

# Novel dimethylsilylene isopropylidene doubly bridged metallocenes: Syntheses, identifications, and activities for olefin polymerizations

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## Abstract

Novel doubly bridged metallocene complexes  $(\text{Me}_2\text{Si})(\text{Me}_2\text{C})(\text{C}_5\text{H}_3)_2\text{MCl}_2$  ( $\text{M} = \text{Ti}(\mathbf{4})$ ,  $\text{Zr}(\mathbf{8})$ ), were synthesized by reactions of the dilithium salt of the corresponding ligand with  $\text{MCl}_4$ . When  $(\text{Me}_2\text{Si})(\text{Me}_2\text{C})(\text{C}_5\text{H}_3\text{SnMe}_3)_2$  compound was used instead of the corresponding dilithium salt, the complex  $\mathbf{4}$  was obtained in high yield. The structures were determined by X-ray analysis ( $\mathbf{4}$ : triclinic,  $P(-1)$ ,  $a = 9.063(2)$ ,  $b = 11.238(2)$ ,  $c = 8.956(2)$  Å,  $\alpha = 91.29(1)$ ,  $\beta = 118.56(1)$ ,  $\gamma = 77.66(2)^\circ$ ,  $Z = 2$ ;  $\mathbf{8}$ : monoclinic,  $P2_1/n$ ,  $a = 12.743(2)$ ,  $b = 9.149(3)$ ,  $c = 14.678(2)$  Å,  $\beta = 110.62(1)^\circ$ ,  $Z = 4$ ). As expected, each of them showed the smallest bite-angle ( $\mathbf{4}$ :  $120^\circ$ ;  $\mathbf{8}$ :  $114^\circ$ ) in the bis(cyclopentadienyl) type of Ti or Zr complexes. Singly bridged and doubly bridged metallocenes were synthesized to study the influence of the bite-angle on ethylene/1-octene copolymerization. Copolymerizations of ethylene/1-octene were carried out using these metallocenes in the presence of cocatalyst (methylaluminoxane (MAO) or  $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{triisobutylaluminium}$  ( $\text{Al}(i\text{-Bu})_3$ )). These complexes showed high 1-octene incorporation abilities.

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**Keywords:** Copolymerization; Metallocene catalyst

## 1. Introduction

LLDPE, which is composed of both ethylene and  $\alpha$ -olefin such as 1-butene, 1-hexene and 1-octene, is used for various purposes such as the modifier for thermoplastic general-purpose resin, material for miscellaneous-goods, containers, films, coating materials, bottle caps, large-sized tanks, autoparts, electric wire coverings, waterproofing sheets, engineering-works construction articles, home electrical machinery parts, sporting goods, etc. These materials are properly used depending on the molecular weights, the molecular weight distributions, the kind of comonomers, the amount of the comonomer and the kind of additives, etc. The physical properties of polymers are greatly influenced by the content of the comonomer. For example, if the

content of the comonomer was increased, crystallinity, melting point, and elasticity would be decreased and the elastic recovery nature would be raised.

In industry, the comonomer must be used efficiently, because comonomer is expensive compared to ethylene. The catalyst with high comonomer incorporation ability could give the polymer with a high comonomer content under the same concentration of the comonomer. Therefore, the use of the catalyst with high incorporation ability would be able to decrease the amount of comparatively expensive  $\alpha$ -olefin used.

As the catalysts with high incorporation ability, the constrained geometry catalyst (CGC) [1] and the CpTi (Cp = cyclopentadienyl) aryloxy complex [2] are known. In general, the metallocene complexes with two cyclopentadienyl ligands show higher incorporation ability than Ziegler-Natta catalysts, but lower ability than the CGC. One of the main reasons for this difference in the incorporation abilities is the difference in the coordination spaces on the catalysts, the so-called open space. That is, for increasing the incorporation ability of metallocene, it would be necessary to make an angle of

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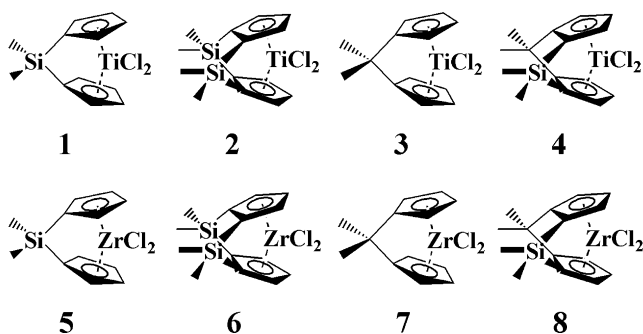


Fig. 1. The structures of the estimated complexes.

ligand–metal–ligand, the so-called bite-angle, narrow in order to extend the open space. The complex which has the narrowest bite-angle among the metallocene complexes was *i*PrCp<sub>2</sub>ZrCl<sub>2</sub> (7) (120°) [3]. We report herein the novel doubly bridged metallocene complexes, which have the narrowest bite-angles in bis(cyclopentadienyl) type of Ti (4) and Zr (8) complexes (Fig. 1).

## 2. Experimental

### 2.1. Materials

All reactions were carried out under exclusion of air by using the standard Schlenk equipment and oxygen-free solvents, which were purified by standard methods. MAO was purchased from Albemarle Corporation. Toluene was dried and degassed by bubbling pure nitrogen (>99.99%). Dimethylsilylene bridged complex (5) was synthesized by the method described by Petersen and co-workers [4]. Isopropylidene bridged complexes (3, 7) were synthesized by the methods described by Nifant'ev et al. [5]. The (dimethylsilylene)(dimethylsilylene) doubly bridged complexes (2, 6) were synthesized by the method described by Royo and co-workers [6]. The contents of 1-octene in the copolymers were measured on a Lambda 500 in C<sub>6</sub>D<sub>6</sub> solutions according to the literature [7].

### 2.2. Synthesis of (1,1'-dimethylsilylene)(2,2'-isopropylidene)bis(cyclopentadienyl)titanium dichloride ((Me<sub>2</sub>C)(Me<sub>2</sub>Si)Cp<sub>2</sub>TiCl<sub>2</sub>) (4) method A

(1,1'-Dimethylsilylene)(2,2'-isopropylidene)bis(cyclopentadiene) was synthesized according to the method reported in Ref. [8]. After (1,1'-dimethylsilylene)(2,2'-isopropylidene)bis(cyclopentadiene) (5.57 g, 24.2 mmol) was dissolved in 30 mL of hexane, *n*-butyllithium (48.8 mmol, 1.5 mol/L hexane solution) was dropwise added to this solution at –78 °C, and the mixture was stirred at room temperature for 8 h. Subsequently, after the solvent was removed, 1.00 g (4.16 mmol) of white solids of the dilithium salt was obtained by evaporation and washing with hexane (100 mL) and tetrahydrofuran (100 mL). This solid was suspended in tetrahydrofuran (50 mL), and to this suspension was added at room temperature tetrahydrofuran

solution (60 mL) of titanium trichloride tris(tetrahydrofuranate) (1.54 g, 4.16 mmol), and the mixture was stirred for 12 h. Silver chloride (11.08 g, 77 mmol) was added to this suspension, and the mixture was stirred at room temperature for 3 h. The solvent was removed and (1,1'-dimethylsilylene)(2,2'-isopropylidene)bis(cyclopentadienyl)titanium dichloride (35 mg) was obtained as red powder by extraction with ether followed by removing the solvent and hexane washing. (C<sub>15</sub>H<sub>18</sub>SiTiCl<sub>2</sub> (345.20) elemental analysis (%), found: C 52.32, H 5.35; calc.: C 52.19, H 5.26, <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>): δ 0.43 (3H, s, (CH<sub>3</sub>)<sub>2</sub>Si), 1.02 (3H, s, (CH<sub>3</sub>)<sub>2</sub>Si), 1.36 (3H, s, (CH<sub>3</sub>)<sub>2</sub>C), 2.18 (3H, s, (CH<sub>3</sub>)<sub>2</sub>C), 6.3–7.1 (6H, m, –CH–).

### 2.3. Synthesis of (1,1'-dimethylsilylene)(2,2'-isopropylidene)bis(cyclopentadienyl)titanium dichloride ((Me<sub>2</sub>C)(Me<sub>2</sub>Si)Cp<sub>2</sub>TiCl<sub>2</sub>) (4) method B

To (1,1'-dimethylsilylene)(2,2'-isopropylidene)bis(cyclopentadiene) (8.55 g, 37.4 mmol) placed in a 300 mL schlenk tube, dried diethyl ether (150 mL) was added under nitrogen atmosphere, and the mixture was cooled to –78 °C using dry ice-methanol bath. *n*-Butyl lithium (45.9 mL, 74.8 mmol, 1.63 mol/L hexane solution) was dropwise added to this solution, and the mixture was stirred at room temperature for 12 h. Subsequently, the reaction mixture was washed by hexane (100 mL), filtered, and the residual substance was dried under reduced pressure to obtain dilithium salt. The dilithium salt (8.90 g, 37.0 mmol) was suspended in 150 mL of dried tetrahydrofuran and cooled to –78 °C by dry ice-methanol bath. Trimethyltin chloride (14.8 g, 74.8 mmol) dissolved in 100 mL of dried tetrahydrofuran was dropwise added to this stirred suspension. The mixture was stirred under room temperature for further 4 h, and the solvent was removed under reduced pressure. The residue was extracted with 150 mL of dried hexane, and the solvent is removed under reduced pressure to give (1,1'-dimethylsilylene)(2,2'-isopropylidene)-4,4'-bis(trimethyltin)bis(cyclopentadiene) (15.07 g, 27.2 mmol). Yield, 73%. (<sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>): δ –0.07 (18H, s, (CH<sub>3</sub>)<sub>3</sub>Sn), –0.04 (6H, s, (CH<sub>3</sub>)<sub>2</sub>Si), 1.49 (6H, s, (CH<sub>3</sub>)<sub>2</sub>C), 5.28 (2H, br, –CH–), 6.3–6.8 (4H, m, –CH–).

(1,1'-Dimethylsilylene)(2,2'-isopropylidene)-4,4'-bis(trimethyltin)bis(cyclopentadiene) (6.15 g, 11.1 mmol) was placed in a 300 mL 3 necked round flask equipped with a flowing-back cooling pipe and dried toluene (100 mL) was added under nitrogen atmosphere. After the addition of 1.22 mL (11.1 mmol) of titanium tetrachloride in 50 mL of dried toluene to this solution under nitrogen atmosphere, this solution was heated to reflux for 4 h. Subsequently, the solvent was removed under reduced pressure and the residue was washed with 100 mL of dried hexane and then 100 mL of dried diethyl ether. The solid was dried in a vacuum and extracted with 200 mL of dried toluene. The filtrate was concentrated under reduced pressure and cooled to –20 °C. (1,1'-Dimethylsilylene)(2,2'-isopropylidene)bis(cyclopentadienyl)titanium dichloride (1.81 g, 5.24 mmol, yield 47.2%) was obtained as dark red crystals.

2.4. Synthesis of (1,1'-dimethylsilylene)(2,2'-isopropylidene)bis(cyclopentadienyl)zirconium dichloride ((Me<sub>2</sub>C)(Me<sub>2</sub>Si)Cp<sub>2</sub>ZrCl<sub>2</sub>) (**8**)

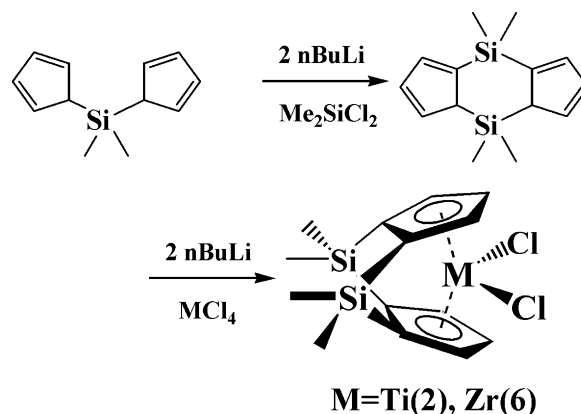
After (1,1'-dimethylsilylene)(2,2'-isopropylidene)bis(cyclopentadiene) (0.7 g, 3.2 mmol) was dissolved in 30 mL of hexane, *n*-butyllithium (6.48 mmol, 1.5 mol/L hexane solution) was dropwise added to this solution at  $-78^{\circ}\text{C}$ , and the mixture was stirred at room temperature for 5 h. Subsequently, after the solvent was removed, the residual white solid was dried under reduced pressure after washing by 20 mL of hexane, and then suspended in toluene (20 mL). Zirconium tetrachloride (0.8 g, 3.2 mmol) was added to the suspension, and the mixture was stirred at room temperature for 12 h. Then, the solvent was removed and 0.3 g of (1,1'-dimethylsilylene)(2,2'-isopropylidene)bis(cyclopentadienyl)zirconium dichloride was obtained as pale yellow crystals by recrystallization from dichloromethane/hexane solvent. (C<sub>15</sub>H<sub>18</sub>SiZrCl<sub>2</sub> (388.52) elemental analysis (%), found: C 46.50, H 4.81; calc.: C 46.37, H 4.67, <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>):  $\delta$  1.01 (3H, s, (CH<sub>3</sub>)<sub>2</sub>Si), 0.54 (3H, s, (CH<sub>3</sub>)<sub>2</sub>Si), 1.52 (3H, s, (CH<sub>3</sub>)<sub>2</sub>C), 2.16 (3H, s, (CH<sub>3</sub>)<sub>2</sub>C), 6.17 (2H, m, -CH-), 6.53 (2H, m, -CH-), 6.82 (2H, m, -CH-).

2.5. Crystal and molecular structures of complexes **4** and **8**

Crystals of **4** and **8** were obtained by recrystallization from toluene at  $-20^{\circ}\text{C}$  and sealed in thin-walled capillaries. The crystallographic and experimental data for both complexes are summarized in Table 1. The structures were solved by direct methods and refined by full-matrix least-squares techniques.

2.6. General procedure of copolymerization of ethylene and 1-octene

Toluene (360 mL), 1-octene (40 mL), MAO (0.67 mL, 1.0 mmol in toluene) and Al(*i*-Bu)<sub>3</sub> (1.0 mL, 1.0 mmol in toluene) were introduced into a 1 L autoclave under nitrogen atmosphere. The solution was heated to  $80^{\circ}\text{C}$ , and then ethylene (0.8 MPa) was introduced in it. Subsequently, the catalyst



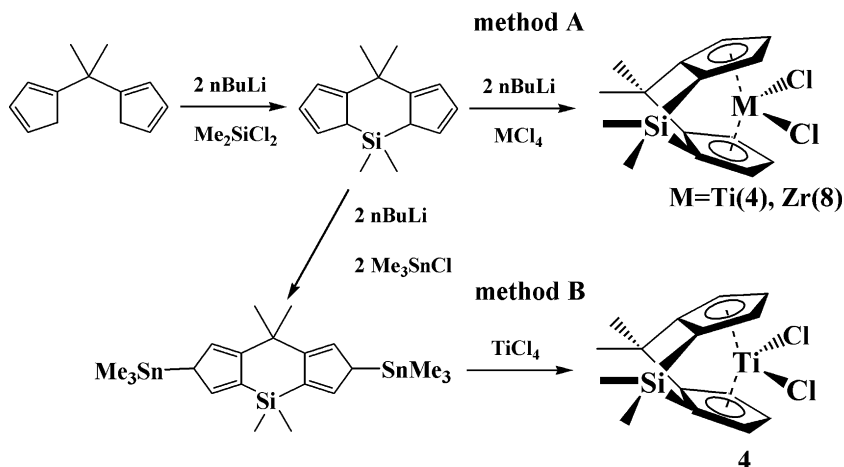
Scheme 1. The preparation of doubly silylene bridged metallocenes.

solution (1.0 mL, 1.0  $\mu\text{mol}$  in toluene) was thrown in and polymerization was started. After 60 min, methanol was added and polymerization was quenched. The obtained slurry was poured in hydrochloric acid/methanol mixture solution (1000 mL), and was stirred for 6 h. Obtained polymer was washed with methanol after filtration, and then dried for 8 h in a vacuum at  $80^{\circ}\text{C}$ .

### 3. Results and discussion

#### 3.1. Synthesis of the doubly bridged complexes

Some doubly bridged metallocene complexes of group 4 metals have been reported, i.e. (C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>3</sub>)<sub>2</sub>MCl<sub>2</sub> (M = Ti [9], Zr [9,10]), (Me<sub>2</sub>SiOSiMe<sub>2</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>3</sub>)<sub>2</sub>MCl<sub>2</sub> (M = Zr, Hf) [11]. The (dimethylsilylene)(dimethylsilylene) doubly bridged complexes (**2**, **6**) were synthesized by reacting lithium salt of the ligand with metal chloride (MCl<sub>4</sub>) as shown in Scheme 1 [6]. In our study, the new (dimethylsilylene)(isopropylidene) doubly bridged complexes (**4**, **8**) were synthesized via a similar method (method A in Scheme 2). The titanium complex (**4**) was obtained in very low yield (2.4%) with the method A. However, when the bis(trimethyltin) compound was used instead of the corresponding dilithium salt under the reflux condition, the complex (**4**) was obtained in high yield (47.2%, method B in



Scheme 2. The preparation of (Me<sub>2</sub>Si)(Me<sub>2</sub>C) bridged metallocenes.

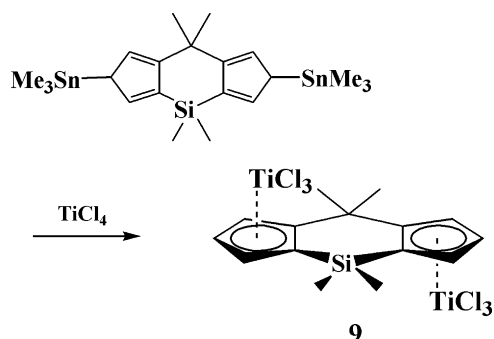
Table 1  
Crystallographic and experimental data for complexes **4** and **8**

|   | <b>4</b>  | <b>8</b>  |
|---|---|---|
| Formula   | C <sub>15</sub> H <sub>18</sub> SiTiCl <sub>2</sub> | C <sub>15</sub> H <sub>18</sub> SiZrCl <sub>2</sub> |
| Formula weight (g mol <sup>-1</sup> )                     | 345.20  | 388.52  |
| Crystal color; form                                       | Black; prism  | Yellow, prism                                       |
| Crystal system  | Triclinic   | monoclinic  |
| Space group   | <i>P</i> (-1) (#2)                                  | <i>P</i> 2 <sub>1</sub> / <i>n</i> (#14)            |
| Lattice parameters:                                       |   |   |
| <i>a</i> (Å)  | 9.063(2)  | 12.743(2)   |
| <i>b</i> (Å)  | 11.238(2)   | 9.149(3)  |
| <i>c</i> (Å)  | 8.956(2)  | 14.678(2)   |
| $\alpha$ (°)  | 91.29(1)  |   |
| $\beta$ (°)   | 118.56(1)   | 110.62(1)   |
| $\gamma$ (°)  | 77.66(2)  |   |
| <i>V</i> (Å <sup>3</sup> )                                | 779.3(3)  | 1601.5(7)   |
| <i>Z</i>  | 2   | 4   |
| <i>D</i> <sub>calcd.</sub> (g cm <sup>-3</sup> )          | 1.471   | 1.611   |
| <i>F</i> <sub>000</sub>                                   | 356   | 784   |
| $\mu$ (cm <sup>-1</sup> )                                 | 9.48  | 10.70   |
| Temperature (°C)  | 23  | 23  |
| Diffractometer  | Rigaku AFC5R  | Rigaku AFC5R  |
| Radiation   | Mo K $\alpha$ ( $\lambda$ = 0.71069 Å)              | Mo K $\alpha$ ( $\lambda$ = 0.71069 Å)              |
| Attenuators   | Ni foil (factors: 3.5, 12.3, 43.8)                  | Ni foil (factors: 3.5, 12.3, 43.8)                  |
| Scan-type, scan width                                     | $w - 2\theta$ , (1.73 + 0.30 tan $\theta$ )°        | $w - 2\theta$ , (1.84 + 0.30 tan $\theta$ )°        |
| $2\theta_{\max}$  | 55.0°   | 55.0°   |
| No. of reflections measured                               |   |   |
| Total   | 3801  | 4088  |
| Unique  | 3574 ( <i>R</i> <sub>int</sub> = 0.037)             | 3921 ( <i>R</i> <sub>int</sub> = 0.017)             |
| No. observations ( <i>I</i> > 1.00 $\sigma$ ( <i>I</i> )) | 2800  | 3189  |
| No. variables   | 227   | 227   |
| Residuals: <i>R</i> ; <i>R</i> <sub>w</sub>               | 0.044; 0.048  | 0.028; 0.037  |
| Goodness of fit indicator                                 | 1.79  | 1.67  |

**Scheme 2**). The reaction of the bis(trimethyltin) compound and TiCl<sub>4</sub> at room temperature mainly produced a bimetallic complex (**9**) (**Scheme 3**, <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>):  $\delta$  0.73 (6H, s, (CH<sub>3</sub>)<sub>2</sub>Si), 1.83 (6H, s, (CH<sub>3</sub>)<sub>2</sub>C), 7.01–7.34 (6H, m, –CH–)). When the method B was applied to the synthesis of a (dimethylsilylene)(dimethylsilylene) doubly bridged complex, the complex **2** was also obtained in high yield.

### 3.2. X-ray structure of the complexes

For the complexes obtained here (**4** and **8**), X-ray crystal structure analyses were performed. The resulting structural



Scheme 3. The reaction of (Me<sub>3</sub>Sn) compound and TiCl<sub>4</sub> at room temperature.

models are represented in **Figs. 2 and 3**. These systems are characterized by a pseudotetrahedral ligand arrangement about the metal. Ti–Cp(*centr.*) distance is 2.052 Å, and is equal to that for the typical titanocenes (**1**: 2.075, **2**: 2.070, **3**: 2.056 Å **Table 2**). However, the bite-angle of this complex is the narrowest 119.7° in titanocenes. Zr–Cp(*centr.*) distance is 2.197 Å, and is equal to that for the typical zirconocenes (**5**: 2.197, **6**: 2.199, **7**: 2.192 Å).

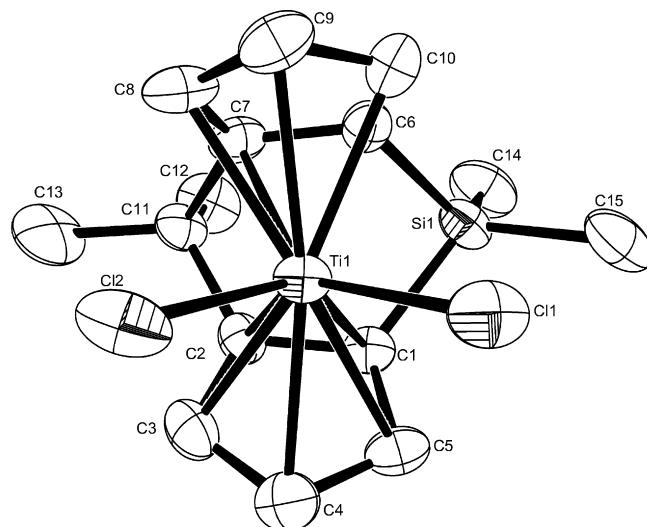


Fig. 2. X-ray structure of (Me<sub>2</sub>C)(Me<sub>2</sub>Si)Cp<sub>2</sub>TiCl<sub>2</sub> (**4**).

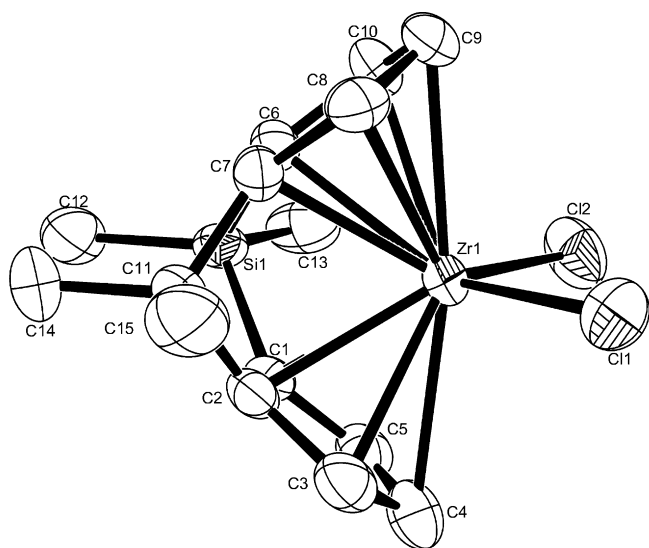


Fig. 3. X-ray structure of  $(\text{Me}_2\text{C})(\text{Me}_2\text{Si})\text{Cp}_2\text{ZrCl}_2$  (**8**).

However, the bite-angle of this complex is the narrowest  $113.8^\circ$  in zirconocenes just like the titanium complex **4**. That is, the complex **8** has the largest open space among these metallocenes.

The difference between the shortest Zr–C(Cp) distance and the longest one in **8** are  $0.186 \text{ \AA}$  (**6**:  $0.175$ , **7**:  $0.118 \text{ \AA}$ ). The bent angle between the  $\text{sp}^2$  plane of C2 and C11–C2 bond in **8** is  $16.2^\circ$  ( $\text{Me}_2\text{CCp}_2\text{ZrCl}_2$  (**7**):  $15.8^\circ$ ). The bent angle between the  $\text{sp}^2$  plane of C1 and Si1–C1 bond in **8** is  $21^\circ$  ( $(\text{Me}_2\text{Si})_2\text{Cp}_2\text{ZrCl}_2$  (**6**):  $20^\circ$ ). These show that **8** is slightly distorted than the other zirconocenes. On the other hand, the difference between the shortest Ti–C(Cp) distance and the longest one in **4** are  $0.170 \text{ \AA}$

(**2**:  $0.159$ , **3**:  $0.125 \text{ \AA}$ ). The bent angle between the  $\text{sp}^2$  plane of C2 and C11–C2 bond in **4** is  $9.9^\circ$  ( $\text{Me}_2\text{CCp}_2\text{TiCl}_2$  (**3**):  $9.9^\circ$ ). The bent angle between the  $\text{sp}^2$  plane of C1 and Si1–C1 bond in **4** is  $14^\circ$  ( $(\text{Me}_2\text{Si})_2\text{Cp}_2\text{TiCl}_2$  (**2**):  $13^\circ$ ). It would be easy for the complex **4** to decompose compared with the other titanocenes, but the Ti complex **4** would be more stable compared with the zirconocene **8**.

### 3.3. Polymerization results

Previously the catalytic behavior of dimethylsilylene doubly bridged zirconocenes in the stereospecific polymerization of propylene was studied [12]. We carried out studies on the copolymerization of ethylene with 1-octene using the zirconocene complexes. The use of complexes with a narrower bite-angle tends to increase the content of 1-octene (Tables 3 and 4). However, the complex **8**, which has the narrowest bite-angle, leads to lower contents of 1-octene than **7**. The wide molecular weight distributions ( $M_w/M_n$ ) of runs no. **4** and **8** showed that the catalyst might have the multiple active species. Since the bridging moieties in the complex **8** are distorted, a part of the catalyst systems of **8** could be decomposed and the decomposed catalysts might give the copolymer with lower 1-octene contents than the expected content. Moreover, the incorporation ability was influenced not only by the bite-angles of complexes but also by a kind of cocatalyst. In the copolymers made by borate cocatalyst, 1-octene contents were less than in the copolymers made by MAO (Tables 3 and 4). It is known that the F atom of pentafluorophenyl group in the borate complex coordinates to the Zr cation [13]. Therefore, the borate which existed near the active

Table 2  
Structural data for metallocenes with various bridging ligands

| Complex  | Bite-angle ( $^\circ$ ) | Cp( <i>centr.</i> )–M ( $\text{\AA}$ ) | M–Cl ( $\text{\AA}$ ) | $\angle(\text{Cl–M–Cl})$ ( $^\circ$ ) | Reference |
|--|-------------------------|--|-----------------------|---------------------------------------|-----------|
| $\text{Me}_2\text{SiCp}_2\text{TiCl}_2$ ( <b>1</b> )                               | 128.7                   | 2.075                                  | 2.356                 | 95.8                                  | [4]       |
| $(\text{Me}_2\text{Si})_2\text{Cp}_2\text{TiCl}_2$ ( <b>2</b> )                    | 126.0                   | 2.070                                  | 2.344                 | 96.7                                  | [6]       |
| $\text{Me}_2\text{CCp}_2\text{TiCl}_2$ ( <b>3</b> )                                | 121.5                   | 2.056                                  | 2.340                 | 98.0                                  | [3]       |
| $(\text{Me}_2\text{C})(\text{Me}_2\text{Si})\text{Cp}_2\text{TiCl}_2$ ( <b>4</b> ) | 119.7                   | 2.052                                  | 2.339                 | 96.3                                  | This work |
| $\text{Me}_2\text{SiCp}_2\text{ZrCl}_2$ ( <b>5</b> )                               | 125.4                   | 2.197                                  | 2.435                 | 98.0                                  | [4]       |
| $(\text{Me}_2\text{Si})_2\text{Cp}_2\text{ZrCl}_2$ ( <b>6</b> )                    | 120.6                   | 2.199                                  | 2.428                 | 99.6                                  | [6]       |
| $\text{Me}_2\text{CCp}_2\text{ZrCl}_2$ ( <b>7</b> )                                | 116.6                   | 2.192                                  | 2.434                 | 100.1                                 | [3]       |
| $(\text{Me}_2\text{C})(\text{Me}_2\text{Si})\text{Cp}_2\text{ZrCl}_2$ ( <b>8</b> ) | 113.8                   | 2.197                                  | 2.432                 | 98.5                                  | This work |

Cp(*centr.*) denotes the *centroid* of the cyclopentadienyl ring.

Table 3  
Ethylene/1-octene copolymerization using zirconium complexes with borate as cocatalyst

| Run no. | Catalyst  | Bite-angle ( $^\circ$ ) | Time (min) | Yield (g) | Activity <sup>a</sup> | C8 content <sup>b</sup> (mol%) | $T_m$ <sup>c</sup> ( $^\circ\text{C}$ ) | $M_w$ <sup>d</sup> | $M_w/M_n$ <sup>d</sup> |
|---------|---|-------------------------|------------|-----------|-----------------------|--------------------------------|---|--------------------|------------------------|
| 1       | $\text{Me}_2\text{SiCp}_2\text{ZrCl}_2$ ( <b>5</b> )  | 125.4                   | 10         | 28.3      | 169.8                 | 2.9                            | 115.9                                   | 21,000             | 3.2                    |
| 2       | $(\text{Me}_2\text{Si})_2\text{Cp}_2\text{ZrCl}_2$ ( <b>6</b> )                                 | 120.6                   | 60         | 29.5      | 29.5                  | 4.4                            | 115.6                                   | 43,000             | 2.9                    |
| 3       | $\text{Me}_2\text{CCp}_2\text{ZrCl}_2$ ( <b>7</b> )   | 116.6                   | 60         | 32.1      | 32.1                  | 6.2                            | 91.3                                    | 3,500              | 2.9                    |
| 4       | $(\text{Me}_2\text{C})(\text{Me}_2\text{Si})\text{Cp}_2\text{ZrCl}_2$ ( <b>8</b> ) <sup>e</sup> | 113.8                   | 60         | 45.7      | 45.7                  | 5.8                            | 108.7                                   | 52,000             | 6.1                    |

Polymerization conditions: catalyst,  $1.0 \mu\text{mol}$ ;  $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ ,  $1.0 \mu\text{mol}$ ;  $\text{Al}(i\text{-Bu})_3$ ,  $1.0 \text{ mmol}$ ; 1-octene, (C8)  $40 \text{ mL}$ ; ethylene,  $0.8 \text{ MPa}$ ; toluene,  $360 \text{ mL}$ ;  $80^\circ\text{C}$ .

<sup>a</sup> Activity  $\times 10^3 \text{ kg/molZr hr}$ .

<sup>b</sup> C8 contents were determined by  $^{13}\text{C}$  NMR analysis [7].

<sup>c</sup>  $T_m$  melting temperature.

<sup>d</sup>  $M_w$  and  $M_w/M_n$ , weight average molecular weight and molecular weight distribution calculated from GPC measurement.

<sup>e</sup> Analytical data were estimated for whole copolymer mixture.

Table 4

Ethylene/1-octene copolymerization using zirconium complexes with MAO as cocatalyst

| Run no. | Catalyst   | Bite-angle (°) | Time (min) | Yield (g) | Activity <sup>a</sup> | C8 content (mol%) | T <sub>m</sub> (°C) | M <sub>w</sub> | M <sub>w</sub> /M <sub>n</sub> |
|---------|--|----------------|------------|-----------|-----------------------|-------------------|---------------------|----------------|--------------------------------|
| 5       | Me <sub>2</sub> SiCp <sub>2</sub> ZrCl <sub>2</sub> ( <b>5</b> )                                   | 125.4          | 10         | 69.4      | 416.4                 | 3.7               | 113.0               | 13,200         | 3.3                            |
| 6       | (Me <sub>2</sub> Si) <sub>2</sub> Cp <sub>2</sub> ZrCl <sub>2</sub> ( <b>6</b> )                   | 120.6          | 60         | 27.3      | 27.3                  | 4.8               | 115.5               | 47,000         | 3.3                            |
| 7       | Me <sub>2</sub> CCp <sub>2</sub> ZrCl <sub>2</sub> ( <b>7</b> )                                    | 116.6          | 60         | 41.5      | 41.5                  | 9.0               | 71.1                | 2,100          | 2.4                            |
| 8       | (Me <sub>2</sub> C)(Me <sub>2</sub> Si)Cp <sub>2</sub> ZrCl <sub>2</sub> ( <b>8</b> ) <sup>b</sup> | 113.8          | 60         | 15.6      | 15.6                  | 7.3               | 110.0               | 52,000         | 7.5                            |

Polymerization conditions: catalyst, 1.0 μmol; MAO, 1.0 mmol; 1-octene (C8), 40 mL; ethylene, 0.8 MPa; toluene, 360 mL; 80 °C.

<sup>a</sup> Activity × 10<sup>3</sup> kg/molZr hr.<sup>b</sup> Analytical data were estimated for whole copolymer mixture.

Table 5

Ethylene/1-octene copolymerization using titanium complexes with borate as cocatalyst

| Run no. | Catalyst  | Bite-angle (°) | Time (min) | Yield (g) | Activity <sup>a</sup> | C8 content (mol%) | T <sub>m</sub> (°C) | M <sub>w</sub> | M <sub>w</sub> /M <sub>n</sub> |
|---------|---|----------------|------------|-----------|-----------------------|-------------------|---------------------|----------------|--------------------------------|
| 9       | Me <sub>2</sub> CCp <sub>2</sub> TiCl <sub>2</sub> ( <b>3</b> )                       | 122            | 60         | 12.7      | 12.7                  | 2.47              | 106                 | 198,000        | 2.0                            |
| 10      | (Me <sub>2</sub> C)(Me <sub>2</sub> Si)Cp <sub>2</sub> TiCl <sub>2</sub> ( <b>4</b> ) | 120            | 60         | 4.3       | 4.3                   | 10.0              | 67                  | 40,000         | 2.2                            |

Polymerization conditions: catalyst, 1.0 μmol; [PhNMe<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], 1.0 μmol; Al(*i*-Bu)<sub>3</sub>, 1.0 mmol; 1-octene (C8), 40 mL; ethylene, 0.8 MPa; toluene, 360 mL; 80 °C.<sup>a</sup> Activity × 10<sup>3</sup> kg/molTi hr.

Table 6

Ethylene/1-octene copolymerization using titanium complexes with MAO as cocatalyst

| Run no. | Catalyst  | Bite-angle (°) | Time (min) | Yield (g) | Activity <sup>a</sup> | C8 content (mol%) | T <sub>m</sub> (°C) | M <sub>w</sub> | M <sub>w</sub> /M <sub>n</sub> |
|---------|---|----------------|------------|-----------|-----------------------|-------------------|---------------------|----------------|--------------------------------|
| 11      | (Me <sub>2</sub> Si) <sub>2</sub> Cp <sub>2</sub> TiCl <sub>2</sub> ( <b>2</b> )      | 126            | 60         | 0.7       | 0.7                   | 14.9              | 10                  | 27,400         | 2.9                            |
| 12      | Me <sub>2</sub> CCp <sub>2</sub> TiCl <sub>2</sub> ( <b>3</b> )                       | 122            | 60         | 39.8      | 39.8                  | 2.7               | 70                  | 175,000        | 2.0                            |
| 13      | (Me <sub>2</sub> C)(Me <sub>2</sub> Si)Cp <sub>2</sub> TiCl <sub>2</sub> ( <b>4</b> ) | 120            | 60         | 9.6       | 9.6                   | 9.1               | 60                  | 144,000        | 2.2                            |

Polymerization conditions; catalyst 1.0 μmol, MAO 1.0 mmol, 1-octene (C8) 40 mL, ethylene 0.8 MPa, toluene 360 mL, 80 °C.

<sup>a</sup> Activity × 10<sup>3</sup> kg/molTi hr.

species would disturb the coordination of 1-octene comonomer. The low 1-octene content in the copolymer obtained with the borate cocatalyst might be due to stronger interaction between the ionized metal and the borate compared with MAO.

The results of titanium complexes are shown in Tables 5 and 6. The titanium complexes with the isopropylidene bridging ligand (**3**), unlike the zirconium complexes, had very low 1-octene incorporation ability. Moreover, the complex **2** with a large bite-angle, which meant a narrow open space, showed higher incorporation ability than either the complex **3** or the complex **4**. It is difficult to explain this phenomenon by the steric factor. Hence, it is thought that the incorporation ability of titanium complexes was due to the electronic influence of the bridging moieties in the ligands rather than a steric effect.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcaa.2007.02.020.

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