APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2006; **20**: 130–137
Published online 12 December 2005 in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.1025

Ethylene and propylene polymerization by the new substituted bridged (cyclopentadienyl)(fluorenyl) zirconocenes

Xiaoxia Yang, Yong Zhang and Jiling Huang*

Laboratory of Organometallic Chemistry, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, People's Republic of China

Received 1 October 2005; Revised 5 October 2005; Accepted 25 October 2005

Eight *Cs*-symmetric complexes, $R_1R_2C(Cp)(Flu)MCl_2$ [$R_1 = R_2 = CH_3CH_2CH_2$, M = Zr (1), Hf (2); $R_1 = R_2 = p\text{–}CH_3OC_6H_4$, M = Zr (3), Hf (4); $R_1 = p\text{–}{}^tBuC_6H_4$, R_2 = Ph, M = Zr (5), Hf (6); $R_1 = R_2 = p\text{–}{}^tBuC_6H_4$, M = Zr (7); $R_1 = R_2 = PhCH_2$, M = Zr (8)] have been synthesized and characterized. Zirconocenes all showed the same high catalytic activities in ethylene polymerization as complex $Ph_2C(Cp)(Flu)ZrCl_2$ (9). However, in the propylene polymerization, the catalytic activities decreased in the order 5 ≈ 9 > 7 > 8. Introduction of ^{t}Bu decreased the activities, probably due to the bulk steric hindrance. The polypropylene produced by 5 and 7 with ^{t}Bu substituent showed a higher molecular weight ($M\eta$) than that produced by 9. The ^{13}C NMR spectrum revealed the polymers from 7 and 8 to have shorter average syndiotactic block length than polymer produced by 9. It was noted that [*mm*] stereodefect of polypropylene by 8 could not be observed from ^{13}C NMR, which showed that the benzyl on bridge carbon 8 prevented chain epimerization and enatiofacial misinsertion in polymerization. Copyright © 2005 John Wiley & Sons, Ltd.

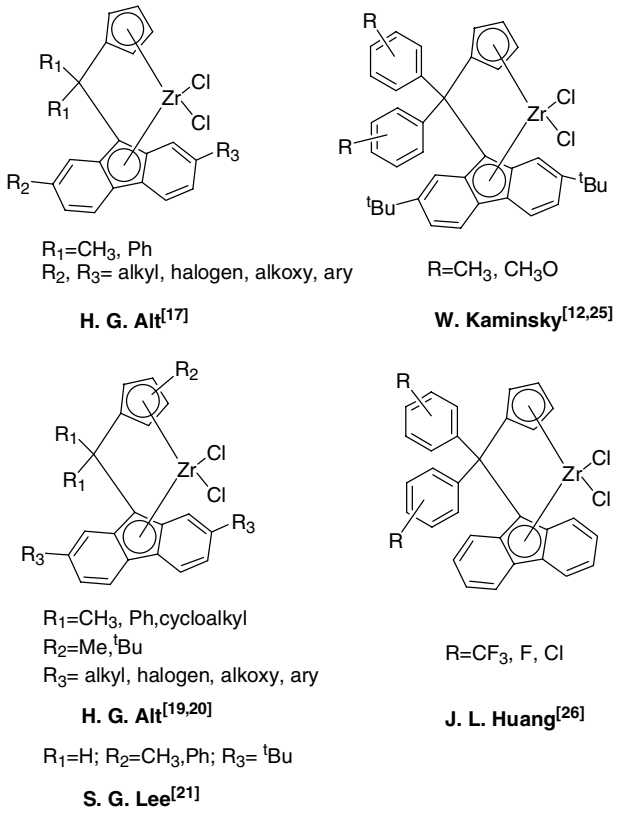
KEYWORDS: ethylene polymerization; propylene polymerization; zirconocene; bridge

INTRODUCTION

Polyolefins are important commercial materials, and the products of polyolefin have become indispensable. Nowadays, polyolefins are successfully prepared using a metallocene–methylaluminoxane (MAO) catalytic system because they have high catalytic activity and can produce narrow molecular weight distribution polyolefin. In order to seek appropriate catalysts, large numbers of complexes have been designed. The microstructure and physical character of polymers can be controlled by modification of the ligand structure of metallocene, and the unbridged metallocene complex is usually considered to show high catalytic activity on ethylene polymerization.[1–5] The bridged metallocene complex exhibits high catalytic activity on propylene polymerization[6–11] and high incorporation on copolymerization.[12–14] It could not be ignored that some complexes possess high catalytic activity on different olefin polymerizations simultaneously.[15,16] As the classical propylene polymerization catalyst, Cs-symmetric complex $R_2C(Cp)(Flu)ZrCl_2$ (**9**) can also exhibit high catalytic activity for ethylene polymerization in certain conditions.[17,18] Owing to their high catalytic activity and high stereoselectivity, they have been extensively investigated (Scheme 1). Alt found that the variety of substituents on the bridge carbon or on the fluorenyl could change the catalytic activity.[17,19–21] Otherwise, by introducing the substituents on the cyclopentadienyl, Cs-symmeric complexes were converted to C_1-symmeric complexes, which produced isotactic or hemiisotactic polypropylene.[22–24]

Recently Kaminsky found that the substituents (CH_3, CH_3O) on the phenyl groups of bridge carbon and ^{t}Bu on the fluorenyl affect the melting point of polypropylene.[12,25] In our report, it was found that the complex with withdrawing electron substituent (CF_3) on the phenyl groups of the bridge carbon showed higher catalytic activity than that with no substituted complex, $Ph_2C(Cp)(Flu)ZrCl_2$ (**9**), and produced the partial crystalline polypropylene.[26] In this paper, we

*Correspondence to: Jiling Huang, Laboratory of Organometallic Chemistry, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, People's Republic of China.
E-mail: qianling@online.sh.cn
Contract/grant sponsor: Special Funds for Major State Basic Research Projects; Contract/grant number: 2005 CB623801.
Contract/grant sponsor: National Natural Science Foundation of China; Contract/grant number: 20372022.



Scheme 1. Modification of Cs-symmetric complex $R_2C(Cp)(Flu)MCl_2$.

synthesized eight Cs-symmeric new complexes containing electron donating substituents (CH_3O, ^{t}Bu) on the phenyl groups of bridge carbon and the long alkyl substituted on the bridge carbon, and studied the ethylene and propylene polymerization with them further.

RESULTS AND DISCUSSION

Synthesis of complexes

As shown in Scheme 2, the bridged complexes **1–8** were prepared by the reaction of corresponding substituted dilithium salt of $R_2C(C_5H_4)(C_{13}H_8)$ with MCl_4 (M = Zr, Hf) in Et_2O, and recrystallization from toluene as red crystals in 27–76% yields. For comparison, the complex $Ph_2C(C_5H_4)(C_{13}H_8)ZrCl_2$ **9** was prepared according to Razavi and Atwood.[8] It was noted that different substituted fulvenes were obtained by different methods. The 6,6-dipropylfulvene (**ful 1**) was synthesized by the reaction of *n*-heptanone and cyclopentadiene in methylamine ethanol solution, and 6,6-substituted diphenylfulvenes (**ful 2, 3, 4**) were synthesized by the reaction of CpNa and substituted benzophenones. The 6,6-dibenzylfulvene (**ful 5**) was prepared by the reaction of dibenzyl ketone and cyclopentadiene in the fresh sodium ethoxide solution.

Polymerization results

Ethylene polymerization

Table 1 summarizes the results for the ethylene polymerization with the complexes **1–9**–MAO systems. All complexes showed high catalytic activities on ethylene polymerization. Zirconocenes obviously showed higher catalytic activity than hafnocenes (**1 > 2**, **3 > 4**, **5 > 6**), in agreement with other reports.[7,27,28] The catalytic activities of complexes **1–9** increased with polymerization temperature rising from 60 to 80 °C. This might be due to acceleration of the chain propagation rate and increasing concentration of the active center actived by MAO when the temperature rose.

For zirconocenes, complexes **1**, **3**, **5**, **7** and **8** exhibited the same high catalytic activity as complex **9** at 80 °C (runs 2, 7, 15, 24, 26 and 28). Complex $(CH_3)_2C(Cp)(Flu)ZrCl_2$ shows lower catalytic activity than $Ph_2C(Cp)(Flu)ZrCl_2$ in propylene polymerization.[29] However, in Table 1 the complex **1** containing the long alkyl on the bridge carbon $[(C_3H_7)_2C(Cp)(Flu)ZrCl_2]$ exhibited the same activity as $Ph_2C(Cp)(Flu)ZrCl_2$ in ethylene polymerization. In addition, complexes **3**, **5** and **7** containing the substituents (CH_3O or ^{t}Bu) on the phenyl groups of bridge carbon also had similar catalytic activities to **9**. It seemed that the effect of substituents on phenyl groups of bridge carbon on catalytic activity was insignificant, according to the results. However, Alt has observed that cycloalkyl-substituted bridge carbon complexes showed discrepant catalytic activity:[17] the cyclohexane-substituted complex showed higher activity than alkyl- or phenyl-substituted complex.

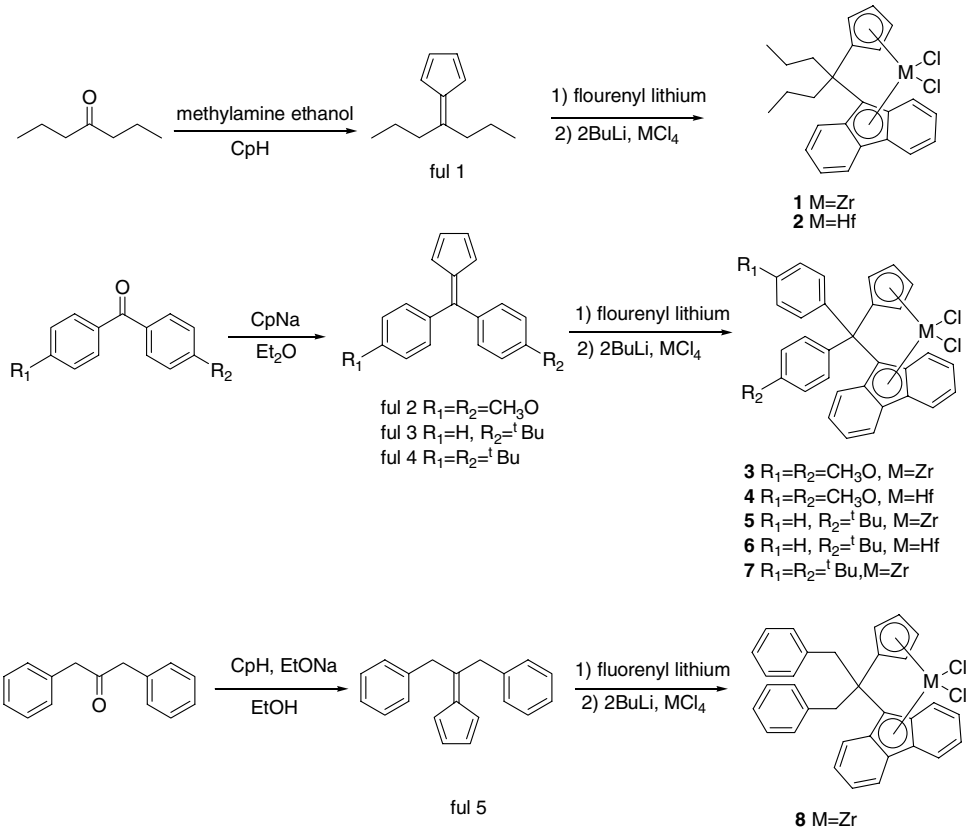
Table 1 also showed the dependence of polymerization activity on polymerization time. Complexes **1**, **3**, **5** and **6** exhibited the higher activities in 10 min than in 30 min (runs 3 > 2, 8 > 7, 16 > 15, 21 > 20). This might be due to the highest concentration of the active center at the beginning of polymerization, and the active center might be deactived during polymerization.

The catalytic activity was directly proportional to the chain propagation rate, so it was expected that activity would increase with the monomer concentration. From Table 1 (runs 9 and 11, 16 and 18), when ethylene pressure increased, higher activities were observed at 11 atm than at 5 atm for **3** and **5**, because higher ethylene pressure means a higher ethylene concentration in the toluene solution.

In addition, with the concentration of catalyst decreasing from 1.0×10^{-4} to 0.5×10^{-4}, the activity decreased slightly (runs 8 > 9, 16 > 17 and 21 > 22). This was because the decrease in catalyst concentration reduced the chain propagation rate and decreased the activity further.

Propylene polymerization

Substituents on the phenyl, fluorenyl or cyclopentadienyl groups could vary the catalytic activity. Alt observed that the substituents on the fluorenyl group enhanced the catalytic activity in propylene polymerization.[19] Kaminsky found that the catalytic activity of propylene polymerization was influenced by the substituents on phenyl groups of bridge



Scheme 2. Synthesis of the complexes **1–8**.

carbon.[25] In this report, propylene polymerizations were studied with complexes **5**, **7**, **8**, **9**–MAO at 30 °C. Complex **5** containing one ^{t}Bu-substituted phenyl showed the same activity as **9** (Table 2, runs 29 and 32), but **7** containing two ^{t}Bu substituted phenyl exhibited lower catalytic activity than **9**. We have reported that withdrawing the electron-substituted complex (p-F-Ph)$_2$(Cp)(Flu)ZrCl$_2$ (Table 2, run 34) was not beneficial to the activity;[26] neither was the electron donating substituent ^{t}Bu here. Therefore, the steric hindrances of ^{t}Bu may have reduced the catalytic activity. In addition, **8** containing benzyl on bridge carbon had lower activity than **9**. The reason for this lay in the abnormal configuration of two benzyls on the bridge carbon. The phenyl of **9** was vertical to the fluorenyl plane according to the X-ray,[8] and there were five signals of phenyl in ^{1}H NMR spectrum. Interestingly, there were only three signals of phenyl in ^{1}H NMR spectra data of **8**. Therefore, it was possible the phenyl of **8** might be parallel to the fluorenyl plane. Possibly it was the special structure influencing the catalytic activity.

Endothermic enthalpy was the important parameter of the crystallinity of polymer. Polypropylene obtained by Cs-symmeric complex **9** or $(CH_3)_2$C(Cp)(Flu)ZrCl$_2$ was highly crystalline. In our prior report, complex (m-CF$_3$-Ph)$_2$C(Cp)(Flu)ZrCl$_2$ produced the partially crystalline polypropylene with the 24.92 J/g endothermic enthalpy (run 33). However, the polypropylene from **5** containing electron donating substituents ^{t}Bu had even higher ΔH_f than that from **9** (59.10 > 45.6 J/g), which was more crystalline polypropylene. In addition, it was noted that polypropylene by **7** showed a high melting point (147 °C), which was 20 °C higher than that by **9**.

On the other hand, the substituents on the phenyl of bridge carbon also affected the viscosity molecular weights ($M\eta$) of polypropylene; **5** and **7** containing electron-donating substituents produced syndiotactic polypropene with higher viscosity molecular weights compared with complex **9**, but the polypropylene produced by (m-CF$_3$-Ph)$_2$C(Cp)(Flu)ZrCl$_2$ and **8** possessed lower-viscosity molecular weight ($M\eta$) than that by **9**.

Cs-symmetric metallocene complex produces syndiotactic polypropylene. From Table 3, the polypropylenes by **7** and **8** were syndiotactic with low syndiotactic block length (Lsyn). However, the polymer from **9** was highly crystalline syndiotactic polypropylene with very high tacticity ([r] = 97.5%)[8] and relatively long average syndiotactic block length (Lsyn = 50).[30] Average block length, as determined by a numerical integration of the pentads, has a great effect on the properties of the polymer.[15,31–33] Relatively short average block lengths, i.e. 6–15 tend to occur in a flexible and rubbery polymer which exhibits good elastic properties as reported by Job.[30] Complex **7** could produce crystalline syndiotactic

Table 1. Ethylene polymerization by complexes **1–9**–MAO catalyst system[a]

Run	Complex	Pressure (atm)	Temperature (°C)	[M][b] /10^{-4}	Time (min)	Activity[c] /10^5
1	**1**	11	60	1.0	30	8.10
2		11	80	1.0	30	9.11
3		11	80	1.0	10	21.98
4	**2**	11	60	1.0	30	0.29
5		11	80	1.0	30	0.44
6	**3**	11	60	1.0	30	7.29
7		11	80	1.0	30	8.64
8		11	80	1.0	10	20.71
9		11	80	0.5	10	17.67
10		5	80	1.0	10	16.80
11		5	80	0.5	10	5.43
12	**4**	11	60	1.0	30	2.17
13		11	80	1.0	30	2.89
14	**5**	11	60	1.0	30	5.01
15		11	80	1.0	30	8.92
16		11	80	1.0	10	20.08
17		11	80	0.5	10	17.54
18		5	80	1.0	10	7.49
19	**6**	11	60	1.0	10	3.44
20		11	80	1.0	30	5.45
21		11	80	1.0	10	17.03
22		11	80	0.5	10	14.27
23	**7**	11	60	1.0	30	7.98
24		11	80	1.0	30	8.86
25	**8**	11	60	1.0	30	3.96
26		11	80	1.0	30	7.97
27	$Ph_2C(Cp)(Flu)ZrCl_2$	11	60	1.0	30	6.73
28		11	80	1.0	30	8.13

[a] Conditions: [Al]/[M] = 1000, 20 ml toluene.
[b] Concentration of catalyst in toluene.
[c] g PE/mol M h.

Table 2. Propylene polymerization by complexes **5**, **7**, **8**–MAO catalyst system[a]

Run	Complex	Activity[b] /10^5	$M\eta/10^5$	T_m[c]	ΔH_f[d] (J/g)
29	(p-^{t}BuPh)(Ph)C(Cp)(Flu)$ZrCl_2$ **5**	19.62	3.02	128	59.10
30	(p-^{t}BuPh)$_2$C(Cp)(Flu)$ZrCl_2$ **7**	13.89	3.15	147	—
31	$(PhCH_2)_2C(Cp)(Flu)ZrCl_2$ **8**	2.04	2.45	125	—
32	$Ph_2C(Cp)(Flu)ZrCl_2$ **9**	19.2	2.96	127	45.6
33[e]	(m-CF_3-Ph)$_2$C(Cp)(Flu)$ZrCl_2$	26.0	2.46	120	24.6
34[e]	(p-F-Ph)$_2$C(Cp)(Flu)$ZrCl_2$	7.11	2.46	137	38.5

[a] Conditions: $P_{propylene}$ = 1 atm, time = 0.5 h, [Al]/[Zr] = 1000, [Zr] = 0.5×10^{-4} mol/l, temperature = 30 °C, 50 ml toluene.
[b] g PP/mol Zr h.
[c] Melting peak temperature of the DSC curve.
[d] Endothermic enthalpies determined by DSC as a parameter of the crystallinity of polymer.
[e] According to Huang *et al.*[26]

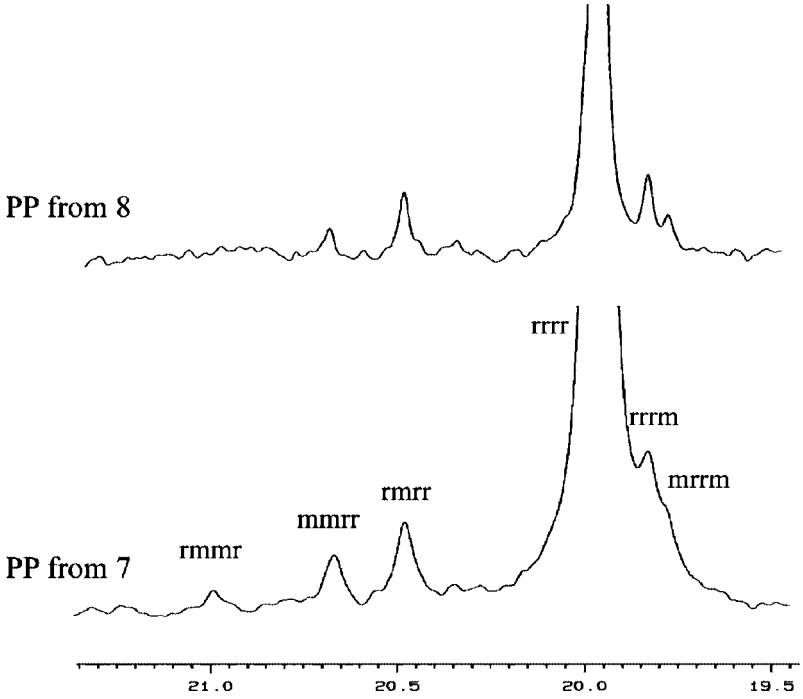
polypropylene with [*rrrr*] = 72.7% ([*r*] = 93.7%) and short average syndiotactic block length (Lsyn = 18) here.

From ^{13}C NMR (Scheme 3), it should be noted that the [*m*] stereodefect of PP from **8** was similar to that from **7**, but the [*mm*] stereodefect of polypropylene by **8** could not be observed. The [*m*] stereodefect was produced by the site epimerization, and [*mm*] stereodefect was produced by two routes in the polymerization. One was the existence of

Table 3. The distribution of pentads of polypropylene by complex **7** and **8**–MAO system

Run	Complex	*rmmr* (%)	*mmrr* (%)	*rmrr* (%)	*rrrr* (%)	*rrrm* (%)	*mrrm* (%)	*r* (%)[a]	Lsyn[b]
30	**7**	1.4	4.0	5.6	72.7	9.8	6.4	93.7	18
31	**8**	—	2.4	5.4	81.9	6.6	3.7	95.1	27

[a] $r = 1/2mr + rr$, $mr = mmrm + mmrr + rmrm + rmrr$, $rr = mrrm + mrrr + rrrr$.
[b] Lsyn (average syndiotactic block length) $= 3 + 2 \times rrrr/rrrm$.



Scheme 3. ^{13}C NMR of polypropylene from complexes **7** and **8**–MAO.

enatiofacial misinsertion after the monomer was coordinated to the metal center; another was the chain epimerization occurring in polymerization (Scheme 4). Therefore, the benzyl on the bridge carbon of **8** did not change the site epimerization, but prevented the chain epimerization and enatiofacial misinsertion.[10]

EXPERIMENTAL

Measurements

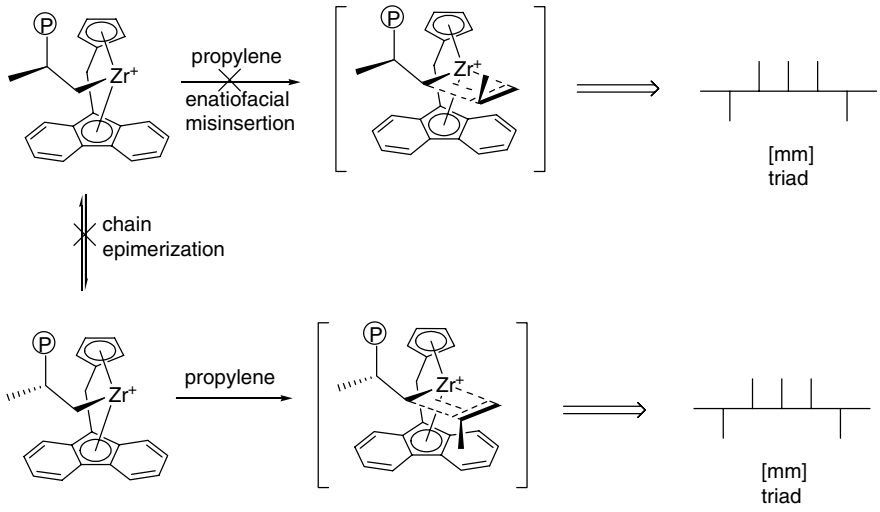
All experiments were carried out under a dry argon atmosphere using standard Schlenk techniques. Toluene, diethyl ether (Et_2O) and tetrahydrofuran (THF) were refluxed over sodium/benzophenone, and distilled before use. The cocatalyst 1.53 M MAO in toluene was purchased from Witco. Ethylene was used after passing it through P_2O_5 powder and KOH pellets.

Infrared (IR) spectra were taken on Nicolet Magna IR 550 and Nicolet 5SXC spectrometers as KBr disks. Elemental analysis was carried out on an EA-1106 analyzer. ^1H NMR was recorded on a Bruker Avance 500 MHz spectrometer with TMS as internal standard. Mass spectra (MS) were recorded on a HP 5989A instrument. Differential scanning calorimetry was performed on a Universal V2.3C TA instrument at a heating rate of 10 °C/min. ^{13}C NMR spectra were recorded on a DR 500 Bruker spectrometer operating at 125.78 MHz in *o*-dichlorodeuterobenzene.

Synthesis of ful 1–5

$(CH_3CH_2CH_2)_2C = C_5H_4$ (*ful 1*)

n-Heptanone (10 g, 87.6 mmol) and cyclopentadiene (8.0mL, 87.6 mmol) were added into a 50 ml flask, then the methylamine ethanol solution (30–32%; 8 g, 87.6 mmol) was dropped into the reaction solution at room temperature and stirred overnight. Then the reaction was quenched by addition of water (50 ml) at 0 °C; the organic layer was washed well (three times) with water and dried over $MgSO_4$, filtered and concentrated to produce dark red viscous oil in *vacuo*. The oil was purified by reduced pressure distillation to produce the red oil (**Ful 1**), 8.9 g (yield 63%).



Scheme 4. Chain epimerization and enatiofacial misinsertion were not occured in the propylene polymerization by complex **8**.

*(p-CH$_3$O-C$_6$H$_4$)$_2$ = C$_5$H$_4$ (**ful 2**)*

A solution of CpNa (1.8 mol/l, 13.7 ml, 24.8 mmol) in THF was added to the solution of bis-(4-methoxyl-phenyl) methanone (6 g, 24.8 mmol) in Et_2O (30 ml). The reaction mixture was warmed to room temperature and stirred overnight. Then the reaction was quenched by addition of water (50 ml) at 0 °C, the organic layer was washed well (three times) with water and dried over $MgSO_4$, filtered and concentrated to produce yellow viscous oil *in vacuo*. The product was purified by chromatography on alumina (petroleum ether as developer). Red crystals (**Ful 2**) 3.8 g (yield 53%) were obtained.

Synthesis of (*p*-^{t}Bu-Ph)(Ph)C = C_5H_4 (**ful 3**) was obtained using a similar procedure (yield 69%). Synthesis of (*p*-^{t}Bu-Ph)$_2$C = C_5H_4 (**ful 4**) was obtained using a similar procedure (yield 67%).

*(PhCH$_2$)$_2$C = C$_5$H$_4$ (**ful 5**)*

The fresh sodium ethoxide was prepared by adding 0.6 g (23.8 mmol) sodium to 20 ml ethanol, and cyclopentadiene (2 ml, 23.8 mmol) was added into the solution. A solution of dibenzene methanone (5.0 g, 23.8 mmol) was dropped into the reaction at 0 °C. After stirring for 4 h, the yellow solution was concentrated *in vacuo*. Then the reaction was quenched by addition of water and Et_2O, the organic layer was washed well (three times) with water and dried over $MgSO_4$, filtered and concentrated *in vacuo* to produce yellow viscous oil. The product was purified by chromatography on alumina with petroleum ether as developer. Yellow crystals (**Ful 5**) 1.6 g (yield 25%) were obtained.

Synthesis of complexes 1–8

*(CH$_3$CH$_2$CH$_2$)$_2$C(C$_5$H$_4$)(C$_{13}$H$_8$)ZrCl$_2$ **1***

The solution of 3.5 mmol fluorenyl lithium salt in 20 ml Et_2O was added dropwise to a solution of 0.6 g (3.5 mmol) **ful 1** in 30 ml Et_2O. After stirring for about 2 h, the solution was hydrolyzed by 20 ml water. The white solid 1.0 g was precipitated (yield, 87%). To a solution of 1.0 g (2.9 mmol) solid in 30 ml Et_2O, 3.2 ml (5.8 mmol) *n*-butyllithium (1.8 M solution in *n*-hexane) was added dropwise at −78 °C. After stirring overnight, 0.67 g (2.9 mmol) $ZrCl_4$ was added and the solution was stirred for 8 h at room temperature, and then evaporated to dryness. The residue was recrystallized by toluene to give 630 mg (yield, 48%) complex **1** as a red crystal.

^{1}H NMR ($CDCl_3$, 500 Hz, δ): 8.13 (d, J = 8.35 Hz, 2H, Flu), 7.82 (d, J = 8.96 Hz, 2H, Flu), 7.56 (m, 2H, Flu), 7.28 (m, 2H, Flu), 6.33 (t, J_1 = 2.68 Hz, J_2 = 2.68 Hz, 2H, Cp,), 5.76 (t, J_1 = 2.68 Hz, J_2 = 2.68 Hz, 2H, Cp), 2.80 (m, 2H, CH_2), 2,71 (m, 2H, CH_2), 1.78 (m, 4H, CH_2), 1.18 (t, J_1 = 7.31 Hz, J_2 = 7.31 Hz, 6H, CH_3). MS (*m*/*e*): 486 (78, M^+), 451 (18, M^+-Cl), 445 (100, M^+-$CH_3CH_2CH_2$), 422 (9, M^+-Cp), 399 (13, M^+-2$CH_3CH_2CH_2$), 326 (7, M^+-$ZrCl_2$), 321 (23, M^+-Flu). IR (cm^{-1}, KBr): 3092w, 2953s, 2926m, 2868m, 1596m, 1447s, 1426m, 1379w, 1317w, 1207w, 1150w, 1126w, 1047m, 823s, 745s, 712w, 473m, 423w. Anal. calcd for $C_{25}H_{26}Cl_2Zr$: C, 61.45, H, 5.36; found: C, 61.61, H, 5.48%.

*(CH$_3$CH$_2$CH$_2$)$_2$C(C$_5$H$_4$)(C$_{13}$H$_8$)HfCl$_2$ **2***

Complex **2** was obtained as yellow crystal by the procedure similar to that used for **1** (yield, 40%). ^{1}H NMR ($CDCl_3$, 500 Hz, δ): 8.10 (d, J = 8.40 Hz, 2H, Flu), 7.85 (d, J = 8.99 Hz, 2H, Flu), 7.52 (m, 2H, Flu), 7.26 (m, 2H, Flu), 6.27 (t, J_1 = 2.64 Hz, J_2 = 2.64 Hz, 2H, Cp), 5.72 (t, J_1 = 2.64 Hz, J_2 = 2.64 Hz, 2H, Cp), 2.82 (m, 2H, CH_2), 2,71 (m, 2H, CH_2), 1.78 (m, 4H, CH_2), 1.18 (t, J_1 = 7.29 Hz, J_2 = 7.29 Hz, 6H, CH_3). MS (*m*/*e*): 576 (70, M^+), 533 (100, M^+-$CH_3CH_2CH_2$), 490 (42, M^+-2$CH_3CH_2CH_2$), 412 (18, M^+-Flu). IR (cm^{-1}, KBr): 2954s, 2869s, 1615m, 1448m, 1428m, 1379w, 1317w, 1207w, 1151w, 1047w, 827s, 744s, 621w, 470w, 422w. Anal. calcd for $C_{25}H_{26}Cl_2Zr$: C, 52.14, H, 4.55; found: C, 51.74, H, 4.66%.

(p-CH$_3$O-C$_6$H$_4$)$_2$C(C$_5$H$_4$)(C$_{13}$H$_8$)ZrCl$_2$ ***3***

Complex **3** was obtained as red crystal by the procedure similar to that used for **1** (yield, 37%). ^{1}H NMR (CDCl$_3$, 500 Hz, δ): 8.19 (d, J = 8.37 Hz, 2H, Flu), 7.80 (dd, J_1 = 8.60 Hz, J_2 = 2.61 Hz, 2H, Ph), 7.72 (dd, J_1 = 8.60 Hz, J_2 = 2.44 Hz, 2H, Ph), 7.58 (t, J_1 = 7.60 Hz, J_2 = 7.60 Hz, 2H, Flu), 7.03 (t, J_1 = 7.60 Hz, J_2 = 7.60 Hz, 2H, Flu), 6.95 (dd, J_1 = 8.60 Hz, J_2 = 2.61 Hz, 2H, Ph), 6.89 (dd, J_1 = 8.60 Hz, J_2 = 2.61 Hz, 2H, Ph), 6.49 (d, J = 8.78 Hz, 2H, Flu), 6.38 (t, J_1 = 2.69 Hz, J_2 = 2.69 Hz, 2H, Cp), 5.79 (t, J_1 = 2.69 Hz, J_2 = 2.69 Hz, 2H, Cp), 3.82 (s, 6H, CH$_3$). MS (*m/e*): 614 (20, M$^+$), 507 (23, M$^+$-MeOPh), 454 (100, M$^+$-ZrCl$_2$), 390 (17, M$^+$-ZrCl$_2$-Cp). IR (cm^{-1}, KBr): 2930w, 1604m, 1507s, 1460m, 1443m, 1428m, 1247s, 1177m, 1123w, 1027m, 819s, 755m, 734s, 697m, 587w, 467w. Anal. calcd for C$_{33}$H$_{26}$Cl$_2$ZrO$_2$: C, 64.27, H, 4.25; found: C, 64.31, H, 5.14%.

(p-CH$_3$O-C$_6$H$_4$)$_2$C(C$_5$H$_4$)(C$_{13}$H$_8$)HfCl$_2$ ***4***

Complex **4** was obtained as yellow crystal by the procedure similar to that used for **1** (yield, 27%). ^{1}H NMR (CDCl$_3$, 500 Hz, δ): 8.17 (d, J = 8.41 Hz, 2H, Flu), 7.80 (dd, J_1 = 8.60 Hz, J_2 = 2.61 Hz, 2H, Ph), 7.72 (dd, J_1 = 8.60 Hz, J_2 = 2.44 Hz, 2H, Ph), 7.54 (t, J_1 = 7.60 Hz, J_2 = 7.60 Hz, 2H, Flu), 7.00 (t, J_1 = 7.60 Hz, J_2 = 7.60 Hz, 2H, Flu), 6.95 (dd, J_1 = 8.60 Hz, J_2 = 2.61 Hz, 2H, Ph), 6.89 (dd, J_1 = 8.60 Hz, J_2 = 2.61 Hz, 2H, Ph), 6.52 (d, J = 8.83 Hz, 2H, Flu), 6.32 (t, J_1 = 2.66 Hz, J_2 = 2.66 Hz, 2H, Cp), 5.79 (t, J_1 = 2.66 Hz, J_2 = 2.66 Hz, 2H, Cp), 3.82 (s, 6H, CH$_3$). MS (*m/e*): 704 (85, M$^+$), 597 (100, M$^+$-MeOPh), 454 (18, M$^+$-HfCl$_2$), 390 (10, M$^+$-HfCl$_2$-Cp). IR (cm^{-1}, KBr): 2931m, 2855w, 1607s, 1509s, 1461m, 1445m, 1430m, 1329w, 1249s, 1179s, 1030s, 823s, 753m, 734s, 697m, 588w, 467w. Anal. calcd for C$_{33}$H$_{26}$Cl$_2$HfO$_2$: C, 56.30, H, 3.72; found: C, 56.60, H, 4.03%.

(p-^{t}Bu-C$_6$H$_4$)(Ph)C(C$_5$H$_4$)(C$_{13}$H$_8$)ZrCl$_2$ ***5***

Complex **5** was obtained as red crystal by the procedure similar to that used for **1** (yield, 42%). ^{1}H NMR (CDCl$_3$, 500 Hz, δ): 8.20 (d, J = 8.36 Hz, 2H, Flu), 7.93 (d, J = 7.90 Hz, 1H, Ph), 7.88 (d, J = 7.90 Hz, 1H, Ph), 7.82 (dd, J_1 = 8.22 Hz, J_2 = 2.20 Hz, 1H, Ph), 7.76 (dd, J_1 = 8.22 Hz, J_2 = 2.20 Hz, 1H, Ph), 7.57 (t, J_1 = 7.80 Hz, J_2 = 7.80 Hz, 2H, Flu), 7.46–7.41 (m, 2H, Ph), 7.35 (d, J = 2.04 Hz, 1H, Ph), 7.33 (d, J = 2.04 Hz, 1H, Ph), 7.30 (m, 1H, Ph), 7.28–7.24 (m, 2H, toluene-Ph), 7.18–7.16 (m, 3H, toluene-Ph), 7.02–7.00 (m, 2H, Cp), 6.41–6.38 (m, 4H, Flu-Ph), 5.83–5.79 (m, 2H, Cp), 2.35 (s, 3H, toluene-CH$_3$), 1.31 (s, 9H, ^{t}Bu). MS (*m/e*): 610 (92, M$^+$), 575 (13, M$^+$-Cl), 553 (4, M$^+$-^{t}Bu), 533 (44, M$^+$-Ph), 477 (46, M$^+$-^{t}BuPh). IR (cm^{-1}, KBr): 2956s, 2865w, 1596w, 1462m, 1446m, 1428m, 1363w, 1326w, 1212w, 1127w, 1016w, 861w, 819s, 752m, 736s, 714m, 696m, 634w, 566w, 474m. Anal. calcd for C$_{35}$H$_{30}$Cl$_2$Zr · CH$_3$C$_6$H$_5$: C, 71.57, H, 5.43; found: C, 71.21, H, 5.66%.

(p-^{t}Bu-C$_6$H$_4$)(Ph)C(C$_5$H$_4$)(C$_{13}$H$_8$)HfCl$_2$ ***6***

Complex **6** was obtained as yellow crystal by the procedure similar to that used for **1** (yield, 76%). ^{1}H NMR (CDCl$_3$, 500 Hz, δ): 8.17 (d, J = 8.41 Hz, 2H, Flu), 7.94 (d, J = 7.90 Hz, 1H, Ph,), 7.87 (d, J = 7.90 Hz, 1H, Ph), 7.82 (dd, J_1 = 8.23 Hz, J_2 = 2.23 Hz, 1H, Ph), 7.76 (dd, J_1 = 8.23 Hz, J_2 = 2.23 Hz, 1H, Ph), 7.53 (t, J_1 = 7.57 Hz, J_2 = 7.57 Hz, 2H, Flu), 7.46– 7.41 (m, 2H, Ph), 7.35– 7.31 (m, 3H, Ph), 7.28– 7.16 (m, 3.75H, toluene-Ph), 7.00– 6.97 (m, 2H, Cp), 6.44 (dd, J_1 = 8.84 Hz, J_2 = 3.57 Hz, 2H, Flu-Ph), 6.32 (t, J_1 = 3.19 Hz, J_2 = 3.57 Hz, 2H, Flu-Ph), 5.78– 5.74 (m, 2H, Cp), 2.35 (s, 2.25H, toluene-CH$_3$), 1.31 (s, 9H, ^{t}Bu). MS (*m/e*): 700 (59, M$^+$), 623 (26, M$^+$-Ph), 567 (33, M$^+$-^{t}BuPh), 450 (70, M$^+$-HfCl$_2$), 393 (100, M$^+$-HfCl$_2$-^{t}Bu). IR (cm^{-1}, KBr): 2955m, 2864w, 1596w, 1492w, 1461w, 1446w, 1327w, 1211w, 1127w, 1039w, 860w, 822s, 735s, 713m, 633w, 468m. Anal. calcd for C$_{35}$H$_{30}$Cl$_2$Hf · 0.75C$_7$H$_8$: C, 62.86, H, 4.72; found: C, 62.85, H, 5.06%.

(p-^{t}Bu-C$_6$H$_4$)$_2$C(C$_5$H$_4$)(C$_{13}$H$_8$)ZrCl$_2$ ***7***

Complex **7** was obtained as red crystal by the procedure similar to that used for **1** (yield, 28%). ^{1}H NMR (CDCl$_3$, 500 Hz, δ): 8.19 (d, J = 8.40 Hz, 2H, Flu), 7.82 (dd, J_1 = 2.21 Hz, J_2 = 10.5 Hz, 2H, Ph), 7.77 (dd, J_1 = 2.21 Hz, J_2 = 10.5 Hz, 2H, Ph), 7.56 (t, J = 7.30 Hz, 2H, Flu), 7.44 (dd, J_1 = 2.21 Hz, J_2 = 10.5 Hz, 2H, Ph), 7.36 (dd, J_1 = 2.21 Hz, J_2 = 10.5 Hz, 2H, Ph), 7.00 (t, J = 6.93 Hz, 2H, Flu), 6.35– 6.37 (m, 4H, Cp and Flu), 5.81 (t, J = 2.72 Hz, 2H, Cp), 1.32 (s, 18H, t-Bu). MS (*m/e*): 666 (3, M$^+$), 533 (8, M$^+$-^{t}Bu-C$_6$H$_4$), 506 (3, M$^+$-ZrCl$_2$), 285 (100, M$^+$-ZrCl$_2$-Flu-^{t}BuC$_6$H$_4$). IR (cm^{-1}, KBr): 3103m, 3028m, 2959s, 1640w, 1593w, 1509m, 1462s, 1444m, 1428s, 1407m, 1359m, 1327m, 1268m, 1237w, 1213m, 1168w, 1128m, 1110m, 1058w, 1043m, 1017m, 950w, 868w, 821s, 751s, 739s, 726m, 713m, 647m, 634m, 589s, 558w, 475s, 451w, 438w, 422w, 409w. HRMS for C$_{39}$H$_{38}$Cl$_2$Zr: 666.1398; found: 666.1378.

(PhCH$_2$)$_2$C(C$_5$H$_4$)(C$_{13}$H$_8$)ZrCl$_2$ ***8***

Complex **8** was obtained as crystal by the procedure similar to that used for **1** (yield, 67%). ^{1}H NMR (CDCl$_3$, 500 Hz, δ): 8.21 (d, J = 8.40 Hz, 2H, Flu), 7.88 (d, J = 8.90 Hz, 2H, Flu), 7.61 (t, J = 7.41 Hz, 2H, Ph), 7.28 (t, J = 9.73 Hz, 2H, Flu), 7.23 (d, J = 7.20 Hz, 2H, Flu), 7.17 (t, J = 7.41 Hz, 4H, Ph), 7.11 (d, J = 7.41 Hz, 4H, Ph), 6.46 (t, J = 2.51 Hz, 2H, Cp), 5.98 (t, J = 2.51 Hz, 2H, Cp), 4.22 (d, J = 15.5 Hz, 2H, CH$_2$), 4.05 (d, J = 15.5 Hz, 2H, CH$_2$). MS (*m/e*): 582 (1, M$^+$), 491 (44, M$^+$-PhCH$_2$), 422 (5, M$^+$-ZrCl$_2$), 456 (8, M$^+$-PhCH$_2$-Cl), 331 (14, M$^+$-ZrCl$_2$-PhCH$_2$), 258 (13, M$^+$-ZrCl$_2$-Flu), 91 (75, PhCH$_2$), 240 (100, M$^+$-ZrCl$_2$-2PhCH$_2$). IR (cm^{-1}, KBr): 3112m, 3086m, 3060m, 3026m, 2967w, 2932w, 1599m, 1495m, 1463m, 1451m, 1425m, 1403w, 1327w, 1299w, 1245w, 1230w, 1213m, 1183w, 1159w, 1128w, 1089m, 1076w, 1045m, 1031w, 934w, 821s, 752s, 739s, 725s, 696s, 631w, 505w, 474m. Anal. calcd for C$_{33}$H$_{26}$Cl$_2$Zr: C, 67.79, H, 4.48; found: C, 67.49, H, 4.66%.

Polymerization procedure

Ethylene polymerization

A 100 ml autoclave, equipped with a magnetic stirrer, was evacuated on a vacuum, and then filled with ethylene. Toluene was injected into the reactor. After equilibrating, the appropriate volume of catalyst solution and cocatalyst

were injected to start the reaction. The ethylene pressure was kept constant during the reaction. The polymerization was carried out for 0.5 h and then quenched with 3% HCl in ethanol (50 ml). The precipitated polymer was filtered and then dried overnight in a vacuum oven at 80 °C.

Propylene polymerization

A 100 ml flask was equipped with a propylene inlet, a magnetic stirrer, and a vacuum line. The flask was filled with 50 ml of freshly distilled toluene was added. MAO was added, and the flask was placed in a bath at the desired polymerization temperature for 10 min. The polymerization reaction was started by adding a solution of the catalyst precursor with a syringe. The polymerization was carried out for 0.5 h and then quenched with 3% HCl in ethanol (50 ml). The precipitated polymer was filtered and then dried overnight in a vacuum oven at 80 °C.

CONCLUSION

Eight various substituted bridged (cyclopentadienyl) (fluorenyl) complexes were prepared. Zirconocenes all showed the same high catalytic activities in ethylene polymerization as complex $Ph_2C(C_5H_4)(C_{13}H_8)ZrCl_2$ (**9**). With complexes **1**, **3**, **5** and **6**, it was observed the activities increased with the increasing concentration of catalyst or ethylene pressure, and the activities decreased with the polymerization time. On the other hand, the catalytic activities decreased in the order (p-^{t}Bu-C_6H_4)(Ph)$C(C_5H_4)(C_{13}H_8)ZrCl_2$ (**5**) $\approx Ph_2C(C_5H_4)(C_{13}H_8)ZrCl_2$ (**9**) $>$ (p-^{t}Bu-$C_6H_4)_2C(C_5H_4)(C_{13}H_8)ZrCl_2$ (**7**) $>>$ $(PhCH_2)_2C(C_5H_4)(C_{13}H_8)ZrCl_2$ (**8**) on the propylene polymerization. Different from ethylene polymerization, the introduction of ^{t}Bu decreased the activities on propylene polymerization, possibly due to the bulk steric hindrance. The polypropylene produced by **5** and **7** showed a higher molecular weight ($M\eta$) than that by **9**, and endothermic enthalpy (ΔH_f) of polypropylene produced by **5** was higher than that of **9**, which indicated that the polymer by **5** possesssed highly crystallinity. The ^{13}C NMR spectrum revealed polymers from **7** and **8** were syndiotactic polypropylenes with $[r] = 93.7\%$ and $[r] = 95.1\%$, respectively, and they had the shorter average syndiotactic block length than polymer from **9**, which would influence the elastic properties of polypropylene. It was noted that the [*mm*] stereodefect of polypropylene by **8** could not be observed from ^{13}C NMR, which showed that the benzyl of **8** prevented the chain epimerization and enatiofacial misinsertion in polymerization.

Acknowledgments

We gratefully acknowledge the financial support from the Special Funds for Major State Basic Research Projects (2005 CB623801) and the National Natural Science Foundation of China (NNSFC) (20372022).

REFERENCES

1. Schmid MA, Alt HG, Milius W. *J. Organomet. Chem.* 1995; **501**: 101.
2. Schmid MA, Alt HG, Milius W. *J. Organomet. Chem.* 1996; **514**: 45.
3. Licht EH, Alt HG, Karim MM. *J. Organomet. Chem.* 2000; **599**: 275.
4. Lee MH, Do Y. *J. Organomet. Chem.* 2005; **690**: 1240.
5. Zhang Y, Huang JL, Yang XX, Zhang J, Qian YY. *J. Polym. Sci. Part A: Polym. Chem.* 2005; **43**: 1261.
6. Kaminsky W, Kulper K, Brintzinger HH, Wild FR. *Angew. Chem. Int. Edn Engl.* 1985; **24**: 507.
7. Ewen JA, Johnes RL, Razavi A, Ferrara JD. *J. Am. Chem. Soc.* 1988; **110**: 6255.
8. Razavi A, Atwood JL. *J. Organomet. Chem.* 1993; **459**: 117.
9. Hopf A, Kaminsky W. *Catal Comm.* 2002; **3**: 459.
10. Leino R, Gomez FJ, Cole AP, Waymouth RM. *Macromolecules.* 2001; **34**: 2072.
11. Brintzinger HH. *J. Organomet. Chem.* 1985; **288**: 53.
12. Kaminsky W, Piel C, Scharlach K. *Macromol Symp.* 2005; **226**: 25.
13. Reybuck SE, Waymouth RM. *Macromolecules.* 2004; **37**: 2342.
14. Shapior PJ, Bunel E, Schaefer WP, Bercaw JE. *Organometallics.* 1990; **9**: 867.
15. Coates GW, Waymouth RM. *Science.* 1995; **267**: 217.
16. Reybuck SE, Meyer A, Waymouth RM. *Macromolecules.* 2002; **35**: 637.
17. Alt HG, Jung M. *J. Organomet. Chem.* 1998; **568**: 87.
18. Yano A, Hasegawa S, Akimoto A. *J. Mol. Catal A: Chem.* 1999; **148**: 77.
19. Alt HG, Zenk R. *J. Organomet. Chem.* 1996; **522**: 39.
20. Alt HG, Zenk R. *J. Organomet. Chem.* 1996; **526**: 295.
21. Lee SG, Hong SD, Park YW, Jeong BG, Nam DW, Jung HY, Lee H, Song KH. *J. Organomet. Chem.* 2004; **689**: 2586.
22. Ewen JA. *ACS Polym. Prepr.* 1991; **32**: 469.
23. Fink G. *Makromol. Chem. Macromol. Symp.* 1993; **66**: 157.
24. Spaleck W. In *Catalytic Olefin Polymerization*. Elseiver, Amsterdam: Kodansha, Tokyo, 1990; 501.
25. Kaminsky W, Hopf A, Piel C. *J. Organomet. Chem.* 2003; **684**: 200.
26. Huang JL, Zhang Y, Yang XX, Chen W, Qian YL. *J. Mol. Catal A: Chem.* 2005; **227**: 147.
27. Ewen JA, Haspeslagh L. *J. Am. Chem. Soc.* 1987; **109**: 6544.
28. Gauthier WJ, Corrigan JF, Taylor NJ, Collins S. *Macromolecules* 1995; **28**: 3771.
29. Hopf A, Kaminsky W. *Catal. Commun.* 2002; **3**: 459.
30. Job RC. US 5 270 410 1993; [*Chem. Abstr.* 1991; **114**: 145 225.]
31. Yoon JS, Lee YS, Park ES, Lee IM, Park DK, Jung SO. *Eur Polym J.* 2000; **36**: 1271.
32. Llinas GH, Day RO, Rausch MD, Chien JCW. *Organometallics.* 1993; **12**: 1283.
33. Schmidt R, Alt HG. *J. Organomet. Chem.* 2001; **621**: 304.