Synthesis of hetero-bimetallic metallocene complexes and their catalytic activities for ethylene polymerization

Jiling Huang [a], Zuofeng Feng [a], Hong Wang [a], Yanlong Qian [a,*], Junquan Sun [b], Yongjin Xu [b], Wei Chen [c], Gang Zheng [c]

[a] *Laboratory of Organometallic Chemistry, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, PR China*
[b] *Department of Chemical Engineering, Zhejiang University, Hangzhou 310027, PR China*
[c] *Research Institute of Petroleum Processing, SINOPEC, 18 Xueyuan Road, Beijing 100083, PR China*

Abstract

Five new hetero-bimetallic metallocene complexes were synthesized by the reaction of $RCpTiCl_3$ and a Si-bridged zirconocene complex in refluxing toluene. They were all well characterized. These complexes activated with methylaluminoxane (MAO) are highly active catalysts for the polymerization of ethylene. The molecular weight ($M_w = 28{,}957$–$124{,}089$) and the molecular weight distribution (MWD = 2.04–3.01) of the polymer generated from the bimetallic catalytic system were higher than that obtained by Cp_2ZrCl_2.
© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Bimetallic; Zirconium; Titanium; Metallocene; Catalysis; Polyethylene

1. 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 distributions of the polymer produced by metallocene catalyst are so narrow to cause some disadvantages on the processability, such as the high shear viscosity and low melt extensional viscosity of the product. In order to overcome those problems, some combined metallocene catalysts, such as Cp_2TiCl_2/Cp_2ZrCl_2 [5] have been studied.

On the other hand, another method to solve this problem is to combine two different metal centers in one complex.

In recent years, much attention has been focused on the formation of bimetallic metallocene complexes due to their special features. Cooperative effect may exist between the two metal centers that allow electronic interaction via the ligands, therefore, behaving differently in catalysis when compared with the mononuclear complex [6–14].

In our previous work, we found that differentially substituted cyclopentadienyl (Cp) titanocenes gave good result on the polymerization of olefins [15,16]. In the present research, we combined two metals (Ti and Zr) with different substituent groups in one complex in order to study their behaviors on the polymerization of ethylene.

* Corresponding author. Fax: +86-21-6470-2573.
E-mail address: qianling@online.sh.cn (Y. Qian).

We report here the synthesis and polymerization behaviors of these new hetero-bimetallic metallocenes, which combine the effects of having two active centers and also the influence of having different substituent groups on the Cp ligand.

2. Results and discussion
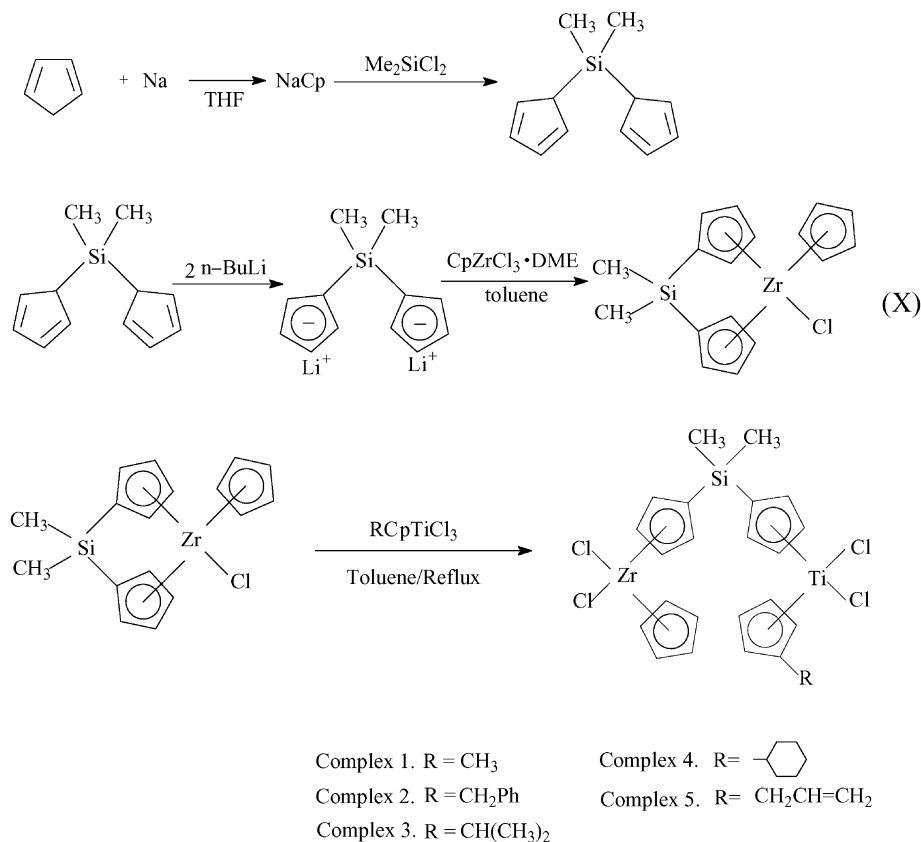
2.1. Synthesis of complexes 1–5

The general method to prepare complexes 1–5 is the reaction of 1 eq. of RCpTiCl$_3$ with complex (X) in refluxing toluene. Complex (X) was synthesized by the procedure described by Ushioda et al. [8]. The titanium complexes RCpTiCl$_3$ were synthesized from the reaction of RCpSiMe$_3$ with TiCl$_4$ in toluene as reported in the literature [19].

The reaction of the known compound Me$_2$Si(C$_5$H$_5$)$_2$ with 2 eq. of *n*-BuLi in hexanes produced Li$_2$[Me$_2$Si (C$_5$H$_4$)$_2$], which was separated as a white powder. Subsequent reaction of this dilithium salt with 1 eq. of CpZrCl$_3$·DME in toluene provided complex (X) as yellow crystals (Scheme 1).

All these complexes were characterized by ^{1}HNMR, MS, IR and EA. They are soluble in CH$_2$Cl$_2$ and toluene, and are sensitive to air and moisture.

2.2. Ethylene polymerization

The synthesized bimetallic complexes are suitable as catalysts for the polymerization of olefins and were used for the homogeneous polymerization of ethylene. The catalytic system was formed by mixing the complex with an excess of MAO.

Complex 1. R = CH$_3$
Complex 2. R = CH$_2$Ph
Complex 3. R = CH(CH$_3$)$_2$
Complex 4. R = ⬡
Complex 5. R = CH$_2$CH=CH$_2$

Scheme 1. Complexes 1–5 were synthesized by the reaction of complex (X) with RCpTiCl$_3$ in refluxing toluene, at 140 °C. Pure products were obtained by recrystallization from toluene/hexane.

Table 1
The result of ethylene polymerization by complexes (1–5)

Number	Catalyst	A (10^5 gPE/mol cat h)	M_n[a]	M_w[b]	M_w/M_n
1	1	1.87	30894	93137	3.01
2	2	8.15	11211	28957	2.58
3	3	2.39	37201	109024	2.93
4	4	1.89	44120	124089	2.81
5	5	2.80	15999	32641	2.04
6	Cp_2ZrCl_2	2.33	14731	24956	1.69
7	Cp_2TiCl_2	1.03	–	–	–

Conditions: Al/M = 500, $T = 60\,°C$, $t = 60\,min$, $V = 25\,ml$, catalyst = 0.004 mmol.
[a] Number average molecular weight, determined by GPC.
[b] Weight average molecular weight, determined by GPC.

The result of ethylene polymerization using these bimetallic complexes (1–5) is shown in Table 1 and Figs. 1–6. All complexes gave high catalytic activity ((1.87–8.15) × 10^5 gPE/mol cat h). Under

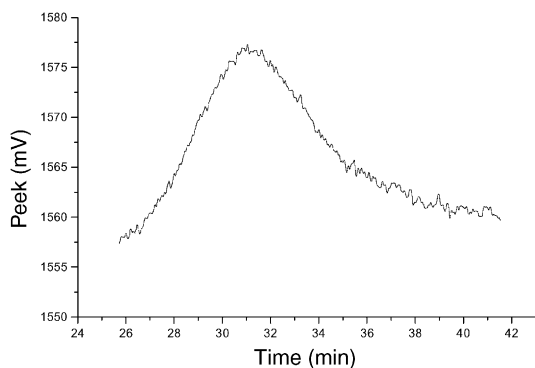Fig. 3. GPC of polymerization of ethylene by complex 3.

Fig. 1. GPC of polymerization of ethylene by complex 1.

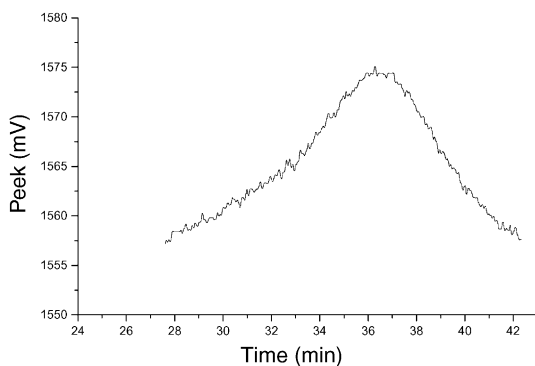Fig. 4. GPC of polymerization of ethylene by complex 4.
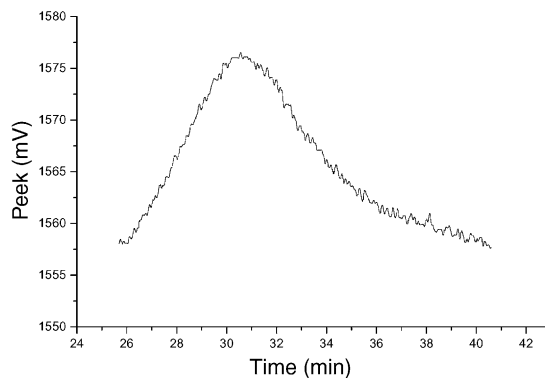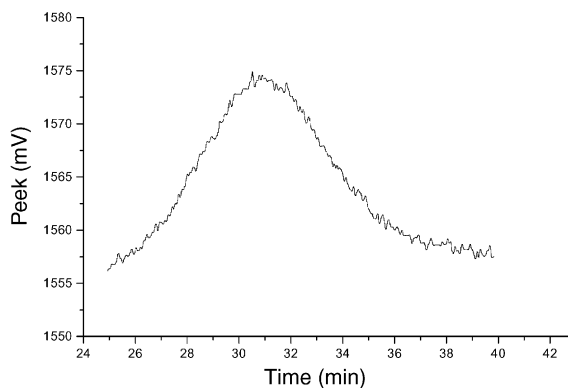

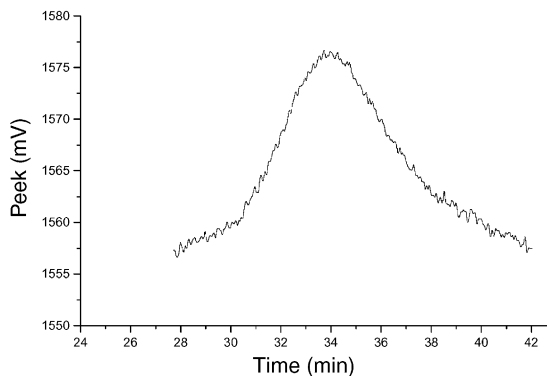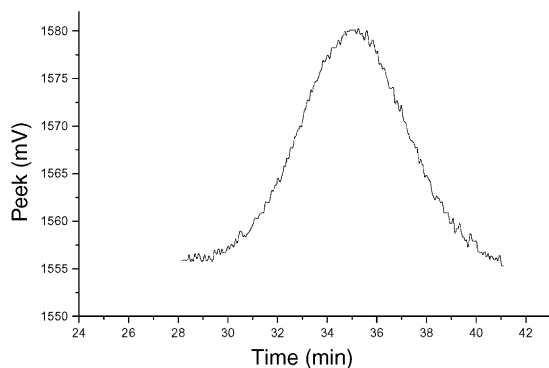Fig. 2. GPC of polymerization of ethylene by complex 2.

Fig. 5. GPC of polymerization of ethylene by complex 5.

Fig. 6. GPC of polymerization of ethylene by complex Cp.

the same conditions, the activity of Cp_2TiCl_2 is 1.03×10^5 gPE/mol cat h and the activity of Cp_2ZrCl_2 is 2.33×10^5 gPE/mol cat h.

All the complexes gave high activity for the polymerization of ethylene. Under similar experimental conditions, the title complexes show activities varying between that of Cp_2TiCl_2 and Cp_2ZrCl_2. This illustrates the interaction between the two metal centers. The activity is highest when R is benzyl (complex 2, $A = 8.15 \times 10^5$ gPE/mol cat h).

The molecular weight and molecular weight distribution of the polymer generated from the bimetallic complexes were different from that obtained from Cp_2ZrCl_2 ($M_w = 24956$; MWD = 1.69). The molecular weight (28,957–124,089) is much higher and the

molecular weight distribution (2.04–3.01) is broader. When complex 1 and MAO were used as the catalytic system, the molecular weight distribution (3.01) of the polymer is highest. We assume that there is more than one active site or dormain during the polymerization process. When complexes 3 or 4 with MAO were used as the catalytic system, the molecular weight of the polymer is about five times that produced using Cp_2ZrCl_2. This is a new catalytic system for the production of high molecular weight polymers.

There is an interesting observation that at higher activity levels M_w is lower. The lower M_w indicate higher rate of β-hydride elimination. We think that this higher rate constant for the β-hydride elimination is the result of the different electronic environments of the metal sites. The electron withdrawing effect of one metal center reduces the electron density on the Cp ligand at the adjacent metal center. This in turn the reduced electron density at the other metal center resulting in higher rate of β-hydride elimination [13].

From the result of polymerization, we observe that different substituent groups on the Cp would influence the polymerization behaviors remarkably. In general, unsaturated substituent group (benzyl or allyl) on Cp would improve the activity of polymerization. We think that the electronic distribution on the Cp ring was affected by the unsaturated substituent group. Consequently, the coordination atmosphere around the metal center was satisfied.
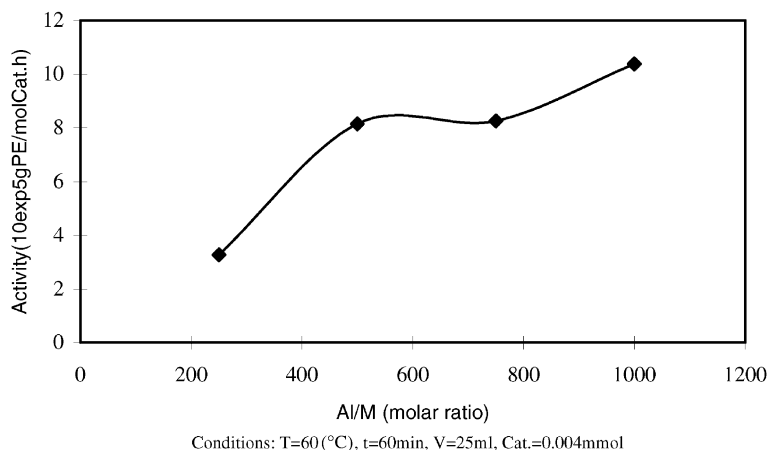

Conditions: T=60 (°C), t=60min, V=25ml, Cat.=0.004mmol

Fig. 7. The effect of Al/M to the polymerization of ethylene.

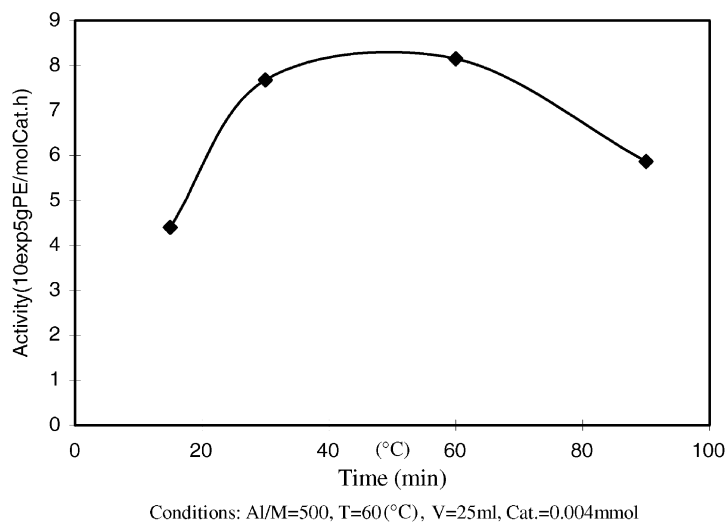Conditions: Al/M=500, T=60(°C), V=25ml, Cat.=0.004mmol

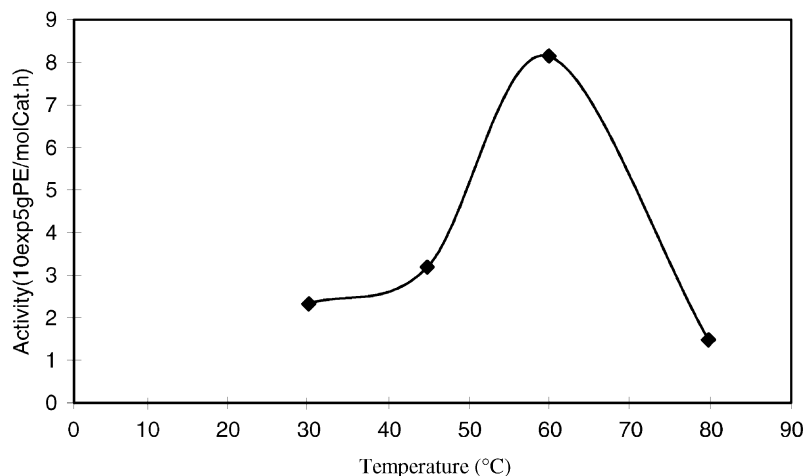Fig. 8. The effect of time to the polymerization of ethylene.

When the substituent groups are benzyl (complex 2) and allyl (complex 5), the activity (A) is somewhat higher ($A_2 = 8.15 \times 10^5$ gPE/mol cat h, $A_5 = 2.80 \times 10^5$ gPE/mol cat h). The benzyl substituted complex 2 show the highest activity. We used complex 2 to test the effect of different condition on the polymerization of ethylene. The conditions varied in our study are MAO/metal (Al/M) molar ratio, time of polymerization, temperature and pressure of ethylene monomer.

The dependence of activity (A) on the Al/M molar ratio is presented in Fig. 7. There is a direct relationship between A and Al/M. The figure shows an initial steep slope at Al/M = 250–500 that later normalized as Al/M reached 500–1000. This implies that for practical purpose Al/M molar ratio roughly 500 is ideal for polymerization, any further increase will have very little impact on activity as we can see increasing Al/M molar ratio from 500 to 1000 only increases the activity from 8.15–10.38 $\times 10^5$ gPE/mol cat h, i.e. less than 25% increment for a 100% increase in Al/M molar ratio. This fact was observed by other researchers and Koltzenburg [17] gave the explanation that it is due to the mechanism of chain termination under different aluminum concentrations. From Fig. 7 we can also ascribe the slowing of rate of activity with an increase in Al/M molar ratio to over-alkylation, which drastically deactivates the metal centers [18].

The result of the effect of time on polymerization is presented in Fig. 8. From the figure it can be seen that catalyst activity increases with time up to a maximum (roughly 1 h) after which a steady decline ensues, due probably to deactivation of catalyst. Jüling et al. [13] reported one bimetallic metallocene, when used as the catalyst for the propene polymerization observed that the polymerization rate decreased rapidly in a few minutes after initiation. Compared to their system, the catalytic system we have employed was much more stable. The length of time over which the catalyst was stable is very impressive and is very important for an industrial application of the system.

The result on variation of activity with temperature is presented in Fig. 9. From where it is obvious that 60 °C is an optimum point below or above which the activity is lower. We supposed that the catalytic system was not stable under high temperature, so the activity decreased when the temperature was above 60 °C.

In order to fully understand the effect of all variants on the polymerization, we carried out a study on the role of variation in pressure and the result is presented in Table 2. Keeping all other conditions constant, it is clear that activity increases directly with pressure. Increased pressure generally implies much more monomer, since more monomer

Conditions: Al/M=500, t=60min, V=25ml, Cat.=0.004mmol

Fig. 9. The effect of temperature to the polymerization of ethylene.

Table 2
Effect of pressure to the polymerization of ethylene

Number	Al/M	Pressure (atm)	A (10^5 gPE/mol cat h)
1	500	1	8.15
2	500	6	9.73
3	1000	1	7.52
4	1000	6	10.90

Conditions: $T = 65\,°C$, $t = 60\,min$, $V = 50\,ml$.

is converted per mole of catalyst by increasing the pressure, i.e. making more monomer available for polymerization.

3. Experimental section

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. $Cp'TiCl_3$ was prepared by the reaction of $Cp'SiMe_3$ with $TiCl_4$ in toluene according to literature methods [19]. $CpZrCl_3·DME$ was prepared by literature methods [19].

^1H NMR was recorded in $CDCl_3$ on a Bruker AVANCHE500 500 MHz NMR spectrometer. 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 was recorded from an EA-1106 elemental analyzer.

3.1. Synthesis of catalysts

3.1.1. Synthesis of complex X ($>Si<^{Cp}_{Cp}>Zr<^{Cp}_{Cl}$)
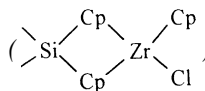
Me_2SiCp_2 (5.0 g, 26.6 mmol) was dissolved in 80 ml hexane, and then 0.0532 mol n-BuLi was added dropwise. This mixture was stirred overnight. After removal of volatiles, 150 ml toluene was added. $CpZrCl_3·DME$ (9.36 g) was then added to the system, and the mixture was stirred at room temperature overnight. The resulting yellow solution was then filtered from solid residues, which was further extracted with CH_2Cl_2 (50 ml × 2 ml). The combined filtrate was concentrated under reduced pressure and cooled to $-20\,°C$ to give pale yellow crystals of compound X.

3.1.2. Synthesis of complex 1 ($R = CH_3$)

A mixture of compound X (511.3 mg, 1.35 mmol) and $CH_3CpTiCl_3$ (315.2 mg, 1.35 mmol) was refluxed in toluene (80 ml) for 20 h. The solution was then filtered and concentrated in vacuo to half the original volume. The filtrate was cooled to $-20\,°C$ to

afford complex 1 as brown crystals (362.3 mg). Yield: 44.5%.

^{1}HNMR: 6.83 (t, $J = 2.4$, 2H); 6.74 (t, $J = 2.4$, 2H); 6.59 (m, 4H); 6.43 (s, 5H); 6.31 (t, $J = 2.6$, 2H); 6.22 (t, $J = 2.6$, 2H); 2.35 (s, 3H); 0.64 (s, 6H).

IR: 3423.3w, 3104.5m, 2957.4w, 2920.2w, 2855.3w, 1499.7w, 1445.0w, 1409.1m, 1371.5w, 1351.9w, 1248.0m, 1176.3m, 1042.7m, 1017.6w, 933.4w, 905.7w, 818.6s, 781.6s, 730.0w, 675.9w.

MS: 573 (26.06, $M^{\bullet+}$–Cl); 543 (9.61, $M^{\bullet+}$–Cp); 538 (16.42, $M^{\bullet+}$–2Cl); 528 (12.05, $M^{\bullet+}$–MeCp); 313 (59.43, $M^{\bullet+}$–ZrCl$_2$Cp–2Cl); 311 (54.61, $M^{\bullet+}$–TiCl$_2$CpMe–Cl–Cp); 269 (56.24, $M^{\bullet+}$–ZrCl$_2$Cp–Cl–MeCp); 234 (100, $M^{\bullet+}$–ZrCl$_2$Cp–2Cl–MeCp); 225 (8.55, ZrCl$_2$Cp); 79 (10.67, MeCp).

E.A. calculated: C 45.17%; H 4.29%; found: C 45.19%; H 4.29%.

3.1.3. Synthesis of complex 2 (R = CH$_2$Ph)

A mixture of compound X (512.7 mg, 1.35 mmol) and PhCH$_2$CpTiCl$_3$ (419.2 mg, 1.35 mmol) was refluxed in toluene (80 ml) for 20 h. The solution was then filtered and concentrated in vacuo to half the original volume. The filtrate was cooled to $-20\,^\circ$C to afford complex 2 as a red solid (354.2 mg). Yield: 38.2%.

^{1}HNMR: 7.32–7.17 (m, 5H); 6.82 (t, $J = 2.3$, 2H); 6.74 (t, $J = 2.3$, 2H); 6.56 (t, $J = 2.2$, 2H); 6.50 (t, $J = 2.2$, 2H); 6.44 (s, 5H); 6.32 (d, $J = 2.2$, 2H); 6.29 (d, $J = 2.2$, 2H); 4.10 (s, 2H); 0.65 (s, 6H).

IR: 3442.8m, 3104.8m, 3024.4w, 2958.1w, 2923.1m, 2852.5w, 1736.9w, 1640.5w, 1600.9w, 1582.5w, 1492.8m, 1449.6m, 1409.8m, 1369.5m, 1351.2w, 1252.1s, 1175.7m, 1068.7w, 1039.8m, 900.1w, 814.5s, 788.6m, 728.5w, 702.3m, 674.2m

MS: 650 (7.05, $M^{\bullet+}$–Cl +1); 529 (12.79, $M^{\bullet+}$–CpCH$_2$Ph); 346 (51.16, $M^{\bullet+}$–TiCl$_2$[CpCH$_2$Ph]–Cp); 311(100, $M^{\bullet+}$–TiCl$_2$[CpCH$_2$Ph]–Cl–Cp); 269 (45.02, $M^{\bullet+}$–ZrCl$_2$Cp–Cl–CpCH$_2$Ph); 234 (50.45, $M^{\bullet+}$–ZrCl$_2$Cp–2Cl–CpCH$_2$Ph); 225 (23.26, ZrCl$_2$Cp); 155 (19.34, CpCH$_2$Ph).

E.A. calculated: C 50.65%; H 4.41%; found: C 50.60%; H 4.60%.

3.1.4. Synthesis of complex 3 [R = CH(CH$_3$)$_2$]

A mixture of compound X (792.7 mg, 2.09 mmol) and (CH$_3$)$_2$CHCpTiCl$_3$ (546.2 mg, 2.09 mmol) was refluxed in toluene (80 ml) for 20 h. The solution was then filtered and concentrated in vacuo to half the original volume. The filtrate was cooled to $-20\,^\circ$C to afford complex 3 as a red solid (323.5 mg). Yield: 24.2%.

^{1}HNMR: 6.80 (t, $J = 2.4$, 2H); 6.74 (t, $J = 2.4$, 2H); 6.58–6.56 (m, 4H); 6.43 (s, 5H); 6.32–6.30 (m, 4H); 3.23 (m, 1H); 1.21 (d, $J = 7.0$, 6H); 0.64 (s, 6H).

IR: 3422.4w, 3105.2m, 2959.5m, 2923.9w, 2869.3w, 1491.9w, 1442.4w, 1408.1m, 1369.7w, 1317.7w, 1249.0m, 1175.7m, 1153.0w, 1073.0w, 1041.8m, 1018.3m, 907.1w, 817.5s, 782.4m, 730.7m, 673.7m.

MS: 601 (52.18, $M^{\bullet+}$–Cl); 529 (41.58, $M^{\bullet+}$–C$_3$H$_7$Cp); 566 (29.80, $M^{\bullet+}$–2Cl); 376 (9.54, $M^{\bullet+}$–ZrCl$_2$Cp–Cl); 341 (14.84, $M^{\bullet+}$–ZrCl$_2$Cp–2Cl); 311 (100, $M^{\bullet+}$–TiCl$_2$[C$_3$H$_7$Cp]–Cl–Cp); 304 (20.73, $M^{\bullet+}$–ZrCl$_2$Cp–C$_3$H$_7$Cp); 276 (7.89, $M^{\bullet+}$–TiCl$_2$[C$_3$H$_7$Cp]–2Cl–Cp); 269 (73.62, $M^{\bullet+}$–ZrCl$_2$Cp–Cl–C$_3$H$_7$Cp); 234 (61.72, $M^{\bullet+}$–ZrCl$_2$Cp–Cl–C$_3$H$_7$Cp) 225 (50.41, ZrCl$_2$Cp); 107 (30.86, C$_3$H$_7$Cp).

E.A. calculated: C 46.95%; H 4.74%; found: C 46.76%; H 4.90%.

3.1.5. Synthesis of complex 4 (R = –⬡)

A mixture of compound X (530.4 mg, 1.41 mmol) and (hexamethyleneCp)TiCl$_3$ (423.1 mg, 1.40 mmol) was refluxed in toluene (80 ml) for 20 h. The solution was then filtered and concentrated in vacuo to half the original volume. The filtrate was cooled to $-20\,^\circ$C to afford complex 4 as a red solid (171.0 mg). Yield: 17.8%.

^{1}HNMR: 6.78 (t, $J = 2.4$, 2H); 6.74 (t, $J = 2.4$, 2H); 6.57–6.55 (m, 4H); 6.42 (s, 5H), 6.30 (s, 4H); 2.88 (m, 1H); 2.00–1.98 (m, 2H); 1.77–1.68 (m, 3H); 1.43–1.37 (m, 2H); 1.28–1.16 (m, 3H); 0.64 (s, 6H).

IR: 3417.7w, 3106.6m, 2922.0m, 2849.2m, 1489.9w, 1445.1m, 1407.9m, 1370.1m, 1321.4w, 1249.9m, 1177.0m, 1051.3m, 1041.5m, 1016.8m, 956.5w, 933.4w, 909.5m, 895.6w, 829.7s, 819.8s, 782.7m, 730.9w, 675.6m.

MS: 641 (22.51, $M^{\bullet+}$–Cl); 606 (7.17, $M^{\bullet+}$–2Cl); 529 (52.03, $M^{\bullet+}$–⬡–Cp); 311 (63.10, $M^{\bullet+}$–TiCl$_2$[⬡–Cp]–Cl); 304 (3.43, –ZrCl$_2$Cp–⬡–Cp); 276 (4.96, $M^{\bullet+}$–TiCl$_2$[⬡–Cp]–2Cl); 269 (79.96,

$M^{\bullet+}$–ZrCl$_2$Cp–⬡–Cp–Cl); 234 (100, $M^{\bullet+}$–ZrCl$_2$Cp–⬡–Cp–2Cl); 225 (17.86, ZrCl$_2$Cp); 147 (4.70, ⬡–Cp).

E.A. calculated: C 49.48%; H 5.05%; found: C 49.29%; H 5.33%.

3.1.6. Synthesis of complex 5 (R = CH$_2$CH = CH$_2$)

A mixture of compound X (473.1 mg, 1.25 mmol) and CH$_2$=CHCH$_2$CpTiCl$_3$ (339.9 mg, 1.31 mmol) was refluxed in toluene (80 ml) for 20 h. The solution was then filtered and concentrated in vacuo to half the original volume. The filtrate was cooled to $-20\,^\circ$C to afford complex 5 as a red solid (145.0 mg). Yield: 18.2%.

^{1}HNMR: 6.83 (s, 2H); 6.73 (d, $J = 5.8$, 2H); 6.59 (s, 2H); 6.56 (s, 2H); 6.43 (s, 5H); 6.32 (d, $J = 2.1$, 2H); 6.28 (s, 2H); 5.95 (m, 1H); 3.51 (d, $J = 6.5$, 2H); 2.35 (s, 2H); 0.64 (s, 6H).

IR: 3419.8w, 3106.6m, 3084.8m, 2956.9m, 2923.7m, 2901.4m, 2853.7w, 1638.6w, 1438.6m, 1409.2m, 1368.8m, 1315.1w, 1209.6w, 1250.3s, 1174.2m, 1126.1w, 1112.2w, 1089.3w, 1072.4w, 1046.5m, 1017.7m, 986.6m, 951.2m, 908.3m, 851.6m, 823.2s, 762.0m, 728.5m, 690.8m.

MS: 564 (9.71, $M^{\bullet+}$–2Cl); 529 (14.51, $M^{\bullet+}$–C$_3$H$_5$Cp); 494 (10.95, $M^{\bullet+}$–Cl–C$_3$H$_5$Cp); 376 (7.60, $M^{\bullet+}$–TiCl$_2$[C$_3$H$_5$Cp]–Cl); 341 (15.46, $M^{\bullet+}$–TiCl$_2$[C$_3$H$_5$Cp]–2Cl–Cp); 311 (100, $M^{\bullet+}$–TiCl$_2$[C$_3$H$_5$Cp]–Cl–Cp); 304 (12.60, $M^{\bullet+}$–ZrCl$_2$Cp–C$_3$H$_5$Cp); 269 (34.93, $M^{\bullet+}$–ZrCl$_2$Cp–Cl–C$_3$H$_5$Cp) 234 (49.16, $M^{\bullet+}$–ZrCl$_2$Cp–2Cl–C$_3$H$_5$Cp); 225 (20.22, ZrCl$_2$Cp).

E.A. calculated: C 47.09%; H 4.44%; found: C 47.29%; H 4.70%.

3.2. Polymerization of ethylene

Ethylene was purified by passage through 4 Å molecular sieves and Mn sieves. Polymerizations were carried out in a reactor placed in a thermostatically heated bath and equipped with a magnetic stirrer.

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 $60\,^\circ$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 using HCl was adjusted to pH 7. The polymer was then separated from the solution then dried in vacuo at $60\,^\circ$C to constant weight.

References

[1] W. Kaminsky, M. Miri, H. Sinn, R. Woldt, Makromol. Chem. Repid Commun. 4 (1983) 417.
[2] J.A. Ewen, J. Am. Chem. Soc. 106 (1984) 6355.
[3] J.C.W. Chien, B.P. Wang, J. Poly Sci. Part A: Polym. Chem 26 (1988) 3089.
[4] F.R.W.P. Wild, L. Zsolnai, G. Huttner, H.H. Brintzinger, J. Organomet. Chem. 232 (1982) 233.
[5] J.A. Ewen, in: T. Keii, K. Soga (Eds.), Proceedings of the International Symposium on Catalytic Polymerization of Olefins, Kondansha, 1986, p. 239.
[6] K.P. Reddy, J.L. Petersen, Organometallics 8 (1989) 2107.
[7] J.L. Huhmann, J.Y. Corey, N.P. Rath, Organometallics 15 (1996) 4063.
[8] T. Ushioda, M.L.H. Green, J. Haggitt, X.F. Yan, J. Organomet. Chem. 518 (1996) 155.
[9] J.L. Huhmann, J.Y. Corey, N.P. Rath, J. Organomet. Chem. 533 (1997) 61.
[10] K. Soga, H.T. Ban, T. Uozumi, J. Mol. Cat. A: Chem. 128 (1998) 273.
[11] S.K. Noh, G.G. Byun, G.S. Lee, D. Lee, K.B. Yoon, K.S. Kang, J. Organomet. Chem. 518 (1996) 1.
[12] R. Feng, L.M. Su, D.W. He, B.Q. Wang, G.L. Tian, S.S. Xu, X.Z. Zhou, Acta Polym. Sinica 6 (1998) 360.
[13] S. Jüling, R. Mlhaupt, H. Plenio, J. Organomet. Chem. 460 (1993) 191.
[14] J.C. Flores, T.E. Ready, J.C.W. Chien, M.D. Rausch, J. Organomet. Chem. 562 (1998) 11.
[15] J. Liu, H. Ma, J. Huang, Y. Qian, A.S.C. Chan, Eur. Polym. J. 35 (1999) 543.
[16] J. Liu, H. Ma, J. Huang, Y. Qian, Eur. Polym. J. 36 (2000) 2055.
[17] S. Koltzenburg, J. Mol. Cat. A: Chem. 116 (1997) 355.
[18] L. Jiang, Z. Shen, Y. Zhang, Eur. Polym. J. 36 (2000) 2513.
[19] E.C. Lund, T. Livinghouse, Organometallics 9 (1990) 2426.