

# Mono, di and tetranuclear ansa zirconocene complexes as catalysts for the homogeneous and heterogeneous polymerization of ethylene

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## Abstract

Mono, di and tetranuclear ansa zirconocene complexes have been synthesized and characterized. After activation with methylalumoxane (MAO) these catalysts were used for the homogeneous and heterogeneous polymerization of ethylene. The properties of the catalysts and the produced polymers were compared. The multinuclear catalysts show a different performance than the corresponding mononuclear derivatives. The tetranuclear catalysts have the lowest activities because of steric crowding.

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*Keywords:* Multinuclear catalysts; Ansa zirconocene complexes; Homogeneous and heterogeneous ethylene polymerization

## 1. Introduction

Mononuclear metallocene complexes of group IV metals have established as excellent single site catalysts for the polymerization of ethylene [1–6]. In order to investigate the influence of more than one metal center on the properties of a homogeneous catalyst, di and tetranuclear ansa metallocene complexes appeared as excellent model compounds.

## 2. Synthesis of the metallocene complexes

### 2.1. Synthesis of the mononuclear complexes

For comparisons mononuclear complexes were synthesized according to [Scheme 1](#) [7–13]. The corre-

ponding fluorenylidene derivative **2** was prepared in an analogous manner.

### 2.2. Synthesis of the dinuclear complexes

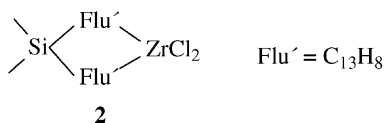
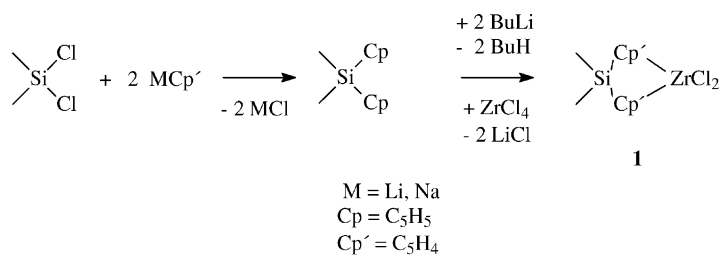
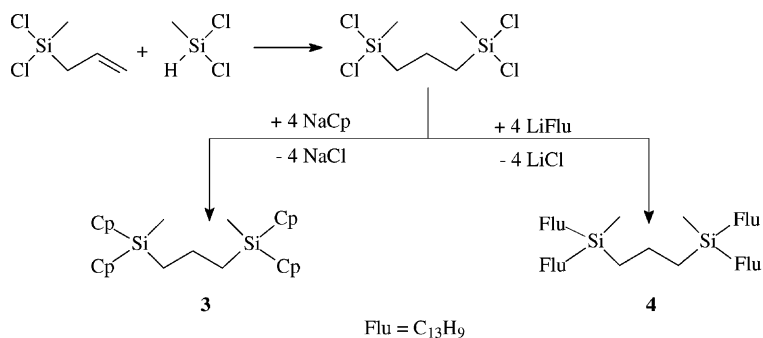
Dinuclear silylene bridged metallocene complexes were synthesized by catalytic hydrosilylation reactions of  $\omega$ -alkenyl substituted silanes with other silane derivatives. The reaction of the product with four equivalents of sodium cyclopentadienide forms the ligand precursor **3** in almost quantitative yield ([Scheme 2](#)). In the same manner the fluorenyl derivative **4** was synthesized [14–16].

Treatment of the ligand precursors **3** and **4** with four equivalents of *n*-butyllithium and two equivalents of zirconium tetrachloride forms the silylene bridged dinuclear complexes **5** and **6** ([Scheme 3](#)) [12,13]. The corresponding fluorenylidene derivative **6** was prepared in an analogous manner.

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Scheme 1. Synthesis of the mononuclear metallocene complexes **1** and **2**.

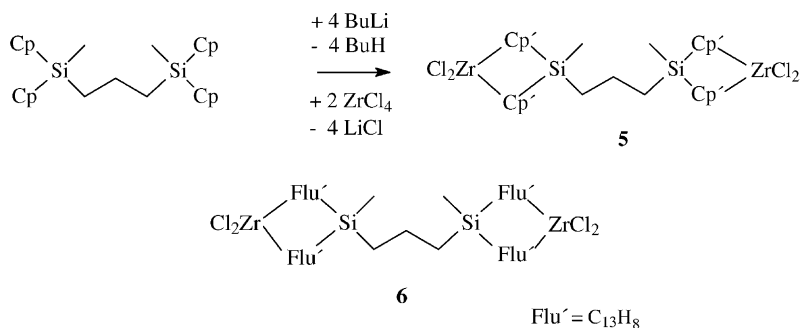
Scheme 2. Synthesis of the ligand precursors for dinuclear complexes.

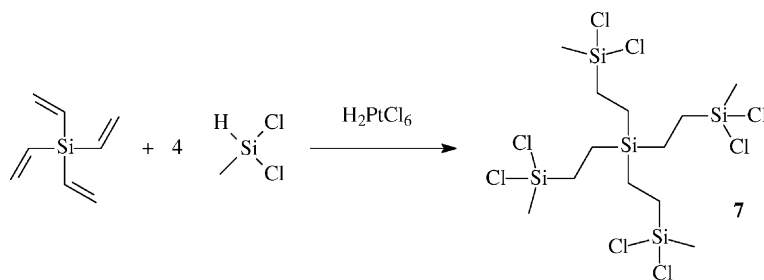
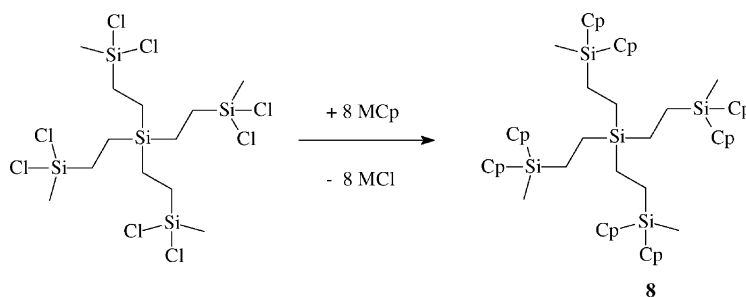
### 2.3. Synthesis of the tetranuclear complexes

The tetranuclear compounds were synthesized via the same route (Scheme 4) [17,18].

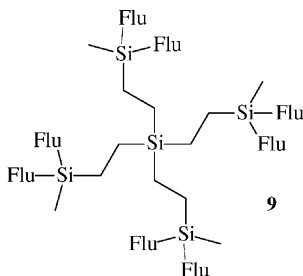
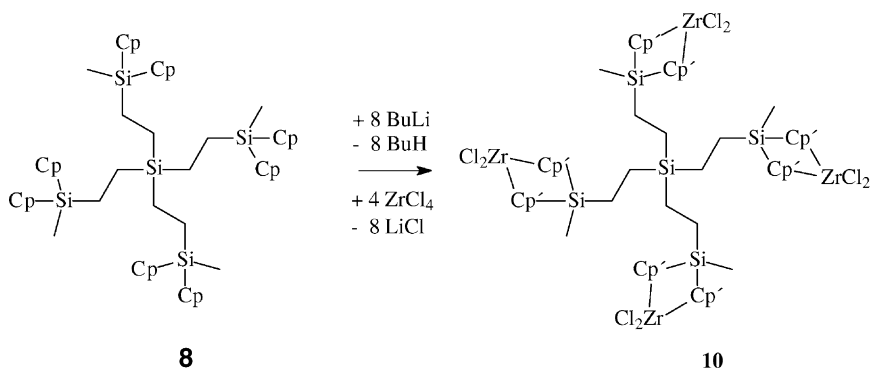
The treatment of **7** with an eight-fold excess of sodium cyclopentadienide or fluorenyllithium yields

the ligand precursors **8** and **9**. An analogous complexation reaction (see Schemes 1 and 3) leads to the tetranuclear complexes **10** and **11** (Schemes 5 and 6) [12,13]. The fluorenyl derivative **9** was prepared in an analogous manner. The fluorenylidene derivative **11** was prepared in an analogous manner.

Scheme 3. Synthesis of the dinuclear metallocene complexes **5** and **6**.

Scheme 4. Synthesis of tetrakis(1-(3,3-dichloro-3-sila)-butyl)-silane (**7**).

The analogous fluorenyl derivative **9** was prepared in an analogous manner.

Scheme 5. Formation of the ligand precursors **8** and **9**.Scheme 6. Synthesis of the tetranuclear complexes **10** and **11** [12,13].

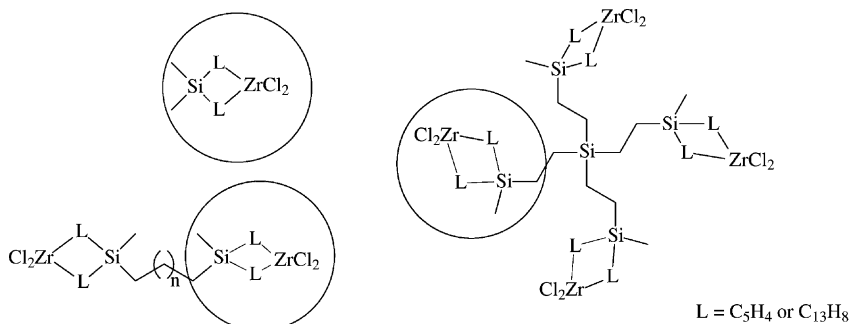
The low solubility of **10** and **11** made the characterization by NMR spectroscopy difficult. Mass spectrometry mainly showed fragments such as  $\text{Flu}^+$  and  $\text{FluZrCl}_2^+$ ; the molecular peak was observed with very low intensity.

### 3. Polymerization Results

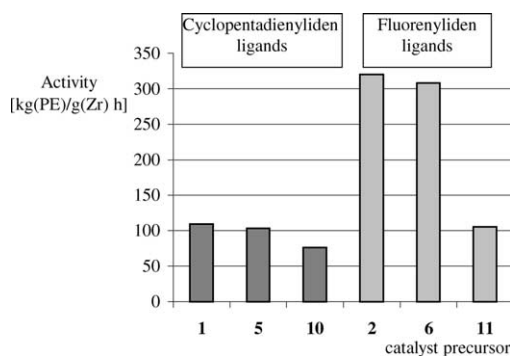
The following scheme will elucidate the relationship between the mono, di and tetra nuclear complexes. Each of the complexes contains the same highlighted basic structural element (Scheme 7).

Thus, a similar polymerization behaviour should be expected. However, the experimental data showed different results (Table 1).

In the homogeneous polymerization runs, the mono and the dinuclear catalysts showed almost the same activity. This is an indication that in the dinuclear species both metal centers are activated by MAO to the same extent as the metal in the mononuclear species.



Scheme 7. Basic structural elements in the mono, di and tetranuclear complexes.



Scheme 8. Polymerization activities under homogeneous polymerization conditions.

The tetranuclear catalysts **10** and **11**, however, had a lower activity than both the mono- and the dinuclear species. This becomes obvious in case of the fluorenyl complex **11** [19–23] (Scheme 8).

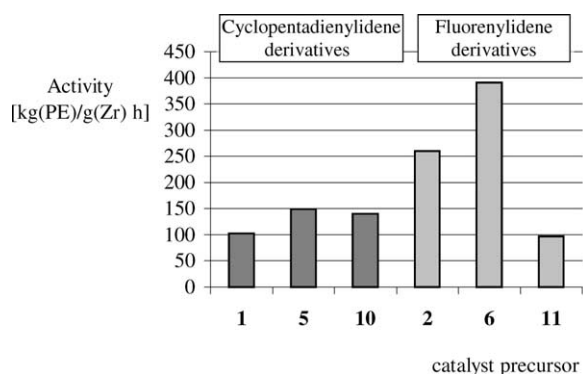
Fluorenyl complexes usually show a much higher catalytic activity in the olefin polymerization than

Table 1  
Results of the homogeneous ethylene polymerization reactions<sup>a</sup>

Compound	Activity (g(PE)/g(Zr)·h)	HT-GPC				
		$M_n$ (g/mol)	$M_w$ (g/mol)	$M_z$ (g/mol)	$M_\eta$ (g/mol)	$D (M_w/M_n)$
<b>1</b>	109000	95120	266400	851600	217200	2.8
<b>2</b>	320000	413800	1239000	3557000	1053000	3.0
<b>5</b>	103000	ND				
<b>6</b>	308000	ND				
<b>10</b>	76000	72930	461700	1658000	366500	6.3
<b>11</b>	105000	119700	631200	1938000	527300	5.3

<sup>a</sup> At 60 °C, 30 min, 10 bar ethylene pressure, Zr:Al = 1:2500, pentane solution.

D: polydispersity; ND: not determined.



Scheme 9. Polymerization activities under heterogeneous polymerization conditions.

the corresponding cyclopentadienyl derivatives [24] because of their ring slippage potential. The reason for the rather low activity of the tetranuclear **11** could derive from the “steric stress” of the molecule (molar mass: 2275 g/mol) in combination with the MAO counter anions that are formed in the activation step. As a consequence, it is hard for the monomer to reach a metal center for complexation. In addition, the growth and the orientation of the polymer chain during the polymerisation process is limited because of these steric conditions. All these disadvantageous parameters compensate the “fluorenyl bonus” of mononuclear homogeneous catalysts.

The tetranuclear compounds, however, show divergent results: in case of the cyclopentadienylidene derivative **10** an increase, in case of the fluorenylidene derivative **11**, a decrease of activity was observed in comparison to the homogeneous catalysts (Scheme 9).

This result emphasizes again that steric crowding should be avoided in order to obtain good activities.

The heterogeneous polymerization of ethylene with the same catalysts supported on silica gel gave different results.

It is well-known that metallocene catalysts can lose up to 90% of their original activity when they are supported on silica gel. One reason could be the fact that OH functions on the surface of the silica provide Lewis basic centers that poison the activated catalysts that are strong Lewis acids. In our experiments the mononuclear catalysts lost about 20% of their activity while the dinuclear catalysts gained about 50%. Such a behavior was already observed with dissymmetric dinuclear complexes [25] and interpreted with a favorable interaction of the MAO anion and the support providing an easily accessible active center for the monomer.

The polyethylenes produced with the homogeneous or heterogeneous catalysts (Tables 1 and 2) have comparatively narrow molecular weight distributions ( $D = 2.3\text{--}3.0$ ) when the mononuclear catalysts were applied. The polydispersity is higher ( $D = 4.6\text{--}6.3$ ) for the resins that were obtained from the tetranuclear catalysts. The homogeneous runs produced polyethylene with somewhat higher polydispersities and lower molecular weights than the heterogeneous runs. An explanation for this phenomenon could be the existence of slightly different active sites in these bulky molecules. On a support the variations of active sites could be limited because of steric reasons. The slightly higher molecular weights could be the consequence of a less favored termination reaction of the polymerization process.

Table 2  
Results from the heterogeneous ethylene polymerization reactions<sup>a</sup>

Compound	Activity (g(PE)/g(Zr)·h)	HT-GPC				
		$M_n$ (g/mol)	$M_w$ (g/mol)	$M_z$ (g/mol)	$M_\eta$ (g/mol)	$D$ ( $M_w/M_n$ )
<b>1</b>	102000	104000	271200	1075000	258900	2.6
<b>2</b>	260000	396000	911500	3854000	826600	2.3
<b>5</b>	149000	ND				
<b>6</b>	391000	ND				
<b>10</b>	140000	78270	459900	1623000	369300	5.9
<b>11</b>	97000	164500	755600	2736000	632800	4.6

<sup>a</sup> At 60 °C, 30 min, 10 bar ethylene pressure, Zr:Al = 1:2500, in pentane slurry.

D: polydispersity; ND: not determined.

## 4. Experimental

All experimental work was routinely carried out using Schlenk technique. Dried and purified argon was used as inert gas. Toluene, pentane, diethylether and tetrahydrofuran were purified by distillation over Na/K alloy. Ether was additionally distilled over lithium aluminum hydride. Methylene chloride was dried with CaH<sub>2</sub>. Deuterated solvents such as chloroform-d<sub>1</sub> and benzene-d<sub>6</sub> 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 toluene) was supplied by Witco Company, Bergkamen. All the other starting materials were commercially available and were used without further purification.

### 4.1. 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 (argon). The spectra were recorded at 25 °C. The chemical shifts in the <sup>1</sup>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 <sup>13</sup>C NMR spectra to the solvent signal ( $\delta = 77.0$  ppm for chloroform-d<sub>1</sub>,  $\delta = 128.0$  ppm for benzene-d<sub>6</sub>). Tetramethylsilane ( $\delta = 0.0$  ppm) was used as external calibration for <sup>29</sup>Si NMR spectra.

### 4.2. 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  $\mu$ m) 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).

### 4.3. 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.

### 4.4. Gas chromatography

Gas chromatograms were recorded using a Perkin–Elmer Auto System gas chromatograph with flame ionization detector (FID) and helium as carrier gas (1 ml/min).

Temperature program:

starting phase: 3 min at 50 °C;  
heating phase: 5 °C/min (15 min);  
plateau phase: 310 °C (15 min).

### 4.5. Synthesis of the ligand precursors for the mononuclear complexes

General procedure: 2.58 g (20 mmol) of dichlorodimethylsilane in 200 ml of diethylether and 10 mmol of sodium cyclopentadienide (or 10 mmol of fluorenyllithium) were mixed at room temperature in a Schlenk tube. The mixture was stirred for 8 h, then filtered through sodium sulfate and silica gel. The solvent was removed in vacuo. Yields: ca. 95%.

### 4.6. Preparation of the mononuclear zirconocene complexes **1** and **2**

The 10 mmol of the ligand precursor were dissolved in 200 ml of diethylether. A volume of 12.5 ml of butyllithium solution (1.6 M in hexane; 20 mmol) was added. The mixture was stirred for at least 8 h at room temperature. Then the solution was cooled to –78 °C and 2.33 g (10 mmol) of zirconium tetrachloride were added. The mixture was brought to room temperature within 6 h and stirred for another 6 h. The solvent was removed in vacuo, the residue was suspended in methylene chloride and the suspension was filtered over sodium sulfate. The solvent of the methylene chloride phase was removed in vacuo, the residue was washed with pentane and diethylether several times and then crystallized at –28 °C from methylene chloride. Yields: 50–70%. The complexes were characterized by NMR spectroscopy (Table 3).

### 4.7. Preparation of the tetrachlorodisilane precursor for dinuclear complexes

The 3.1 g (20 mmol) of allyldichloromethylsilane and 3.45 g (30 mmol) of dichloromethylsilane were dissolved in 10 ml of pentane. Approximately 50 mg

Table 3  
NMR data<sup>a</sup> of compounds 1–11

Compound	<sup>1</sup> H NMR (δ in ppm)	<sup>13</sup> C NMR (δ in ppm)	<sup>29</sup> Si NMR (δ in ppm)
1	6.88–6.46 (m, 8H, Cp); 0.16 (s, 6H, Si–CH <sub>3</sub> )	129.5, 128.1, 127.2, 125.6 (CH, Cp), –4.6 (Si–CH <sub>3</sub> )	–10.2
2	7.89–7.15 (m, 16H, Flu), –0.10 (s, 6H, Si–CH <sub>3</sub> )	144.3, 144.1 (C <sub>q</sub> , Flu), 129.9, 127.2, 125.4, 124.0, 121.5 (CH, Flu), –5.1 (Si–CH <sub>3</sub> )	–11.0
3	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 <sub>3</sub> )	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 <sub>2</sub> , al, Cp), 26.3, 6.3, 6.6, 6.3, 6.1 (CH <sub>2</sub> , bridge), –6.9, –7.3, –7.4 (Si–CH <sub>3</sub> )	6.0, –5.0
4	7.38–6.63 (m, 32H, Flu), 3.57 (s, 4H, al H, Flu), 1.34–1.19 (m, 6H, bridge), 0.13 (s, 6H, Si–CH <sub>3</sub> )	143.8, 142.9, 142.1, 140.1 (C <sub>q</sub> , Flu), 128.3, 127.1, 126.1, 124.7, 120.4 (CH, Flu), 38.3 (CH, al, Flu), 27.3, 26.8, 22.1 (CH <sub>2</sub> , bridge), –0.2 (Si–CH <sub>3</sub> )	–5.8
5	6.80–5.79 (m, 16H, Cp), 2.11–1.37 (m, 6H, bridge), 0.72 (s, 6H, Si–CH <sub>3</sub> )	129.3, 128.0, 115.1, 114.1 (CH, Cp), 108.1 (C <sub>q</sub> , Cp), 16.7, 15.5 (CH <sub>2</sub> , bridge), –7.0 (Si–CH <sub>3</sub> )	–12.9
6	7.79–7.55, 7.40–7.19, 7.03–6.64 (m, 32H, Flu), 1.25–0.23 (m, 6H, bridge), –0.26 (s, 6H, Si–CH <sub>3</sub> )	145.4, 141.0, 131.7 (C <sub>q</sub> , Flu), 127.5, 126.1, 125.7, 125.3, 124.6, 124.2, 120.2, 120.0 (CH, Flu), 33.3, 12.4 (CH <sub>2</sub> , bridge), –7.1 (Si–CH <sub>3</sub> )	–12.3
7	1.22–0.70 (m, 16H, bridges), 0.74, 0.73 (s, 12H, Si–CH <sub>3</sub> )	14.2, 4.5 (Si–CH <sub>3</sub> ), 2.7, 2.2 (CH <sub>2</sub> , bridges)	33.4, 32.8 (Cl–Si), 1.28 (alkyl–Si)
8	6.61–6.02 (m, 32H, ar H), 3.77–3.72 (m, 8H, al H, Cp), 1.28–0.27 (m, 16H, bridges), –0.16, –0.20 (s, 12H, Si–CH <sub>3</sub> )	142.3, 132.9, 131.1 (CH, ar, Cp), 47.1 (CH <sub>2</sub> , al, Cp), 24.4, 24.3 (CH <sub>2</sub> , bridges), –7.8 (Si–CH <sub>3</sub> )	5.9 (alkyl–Si), –5.3, –5.8 (Cp–Si)
9	7.96–7.34 (m, 64H, ar H, Flu), 4.33–4.31 (8H, al H, Flu), 1.35–0.44 (m, 16H, bridges), –0.02, –0.19 (s, 12H, Si–CH <sub>3</sub> )	144.3, 143.9 (C <sub>q</sub> , Flu), 132.4, 130.1, 129.7, 126.4, 122.1 (CH, ar, Flu), 39.6 (CH, al, Flu), 25.5, 16.4 (CH <sub>2</sub> , bridges), –7.5 (Si–CH <sub>3</sub> )	5.3 (alkyl–Si), –6.4, –6.7 (Flu–Si)
10	7.15–6.87 (m, 16H, Cp), 5.90–5.82 (m, 16H, Cp), 1.39–0.65 (m, 16H, bridges), 1.14 (s, 12H, Si–CH <sub>3</sub> )	135.4, 131.7, 129.1 (CH, Cp), 42.1, 22.6 (CH <sub>2</sub> , bridges), –7.5 (Si–CH <sub>3</sub> )	–11.4 (Cp–Si) 0.7 (alkyl–Si)
11	7.70–6.98 (m, 64H, Flu), 1.51–0.34 (m, 16H, bridges), 0.95 (s, 12H, Si–CH <sub>3</sub> )	146.1, 140.9 (C <sub>q</sub> , Flu), 129.2, 128.3, 127.5, 125.1, 120.0 (CH, Flu), 26.8, 22.5 (CH <sub>2</sub> , bridges), –7.2 (Si–CH <sub>3</sub> )	–12.1 (Flu–Si) 0.8 (alkyl–Si)

<sup>a</sup> In CDCl<sub>3</sub>, at 25 °C.

of hexachloroplatinic acid hydrate were added. The mixture was stirred at room temperature for 40 h, then filtered through sodium sulfate. The solvent and the excess silane were removed in vacuo. Yield: 95%.

#### 4.8. Preparation of the ligand precursors 3 and 4 for the dinuclear complexes

The 2.7 g (10 mmol) of 2,2,7,7-tetrachloro-2,7-disila-heptane were dissolved in 200 ml of diethylether at room temperature. Then 40 mmol of sodium cyclopentadienide (or fluorenyllithium) were added. The mixture was stirred for 8 h, then filtered over

sodium sulfate and silica gel. The solvent was removed in vacuo. The crude products were crystallized from pentane at –28 °C. Yields: 85–90%. The compounds were characterized by NMR spectroscopy (Table 3).

#### 4.9. Synthesis of the dinuclear complexes 5 and 6

The 5 mmol of the fluorenyl or cyclopentadienyl substituted ligand precursor were dissolved in 400 ml of diethylether and 25 ml (40 mmol) of *n*-butyllithium (1.6 M in hexane) were added. The reaction mixture was stirred for a minimum of 8 h at room temperature.

The solution was cooled to  $-78^{\circ}\text{C}$ . Then 2.33 g (10 mmol) of zirconium tetrachloride were added. The reaction mixture was brought to room temperature within 6 h and stirred for another 6 h. The solvent was removed in vacuo, the residue suspended in methylene chloride and the solution filtered over  $\text{Na}_2\text{SO}_4$ . The solvent of the methylene chloride phase was again removed in vacuo, the residue was washed with pentane and the product crystallized from methylene chloride/pentane. Yield: 60–70%. The complexes were characterized by NMR spectroscopy (Table 3).

#### 4.10. Synthesis of tetrakis(1-(3,3-dichloro-3-sila-butyl))-silane (7)

The 1.36 g (10 mmol) of tetravinylsilane in 10 ml of pentane and approximately 50 mg of hexachloroplatinic acid hydrate were given to a Schlenk vessel at room temperature. The 4.6 g (40 mmol) of methylchlorosilane were added and the mixture was stirred for 40 h, then filtered through  $\text{Na}_2\text{SO}_4$  and the solvent was removed in vacuo. Yield: 95%. Compound 7 was characterized by NMR spectroscopy (Table 3).

#### 4.11. Synthesis of tetrakis(1-(3,3-bis(cyclopentadienyl)-3-sila-butyl))-silane (8) and tetrakis(1-(3,3-bis(flourenyl)-3-sila-butyl))-silane (9)

The 24 mmol of cyclopentadienylsodium (resp. fluorenyllithium) in 10 ml of thf (resp. diethylether) were added to 2 g (6 mmol) of 1,1,5,5-tetrachloro-1-phenyl-1,5-disilahexane in 100 ml of ether. The mixture was stirred at room temperature for 6 h. The solvent was removed in vacuo, the residue taken up in ether, the suspension filtered through  $\text{Na}_2\text{SO}_4$  and  $\text{SiO}_2$  and the solvent removed in vacuo. Yield: 90–95%. The compounds 8 and 9 were characterized by NMR spectroscopy (Table 3).

#### 4.12. Synthesis of the tetra nuclear metallocene complexes 10 and 11

General procedure: 5 mmol of the cyclopentadienyl or fluorenyl substituted ligand precursor were dissolved in 800 ml of diethylether and 25 ml (40 mmol) of *n*-butyllithium (1.6 M in hexane) were added. The

reaction mixture was stirred for a minimum of 8 h at room temperature.

The solution was cooled to  $-78^{\circ}\text{C}$ . Then 4.66 g (20 mmol) of zirconium tetrachloride were added. The reaction mixture was brought to room temperature within 6 h and stirred for another 6 h. The solvent was removed in vacuo, the residue suspended in methylene chloride and the suspension filtered through  $\text{Na}_2\text{SO}_4$ . The methylene chloride was removed in vacuo, the residue washed with pentane and the product crystallized from methylene chloride/pentane. Yield: 40–80%. The complexes were characterized by NMR spectroscopy (Table 3).

#### 4.13. 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 complex was taken and activated with MAO (30% in toluene; Al:Zr = 2500:1).

For heterogeneous polymerization, silica gel was added (1 g  $\text{SiO}_2/\mu\text{mol}(\text{Zr})$ ) to this solution and stirred for 3 min. Both for homogeneous and heterogeneous polymerization reactions the catalyst suspension was added to 250 ml of pentane and charged to a 1 l Büchi laboratory autoclave thermostated at  $60^{\circ}\text{C}$ . An ethylene pressure of 10 bar was applied to the reactor and the polymerization was conducted 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 are presented in Tables 1 and 2.

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