

Synthesis of Mixed-ring Zirconocene Complexes Containing Alkenyl Group and Ethylene Polymerization Catalyzed with Them

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Four new mixed-ring zirconium complexes, $[\text{CH}_2 = \text{CH}(\text{CH}_2)_n\text{-C}_5\text{H}_4](\text{RC}_3\text{H}_4)\text{ZrCl}_2$ [$n = 1$, $\text{R} = \text{CH}_3\text{OCH}_2\text{CH}_2$ (3); $n = 2$, $\text{R} = \text{CH}_3\text{OCH}_2\text{CH}_2$ (4); $n = 2$, $\text{R} = \text{Me}_3\text{Si}$ (5); $n = 2$, $\text{R} = \text{allyl}$ (6)], have been prepared by the reaction of $\text{CH}_2 = \text{CH}(\text{CH}_2)_n\text{C}_5\text{H}_4\text{ZrCl}_3 \cdot \text{DME}$ [$n = 1$ (1); $n = 2$ (2)] with $\text{RC}_3\text{H}_4\text{Li}$. When activated with methylaluminoxane (MAO), the catalytic activities of the above complexes in ethylene polymerization were tested. Complexes 5 and 6 show high activities similar to Cp_2ZrCl_2 . Introduction of methoxyethyl group into Cp-ligand dramatically decreases the catalytic activities of complexes 3 and 4, which can be overcome by increasing the amount of MAO. For complex 5, the dependence of activity and molecular weight (M_n) on the Al/Zr ratio, the polymerization time (t_p), polymerization temperature (T_p) and the polymerization solvent volume (V) was investigated.

Keywords zirconocene, ethylene polymerization, alkenyl group, methoxyethyl group, catalyst

Introduction

In recent years, Group 4 zirconocenes that possess alkenyl group in Cp, Ind or bridged-atom have been studied very intensively. The presence of the double bond in the side chain allows further reactions (such as halide addition,^{1,2} hydroboration,³⁻⁵ hydrosilylation,^{6,7} coupling reaction^{8,9}) and self-immobilization of the catalysts during the polymerization, which could overcome the polymer fouling of the inter surfaces of the reactor and improve the polymer properties.¹⁰⁻¹⁴

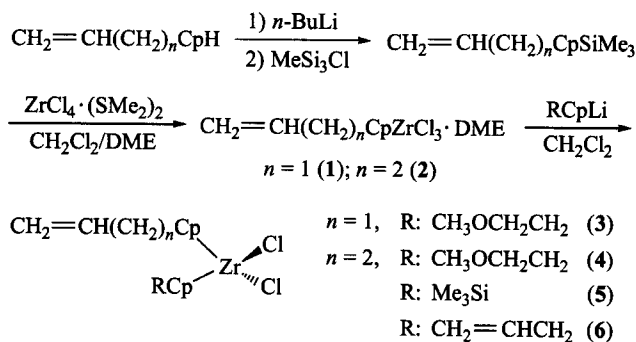
Until now, compared with ansa/non-ansa alkenyl-substituted indenyl zirconium complexes,¹⁰⁻¹⁶ there were fewer studies on ethylene polymerization with alkenylcyclopentadienyl zirconium complexes.^{16,17} Here we report on the preparation of some new mixed-ring zirconocene complexes containing alkenyl group. Special emphasis is placed on catalytic activities using such compounds as precursors in ethylene polymerization.

Results and discussion

Synthesis of catalyst precursors

As shown in Scheme 1, the reaction of alkenylcyclopentadienyltrimethylsilane with $\text{ZrCl}_4 \cdot (\text{SMe}_2)_2$ in $\text{CH}_2\text{Cl}_2/\text{DME}$ gave the alkenylcyclopentadienyl zirconium trichlorides (1, 2), which can be recrystallized from DME/ n -hexane as white crystals in 62%—69% yields. Treatment of a CH_2Cl_2 solution of 1 or 2 with one equivalent of $\text{RC}_3\text{H}_4\text{Li}$ led to the formation of the desired mixed-ring zirconocene (3—6), which can be easily recrystallized from hot n -hexane as white or pale yellow crystals with yields from 51% to 65%.

Scheme 1



Complexes 1 to 6 are characterized by elemental analysis, ¹H NMR, IR and mass spectra. ¹H NMR spectra: the resonance for hydrogen of vinyl and methoxyl does not shift to higher field (low frequency). IR spectra: complexes show a band at 1620—1640 cm⁻¹ due to an uncoordinated ν_{C=C} and a band at 1100—1120 cm⁻¹ due to an uncoordinated ν_{C-O}. These phenomena indicate that the C = C bond of alkenyl group and the oxygen of methoxyethyl group in complexes 1 to

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6 are not coordinated to the metal center.^{18,19} EI MS spectra: the molecular ion peaks do not appear for all complexes **1** to **6**, indicating that they are not stable to heat, and easily to fall off chlorine, substituent group or Cp-moiety during electron impact ionization.

Polymerization results

Table 1 summarizes the results of ethylene polymerization at the polymerization temperature of 50 °C. Complexes **5** to **8** show high activities of ethylene polymerization, whose activities are on the same order as that of the parent complex Cp₂ZrCl₂/MAO system. The reason for the difference of the catalytic activities is not very clear. It may be caused by the existence of diffusion-controlled processes during the polymerization because of the higher catalyst concentrations.²⁰ In addition, the molecular weights of polyethylenes made by using complexes **5** to **8** as catalyst are higher than that with Cp₂ZrCl₂. It reflects that the introduction of substituent group into Cp-moiety can block the chain-termination reaction.

Complexes **3** and **7** containing allyl group show higher activities than complexes **4** and **8** containing 3-butenyl group, respectively. In general, substituent groups in Cp-moiety have an important effect on polymerization activities through both electronic and steric effects. Owing to the similar electronic effects of allyl and 3-butenyl groups, their steric effects perhaps play a key role in activities. Because 3-butenyl group has a longer chain length and a more flexible chain than allyl group, the steric hindrance of 3-butenyl group is larger. We previously reported that the activity of (CH₂=CHCH₂CH₂C₅H₄)₂ZrCl₂ is higher than that of (CH₂=CHCH₂CH₂CH₂C₅H₄)₂ZrCl₂.¹⁷ It indicates that the activity decreased with longer chain lengths of the ω-alkenyl group. A similar result has been observed in the literature.¹⁶ For indenyl zirconium complexes, they often exhibited the opposite trend.¹⁰⁻¹⁶

Introduction of methoxyethyl group into Cp-ligand dramatically decreases the catalytic activities of complexes **3** and **4** due to the strong coordination of oxygen atom to zirconium cation, which blocks ethylene coordination to the metal center. On increasing the Al/Zr ratio from 1000 to 3000, the

activity of complexes **3** is enhanced 5 times (Run 1, Run 2). It indicates that increasing the amount of MAO could weaken the ability of coordination between oxygen atom and zirconium cation, because Lewis-acidic aluminium centers of MAO can coordinate to the Lewis-basic oxygen atom of methoxyethyl group.

For complexes **3** and **5**, we further determined the corresponding GPC data of polymers. It was found that a broader molecular weight distribution of the polymer made with complex **3** (MWD = 4.11) was obtained at the Al/Zr ratio of 1000, compared with complex **5** (MWD = 1.71). There maybe exist two active centers in complex **3**/MAO system like in Me₂Si[Cp(*i*-Pr₂NC₂H₄Cp)]ZrCl₂/MAO system.²¹ A more detailed research about the influence of oxygen-containing substituent group on the catalytic properties is now in progress.

The dependence of the activities and molecular weights (*M*_η) on the Al/Zr ratio, the polymerization time (*t*_p), polymerization temperature (*T*_p) and the polymerization solvent volume (*V*) with complex **5** was investigated and presented in Figs. 1–4, respectively. Increasing the Al/Zr ratio from 500 to 2000 leads to an increase of the activity, and a decrease in *M*_η due to aggravation of chain transfer reaction at high Al/Zr ratio (Fig. 1). Similar results have been reported elsewhere.^{17,22}

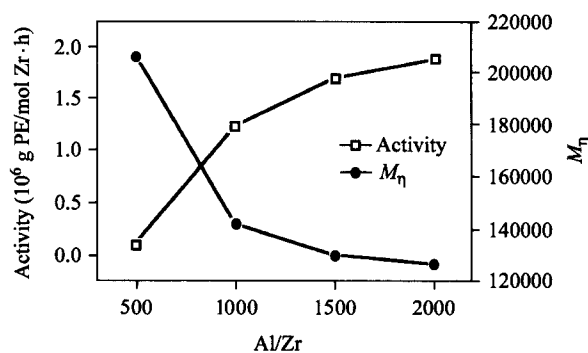


Fig. 1 Dependence of the activity and *M*_η on the Al/Zr ratio with the complex **5**. Condition: [Zr] = 0.1 mmol/L, 50 °C for 0.5 h, *V* = 25 mL.

Table 1 Ethylene polymerization results^a

Run	Catalyst	Al/Zr	PE (g)	Activity ^b	<i>M</i> _η
1	3	1000	0.0740	0.592	
2	3	3000	0.3654	2.92	408000
3	4	1000	0.0511	0.409	198000
4	5	1000	1.5561	12.4	142000
6	6	1000	1.3752	11.0	91000
7	(CH ₂ =CHCH ₂ C ₅ H ₄) ₂ ZrCl ₂ (7)	1000	1.6813	13.4	131000
8	(CH ₂ =CHCH ₂ CH ₂ C ₅ H ₄) ₂ ZrCl ₂ (8)	1000	1.5244	12.2	104000
9	Cp ₂ ZrCl ₂	1000	1.5799	12.6	66000

^a Polymerization conditions: [Zr] = 0.1 mmol/L, *p* = 0.1 MPa, *T*_p = 50 °C for 0.5 h, *V* = 25 mL (toluene); ^b unit in 10⁵ g PE/(mol Zr·h)

As shown in Fig. 2, a maximum activity was reached after a short induction time, thereafter the activity decreased. On the other hand, M_n increased with increasing reaction time at 50 °C.

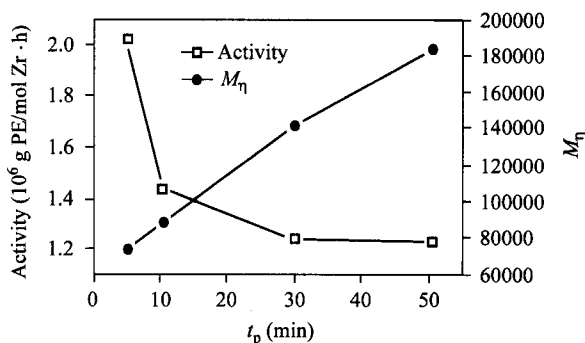


Fig. 2 Dependence of the activity and M_n on the polymerization time with the complex **5**. Condition: $[Zr] = 0.1$ mmol/L, Al/Zr = 1000, 50 °C, $V = 25$ mL.

Fig. 3 clearly indicates that the highest activity was obtained at 65 °C, below and above which the activity decreases due to the lower propagation rate and the thermal instability of the active species. In addition, temperature has a large effect on M_n because of β -H elimination. Increasing temperature from 30 °C to 80 °C decreases M_n from 469500 to 283000.

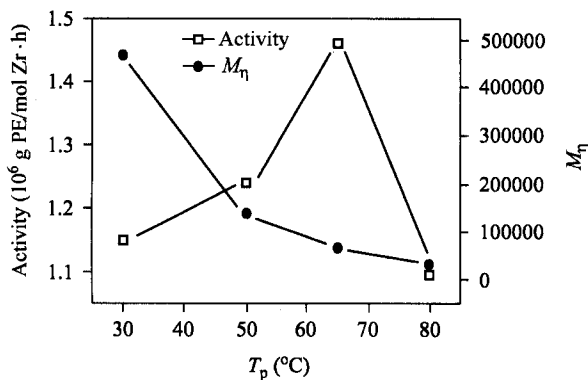


Fig. 3 Dependence of the activity and M_n on the polymerization temperature with the complex **5**. Condition: $[Zr] = 0.1$ mmol/L, Al/Zr = 1000, 0.5 h, $V = 25$ mL.

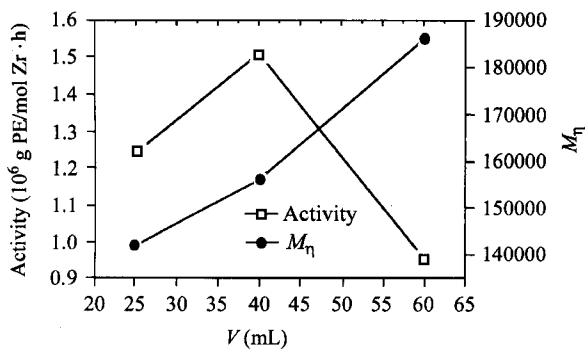


Fig. 4 Dependence of the activity and M_n on the polymerization solvent volume with the complex **5**. Condition: $n(Zr) = 2.5 \times 10^{-6}$ mol, Al/Zr = 1000, 50 °C for 0.5 h.

From Fig. 4, the highest activity is observed at the polymerization solvent volume of 40 mL, and M_n enhances with increasing polymerization volume, which indicates that the ratio between the rates of propagation and termination is influenced by the polymerization volume.

Experimental

General procedures

All manipulations were carried out under a dry argon atmosphere using standard Schlenk techniques. Solvents were purified by distillation over sodium benzophenone (diethyl ether, THF, toluene and *n*-hexane) and CaH_2 (CH_2Cl_2). MAO was purchased from Akzo. $CH_2 = CHCH_2C_5H_4SiMe_3$,²³ $CH_2 = CHCH_2CH_2C_5H_5$,²⁴ $CH_3OCH_2CH_2C_5H_4Li$,¹⁹ $(CH_2 = CHCH_2C_5H_4)_2ZrCl_2$,²⁵ and $(CH_2 = CHCH_2CH_2C_5H_4)_2ZrCl_2$ ²⁶ were synthesized by using reported methods. Cp_2ZrCl_2 was used as received. The general procedure for the preparation of complexes **1** and **2** was carried out as that in the literature.²⁷

Mass spectra were measured on an HP5989A spectrometer. IR spectra were recorded on a Nicolet FTIR 5SXC spectrometer. 1H NMR spectra were measured on a Varian GRMNI-300A NMR spectrometer using tetramethylsilane (TMS) as an internal standard. Elemental analyses were performed by Shanghai Institute of Organic Chemistry. Melting points were uncorrected.

Synthesis of $CH_2 = CHCH_2CH_2C_5H_4SiMe_3$

A solution of 42.3 mL of *n*-BuLi (0.0656 mol, 1.55 mol/L) was added dropwise to a THF (100 mL) solution of 7.87 g (0.0656 mol) of 3-butenylcyclopentadiene at 0 °C. The solution was allowed to warm to room temperature and stirred for 3 h. Then 8.4 mL (0.0656 mol) of chlorotrimethylsilane was added dropwise to the stirred solution at r. t., and the mixture was stirred for 2 h. The solution was filtered and the solvent was removed under vacuum. The residual oil was distilled at 83–85 °C/1.2 kPa to give 9.65 g (77%) of pale yellow oil. 1H NMR ($CDCl_3$) δ : 0.02–0.17 [m, 9H, Si(CH_3)₃], 2.30–2.36 (m, 2H, CH_2), 2.53 (t, $J = 7.2$ Hz, 2H, CH_2Cp), 3.28 (s, 1H, Cp), 4.97–5.10 (m, 2H, $CH_2 =$), 5.84–5.97 (m, 1H, $CH =$), 6.13–6.50 (m, 3H, Cp).

Synthesis of $CH_2 = CHCH_2C_5H_4ZrCl_3 \cdot DME$ (**1**)

To a stirred suspension of $ZrCl_4$ (4.67 g, 20 mmol) in 60 mL of dichloromethane was added Me_2S (2.75 g, 44 mmol) at 0 °C. To the resulting clear solution was then added dropwise 3.58 g (20 mmol) of $CH_2 = CHCH_2C_5H_4SiMe_3$. The solution was allowed to warm to room temperature, and stirred overnight. The mixture was filtered, and the filtrate was evaporated to dryness under vacuum. The solid was recrystallized with DME/*n*-hexane to yield 5.43 g (69%) of white needle

crystals. M.p. 121 °C (dec.); $^1\text{H NMR}$ (CDCl_3) δ : 3.62 (d, $J = 6.5$ Hz, 2H, CH_2), 3.81 (br. s, 6H, OCH_3), 4.03 (br. s, 4H, OCH_2), 5.06–5.11 (m, 2H, $\text{CH}_2 =$), 5.95–6.08 (m, 1H, $\text{CH} =$), 6.44 (s, 2H, Cp), 6.55 (s, 2H, Cp); IR (KBr) ν : 3102 (m), 2977 (m), 2935 (m), 2842 (w), 1638 (m), 1614 (m), 1492 (w), 1450 (w), 1429 (m), 1244 (w), 1194 (w), 1072 (m), 1042 (m), 994 (w), 914 (m), 842 (m), 742 (w) cm^{-1} ; MS m/z (%): 355 ($\text{M}^+ - \text{Cl}$, 4), 300 ($\text{M}^+ - \text{DME}$, 6), 265 ($\text{M}^+ - \text{Cl} - \text{DME}$, 36). Anal. calcd for $\text{C}_{12}\text{H}_{19}\text{Cl}_3\text{O}_2\text{Zr}$: C 36.69, H 4.87; found C 36.37, H 4.87.

Synthesis of $\text{CH}_2 = \text{CHCH}_2\text{CH}_2\text{C}_5\text{H}_4\text{ZrCl}_3 \cdot \text{DME}$ (2)

White crystal, yield 62%, m.p. 82–84 °C; $^1\text{H NMR}$ (CDCl_3) δ : 2.41–2.49 (m, 2H, CH_2), 3.02 (t, $J = 7.6$ Hz, 2H, CH_2Cp), 3.92 (brs, 6H, OCH_3), 4.14 (brs, 4H, OCH_2), 5.03–5.12 (m, 2H, $\text{CH}_2 =$), 5.83–5.98 (m, 1H, $\text{CH} =$), 6.49 (s, 2H, Cp), 6.58 (s, 2H, Cp); IR (KBr) ν : 3100 (m), 2915 (m), 1640 (m), 1613 (m), 1494 (w), 1452 (m), 1284 (w), 1250 (w), 1183 (w), 1065 (m), 1012 (m), 971 (m), 917 (m), 839 (m), 658 (w) cm^{-1} ; MS m/z (%): 279 ($\text{M}^+ - \text{Cl} - \text{DME}$, 15), 244 ($\text{M}^+ - 2\text{Cl} - \text{DME}$, 9), 55 (C_4H_7^+ , 39). Anal. calcd for $\text{C}_{13}\text{H}_{21}\text{Cl}_3\text{O}_2\text{Zr}$: C 38.37, H 5.20; found C 38.39, H 5.27.

Synthesis of $(\text{CH}_2 = \text{CHCH}_2\text{C}_5\text{H}_4)(\text{CH}_3\text{OCH}_2\text{CH}_2\text{C}_5\text{H}_4)\text{ZrCl}_2$ (3)

To a THF solution (30 mL) of **1** (1.31 g, 3.334 mmol) was added dropwise a THF solution of $\text{CH}_3\text{OCH}_2\text{CH}_2\text{C}_5\text{H}_4\text{Li}$ (6.1 mL, 0.5501 mol/L) at -30 °C. The solution was allowed to warm to room temperature, and stirred overnight. The solvent was removed under vacuum, and the residue was taken up in hot *n*-hexane (80 mL) and filtered. Cooling the filtrate at 0 °C afforded the desired product as white needle crystals (yield 0.66 g, 51%). M.p. 65–67 °C; $^1\text{H NMR}$ (CDCl_3) δ : 2.92 (t, $J = 6.3$ Hz, 2H, CH_2), 3.35 (s, 3H, CH_3O), 3.42 (d, $J = 6.6$ Hz, 2H, CH_2), 3.59 (t, $J = 6.3$ Hz, 2H, CH_2O), 5.06–5.10 (m, 2H, $\text{CH}_2 =$), 5.88–5.96 (m, 1H, $\text{CH} =$), 6.23 (t, $J = 2.6$ Hz, 2H, Cp), 6.29 (t, $J = 2.6$ Hz, 2H, Cp), 6.32 (t, $J = 2.6$ Hz, 2H, Cp), 6.34 (t, $J = 2.6$ Hz, 2H, Cp); IR (KBr) ν : 3098 (m), 2925 (m), 2882 (m), 2844 (m), 1635 (m), 1493 (m), 1462 (w), 1429 (m), 1376 (w), 1244 (w), 1208 (w), 1157 (w), 1111 (s), 1076 (w), 1033 (m), 994 (m), 907 (m), 881 (s), 821 (m), 736 (w), 686 (w) cm^{-1} ; MS m/z (%): 357 ($\text{M}^+ - \text{OCH}_3$, 44), 353 ($\text{M}^+ - \text{Cl}$, 100), 283 ($\text{M}^+ - \text{C}_3\text{H}_5\text{Cp}$, 58), 265 ($\text{M}^+ - \text{CH}_3\text{OCH}_2\text{CH}_2\text{Cp}$, 8), 248 ($\text{M}^+ - \text{Cl} - \text{C}_3\text{H}_5\text{Cp}$, 17). Anal. calcd for $\text{C}_{16}\text{H}_{20}\text{Cl}_2\text{OZr}$: C 49.22, H 5.16; found C 49.11, H 5.21.

Synthesis of $(\text{CH}_2 = \text{CHCH}_2\text{CH}_2\text{C}_5\text{H}_4)(\text{CH}_3\text{OCH}_2\text{CH}_2\text{C}_5\text{H}_4)\text{ZrCl}_2$ (4)

The same procedure as described for **3** was used. The compound **2** (1.66 g, 4.080 mmol) and $\text{CH}_3\text{OCH}_2\text{CH}_2\text{C}_5\text{H}_4\text{Li}$ (7.4 mL, 0.5501 mol/L) were reacted to give 0.85 g (52%) of a pale yellow flat crystal. M.p. 68–70 °C; $^1\text{H NMR}$ (CDCl_3) δ : 2.30–2.35 (m, 2H, CH_2), 2.75 (t, $J = 7.8$ Hz, 2H, CH_2Cp), 2.92 (t, $J = 6.3$ Hz, 2H, CH_2Cp), 3.35 (s, 3H, CH_3O), 3.59 (t, $J = 6.3$ Hz, 2H, CH_2O), 4.98–5.05 (m, 2H, $\text{CH}_2 =$), 5.78–5.86 (m, 1H, $\text{CH} =$), 6.23 (t, $J = 2.7$ Hz, 2H, Cp), 6.29 (t, $J = 2.7$ Hz, 2H, Cp), 6.31–6.32 (m, 4H, Cp); IR (KBr) ν : 3092 (m), 2927 (m), 2882 (m), 2841 (w), 1637 (w), 1492 (m), 1434 (m), 1419 (w), 1243 (w), 1208 (w), 1157 (w), 1113 (s), 1074 (w), 1050 (w), 1032 (m), 992 (m), 878 (w), 840 (s), 816 (m), 685 (w), 638 (w) cm^{-1} ; MS m/z (%): 371 ($\text{M}^+ - \text{OCH}_3$, 43), 367 ($\text{M}^+ - \text{Cl}$, 100), 283 ($\text{M}^+ - \text{C}_4\text{H}_7\text{Cp}$, 36), 248 ($\text{M}^+ - \text{Cl} - \text{C}_4\text{H}_7\text{Cp}$, 8). Anal. calcd for $\text{C}_{17}\text{H}_{22}\text{Cl}_2\text{OZr}$: C 50.48, H 5.48; found C 50.56, H 5.66.

Synthesis of $(\text{CH}_2 = \text{CHCH}_2\text{CH}_2\text{C}_5\text{H}_4)(\text{Me}_3\text{SiC}_5\text{H}_4)\text{ZrCl}_2$ (5)

The same procedure as described for **3** was used. The compound **2** (1.59 g, 3.909 mmol) and $\text{Me}_3\text{SiC}_5\text{H}_4\text{Li}$ (7.8 mL, 0.5064 mol/L) were reacted to give 1.05 g (65%) of white crystals. M.p. 90–92 °C; $^1\text{H NMR}$ (CDCl_3) δ : 0.44 [s, 9H, $\text{Si}(\text{CH}_3)_3$], 2.27–2.32 (m, 2H, CH_2), 2.73 (t, $J = 7.6$ Hz, 2H, CH_2Cp), 4.95–5.02 (m, 2H, $\text{CH}_2 =$), 5.75–5.83 (m, 1H, $\text{CH} =$), 6.17 (t, $J = 2.7$ Hz, 2H, Cp), 6.27 (t, $J = 2.7$ Hz, 2H, Cp), 6.49 (t, $J = 2.5$ Hz, 2H, Cp), 6.67 (t, $J = 2.5$ Hz, 2H, Cp); IR (KBr) ν : 3106 (w), 3077 (w), 2953 (w), 2930 (w), 2889 (w), 1640 (w), 1410 (w), 1369 (w), 1246 (m), 1174 (w), 1046 (m), 995 (w), 915 (m), 905 (m), 838 (s), 825 (s), 759 (m), 637 (w), 553 (w) cm^{-1} ; MS m/z (%): 401 ($\text{M}^+ - \text{CH}_3$, 100), 381 ($\text{M}^+ - \text{Cl}$, 18), 297 ($\text{M}^+ - \text{C}_4\text{H}_7\text{Cp}$, 27), 279 ($\text{M}^+ - \text{Me}_3\text{SiCp}$, 50). Anal. calcd for $\text{C}_{17}\text{H}_{24}\text{Cl}_2\text{SiZr}$: C 48.78, H 5.78; found C 48.63, H 5.72.

Synthesis of $(\text{CH}_2 = \text{CHCH}_2\text{CH}_2\text{C}_5\text{H}_4)(\text{CH}_2 = \text{CHCH}_2\text{C}_5\text{H}_4)\text{ZrCl}_2$ (6)

The same procedure as described for **3** was used. The compound **2** (1.20 g, 2.949 mmol) and $\text{CH}_2 = \text{CHCH}_2\text{C}_5\text{H}_4\text{Li}$ (7.2 mL, 0.4128 mol/L) were reacted to give 0.85 g (55%) of a pale yellow flat crystal. M.p. 58–60 °C; $^1\text{H NMR}$ (CDCl_3) δ : 2.30–2.34 (m, 2H, CH_2), 2.75 (t, $J = 7.5$ Hz, 2H, CH_2Cp), 3.42 (d, $J = 6.2$ Hz, 2H, CH_2Cp), 4.98–5.10 (m, 4H, $\text{CH}_2 =$), 5.78–5.85 (m,

¹H, CH=), 5.88—5.96 (m, 1H, CH=), 6.23 (s, 4H, Cp), 6.30 (d, *J* = 3.3 Hz, 2H, Cp), 6.33 (d, *J* = 3.3 Hz, 2H, Cp); IR (KBr) ν : 3104 (m), 2975 (w), 2923 (m), 2852 (w), 1639 (m), 1488 (w), 1420 (m), 1384 (w), 1365 (w), 1043 (m), 992 (m), 911 (m), 837 (s), 818 (s), 742 (w), 568 (w) cm^{-1} ; MS *m/z* (%): 349 ($\text{M}^+ - \text{Cl}$, 53), 279 ($\text{M}^+ - \text{C}_3\text{H}_5\text{Cp}$, 100), 265 ($\text{M}^+ - \text{C}_4\text{H}_7\text{Cp}$, 80), 243 ($\text{M}^+ - \text{HCl} - \text{C}_3\text{H}_5\text{Cp}$, 39), 229 ($\text{M}^+ - \text{HCl} - \text{C}_4\text{H}_7\text{Cp}$, 67). Anal. calcd for $\text{C}_{17}\text{H}_{20}\text{Cl}_2\text{Zr}$: C 52.83, H 5.22; found C 52.77, H 5.12.

Ethylene polymerization

Ethylene polymerization was carried out in a Schlenk bottle equipped with a magnetic stirrer. MAO, toluene solution of catalyst and toluene were sequentially injected, and the bottle was placed in an oil bath at the desired polymerization temperature. The reaction was initiated by piping pre-dried ethylene into the solution at atmospheric pressure. After 30 min, the polymerization was terminated by the addition of acidified ethanol. The resultant precipitate was collected by filtration, washed with ethanol, and dried under vacuum at 80 °C for 5 h to give polyethylene.

The molecular-weight (M_η) determination of the polyethylene samples was performed using an Ubbelohde precision capillary viscometer in decalin at $(135 \pm 0.1) \text{ }^\circ\text{C}$ ²⁸ as $[\eta] = 6.77 \times 10^{-4} M_\eta^{0.67}$

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