

# Aromatic Substituted Group 4 Metallocene Catalysts for the Polymerization of $\alpha$ -Olefins

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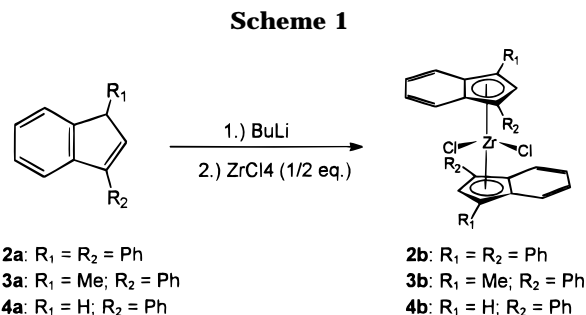
Received June 28, 1996<sup>⊗</sup>

Six new group 4 metallocene complexes were synthesized as precursors for the polymerization of  $\alpha$ -olefins. The phenyl-substituted precursors **2b–4b** when activated by methylaluminoxane (MAO) were highly active for the polymerization of ethylene but exhibited no activity for the polymerization of propylene. Bis(2-methylbenz[e]indenyl)zirconium dichloride (**5b**) was activated with both MAO and triphenylcarbenium tetrakis(pentafluorophenyl)borate (trityl)/triisobutylaluminum producing polypropylene with varying molecular weight depending on polymerization temperature. The titanium precursor **6b** had lower activity for ethylene as compared to the zirconium analog **5b** and virtually no activity for propylene when activated with either MAO or trityl.

## Introduction

In 1980, Kaminsky et al.<sup>1</sup> reported that group 4 metallocenes when activated by methylaluminoxane were efficient catalysts for the polymerization of  $\alpha$ -olefins. Subsequently, it was found that bridging the two hapto ligands in the metallocene precursor produced catalysts which polymerized propylene in a stereospecific manner when activated with MAO.<sup>2</sup> A variety of bridges have been used in studies of these systems; however the most commonly used bridges are the methylene,<sup>3</sup> ethylene,<sup>2,4</sup> and dimethylsilylene<sup>5</sup> units.

Recently, Waymouth et al.<sup>6</sup> found that unbridged bis( $\eta^5$ -2-phenylindenyl)zirconium dichloride (**1**) activated with MAO produced elastomeric polypropylene. Elastomeric polypropylene was first reported by Natta in 1957,<sup>7</sup> and subsequently Chien et al.<sup>3b,8</sup> found that



elastomeric polypropylene could be produced using a bridged titanocene catalyst. The explanation by Rausch et al. for the production of elastomeric polypropylene is the existence of two separate catalytic sites. The aspecific site produces blocks of atactic polypropylene, while the isospecific site produces isotactic blocks. In the case of **1**, the formation of elastomeric polypropylene is thought to be due to the fact that two isomers of **1** are possible which can interconvert by rotation of the indenyl rings. The *meso*-like form produces atactic blocks of polypropylene while the *rac*-like form produces isotactic blocks.

In the present study, a series of unbridged bis(indenyl)zirconium and -titanium dichlorides containing phenyl and benzo substituents have been synthesized and evaluated as catalyst precursors for the polymerization of ethylene and propylene.

## Results and Discussion

**Synthesis of Catalyst Precursors.** The precursors **2b–4b** were prepared by the same general procedure (Scheme 1). The appropriately substituted indene was deprotonated with 1 equiv of butyllithium in diethyl ether solution, and  $1/2$  equiv of zirconium tetrachloride was added in the same solvent. Recrystallization of the complexes from either toluene or CH<sub>2</sub>Cl<sub>2</sub> gave **2b–4b** in 50–55% yield.

The complexes **5b** and **6b** were prepared by deprotonation of 2-methylbenz[e]indene (**5a**) in diethyl ether and toluene, respectively, followed by addition of  $1/2$

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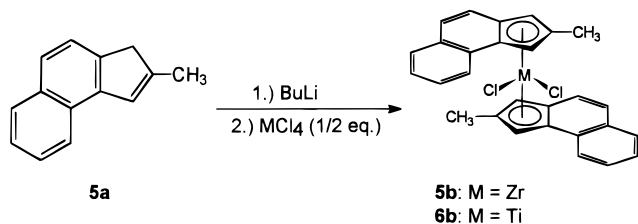
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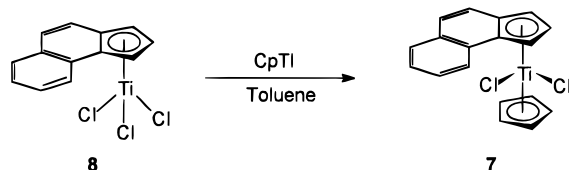
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Scheme 2



Scheme 3

Table 1. Polymerization of Ethylene with Precursors 2b–4b Activated with MAO<sup>a</sup>

compd	time (min)	10 <sup>-7</sup> A <sup>b</sup>	yield (g)	T <sub>m</sub> (°C)
<b>2b</b>	30	0.4	1.38	130.1
<b>3b</b> (isomer 1)	1	5.1	0.62	133.0
<b>3b</b> (isomer 2)	1	5.0	0.60	132.2
<b>4b</b>	1	8.8	1.05	134.7

<sup>a</sup> Polymerization conditions: [Zr] = 50 μM; Al/Zr = 4000:1; T<sub>p</sub> = 50 °C; 15 psi of C<sub>2</sub>H<sub>4</sub>. <sup>b</sup> Activity = g of PE/(mol of Zr·[C<sub>2</sub>H<sub>4</sub>]<sup>h</sup>).

equiv of MCl<sub>4</sub> (M = Zr, Ti) in the same solvent. Crystallization of the products from toluene gave **5b** and **6b** in 60% and 47% yield, respectively (Scheme 2).

The mixed-ring complex **7** was synthesized from 2-methylbenz[e]indenyltitanium trichloride (**8**), which we have previously reported,<sup>10</sup> and CpTi in toluene solution. Crystallization of the product from toluene gave **7** in 42% yield (Scheme 3).

**Polymerization Results.** Precursors **2b–4b** were activated with MAO and used to polymerize both ethylene and propylene. No visible polypropylene was produced by precursors **2b–4b**, and variation of polymerization conditions (i.e., temperature, concentration of catalyst, etc.) failed to produce any satisfactory result. However, precursors **2b–4b** are highly active catalysts for the polymerization of ethylene when activated by MAO (Table 1). Catalyst **2b**/MAO exhibited an activity of 4.0 × 10<sup>6</sup> g of PE/(mol Zr·[C<sub>2</sub>H<sub>4</sub>]<sup>h</sup>) at a polymerization temperature (T<sub>p</sub>) of 50 °C. When one of the phenyl rings in **2b** was replaced by a methyl group, two isomers of the desired complex (**3b**) were obtained. However, both isomers exhibited comparable polymerization behavior. The catalyst **3b**/MAO exhibited higher activity as compared to **2b**/MAO. In addition, the melting point (T<sub>m</sub>) of the polyethylene (PE) increased when **3b**/MAO was used as the catalyst. In order to further reduce steric factors at the C-3 position on the indenyl ring, the precursor **4b** was synthesized. The catalyst **4b**/MAO exhibited higher activity and T<sub>m</sub> of the PE produced as compared to both **2b**/MAO and **3b**/MAO. Therefore, a comparison of these catalyst systems shows that phenyl substitution on both the C-1 and C-3 positions leads to catalysts with lower activity and lower T<sub>m</sub> of PE, while removal of the steric bulk from the C-3 position increased both activity and T<sub>m</sub> of PE.

Table 2. Polymerization of Ethylene and Propylene with Precursors **5b**, **6b**, and **7** Activated by MAO or Triphenylcarbenium Tetrakis(pentafluorophenyl)borate (Trityl)/Triisobutylaluminum (TIBA)<sup>a</sup>

compd	monomer	cocatalyst	T <sub>p</sub> (°C)	yield (g)	10 <sup>-7</sup> A <sup>b</sup>	10 <sup>-5</sup> M <sub>w</sub> <sup>c</sup>
<b>5b</b>	C <sub>2</sub> H <sub>4</sub>	MAO	25	2.32	1.0	3.0
<b>5b</b>	C <sub>2</sub> H <sub>4</sub>	trityl/TIBA	25	3.02	1.3	
<b>5b</b>	C <sub>3</sub> H <sub>6</sub>	MAO	25	1.25	0.3	
<b>5b</b>	C <sub>3</sub> H <sub>6</sub>	trityl/TIBA	25	4.58	1.1	0.4
<b>5b</b>	C <sub>3</sub> H <sub>6</sub>	trityl/TIBA	0	6.76	1.2	5.0
<b>6b</b>	C <sub>2</sub> H <sub>4</sub>	trityl/TIBA	25	0.16	0.07	2.1
<b>6b</b>	C <sub>3</sub> H <sub>6</sub>	trityl/TIBA	0	trace		
<b>7</b>	C <sub>2</sub> H <sub>4</sub>	trityl/TIBA	25	4.18	1.8	
<b>7</b>	C <sub>3</sub> H <sub>6</sub>	trityl/TIBA	0	trace		

<sup>a</sup> For MAO polymerizations: [Zr] or [Ti] = 50 μM; Al/Zr or Ti = 4000:1; 15 psi of C<sub>2</sub>H<sub>4</sub> or C<sub>3</sub>H<sub>6</sub>. For trityl polymerizations: [Zr] or [Ti] = 50 μM; Al/Zr or Ti = 20:1; [Zr] or [Ti]/trityl = 1:1; 15 psi of C<sub>2</sub>H<sub>4</sub> or C<sub>3</sub>H<sub>6</sub>; time of polymerization = 15 min. <sup>b</sup> Activity = g of polymer/(mol of catalyst·[monomer]<sup>h</sup>·h). <sup>c</sup> Molecular weights determined by GPC.

Precursors **5b** and **6b** were activated using either MAO or triphenylcarbenium tetrakis(pentafluorophenyl)borate (trityl)/triisobutylaluminum. The catalysts **5b**/MAO and **5b**/trityl were both used to polymerize ethylene and propylene (Table 2). Both systems showed high activity for the polymerization of ethylene; however, in propylene polymerizations, **5b**/trityl exhibited higher activity than did the **5b**/MAO system (Table 2). The polypropylene (PP) produced by **5b**/trityl and **5b**/MAO was atactic as shown by <sup>13</sup>C NMR at both T<sub>p</sub> investigated. However, the molecular weight (M<sub>w</sub>) varied greatly at different T<sub>p</sub>. At T<sub>p</sub> = 25 °C, the catalyst **5b**/trityl had an activity of 1.1 × 10<sup>7</sup> g of PP/(mol Zr·[C<sub>3</sub>H<sub>6</sub>]<sup>h</sup>) and the M<sub>w</sub> of the PP was 0.4 × 10<sup>5</sup>. When T<sub>p</sub> was lowered to 0 °C, the activity of the catalyst **5b**/trityl was comparable to **5b**/trityl at 25 °C; however, the M<sub>w</sub> of the PP increased to 5.0 × 10<sup>5</sup>. The large increase in M<sub>w</sub> could be attributed to the fact that at lower temperature rotation of the haptic ligands is decreased allowing monomer coordination and insertion to proceed with less steric interaction. In addition, since β-hydride elimination requires a significant activation energy, lowering the T<sub>p</sub> should decrease the rate of β-hydride elimination and increase the molecular weight of the polymer.

The titanium-based catalyst system **6b**/trityl exhibited lower activity for the polymerization of ethylene and virtually no activity for propylene (Table 2). This phenomenon can be attributed to the smaller size of the titanium metal center as compared to the zirconium analog which would decrease the angle between the two bulky haptic ligands and make monomer coordination more difficult. Therefore, precursor **7** was synthesized in order to decrease the steric bulk around the metal center. For the polymerization of ethylene, the activity of **7**/trityl was 30 times that exhibited by **6b**/trityl under similar polymerization conditions (Table 2). However, only trace amounts of polypropylene were produced by **7**/trityl at various polymerization conditions.

## Experimental Section

**General Procedures.** Reactions were carried out under an argon atmosphere using standard Schlenk techniques. Methylaluminoxane (MAO) was purchased from Akzo, and all other reagents were purchased from Aldrich and used without

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further purification. Toluene, diethyl ether, tetrahydrofuran (THF), hexane, and pentane were distilled from Na/K alloy under argon. Methylene chloride and styrene were distilled from CaH<sub>2</sub>. **2a**,<sup>9</sup> **3a**,<sup>9</sup> **4a**,<sup>10</sup> **5a**,<sup>5d</sup> **8**,<sup>10</sup> and CpTi<sup>11</sup> were synthesized by literature procedures. <sup>1</sup>H NMR spectra were recorded on a Varian XL-200 or a Bruker NR-80 spectrometer. <sup>13</sup>C NMR spectra were recorded on a Bruker MSL-300 spectrometer. Elemental analyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA. The procedure used to polymerize ethylene and propylene has been reported in detail.<sup>12</sup>

**Bis( $\eta^5$ -1,3-diphenylindenyl)zirconium Dichloride (**2b**).** To a solution of 1,3-diphenylindene (**2a**) (3.33 g, 12.4 mmol) in diethyl ether (75 mL) at 0 °C was added 1.6 M butyllithium (7.8 mL, 12.4 mmol). The reaction mixture was warmed to room temperature and stirred overnight. The solvent was removed, and the solid residue was washed with pentane (2 × 20 mL) and dried in vacuo. The lithium salt was redissolved in diethyl ether (50 mL), the solution was cooled to 0 °C, and a suspension of ZrCl<sub>4</sub> (1.44 g, 6.18 mmol) in diethyl ether (10 mL) was added. The mixture was warmed to room temperature and stirred overnight. The suspension was filtered and the solid residue extracted with toluene. Concentration of the solvent and cooling to -20 °C gave **2b** (2.24 g, 52%) as orange crystals. <sup>1</sup>H NMR (C<sub>7</sub>D<sub>8</sub>):  $\delta$  7.85–7.37 (m, 8H, Ind-arom H), 7.09–6.79 (m, 20H, Ph), 6.69 (s, 2H, Ind-C<sub>5</sub>). Anal. Calcd for C<sub>42</sub>H<sub>30</sub>Cl<sub>2</sub>Zr: C, 72.39; H, 4.34. Found: C, 71.98; H, 4.77.

**Bis( $\eta^5$ -1-methyl-3-phenylindenyl)zirconium Dichloride (**3b**).** 1-Methyl-3-phenylindene (**3a**) (3.38 g, 16.4 mmol) was dissolved in diethyl ether (50 mL) and cooled to 0 °C. After addition of 1.6 M butyllithium (10.2 mL, 16.4 mmol), the solution was warmed to room temperature and stirred for 8 h. The reaction mixture was recooled to 0 °C, ZrCl<sub>4</sub> (1.91 g, 8.20 mmol) was added, and the solution was stirred overnight at room temperature. The suspension was filtered, and the solid residue was extracted with toluene. Concentration of the solvent and cooling to -20 °C gave a mixture of isomers of **3b** (2.52 g, 55%) as an orange-yellow powder. Anal. Calcd for C<sub>32</sub>H<sub>26</sub>Cl<sub>2</sub>Zr: C, 67.11; H, 4.58. Found: C, 66.83; H, 4.50. The mixture of isomers was separated by fractional crystallization

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from CH<sub>2</sub>Cl<sub>2</sub>. Isomer 1: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  7.74–7.23 (m, 18H, arom H), 6.10 (s, 2H, C<sub>5</sub>-H), 2.02 (s, 6H, CH<sub>3</sub>). Isomer 2: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  7.85–7.12 (m, 18H, arom H), 6.45 (s, 2H, C<sub>5</sub>-H), 2.18 (s, 6H, CH<sub>3</sub>).

**Bis( $\eta^5$ -1-phenylindenyl)zirconium Dichloride (**4b**).** Following the procedure described for **2b**, 3-phenylindene (**4a**) (2.50 g, 13.0 mmol), 1.6 M butyllithium (8.13 mL, 13.0 mmol), and ZrCl<sub>4</sub> (1.51 g, 6.50 mmol) gave **4b** (1.66 g, 47%) as yellow crystals. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.83–7.16 (m, 18H, arom H), 6.59 (d, 2H, C<sub>5</sub>-H), 6.03 (d, 2H, C<sub>5</sub>-H). Anal. Calcd for C<sub>30</sub>H<sub>22</sub>Cl<sub>2</sub>Zr: C, 66.16; H, 4.07. Found: C, 65.69; H, 3.88.

**Bis( $\eta^5$ -2-methylbenz[e]indenyl)zirconium Dichloride (**5b**).** Following the procedure described for **2b**, 2-methylbenz[e]indene (**5a**) (5.25 g, 29.1 mmol), 1.6 M butyllithium (18.2 mL, 29.1 mmol), and ZrCl<sub>4</sub> (3.38 g, 14.5 mmol) gave **5b** (5.40 g, 60%) as a yellow solid. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  8.08–7.11 (m, 12H, arom H), 6.67 (m, 2H, C<sub>5</sub>-H), 6.02 (m, 2H, C<sub>5</sub>-H), 1.92 (m, 6H, CH<sub>3</sub>). Anal. Calcd for C<sub>28</sub>H<sub>22</sub>Cl<sub>2</sub>Zr: C, 64.60; H, 4.23. Found: C, 64.82; H, 4.49.

**Bis( $\eta^5$ -2-methylbenz[e]indenyl)titanium Dichloride (**6b**).** To a solution of **5a** (3.79 g, 21.0 mmol) in toluene (75 mL) at 0 °C was added 1.6 M butyllithium (13.1 mL, 21.0 mmol). The solution was warmed to room temperature and stirred overnight. The reaction mixture was recooled to 0 °C, TiCl<sub>4</sub> (1.99 g, 10.5 mmol) was added via a syringe, and the solution was stirred overnight at room temperature. The suspension was filtered, and the solution was concentrated to 1/4 its original volume. Cooling to -20 °C gave **6b** (2.36 g, 47%) as a red solid. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.77–7.47 (m, 12H, arom H), 6.67 (m, 2H, C<sub>5</sub>-H), 6.02 (m, 2H, C<sub>5</sub>-H), 1.91 (m, 6H, CH<sub>3</sub>). Anal. Calcd for C<sub>28</sub>H<sub>22</sub>Cl<sub>2</sub>Ti: C, 70.46; H, 4.65. Found: C, 70.02; H, 4.71.

**( $\eta^5$ -Benz[e]indenyl)( $\eta^5$ -cyclopentadienyl)titanium Dichloride (**7**).** Benz[e]indenyltitanium trichloride (**8**) (300 mg, 0.94 mmol) was dissolved in toluene (40 mL), CpTi (253 mg, 0.94 mmol) was added, and the reaction mixture was stirred overnight. The resulting suspension was filtered to give a red solution and a gray solid. Concentration of the solution and cooling to -20 °C gave **7** (138 mg, 42%) as red crystals. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.25–7.58 (m, 6H, arom H), 7.06–7.02 (m, 2H, C<sub>5</sub>-H), 6.80 (m, 1H, C<sub>5</sub>-H), 6.16 (s, 5H, Cp). Anal. Calcd for C<sub>18</sub>H<sub>14</sub>Cl<sub>2</sub>Ti: C, 61.93; H, 4.04. Found: C, 61.28; H, 3.97.

OM960519X