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# Synthesis, structures and catalytic properties of Group 4 metallocenes based upon $[Me_2E(C_5H_4)(C_5Me_4)]_2$ (E = Si, Ge) supporting coordination

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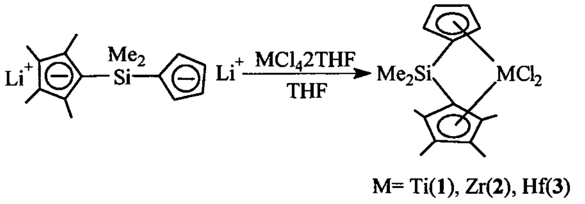
## Abstract

The *ansa*-metallocene complexes $Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5Me_4)MCl_2$ [M = Ti (**1**), Zr (**2**), Hf (**3**)] were prepared by the reaction of $[Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5Me_4)]Li_2$ with $MCl_4{\cdot}2THF$. Complexes $Me_2Ge(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5Me_4)MCl_2$ [M = Ti (**4**), Zr (**5**)] were synthesized using similar method from the germyl-bridged ligand. The molecular structures of **1**–**3** and **5** have been determined by X-ray diffraction. Complexes **1**–**3** and **5** in combination with MAO were studied as catalysts for ethylene polymerization and it was found that zirconocene catalysts show much higher activities than the titanocene and hafnocene and the activities reach the maximum at high temperature. This indicates that the zirconocene system based upon $[Me_2E(C_5H_5)(C_5Me_4)]_2$ (E = Si, Ge) supporting coordination is a highly stable ethylene polymerization catalyst system. The relationship between structures and catalytic properties of catalysts is discussed. © 2001 Published by Elsevier Science B.V.

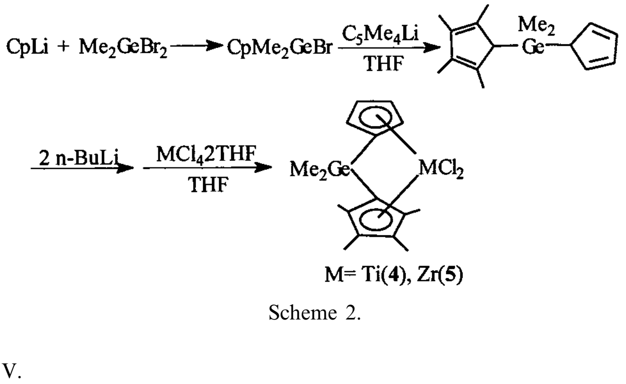
*Keywords:* Titanocene; Zirconocene; Metallocene; Polymerization

## 1. Introduction

Metallocene catalysts have been one of the most widely studied topics for more than 20 years [1]. As a great advantage over the traditional heterogeneous Ziegler–Natta catalysts, metallocene catalysts show super high activities and can produce polymers with narrow molecular weight distribution in high yield, since the active species in these catalyst systems is the single-site active center. It has been found that, upon introduction of positional substituents with various degrees of steric bulk in the aromatic rings or by modifying the size, number of atoms, and nature of atoms constituting its bridge, the catalytic performance can be altered in a predictable manner. It is now generally recognized that metallocenes with a short single-atom rigid bridge structure exhibit high activities and stereoselectivities in olefin polymerization and a lot of singe-atom bridged metallocenes, especially single-car-



Scheme 1.



Scheme 2.

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Table 1
$^1$H-NMR spectral data for complexes **1**–**5** (in $CDCl_3$)

| | $\delta$ $C_5H_4$ ($\Delta\delta$) | $\delta$ $C_5Me_4$ ($\Delta\delta$) | $\delta$ Si(Ge)$Me_2$ |
|---|---|---|---|
| **1** | 7.17 (t, 2)<br>5.57 (t, 2) (1.60) | 2.10 (s, 6)<br>1.82 (s, 6) (0.28) | 0.85 (s, 6) |
| **2** | 6.99 (t, 2)<br>5.69 (t, 2) (1.30) | 2.01 (s, 6)<br>1.91 (s, 6) (0.10) | 0.83 (s, 6) |
| **3** | 92 (t, 2)<br>5.65 (t, 2) (1.27) | 2.03 (s, 6)<br>1.99 (s, 6) (0.04) | 0.82 (s, 6) |
| **4** | 5.56 (t, 2)<br>7.13 (t, 2) (1.57) | 1.84 (s, 6)<br>2.10 (s, 6) (0.26) | 1.10 (s, 6) |
| **5** | 5.68 (t, 2)<br>6.97 (t, 2) (1.29) | 1.91 (s, 6)<br>2.01 (s, 6) (0.10) | 0.97 (s, 6) |

bon or silicon bridged metallocenes have been synthesized and studied for olefin polymerization [2,3]. However, there are still a few reports on the full structural characterization of titanium, zirconium and hafnium complexes with the same ligand and comparison of their catalytic behavior [4]. Based on our early work about silyl-bridged Group 4 metallocenes [5], herein we report the synthesis, crystal structures and catalytic behavior of single-silicon-bridged or germanium-bridged $C_s$ symmetric cyclopentadienyl and tetramethylcyclopentadienyl titanium, zirconium and hafnium complexes.

## 2. Results and discussion

The *ansa*-metallocene complexes $Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5Me_4)MCl_2$ (M = Ti (**1**), Zr (**2**), Hf (**3**) were synthesized by the reaction of $[Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5Me_4)]Li_2$ with $MCl_4{\cdot}2THF$ (Scheme 1). Complexes **4** and **5** were synthesized using similar method from the germyl-bridged ligand (Scheme 2).

The $^1$H-NMR spectra of **1**–**5** (Table 1) show two triplets for the α-H and β-H of cyclopentadienyl ring protons corresponding to the AA′BB′ system and two singlets for the methyl groups of the tetramethylcyclopentadienyl moiety. The differences ($\Delta\delta$) of the chemical shift between the α-H and β-H of cyclopentadienyl ring and the α- and β-methyl groups of the tetramethylcyclopentadienyl decrease with increasing atomic number of the metals. The methyl groups of the $SiMe_2$ or $GeMe_2$ bridging unit are equivalent and give a singlet.

The molecular structures of **1**–**3** and **5** are presented in Figs. 1–4, respectively. Table 2 provides the selected bond distances and angles. The molecules of **1**–**3** and **5** have $C_s$ symmetry. The metal atoms, silicon or germanium atom and two bridge-head carbon atoms are in a same plane which is nearly upright with the two $C_5$-ring planes. Because the ionic radii of zirconium and halfnium are very close, zirconocene **2** and hafnocene **3**

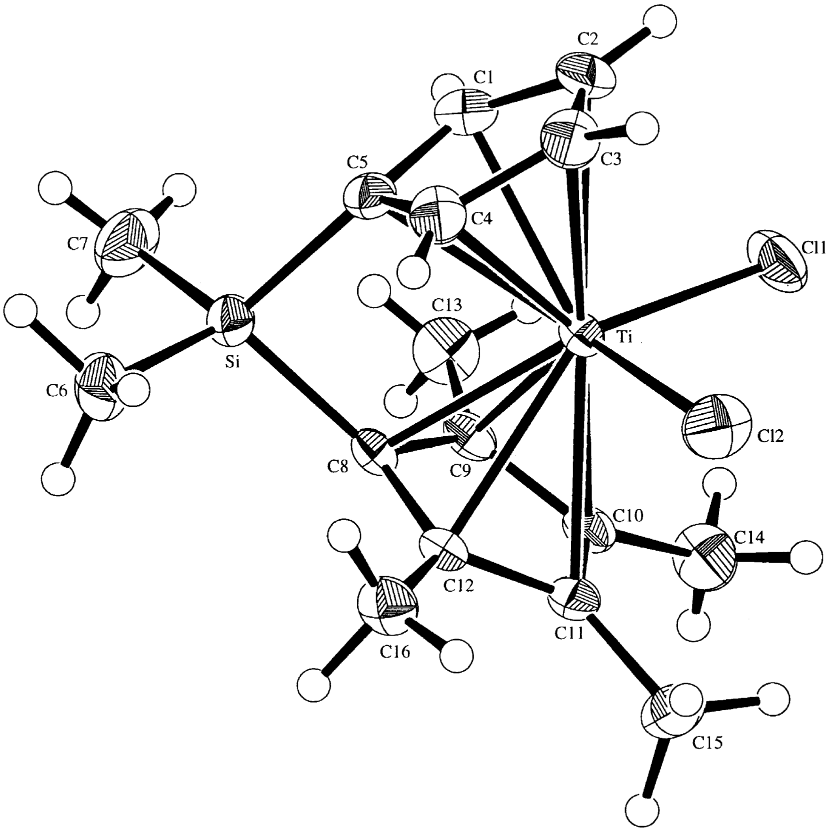

Fig. 1. ORTEP diagram of the molecular structure of **1**.

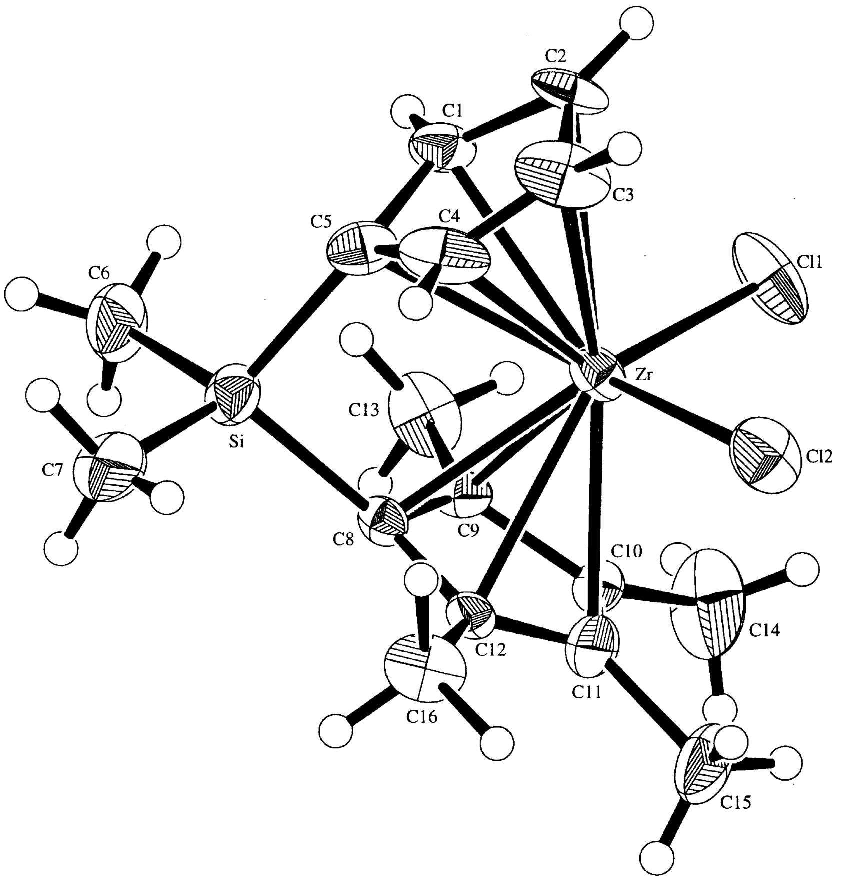

Fig. 2. ORTEP diagram of the molecular structure of **2**.

have similar structural parameters, which are very different from that of titanocene **1**.

Complexes **1**–**3** and **5** in combination with MAO were studied as catalysts for ethylene polymerization. The results are given in Table 3. From Table 3 it can be seen that zirconocenes show much higher activity than the titanocene and hafnocene. In general, the larger dihedral angle of a metallocene enlarges the reaction space between the two cyclopentadienyl ligands and increases the catalytic activity. With increasing ionic radius of metals, $Ti < Zr$, the dihedral angle between two cyclopentadienyl planes ($57.56 < 60.05°$) increases. So zirconocene **2** shows higher activity than titanocene **1**. Replacement of the dimethylsilyl bridge in **2** by the dimethylgermyl bridge in **5** results in an increase in the bridge and decrease of the dihedral angle (57.8°), and makes the activity decrease. The difference of ionic radius between Zr and Hf is very small due to the 4f lanthanide contraction, so the higher activity of zirconocene **2** than hafnocene **3** can be attributed to the higher electrophilicity of Zr metal center than that of Hf. The activity of **2** increases with increasing temperature and reaches the maximum at about 70 °C. The activity of **5** increases with increasing temperature from 20 to 80 °C. In contrast, the corresponding unbridged zirconocene $Cp(C_5Me_4H)ZrCl_2$ shows the highest activity at about 40 °C. This indicates that the presence of silyl or germyl bridge increases the stability of catalysts and the zirconocenes system based upon $[Me_2E(C_5H_5)(C_5Me_4)]_2$ ($E = Si$, Ge) supporting coordination is a highly stable ethylene polymerization catalyst system.

## 3. Experimental

Schlenk and vacuum line techniques were employed for all manipulations of air- and moisture-sensitive compounds. Hexane, toluene and THF were purified by refluxing over $Na/(C_6H_5)_2CO$ system under argon. $CH_2Cl_2$ was distilled from $P_2O_5$ under argon before use. $^1H$-NMR spectra were recorded on a Bruker AC-200 spectrometer and MS spectra on a VG-7070E HF. Elemental analysis was performed on a CHN CORDER MF-3 instrument. Molecular weight and molecular weight distribution of the polyethylene were measured by means of a Waters 150C/GPC in *o*-dichlorobenzene solution at 135 °C. Polymerization grade ethylene (Yanshan Petrochem. Co., China) was used without further purification. MAO was purchased from Aldrich Co. $Cp(C_5Me_4H)ZrCl_2$ [5e], $LiC_5H_4$-

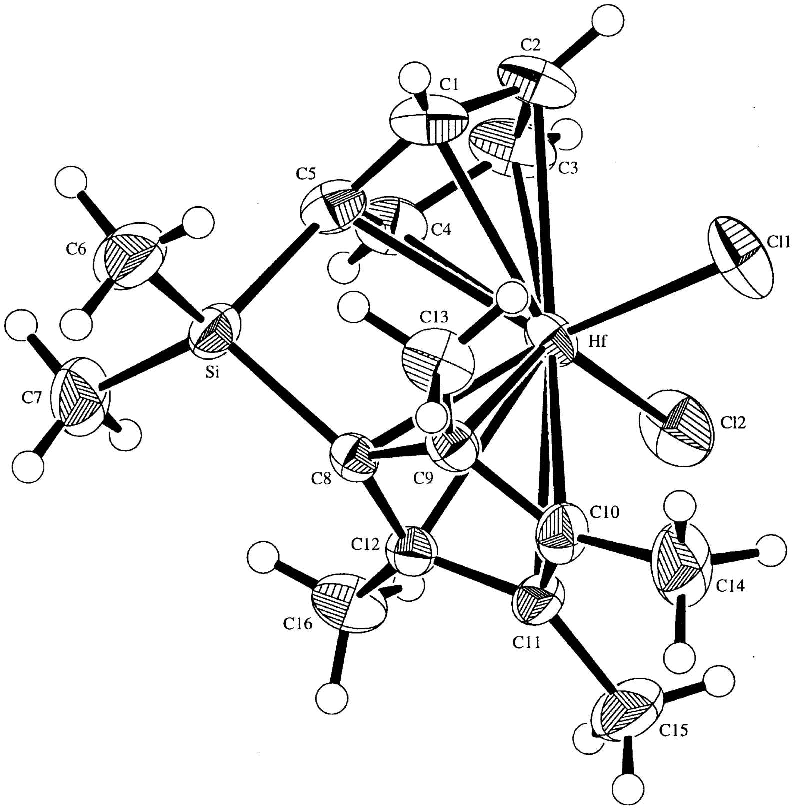

Fig. 3. ORTEP diagram of the molecular structure of **3**.

$SiMe_2C_5Me_4Li$ [6] and $MCl_4{\cdot}2THF$ (M = Ti, Zr, Hf) [7] were prepared according to literature.

### 3.1. Preparation of $Me_2Si(C_5H_4)(C_5Me_4)TiCl_2$ (1)

To a solution of 3.34 g (10.0 mmol) of $TiCl_4{\cdot}2THF$ in 50 mL of THF was added 10.0 mmol of $LiC_5H_4SiMe_2C_5Me_4Li$ in 20 ml of THF at 0 °C. The mixture was stirred at room temperature (r.t.) for 2 h and maintained under reflux for 24 h. After removal of solvents the residue was extracted with $CH_2Cl_2$. Upon concentration and cooling down 1.1 g (31%) of **1** was obtained as red crystals. M.p.: 197–199 °C. Anal. Calc. for $C_{16}H_{22}Cl_2SiTi$: C, 53.20; H, 6.14. Found: C, 52.99; H, 5.97%. MS (EI): *m*/*z* 360 ([$M^+$], 40), 324 ($M^+ - HCl$, 49), 288 ($M^+ - 2HCl$, 73), 120 ($[C_5Me_4]^+$, 40), 93 ($[Me_2SiCl]^+$, 100).

### 3.2. Preparation of $Me_2Si(C_5H_4)(C_5Me_4)MCl_2$ (M = Zr, 2; Hf, 3)

Metallocenes **2** and **3** were synthesized using a similar method. **2**: Light yellow–green crystals, yield 49%. M.p.: 252–254 °C. Anal. Calc. for $C_{16}H_{22}Cl_2SiZr$: C, 47.50; H, 5.48. Found: C, 47.39; H, 5.44%. MS (EI): *m*/*z* 402 ([$M^+$], 34), 367 ($M^+ - Cl$, 47), 366 ($M^+ - HCl$, 84), 93 ($[Me_2SiCl]^+$, 100). **3**: White crystals, yield 41%. M.p.: 255–258 °C. Anal. Calc. for $C_{16}H_{22}Cl_2SiHf$: C, 39.09; H, 4.51. Found: C, 38.88; H, 4.69%. MS (EI): *m*/*z* 492 ([$M^+$], 1), 178 ($[(C_5Me_4)SiMe_2]^+$, 100), 93 ($[Me_2SiCl]^+$, 20).

### 3.3. Preparation of $Me_2Ge(C_5H_4)(C_5Me_4)TiCl_2$ (4)

To a solution of 9.5 ml of cyclopentadiene in 150 ml of THF cooled down to 0 °C, 50.0 ml of *n*-BuLi (2.0 N, 0.1 mol) in hexane was added dropwise. After stirring at r.t. for 2 h, the solvents were removed and 350 ml of benzene was added. The resulting suspension was transferred via a cannula to a solution of 26.2 g (0.1 mol) of $Me_2GeBr_2$ in 50 ml of THF at 0 °C. The mixture was stirred at r.t. overnight and maintained under reflux for 4 h. After filtration and removal of solvents the residue was distilled under reduced pressure. The fraction of b.p. 62–64 °C/4 mmHg was collected to give 17.2 g (70%) of $CpGeMe_2Br$ as a yellow–green liquid. $^1H$-NMR ($CDCl_3$) $\delta$: 5.8–7.2 (m, 4H, $C_5H_5$), 2.65 (m, 1H, $C_5H_5$), 0.65 (s, 6H, $GeMe_2$).

To a solution of 6.07 g (24.5 mmol) of $CpGeMe_2Br$ in 80 ml of THF cooled down to 0 °C, 24.5 mmol of $C_5Me_4HLi$ (prepared from $C_5Me_4H_2$ and *n*-BuLi in 70 ml of THF) solution was added dropwise. The mixture was refluxed for 4 h and then hydrolyzed. After separation, drying and removal of solvents the residue was

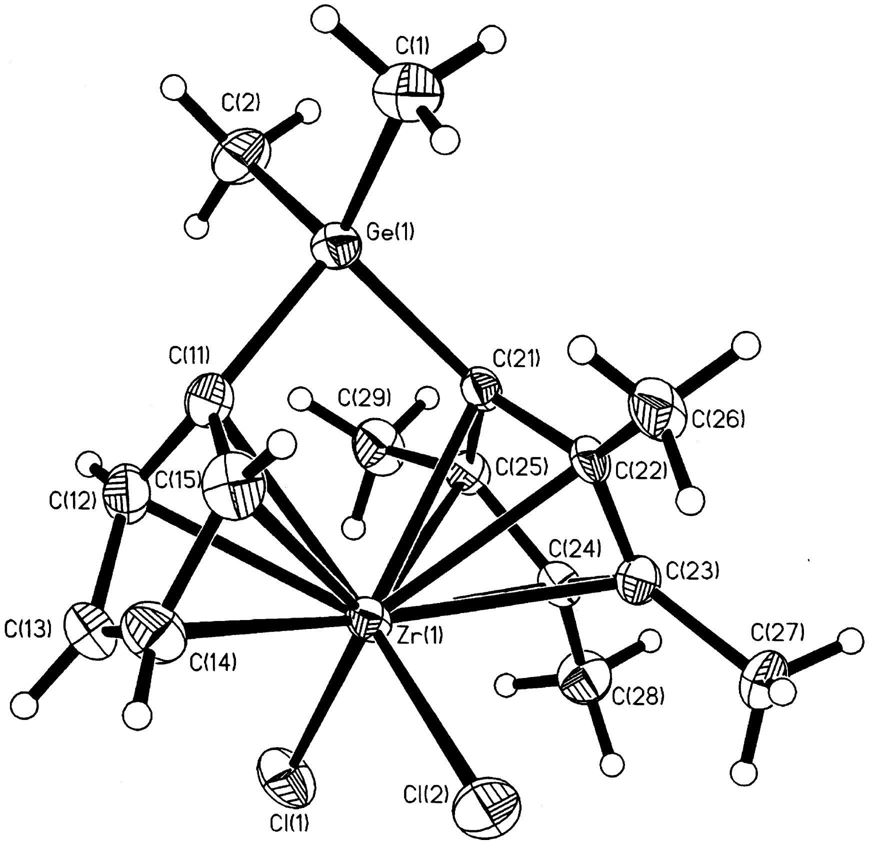

Fig. 4. ORTEP diagram of the molecular structure of **5**.

Table 2
Selected bond lengths (Å) and bond angles (°) for **1**–**3** and **5**

| | M = Ti (**1**) | M = Zr (**2**) | M = Hf (**3**) | M = Zr (**5**) |
|---|---|---|---|---|
| M–Cl (Å) | 2.336(1)<br>2.3492(9) | 2.430(4)<br>2.448(4) | 415(2)<br>2.411(2) | 2.426(2)<br>2.437(2) |
| M–PL ($C_5H_4$) (Å) | 2.081 | 2.213 | 2.201 | 2.2167 |
| M–PL ($C_5Me_4$) (Å) | 2.101 | 2.206 | 2.193 | 2.2066 |
| Si(Ge)–PL ($C_5H_4$) (Å) | 0.560 | 0.578 | 0.606 | 0.6220 |
| Si(Ge)–PL ($C_5Me_4$) (Å) | 0.464 | 0.458 | 0.461 | 0.4998 |
| Average M–C ($C_5H_4$) (Å) | 2.402 | 2.518 | 2.511 | 2.521 |
| Average M–C ($C_5Me_4$) (Å) | 2.433 | 2.519 | 2.509 | 2.521 |
| Si(Ge)–C (bridge head of $C_5H_4$) (Å) | 1.865(3) | 1.871(4) | 1.872(6) | 1.954(8) |
| Si(Ge)–C (bridge head of $C_5Me_4$) (Å) | 1.883(3) | 1.878(4) | 1.873(5) | 1.964(7) |
| ∠Cl–M–Cl (°) | 97.33 | 101.08(6) | 99.96 | 99.5(1) |
| ∠($C_5H_4$)–($C_5Me_4$) (°) | 57.56 | 60.95 | 60.05 | 57.8 |
| ∠C–Si–C (°) (C: bridge head atom) | 90.3(1) | 93.9(2) | 94.1(2) | 92.0(3) |

chromatographed on silica gel using petroleum ether as eluent and to give 3.6 g (51%) of $CpGeMe_2C_5Me_4H$ as an orange liquid. $^1$H-NMR ($CDCl_3$) $\delta$: 6.1–7.1 (m, 4H, $C_5H_5$), 2.8–3.0 (m, 2H, $C_5H_5$), 1.95 (s, 6H, $CpMe_4$), 1.85 (s, 6H, $CpMe_4$), −0.06 (s, 6H, $GeMe_2$).

To a solution of 1.28 g (4.4 mmol) of $C_5H_5GeMe_2C_5Me_4H$ in 30 ml of THF cooled down to 0 °C, 4.4 ml of *n*-BuLi (2.0 N, 8.8 mmol) in hexane was added dropwise. After stirring at r.t. overnight, the resulting solution was transferred via a cannula to a solution of 1.48 g (4.4 mmol) of $TiCl_4 \cdot 2THF$ in 25 ml of THF at 0 °C. The mixture was stirred at r.t. for 5 h and maintained under reflux for 2 h. After removal of solvents the residue was extracted with toluene. Upon concentration and cooling down afforded purple crude product. After recrystallization with $CH_2Cl_2$ 0.3 g (17%) of **4** was obtained as purple crystals. M.p.: 292–294 °C. Anal. Calc. for $C_{16}H_{22}Cl_2GeTi$: C, 47.33;

H, 5.47. Found: C, 47.16; H, 5.62%. MS (EI): *m*/*z* 404 ([M$^+$], 21), 368 (M$^+$ − HCl, 10), 332 (M$^+$ − 2HCl, 17), 267 (M$^+$ − GeMe$_2$Cl, 16), 232 (M$^+$ − Me$_2$GeCl$_2$, 100).

### 3.4. Preparation of $Me_2Ge(C_5H_4)(C_5Me_4)ZrCl_2$ (5)

Using a similar method **5** was synthesized as yellow–green crystals. The yield is 14%. M.p.: 290–292 °C. Anal. Calc. for $C_{16}H_{22}Cl_2GeZr$: C, 42.76; H, 4.94. Found: C, 42.67; H, 5.06%. MS (EI): *m*/*z* 448 ([M$^+$], 65), 412 (M$^+$ − HCl, 100), 223 ([(C$_5$Me$_4$)GeMe$_2$]$^+$, 35), 165 ([C$_5$H$_4$GeMe$_2$]$^+$, 21).

### 3.5. Crystallographic studies

Crystals of **1**–**3** and **5** suitable for X-ray diffraction were obtained from $CH_2Cl_2$ solutions. All data sets were collected on a Rigaku AFC7R (**1**–**3**) or Enraf–Nonius CAD-4 (**5**) diffractometer with graphite monochromated Mo–K$_\alpha$ radiation. The corrections for empirical absorption were applied to intensity data. The structures were solved by direct methods (**1** and **5**) and heavy-atom Patterson methods (**2** and **3**) [8] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. All calculations for **1**–**3** were performed using the TEXSAN crystallographic

Table 3
Results of ethylene polymerization catalyzed with **1**–**3** and **5**/MAO

| Catalyst | $T_p$ (°C) | $A$ | $M_w$ ×10$^{-4}$ | $M_w/M_n$ |
|---|---|---|---|---|
| **1** | 20 | 0.31 | | |
| | 40 | 0.42 | | |
| | 60 | 0.35 | | |
| **2** | 30 | 2.00 | 22.0 | 2.60 |
| | 40 | 1.82 | 13.7 | 2.86 |
| | 50 | 1.83 | 9.18 | 2.77 |
| | 60 | 4.64 | 7.12 | 2.59 |
| | 70 | 10.8 | 5.71 | 2.21 |
| | 80 | 6.72 | 3.70 | 2.44 |
| **3** | 40 | 0.40 | | |
| | 60 | 0.60 | 20.7 | 2.27 |
| | 20 | 1.58 | | |
| **5** | 40 | 1.73 | | |
| | 60 | 2.95 | | |
| | 80 | 4.48 | | |
| $Cp(C_5Me_4H)ZrCl_2$ | 30 | 2.48 | | |
| | 40 | 6.49 | 43.3 | 2.60 |
| | 50 | 3.65 | | |
| | 60 | 2.03 | | |
| $Cp_2ZrCl_2$ | 40 | 4.35 | 44.8 | 2.53 |

Polymerization conditions: [M] = 3.0 × 10$^{-6}$ mol, Al/Zr = 2500, $t$ = 30 min, 1 atm of monomer pressure, in 100 ml toluene. $A$, activity (kg PE mmol$^{-1}$ Zr h); $M_w$, g mol$^{-1}$, determined by GPC in *o*-$C_6H_4Cl_2$ at 135 °C.

Table 4
Crystal data and structure refinement parameters for **1**–**3** and **5**

| | **1** | **2** | **3** | **5** |
|---|---|---|---|---|
| Empirical formula | $C_{16}H_{22}Cl_2SiTi$ | $C_{16}H_{22}Cl_2SiZr$ | $C_{16}H_{22}Cl_2HfSi$ | $C_{16}H_{22}Cl_2GeZr$ |
| Formula weight | 361.24 | 404.56 | 491.83 | 449.07 |
| Crystal system | Triclinic | Orthorhombic | Monoclinic | Monoclinic |
| Space group | $P\bar{1}$ (#2) | $Pna2_1$ (#33) | $P2_1/a$ (#14) | $P2_1/n$ (#14) |
| Unit cell dimensions | | | | |
| $a$ (Å) | 8.987(3) | 10.155(3) | 10.137(2) | 13.560(3) |
| $b$ (Å) | 11.908(3) | 12.814(4) | 12.795(4) | 9.101(2) |
| $c$ (Å) | 8.850(2) | 13.438(3) | 13.452(1) | 14.810(3) |
| $\alpha$ (°) | 102.73(2) | 90 | 90 | 90 |
| $\beta$ (°) | 116.26(1) | 90 | 90.16(1) | 110.71(3) |
| $\gamma$ (°) | 85.68(2) | 90 | 90 | 90 |
| $V$ (Å$^3$) | 828.2(4) | 1748(1) | 1744.7(6) | 1710(1) |
| $Z$ | 2 | 4 | 4 | 4 |
| $D_{calc}$ (g cm$^{-3}$) | 1.448 | 1.537 | 1.872 | 1.745 |
| $\mu$ (cm$^{-1}$) | 8.99 | 9.9 | 63.31 | 26.399 |
| Crystal size (mm) | 0.20 × 0.20 × 0.30 | 0.20 × 0.20 × 0.30 | 0.20 × 0.20 × 0.30 | 0.15 × 0.2 × 0.5 |
| Radiation (Å) | Mo–K$_\alpha$ (0.71069) | Mo–K$_\alpha$ (0.71069) | Mo–K$_\alpha$ (0.71069) | Mo–K$_\alpha$ (0.71073) |
| Data collection method | $\omega$–2$\theta$ | $\omega$–2$\theta$ | $\omega$–2$\theta$ | $\omega$–2$\theta$ |
| Max. 2$\theta$ (°) | 50 | 55 | 55 | 46 |
| Total no. of observations | 2913 | 2306 | 3698 | 2644 |
| No. of unique data [$I > 3\sigma(I)$] | 2573 | 1714 | 2827 | 1983 |
| Final no. of variables | 182 | 181 | 182 | 181 |
| $R$ | 0.036 | 0.033 | 0.031 | 0.05 |
| $R_w$ | 0.053 | 0.04 | 0.044 | 0.06 |
| Goodness-of-fit | 2.29 | 1.62 | 1.39 | 1.28 |

software package of Molecular Structure Corporation, while for **5** PDP11/44 and Pentium MMX/166 computers was used. A summary of the crystallographic results is presented in Table 4.

### 3.6. Ethylene polymerization

Polymerization was carried out in a 250 ml glass reactor with a magnetic stirring bar at about 780 mmHg. Toluene (100 ml) was introduced into the reactor, the temperature was increased to polymerization temperature, and then toluene was saturated with ethylene. A prescribed amount of MAO and a given metallocene dissolved in toluene were injected into the reactor to initiate the polymerization. The polymerization was stopped by adding 100 ml of methanolic hydrochloric acid solution. The polymer product was washed with ethanol and dried in vacuo at 60 °C.

## 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 163463–163466 for compounds **1**–**3** and **5**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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