

# Synthesis and polymerization catalytic properties of aryl-substituted tetramethylcyclopentadienyl zirconocenes

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## Abstract

A series of aryl-substituted tetramethylcyclopentadienyl zirconocenes ( $C_5Me_4C_6H_4X-4$ )Cp'MCl<sub>2</sub> [Cp' = C<sub>5</sub>H<sub>5</sub>, X = H (**5**), Me (**6**), Cl (**7**) or OMe (**8**); Cp' = Ind, X = H (**9**), Me (**10**) or Cl (**11**); Cp' = 2-Ph-Ind, X = H (**12**)] and ( $C_5Me_4C_6H_4X-4$ )<sub>2</sub>ZrCl<sub>2</sub> [X = H (**13**), Me (**14**), Cl (**15**)], with different substituents at the 4-position of phenyl, have been prepared by the reaction of the corresponding ligands ( $C_5Me_4HC_6H_4X-4$ ) [X = H (**1**), Me (**2**), Cl (**3**) or OMe (**4**)] with *n*-BuLi, ZrCl<sub>4</sub> and Cp'Li or with *n*-BuLi and ZrCl<sub>4</sub>. Ethylene polymerization with these complexes in combination with MAO has been studied. The electron donor (Me) at the 4-position of phenyl led to an increase in catalytic activity while the electron-withdrawing group (Cl) and the strong  $\pi$  donor (OMe) led to its decrease. Complexes **5**, **6**, **9** and **10** exhibited very high activities, but **13–15** showed much lower activities due to the bulky steric effect. The molecular structure of **5** has been determined by X-ray diffraction. The relationship between structures of catalysts and catalytic activities were discussed. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Zirconocene; Metallocene; Ethylene polymerization; Polyethylene; Electronic effect

## 1. Introduction

Metallocene catalysts have been one of the most widely studied topics for more than 20 years [1–7]. Various types of metallocene complexes have been studied as olefin polymerization catalysts. It was found that the unbridged species generally show higher

catalytic activity than the bridged ones for group 4 metallocenes [8]. The steric and electronic effects of cyclopentadienyl ring substituents greatly influence catalytic activity [9]. Thus the variation of cyclopentadienyl ligands is the first strategy for efficient catalysts. Because of the special electronic and steric effect of the phenyl group [10–17], in this study, a series of aryl-substituted tetramethylcyclopentadienyl zirconocenes, with different substituents at the 4-position of phenyl, has been synthesized. Ethylene polymerization was investigated with these complexes in combination with MAO in order to examine the electronic effect of the substituents of phenyl on catalytic activities.

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## 2. Experimental

### 2.1. General procedures

All operations were carried out under an argon atmosphere using the standard Schlenk techniques. Diethyl ether, toluene and DME were distilled from sodium/benzophenone ketyl under argon prior to use.  $^1\text{H-NMR}$  spectra were recorded on a Bruker AC-200, and MS spectra on a VG-7070E HF spectrometer. Elemental analyses were made on a CHN Corder MF-3 spectrometer. The molecular structure of **5** was determined by X-ray diffraction on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Polymerization grade ethylene (Yanshan Petrochem, China) was used without further purification. MAO was purchased from Aldrich. The molecular weight of the polyethylene was measured in decalin solution using an AVS 300 viscometer at  $135 \pm 0.1 \text{ }^\circ\text{C}$ . 2,3,4,5-Tetramethylcyclopent-2-enone [18] and 2-phenylindene [11] were prepared according to literature.

### 2.2. Preparation of $\text{C}_5\text{Me}_4\text{HPh}$ (**1**)

To 45.7 ml (2.19 M, 0.10 mol) of *n*-BuLi/hexane solution and 100 ml of diethyl ether, 15.7 g (0.10 mol) of bromobenzene in 100 ml of diethyl ether was added dropwise at  $0 \text{ }^\circ\text{C}$ . After heating under reflux for 1 h, the mixture was cooled down to  $0 \text{ }^\circ\text{C}$  and 13.8 g (0.10 mol) of 2,3,4,5-tetramethylcyclopent-2-enone was added. After stirring overnight at room temperature (RT), the mixture was hydrolyzed. The organic phase was washed with 20 ml of hydrochloric acid and dried with  $\text{Na}_2\text{CO}_3$ . After removal of the solvents, the residue was distilled at  $88\text{--}92 \text{ }^\circ\text{C}/0.3 \text{ mmHg}$  to give 15.5 g (78%) of **1** as yellow liquid.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.32–7.06 (m, 5H, Ph-H), 3.24–3.11 (m, 1H,  $\text{C}_5\text{Me}_4\text{H}$ ), 2.00 (s, 3H, Me), 1.91 (s, 3H, Me), 1.85 (s, 3H, Me), 0.95, 0.91 ppm (s, s, 3H, Me).

### 2.3. Preparation of $\text{C}_5\text{Me}_4\text{HC}_6\text{H}_4\text{Me-4}$ (**2**) and $\text{C}_5\text{Me}_4\text{HC}_6\text{H}_4\text{Cl-4}$ (**3**)

Complexes **2** and **3** were prepared from 4-bromotoluene or 4-bromochlorobenzene with *n*-BuLi and

2,3,4,5-tetramethylcyclopent-2-enone using a method similar to that as described for **1**. **2**: b.p. =  $100\text{--}104 \text{ }^\circ\text{C}/0.4 \text{ mmHg}$ , yellow liquid (71%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.32–7.06 (m, 4H, Ph-H), 3.24–3.11 (m, 1H,  $\text{C}_5\text{Me}_4\text{H}$ ), 2.34 (s, 3H, Ph-Me), 2.00 (s, 3H, Me), 1.91 (s, 3H, Me), 1.85 (s, 3H, Me), 0.95, 0.91 ppm (s, s, 3H, Me). **3**: b.p. =  $111\text{--}113 \text{ }^\circ\text{C}/0.6 \text{ mmHg}$ , yellow waxy solid (82%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.29 (d,  $J = 8.4 \text{ Hz}$ , 2H, Ph-H), 7.13 (d,  $J = 8.4 \text{ Hz}$ , 2H, Ph-H), 3.24–3.04 (m, 1H,  $\text{C}_5\text{Me}_4\text{H}$ ), 1.98 (s, 3H, Me), 1.90 (s, 3H, Me), 1.84 (s, 3H, Me), 0.93, 0.90 ppm (s, s, 3H, Me). Anal. found: C, 77.17%; H, 7.13%.  $\text{C}_{15}\text{H}_{17}\text{Cl}$  (calc.): C, 77.41%; H, 7.36%.

### 2.4. Preparation of $\text{C}_5\text{Me}_4\text{HC}_6\text{H}_4\text{OMe-4}$ (**4**)

To 1.2 g (0.05 mol) of magnesium turnings and 20 ml of diethyl ether, 9.35 g (0.05 mol) of 4-bromoanisole in 40 ml of diethyl ether was added with vigorous stirring. After stirring at RT for 1 h, the mixture was cooled down to  $0 \text{ }^\circ\text{C}$  and 6.9 g (0.05 mol) of 2,3,4,5-tetramethylcyclopent-2-enone was added. After stirring overnight at RT, the mixture was hydrolyzed. The organic phase was washed with 20 ml of hydrochloric acid and dried with  $\text{Na}_2\text{CO}_3$ . After removal of the solvents, the residue was distilled at  $126\text{--}130 \text{ }^\circ\text{C}/0.7 \text{ mmHg}$  to give 7.0 g (61%) of **4** as light yellow liquid.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.21–7.00 (m, 2H, Ph-H), 7.00–6.76 (m, 2H, Ph-H), 3.80 (s, 3H, OMe), 3.21–3.04 (m, 1H,  $\text{C}_5\text{Me}_4\text{H}$ ), 1.98 (s, 3H, Me), 1.90 (s, 3H, Me), 1.84 (s, 3H, Me), 0.94, 0.90 ppm (s, s, 3H, Me).

### 2.5. Preparation of $(\text{C}_5\text{Me}_4\text{Ph})\text{CpZrCl}_2$ (**5**)

To a solution of 1.98 g (10 mmol) of **1** in 40 ml of toluene, 4.57 ml (2.19 M, 10 mmol) of *n*-BuLi/hexane solution was added dropwise. After stirring at RT overnight, 2.33 g (10 mmol) of  $\text{ZrCl}_4$  was added to the resulting suspension. After heating under reflux for 24 h, 10 mmol of CpLi (prepared from cyclopentadiene and *n*-BuLi) was added to the resulting red suspension. The mixture was refluxed for 24 h. After removal of solvents, 40 ml of  $\text{CH}_2\text{Cl}_2$  and 10 ml of HCl (6N) was added to the residue. After separation, the organic phase was washed with water and dried with  $\text{Na}_2\text{SO}_4$ . Upon concentration and addition of hexane, 2.3 g (52%) of **5** was obtained as yellow

crystals; m.p.: 225–227 °C. Anal. found: C, 56.33%; H, 5.37%.  $C_{20}H_{22}Cl_2Zr$  (calc.): C, 56.59%; H, 5.22%.  $^1H$ -NMR ( $CDCl_3$ ):  $\delta$  7.49–7.11 (m, 5H, Ph-H), 6.14 (s, 5H,  $C_5H_5$ ), 2.22 (s, 6H, Me), 2.05 ppm (s, 6H, Me). MS (EI):  $m/z$  422 (22,  $M^+$ ), 386 (14,  $M^+ - HCl$ ), 357 (100,  $M^+ - C_5H_5$ ), 321 (21,  $M^+ - HCl - C_5H_5$ ), 225 (24,  $M^+ - C_5Me_4Ph$ ), 197 (11,  $[C_5Me_4Ph]^+$ ), 165 (49,  $[C_5MeZr]^+$ ), 91 (16,  $[C_7H_7]^+$ ), 77 (12,  $[C_6H_5]^+$ ), 65 (8,  $[C_5H_5]^+$ ).

#### 2.6. Preparation of $(C_5Me_4C_6H_4X-4)CpZrCl_2$ [X = Me (**6**), Cl (**7**), OMe (**8**)]

Complexes **6–8** were synthesized from the corresponding ligands **2–4**, *n*-BuLi,  $ZrCl_4$  and CpLi using a method similar to that as described for **5**.

**6**: Light yellow solid (77%); m.p.: 162–164 °C. Anal. found: C, 57.24%; H, 5.21%.  $C_{21}H_{24}Cl_2Zr$  (calc.): C, 57.51%; H, 5.52%.  $^1H$ -NMR ( $CDCl_3$ ):  $\delta$  7.21 (d,  $J = 8.0$  Hz, 2H, Ph-H), 7.02 (d,  $J = 8.0$  Hz, 2H, Ph-H), 6.13 (s, 5H,  $C_5H_5$ ), 2.38 (s, 3H, Ph-Me), 2.22 (s, 6H, Me), 2.04 ppm (s, 6H, Me). MS (EI):  $m/z$  436 (20,  $M^+$ ), 400 (8,  $M^+ - HCl$ ), 371 (100,  $M^+ - C_5H_5$ ), 335 (21,  $M^+ - HCl - C_5H_5$ ), 225 (10,  $M^+ - C_5Me_4C_6H_4Me$ ), 211 (16,  $M^+ - CpZrCl_2$ ), 196 (15,  $[C_5Me_4C_6H_4]^+$ ), 179 (29,  $[C_5MeCH_2Zr]^+$ ), 165 (57,  $[C_5MeZr]^+$ ), 91 (12,  $[C_7H_7]^+$ ), 65 (10,  $[C_5H_5]^+$ ).

**7**: White crystals (71%); m.p.: 135–137 °C. Anal. found: C, 52.14%; H, 4.48%.  $C_{20}H_{21}Cl_3Zr$  (calc.): C, 52.34%; H, 4.61%.  $^1H$ -NMR ( $CDCl_3$ ):  $\delta$  7.37 (d,  $J = 8.4$  Hz, 2H, Ph-H), 7.08 (d,  $J = 8.4$  Hz, 2H, Ph-H), 6.15 (s, 5H,  $C_5H_5$ ), 2.19 (s, 6H, Me), 2.04 ppm (s, 6H, Me). MS (EI):  $m/z$  456 (7,  $M^+$ ), 420 (4,  $M^+ - HCl$ ), 391 (20,  $M^+ - C_5H_5$ ), 355 (4,  $M^+ - HCl - C_5H_5$ ), 225 (81,  $M^+ - C_5Me_4C_6H_4Cl$ ), 165 (100,  $[C_5MeZr]^+$ ), 65 (19,  $[C_5H_5]^+$ ).

**8**: Yellow crystals (46%); m.p.: 162–164 °C. Anal. found: C, 55.33%; H, 4.72%.  $C_{21}H_{24}Cl_2OZr$  (calc.): C, 55.49%; H, 5.32%.  $^1H$ -NMR ( $CDCl_3$ ):  $\delta$  7.07 (d,  $J = 8.7$  Hz, 2H, Ph-H), 6.93 (d,  $J = 8.7$  Hz, 2H, Ph-H), 6.13 (s, 5H,  $C_5H_5$ ), 3.83 (s, 3H, OMe), 2.21 (s, 6H, Me), 2.03 ppm (s, 6H, Me). MS (EI):  $m/z$  452 (25,  $M^+$ ), 416 (6,  $M^+ - HCl$ ), 387 (96,  $M^+ - C_5H_5$ ), 389 (100,  $M^+ + 2 - C_5H_5$ ), 351 (18,  $M^+ - HCl - C_5H_5$ ), 225 (39,  $M^+ - C_5H_5Me_4C_6H_4OMe$ ), 179 (23,  $[C_5MeCH_2Zr]^+$ ), 165 (62,  $[C_5MeZr]^+$ ), 91 (15,  $[C_7H_7]^+$ ), 65 (11,  $[C_5H_5]^+$ ).

#### 2.7. Preparation of $(C_5Me_4C_6H_4X-4)(Ind)ZrCl_2$ [X = H (**9**), Me (**10**), Cl (**11**)]

Complexes **9–11** were synthesized from the corresponding ligands **1–3**, *n*-BuLi,  $ZrCl_4$  and IndLi using a method similar to that as described for **5**.

**9**: Yellow crystals (84%); m.p.: 280–281 °C. Anal. found: C, 60.44%; H, 5.04%.  $C_{24}H_{24}Cl_2Zr$  (calc.): C, 60.74%; H, 5.10%.  $^1H$ -NMR ( $CDCl_3$ ):  $\delta$  7.64–7.16 (m, 9H, Ar-H), 6.09 (d, 2H, Ind-H), 5.87 (t, 1H, Ind-H), 2.26 (s, 6H, Me), 2.00 ppm (s, 6H, Me). MS (EI):  $m/z$  472 (4,  $M^+$ ), 357 (99,  $M^+ - Ind$ ), 359 (100,  $M^+ + 2 - Ind$ ), 321 (27,  $M^+ - HCl - Ind$ ), 275 (19,  $[IndZrCl_2]^+$ ), 197 (6,  $[C_5Me_4Ph]^+$ ), 165 (31,  $[C_5MeZr]^+$ ), 115 (67,  $[Ind]^+$ ), 77 (8,  $[C_6H_5]^+$ ).

**10**: Yellow crystals (79%); m.p.: 209–210 °C. Anal. found: C, 61.60%; H, 5.23%.  $C_{25}H_{26}Cl_2Zr$  (calc.): C, 61.45%; H, 5.36%.  $^1H$ -NMR ( $CDCl_3$ ):  $\delta$  7.64–7.51 (m, 2H, Ar-H), 7.37–7.22 (m, 4H, Ar-H), 7.10 (d, 2H, Ar-H), 6.09 (d, 2H, Ind-H), 5.87 (t, 1H, Ind-H), 2.41 (s, 3H, Ph-Me), 2.26 (s, 6H, Me), 2.00 ppm (s, 6H, Me). MS (EI):  $m/z$  486 (3,  $M^+$ ), 371 (96,  $M^+ - Ind$ ), 373 (100,  $M^+ + 2 - Ind$ ), 335 (26,  $M^+ - HCl - Ind$ ), 275 (22,  $[IndZrCl_2]^+$ ), 165 (30,  $[C_5MeZr]^+$ ), 115 (54,  $[Ind]^+$ ).

**11**: Yellow solid (37%); m.p.: 209–210 °C. Anal. found: C, 56.13%; H, 4.90%.  $C_{24}H_{23}Cl_3Zr$  (calc.): C, 56.63%; H, 4.55%.  $^1H$ -NMR ( $CDCl_3$ ):  $\delta$  7.58 (m, 2H, Ar-H), 7.41 (d,  $J = 8.32$  Hz, 2H, Ar-H), 7.28 (m, 2H, Ar-H), 7.15 (d,  $J = 8.32$  Hz, 2H, Ar-H), 6.10 (d, 2H, Ind-H), 5.93 (t, 1H, Ind-H), 2.23 (s, 6H, Me), 2.01 ppm (s, 6H, Me). MS (EI):  $m/z$  506 (4,  $M^+$ ), 391 (75,  $M^+ - Ind$ ), 393 (100,  $M^+ + 2 - Ind$ ), 355 (16,  $M^+ - HCl - Ind$ ), 275 (22,  $[IndZrCl_2]^+$ ), 165 (54,  $[C_5MeZr]^+$ ), 115 (69,  $[Ind]^+$ ).

#### 2.8. Preparation of $(C_5Me_4C_6H_5)(2-Ph-Ind)ZrCl_2$ (**12**)

Complex **12** was synthesized from the ligand **1**, *n*-BuLi,  $ZrCl_4$  and 2-Ph-IndLi (prepared from 2-Ph-indene and *n*-BuLi) using a method similar to that as described for **5** as yellow crystals (36%); m.p.: 125–127 °C. Anal. found: C, 64.97%; H, 5.37%.  $C_{30}H_{28}Cl_2Zr$  (calc.): C, 65.43%; H, 5.12%.  $^1H$ -NMR ( $CDCl_3$ ):  $\delta$  7.64 (m, 2H, Ar-H), 7.46–7.12 (m, 10H, Ar-H), 6.94 (m, 2H, Ar-H), 6.71 (s, 2H, Ind-H), 2.01 (s, 6H, Me), 1.79 ppm (s, 6H, Me). MS (EI):  $m/z$  548 (1,  $M^+$ ), 357 (70,  $M^+ - (2-Ph-Ind)$ ), 351 (5,

[2-Ph-IndZrCl<sub>2</sub>]<sup>+</sup>, 321 (20, M<sup>+</sup> – HCl–(2-Ph-Ind)), 197 (5, [C<sub>5</sub>Me<sub>4</sub>Ph]<sup>+</sup>), 191 (100, [2-Ph-Ind]<sup>+</sup>), 165 (57, [C<sub>5</sub>MeZr]<sup>+</sup>), 91 (11, [C<sub>7</sub>H<sub>7</sub>]<sup>+</sup>), 77 (7, [C<sub>6</sub>H<sub>5</sub>]<sup>+</sup>), 65 (3, [C<sub>5</sub>H<sub>5</sub>]<sup>+</sup>).

### 2.9. Preparation of (C<sub>5</sub>Me<sub>4</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>ZrCl<sub>2</sub> (**13**)

To a solution of 3.97 g (15 mmol) of **1** in 40 ml of DME, 6.85 ml (2.19 N, 15 mmol) of *n*-BuLi/hexane solution was added dropwise. After stirring at RT overnight, the mixture was cooled down to –78 °C and 1.74 g (7.5 mmol) of ZrCl<sub>4</sub> was added. After heating under reflux for 6 h, the solvents were removed and 40 ml of CH<sub>2</sub>Cl<sub>2</sub> and 10 ml of HCl (6 N) was added to the residue. After separation, the organic phase was washed with water and dried with Na<sub>2</sub>SO<sub>4</sub>. Upon concentration and addition of hexane, 2.1 g (54%) of **13** was obtained as yellow crystals; m.p.: 242–243 °C. Anal. found: C, 64.47%; H, 5.89%. C<sub>30</sub>H<sub>34</sub>Cl<sub>2</sub>Zr (calc.): C, 64.72%; H, 6.16%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.40–7.24 (m, 6H, Ph-H), 7.05 (d, 4H, Ph-H), 1.99 (s, 12H, Me), 1.79 ppm (s, 12H, Me). MS (EI): *m/z* 554 (4, M<sup>+</sup>), 357 (99, M<sup>+</sup> – C<sub>5</sub>Me<sub>4</sub>Ph), 359 (100, M<sup>+</sup> + 2-C<sub>5</sub>Me<sub>4</sub>Ph), 321 (26, M<sup>+</sup> – HCl–C<sub>5</sub>Me<sub>4</sub>Ph), 197 (21, [C<sub>5</sub>Me<sub>4</sub>Ph]<sup>+</sup>), 165 (44, [C<sub>5</sub>MeZr]<sup>+</sup>), 91 (14, [C<sub>7</sub>H<sub>7</sub>]<sup>+</sup>), 77 (6, [C<sub>6</sub>H<sub>5</sub>]<sup>+</sup>).

### 2.10. Preparation of (C<sub>5</sub>Me<sub>4</sub>C<sub>6</sub>H<sub>4</sub>X-4)<sub>2</sub>ZrCl<sub>2</sub> [X = Me (**14**), Cl (**15**)]

Complexes **14** and **15** were synthesized from the corresponding ligands **2** and **3**, *n*-BuLi and ZrCl<sub>4</sub> using a method similar to that as described for **13**.

**14**: Yellow crystals (71%); m.p.: 261–263 °C. Anal. found: C, 65.50%; H, 6.45%. C<sub>32</sub>H<sub>38</sub>Cl<sub>2</sub>Zr (calc.): 65.73%; H, 6.55%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.14 (d, *J* = 7.95 Hz, 4H, Ph-H), 6.93 (d, *J* = 7.95 Hz, 4H, Ph-H), 2.36 (s, 6H, Ph-Me), 1.98 (s, 12H, Me), 1.79 ppm (s, 12H, Me). MS (EI): *m/z* 582 (2, M<sup>+</sup>), 371 (100, M<sup>+</sup> – C<sub>5</sub>Me<sub>4</sub>C<sub>6</sub>H<sub>4</sub>Me), 335 (23, M<sup>+</sup> – HCl–C<sub>5</sub>Me<sub>4</sub>C<sub>6</sub>H<sub>4</sub>Me), 211 (28, [C<sub>5</sub>Me<sub>4</sub>C<sub>6</sub>H<sub>4</sub>Me]<sup>+</sup>), 181 (27, [C<sub>5</sub>Me<sub>3</sub>C<sub>6</sub>H<sub>4</sub>]<sup>+</sup>), 165 (36, [C<sub>5</sub>MeZr]<sup>+</sup>).

**15**: Yellow crystals (82%); m.p.: 267–268 °C. Anal. found: C, 57.56%; H, 5.25%. C<sub>30</sub>H<sub>32</sub>Cl<sub>4</sub>Zr (calc.): 57.60%; H, 5.16%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.33 (d, *J* = 8.40 Hz, 4H, Ar-H), 7.00 (d, *J* = 8.40 Hz, 4H, Ar-H), 1.97 (s, 12H, Me), 1.82 ppm (s, 12H, Me). MS (EI):

*m/z* 622 (1, M<sup>+</sup>), 391 (22, M<sup>+</sup> – C<sub>5</sub>Me<sub>4</sub>C<sub>6</sub>H<sub>4</sub>Cl), 355 (15, M<sup>+</sup> – HCl–C<sub>5</sub>Me<sub>4</sub>C<sub>6</sub>H<sub>4</sub>Cl), 319 (10, M<sup>+</sup> – 2HCl–C<sub>5</sub>Me<sub>4</sub>C<sub>6</sub>H<sub>4</sub>Cl), 231 (18, [C<sub>5</sub>Me<sub>4</sub>C<sub>6</sub>H<sub>4</sub>Cl]<sup>+</sup>), 196 (34, [C<sub>5</sub>Me<sub>4</sub>C<sub>6</sub>H<sub>4</sub>]<sup>+</sup>), 181 (43, [C<sub>5</sub>Me<sub>3</sub>C<sub>6</sub>H<sub>4</sub>]<sup>+</sup>), 165 (100, [C<sub>5</sub>MeZr]<sup>+</sup>).

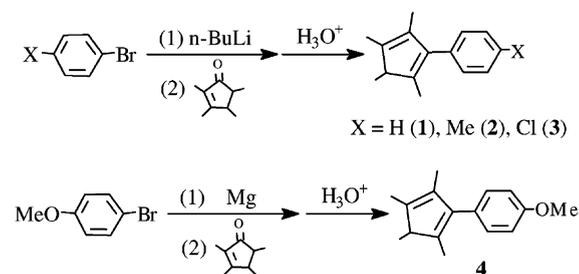
### 2.11. Ethylene polymerization

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 terminated by addition of acidified EtOH. The polymer product obtained was washed with ethanol and dried in vacuo at 60 °C.

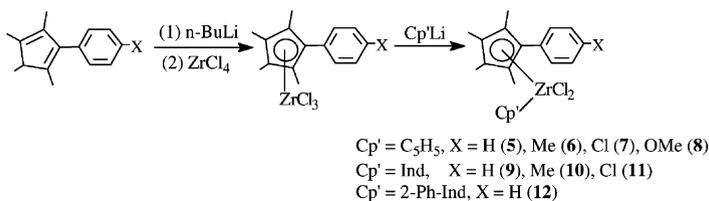
## 3. Results and discussion

The ligands **1–3** were synthesized by the reaction of 4-substituted bromobenzene with *n*-BuLi and 2,3,4,5-tetramethylcyclopent-2-enone. 4-Bromoanisole reacted with magnesium turnings to form the Grignard reagent, which further reacted with 2,3,4,5-tetramethylcyclopent-2-enone to give the ligand **4** (Scheme 1).

The ligands **1–4** reacted with *n*-BuLi and 1 equiv. of ZrCl<sub>4</sub> to form the corresponding aryl-substituted tetramethylcyclopentadienyl zirconium trichlorides, which further reacted in situ with CpLi, IndLi or 2-Ph-IndLi to give the mixed-ring zirconocene complexes **5–12** in high yield, respectively (Scheme 2).



Scheme 1.

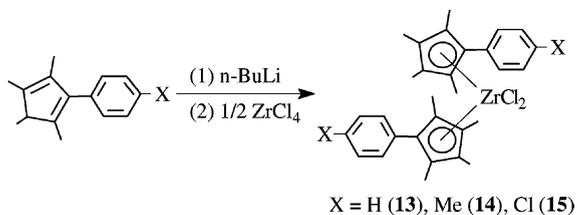


Scheme 2.

The zirconocene complexes **13–15** were synthesized by the reaction of the corresponding ligands **1–3** with *n*-BuLi and 0.5 equiv. of  $\text{ZrCl}_4$  in DME (Scheme 3).

The mass spectrum of a compound reflects the relative stability of the fragment ions. The fragment ion  $[\text{M} - \text{C}_5\text{H}_5]^+$  is the base peak in the mass spectra of **5**, **6** and **8**, indicating the ligands  $\text{C}_5\text{Me}_4\text{C}_6\text{H}_4\text{X}-4$  ( $\text{X} = \text{H, Me and MeO}$ ) complex with zirconium atom more strongly than the cyclopentadienyl ligand. In the mass spectrum of **7**, the abundance of the fragment ion  $[\text{M} - \text{C}_5\text{H}_5]^+$  (20%) is much smaller than that of  $[\text{M} - \text{C}_5\text{Me}_4\text{C}_6\text{H}_4\text{Cl}-4]^+$  (81%). This indicates that the introduction of an electron-withdrawing substituent (Cl) at the 4-position of phenyl decreases the electronic density of the cyclopentadienyl ring and weakens the complexing ability of the ligand. Similarly, the abundance of the fragment ion  $[\text{M} - \text{Ind}]^+$  (99, 96 and 75%) are much larger than that of  $[\text{M} - \text{C}_5\text{Me}_4\text{C}_6\text{H}_4\text{X}-4]^+$  (19, 22 and 22%) in the mass spectra of **9–11**, indicating the stronger complexing ability of  $\text{C}_5\text{Me}_4\text{C}_6\text{H}_4\text{X}-4$  than the indenyl ligand. Based on the mass spectra data, the complexing ability order of these ligands can be concluded as follows:  $\text{C}_5\text{Me}_4\text{C}_6\text{H}_4\text{X}-4$  ( $\text{X} = \text{H, Me and MeO}$ ) > Cp >  $\text{C}_5\text{Me}_4\text{C}_6\text{H}_4\text{Cl}-4$  > Ind.

Complexes **5–15** in combination with MAO were studied as catalysts for ethylene polymerization (Table 1). From the polymerization results it is



Scheme 3.

Table 1  
Results of ethylene polymerization catalyzed with zirconocenes/MAO<sup>a</sup>

Catalyst	$T_p$ (°C)	$A^b$ ( $\times 10^{-6}$ )	$M_n$ ( $\times 10^{-5}$ g/mol)	
$(\text{C}_5\text{Me}_4\text{H})\text{CpZrCl}_2^c$	40	6.47	3.67	
<b>5</b>	30	2.48		
	60	16.1	1.12	
	50	23.9	1.89	
	40	21.1	2.41	
	30	15.6	5.44	
<b>6</b>	20	14.1	5.92	
	30	15.9	3.35	
<b>7</b>	30	3.74	1.63	
	30	0.997	3.32	
$(\text{C}_5\text{Me}_4\text{H})\text{IndZrCl}_2^c$	40	4.20	2.90	
	30	3.67	3.43	
	<b>9</b>	60	9.88	0.84
		50	12.4	0.73
	<b>10</b>	40	16.6	1.61
30		19.8	2.11	
20		15.3	2.38	
60		10.6	0.74	
50		14.4	0.58	
40		19.2	1.76	
30		26.1	2.55	
<b>11</b>	20	23.8	3.13	
	30	5.15	2.51	
<b>12</b>	50	1.43	1.02	
	40	2.52	1.23	
	30	3.96	1.53	
	20	5.23	1.46	
	10	4.80	2.68	
<b>13</b>	30	1.03	0.198	
<b>14</b>	30	1.63	0.224	
<b>15</b>	30	0.422	0.280	

<sup>a</sup> Polymerization conditions:  $[\text{Zr}] = 1.0 \times 10^{-6}$  mol;  $\text{Al/Zr} = 2000$ ;  $t = 15$  min; 1 atm ethylene pressure; in 100 ml toluene.

<sup>b</sup> Activity (g PE/mol Zr h).

<sup>c</sup> Ref. [19],  $[\text{Zr}] = 3.0 \times 10^{-6}$  mol;  $\text{Al/Zr} = 2500$ ;  $t = 30$  min.

found that the introduction of a substituent at the 4-position of phenyl greatly influences the activities of catalysts for ethylene polymerization. At 30 °C, the activities decrease in the following order: for  $(C_5Me_4C_6H_4X-4)CpZrCl_2$ , **6** ( $X = Me$ ) > **5** ( $X = H$ ) > **7** ( $X = Cl$ ) >  $(C_5Me_4)CpZrCl_2 \gg$  **8** ( $X = OMe$ ); for  $(C_5Me_4C_6H_4X-4)(Ind)ZrCl_2$ , **10** ( $X = Me$ ) > **9** ( $X = H$ ) > **11** ( $X = Cl$ ) > **12** >  $(C_5Me_4)(Ind)ZrCl_2$ ; for  $(C_5Me_4C_6H_4X-4)_2ZrCl_2$ , **14** ( $X = Me$ ) > **13** ( $X = H$ ) > **15** ( $X = Cl$ ). For these complexes, the substituents are at the 4-position of phenyl, which is far from the metal center, so the steric effects are similar and the catalytic activity differences depend mainly on the electronic effect of the substituents. The electron donor (Me) increases the electron density of the metal center, which leads to an increase in catalytic activity. In contrast, the electron-withdrawing group (Cl) decreases the electron density of the metal center and leads to a decrease in catalytic activity. However, complex **8** with a strong  $\pi$  donor (OMe) shows much lower activity. This can be attributed to the coordination of the donor to MAO leading to inductive electron withdrawal [21,22]. The introduction of a phenyl at 2-position of indenyl in **12** increases the steric hindrance and leads to a decrease in catalytic activity. The much lower catalytic activities of **13–15** than that of the mixed-ring zirconocenes can be attributed to the large steric effect of the aryl-substituted tetramethylcyclopentadienyl ligand than the cyclopentadienyl ligand.

The relationship between the molecular weight of polyethylene with the electronic effects of substituents in phenyl is not clear. It seems that the molecular weight of polyethylene is more sensitive to the steric effect of catalysts. For  $(C_5Me_4C_6H_4X-4)CpZrCl_2$ , the introduction of substituents at the 4-position of phenyl, both electron-withdrawing and donating, leads to a decrease in the molecular weight of polyethylene; especially for complex **8** with a strong  $\pi$  donor (OMe), much lower molecular weight of polyethylene was produced. For  $(C_5Me_4C_6H_4X-4)IndZrCl_2$ , polyethylenes with similar molecular weight were obtained. The introduction of the bulky phenyl at 2-position of indenyl decreases the molecular weight of polyethylene. For  $(C_5Me_4C_6H_4X-4)_2ZrCl_2$ , polyethylenes with very low molecular weight were obtained. This indicates

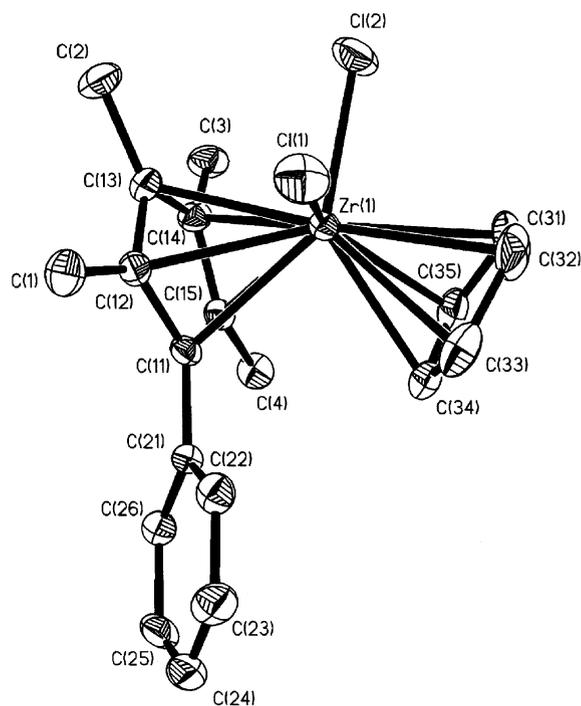


Fig. 1. The molecular structure of **5**.

that although bulky substituents in the ligand, such as  $(C_5Me_5)_2ZrCl_2$ , may partially block the free coordination site, suppress  $\beta$ -hydrogen elimination reactions and increase the molecular weight of the produced polymer [8]. However, the too bulky substituents led to a decrease in the molecular weight of polyethylene.

From Table 1 it is also found that the introduction of phenyl makes complexes **5**, **6**, **9** and **10** show much higher activities than  $(C_5Me_4)CpZrCl_2$ . In the molecular structure of **5** (Fig. 1), the dihedral angle between phenyl and tetramethylcyclopentadienyl planes is 47.2°, showing that there is no conjugation effect between phenyl ring and tetramethylcyclopentadienyl ring. This indicates that the electronic effect is not responsible mainly for the high activity. In comparison with  $(C_5Me_5)CpZrCl_2$ , the introduction of a phenyl increases the distance between zirconium atom and the center of cyclopentadienyl ring (Zr–Cen: 2.219 Å vs. 2.209 Å) (Table 2). This enlarges the reaction space of the metal center and increases the catalytic activity of **5**.

Table 2  
Selected bond lengths (Å) and bond angles (°) for **5** and (C<sub>5</sub>Me<sub>5</sub>)CpZrCl<sub>2</sub><sup>a</sup>

	<b>5</b>	(C <sub>5</sub> Me <sub>5</sub> )CpZrCl <sub>2</sub>
Zr–C(Cp)	2.516	2.507(31)
Zr–C(Cp'')	2.524	2.524(14)
Zr–Cen(Cp)	2.219	2.209(2)
Zr–Cen(Cp'')	2.219	2.219(2)
Zr–Cl	2.437(2) 2.429(2)	2.442(1)
∠Cen–Zr–Cen	131.1	130.01(7)
∠Cp–Cp''	52.4	53.4(2)
∠Cl–Zr–Cl	96.8(1)	97.78(3)
Reference	This work	[20]

<sup>a</sup> Cen: the center of C<sub>5</sub> ring.

Table 3  
The effects of Al/Zr ratio on polymerization activities for **5** and **9**<sup>a</sup>

Catalyst	Al/Zr	A (×10 <sup>-6</sup> )	M <sub>η</sub> (×10 <sup>-5</sup> g/mol)
<b>5</b>	3200	31.4	3.08
	2500	26.5	2.46
	2000	21.1	2.46
	1200	17.2	2.47
	640	1.66	1.22
<b>9</b>	3200	18.8	1.83
	2500	32.4	2.14
	2000	29.1	2.50
	1200	18.6	2.71
	640	3.74	1.82

<sup>a</sup> Polymerization conditions: [Zr] = 5.0 × 10<sup>-7</sup> mol; T<sub>p</sub> = 50 °C for **5**, 30 °C for **9**; t = 15 min; 1 atm ethylene pressure; in 100 ml toluene.

Complex **5** shows the highest activity at 50 °C, while complexes **9–12** reach the maximum activities at low temperature, due to the poor thermal stabilities of indenyl zirconocene complexes. For complexes **5** and **9**, the effects of Al/Zr ratio on catalytic activities were also examined (Table 3). The activity increases with increasing Al/Zr ratio for **5**, but the highest activity is obtained at Al/Zr = 2500 for **9**.

#### 4. Conclusions

In this study, we demonstrated that mixed-ring aryl-substituted tetramethylcyclopentadienyl zircono-

cenes **5**, **6**, **9** and **10** displayed very high ethylene polymerization activities. The X-ray crystallographic structure of **5** revealed that the introduction of phenyl increased the distance between zirconium atom and the center of cyclopentadienyl ring and enlarged the reaction space of the metal center. The electronic effects of the substituents at the 4-position of phenyl were examined and it was found that the electron donor (Me) led to an increase while the electron-withdrawing group (Cl) and the strong π donor (OMe) led to a decrease in catalytic activity.

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