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Synthesis, structure and polymerization catalytic properties of doubly bridged bis(cyclopentadienyl) dinuclear titanium and zirconium complexes

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Abstract

A series of doubly bridged dinuclear titanium and zirconium complexes $(Me_2C)(Me_2E)(C_5H_3)_2(Cp'MCl_2)_2$ [E = Si, Cp′ = C_5H_5, M = Ti (**1**), Zr (**2**); E = Ge, Cp′ = C_5H_5, M = Ti (**3**), Zr (**4**); Cp′ = C_5Me_4H, M = Zr, E = Si (**5**), Ge (**6**)] and $(Me_2SiOSiMe_2)_2(C_5H_3)_2(Cp'MCl_2)_2$ [Cp′ = C_5H_5, M = Ti (**7**), Zr (**8**); Cp′ = C_5Me_4H, M = Zr (**9**)] were synthesized by the reaction of the lithium compounds of the corresponding doubly bridged cyclopentadienyl ligands with $CpTiCl_3$, $CpZrCl_3(THF)_2$ or $C_5Me_4HZrCl_3$, respectively. These complexes were characterized by ^{1}H-NMR, MS and elemental analysis. The crystal structure of **4** was determined by the X-ray diffraction. Their catalytic properties for ethylene polymerization were also studied in the presence of MAO. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Titanium; Zirconium; Doubly bridged; Dinuclear; Polymerization

1. Introduction

Metallocene catalysts have been one of the most widely studied topics for 20 years [1]. It has been found that catalytic properties have a close relationship with structures of catalysts, concerning the ring substituents and the nature of bridges. In order to develop effective catalysts for olefin polymerization, considerable attentions have been paid to the complexes with single bridged cyclopentadienyl ligands [2]. Meanwhile, there are also some reports about doubly bridged metallocenes [3] or single bridged dinuclear metallocenes [4]. If the two cyclopentadienyl ligands are linked with two alkyl or silyl groups, they might show the different catalytic properties from those of single bridged or single site catalysts [5,6]. Herein we report the synthesis, structure and catalytic behavior of a series of doubly bridged biscyclopentadienyl dinuclear titanium and zirconium complexes.

2. Results and discussion

Complexes **1**–**9** were prepared by the reaction of the lithium compounds of the corresponding doubly bridged cyclopentadienyl ligands with $CpTiCl_3$, $CpZrCl_3(THF)_2$ or $C_5Me_4HZrCl_3$, according to Schemes 1 and 2.

The doubly bridged bis(cyclopentadienyl) dinuclear complexes **1**–**9** are thermally very stable both in the solid and solution states. Complexes **1**–**6** are not very soluble in conventional organic solvents, but complexes **7**–**9** with two long siloxane bridges show much better solubility than complexes **1**–**6**. The complexes **1**–**6** exhibit similar ^{1}H-NMR spectra. The protons of C_5H_5 of complexes **1**–**4**, **7** and **8** show a single signal and the protons of C_5Me_4 of complexes **5**, **6** and **9** show a single and a double peaks at about $\delta = 2.0$ and 1.92 ppm. The protons of CMe_2 and $SiMe_2$ exhibit a single signal. There are two multiplets resulted from a A_2B splitting pattern for **1**–**4** and **7**–**9** and three multiplets resulted from a ABC splitting for **5** and **6**. The methyl substitutions increase the electron density of the cyclopentadi-

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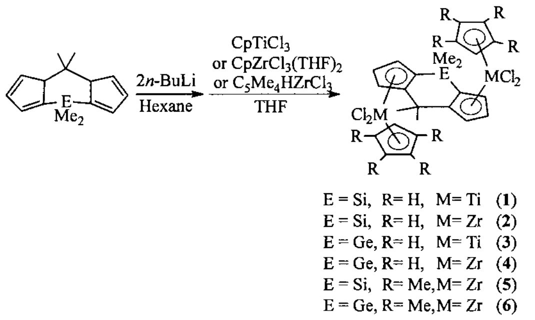
enyl ring and enhance the shielding effect, so that the chemical shift of C_5H_3 protons of the tetramethylcyclopentadienyl complexes **5**, **6** and **9** shifted upfield evidently than that of the cyclopentadienyl complexes **1**–**4**, **7** and **8**.

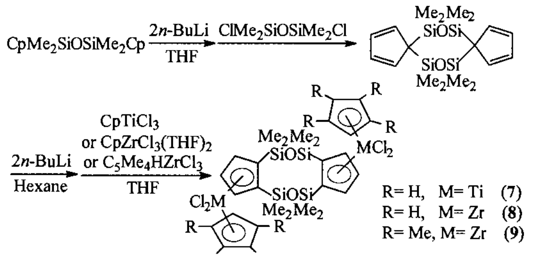
We could not detect the parent molecular ion peaks in all the Mass spectra (EI, 70 eV) of complexes **1**–**9**. The most important character in the Mass spectra is that all the complexes contain the fragment ion peaks of the corresponding mononuclear complexes (Scheme 3, Table 1) indicating that the mononuclear complexes are more stable in the Mass spectra condition. Especially in the Mass spectra of the complexes containing, both carbon and silicon bridges, **2** and **5**, the fragment ion *m/z* 351 ($[(Me_2C)(Me_2Si)(C_5H_3)_2ZrCl]^+$) peak of the corresponding mononuclear complex is the base peak. From the abundances of the fragment ion peaks of the corresponding mononuclear complexes, it can also estimate that, for the doubly bridged mononuclear complexes, the zirconium complexes are more stable than the titanium complexes, the complexes with carbon and silicon doubly bridge are more stable than that with carbon and germanium doubly bridge. Although, the Mass spectra of the doubly siloxane bridged complexes **7**–**9** also contain the fragment ion peaks of the corresponding mononuclear complexes, but the abundances of the peaks are much less than the complexes with carbon and silicon or carbon and germanium doubly bridges. All the Mass spectra of complexes **7**–**9** contain the fragment ion *m/z* 73 (Me_3Si^+) peak indicating the occurrence of rearrangement of $SiMe_2$ to $SiMe_3$ group [7].

Table 1
The fragment ion peaks of the mononuclear complexes in mass spectra

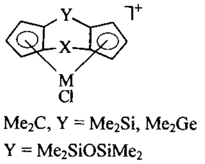
Complex	*m/z*	Composition	Relative abundance
1	309	$[(Me_2C)(Me_2Si)(C_5H_3)_2TiCl]^+$	83
2	351	$[(Me_2C)(Me_2Si)(C_5H_3)_2ZrCl]^+$	100
3	355	$[(Me_2C)(Me_2Ge)(C_5H_3)_2TiCl]^+$	15
4	397	$[(Me_2C)(Me_2Ge)(C_5H_3)_2ZrCl]^+$	28
5	351	$[(Me_2C)(Me_2Si)(C_5H_3)_2ZrCl]^+$	100
6	397	$[(Me_2C)(Me_2Ge)(C_5H_3)_2ZrCl]^+$	43
7	473	$[(Me_2SiOSiMe_2)_2(C_5H_3)_2TiCl]^+$	2
8	515	$[(Me_2SiOSiMe_2)_2(C_5H_3)_2ZrCl]^+$	3
9	515	$[(Me_2SiOSiMe_2)_2(C_5H_3)_2ZrCl]^+$	4



Scheme 1.



Scheme 2.



Scheme 3.

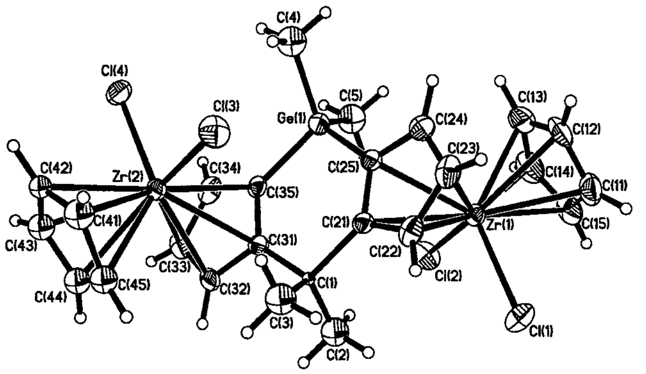


Fig. 1. The molecular structure of **4**.

Fig. 1 illustrates the molecular structure of **4**. Table 2 provides the selected bond lengths and angles. The molecule of **4** assumes the *trans* configuration. Similar to the structure of the analogue reported by J.Y. Corey [5c], C(1), C(21), C(25), Ge(1), C(35) and C(31) form a planar six-membered ring. The dihedral angles between the six-membered ring plane and two connected cyclopentadienyl ring planes are 12.57 and 3.46°, respectively. The average Zr–C bond lengths of the bridged cyclopentadienyl ring (2.532, 2.516 Å) are much longer than that of the free cyclopentadienyl ring (2.504, 2.505 Å).

These doubly bridged dinuclear zirconocenes **2**, **4**, **5**, **6**, **8** and **9** in combination with MAO were studied as catalysts for ethylene polymerization. The results are given in Table 3. As we can see from it, the cyclopentadienyl zirconium complexes **2**, **4** and **8** show high activities toward ethylene polymerization. The silicon and germanium bridged zirconocenes **2** and **4** show the highest activity at lower temperature (40 °C) but the doubly siloxane bridged zirconocene **8** shows the highest activity at higher temperature (60 °C). This can be contributed to that complex **8** with longer bridge, ligand experiences slow bimolecular deactivation processes [1b] than the ones with a shorter bridge ligand. After carrying four methyl groups in the cyclopentadienyl ring, the catalytic activities are decreased significantly due to the steric effect.

Table 2
Selected bond lengths (Å) and angles (°) for **4**

Bond lengths			
Zr(1)–Cl(1)	2.456(2)	Zr(1)–Cl(2)	2.4239(19)
Zr(2)–Cl(3)	2.438(2)	Zr(2)–Cl(4)	2.4609(19)
C(1)–C(21)	1.661(8)	C(1)–C(31)	1.606(8)
Ge(1)–C(25)	1.921(7)	Ge(1)–C(35)	1.920(7)
Zr(1)–C(21)	2.637(6)	Zr(2)–C(31)	2.580(7)
Zr(1)–C(22)	2.546(7)	Zr(2)–C(32)	2.497(7)
Zr(1)–C(23)	2.451(7)	Zr(2)–C(33)	2.460(7)
Zr(1)–C(24)	2.470(7)	Zr(2)–C(34)	2.504(7)
Zr(1)–C(25)	2.557(6)	Zr(2)–C(35)	2.567(6)
Zr(1)–C(11–15)	2.505	Zr(1)–C(21–25)	2.532
Zr(2)–C(31–35)	2.516	Zr(2)–C(41–45)	2.504
Bond angles			
C(31)–C(1)–C(21)	105.7(4)	C(35)–Ge(1)–C(25)	97.9(3)
Cl(2)–Zr(1)–Cl(1)	96.96(8)	Cl(3)–Zr(2)–Cl(4)	95.32(8)

Table 3
Results of ethylene polymerization catalyzed with zirconocenes/MAO

Catalyst	Tp (°C)	Yield (g)	*A*
2	20	6.63	4.42
	40	8.33	5.55
	60	4.01	2.67
	80	3.66	2.44
4	20	3.98	2.65
	40	5.91	3.94
	60	5.16	3.44
	80	3.39	2.26
5	20	1.71	1.14
	40	1.96	1.31
	60	2.07	1.38
	80	1.29	0.86
6	20	2.24	1.49
	40	2.16	1.44
	60	2.28	1.52
	80	1.64	1.09
8	20	3.18	2.12
	40	3.52	2.35
	60	7.02	4.68
	80	3.21	2.14
9	20	1.26	0.84
	40	1.27	0.85
	60	0.67	0.45

Tp, polymerization temperature; *A*, activity (10^6 gPE per molZr h). Polymerization conditions, $[\mathrm{Cat.}] = 0.5 \times 10^{-6}$ mol; Al–Zr = 2500; $t = 30$ min; 1 atm of monomer pressure; in 100 ml toluene.

3. Experimental

All operations were carried out under an argon atmosphere using standard Schlenk techniques. Toluene and THF were purified by refluxing over Na–$(C_6H_5)_2CO$ system under argon. Polymerization grade ethylene (Yanshan Petrochem. Co, China) was used without further purification. ^{1}H-NMR spectra were recorded on a Bruker AC-200 spectrometer and MS spectra on a VG-7070E HF. Elemental analyses were carried out on the CHN Corder MF-3 Elemental Analysis Facility. $(Me_2C)(Me_2Si)(C_5H_4)_2$ [8], $(Me_2C)(Me_2Ge)(C_5H_4)_2$ [8], $CpTiCl_3$ [9], $CpZrCl_3(THF)_2$ [10], $C_5Me_4HZrCl_3$ [11], $CpMe_2SiOSiMe_2Cp$ [12] and $ClMe_2SiOSiMe_2Cl$ [13] were prepared according to the literatures.

3.1. Preparation of *(Me₂C)(Me₂Si)[(C₅H₃)TiCl₂Cp]₂* (**1**)

To a solution of 1.6 g (7.0 mmol) of $(Me_2C)(Me_2Si)(C_5H_4)_2$ in 60 ml of hexane cooled down to 0 °C was gradually added 7.0 ml (14.0 mmol, 2.0 N in hexane) of *n*-BuLi. After stirring at room temperature (r.t.) overnight, the resulting suspension was filtered and the solvent was evaporated to dryness. THF (60 ml) and 3.05 g (14.0 mmol) of $CpTiCl_3$ were added to the solid. After stirring at r.t. for 0.5 h, the resulting suspension was filtered and the solid was extracted with CH_2Cl_2. Upon cooling, 0.93 g (22%) of **1** was obtained as brown red solid. $(Me_2C)(Me_2Si)[(C_5H_3)TiCl_2Cp]_2$ (**1**) Melting point (m.p.): 290 °C (dec). Anal. Found: C, 50.25; H, 4.54. $C_{25}H_{28}Cl_4SiTi_2$ Calc.: C, 50.54; H, 4.75%. ^{1}H-NMR ($CDCl_3$): δ 6.80 (m, 4H, C_5H_3), 6.49 (s, 10H, C_5H_5), 6.34 (m, 2H, C_5H_3), 1.73 (s, 6H, C–Me), 0.51 (s, 6H, Si–Me). MS (EI): m/z 409 (9, $M^+ - CpTiCl_2$), 373 (32, $M^+ - CpTiCl_2 - HCl$), 338(40, $M^+ - CpTiCl_3 - HCl$), 309 (83, $[(Me_2C)(Me_2Si)(C_5H_3)_2TiCl]^+$), 226 (49, $M^+ - 2CpTiCl_2$), 211(38, $M^+ - 2CpTiCl_2 - Me$), 183 (40, $[CpTiCl_2]^+$), 148 (42, $[CpTiCl]^+$), 65 (100, $[C_5H_5]^+$).

3.2. Preparation of *(Me₂C)(Me₂Si)[(C₅H₃)ZrCl₂Cp]₂* (**2**)

Described for **1**, desired complex **2** (1.0 g) was prepared from 1.6 g (7.0 mmol) of $(Me_2C)(Me_2Si)(C_5H_4)_2$, 14.0 mmol of n-BuLi and 5.65 g (14.0 mmol) of $CpZrCl_3(THF)_2$ in 21% yield as white solid. M.p.: > 300 °C. Anal. Found: C, 44.01; H, 3.89. $C_{25}H_{28}Cl_4SiZr_2$ Calc.: C, 44.10; H, 4.14%. ^{1}H-NMR ($CDCl_3$): δ 6.67 (m, 4H, C_5H_3), 6.40 (s, 10H, C_5H_5), 6.32 (m, 2H, C_5H_3), 1.71 (s, 6H, C–Me), 0.49 (s, 6H, Si–Me). MS (EI): m/z 663 (12, $M^+ + 2$-Me), 661 (5, [M^+]), 421 (9, $M^+ - CpZrCl_2 - 2Me$), 401 (30, $M^+ - CpZrCl_2 - Me - Cl$), 351 (100, $[(Me_2C)(Me_2Si)(C_5H_3)_2ZrCl]^+$), 335 (42, $[(CH_2C)(Me_2Si)(C_5H_3)_2ZrCl]^+$), 225 (81, $[CpZrCl_2]^+$), 65 (17, $[C_5H_5]^+$).

3.3. *Preparation of* $(Me_2C)(Me_2Ge)[(C_5H_3)MCl_2Cp]_2$ [$M = Ti$ (**3**), Zr (**4**)]

The compounds, **3** and **4**, were prepared using a similar method to that described for **1** from $(Me_2C)(Me_2Ge)(C_5H_4)_2$, n-BuLi and $CpTiCl_3$ or $CpZrCl_3(THF)_2$. **3**, Brown–red solid, yield 42%. M.p.: 298 °C (dec). Anal. Found: C, 46.77; H, 4.65. $C_{25}H_{28}Cl_4GeTi_2$ Calc.: C, 47.02; H, 4.42%. ^{1}H-NMR ($CDCl_3$): δ 6.70 (m, 4H, C_5H_3), 6.48 (s, 10H, C_5H_5), 6.34 (m, 2H, C_5H_3), 1.73 (s, 6H, C–Me), 0.67 (s, 6H, Ge–Me). MS (EI): m/z 355 (15, $[(Me_2C)(Me_2Ge)(C_5H_3)_2TiCl]^+$), 272 (5, $M^+ - 2CpTiCl_2$), 183 (29, $[CpTiCl_2]^+$), 65 (100, $[C_5H_5]^+$). **4**, White solid, yield 17%. M.p.: > 300 °C. Anal. Found: C, 41.27; H, 3.51. $C_{25}H_{28}Cl_4GeZr_2$ Calc.: C, 41.40; H, 3.89%. ^{1}H-NMR ($CDCl_3$): δ 6.60 (m, 4H, C_5H_3), 6.39 (s, 10H, C_5H_5), 6.30 (m, 2H, C_5H_3), 1.71 (s, 6H, C–Me), 0.16 (s, 6H, Ge–Me). MS (EI): m/z 707 (10, $M^+ - Me$), 397 (28, $[(Me_2C)(Me_2Ge)(C_5H_3)_2ZrCl]^+$), 307 (100, $[(MeGeC_5H_3)ZrCp]^+$), 277 (72, $[(MeGeC_5H_3)ZrCl]^+$), 225 (83, $[CpZrCl_2]^+$), 65 (41, $[C_5H_5]^+$).

3.4. *Preparation of* $(Me_2C)(Me_2E)[(C_5H_3)ZrCl_2(C_5Me_4H)]_2$ [$E = Si$ (**5**), Ge (**6**)]

Using a similar method to that described for **1**, **5** and **6** were prepared from $(Me_2C)(Me_2E)(C_5H_4)_2$ ($E = Si$, Ge), n-BuLi and $C_5Me_4HZrCl_3$. After the removal of solvents the residue was extracted with toluene. Upon concentration and cooling, **5** and **6** were obtained as light yellow solid. **5**, Yield 8%. M.p.: 300 °C (dec). Anal. Found: C, 49.80; H, 5.64. $C_{33}H_{44}Cl_4SiZr_2$ Calc.: C, 49.98; H, 5.59%. ^{1}H-NMR ($CDCl_3$): δ 6.53 (m, 2H, C_5H_3), 6.45 (m, 2H, C_5H_3), 6.10 (m, 2H, C_5H_3), 5.83 (s, 2H, C_5Me_4H), 2.00 (d, 12H, C_5Me_4), 1.93 (s, 12H, C_5Me_4), 1.72 (s, 6H, C–Me), 0.45 (s, 6H, Si–Me). MS (EI): m/z 457(14, $M^+ - C_5Me_4HZrCl_2 - Cl - Me$), 351(100, $[(Me_2C)(Me_2Si)(C_5H_3)_2ZrCl]^+$), 335 (33, $[(CH_2C)(Me_2Si)(C_5H_3)_2ZrCl]^+$), 281(48, $[C_5Me_4HZrCl_2]^+$), 121(60, $[C_5Me_4H]^+$). **6**, Yield 8%. M.p.: 295 °C (dec). Anal. Found: C, 47.14; H, 5.32. $C_{33}H_{44}Cl_4GeZr_2$ Calc.: C, 47.32; H, 5.30%. ^{1}H-NMR ($CDCl_3$): δ 6.51 (m, 2H, C_5H_3), 6.36 (m, 2H, C_5H_3), 6.12 (m, 2H, C_5H_3), 5.84 (s, 2H, C_5Me_4H), 2.00 (d, 12H, C_5Me_4), 1.92 (s, 12H, C_5Me_4), 1.73 (s, 6H, C–Me), 0.60 (s, 6H, Si–Me). MS (EI): m/z 819 (5, $M^+ - Me$), 397(43, $[(Me_2C)(Me_2Ge)(C_5H_3)_2ZrCl]^+$), 281(100, $[C_5Me_4HZrCl_2]^+$), 243 (56, $[MeC(C_5H_3)_2Zr]^+$), 121(46, $[C_5Me_4H]^+$).

3.5. *Preparation of* $(Me_2SiOSiMe_2)_2[(C_5H_3)MCl_2Cp]_2$ [$M = Ti$ (**7**), Zr (**8**)]

To a solution of 12.2 g (46.5 mmol) of $CpMe_2SiOSiMe_2Cp$ in 200 ml of hexane cooled down to 0 °C was gradually added 46.5 ml (93.0 mmol, 2.0 N in hexane) of n-BuLi. After stirring at r.t. overnight, the resulting suspension was filtered and the solvent was removed from the filtrate. THF (200 ml) was added to the residue, then the solution of 9.45 g (46.5 mmol) of $ClMe_2SiOSiMe_2Cl$ in 50 ml of THF were added to the mixture. After stirring at r.t. for 20 h, the solvents were evaporated and the residue was extracted with pentane. Upon concentration and cooling, 3.7 g (20%) of $(Me_2SiOSiMe_2)_2(C_5H_4)_2$ was obtained as white crystals. M.p.: 97–98 °C. Anal. Found: C, 54.85; H, 8.09. $C_{18}H_{32}O_2Si_4$ Calc.: C, 55.04; H, 8.21%. ^{1}H-NMR ($CDCl_3$): δ 6.74 (m, 4H, C_5H_4), 6.24 (m, 4H, C_5H_4), −0.08 (s, 24H, Si–Me).

The compounds, **7** and **8**, were prepared using a similar method as described for **1** from $(Me_2SiOSiMe_2)_2(C_5H_4)_2$, n-BuLi and $CpTiCl_3$ or $CpZrCl_3(THF)_2$. **7**, as red solid in 15% yield. M.p.: > 300 °C. Anal. Found: C, 44.08; H, 5.62. $C_{28}H_{40}Cl_4O_2Si_4Ti_2$ Calc.: C, 44.33; H, 5.32%. ^{1}H-NMR ($CDCl_3$): δ 6.78 (m, 4H, C_5H_3), 6.62 (m, 2H, C_5H_3), 6.46 (s, 10H, C_5H_5), 0.36 (s, 12H, Si–Me), 0.28 (s, 12H, Si–Me). MS (EI): m/z 473 (2, $[(Me_2SiOSiMe_2)_2(C_5H_3)_2TiCl]^+$), 183 (21, $[CpTiCl_2]^+$), 73 (100, $[SiMe_3]^+$), 65 (41, $[C_5H_5]^+$). **8**, as white solid in 10% yield. M.p.: > 300 °C. Anal. Found: C, 40.01; H, 5.08. $C_{28}H_{40}Cl_4O_2Si_4Zr_2$ Calc.: C, 39.79; H, 4.77%. ^{1}H-NMR ($CDCl_3$): δ 6.76 (m, 4H, C_5H_3), 6.55 (m, 2H, C_5H_3), 6.36 (s, 10H, C_5H_5), 0.37 (s, 12H, Si–Me), 0.29 (s, 12H, Si–Me). MS (EI): m/z 515 (3, $[(Me_2SiOSiMe_2)_2(C_5H_3)_2ZrCl]^+$), 225 (25, $[CpZrCl_2]^+$), 73 (100, $[SiMe_3]^+$), 65 (35, $[C_5H_5]^+$).

3.6. *Preparation of* $(Me_2SiOSiMe_2)_2[(C_5H_3)ZrCl_2(C_5Me_4H)]_2$ (**9**)

The compound **9** was prepared using a similar method as described for **5** from $(Me_2SiOSiMe_2)_2(C_5H_4)_2$, n-BuLi and $C_5Me_4HZrCl_3$ as light yellow powder in 10% yield. M.p.: 300 °C (dec). Anal. Found: C, 44.86; H, 5.67. $C_{36}H_{56}Cl_2OSi_2Zr_2$ Calc.: C, 45.16; H, 5.86%. ^{1}H-NMR ($CDCl_3$): δ 6.52 (m, 4H, C_5H_3), 6.17 (m, 2H, C_5H_3), 5.80 (s, 2H, C_5Me_4H), 1.96 (s, 12H, C_5Me_4), 1.92 (d, 12H, C_5Me_4), 0.51 (s, 12H, Si–Me), 0.32 (s, 12H, Si–Me). MS (EI): m/z 515 (4, [(Me₂Si-

Table 4
Crystal data and refinement parameters for (**4**)

Empirical formula	$C_{25}H_{28}Cl_4GeZr_2$
Formula weight	725.304
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	15.1838(12)
b (Å)	13.5245(11)
c (Å)	14.6202(12)
β (°)	93.110(2)
V (Å^3)	2997.9(4)
Z	4
D_{calc} (g cm^{-3})	1.791
μ (mm^{-1})	2.229
Crystal size (mm)	$0.02\times0.08\times0.22$
Radiation (Å^3)	Mo–K$_\alpha$ (0.71073)
Data collection method	ω-2θ
Max. 2θ (°)	46.56
Total number of observations	4306
Number of unique data [$I>3\sigma(I)$]	4306
Final number of variables	273
R [$I>2\sigma(I)$]	$R=0.0493$, $wR=0.1386$
R (all data)	$R=0.0581$, $wR=0.11518$
Goodness-of-fit	0.697

$OSiMe_2)_2(C_5H_3)_2ZrCl]^+$), 281 (30, $[C_5Me_4HZrCl_2]^+$), 121 (100, $[C_5Me_4H]^+$), 73 (45, $[SiMe_3]^+$).

3.7. Crystallographic studies

Crystals of **4** suitable for X-ray diffraction were obtained from CH_2Cl_2 solution. All data were collected on Bruker Smart 1000 diffractometer with graphite monochromated Mo–K$_\alpha$ radiation ($\lambda=0.71073$ Å). All calculations were made using the SHELXS-97 program system. The structure was solved by direct method and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were not included in the refinement and calculations of structure factors. A summary of the crystallographic results is presented in Table 4.

3.8. Ethylene polymerization

Ethylene was introduced into a 250 ml glass reactor with a magnetic stirring bar at about 780 mmHg and 100 ml of toluene was added. When the temperature was increased to polymerization temperature, 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 methanol containing a small amount of hydrochloric acid. The polymer product was washed with ethanol and dried in vacuo at 60 °C.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 157599 for compound **4**. 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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