

# Synthesis of zirconocenes bearing benz[*f*]indenyl ligand and their use as a catalyst in ethylene polymerization

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## Abstract

Benz[*f*]indenyl zirconium complexes have been successfully synthesized and characterized. Their catalytic activities were evaluated for the polymerization of ethylene. The complexes combined with MAO can be highly active single site catalysts, which display activities comparable with that of the Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO system and provide very high molecular weight polyethylenes. The melting point of the polymers indicates the formation of linear polyethylene.

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## 1. Introduction

The discovery of the combination of group 4 metallocenes and methylaluminoxane (MAO) as catalysts in the olefin polymerization opens the gateway to a new world of polymers [1]. Thus, there has been active research aimed at discovering analogues or alternatives for the cyclopentadienyl (Cp) ring since changes to the ligand skeleton provides access to more unusual materials, which are unachievable using conventional Ziegler–Natta catalysts (For reviews on metallocene olefin polymerization, see: [2]). For example, indenyl, fluorenyl, cyclohexadienyl, boratabenzene anion, borole, azaborolanyl, cyclooctatetraenyl dianion, trimethylene dianion, and tripyrazolyl anion have been used instead of Cp [3]. Nowadays, the well-defined nature

of metallocenes allows rational catalyst design to elucidate a qualitative relationship between catalyst structure and the resulting polymer microstructure [4].

Benz[*f*]indenyls, isomer to fluorenyls, have not been used as alternatives or substitutes for Cp until we recently reported [5] the first synthesis of zirconium complexes of benz[*f*]indenyl ligands. There had been some efforts to synthesize metallocenes bearing benz[*f*]indenyls [6]. However, their attempts were not successful presumably due to the low stability of benz[*f*]indenyl anions. In order to overcome this problem, we introduced some substituents to the benz[*f*]indenyl skeleton. Finally, several zirconium compounds of benz[*f*]indenyls were synthesized and one of them was characterized by X-ray crystallography. Thus, we expect that the use of benz[*f*]indenyl ligands in the synthesis of metallocenes will be quite common in the near future. Herein, we report the synthesis of Zr complexes of benz[*f*]indenyls and their catalytic activity in ethylene polymerization in detail.

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## 2. Results and discussion

### 2.1. Synthesis

Zirconium complexes synthesized in this study were drawn in Chart 1. Schemes 1 and 2 show the synthetic pathway to benz[*f*]indenyl zirconium compounds **1** and **4**, respectively. For the synthesis of **2** and **3**, the same procedure as the synthesis of **1** was applied and for **5** and **6** the same procedure as the synthesis of **4** was applied. In order to know the effect of a substituent of the benz[*f*]indene on the catalytic activity and the molecular weight of polymers, two kinds of benz[*f*]indene compounds, i.e., both with and without substituents, were used in the synthesis of zirconium complexes. Substituted benz[*f*]indenes [5] and unsubstituted benz[*f*]indene [7] were prepared by the procedure of the literature. The benz[*f*]indenes having substituents were not soluble in diethyl ether but soluble in THF at  $-78\text{ }^{\circ}\text{C}$ . Lithiation was conducted in THF solution. However, benz[*f*]indene without substituents was soluble in diethyl ether and THF at  $-78\text{ }^{\circ}\text{C}$ . Thus, lithiation could be carried out in either solution. After evaporation, gummy solids were obtained. The gummy solids were transferred into a dry box and dissolved in toluene. In order to synthesize zirconium metallocene compounds, three kinds of zirconium chloride compounds,  $(\text{Ind})\text{ZrCl}_3$  (Ind = indenyl),  $\text{Cp}^*\text{ZrCl}_3$ , and  $\text{CpZrCl}_3$ , were used. They were not very soluble in toluene, but slowly dissolved in toluene as the reaction proceeded. For example, as the reaction of gummy solids with  $(\text{Ind})\text{ZrCl}_3$  proceeded,  $(\text{Ind})\text{ZrCl}_3$  was slowly dissolved in toluene. After evaporation of toluene, the residue

was extracted with dichloromethane and filtered off to remove lithium chloride. After removal of the solvent, a crude product was obtained. None of the zirconium compounds were soluble in diethyl ether and hexane but all soluble in dichloromethane. Compounds **1–3** were soluble in toluene but **4–6** were almost insoluble in toluene. Thus, the solubility was highly dependent upon the presence of the substituents. After recrystallization in toluene/ $\text{Et}_2\text{O}$ , reddish crystalline solids were obtained for **1**, **2**, and **3**. Yellowish powders were obtained for **4**, **5**, and **6**.

### 2.2. X-ray diffraction study

Single crystals of **1** and **2** were obtained by recrystallization from a dichloromethane/toluene mixture at  $-20\text{ }^{\circ}\text{C}$ . The crystal structure of **2** was previously communicated [5]. Figs. 1 and 2 give ORTEP views of the structures of **1** and **2** together with the atom labeling. Crystal data, details of the data collection, and refinement parameters are listed in Table 1 and selected bond distances and angles are given in Table 2. The geometry around Zr, as defined by the centroids of the cyclopentadienyl, benz[*f*]indenyl and Cl atoms, is roughly tetrahedral. Although the substitution of the methyl group on the cyclopentadienyl causes no apparent distortion of the structure, all the Zr–C bond lengths for **2** are longer than those found in **1** presumably due to the steric bulkiness of  $\text{Cp}^*$ . For a bent metallocene, geometric parameters ( $\alpha$ ,  $\beta$ , and  $\gamma$ ) were proposed [8]. The angle between the ring planes ( $\alpha$ ) was  $52.8^{\circ}$  and  $48.6^{\circ}$  for **1** and **2**, respectively. The ring centroid–metal–ring centroid ( $\gamma$ ) was  $130.5^{\circ}$  and  $134.5^{\circ}$  for **1** and **2**, respectively. The

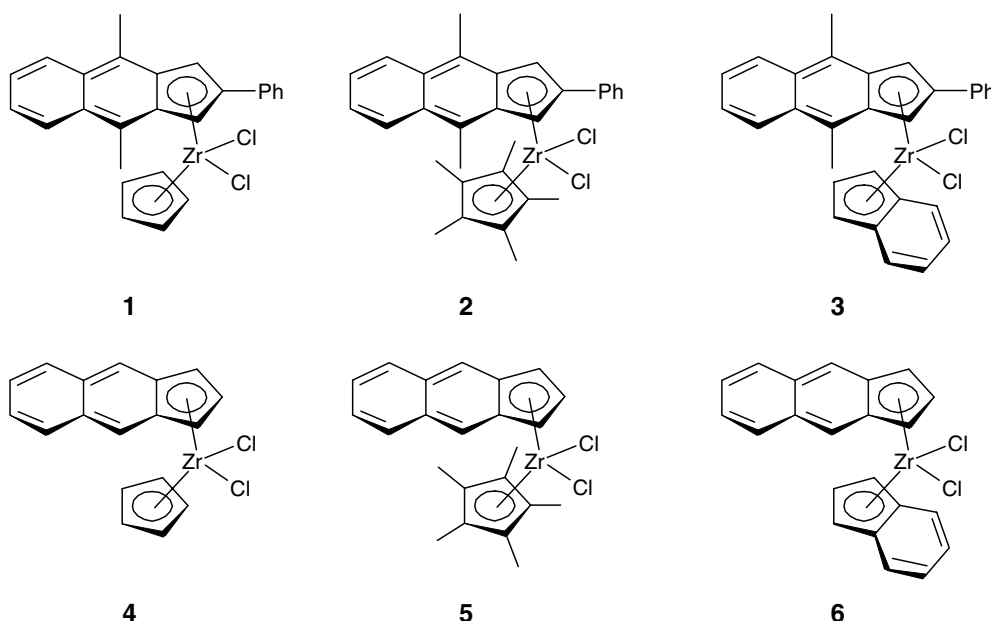
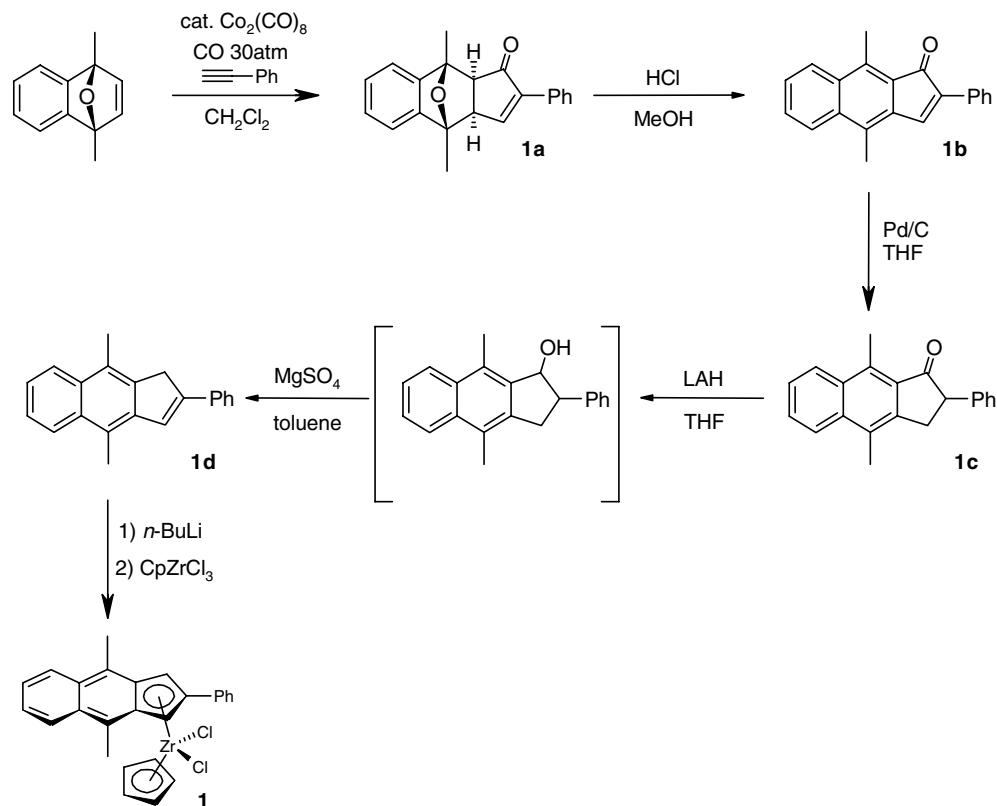
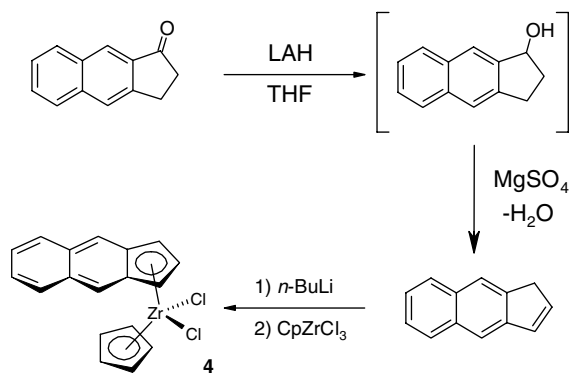
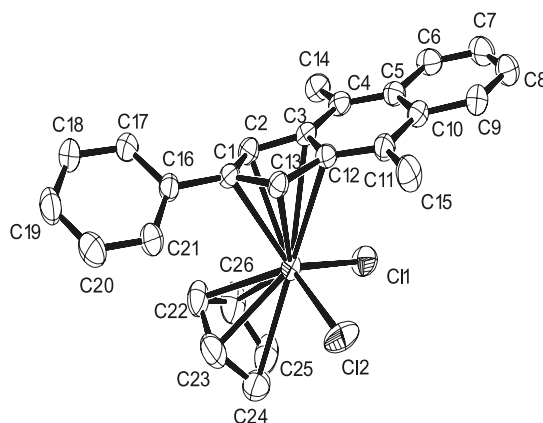


Chart 1. Structures of synthesized zirconium complexes.

Scheme 1. Syntheses of substituted benz[f]indenyl zirconium complex **1**.Scheme 2. Syntheses of benz[f]indenyl zirconium complex **4**.Fig. 1. Drawing of compound **1**. Atoms are represented by anisotropic displacement ellipsoids at the 30% probability level.

angle  $\beta$  between the normals from the metal to the ring planes, is another useful parameter, because its difference from  $\gamma$  reflects the amount of slippage of the metal from an ideal  $\eta^5$  coordination to each ring [9]. The  $\beta$  value was  $127.2^\circ$  and  $131.4^\circ$  for **1** and **2**, respectively. Thus, the angle is greater than the angle  $\beta$ . Interestingly, the difference between  $\beta$  and  $\gamma$  for **1** and **2** was almost the same.

The benz[f]indenyl groups are displaced from symmetric  $\eta^5$ -coordination toward  $\eta^3$ -coordination: for example, the Zr is significantly closer to carbons C(1), C(2), and C(13) than carbons C(3) and C(12). We

expected that this modified  $\eta^3$ - $\eta^2$  coordination geometry creates a more electrophilic metal center [8].

### 2.3. Polymerization of ethylene

The dichloride complexes **1–6** are active to ethylene polymerization when activated with MAO. The activities of unsubstituted benz[f]indenyl zirconium complexes (**4–6**) were greater than those of substituted benz[f]indenyl zirconium complexes (**1–3**). The highest activity

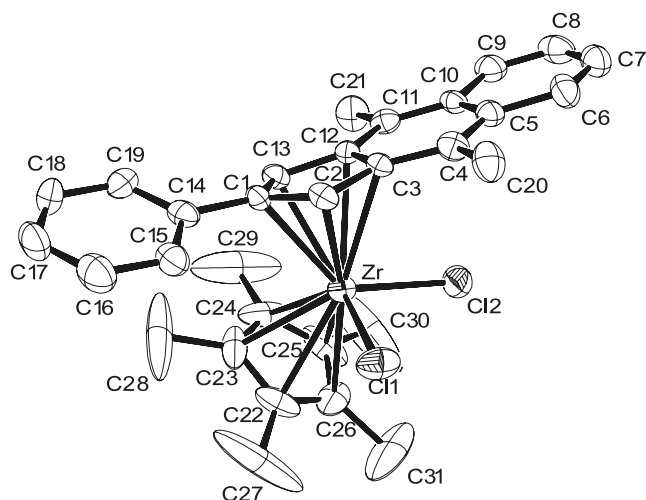


Fig. 2. Drawing of compound **2**. Atoms are represented by anisotropic displacement ellipsoids at the 30% probability level.

Table 1  
Crystal data and structure refinement for **1** and **2**<sup>a</sup>

Compound	1	2
Formula	C <sub>26</sub> H <sub>22</sub> ZrCl <sub>2</sub>	C <sub>31</sub> H <sub>32</sub> ZrCl <sub>2</sub>
<i>M<sub>w</sub></i>	496.59	566.72
Unit cell dimensions		
<i>a</i> (Å)	8.5676(3)	9.3370(10)
<i>b</i> (Å)	10.2271(4)	18.0230(10)
<i>c</i> (Å)	13.1520(5)	16.1490(10)
$\alpha$ (°)	98.134(2)	90
$\beta$ (°)	91.938(2)	100.296(2)
$\gamma$ (°)	108.011(2)	90
<i>V</i> Å <sup>3</sup>	1081.22(7)	2673.8(4)
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> – 1	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>Z</i>	2	4
$\mu$ /mm <sup>-1</sup>	0.766	0.629
No. of data collected	7296	7826
No. of unique data	4971	4445
No. of variables	266	315
<i>R</i>	0.0619	0.0409
<i>R<sub>w</sub></i>	0.1888	0.0679

<sup>a</sup> Data collected at 293(2) K with Mo K $\alpha$  radiation ( $\lambda(K\alpha) = 0.7107\text{Å}$ ),  $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$  with  $F_o > 2.0\sigma(I)$ ,  $R_w = [\sum [w(F_o^2 - F_c^2)]^2] / \sum [w(F_o^2)]^2]^{1/2}$  with  $F_o > 2.0\sigma(I)$ .

( $39 \times 10^6$  g/mol of Zr h) was observed for **5** and **3** shows the lowest activity ( $7.9 \times 10^6$  g/mol of Zr h) with the highest molecular weight,  $10.3 \times 10^5$ . Interestingly, the activity of **6** and the molecular weight of polyethylene produced by **6** are comparable to that of Cp<sub>2</sub>ZrCl<sub>2</sub> but **4** and **5** have much higher activities. Molecular weights of the obtained polyethylenes are fairly high in the cases of **2** and **3**. In many cases, high molecular weight polyethylenes are produced by the catalysts with bulky substituents in the ligand sphere with substantial loss of activity [10]. The molecular weight distributions are narrow ( $M_w/M_n$ , 1.7–2.6) indicating a single active species is present in the polymerization solution. More-

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

	1	2
Zr–Cl1	2.4243(18)	2.4591(11)
Zr–Cl2	2.4390(16)	2.4218(15)
Zr–C1	2.556(5)	2.576(5)
Zr–C2	2.487(6)	2.572(4)
Zr–C3	2.614(5)	2.643(5)
Zr–C12	2.602(5)	2.592(4)
Zr–C13	2.524(6)	2.465(4)
Zr–C22	2.488(6)	2.510(6)
Zr–C23	2.473(7)	2.514(6)
Zr–C24	2.508(8)	2.515(6)
Zr–C25	2.497(8)	2.532(6)
Zr–C26	2.471(8)	2.511(6)
Cl1–Zr–Cl2	96.40(7)	95.25(5)
Zr–Cp(c) <sup>a</sup>	2.194	2.232
Zr–benzind(c) <sup>b</sup>	2.250	2.267
Cpbenzind(c)–Zr–Cp(c)	130.58	134.52

<sup>a</sup> Centroid of cyclopentadienyl group.

<sup>b</sup> Centroid of benz[*f*]indenyl group.

Table 3  
Ethylene polymerizations by benz[*f*]indenyl zirconium complexes<sup>a</sup>

Entry	Compound	Activity <sup>b</sup>	<i>M<sub>w</sub></i> ( $\times 10^5$ )	<i>M<sub>w</sub></i> / <i>M<sub>n</sub></i>	Melting point (°C)
1	Cp <sub>2</sub> ZrCl <sub>2</sub>	24	3.8	1.92	134.3
2	<b>1</b>	24	1.9	1.88	134.6
3	<b>2</b>	22	7.5	2.23	134.2
4	<b>3</b>	7.9	10.3	1.72	133.7
5	<b>4</b>	30	6.3	2.07	134.4
6	<b>5</b>	39	2.8	2.64	136.2
7	<b>6</b>	26	3.4	2.43	135.4

<sup>a</sup> Polymerization conditions: 30 mL of toluene, 0.29  $\mu$ mol of complex, [Al]/[Zr] = 5000, 60 °C, 5 min.

<sup>b</sup> Activity in 10<sup>6</sup> gmol Zr · h.

over, the PEs produced by this study are highly linear with  $T_m = 133$ – $136$  °C. The above results show that the activity, molecular weight, and PDI value of the (benz[*f*]indenyl)zirconium complexes are highly dependent upon the steric effect of an ancillary ligand. For **1**–**3**, as the steric effect of the ancillary ligand increases (Indenyl > Cp\* > Cp), the activity decreases but the molecular weight increases. However, for **4**–**6**, there is an optimum steric crowdedness for the maximum activity: the activity decreases in the order of **5** > **4** > **6** and the molecular weight decreases in the order **4** > **6** > **5** (Table 3).

### 3. Conclusions

A new series of benz[*f*]indenyl zirconium complexes were successfully prepared and characterized. They were highly active catalysts in the presence of MAO for polymerization of ethylene. They display activities comparable with that of Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO systems. We

expect that the benz[*f*]indenyl zirconium catalysts are an important addition to the list of group 4 metallocene catalysts. Efforts to synthesize catalysts with substitution in the special positions of benz[*f*]indenyl framework and their influence on the polymer properties are in progress.

## 4. Experimental

### 4.1. General remarks

Toluene used for polymerization reaction was purchased from Aldrich (anhydrous grade) and purified further over Na/K alloy. Ethylene was purchased from Conley Gas (99.9%) and purified by contacting with molecular sieves and copper overnight under the pressure of 150 psig. Methylaluminoxane (MAO) was purchased as a solution in toluene from Akzo (7.6 wt% of Al, MMAO type 4). Gel permeation chromatograms (GPC) were obtained at 140 °C in trichlorobenzene using Waters Model 150-C+ GPC and the data were analyzed using a polystyrene analyzing curve.

### 4.2. 4,9-Dimethyl-2-phenyl-4,9-epoxycyclopenta[*b*]naphthalen-1-one (**1a**)

To a 100 mL high-pressure reactor were added oxabenzonorbornadiene (1.3 g, 9.1 mmol), phenyl acetylene (0.50 mL, 4.6 mmol), 30 mL of CH<sub>2</sub>Cl<sub>2</sub>, and Co<sub>2</sub>(CO)<sub>8</sub> (78 mg, 0.23 μmol). After the solution was flushed with CO gas in several seconds, the reactor was pressurized with 30 atm of CO. The reactor was heated at 130 °C for 18 h. After the reactor was cooled to rt and excess gas was relieved, the solution was transferred into a flask and then evaporated to dryness. The residue was chromatographed on a silica gel column eluting with hexane and ethyl acetate (v/v, 8:1). Yield: 92%; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.76 (d, *J* = 3.0 Hz, 1H), 7.72 (m, 2H), 7.40–6.90 (m, 7H), 3.06 (dd, *J* = 5.1, 2.9 Hz, 1H), 2.57 (d, *J* = 5.1 Hz, 1H), 1.89 (s, 3H), 1.84 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 204.2, 155.5, 148.5, 147.6, 131.3, 128.7, 128.4, 127.3, 127.2, 126.9, 125.8, 118.2, 118.1, 85.8, 85.1, 57.5, 52.6, 14.7, 14.4; IR ν(C=O) 1698 cm<sup>-1</sup>; HRMS for C<sub>21</sub>H<sub>18</sub>O<sub>2</sub>: Calc. 302.1307, obsd. 302.1306.

### 4.3. 4,9-Dimethyl-2-phenylbenz[*f*]inden-1-one (**1b**)

To a 100 mL of round-bottom flask was added **1a** (0.50 g, 1.8 mmol). To the solution was added MeOH and hydrochloric acid (2 mL of HCl in 30 mL of MeOH). After the resulting solution was refluxed for 5 h, the solution was cooled to rt. To the solution were added ice water and saturated aqueous NaOH. Ethyl acetate was added to extract organic com-

pounds. The ethyl acetate extract was dried over anhydrous MgSO<sub>4</sub>, filtered, and chromatographed on a silica gel column eluting with hexane and ethyl acetate (v/v, 10:1). Yield: 90%; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.07 (d, *J* = 6.8 Hz, 1H), 7.98 (s, 1H), 7.92 (d, *J* = 7.7 Hz, 1H), 7.88 (d, *J* = 7.0 Hz, 2H), 7.58 (t, *J* = 7.0 Hz, 1H), 7.49 (t, *J* = 7.1 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 2.92 (s, 3H), 2.58 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 197.2, 141.7, 141.6, 139.1, 136.1, 135.9, 135.8, 134.7, 132.2, 128.7, 128.6, 128.5, 127.5, 126.9, 126.7, 126.3, 125.5, 13.8, 12.0; IR ν(C=O) 1694 cm<sup>-1</sup>; HRMS for C<sub>21</sub>H<sub>16</sub>O: Calc. 284.1201, obsd. 284.1201.

### 4.4. 4,9-Dimethyl-2-phenylbenz[*f*]indan-1-one (**1c**)

To a 50 mL schlenk flask filled with nitrogen were added a solution of **1b** (0.30 g, 1.06 mmol) in 25 mL of THF and Pd/C (0.30 g, Pd 10%, dry wt. basis Water ~50%). The solution was flushed with a balloon of H<sub>2</sub> gas. When the yellow color of the solution was disappeared, the reaction was completed. Pd/C was recovered by filtration and reused for other reaction. Filtrate was concentrated and chromatographed on a silica gel column eluting with hexane and ethyl acetate (v/v, 9:1). Yield: 93%; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.27 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.66 (t, *J* = 8.4 Hz, 1H), 7.56 (t, *J* = 8.4 Hz, 1H), 7.32–7.20 (m, 5H), 3.95 (dd, *J* = 4.8, 9.1 Hz, 1H), 3.73 (dd, *J* = 9.1, 17 Hz, 1H), 3.28 (dd, *J* = 4.7, 17 Hz, 1H), 3.07 (s, 3H), 2.65 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 208.2, 144.5, 140.6, 136.6, 135.6, 132.8, 130.1, 128.9, 128.4, 128.1, 127.1, 126.7, 126.0, 125.6, 124.4, 54.7, 34.2, 14.2, 12.7; IR ν(C=O) 1705 cm<sup>-1</sup>; HRMS for C<sub>21</sub>H<sub>18</sub>O: Calc. 286.1358, obsd. 286.1363.

### 4.5. 4,9-Dimethyl-2-phenylbenz[*f*]indene (**1d**)

To a 50 mL schlenk flask filled with nitrogen in an ice-bath were added a solution of **1c** (0.28 g, 0.98 mmol) in 15 mL of THF and LiAlH<sub>4</sub> (23 mg, 0.59 mmol). The resulting solution was allowed to warm to rt. After the solution was stirred for 4 h, several drops of sat. aqueous NH<sub>4</sub>Cl solution were added. As the NH<sub>4</sub>Cl solution was added, fluorescence was disappeared. The resulting solution was filtered over a MgSO<sub>4</sub> pad and the filtrate was evaporated to dryness. The residue was used further reactions without further purification. To a 100 mL round-bottom flask were added the residue, MgSO<sub>4</sub> (5.0 g), and 60 mL of hexane. After the resulting solution was refluxed, the solution was filtered, evaporated, and chromatographed on a silica gel column eluting with hexane and ethyl acetate (v/v, 24:1). Yield: 70%; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.03 (m, 2H), 7.69 (d, *J* = 7.2 Hz, 2H), 7.49 (s, 1H), 7.47 (m, 2H), 7.40

(t,  $J = 7.8$  Hz, 2H), 7.28 (t,  $J = 7.3$  Hz, 1H), 3.81 (s, 2H), 2.73 (s, 3H), 2.64 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$ 146.1, 141.9, 138.9, 136.2, 132.8, 131.5, 128.8, 127.8, 125.9, 125.8, 124.9, 124.6, 124.3, 123.1, 38.4, 15.3, 15.0; HRMS for  $\text{C}_{21}\text{H}_{18}$ : Calc. 270.1409, obsd. 270.1405.

#### 4.6. (4,9-Dimethyl-2-phenylbenz[*f*]indenyl)cyclopentadienylzirconium dichloride (**1**)

To a 50 mL schlenk filled with nitrogen was added a solution of 4,9-dimethyl-2-phenyl-benz[*f*]indene (0.1 g, 0.37 mmol) in THF (8 ml). The solution was cooled by a dry ice/acetone bath. After *n*-BuLi (0.15 ml, 2.5 M in hexane) was added at  $-78$  °C, the solution was allowed to warm to rt. After the solution was stirred for 1 h, the solution was evaporated to dryness. To the residue were added  $\text{CpZrCl}_3$  (97 mg, 0.37 mmol) and 6 ml of toluene. The resulting solution was stirred overnight. During the stirring, the solution became red. After the solvent was removed, the residue was dissolved in dichloromethane, filtered, and dried. The residue was redissolved in toluene and recrystallized by diffusion of  $\text{Et}_2\text{O}$  at  $-20$  °C. Red crystalline solids were obtained as a product. Yield: 70%.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$ 8.24 (d,  $J = 6.9$  Hz, 1H), 8.22 (d,  $J = 6.9$  Hz, 1H), 7.77 (d,  $J = 7.0$  Hz, 1H), 7.76 (d,  $J = 7.0$  Hz, 1H), 7.53–7.39 (m, 5H), 7.09 (s, 2H), 5.99 (s, 5H), 3.04 (s, 6H); Anal. Calc. for  $\text{C}_{26}\text{H}_{22}\text{ZrCl}_2$ : C, 62.89; H, 4.47. Found: C, 63.22; H, 4.52%.

#### 4.7. (4,9-Dimethyl-2-phenylbenz[*f*]indenyl)indenylzirconium dichloride (**3**)

The reaction procedure was exactly the same as the synthesis of **1** except the use of  $(\text{Ind})\text{ZrCl}_3$  instead of  $\text{CpZrCl}_3$ . Yield: 50%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$ 8.04 (d,  $J = 6.9$  Hz, 1H), 8.03 (d,  $J = 6.9$  Hz, 1H), 7.81 (d,  $J = 7.0$  Hz, 1H), 7.80 (d,  $J = 7.0$  Hz, 1H), 7.47 (m, 2H), 7.42 (m, 2H), 7.31–7.18 (m, 5H), 6.90 (m, 2H), 6.60 (s, 2H), 5.77 (m, 1H), 2.54 (s, 6H); Anal. Calc. for  $\text{C}_{30}\text{H}_{24}\text{ZrCl}_2$ : C, 65.92, H, 4.43. Found: C, 66.31; H, 4.72%.

#### 4.8. Benz[*f*]indenylcyclopentadienylzirconium dichloride (**4**)

The reaction procedure was exactly the same as the synthesis of **1** except the use of benz[*f*]indene instead of 4,9-dimethyl-2-phenylbenz[*f*]indene. Yield: 63%.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$ 8.21 (s, 2H), 7.79 (d,  $J = 6.3$  Hz, 1H), 7.78 (d,  $J = 6.3$  Hz, 1H), 7.29 (d,  $J = 6.6$  Hz, 1H), 7.28 (d,  $J = 6.6$  Hz, 1H), 7.04 (t,  $J = 3.3$  Hz, 1H), 6.64 (d,  $J = 3.3$  Hz, 2H), 6.05 (s, 5H); Anal. Calc. for

$\text{C}_{18}\text{H}_{14}\text{ZrCl}_2$ : C, 55.09; H, 3.60. Found: C, 54.75; H, 3.64%.

#### 4.9. Benz[*f*]indenylpentamethylcyclopentadienylzirconium dichloride (**5**)

The reaction procedure was exactly the same as the synthesis of **2** except the use of benz[*f*]indene instead of 4,9-dimethyl-2-phenylbenz[*f*]indene. Yield: 46%.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$ 8.44 (s, 2H), 7.91 (d,  $J = 6.7$  Hz, 1H), 7.90 (d,  $J = 6.7$  Hz, 1H), 7.30 (d,  $J = 6.7$  Hz, 1H), 7.29 (d,  $J = 6.7$  Hz, 1H), 6.37 (d,  $J = 3.3$  Hz, 2H), 6.33 (t,  $J = 3.2$  Hz, 1H), 2.03 (s, 15H); Anal. Calc. for  $\text{C}_{23}\text{H}_{24}\text{ZrCl}_2$ : C, 59.72; H, 5.23. Found: C, 59.56; H, 5.52%.

#### 4.10. Benz[*f*]indenylindenylzirconium dichloride (**6**)

The reaction procedure was exactly the same as the synthesis of **3** except the use of benz[*f*]indene instead of 4,9-dimethyl-2-phenylbenz[*f*]indene. Yield: 45%.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$ 8.14 (s, 2H), 7.76 (d,  $J = 6.6$  Hz, 1H), 7.75 (d,  $J = 6.6$  Hz, 1H), 7.54 (d,  $J = 6.6$  Hz, 1H), 7.53 (d,  $J = 6.6$  Hz, 1H), 7.29 (d,  $J = 6.6$  Hz, 1H), 7.28 (d,  $J = 6.6$  Hz, 1H), 7.19 (d,  $J = 6.6$  Hz, 1H), 7.18 (d,  $J = 6.6$  Hz, 1H), 6.62 (t,  $J = 3.4$  Hz, 1H), 6.44 (t,  $J = 3.3$  Hz, 1H), 6.25 (d,  $J = 3.4$  Hz, 2H), 6.12 (d,  $J = 3.3$  Hz, 2H); Anal. Calc. for  $\text{C}_{22}\text{H}_{16}\text{ZrCl}_2$ : C, 59.72; H, 3.64. Found: C, 59.41; H, 3.59%.

#### 4.11. Ethylene polymerization

In a dry box, to a dried 70 ml glass reactor was added 30 ml toluene. Activated complex, prepared by mixing a complex (0.29  $\mu\text{mol}$ ) and MAO (0.492 g,  $\text{Al/Zr} = 5000$ ), was added to the reactor. The reactor was assembled and brought out from the dry box. The reactor was immersed in an oil bath whose temperature had been set to 60 °C and stirred for 5 min, at which time the solution temperature reached to the bath temperature. Ethylene was fed under the pressure of 60 psig for 5 min. During feeding ethylene, the reaction temperature went up to 70–72 °C. Polymerization was quenched by venting ethylene gas and pouring the mixture to acetone. Polyethylene was precipitated from acidified methanol, filtered, washed with methanol, and dried under vacuum at 50 °C. White precipitates were collected by filtration and dried under vacuum.

#### 4.12. Crystallographic studies

A single crystal coated with grease (Apiezon N) were mounted inside a thin glass tube with epoxy glue and placed on an Enraf-Nonius CCD single crystal X-ray diffractometer. The structures were solved by direct

methods (SHELXS-97) [11] and refined against all  $F^2$  data (SHELXS-97). All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were treated as idealized contributions.

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