

Synthesis and Catalytic Application of Homo-bimetallic Metallocene Complexes as Ethylene Polymerization Catalysts[†]

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Three new homo-bimetallic metallocene complexes were prepared by RCpMC_3 ($M = \text{Ti}, \text{Zr}$) and Si-bridged compounds, and were all well characterized structurally. These complexes with the methylaluminoxane (MAO) are highly active catalysts for the polymerization of ethylene. Compared to the polyethylene obtained by Cp_2ZrCl_2 , the molecular weight ($M_w = 78784\text{—}238021$) of the polyethylene was higher and the molecular weight distribution ($M_w/D = 2.10\text{—}2.44$) was broader.

Keywords bimetallic, zirconium, titanium, metallocene, catalysis, polyethylene

Introduction

It is well known that metallocenes activated with methylaluminoxane (MAO) are highly active homogeneous Ziegler-Natta catalysts that produce polyolefin with controlled stereoregularity and narrow molecular weight distribution,¹⁻⁴ however, the molecular weight of the polymer produced by metallocene catalyst is less than that by traditional catalytic system. Moreover, the molecular weight distribution of the polymer produced by metallocene catalyst is so narrow that causes some disadvantages on the processability, such as the high shear viscosity and low melt extensional viscosity of the product. In order to over-

come those problems, some combined metallocene catalysts such as $\text{Cp}_2\text{TiCl}_2/\text{Cp}_2\text{ZrCl}_2$ have been studied.⁵

In recent years, much attention has been focused on the formation of bimetallic metallocene complexes for their special features. Cooperative effect may exist between two metal centers that allow electronic interaction via ligand. So bimetallic catalytic system will give different behaviors compared with the mononuclear complex.⁶⁻¹⁴

In our previous work, it is testified that titanocene with different substituents on Cp has high activity in the polymerization of olefins.^{15,16} In the present research, we combined two metals in one complex in order to study the behaviors of different complexes on the polymerization of ethylene. The synthesis and the polymerization catalytic behaviors of some new homo-bimetallic Metallocene are reported.

Results and discussion

Synthesis of complexes 1—3

The reaction of the known compound $\text{Me}_2\text{Si}(\text{C}_5\text{H}_5)_2$ with *n*-BuLi (2 equiv.) in hexane produced $\text{Li}_2[\text{Me}_2\text{Si}(\text{C}_5\text{H}_5)_2]$, which was separated as white powder.⁶ The

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general method to prepare complexes **1** and **2** was that RCpTiCl_3 (2 equiv.) reacted with $\text{Li}_2[(\text{Me}_2\text{Si})(\text{C}_5\text{H}_5)_2]$ in toluene and refluxed for 20 h (Scheme 1).

Since the two central metals in complex **3** have different coordination environment, complex **3** can not be prepared directly from the reaction of RCpZrCl_3 with $\text{Li}_2[(\text{Me}_2\text{Si})(\text{C}_5\text{H}_5)_2]$, but from the reaction of $\text{CH}_3\text{CpZrCl}_3 \cdot \text{DME}$ and compound **A**, which was synthesized by the method of literature.⁸

The structures of these complexes were well characterized by ^1H NMR, MS, IR and EA. They are soluble in CH_2Cl_2 and toluene, and are sensitive to air and moisture.

Ethylene polymerization

The synthesized bimetallic complexes were used as main catalyst for the homogeneous polymerization of ethylene. The catalytic system was formed by mixing the complex with excess of MAO.

All complexes gave high catalytic activity (1.03×10^5 — 3.09×10^5 gPE/molCat·h). Under the same condi-

tions, the activities of Cp_2TiCl_2 and Cp_2ZrCl_2 are 1.03×10^5 gPE/molCat·h and 2.33×10^5 gPE/molCat·h, respectively. The results of polymerization are shown in Table 1 and Figs. 1—4.

All these complexes gave high activity for the polymerization of ethylene. Under the conditions of experiment, the activities of these complexes are higher than or near to that of Cp_2TiCl_2 and Cp_2ZrCl_2 .

The molecular weight and molecular weight distribution of the polymer generated from the bimetallic complexes were different from those obtained from Cp_2ZrCl_2 ($M_w = 24956$; $M_wD = 1.69$). The molecular weight (78784—238021) is much higher and the molecular weight distribution (2.10—2.44) is broader. When complex **2** with MAO was used as the catalytic system, the molecular weight distribution (2.44) of the polymer is the broadest. We assume that there is more than one active site or dormant during the polymerization process. This phenomenon was also observed by Ushioda *et al.*⁸ in 1996 and they gave the explanation that more than one active site was living in the polymerization process.

Scheme 1

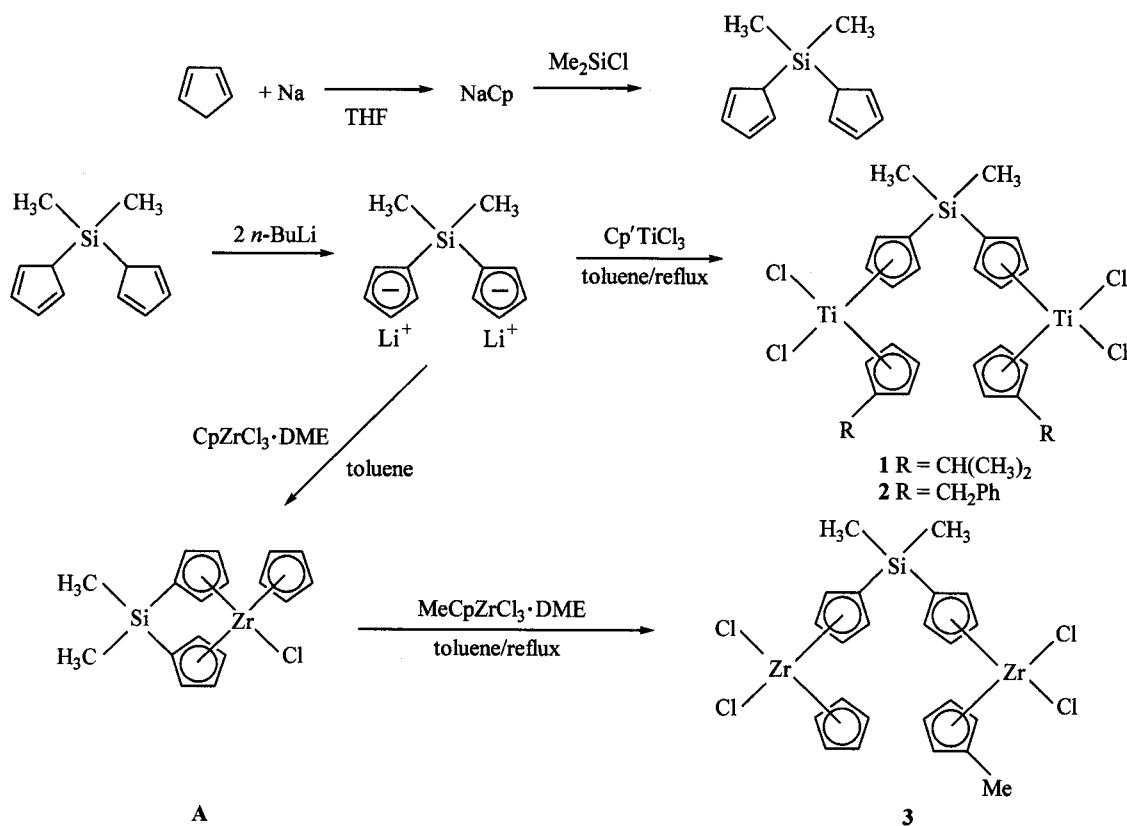
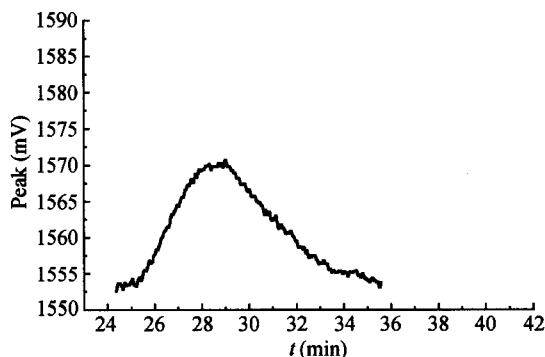
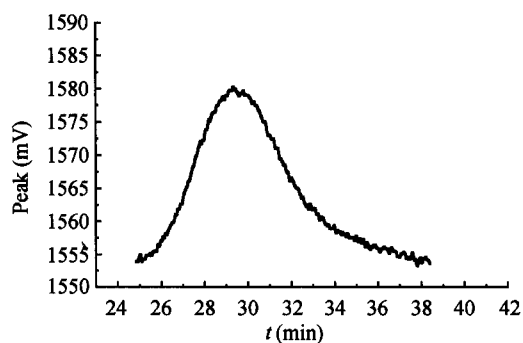
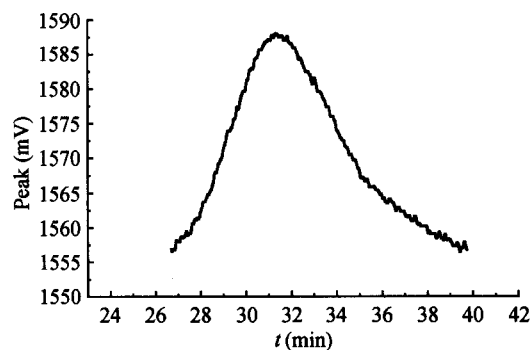
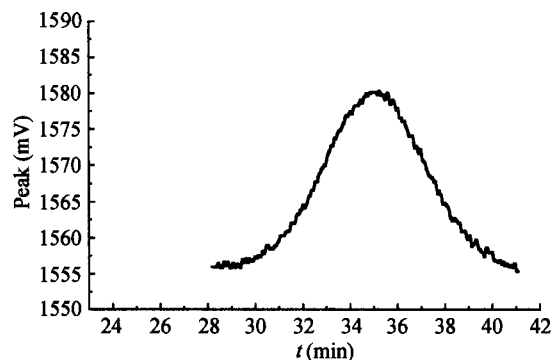


Table 1 Results of ethylene polymerization by complexes 1—3^a

No.	Cat.	A (10 ⁵ gPE/molCat·h)	Mn ^b	Mw ^c	Mw/Mn
1	1	1.03	69129	168812	2.44
2	2	2.44	113533	238021	2.10
3	3	3.09	36427	78784	2.16
4	Cp ₂ ZrCl ₂	2.33	14731	24956	1.69
5	Cp ₂ TiCl ₂	1.03			

^a Conditions: Al/M = 500, T = 60 °C, t = 60 min, V = 25 mL, n_{Cat.} = 0.004 mmol. ^b Number average molecular weight, determined by GPC. ^c Weight average molecular weight, determined by GPC.

**Fig. 1** GPC of polymerization of ethylene by complex 1.**Fig. 2** GPC of polymerization of ethylene by complex 2.**Fig. 3** GPC of polymerization of ethylene by complex 3.**Fig. 4** GPC of polymerization of ethylene by complex Cp₂ZrCl₂.

When complex 1 with MAO was used as the catalytic system, the molecular weight of the polymer was about 10 times that produced using Cp₂ZrCl₂, up to 238021 g/mol. It implied that the use of bimetallic catalytic system in the polymerization would result in the increase of the molecular weight of the polymer.

Experimental

All operations were carried out under a dry argon atmosphere using standard Schlenk techniques. Toluene, diethyl ether, tetrahydrofuran (THF) and hexane were refluxed over sodium/benzophenone ketyl, from which

they were distilled prior to use. Polymerization-grade ethylene was purified before use. The titanium complex RCpTiCl₃ was prepared by the reaction of RCpSiMe₃ with TiCl₄ in toluene according to the reported method.¹⁷ The zirconium complex RCpZrCl₃·DME was prepared from RCpSiMe₃ with ZrCl₄·2Me₂S according to the method as the literature described.¹⁷

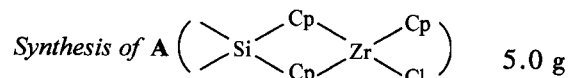
¹H NMR spectra was recorded in CDCl₃ on a Bruker Avance-500 MHz. IR data were collected on a Nicolet Magna-IR550 (KBr). Mass spectral data (EI) were collected on a Hewlett-Packard model 5989A instrument. EA data were collected on EA-1106.

Synthesis of catalysts

Synthesis of complex 1 263 mg of $\text{Li}_2[\text{Me}_2\text{Si}(\text{C}_5\text{H}_5)_2]$ (1.30 mmol) was dissolved in 70 mL of toluene. Then 560 mg of $(\text{CH}_3)_2\text{CHCpTiCl}_3$ (2.14 mmol) was added to the solution. The reaction mixture was refluxed at 140 °C for 20 h. The solution was then filtered and concentrated *in vacuo* to 1/2 *V*. The filtrate was cooled to -20 °C to give orange solid which was then recrystallized with toluene/hexane to afford complex 1 as brown crystals. 324 mg, yield 54.6%, m. p. 224 °C; $^1\text{H NMR}$ (CDCl_3 , 500 MHz) δ : 6.83 (t, $J = 2.4$ Hz, 4H), 6.57 (t, $J = 2.4$ Hz, 4H), 6.36 (t, $J = 2.6$ Hz, 4H), 6.31 (t, $J = 2.6$ Hz, 4H), 3.22–3.25 (m, 2H), 1.21 (d, $J = 7.0$ Hz; 12H), 0.62 (s, 6H); IR (KBr) ν : 3442.0, 3113.2, 2961.6, 2869.8, 1491.2, 1454.3, 1412.6, 1390.9, 1373.2, 1316.8, 1251.5, 1182.5, 1086.8, 1055.9, 1041.2, 960.4, 925.9, 899.3, 874.8, 849.5, 836.1, 818.6, 792.1, 672.7, 641.0, 621.8 cm^{-1} ; MS (70 eV) m/z (%): 566 ($\text{M}^+ - 2\text{Cl}$, 29), 531 ($\text{M}^+ - 3\text{Cl}$, 8), 304 ($\text{M}^+ - \text{TiCl}_2[\text{C}_3\text{H}_7\text{Cp}] - \text{C}_3\text{H}_7\text{Cp}$, 70), 269 ($\text{M}^+ - \text{TiCl}_2[\text{C}_3\text{H}_7\text{Cp}] - \text{C}_3\text{H}_7\text{Cp} - \text{Cl}$, 69), 234 ($\text{M}^+ - \text{TiCl}_2[\text{C}_3\text{H}_7\text{Cp}] - \text{C}_3\text{H}_7\text{Cp} - 2\text{Cl}$, 100), 225 ($\text{TiCl}_2[\text{C}_3\text{H}_7\text{Cp}]$, 30), 110 ($\text{TiCl}[\text{C}_3\text{H}_7\text{Cp}]$, 17). Anal. calcd for $\text{C}_{28}\text{H}_{36}\text{Cl}_4\text{SiTi}_2$: C 52.69, H 5.69; found C 52.64, H 5.85.

Synthesis of complex 2 239.2 mg of $\text{Li}_2[\text{Me}_2\text{Si}(\text{C}_5\text{H}_5)_2]$ (1.20 mmol) was dissolved in 70 mL of toluene. Then 603.8 mg of $\text{PhCH}_2\text{CpTiCl}_3$ (1.95 mmol) was added to the solution. The reaction mixture was refluxed at 140 °C for 20 h. The solution was then filtered and concentrated *in vacuo* to 1/2 *V*. The filtrate was cooled to -20 °C to give red solid which was then recrystallized with toluene/hexane to afford complex 2 as red crystals. 370.2 mg, yield 51.7%, m. p. 190–192 °C; $^1\text{H NMR}$ (CDCl_3 , 500 MHz) δ : 7.31–7.20 (m, 10H), 6.84 (d, $J = 2.3$ Hz, 4H), 6.50 (t, $J = 2.3$ Hz, 4H), 6.37 (t, $J = 2.5$ Hz, 4H), 6.30 (t, $J = 2.5$, 4H), 4.10 (s, 4H), 0.63 (s, 6H); IR (KBr) ν : 3442.2, 3111.6, 3059.5, 3027.1, 2922.1, 2852.7, 1601.2, 1582.7, 1550.5, 1491.9, 1451.7, 1424.4, 1411.6, 1381.0, 1371.7, 1315.9, 1251.9, 1179.2, 1070.9, 1053.5, 1040.7, 827.7, 896.5, 873.6, 852.3, 834.6, 818.9, 790.6, 767.6, 698.4,

673.7, 641.6, 613.6 cm^{-1} ; MS (70 eV) m/z (%): 662 ($\text{M}^+ - 2\text{Cl}$, 2), 395 ($\text{M}^+ - \text{CpTiCl}_2[\text{CpCH}_2\text{Ph}]$, 13), 304 ($\text{M}^+ - \text{TiCl}_2[\text{CpCH}_2\text{Ph}] - \text{CpCH}_2\text{Ph}$, 44), 273 ($\text{TiCl}_2[\text{CpCH}_2\text{Ph}]$, 100), 269 ($\text{M}^+ - \text{TiCl}_2[\text{CpCH}_2\text{Ph}] - \text{CpCH}_2\text{Ph} - \text{Cl}$, 36), 240 ($\text{M}^+ - \text{CpTiCl}_2[\text{CpCH}_2\text{Ph}] - \text{CpCH}_2\text{Ph}$, 23), 238 ($\text{TiCl}[\text{CpCH}_2\text{Ph}]$, 64), 91 (C_7H_7 , 7). Anal. calcd for $\text{C}_{36}\text{H}_{36}\text{Cl}_4\text{SiTi}_2$: C 58.88, H 4.94; found C 58.44, 5.15.



of $\text{Me}_2\text{Si}(\text{C}_5\text{H}_5)_2$ (26.6 mmol) was dissolved in 80 mL of hexane, and then 53.2 mmol of *n*-BuLi was added dropwise. This mixture was stirred overnight. After solvents removed, 150 mL of toluene was added. $\text{CpZrCl}_3 \cdot \text{DME}$ (9.36 g) was added to the system, and the mixture was stirred at room temperature overnight. The resulting yellow solution was then filtered from solid residues, which were extracted with CH_2Cl_2 (50 mL \times 2). The combined filtrate was concentrated under reduced pressure and cooled to -20 °C to give pale yellow crystals of compound A.

Synthesis of complex 3 513.7 mg of complex A (1.40 mmol) was dissolved in 70 mL of toluene and then added 530 mg of $\text{CH}_3\text{CpZrCl}_3 \cdot \text{DME}$ (1.40 mmol). The reaction mixture was refluxed at 160 °C for 20 h. The solution was then filtered and concentrated *in vacuo* to 1/2 *V*. The filtrate was cooled to -20 °C to give white solid and then recrystallized with CH_2Cl_2 /hexane to afford complex 3 as white crystals. 123.6 mg, yield 13.6%, m. p. 200 °C (decomposed); $^1\text{H NMR}$ (CDCl_3 , 500 MHz) δ : 6.72 (d, $J = 2.2$ Hz, 2H), 6.70 (t, $J = 2.2$ Hz, 2H), 6.56 (d, $J = 2.2$ Hz, 2H), 6.54 (t, $J = 2.2$ Hz, 2H), 6.40 (s, 5H), 6.21 (t, $J = 2.2$ Hz, 2H), 6.12 (d, $J = 2.2$ Hz, 2H), 2.27 (s, 3H), 0.65 (s, 6H); IR (KBr) ν : 3387.0, 3107, 2961.3, 2922.0, 1495.4, 1441.9, 1409.5, 1370.4, 1254.7, 1178.3, 1094.1, 1040.1, 908.6, 816.4, 672.8, 648.4; MS (70 eV) m/z (%): 615 ($\text{M}^+ - \text{Cl}$, 11), 580 ($\text{M}^+ - 2\text{Cl}$, 11), 571 ($\text{M}^+ - \text{MeCp}$, 18), 376 ($\text{M}^+ - \text{ZrCl}_2\text{MeCp} - \text{Cl}$, 4), 311 ($\text{M}^+ - \text{ZrCl}_2\text{MeCp} - \text{Cl} - \text{Cp}$, 100), 276 ($\text{M}^+ - \text{ZrCl}_2\text{MeCp} - 2\text{Cl} - \text{Cp}$, 8), 225 (ZrCl_2Cp , 7). Anal. calcd for $\text{C}_{23}\text{H}_{26}\text{Cl}_4\text{SiZr}_2$: C 42.19, H 4.00; found C 41.92, H 4.22.

Polymerization of ethylene

Ethylene was purified by passage through 0.4 nm molecular sieves and Mn sieves. Polymerizations were carried out in a reactor placed in a thermostatically heated bath and equipped with a magnetic stirrer.

Methylaluminoxane (MAO), toluene solution of metallocene and more toluene to bring the final volume to 25 mL were added to the reactor in that sequence. The reaction mixture was stirred vigorously at 60 °C and pre-dried ethylene at atmospheric pressure was pumped in for a certain time. The polymerization was quenched by venting the ethylene and adding a small amount of ethanol. The contents of the flask were transferred to a beaker and was adjusted to pH 7 using HCl. The polymer was then separated from the solution and then dried *in vacuo* at 60 °C to constant weight.

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