH$_2$, bridge), −7.5 (Si–CH$_3$)	−13.5 (Me–Si) −23.8 (Ph–Si)
31	7.99–6.00 (m, 21H, Cp, Ph), 1.83–1.49 (m, 6H, bridge), 0.19 (s, 3H, Si–CH$_3$)	147.1, 144.8, 144.7 (C$_q$, Cp, Ph), 134.9, 131.4, 129.2, 128.8, 127.9, 115.6, 115.0, 113.8 (CH, Cp, Ph), 26.4, 11.3, 11.2 (CH$_2$, bridge), −7.2 (Si–CH$_3$)	−12.3 (Me–Si) −21.7 (Ph–Si)
32	7.87–7.27 (m, 5H, Ph), 6.98–6.90, 6.22–5.92 (m, 16H, Cp), 1.87–0.62 (m, 10H, bridge), 0.09 (s, 3H, Si–CH$_3$)	144.5, 144.1, 140.5 (C$_q$, Cp, Ph), 134.9, 133.4, 130.6, 129.2, 128.8, 127.9, 127.6, 115.6, 115.0, 113.8 (CH, Cp, Ph), 29.8, 23.4, 22.7, 11.3, 11.2 (CH$_2$, bridge), −6.9 (Si–CH$_3$)	−12.1 (Me–Si) −23.2 (Ph–Si)
33	7.75–7.30 (m, 5H, Ph), 6.90–6.03 (m, 16H, Cp), 2.12–0.59 (m, 12H, bridge), 0.02 (s, 3H, Si–CH$_3$)	145.2, 139.8, 137.6 (C$_q$, Cp, Ph), 129.8, 129.2, 128.9, 128.2, 116.0, 115.9, 114.2, 114.1 (CH, ar, Cp, Ph), 32.9, 26.8, 26.4, 22.9, 11.6, 11.1 (CH$_2$, bridge), −7.8 Si–CH$_3$)	−12.3 (Me–Si) −21.9 (Ph–Si)
34	7.63–7.22 (m, 5H, Ph), 6.81–6.23 (m, 16H, Cp), 2.66–2.46, 2.19–1.73, 1.45–0.59 (m, 16H, bridge), −0.12 (s, 3H, Si–CH$_3$)	144.2, 140.8, 140.1 (C$_q$, Cp, Ph), 135.1, 133.9, 130.2, 129.8, 129.2, 128.9, 128.2, 115.9, 114.2 (CH, ar, Cp, Ph), 32.9, 31.0, 28.5, 26.8, 26.4, 22.9, 11.6, 11.1 (CH$_2$, bridge), −7.2 Si–CH$_3$)	−10.9 (Me–Si) −21.5 (Ph–Si)
35	7.77–7.61 (m, 5H, Ph), 7.36–6.90, 6.12–6.10, 5.81–5.77 (m, 24H, Ind), 1.39–0.86 (m, 4H, bridge), 0.03 (s, 3H, Si–CH$_3$)	146.2, 144.7, 134.1, 134.0 (C$_q$, Ind, Ph), 132.5, 128.5, 127.6, 126.7, 122.1, 105.2, 104.0 (CH, Ind, Ph), 15.1, 12.9 (CH$_2$, bridge), −6.1 (Si–CH$_3$)	−11.6 (Me–Si) −21.5 (Ph–Si)

Table 2 (*Continued*)

Compound	^{1}H NMR	^{13}C NMR	^{29}Si NMR
36	7.75–7.62 (m, 5H, Ph), 7.33–6.76 (m, 24H, Ind), 1.31–0.29 (m, 6H, bridge), 0.11 (s, 3H, Si–CH_3)	145.1, 144.0, 140.2 (C_q, Ind, Ph), 132.5, 131.6, 129.7, 129.1, 128.5, 127.6, 126.7, 122.1, 105.2, 104.0 (CH, Ind, Ph), 23.0, 15.1, 12.9 (CH_2, bridge), −6.4 (Si–CH_3)	−9.3 (Me–Si) −20.1 (Ph–Si)
37	7.69–6.73 (m, 29H, Ind, Ph), 1.41–0.67 (m, 4H, bridge), 0.11 (s, 3H, Si–CH_3)	144.7, 144.0, 140.9, 140.2 (C_q, Ind, Ph), 135.0, 132.5, 131.6, 129.7, 129.1, 128.5, 127.6, 126.7, 122.1, 120.3, 115.2, 114.0 (CH, Ind, Ph), 29.0, 23.0, 22.7, 12.1, 11.9 (CH_2, bridge), −6.8 (Si–CH_3)	−11.9 (Me–Si) −21.3 (Ph–Si)
38	7.89–6.73 (m, 29H, Ind, Ph), 2.05–1.67, 1.41–0.67 (m, 12H, bridge), 0.03 (s, 3H, Si–CH_3)	144.8, 144.0, 141.0, 140.1 (C_q, Ind, Ph), 135.0, 132.3, 131.1, 130.0, 129.5, 128.6, 127.2, 126.8, 122.0, 120.8, 115.1, 113.9 (CH, Ind, Ph), 31.5, 30.7, 29.0, 22.7, 12.1, 11.9 (CH_2, bridge), −7.0 (Si–CH_3)	−11.7 (Me–Si) −22.1 (Ph–Si)
39	7.91–6.99, 6.58–6.49, 6.19–6.13 (m, 29H, Ind, Ph), 1.68–0.72 (m, 16H, bridge), 0.09 (s, 3H, Si–CH_3)	147.0, 146.8, 144.5, 144.3 (C_q, Ind, Ph), 135.9, 135.2, 134.2, 129.1, 127.6, 124.9, 124.4, 123.8, 123.6, 122.6, 122.2, 121.0 (CH, Ind, Ph), 29.7, 29.0, 26.7, 26.0, 23.8, 22.4, 9.6, 9.4 (CH_2, bridge), −6.4 (Si–CH_3)	−11.6 (Me–Si) −20.4 (Ph–Si)
40	7.81–7.58, 7.46–7.01 (m, 37H, Flu, Ph), 2.21–0.93 (m, 4H, bridge), −0.01 (s, 3H, Si–CH_3)	144.5, 144.0, 140.1 (C_q, Flu, Ph), 135.0, 133.4, 130.1, 129.0, 128.1, 127.9, 127.4, 126.8, 126.2, 125.5, 125.1, 124.7, 124.2 (CH, Flu, Ph), 14.2, 12.4 (CH_2, bridge), −6.7 (Si–CH_3)	−11.2 (Me–Si) −21.0 (Ph–Si)
41	7.87–7.47, 7.36–6.91 (m, 37H, Flu, Ph), 2.01–0.52 (m, 6H, bridge), −0.15 (s, 3H, Si–CH_3)	145.0, 144.4, 140.9, 131.4 (C_q, Flu, Ph), 134.0, 129.0, 127.5, 127.0, 126.6, 126.1, 124.5, 124.2, 120.0 (CH, Flu, Ph), 25.3, 11.0, 8.5 (CH_2, bridge), −7.0 (Si–CH_3)	−11.2 (Me–Si) −20.9 (Ph–Si)
42	7.91–7.62, 7.51–7.10 (m, 37H, Flu, Ph), 2.21–1.56, 1.38–0.93, 0.65–0.23 (m, 10H, bridge), −0.01 (s, 3H, Si–CH_3)	144.5, 144.0, 140.1 (C_q, Flu, Ph), 135.0, 133.4, 130.1, 129.0, 128.1, 127.9, 127.4, 126.8, 126.2, 125.5, 125.1, 124.7, 124.2 (CH, Flu, Ph), 14.2, 12.4 (CH_2, bridge), −6.7 (Si–CH_3)	−12.4 (Me–Si) −22.6 (Ph–Si)
43	7.79–7.65, 7.40–7.19, 7.03–6.64 (m, 37H, Flu, Ph), 1.22–0.17 (m, 12H, bridge), −0.38 (s, 3H, Si–CH_3)	146.0, 145.4, 141.0, 131.7 (C_q, Flu, Ph), 134.1, 129.1, 128.5, 127.5, 126.7, 126.2, 125.7, 125.3, 124.6, 124.2, 120.2, 120.0 (CH, Flu, Ph), 33.4, 33.3, 23.6, 23.3, 11.7, 9.3 (CH_2, bridge), −7.1 (Si–CH_3)	−12.0 (Me–Si) −22.6 (Ph–Si)
44	7.78–6.54 (m, 37H, Flu, Ph), 1.31–0.27 (m, 16H, bridge), −0.32 (s, 3H, Si–CH_3)	145.7, 145.6, 145.0, 141.4, 141.3 (C_q, Flu, Ph), 135.8, 134.9, 134.5, 129.6, 127.1, 125.8, 125.1, 124.3, 120.4, 120.3 (CH, Flu, Ph), 34.4, 34.0, 33.6, 29.1, 26.9, 23.6, 11.7, 10.8 (CH_2, bridge), −7.3 (Si–CH_3)	−11.5 (Me–Si) −21.0 (Ph–Si)

n.d., not determined.

[a] δ (ppm) in $CDCl_3$, 25 °C.

3.12. *Preparation of tetrachlorodisilane derivatives **7–12** by hydrosilation reaction*

ω-Alkenyldichloromethylsilane derivative (19.4 mmol) and aryl or alkylsubstituted dichlorosilane (19.4 mmol) derivative were dissolved in 5 ml of C_5H_{12}. Hexachloroplatinic acid (30–50 mg) was added. The mixture was stirred 40 h at r.t., 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).

3.13. *Preparation of the cyclopentadienyl substituted ligand precursors **13–18***

1,1,n,n-Tetrachloro-1-phenyl-1,n-disila-alkane (6 mmol) in 100 ml of Et_2O were placed in a Schlenk vessel and 2.1 g (24 mmol) of cyclopentadienyl sodium (dissolved in 10 ml of THF) were added. The mixture was stirred for 6 h at r.t. The solvent was removed in vacuo, the residue was suspended in Et_2O and the solution 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).

3.14. *Preparation of the indenyl and fluorenyl substituted ligand precursors **19–28***

Fluorenyllithium/indenyllithium (24 mmol) at r.t. was dissolved in 100 ml of Et_2O. 1,1,3,3-Tetrachloro-1-phenyl-1,3-disila-butane (6 mmol) dissolved in 10 ml of Et_2O 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 C_5H_{12} and the solution 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 characterized by NMR spectroscopy (Table 2).

3.15. Preparation of the dinuclear metallocene complexes **29–44**

General procedure: Ligand precursor (5 mmol) was dissolved in 400 ml of Et_2O. Then 12.5 ml of butyllithium solution (1.6 M in C_6H_{14}; 20 mmol) was added at r.t. The reaction mixture was stirred for 8 h. Subsequently, the solution was cooled to −78 °C, the equimolar amount of $ZrCl_4$ was added, then the suspension was brought to r.t. slowly within 6 h and was stirred for another 6 h. The solvent was removed in vacuo, the residue was suspended in CH_2Cl_2 and filtered over Na_2SO_4. The solvent was removed in vacuo to almost dryness, C_5H_{12} 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).

3.16. Polymerization reactions

An amount of 20–25 mg of the corresponding complex was dissolved in 50 ml of $C_6H_5CH_3$. A volume of the solution containing 1–2 mg of the complex was taken and activated with MAO (30% in $C_6H_5CH_3$; Al–Zr = 2500:1).

For heterogeneous polymerization reactions, untreated silica gel (Davison 948) was added (1 g SiO_2/μmol(Zr)) to this solution and the mixture was stirred for 3 min. The colored precipitate contained the activated catalyst; the supernatant solution was colorless and clear. The heterogeneous catalyst was not separated by filtration but applied as suspension. Both for homogeneous and heterogeneous polymerizations the catalyst suspension was charged to 250 ml of C_5H_{12} and filled into a 1l Büchi laboratory autoclave and thermostated at 60 °C. An ethylene pressure of 10 bar was applied to the reactor and polymerization was conducted 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.

4. Supplementary material

The material is available from the authors on request.

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