

# The first synthesised examples of di-siloxy-substituted cyclopentadienyl zirconocenes, their synthesis, structure and activity in ethylene polymerisation

Shaozhong Ge<sup>a</sup>, Ove S. Andell<sup>a,\*</sup>, Antti Penninkangas<sup>a</sup>, Janne Maaranen<sup>b</sup>,  
Tuula Telén<sup>b</sup>, Ilpo Mutikainen<sup>c</sup>

<sup>a</sup> *Laboratory of Polymer Technology, Åbo Akademi University, Biskopsgatan 8, FIN-20500 Åbo, Finland*

<sup>b</sup> *Borealis Polymers Oy, R&D, P.O.Box 330, FIN-06101 Porvoo, Finland*

<sup>c</sup> *Department of Inorganic Chemistry, University of Helsinki, P.O. Box 55, FIN-00014, Finland*

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## Abstract

Bis-(1,2-(RMe<sub>2</sub>SiO)<sub>2</sub>)ZrCl<sub>2</sub> complexes with R = Me-(**5a**), *i*Pr-(**5b**) and *t*Bu-(**5c**) have been synthesised in good yields and characterised. Compounds **5a–c** are the first synthesised examples of multi-siloxy-substituted cyclopentadienyl metallocenes. The siloxy-substituents have a for siloxy substituted metallocenes unique steric arrangement, with one almost in the same plane, and the other nearly perpendicular to the plane of the cyclopentadienyl ligand of the zirconocene. The ethylene/1-hexene co-polymerisation activity using methylalumoxane as co-activator gives low activities, with compound **5c** (262.92 kg(PE)/g(Zr)/h) being the most active.

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## 1. Introduction

Since the invention of methylalumoxane (MAO) in the late 1970s by Sinn and Kaminsky, have a large number of group 4 metallocenes been investigated. The progress in this field has been thoroughly reviewed by several authors over the years [1–6]. The long struggle to find complexes fulfilling the requirements of the polymerisation industry has led to an intellectual property rights situation forcing the polymer industry to build joint ventures in order to have all rights needed to produce and sell the polymer [7–10].

Zirconium metallocene catalyst complexes can be activated by a number of co-catalysts [11–13]. An important group of zirconocenes in this respect is the siloxy substi-

tuted bis-indenyl metallocenes which have been investigated by Leino, Luttikhedde and Kallio et al. who have shown them to be highly active in olefin polymerisation and well behaving in the polymerisation process [14]. The more unusual behaviour of this complex family has been investigated by Kallio et al., [15,16] who reported hexaisobutylalumoxane (HIBAO) as a well functioning co-catalyst in combination with siloxy substituted zirconocenes. Previous research using HIBAO as co-catalyst with zirconocenes did not report this high level of activities [17].

We have earlier studied cyclopentadienyl group 4 metallocenes with mono-siloxy-group substituted cyclopentadienes and unique activity level differences between MAO and HIBAO was demonstrated. Some of the unbridged mono substituted siloxy cyclopentadienyl zirconocenes showed almost no activity with MAO as activator but a quite reasonable activity with HIBAO [18].

In this report, we describe the synthesis and polymerisation results with MAO as co-activator of the novel

\* Corresponding author.

E-mail address: [Ove.Andell@abo.fi](mailto:Ove.Andell@abo.fi) (O.S. Andell).

metallocene complexes, bis-[1,2-di(trimethylsiloxy)cyclopentadienyl] zirconium dichloride (**5a**), bis-[1,2-di(*i*-propyldimethylsiloxy)cyclopentadienyl]zirconium dichloride (**5b**), and bis-[1,2-di(*t*-butyldimethylsiloxy)cyclopentadienyl]zirconium dichloride (**5c**). The molecular structures of **5a** and **5b** are reported. A few reports exist regarding 1,2-disiloxy-substituted- [19–24] and 1,3-di-siloxy-substituted- [25,26] cyclopentadienes, but no previous example of a metallocene with such cyclopentadienyl ligands can be found in the literature.

## 2. Results and discussion

### 2.1. Synthesis of bis-trialkylsiloxy-substituted Cp ligands and their corresponding silylated forms

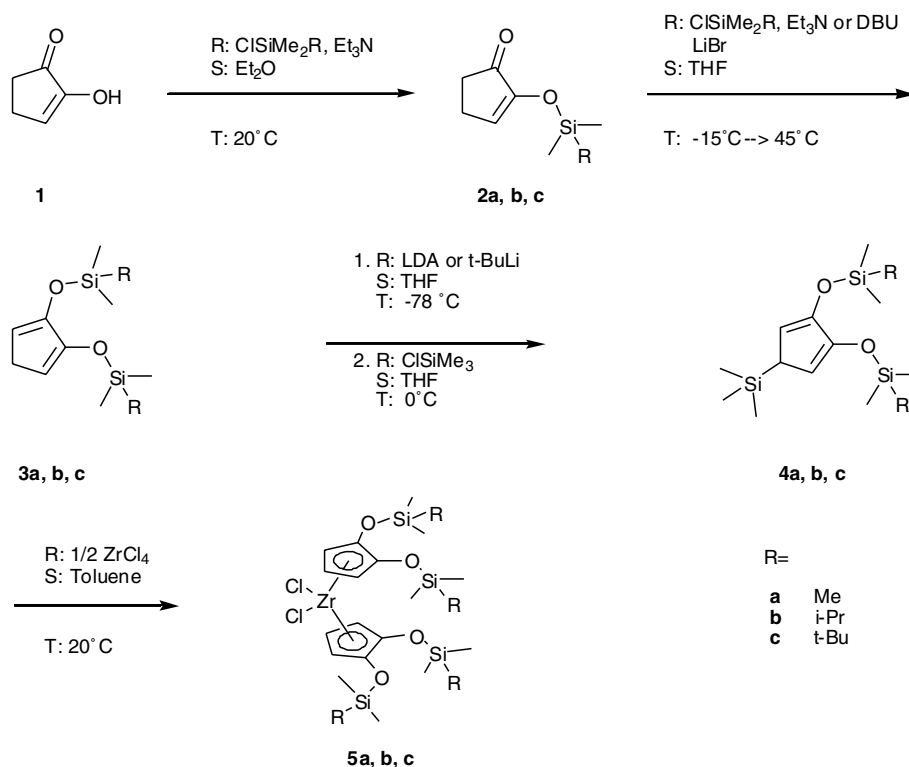
Synthesis of **3a–c** and **4a–c** is illustrated in Scheme 1. 1,2-Cyclopentadiene was prepared according to the reported literature procedure by Acheson [27] and the mono-trialkylsiloxy-substituted compounds **2a–c** were made as described by Sasaki [28]. The second siloxy group was induced according to the slightly modified literature method with high yields by Hansson [19,20]. Although **3b–c** are novel compounds, 2,3-bis-trimethylsiloxy-cyclopenta-1,3-diene **3a** has previously been synthesised by Reetz [24] and 2,3-bis-trimethylsiloxy-1-methyl-cyclopenta-1,3-diene has been synthesised by Hansson [19]. Reetz describes **3a** as sensitive for Diels–Alder reactions during the distillation step or when synthesised by an alternative method to have a tendency to polymerise on storage. Compound **3a** made through the methods described

in this paper is easily distilled as a colourless liquid giving very small amounts of residue. The yield in the last step for **3a–c** varies from 85% to 46%, going down with increasing steric hindrance.

The H NMR spectra of **3a–c** are simple and show 2,3-bis-tri-alkylsiloxy-cyclopenta-1,3-diene as the only isomer present. No isomerisation of the double-bonds was observed even after storage over several months at room temperature.

Metallocene formation by treating zirconium tetrachloride with the lithium cyclopentadienyl salts of **3a–c** gave unclear results, but the trimethylsilyl-cyclopentadiene (**4a–c**) methodology used by Tian [29] performed well.

The silylated bis-trialkylsiloxy-substituted Cp ligands, **4a–c**, were prepared by deprotonating **3a–c** with lithium diisopropylamine (LDA) or *t*-BuLi, followed by Me<sub>3</sub>SiCl giving high yields (**4a**: 71%, **4b**: 79%, **4c**: 79%). Treating **3b** and **3c** with *t*-BuLi resulted in a slightly yellow solution, while **3a** gave a dark solution with a loss of siloxy groups caused by these groups, sensitivity towards lithium alkyls. H NMR spectra from **4a–c** showed that the trimethylsilyl group was introduced exclusively in the 5-position of the (R<sub>3</sub>SiO)<sub>2</sub>CpH ring. The H NMR spectra of these compounds are predictable and symmetric showing only one symmetric olefin isomer. In **4b** the methyl protons and the methine protons from the *iso*-propyl groups were located at the same shift value leading to a broader singlet with shoulders. All compounds **4a–c** could be purified by vacuum distillation as colourless liquids although **4c** requires a system with a good vacuum.



Scheme 1.

## 2.2. Synthesis of bis-trialkylsiloxy-substituted Cp zirconocenes

Treating the silylated ligands **4a–c** with zirconium tetrachloride in toluene at an ambient temperature for 12 h afforded the bis-trialkylsiloxy-cyclopentadienyl zirconocene dichlorides **5a–c** in high isolated yields (**5a**: 72%, **5b**: 65%, **5c**: 66%). Analytically pure material of zirconocenes **5a–c** was isolated as pale yellow crystalline powders from *n*-hexane. Crystallisation from *n*-hexane by slowly lowering the temperature to  $-30\text{ }^{\circ}\text{C}$ , gave colourless crystals suitable for XRD analysis for compounds **5a–b**. We were not able to produce crystals from **5c** due to the high solubility and seemingly low melting point. The compounds were characterised by NMR, electron impact mass spectrum (EIMS), and elemental analyses. The  $^1\text{H}$  NMR of the reaction mixtures just after removal of solvent indicate that the yield of the resulting metallocenes becomes higher with increasing steric bulk in siloxy-substituents on the ligands (**5a**:  $\sim 70\%$ ; **5b**:  $\sim 85\%$ ; **5c**:  $>90\%$ ). Compound **5b** was analysed with  $^{29}\text{Si}$  NMR in  $\text{CD}_2\text{Cl}_2$  and gave one peak at 24.61 ppm.

## 2.3. Molecular structure by X-ray analysis

Crystal structure and refinement data for **5a–b** are shown in Table 1 and selected bond lengths ( $\text{\AA}$ ) and angles ( $^{\circ}$ ) together with some calculated structural angles are presented in Table 2. The solid state structures of **5a** and **5b**

with thermal ellipsoids at the 30% probability level are shown in Figs. 1 and 2.

There are 7 XRD structures of previously published siloxy-substituted-bis-zirconocenes that can be found in the CCDC database [14]. They are all indenyl or tetra-hydro-indenyl type zirconocenes with one siloxy substituent in the 5-ring and having an ethylene bridged structure. One exception to this is one unbridged bis indenyl example.

Structural features of interest for the class of unbridged metallocenes to which **5a–b** belong concerns the siloxy substituent, the metal–chlorine and the (Cp-centroid)–metal bonds, Table 2.

The Cp–O bond lengths for **5a**, C(1)–O(6) = 1.354(2)  $\text{\AA}$ , C(5)–O(11) = 1.368(2)  $\text{\AA}$  and for **5b**, C(1)–O(6) = 1.376(3)  $\text{\AA}$ , C(5)–O(13) = 1.358(3)  $\text{\AA}$  are interesting from the point that the shorter C–O bond lengths in both structures belong to the one siloxy substituent having a torsion angle C–C–O–Si very close to  $0^{\circ}$ . In **5a** is torsion angle C(2)–C(1)–O(6)–Si(7) =  $-4.79^{\circ}$  and in **5b** C(4)–C(5)–O(13)–Si(14) =  $6.88^{\circ}$ . The longer Cp–O bond length belongs to the siloxy substituent with a distinctly “out of plane” torsion angle. In **5a** C(1)–C(5)–O(11)–Si(12) =  $-92.18^{\circ}$  almost totally perpendicular to the Cp plane and in **5b** C(5)–C(1)–O(6)–Si(7) =  $40.35^{\circ}$  which is a value more in between the two extremes represented in this unique complex **5a**. Previously published Cp–O bond lengths for siloxy substituted zirconocenes are between 1.341 and 1.372  $\text{\AA}$ . Here we can observe that the siloxy substituents in **5a** is within the range of this interval and

Table 1  
Crystal Structure and Refinement Data for **5a** and **5b**

	<b>5a</b>	<b>5b</b>
Empirical formula	$\text{C}_{22}\text{H}_{42}\text{Cl}_2\text{O}_4\text{Si}_4\text{Zr}$	$\text{C}_{30}\text{H}_{58}\text{Cl}_2\text{O}_4\text{Si}_4\text{Zr}$
Formula weight	645.04	757.24
Temperature (K)	173(2)	293(2)
Wavelength ( $\text{\AA}$ )	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Colour	Colorless	Colorless
Space group	$P2_1/c$	$Pccn$
$a$ ( $\text{\AA}$ )	13.646(3)	25.818(5)
$b$ ( $\text{\AA}$ )	6.4360(13)	12.374(3)
$c$ ( $\text{\AA}$ )	19.755(4)	12.833(3)
$V$ ( $\text{\AA}^3$ )	1633.3(6)	4099.8(14)
$Z$	2	4
$D_{\text{calc}}$ ( $\text{Mg/m}^3$ )	1.312	1.227
Abs coeff ( $\text{mm}^{-1}$ )	0.670	0.544
$F(000)$	672	1600
Crystal size ( $\text{mm}^3$ )	$0.25 \times 0.25 \times 0.21$	$0.22 \times 0.06 \times 0.06$
$\theta$ Range for data collection ( $^{\circ}$ )	3.11–27.50	3.16–27.57
Index ranges	$-17 < h < 17$ , $-8 < k < 8$ , $-25 < l < 25$	$-33 < h < 32$ , $-16 < k < 16$ , $-16 < l < 16$
Reflections collected	23104	61892
Independent reflections	4758 [ $R_{\text{int}} = 0.0525$ ]	4731 [ $R_{\text{int}} = 0.1276$ ]
Completeness to theta	27.50°, 99.9%	27.57°, 99.5%
Maximum and minimum transmission	0.8720 and 0.8503	0.9681 and 0.8897
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$
Data/restraints/parameters	3758/0/150	4731/24/239
Goodness-of-fit on $F^2$	1.029	0.983
Final $R$ indices [ $I > 2\sigma(I)$ ] $R_1$	$R_1 = 0.0283$ , $wR_2 = 0.0635$	$R_1 = 0.0450$ , $wR_2 = 0.1082$
$R$ indices (all data) $R_1$	$R_1 = 0.0393$ , $wR_2 = 0.0672$	$R_1 = 0.0894$ , $wR_2 = 0.1257$
Largest difference peak and hole ( $e\text{\AA}^{-3}$ )	0.348 and $-0.309$	0.320 and $-0.587$

Table 2  
Selected bond lengths (Å) and angles (°) for compounds **5a** and **5b**

<b>5a</b>	
<i>Bond lengths (Å)</i>	
Zr(1)–Cl(1)	2.4524(6)
Zr(1)–C(1)	2.630(2)
Zr(1)–C(2)	2.4874(18)
Zr(1)–C(3)	2.4308(18)
Zr(1)–C(4)	2.5133(18)
Zr(1)–C(5)	2.6076(19)
C(1)–C(2)	1.414(3)
C(2)–C(3)	1.426(3)
C(3)–C(4)	1.410(3)
C(4)–C(5)	1.415(3)
C(1)–C(5)	1.423(3)
C(1)–O(6)	1.354(2)
C(5)–O(11)	1.368(2)
O(6)–Si(7)	1.6736(14)
O(11)–Si(12)	1.6740(14)
<i>Bond angles (°)</i>	
C(1)–O(6)–Si(7)	128.10(12)
C(5)–O(11)–Si(12)	122.95(11)
Cl(1)–Zr(1)–Cl(1)	100.65(3)
<i>Torsion angles (°)</i>	
C(2)–C(1)–O(6)–Si(7)	–4.79
C(1)–C(5)–O(11)–Si(12)	–92.18
<i>Calculated lengths (Å)</i>	
Cp (centroid)–Zr(1)	2.230
<i>Calculated angles (°)</i>	
Angle between the Cp planes ( $\gamma$ )	55.1
Angle between the Cp plane normals ( $\beta$ )	124.9
Angle between the Cp plane and the metal–Cp(centroid) vector, ( $\delta$ )	85.4
Cp (centroid)–Zr(1)–Cp'(centroid)	134.1
Planes – [(Si(12)–O(11)–C(5))–[(Si(12A)–O(11A)–C(5A))]	9.8

**5b**

<i>Bond lengths (Å)</i>	
Zr(1)–Cl(1)	2.4648(8)
Zr(1)–C(1)	2.622(3)
Zr(1)–C(2)	2.517(3)
Zr(1)–C(3)	2.427(3)
Zr(1)–C(4)	2.489(3)
Zr(1)–C(5)	2.632(2)
C(1)–C(2)	1.408(4)
C(2)–C(3)	1.415(4)
C(3)–C(4)	1.426(4)
C(4)–C(5)	1.423(4)
C(1)–C(5)	1.426(4)
C(1)–O(6)	1.376(3)
C(5)–O(13)	1.358(3)
O(6)–Si(71)	1.683(2)
O(13)–Si(14)	1.695(2)
<i>Bond angles (°)</i>	
C(1)–O(6)–Si(71)	130.59(17)
C(1)–O(6)–Si(72)	123.98(19)
C(5)–O(13)–Si(14)	127.86(17)
Cl(1)–Zr(1)–Cl(1)	101.47(4)
<i>Torsion angles (°)</i>	
C(4)–C(5)–O(13)–Si(14)	6.88
C(5)–C(1)–O(6)–Si(71)	40.35
<i>Calculated lengths (Å)</i>	
Cp (centroid)–Zr(1)	2.233

Table 2 (continued)

<i>Calculated angles (°)</i>	
Angle between the Cp planes	55.4
Angle between the Cp plane normals ( $\beta$ )	124.6
Angle between the Cp plane and the metal–Cp(centroid) vector, ( $\delta$ )	85.3
Cp (centroid)–Zr(1)–Cp'(centroid)	134.1

that in **5b** is the “in plane” siloxy substituent within the interval but the C(1)–O(6) = 1.376(3) Å, with the torsion angle C(5)–C(1)–O(6)–Si(71) = 40.35°, being slightly outside the high end of the interval.

The torsion angles found in previously published structures are from the whole range possible and of those are two examples “close” to in plane arrangement. One example is with a torsion angle of 10.71° and a C–O bond length of 1.341 Å (CCDC code LOPZAR [30]) and another example

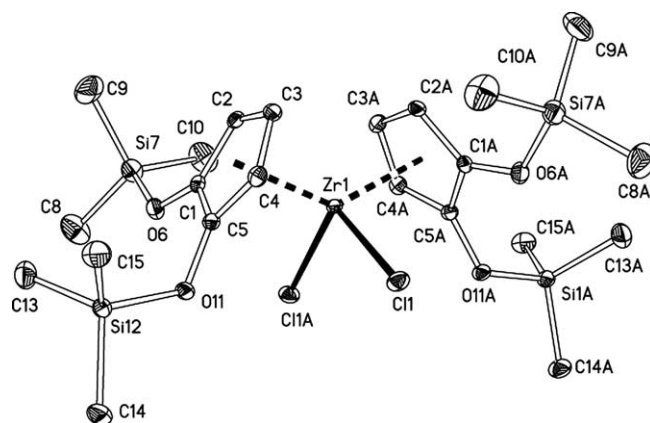


Fig. 1. Solid state structure of **5a** (thermal ellipsoids at the 30% probability level).

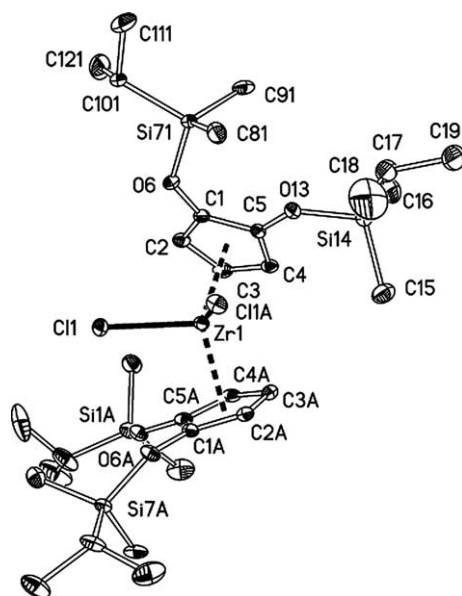


Fig. 2. Solid state structure of **5b** (thermal ellipsoids at the 30% probability level).

has the torsion angle  $8.3^\circ$  and a C–O bond length of 1.356 Å (CCDC code LAWYOX [31]). Both examples belong to the low end of the bond length interval for the C–O bonds.

The next observation we can make is regarding the O–Si bond lengths. In **5a** O(6)–Si(7) = 1.6736(14) Å, O(11)–Si(12) = 1.6740(14) Å and for **5b**, O(6)–Si(71) = 1.683(2) Å, O(13)–Si(14) = 1.695(2) Å. They all belong to the high end of the interval of published structures where O–Si is 1.634–1.696 Å. This observation does not correlate in any way with the C–O bond lengths or the torsion angle of the siloxy substituents of **5a–b**. Instead the O–Si bond lengths of **5a** are both shorter than those of **5b** which could be explained as an effect of the alkyl groups on the silicon atoms.

The general direction of the siloxy groups having the torsion angles with the cyclopentadienyl plane close to  $90^\circ$  is very symmetric in **5a**. The planes in **5a** defined as Si(12)–O(11)–C(5) and Si(12A)–O(11A)–C(5A) form an angle of only  $9.8^\circ$  and are very close to the bisector of the angle formed by Cl–Zr–Cl. A similar arrangement is valid for **5b** in which the C(1)–Zr–C(1A) plane is also very close to the bisecting angle formed from the Cl–Zr–Cl atoms. The close to in plane siloxy-substituents are situated on opposite sides of the described bisecting plane and the silicon atoms are directed towards the back side of the metallocene, away from the direction of the chlorine atoms. XRD analysis from unbridged cyclopentadienyl zirconocenes does not exist in the published literature. XRD structures of 4 different mono siloxy substituted unbridged cyclopentadienyl zirconocenes will be published by us in the near future originating from results in a previous patent disclosure [18]. Among 1,2-di-alkylated unbridged cyclopentadienyl zirconocene dichlorides is (1,2-di-*t*Bu–Cp)<sub>2</sub>ZrCl<sub>2</sub> (CCDC code: TIVMAM) whose structure mostly resembles **5a–b**. The arrangement of the *t*Bu-groups is almost the same with one *t*Bu-group very close to the bisecting angle of the Cl–Zr–Cl. In a very similar complex, (1,2-di-*i*Pr–Cp)<sub>2</sub>ZrCl<sub>2</sub> (CCDC code: KUBXIO) this arrangement is not the case.

When we observe the ligands around the zirconium atom we can note that the Zr–Cl bond lengths in compounds **5a–b** are longer than those observed in previously published siloxy substituted zirconocene structures having bond lengths of 2.411–2.436 Å. In **5a** is Zr(1)–Cl(1) = 2.4524(6) Å and in **5b** is Zr(1)–Cl(1) = 2.4648(8) Å. The distance between the Zr and the centroid of the Cyclopentadienyl ring (Zr–Cp) is in **5a**, 2.230 Å and in **5b**, 2.233 Å. Both of the mentioned distances are within the range of such previously published complexes, 2.228–2.255 Å.

For **5a** and **5b** a unique structural feature is the large angles representing Cl–Zr(1)–Cl, being  $100.65^\circ$  for **5a** and  $101.47^\circ$  for **5b** and the also large angles of the Cp'(centroid)–Zr(1)–Cp''(centroid) being  $134.1^\circ$  for both **5a** and **5b**. Here, the mainly bridged indenyl type siloxy substituted zirconocenes have angles for Cl–Zr–Cl of  $94.28$ – $99.30^\circ$ , (1,2-di-*t*Bu–Cp)<sub>2</sub>ZrCl<sub>2</sub> has  $95.11^\circ$  and (1,2-di-*i*Pr–Cp)<sub>2</sub>ZrCl<sub>2</sub> has  $94.78^\circ$ . The Cp'(centroid)–Zr(1)–Cp''(centroid) angles of the published siloxy complexes are within

the range  $109.22$ – $130.25^\circ$ , and (1,2-di-*t*Bu–Cp)<sub>2</sub>ZrCl<sub>2</sub> has an angle of  $128.68^\circ$  and (1,2-di-*i*Pr–Cp)<sub>2</sub>ZrCl<sub>2</sub> has  $128.42^\circ$ . The angle between the cyclopentadienyl planes for **5a** is,  $55.1^\circ$  and for **5b** it is,  $55.4^\circ$ , which is a normal value for this class of complexes.

#### 2.4. Polymerisation studies

Table 3 shows polymerisation data for the **5a–c** complexes under co-polymerisation conditions using ethylene and 1-hexene, with MAO as co-activator. It shows that all three complexes **5a–c** have a low polymerisation activity compared with previously published structures [14,18]. Molecular weights of the hexene–ethylene copolymers are markedly high in the case of **5a** with  $M_w = 919,000$  and much lower with **5c**,  $M_w = 65,500$ . Compound **5b** has no measured value since the amount of polymer isolated was too small. We can see that a small increase in steric hindrance going from a *i*PrMe<sub>2</sub>SiO– group in **5b** to the *t*Bu–Me<sub>2</sub>SiO– group in **5c** increases the activity 10 times. The hexene incorporation also increases when we go from **5a** (0.3 wt%) to **5c** (3.0 wt%). The broad polydispersity ( $M_w/M_v$ ) especially in **5c** is of a bimodal nature.

Polymerisations were also performed with HIBAO as co-activator with very limited activity. This result was not expected since the mono-siloxy-substituted cyclopentadienyl zirconium dichlorides presented in our patent application [18] show activities up to 2570 (kg(PE)/g(Zr)/h) for polymerisation activated by HIBAO and up to 900 (kg(PE)/g(Zr)/h) for polymerisations activated by MAO.

### 3. Summary

The novel zirconocenes **5a–c** were synthesised in good yields. (1,2-(Me<sub>3</sub>SiO)<sub>2</sub>Cp)<sub>2</sub>ZrCl<sub>2</sub> (**5a**) has a unique arrangement in the torsion angles of the siloxy substituents. One is almost in plane with the cyclopentadienyl ring and the other is almost perpendicular to this plane. The Cl–Zr–Cl

Table 3  
Results of co-polymerisation of ethylene and 1-hexene with compounds **5a–c**

Complex	<b>5a</b>	<b>5b</b>	<b>5c</b>
Complex charged (μmol)	1.0	0.50	1.0
Yield (g)	2.2	0.8	23.6
Activity [kg(PE)/g(Zr)/h]	24.30	25.44	262.92
Crystallinity (%)	49.7	n.d.	59.9
$T_m$ (°C)	130.6	n.d.	125.8
$M_w$ (g mol <sup>-1</sup> )	919000	n.d.	65500
$M_w/M_n$	5.6	n.d.	8.1
Co-monomer Cont. (wt%)	0.4	n.d.	3.0
<i>trans</i> -Vinylene (wt%)	0.03	n.d.	0.30
Vinyl (wt%)	0.47	n.d.	0.95
Vinylidene (wt%)	0.57	n.d.	0.22

Ethylene pressure = 10 bar. Co-monomer is 1-hexene charged as 40 ml from the start. Methylalumoxane is used as co-activator with the amount of Al/Zr = 1000. A stirring rate of 400 rpm/min. is used. The polymerisation is stopped after 30 min. Polymerisation temperature is 80 °C. Polymerisation medium = 1200 ml pentane. n.d., not determined.



and the Cp(centroid)–Zr–Cp(centroid) angles in **5a–c** are larger than what can be found for published values of similar structures. The complexes were active catalysts in ethylene polymerisation with MAO and exhibited low polymerisation activities. The (1,2-(*t*BuMe<sub>2</sub>SiO)<sub>2</sub>Cp)<sub>2</sub>ZrCl<sub>2</sub> complex **5c** showed a higher polymerisation activity than the other examples synthesised. Molecular weights of the polymers obtained were medium to high with (1,2-(Me<sub>3</sub>-SiO)<sub>2</sub>Cp)<sub>2</sub>ZrCl<sub>2</sub> **5a** having  $M_w = 919,000$ . The complexes **5a–c** shows very low activity when activated with HIBAO, which is surprising since previous research on unbridged mono-siloxy-cyclopentadienyl chlorides shows decent activities when activated with HIBAO.

## 4. Experimental

### 4.1. General procedures and materials

All operations were carried out under argon or nitrogen atmosphere by using standard Schlenk-line, vacuum and dry box techniques. Solvents were dried with metallic sodium benzophenone and distilled under argon prior to use. Me<sub>3</sub>SiCl (ABCR) was distilled under argon prior to use. *t*-BuMe<sub>2</sub>SiCl (ABCR), *i*-PrMe<sub>2</sub>SiCl (Aldrich), *t*-BuLi, ZrCl<sub>4</sub> (Acros) were used as received. 1,2-Cyclopentandione was prepared according to Acheson [27] and 2-trimethylsiloxy-cyclopent-2-enone and 2-(*t*-butyl-dimethyl-siloxy)-cyclopent-2-enone [32] were prepared according to the literature procedure by Sasaki [28].

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded at 298 K with a Bruker Avance 600 (<sup>1</sup>H NMR 600 MHz, <sup>13</sup>C NMR 150.9 MHz) or with a Bruker 250 MHz instrument (<sup>1</sup>H NMR 250 MHz). <sup>1</sup>H NMR was referenced to residual hydrogen in deuterated solvents. <sup>29</sup>Si NMR was recorded at 25 °C on a Jeol JNM-A500 (<sup>29</sup>Si NMR 99.36 MHz) using external reference. GC–MS spectra were recorded on a HEWLETT 5971A gas chromatography-mass selective detector apparatus. Direct inlet MS spectra were produced by a high resolution mass spectrometer, Fison's ZapSpec, in an electron impact ionisation mode (EIMS) (70 eV). The elemental analyses were carried out by the Analytische Laboratorien GmbH in Lindlar, Germany. The melting points of the synthesised metallocenes were measured using a TA Instruments DSC Q1000.

Crystal data were collected with a Nonius Kappa CCD area-detector diffractometer at 173(2) K, using graphite monochromatised Mo K $\alpha$  radiation, 0.71073 Å: COLLECT (Nonius, 2002). The crystal was fixed at the fiber using the oil-drop method. A multi-scan absorption correction was made: SADABS (Sheldrick, 1996).

Polymerisations were carried out in a 2 L stainless steel autoclave reactor equipped with a paddle stirrer and a continuous supply of ethylene. Polymerisation temperature was 80 °C and ethylene pressure 10 bar unless otherwise indicated. Methylalumoxane (MAO) 30 wt% solution in toluene was purchased from Albemarle. Hydrogen and

co-monomer, if used, were fed to the reactor simultaneously with ethylene.

**Polymer analysis:** MFRs of the polymers produced were measured according to the ISO 1133 method. The molecular weight averages and molecular weight distributions were determined using a Waters 150C SEC instrument. A set of two mixed bed and one 10.7 Å TSK-Gel columns from TosoHaas was used. The analyses were performed in 1,2,4-trichlorobenzene (TCB) stabilised with BHT at 135 °C with flow rate of 0.7 ml/min. The columns were calibrated with NMWD polystyrene standards and BMWD polyethylenes. DSC analyses were performed using a Mettler Toledo 822 and FTIR analyses with a Nicolet Magna-IR 550 instrument.

### 4.2. 2,3-Bis-trimethylsiloxy-cyclopenta-1,3-diene (**3a**)

To a 250 ml three-necked flask equipped with a water condenser and a 100 ml addition funnel, 20.56 g of LiBr (236.7 mmol) was added and the whole system was flame-dried under vacuum. After cooling to the room temperature under argon, 100 ml of dry THF was added to the flask. When LiBr was dissolved in THF completely, the flask was put into an ethanol bath pre-cooled to –15 °C. After stirring for 30 min, 10.79 g of 2-trimethylsiloxy-cyclopent-2-enone **2a** (63.37 mmol) and 10.37 g of trimethylchlorosilane (95.45 mmol) were added to the flask, then 9.61 g of triethylamine (95.0 mmol) in 20 ml dry THF was added dropwise. After the completion of addition, the mixture was stirred at –15 °C for another 1 h and then put into an oil bath preheated to 45 °C. The mixture was allowed to react for 5 h at this temperature. After reaction, the volatiles were removed under vacuum and the residue was extracted with 100 ml dry pentane. The solids were filtered off and washed with three portions of 20 ml pentane. The solvent was removed under reduced pressure to afford 16.49 g of a brown residue, which was purified by distillation (45–48 °C, 0.15mbar) to give 13.10 g of pure product (54.03 mmol, 85%). (Found:  $M^+$  242. C<sub>11</sub>H<sub>22</sub>O<sub>2</sub>Si<sub>2</sub> requires:  $M^+$  242.12); <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 5.36 (t,  $J = 2.08$  Hz, 2H, CpH) 2.74 (t,  $J = 2.08$  Hz, 2H, CpH<sub>2</sub>) 0.33 (s, 18H, OSi(CH<sub>3</sub>)<sub>3</sub>).

### 4.3. 2,3-Bis-(*i*-propyldimethyl-siloxy)-cyclopenta-1,3-diene (**3b**)

To a 250 ml two-necked flask equipped with a water condenser and a Teflon-coated magnetic stirring bar, 25.36 g of lithium bromide (292 mmol) was added. The whole system was flame-dried under vacuum and cooled to room temperature under argon. The flask was then charged with 100 ml of dry THF. After all the LiBr was dissolved, the solution was cooled to –15 °C. Then the mixture was successively treated with 7.18 g of 1,2-cyclopentandione **1** (73.2 mmol) in 20 ml dry THF, 25.00 g of chloro(dimethyl)isopropylsilane (183 mmol) and 27.86 g of 1,8-diazabicyclo[5.4.0]undec-7-ene (183 mmol). The

resulting heterogeneous mixture was stirred at  $-15\text{ }^{\circ}\text{C}$  for 2 h and then put into an oil bath preheated to  $45\text{ }^{\circ}\text{C}$ . The reaction mixture was then allowed to react for 18 h. The volatiles were then removed under vacuum and the product was extracted twice with 80 ml of dry pentane. The two pentane parts were combined and pentane was pumped away to give 21.35 g of brown oily liquid, which was purified by distillation ( $61\text{--}64\text{ }^{\circ}\text{C}$ , 0.024 mbar) to afford 18.14 g of pure product (60.8 mmol, 83%). (Found: C, 60.09; H, 10.28; Si, 18.46%;  $\text{M}^+$  298.  $\text{C}_{15}\text{H}_{30}\text{O}_2\text{Si}_2$  requires: C, 60.34; H, 10.13; O, 10.72; Si, 18.81%;  $\text{M}^+$  298.18);  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$   $\delta$  ppm): 5.21 (t,  $J = 2.08$  Hz, 2H, CpH) 2.69 (t,  $J = 2.08$  Hz, 2H, CpH<sub>2</sub>) 1.01 (s, 2H, OSiMe<sub>2</sub>(CHMe<sub>2</sub>)) 1.00 (s, 12H, OSi(CH<sub>3</sub>)<sub>2</sub>(i-Pr)) 0.19 (s, 12H, OSiMe<sub>2</sub>(CH(CH<sub>3</sub>)<sub>2</sub>)).  $^{13}\text{C}$  NMR (150.5 MHz,  $\text{CD}_2\text{Cl}_2$   $\delta$  ppm): 152.04, 104.61, 30.49, 16.83, 14.93,  $-3.97$ .

#### 4.4. 2,3-Bis-(*t*-butyldimethyl-siloxy)-cyclopenta-1,3-diene (**3c**)

This compound was synthesised in a manner analogous to the procedure for **3a**. (10.50 g) 2-(*t*-Butyldimethyl-siloxy)-cyclopent-2-enone (49.44 mmol) was treated with 8.00 g of *t*-butyldimethylchlorosilane (73.6 mmol) in the presence of 17.37 g of LiBr (200.0 mmol) and 11.24 g of 1,8-diazabicyclo[5.4.0]undec-7-ene (73.83 mmol) to afford 11.47 g of brown residue, which was purified by distillation ( $69\text{--}72\text{ }^{\circ}\text{C}$ , 0.058 mbar) to give 7.40 g of pure product (22.66 mmol, 46%). (Found:  $\text{M}^+$  326.  $\text{C}_{17}\text{H}_{34}\text{O}_2\text{Si}_2$  requires:  $\text{M}^+$  326.21);  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$   $\delta$  ppm): 5.20 (t,  $J = 2.08$  Hz, 2H, CpH) 2.69 (t,  $J = 2.08$  Hz, 2H, CpH<sub>2</sub>) 0.97 (s, 18H, OSiMe<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>) 0.20 (s, 12H, OSi(CH<sub>3</sub>)<sub>2</sub>(*t*-Bu)).

#### 4.5. 5-Trimethylsilyl-2,3-bis-trimethylsiloxy-cyclopenta-1,3-diene (**4a**)

To a 250 ml flame-dried two-necked flask equipped with a water condenser, 6.60 g of 2,3-bis-trimethylsiloxy-cyclopenta-1,3-diene **3a** (27.2 mmol) and 60 ml dry THF were added. The solution was cooled to  $0\text{ }^{\circ}\text{C}$  and then 13.65 ml lithium diisopropylamide (LDA) solution (2 M in THF/*n*-heptane) was added dropwise to this solution while stirring. After the completion of the addition, the mixture was refluxed for about 18 h. Then the volatiles were removed under reduced pressure, leaving a dark red semisolid. The semisolid was dissolved in 80 ml of dry THF and then cooled to  $0\text{ }^{\circ}\text{C}$ . While stirring this solution, 2.96 g of fresh distilled trimethylchlorosilane (27.2 mmol) was added in one portion and then the resultant mixture was warmed to room temperature and stirred for 6 h. Volatiles were removed under vacuum and the residue was dissolved in 60 ml dry pentane. The formed suspension was filtered and washed with two portions of 20 ml pentane. Pentane was removed under vacuum to give red oily liquid. Purification by distillation ( $58\text{--}62\text{ }^{\circ}\text{C}$ , 0.16 mbar) afforded 6.10 g of pure product (19.4 mmol, 71.3%). (Found: C, 52.78; H, 9.75; Si, 26.20%;  $\text{M}^+$  314;  $\text{C}_{14}\text{H}_{30}\text{O}_2\text{Si}_3$  requires:

C, 53.44; H, 9.61; Si, 26.78%;  $\text{M}^+$  314.16);  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$   $\delta$  ppm): 5.36 (d,  $J = 1.95$  Hz, 2H, CpH) 2.67 (t,  $J = 1.95$  Hz, 1H, CpH-Si) 0.25 (s, 18H, OSi(CH<sub>3</sub>)<sub>3</sub>)  $-0.02$  (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).  $^{13}\text{C}$  NMR (150.9 MHz,  $\text{CD}_2\text{Cl}_2$   $\delta$  ppm): 150.14, 107.51, 37.47, 0.00,  $-2.29$ .

#### 4.6. 5-Trimethylsilyl-2,3-bis-(*i*-propyldimethyl-siloxy)-cyclopenta-1,3-diene (**4b**)

To a 250 ml flame-dried two-necked flask equipped with a 60 ml addition funnel and a Teflon-coated magnetic stirring bar, 14.93 g of 2,3-bis-(*i*-propyldimethyl-siloxy)-cyclopenta-1,3-diene **3b** (50.0 mmol) and 100 ml dry THF were added. Then the mixture was cooled to  $-78\text{ }^{\circ}\text{C}$  and 33.4 ml of *t*-BuLi (1.5 M in pentane) was added dropwise. After completion of addition, the mixture was stirred at room temperature for 2 h and then cooled to  $0\text{ }^{\circ}\text{C}$ . Trimethylchlorosilane (5.56 g, 52.0 mmol) was added to the mixture in one portion and then the mixture was stirred at room temperature for 2 h. The same workup and purification method (distillation,  $72\text{--}75\text{ }^{\circ}\text{C}$ , 0.028 mbar) with 5-trimethylsilyl-2,3-bis-trimethylsiloxy-cyclopenta-1,3-diene gave 14.69 g of product (39.6 mmol, 79%). (Found: C, 57.54; H, 10.52; Si, 22.68%;  $\text{M}^+$  370;  $\text{C}_{18}\text{H}_{38}\text{O}_2\text{Si}_3$  requires: C, 58.31; H, 10.33; Si, 22.73%;  $\text{M}^+$  370.22);  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$   $\delta$  ppm): 5.32 (d,  $J = 1.71$  Hz, 2H, CpH) 2.63 (t,  $J = 1.59$  Hz, 1H, CpH-Si) 1.01(0.97–1.03, narrow m, 14H, OSiMe<sub>2</sub>(CH(CH<sub>3</sub>)<sub>2</sub>)) 0.18 (s, 12H, OSi(CH<sub>3</sub>)<sub>2</sub>(i-Pr))  $-0.02$  (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).  $^{13}\text{C}$  NMR (150.9 MHz,  $\text{CD}_2\text{Cl}_2$   $\delta$  ppm): 150.65, 107.52, 37.54, 17.12, 15.19,  $-2.02$ ,  $-3.64$ ,  $-3.70$ .

#### 4.7. 5-Trimethylsilyl-2,3-bis-(*t*-butyldimethyl-siloxy)-cyclopenta-1,3-diene (**4c**)

To a 100 ml flame-dried Schlenk flask, 5.70 g of 2,3-bis-(*t*-butyldimethyl-siloxy)-cyclopenta-1,3-diene **3c** (17.4 mmol) and 50 ml dry THF were added. The solution was cooled to  $-78\text{ }^{\circ}\text{C}$  and then 11.70 ml of *t*-BuLi (1.5 M in pentane) was added dropwise. After completion of addition, the mixture was stirred at room temperature for 2 h and then cooled to  $0\text{ }^{\circ}\text{C}$ . Trimethylchlorosilane (2.00 g, 18.4 mmol) was added to the mixture in one portion and then the mixture was stirred at room temperature for 2 h. The same workup and purification method (distillation,  $78\text{--}83\text{ }^{\circ}\text{C}$ , 0.035 mbar) with 5-trimethylsilyl-2,3-bis-trimethylsiloxy-cyclopenta-1,3-diene afforded 5.50 g of pure product (13.8 mmol, 79%). (Found:  $\text{M}^+$  398;  $\text{C}_{20}\text{H}_{42}\text{O}_2\text{Si}_3$  requires:  $\text{M}^+$  398.25.  $^1\text{H}$  NMR ( $\text{CDCl}_3$   $\delta$  ppm): 5.29 (d, 2H, CpH); 2.62 (t, 1H, CpH-Si); 0.96 (s, 18H, OSiMe<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>); 0.24 (d, 12H, OSi(CH<sub>3</sub>)<sub>2</sub>(*t*-Bu)); 0.03 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

#### 4.8. Bis-[1,2-(trimethylsiloxy)cyclopentadienyl]zirconium dichloride (**5a**)

A flame-dried 100 ml Schlenk flask was charged with 2.56 g of ZrCl<sub>4</sub> (11.0 mmol), 50 ml of dry toluene and a magnetic stirring bar and was fitted with a rubber septum.

Then, 6.28 g of 5-trimethylsilyl-2,3-bis-trimethylsiloxy-cyclopenta-1,3-diene **4a** (20.0 mmol) was added via a syringe and the resultant heterogeneous mixture was stirred at room temperature for 24 h. The reaction mixture was filtered through a 3 cm pad of Celite and the filtrate was concentrated and cooled to  $-30\text{ }^{\circ}\text{C}$ . The target zirconocene precipitated as a white microcrystalline powder. The solvent was removed by using a Teflon tube fitted with a filter and the solid was vacuum-dried to afford 4.65 g white powder (72.1 mmol, 72% based on the ligand), m.p.  $148.7\text{ }^{\circ}\text{C}$ . (Found: C, 40.92; H, 6.29; Si, 17.82%;  $\text{C}_{22}\text{H}_{42}\text{Cl}_2\text{O}_4\text{Si}_4\text{Zr}$  requires: C, 40.96; H, 6.56; Si, 17.42%);  $^1\text{H}$  NMR (150.9 MHz,  $\text{CD}_2\text{Cl}_2$   $\delta$  ppm): 5.60 (t,  $J = 3.97$  Hz, 2H) 5.51 (d,  $J = 3.78$  Hz, 4H) 0.28 (s, 36H, OSi(CH<sub>3</sub>)<sub>3</sub>).  $^{13}\text{C}$  NMR (150.9 MHz,  $\text{CD}_2\text{Cl}_2$   $\delta$  ppm): 137.62, 100.96, 99.12, 0.86. In the EIMS spectrum, parent ions of the composition  $\text{C}_{22}\text{H}_{42}\text{Si}_4\text{O}_4\text{ZrCl}_2^+$  were observed in the appropriate isotope ratios at  $m/e$  642–650.

#### 4.9. Bis-[1,2-(*i*-propyldimethylsiloxy)-cyclopentadienyl]zirconium dichloride (**5b**)

A flame-dried 100 ml Schlenk flask was charged with 2.56 g of  $\text{ZrCl}_4$  (11.0 mmol), 50 ml of dry toluene and a stirbar and was fitted with a rubber septum. Then 7.41 g of 5-trimethylsilyl-2,3-bis-*i*-propyldimethylsiloxy-cyclopenta-1,3-diene **4b** (20.0 mmol) was added via a syringe and the resultant heterogeneous mixture was stirred at room temperature for 24 h. The reaction mixture was filtered through a 3 cm pad of Celite and the filtrate was concentrated and cooled to  $-40\text{ }^{\circ}\text{C}$ . The target zirconocene precipitated as a slightly yellow microcrystalline powder. The solvent was removed by using a Teflon tube fitted with a filter and the solid was vacuum-dried to afford 4.95 g of powder (65.4 mmol, 65% based on the ligand), m.p.  $60.0\text{ }^{\circ}\text{C}$ . (Found: C, 46.70; H, 7.56; Si, 14.85%;  $\text{C}_{30}\text{H}_{58}\text{Cl}_2\text{O}_4\text{Si}_4\text{Zr}$  requires: C, 47.58; H, 7.72; Si, 14.84%);  $^1\text{H}$  NMR (150.9 MHz,  $\text{CD}_2\text{Cl}_2$   $\delta$  ppm): 5.61 (t,  $J = 4.15$  Hz, 2H) 5.50 (d,  $J = 3.78$  Hz, 4H) 1.03 (s, 4H, OSiMe<sub>2</sub>CH(Me<sub>2</sub>)) 1.02 (s, 24 H, OSiMe<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>) 0.23 (s, 12H, OSi(CH<sub>3</sub>)) 0.21 (s, 12H, OSi(CH<sub>3</sub>)).  $^{13}\text{C}$  NMR (150.9 MHz,  $\text{CD}_2\text{Cl}_2$   $\delta$  ppm): 137.66, 101.17, 98.87, 17.07, 15.34,  $-2.89$ ,  $-3.12$ .  $^{29}\text{Si}$  NMR (99.36 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $\delta$  ppm): 24.61. In the EIMS spectrum, parent ions of the composition  $\text{C}_{30}\text{H}_{58}\text{Si}_4\text{O}_4\text{ZrCl}_2^+$  were observed in the appropriate isotope ratios at  $m/e$  754–763.

#### 4.10. Bis-[1,2-(*t*-butyldimethylsiloxy)-cyclopentadienyl]zirconium dichloride (**5c**)

A flame-dried 100 ml Schlenk flask was charged with 1.82 g of  $\text{ZrCl}_4$  (7.81 mmol), 60 ml of dry toluene and a stirbar and was fitted with a rubber septum. Then, 5.18 g of 5-trimethylsilyl-2,3-bis-*t*-butyldimethylsiloxy-cyclopenta-1,3-diene **4c** (13.0 mmol) was added via a syringe and the resultant heterogeneous mixture was stirred at room temperature for 20 h. The reaction mixture was filtered

through a 3 cm pad of Celite and the volatiles were removed under reduced pressure to give 3.47 g of a almost pure product (4.27 mmol, 66% based on the ligand). Further purification by recrystalliation from *n*-hexane afforded a yellow microcrystalline powder. (Found: C, 50.21; H, 8.14; Si, 13.52%;  $\text{C}_{34}\text{H}_{66}\text{Cl}_2\text{O}_4\text{Si}_4\text{Zr}$  requires: C, 50.21; H, 8.18; Si, 13.81%);  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_2\text{Cl}_2$   $\delta$  ppm): 5.66 (t,  $J = 4.15$  Hz, 2H) 5.49 (d,  $J = 4.16$  Hz, 4H) 0.99 (s, 36H, OSiMe<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>) 0.20 (s, 12H, OSi(CH<sub>3</sub>)), 0.24 (s, 12H, OSi(CH<sub>3</sub>)).  $^{13}\text{C}$  NMR (600 MHz,  $\text{CD}_2\text{Cl}_2$   $\delta$  ppm): 137.74, 100.97, 98.80, 26.09, 18.72,  $-3.43$ ,  $-4.07$ . In the EIMS spectrum, parent ions of the composition  $\text{C}_{34}\text{H}_{66}\text{Si}_4\text{O}_4\text{ZrCl}_2^+$  were observed in the appropriate isotope ratios at  $m/e$  810–819.

## 5. Supplementary material

Crystallographic data for the structural analysis of **5a** and **5b** have been deposited with the Cambridge Crystallographic Data Centre, as CCDC No. 271538 and CCDC No. 271537. A copy of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax.(int. code) +44 1223 336 033 or Email: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>.

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