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Synthesis, structures and polymerization catalytic properties of germyl-bridged bis(cyclopentadienyl) metallocenes

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Abstract

The ansa-metallocene complexes $Me_2Ge(\eta^5\text{-}C_5Me_4)_2MCl_2$ [M = Ti (**1**), Zr (**2**)], $Me_2Ge(\eta^5\text{-}C_5H_3Bu\text{-}t)_2ZrCl_2$ (**3**) and $Me_2Ge(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3R)ZrCl_2$ [R = Me (**4**), *t*-Bu (**5**)] were prepared by the reaction of the corresponding ligands with *n*-BuLi and $MCl_4{\cdot}2THF$, respectively. The molecular structures of **1** and **2** have been determined by the X-ray diffraction method. Complexes **2**–**5** in combination with MAO were studied as catalysts for ethylene polymerization and all the germyl-bridged zirconocene catalysts show high activities at relative high temperatures. This indicates that the germyl-bridged zirconocene systems show thermally stable catalyst systems for polymerization of ethylene.

Keywords: Titanocene; Zirconocene; Metallocene; Polymerization

1. Introduction

Metallocene catalysts have been one of the most widely studied topics in more than 20 years [1]. 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-carbon or silicon bridged metallocenes have been synthesized and studied for olefin polymerization [2,3]. However, there are still a few reports on the germyl-bridged cyclopentadienyl metallocene catalysts [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-germanium bridged substituted cyclopentadienyl titanium and zirconium complexes.

2. Results and discussion

The ansa-metallocene complexes **1**–**5** were synthesized by the reaction of the corresponding ligands with *n*-BuLi and $MCl_4{\cdot}2THF$, respectively (Schemes 1–3).

The solubility of complex **1** is much smaller than that of complex **2** in THF. After reaction complex **1** can easily crystallize from the THF solution. Complex **3** is a mixture of *rac* and *meso* isomers, which cannot be separated thoroughly by recrystallization. However, the *rac* and *meso* isomers can be assigned readily on the ^1H-NMR spectra of the mixture. The mixed cyclopentadienyl complexes **4** and **5** are not very stable, especially in solution, due to the poor symmetry.

The ^1H-NMR spectra of **1** and **2** show two singlets for the α- and β-methyls of cyclopentadienyl ring and a singlet for the germanium methyl groups. The ^1H-NMR spectrum of **3** indicates the presence of a mixture of *rac* and *meso* isomers in a 1:1 ratio. The *t*-butyl protons show two singlets at $\delta = 1.31$ and 1.34 ppm for *rac* and *meso* isomers. The germanium methyl protons show a singlet at $\delta = 0.83$ ppm for *rac* isomer and two singlets at $\delta = 0.76$ and 0.88 ppm for the *meso* isomer. The ^1H-NMR spectra of **4** and **5** show two singlets for the germanium methyl groups. Due to the asymmetry, the cyclopentadienyl protons of **4** and **5** split into four

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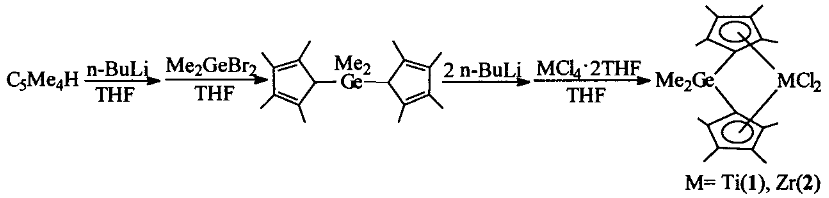
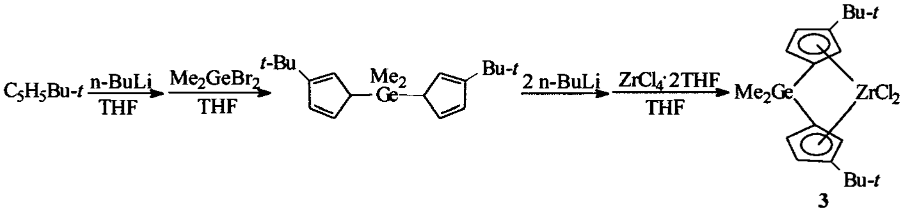


Scheme 1.



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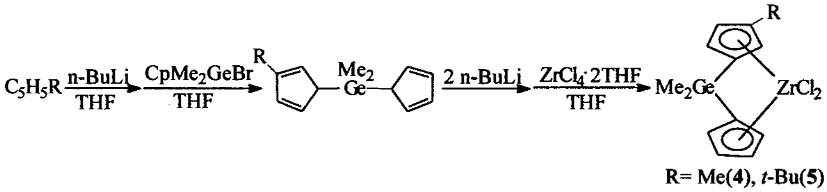
Scheme 2.



Scheme 3.

peaks. The integral ratios are 1:2:1:3 for **4** and 1:3:2:1 for **5**.

There are molecular ion peaks in all the mass spectra (EI, 70 eV) of complexes **1**–**5**. From the mass spectra it also can see that, the zirconium complexes, having larger abundances of the molecular ion peaks, are more stable than the titanium complex. For complexes **4** and **5**, due to the poor stability, the base peaks are very small fragment ions ($m/z = 91$ for **5**).

The molecular structures of **1** and **2** are presented in Figs. 1 and 2, respectively. Table 2 provides the selected bond distances and angles. The molecule of **1** has no symmetry but **2** has C_2 symmetry. This is probably due to that the small ionic radius of titanium increases the steric repulsion between two tetramethylcyclopentadienyl ligands and Ti–Cl bonds which makes the molecule of **1** twisted and lost the symmetry. Replacement of titanium atom in **1** by zirconium, with increasing the ionic radius of metals, $\text{Ti} < \text{Zr}$, all the bond lengths (M–Cl, average M–C), bond angles [Cl–M–Cl, C–Ge–C (bridge head carbon)] and the dihedral angle between two cyclopentadienyl ring planes ($57.9 < 59.3°$) increase (Table 1).

Complexes **2**–**5** in combination with MAO were studied as catalysts for ethylene polymerization. The results are given in Table 2. From Table 2 it can be seen that all the germyl-bridged zirconocenes show high activities for ethylene polymerization and the activities reach the maximum at higher temperature (80 °C for **2** and 60 °C for **3**–**5**). In contrary to the silyl-bridged analogues [5a,5b,5e], after carrying a *t*-butyl, the germyl-bridged zirconocenes **3** and **5** still show high activities for ethylene polymerization. This can be contributed to the larger ionic radius of germanium than that of silicon which decreases the steric effect of *t*-butyl.

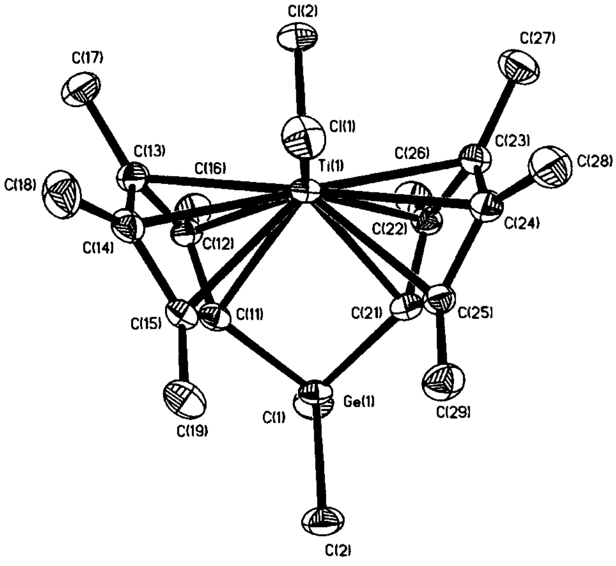


Fig. 1. ORTEP diagram of the molecular structure of **1**.

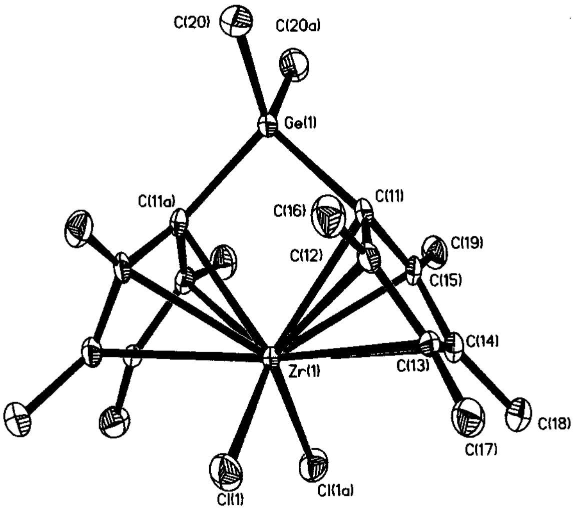


Fig. 2. ORTEP diagram of the molecular structure of **2**.

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

	M = Ti (**1**)	M = Zr (**2**)
Bond lengths		
M–Cl	2.321(2), 2.340(1)	2.433(1)
M–PL (C_5Me_4)	2.1315, 2.1213	2.2297
Ge–PL (C_5Me_4)	0.5363, 0.4971	0.5539
Average M–C (C_5Me_4)	2.4566, 2.4492	2.5426
Ge–C (bridge head carbon)	1.963(4), 1.944(4)	1.968(5)
Bond angles		
∠Cl–M–Cl	96.0(1)	99.1(1)
∠PL–PL	57.9	59.3
∠C–Ge–C (C: bridge head carbon)	89.7(2)	93.0(3)

3. Experimental

Schlenk and vacuum line techniques were employed for all manipulations of air- and moisture-sensitive compounds. C_6H_{14}, $C_6H_5CH_3$ and THF were purified by refluxing over Na–$(C_6H_5)_2CO$ system under Ar. CH_2Cl_2 was distilled from P_2O_5 under Ar before use. ^{1}H-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. Polymerization grade C_2H_4 (Yanshan Petrochem. Co., China) was used without further purification. MAO was purchased from Aldrich Co., $C_5Me_4HGeMe_2C_5Me_4H$ [6], *t*-BuCp [7], $CpGeMe_2Br$ [5f] and $MCl_4 \cdot 2THF$ (M = Ti, Zr) [8] were prepared according to literature.

3.1. Preparation of $Me_2Ge(C_5Me_4)_2TiCl_2$ (1)

To a solution of 1.4 g (4.0 mmol) of $C_5Me_4HGeMe_2$-C_5Me_4H in 40 ml of THF cooled down to 0 °C was dropwise added 8.0 mmol of *n*-BuLi C_6H_{14} solution. After stirring at room temperature (r.t.) for 2 days, the resulting solution was transferred via a cannula to a solution of 1.34 g (4.0 mmol) of $TiCl_4 \cdot 2THF$ in 30 ml of THF at 0 °C. The mixture was stirred at r.t. overnight and maintained under refluxing for 4 h. After the removal of solvents the residue was extracted with $C_6H_5CH_3$. Upon concentration and cooling down, a purple crude product was obtained. After recrystallization with CH_2Cl_2 0.3 g (16%) of **1** was obtained as purple crystals. M.p.: > 300 °C. Anal. Calc. for $C_{20}H_{30}Cl_2GeTi$: C, 51.96; H, 6.55. Found: C, 51.78; H, 6.74%. ^{1}H-NMR ($CDCl_3$): δ 2.07 (s, 12H, C_5Me_4), 1.79 (s, 12H, C_5Me_4), 1.13 (s, 6H, $GeMe_2$). MS (EI): *m*/*z* 462 (13, $[M^+]$), 426 (22, $[M-HCl]^+$), 411 (20, $[M-HCl-Me]^+$), 223 (31, $[(C_5Me_3CH_2)GeMe_2]^+$), 119 (100, $[C_5Me_3CH_2]^+$), 105 (84, $[C_5Me_3]^+$), 91 (56, $[C_7H_7]^+$), 77 (30, $[C_6H_5]^+$).

3.2. Preparation of $Me_2Ge(C_5Me_4)_2ZrCl_2$ (2)

Complex **2** were synthesized using a similar method as described above with $ZrCl_4 \cdot 2THF$ instead of $TiCl_4 \cdot 2THF$. Complex **2**: yellow green crystals, yield 21%. M.p.: > 300 °C. Anal. Calc. for $C_{20}H_{30}Cl_2GeZr$: C, 47.55; H, 5.99. Found: C, 47.65; H, 5.90%. ^{1}H-NMR ($CDCl_3$): δ 2.03 (s, 12H, C_5Me_4), 1.89 (s, 12H, C_5Me_4), 1.10 (s, 6H, $GeMe_2$). MS (EI): *m*/*z* 504 (23, $[M^+]$), 468 (12, $[M-HCl]^+$), 453 (25, $[M-HCl-Me]^+$), 365 (9, $[(C_5Me_4)_2ZrCl]^+$), 245 (16, $[(C_5Me_4)ZrCl]^+$, 223 (14, $[(C_5Me_3CH_2)GeMe_2]^+$), 119 (100, $[C_5Me_3CH_2]^+$), 105 (71, $[C_5Me_3]^+$), 91 (51, $[C_7H_7]^+$), 77 (25, $[C_6H_5]^+$).

Table 2
Results of ethylene polymerization catalyzed with **2**–**5**/MAO

Catalyst	Tp (°C)	Yield (g)	*A*
2	20	3.38	2.25
	40	3.95	2.63
	60	2.87	1.91
	80	5.81	3.87
3 (*rac*:*meso* = 1:1)	20	2.97	1.98
	40	2.48	1.65
	60	6.95	4.63
	80	6.25	4.17
4	20	3.14	2.09
	40	2.84	1.89
	60	13.62	9.08
	80	8.24	5.49
5	20	2.76	1.84
	40	3.41	2.27
	60	15.45	10.3
	80	9.80	6.53

Polymerization conditions: $[M] = 3.0 \times 10^{-6}$ mol, Al–Zr = 2500, t = 30 min, 1 atm of monomer pressure, in 100 ml toluene. *A*, activity (10^6 gPE mol^{-1} Zr^{-1} h^{-1}).

3.3. Preparation of $Me_2Ge(C_5H_3Bu\text{-}t)_2ZrCl_2$ (**3**)

To a solution of 6.1 g (50.0 mmol) of *t*-BuCp in 100 ml of THF cooled down to 0 °C was dropwise added 50.0 mmol of *n*-BuLi C_6H_{14} solution. After stirring at r.t. for 5 h, 6.6 g (25.0 mmol) of Me_2GeBr_2 was added to the mixture at 0 °C. The mixture was stirred overnight and then hydrolyzed. After separation, the mixture was dried over Na_2SO_4. Then the solution was evaporated to dryness and the residue was chromatographed on silica gel using petroleum ether as eluent to give 6.7 g (78%) of $t\text{-}BuC_5H_4GeMe_2C_5H_4Bu\text{-}t$ as orange–red liquid. ^{1}H-NMR ($CDCl_3$): δ 5.8–6.8 (m, 6H, C_5H_4), 2.15 (m, 2H, C_5H_4), 1.18 (s, 18H, *t*-Bu), −0.11 (s, 6H, $GeMe_2$).

To a solution of 3.4 g (9.9 mmol) of $t\text{-}BuC_5H_4GeMe_2C_5H_4Bu\text{-}t$ in 60 ml of THF cooled down to 0 °C was dropwise added 19.8 mmol of *n*-BuLi C_6H_{14} solution. After stirring at r.t. overnight, the resulting solution was transferred via a cannula to a solution of 3.72 g (9.9 mmol) of $ZrCl_4·2THF$ in 50 ml of THF at 0 °C. The mixture was stirred at r.t. for 24 h. After removal of solvents the residue was extracted with C_6H_{14}. Upon concentration and cooling down 2.5 g (51%) of **3** was obtained as yellow–green crystals. M.p.: 162–164 °C. Anal. Calc. for $C_{20}H_{30}Cl_2GeZr$: C, 47.55; H, 5.99. Found: C, 47.35; H, 5.56%. ^{1}H-NMR ($CDCl_3$): δ 6.82 (*meso*), 6.70 (*rac*), 6.02 (*meso*), 5.92 (*meso*), 5.58 (*rac*) (m, m, m, m, m, 6H, C_5H_3), 1.34 (*meso*), 1.31 (*rac*) (s, s, 18H, CMe_3), 0.88 (*meso*), 0.83 (*rac*), 0.76 (*meso*) (s, s, s, 6H, $GeMe_2$). MS (EI): *m*/*z* 504 (19, $[M^+]$), 489 (30, $[M-Me]^+$), 453 (100, $[M-HCl-Me]^+$), 385 (10, $[M-Me-GeMe_2]^+$), 229 (29, $[M-HCl-GeMe_2C_5H_3Bu\text{-}t\text{-}Me]^+$), 200 (24, $[C_5H_3GeC_5H_3]^+$), 91 (14, $[C_7H_7]^+$).

3.4. Preparation of $Me_2Ge(C_5H_4)(C_5H_3Me)ZrCl_2$ (**4**)

To a solution of 5.69 g (23 mmol) of $CpGeMe_2Br$ in 25 ml of THF cooled down to 0 °C was dropwise added 23 mmol of C_5H_4MeLi (prepared from C_5H_5Me and *n*-BuLi in 40 ml of THF) solution. The mixture was refluxed for 4 h and then hydrolyzed. After separation, drying and removal of solvents the residue was chromatographed on silica gel using petroleum ether as eluent to give 4.4 g (78%) of $CpGeMe_2C_5H_4Me$ as orange–yellow liquid. ^{1}H-NMR ($CDCl_3$): δ 5.8–6.8 (m, 7H, C_5H_5 and C_5H_4Me), 2.9–3.0 (m, 2H, C_5H_5 and C_5H_4Me), 2.07 (s, 3H, C_5H_4Me), −0.09 (s, 6H, $GeMe_2$).

Using a similar method for **3**, **4** was synthesized from 2.04 g (8.3 mmol) of $CpGeMe_2C_5H_4Me$, *n*-BuLi and 3.12 g (8.3 mmol) of $ZrCl_4·2THF$. After removal of solvents the residue was extracted with CH_2Cl_2. Upon concentration and cooling down 0.3 g (8%) of **4** was obtained as light-yellow solid. M.p.: 170 °C (dec.). Anal. Calc. for $C_{13}H_{16}Cl_2GeZr$: C, 38.34; H, 3.96. Found: C, 38.10; H, 3.87%. ^{1}H-NMR ($CDCl_3$): δ 6.93 (m, 3H, CpH), 6.68 (m, 1H, CpH), 5.95 (m, 2H, CpH), 5.80 (m, 1H, CpH), 2.16 (s, 3H, C_5H_3Me), 0.99 (s, 3H, $GeMe_2$), 0.88 (s, 3H, $GeMe_2$). MS (EI): *m*/*z* 406 (38, $[M^+]$), 391 (41, $[M-Me]^+$), 370 (91, $[M-HCl]^+$), 355 (22, $[M-HCl-Me]^+$), 297 (28, $[M-C_5H_4-3Me]^+$), 302 (18, $[M-GeMe_2]^+$), 267 (72, $[M-Cl-GeMe_2]^+$), 253 (70, $[M-GeMe_2-HCl-Me]^+$), 229 (100, $[M-2HCl-Zr-Me]^+$), 215 (22, $[M-HCl-Cl-Zr-2Me]^+$), 201 (32, $[C_5H_4GeC_5H_3]^+$).

3.5. Preparation of $Me_2Ge(C_5H_4)(C_5H_3Bu\text{-}t)ZrCl_2$ (**5**)

Using a similar method for $CpGeMe_2C_5H_4Me$, $CpGeMe_2C_5H_4Bu\text{-}t$ was synthesized from *t*-BuCp, *n*-BuLi and $CpGeMe_2Br$ as orange–yellow liquid in 93% yield. ^{1}H-NMR ($CDCl_3$): δ 5.8–6.6 (m, 7H, C_5H_5 and $C_5H_4Bu\text{-}t$), 1.8–1.9 (m, 2H, C_5H_5 and $C_5H_4Bu\text{-}t$), 1.18 (s, 9H, *t*-Bu), −0.10 (s, 6H, $GeMe_2$).

Using a similar method for **3**, **5** was synthesized from 1.7 g (5.9 mmol) of $CpGeMe_2C_5H_4Bu\text{-}t$, *n*-BuLi and 2.22g (5.9 mmol) of $ZrCl_4·2THF$ as light-yellow solid. Yield 8%. M.p.: 154–156 °C. Anal. Calc. for $C_{22}H_{32}Cl_2Si_2Zr$: C, 42.76; H, 4.94. Found: C, 42.35; H, 4.83%. ^{1}H-NMR ($CDCl_3$): δ 6.93 (m, 1H, CpH), 6.83 (m, 2H, CpH), 5.98 (m, 3H, CpH), 5.83 (m, 1H, CpH), 1.33 (s, 9H, CMe_3), 0.89 (s, 3H, $GeMe_2$), 0.82 (s, 3H, $GeMe_2$). MS (EI): *m*/*z* 448 (7, $[M^+]$), 433 (9, $[M-Me]^+$), 412 (6, $[M-HCl]^+$), 397 (30, $[M-HCl-Me]^+$), 291 (10, $[M-2Cl-2Me\text{-}t\text{-}Bu]^+$), 91 (100, $[C_7H_7]^+$).

3.6. Crystallographic studies

Crystals of **1** and **2** suitable for X-ray diffraction were obtained from CH_2Cl_2 solutions. All data sets were collected on Enraf–Nonius CAD-4 diffractometer with graphite monochromated Mo–K_α radiation. The corrections for empirical absorption were applied to intensity data. The structures were solved by direct method and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. All calculations were performed using the SDP-PLUS, SHELXS-86 and SHELXL-93 program on PDP11/44 and Pentium 586/166 computers. A summery of the crystallographic results is presented in Table 3.

3.7. C_2H_4 polymerization

Polymerization was carried out in a 250 ml glass reactor with a magnetic stirring bar at about 780 mmHg. $C_6H_5CH_3$ (100 ml) was introduced into the reactor, the temperature was increased to polymerization temperature, and then $C_6H_5CH_3$ was saturated with C_2H_4. A prescribed amount of MAO (7.5 mmol)

Table 3
Crystal data and structure refinement parameters for **1** and **2**

	1	**2**
Empirical formula	$C_{20}H_{30}Cl_2GeTi$	$C_{20}H_{30}Cl_2GeZr$
Formula weight	461.86	505.18
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$C2/c$ (no. 15)
Unit cell dimensions		
a (Å)	8.764(2)	15.487(3)
b (Å)	8.985(2)	12.352(2)
c (Å)	14.389(3)	11.133(2)
α (°)	92.83(3)	90
β (°)	97.30(3)	104.50(3)
γ (°)	115.19(3)	90
V (Å^3)	1010(1)	2061(1)
Z	4	4
D_{calc} (g cm^{-3})	1.518	1.627
μ (mm^{-1})	2.1265	2.1983
Crystal size (mm)	0.10 × 0.20 × 0.35	0.15 × 0.20 × 0.24
Radiation (Å)	Mo–K$_\alpha$ (0.71073)	Mo–K$_\alpha$ (0.71073)
Data collection method	ω–2θ	ω–2θ
Max. 2θ (°)	46	46
Total no. of observations	2945	1598
No. of unique data [$I \geq 3\sigma(I)$]	2348	1220
Final no. of variables	217	110
R	0.038	0.042
wR	0.046	0.049
Goodness-of-fit	1.00	1.25

dissolved in $C_6H_5CH_3$ (5 ml), metallocene (0.003 mmol) dissolved in $C_6H_5CH_3$ (3 ml) 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 EtOH 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. 169170 and 169171 for compounds **1** and **2**, 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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References

[1] (a) H. Sinn, W. Kaminsky, Adv. Organomet. Chem. 18 (1980) 99;
(b) P.C. Möhring, N.J. Coville, J. Organomet. Chem. 479 (1994) 1;
(c) H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem. Int. Ed. Engl. 34 (1995) 1143;
(d) G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem. Int. Ed. Engl. 38 (1999) 428;
(e) S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169;
(f) U. Siemeling, Chem. Rev. 100 (2000) 1495;
(g) H. Butenschon, Chem. Rev. 100 (2000) 1527;
(h) G.W. Coates, Chem. Rev. 100 (2000) 1223.

[2] Single-carbon bridged: (a) J.A. Ewen, R.L. Jones, A. Razavi, J.D. Ferrara, J. Am. Chem. Soc. 110 (1988) 6255;
(b) A. Razavi, J. Ferrara, J. Organomet. Chem. 435 (1992) 299;
(c) A. Razavi, J.L. Atwood, J. Organomet. Chem. 459 (1993) 117;
(d) G.H. Llinas, R.O. Day, M.D. Rausch, J.C.W. Chien, Organometallics 12 (1993) 1283;
(e) A. Razavi, J.L. Atwood, J. Organomet. Chem. 497 (1995) 105;
(f) R.M. Shaltout, J.Y. Corey, N.P. Rath, J. Organomet. Chem. 503 (1995) 205;
(g) M.L.H. Green, N. Ishihara, J. Chem. Soc. Dalton Trans. (1994) 657;
(h) S.C. Yoon, T.K. Han, B.W. Woo, H. Song, S.I. Woo, J.T. Park, J. Organomet. Chem. 534 (1997) 81;
(i) J.A. Ewen, R.L. Jones, M.J. Elder, A.L. Rheingold, L.M. Liable-Sands, J. Am. Chem. Soc. 120 (1998) 10786;
(j) D. Veghini, L.M. Henling, T.J. Burkhatdt, J.E. Bercaw, J. Am. Chem. Soc. 121 (1999) 564.

[3] Single-silicon bridged: (a) T. Mise, S. Miya, H. Yamazaki, Chem. Lett. (1989) 1853;
(b) W.A. Herrmann, J. Rohrmann, E. Herdtweck, W. Spaleck, A. Winter, Angew. Chem. Int. Ed. Engl. 28 (1989) 1511;
(c) W. Spaleck, M. Antberg, J. Rohrmann, A. Winter, B. Bachmann, P. Kiprof, J. Behm, W.A. Herrmann, Angew. Chem. Int. Ed. Engl. 31 (1992) 1347;
(d) M.A. Giardello, M.S. Eisen, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 115 (1993) 3326;
(e) W. Spaleck, F. Kuber, A. Winter, J. Rohrmann, B. Bachmann, M. Antberg, V. Dolle, E.F. Paulus, Organometallics 13 (1994) 954;
(f) U. Stehling, J. Diebold, R. Kirsten, W. Roll, H.H. Brintzinger, Organometallics 13 (1994) 964;
(g) M.A. Giardello, M.S. Eisen, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 117 (1995) 12114;
(h) Y.-X. Chen, M.D. Rausch, J.C.W. Chien, J. Organomet. Chem. 497 (1995) 1;
(i) T.A. Herzog, D.T. Zubris, J.E. Bercaw, J. Am. Chem. Soc. 118 (1996) 11988;
(j) Y. Obora, C.L. Stern, T.J. Marks, P.N. Nickias, Organometallics 16 (1997) 2503;
(k) N. Suzuki, T. Mise, Y. Yamaguchi, T. Chihara, Y. Ikegami, H. Ohmori, A. Matsumoto, Y. Wakatsuki, J. Organomet. Chem. 560 (1998) 47;
(l) H.G. Alt, M. Jung, W. Milius, J. Organomet. Chem. 558 (1998) 111;
(m) H. Schumann, K. Zietzke, R. Weimann, J. Demtschuk, W. Kaminsky, A.-M. Schauwienold, J. Organomet. Chem. 574 (1999) 228;

(n) C. Muller, D. Lilge, M.O. Kristen, P. Jutzi, Angew. Chem. Int. Ed. Engl. 39 (2000) 789;
(o) A. Antinolo, I. Lopez-Solera, I. Orive, A. Otero, S. Prashar, A.M. Rodriguez, E. Villasenor, Organometallics 20 (2001) 71;
(p) J.A. Ewen, M.J. Elder, R.L. Jones, L. Haspeslagh, J.L. Atwood, S.G. Bott, K. Robinson, Makromol. Chem. Macromol. Symp. 48/49 (1991) 253.
[4] (a) W. Spaleck, M. Antberg, V. Dolle, R. Klein, J. Rohrmann, A. Winter, New J. Chem. 14 (1990) 499;
(b) Y.-X. Chen, M.D. Rausch, J.C.W. Chien, Organometallics 13 (1994) 748;
(c) K. Patsidis, H.G. Alt, W. Milius, S.J. Palackal, J. Organomet. Chem. 509 (1996) 63;
(d) M. Koyama, K. Kimura, M. Nakano, H. Yamazaki, Chem. Lett. (1998) 1139;
(e) Y. Masubuchi, N. Suzuki, A. Fries, T. Mise, H. Koshino, Y. Ikegami, H. Ohmori, A. Matsumoto, J. Polym. Sci. Part A: Polym. Chem. 37 (1999) 283;
(f) N. Suzuki, Y. Masubuchi, Y. Yamaguchi, T. Kase, T.K. Miyamoto, A. Koriuchi, T. Mise, Macromolecules 33 (2000) 754.
[5] (a) B. Wang, L. Su, S. Xu, R. Feng, X. Zhou, D. He, Macromol. Chem. Phys. 198 (1997) 3197;
(b) G. Tian, B. Wang, S. Xu, Y. Zhang, X. Zhou, J. Organomet. Chem. 579 (1999) 24;
(c) B. Wang, S. Xu, X. Zhou, L. Su, R. Feng, D. He, Chem. J. Chin. Univ. 20 (1999) 77;
(d) G. Tian, B. Wang, S. Xu, X. Zhou, Trans. Met. Chem. 25 (2000) 568;
(e) X. Sun, B. Wang, S. Xu, X. Zhou, J. Zhao, Y. Hu, Chem. J. Chin. Univ. 21 (2000) 222;
(f) G. Tian, B. Wang, X. Dai, S. Xu, X. Zhou, J. Sun, J. Organomet. Chem. 634 (2001) 145.
[6] H. Schumann, L. Esser, J. Loebel, A. Dietrich, D. Van der Helm, X. Ji, Organometallics 10 (1991) 2585.
[7] R. Riemschneider, A. Reisch, H. Horak, Monastch 91 (1960) 805.
[8] L. Manzer, Inorg. Synth. 21 (1982) 135.