Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Molecular Catalysis A: Chemical 250 (2006) 145–152
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

ansa-Metallocene (R-Ph)$_2$C(Cp)(Ind)MCl$_2$ with electron withdrawing substituents on phenyl groups for olefin polymerization

Xiaoxia Yang, Yong Zhang, Jiling Huang *

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

Received 14 July 2005; received in revised form 20 January 2006; accepted 21 January 2006
Available online 28 February 2006

Abstract

The new ansa-complexes (R-Ph)$_2$C(Cp)(Ind)MCl$_2$ (R = CF$_3$, F, Cl; M = Ti, Zr or Hf) were synthesized from the reaction of dilithium salt of the corresponding ligands with appropriate group 4 metal halides. They were tested for ethylene homopolymerization and copolymerization in the presence of methylaluminoxane (MAO) at various ethylene pressures and temperatures. In the case of zirconocenes, complexes **2** (R = CF$_3$) and **8** (R = Cl) demonstrated much higher catalytic activity than complexes **10** (Ph$_2$C(Cp)(Ind)ZrCl$_2$) and **5** (R = F) in ethylene polymerization. The same trend was observed in titanocenes and hafnocenes. The electronic and geometric effects of substituents at the phenyl group on the polymerization activity were easily noticed. For the ethylene/1-hexene or 1-octene copolymerization, **2** also showed the highest catalytic activity, and the copolymers from complex **8** possessed the highest 1-hexene and 1-octene contents.

Keywords: Zirconocene; Substituent; Ethylene polymerization; Copolymerization

1. Introduction

After the discovery of methylaluminoxane (MAO) and the chiral *ansa*-metallocene catalyst, the metallocene containing cyclopentadienyl (Cp), indenyl (Ind) or fluorenyl (Flu) received a lot of attention because of the ability to produce polymers with high stereoregularity and good thermal properties [1–6]. R$_2$C(Cp)(Flu)MCl$_2$ (R = CH$_3$, Ph; M = Zr, Hf) complexes were highly active for polymerization of propylene to syndiotactic polypropylene [7,8], and also active for ethylene polymerization [9–11]. Green and Ishihara reported firstly in 1994 the complexes R$_2$C(Cp)(Ind)MCl$_2$ (R = CH$_3$, Ph and cyclohexyl; M = Ti, Zr, Hf) which were used for propylene and styrene polymerizations [12] showing normal activity. We know very well the modification of ligand environment on the metal can change space of the active species and ultimately affect the catalytic activity, stereoregularity and molecular weight. We have recently reported that (R-Ph)$_2$C(Cp)(Flu)MCl$_2$ (R = CF$_3$, F or Cl; M = Zr or Hf) complexes have higher activity in propylene polymerization [13]. The complex with the CF$_3$ substituent at the *meta* positions on the phenyl groups showed the highest activity which was 1.36 times as high as that of Ph$_2$C(Cp)(Flu)ZrCl$_2$. The obtained polymer was syndiotactic polypropylene with lower tacticity than that from classical catalyst Ph$_2$C(Cp)(Flu)ZrCl$_2$.

After we introduced halogen and CF$_3$ substituents into the phenyl groups of Ph$_2$C(Cp)(Ind)MCl$_2$ (M = Ti, Zr, Hf), these complexes exhibited excellent activity in ethylene homopolymerization and ethylene/α-olefin copolymerization. Especially, complexes **2** (R = CF$_3$, M = Zr) and **8** (R = Cl, M = Zr)/MAO showed about two times the catalytic activity of complex **10**/MAO in ethylene polymerization. For ethylene/1-hexene or 1-octene copolymerization, the highest activities from complex **2** reached 4.3×10^6 polymer/mol Zr h and 2.8×10^6 polymer/mol Zr h, respectively. All of these indicated the substituents played an important role in the catalytic activity.

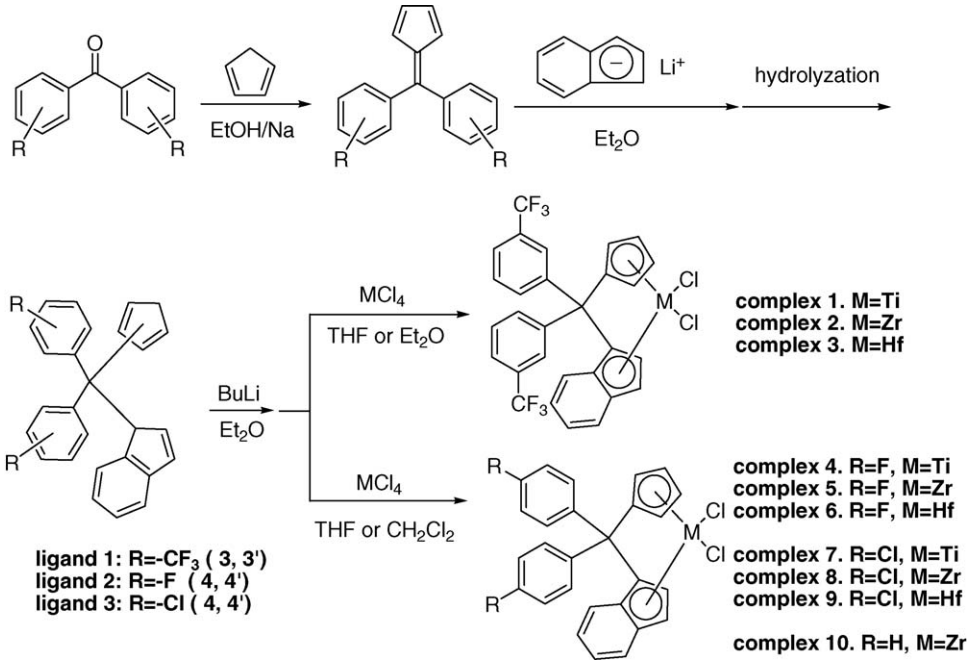
2. Results and discussion

2.1. Synthesis of (R-Ph)$_2$C(Cp)(Ind)MCl$_2$

The substituted diphenylfulvene was obtained according to the previous paper [13]. The new ligands (R-Ph)$_2$C(Cp)(Ind)

* Corresponding author. Tel.: +86 21 6425 3519; fax: +86 21 5428 2375.
E-mail address: qianling@online.sh.cn (J. Huang).

1381-1169/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2006.01.039



Scheme 1. Synthesis of complexes **1**–**10**.

(R = CF_3, F, Cl) were prepared by the reaction between the appropriate fulvene and indenyl lithium, followed by hydrolysis. Then the ligands were treated with two equivalents of *n*-butyllithium and reacted with the equivalent amount of MCl_4 (M = Ti, Zr or Hf). The complexes **1**–**9** were obtained by recrystallization from toluene or diethyl ether (Scheme 1).

The reaction of dilithium salts Li_2[(R-Ph)$_2$C(Cp)(Ind)] (R = F, Cl) with MCl_4 (M = Zr or Hf) must be processed in the CH_2Cl_2 solution. When THF or Et_2O were used in place of CH_2Cl_2, the reaction did not take place. Although dilithium salts Li_2[(*m*-*CF*$_3$-Ph)$_2$C(Cp)(Ind)] reacted with MCl_4 (M = Zr or Hf) in Et_2O, the corresponding complexes were obtained. For comparison the complex $Ph_2C(Cp)(Ind)ZrCl_2$ (**10**) was prepared according to the previous reference [12]. All of these complexes were used for ethylene homopolymerization and ethylene/α-olefin copolymerization in the presence of MAO.

2.2. *Polymerization of ethylene by complex **1**–**10**/MAO catalyst systems*

Ethylene polymerizations by **1**–**10** were performed in toluene in the presence of MAO at different ethylene pressures and different temperatures. The results are summarized in Table 1.

All of these complexes showed high catalytic activities for ethylene polymerization. In general, zirconocenes had the higher catalytic activity than titanocenes and hafnocenes (**2** > **3** > **1**, **5** > **6** > **4**, **8** > **7** > **9**). It was noted that titanocene **7** had catalytic activity similar to zirconcene **10** at 80 °C.

For zirconocenes, the catalytic activity for ethylene polymerization at 60 °C and 11 atm increased in the order **5** < **10** < **8** ≈ **2** (Fig. 1). The substituents on the phenyl groups played an important role in the catalytic activity. Complexes **2** and **8** containing CF_3 and Cl substituents exhibited remarkable catalytic activity (27.16×10^5 g PE/mol Zr h and 26.70×10^5 g PE/mol Zr h), respectively, which were two times as high as complex **10**, and complex **5** containing a F substituent showed the lower activity than **10**. The results of titanocenes and hafnocenes were consistent with zirconocenes. In the case of fluorine atom substituted complex **5**, the fluorine atom with a small radius was at the *para* position on the phenyl group, far away from the metal center, so the electronic effect seemed to be more important than steric hindrance in space. On the one hand, the fluorine atom being a strong electron withdrawing substituent, it led to a more electron positive metal center, which would accelerate coordination and insertion of monomer. On the other hand, a more electron positive metal center should enhance interactions with the counter ion of cocatalyst, leading to slower coordination and insertion of monomer. Which situation was predominant depended on the structure of the complex. If the metal center was incompletely shielded by the ligands, the close association effect of counter ion prevailed, and if the metal center was protected by bulky ligands, the close association effect between the counter ion

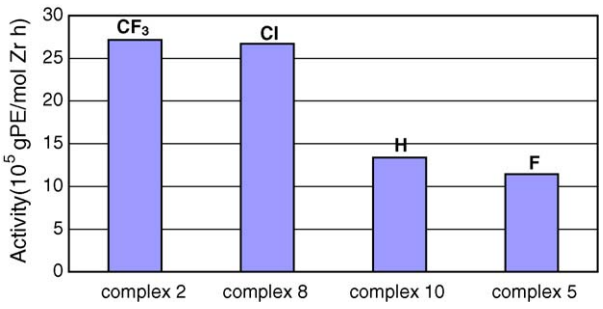


Fig. 1. Effect of substituent of zirconocenes on catalytic activity (*polymerization conditions*: [Zr] = 1×10^{-4} mol/L, time = 30 min, [Al]/[Zr] = 1000, temperature = 60 °C, ethylene pressure = 11 atm, 20 mL toluene).

Table 1
Ethylene polymerization by complexes **1**–**10**/MAO systems[a]

Run	Complex	Pressure (atm)	Temperature (°C)	Activity[b] ($\times 10^5$)	M_η ($\times 10^5$)
1	**10**	11	60	13.35	
2		11	60	3.28	
3	**1**(CF_3,Ti)	11	80	3.51	
4		8	80	3.43	
5		5	80	2.43	
6		11	60	27.16	0.25
7		11	80	20.62	0.13
8	**2**(CF_3,Zr)	8	80	23.31	
9		5	80	5.97	
10		2	80	5.52	
11		11	60	4.89	
12		11	80	10.37	
13	**3**(CF_3,Hf)	8	80	12.49	
14		5	80	2.84	
15		2	80	0.81	
16		11	60	2.01	
17	**4**(F,Ti)	11	80	2.32	
18		8	80	1.94	
19		5	80	1.03	
20		11	60	11.46	0.22
21		11	80	17.63	0.16
22	**5**(F,Zr)	8	80	12.98	
23		5	80	9.22	
24		2	80	1.43	
25		11	60	2.25	
26		11	80	4.99	
27	**6**(F,Hf)	8	80	2.61	
28		5	80	1.35	
29		2	80	1.69	
30		11	60	3.12	
31		11	80	13.64	
32	**7**(Cl,Ti)	8	80	13.24	
33		5	80	10.11	
34		5	60	2.40	
35		11	30	2.38	
36		11	60	26.70	0.31
37	**8**(Cl,Zr)	11	80	28.06	0.19
38		8	80	22.28	
39		5	80	19.63	
40		2	80	5.28	
41		11	60	1.47	
42		11	80	6.47	
43	**9**(Cl,Hf)	8	80	3.77	
44		5	80	2.74	
45		2	80	1.22	

[a] Polymerization conditions: [M] = 1×10^{-4} mol/L, time = 30 min, [Al]/[M] = 1000, 20 mL toluene.
[b] g PE/(mol Zr h).

pair was disfavored. It was reported by Siedle that metallocene (2,7-F_2-Flu-C_2H_4-Flu)$ZrCl_2$ showed higher activity than (Flu-C_2H_4-Flu)$ZrCl_2$ in octene polymerization, because the metal center was protected by bulky fluorenyl ligands and the counter ion pair was disfavoured [14]. But in the case of complex **5** (*p*-F-Ph)$_2$C(Cp)(Ind)$ZrCl_2$ in this work, since the steric bulkness of cyclopentadienyl and indenyl was so small and the metal center was partially exposed, the close association effect of counter ion prevails. So the complex **5** showed lower activity. Furthermore, some studies reported that the introduction of fluorine atoms led to a decrease in catalytic activity [15,16].

In our studies, the complex **8** containing chlorine atoms showed higher catalytic activity than unsubstituted complexes **10** and **5**. The results appeared to be inconsistent with the above results. Although the chlorine atom was an electron withdrawing substituent, the electronegativity of chlorine atom was obviously weaker than the fluorine atom. Then its electron-withdrawing effect was not so strong as the fluorine atom. Normally, it was reasonable to consider the p–π conjugate effect between the chlorine atom and the phenyl group when the chlorine atom is connected directly with the phenyl group. Although the effect of the chlorine atom is complicated, it was surmised that the chlorine atom should be regarded as an electron-donating substituent here according to our results.

On the other hand, for CF_3 substituted complex **2**, because it was substituted at the *meta* position of the phenyl group, its electronic effect could not influence the charge of metal center. It is more reasonable to suggest that the steric hindrance of CF_3 played an essential role in the catalytic activity here. The CF_3 substituent at the *meta* position placed a greater steric hindrance in space. The active center was shielded by the fluorine atoms and kept away from their counter ion charge because the fluorine atoms and their counter ion repelled each other. The loosened ion pairing should prevail and resulted in enhanced interactions between metal center and olefin in polymerization. The results were consistent with our prior report [13]. In our previous works, we also found (*m*-CF_3-Ph)$_2$C(Cp)(Flu)$ZrCl_2$ had the higher catalytic activity than Ph_2C(Cp)(Flu)$ZrCl_2$ in propylene polymerization.

Fig. 2 summarizes the influence of ethylene pressure on the catalytic activity at 80 °C. The catalytic activities increased as the ethylene pressure increases from 2 atm to 8 atm for all catalysts. Especially, when ethylene pressure enhanced from 5 atm to 8 atm, the catalytic activities of complexes (**2**, **3**) containing the CF_3 substituent increased rapidly. Higher ethylene pressure means the enhancement of ethylene concentrations in toluene, which was the main reason for the increase in the catalytic activity. It should be noteworthy that the catalytic activities of complexes **2** and **3** slightly decreased when ethylene pressure increased from 8 atm to 11 atm, and that the catalytic activities of complexes **5**, **6**, **8**, and **9** (see Table 1) increased as usual. It

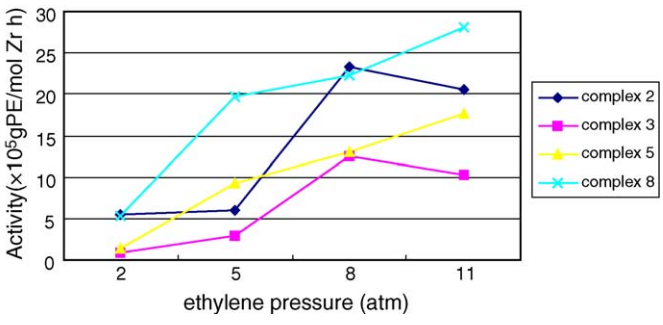


Fig. 2. Influence of ethylene pressure on catalytic activity.

is also noted that complexes **2** and **3** contained CF_3 at the *meta* position on the phenyl groups, so we assume that the reason for the decrease in the catalytic activity would be due to the special structure of complexes **2** and **3**, although we did not have any clear elucidation.

The catalytic activities of all complexes increased as the reaction temperature increased from 60 °C to 80 °C. On the other hand, the active center becomes unstable at high temperature, the compromise of two factors making the activity of complex **2** decreased slightly over 80 °C.

2.3. Copolymerization of ethylene and 1-hexene by complexes (2, 3, 5, 6, 8, 9, 10)/MAO catalyst systems

The results for ethylene/1-hexene copolymerization by complexes **2**, **3**, **5**, **6**, **8**, **9**, **10**/MAO catalytic systems are summarized in Table 2. Zirconocene catalysts showed the higher catalytic activity than hafnocene catalysts.

For these zirconocene catalysts, it was revealed that catalytic activity for the ethylene/1-hexene copolymerization increased in the order **5** < **8** < **10** < **2**. It is important to note that complex **2** showed the highest catalytic activity among these complexes, which was the same as in ethylene polymerization. The copolymer from catalyst **2** showed similar 1-hexene contents to the copolymer from **10**. We also found the catalytic activity of **10** was higher than that of **8**. Copolymer from catalyst **8** (Run 5) possessed the higher 1-hexene contents than that from catalyst **10** (Run 7).

The contents of 1-hexene in the copolymers resulting from these complexes were almost the same as those resulting from complex **10**, except the complex **8** led to higher incorporation of 1-hexene than complex **10**. The contents of 1-hexene were influenced slightly by the substituents. Fig. 3 shows the ^{13}C NMR spectrum for copolymer of ethylene/1-hexene (E–H) obtained from the complex **8**/MAO catalyst. The weak sharp signal near 11 ppm indicated the existence of ethyl branches in the copolymer. This might be explained by a mechanism including β-hydrogen transfer from the growing chain to incoming monomer followed by insertion of the unsaturated terminal into the formed ethyl-zirconium bond [17–20].

Table 2
Ethylene/1-hexene copolymerization by complexes **2**, **3**, **5**, **6**, **8**, **9**, **10**/MAO catalyst systems[a]

Run	Complex	Temperature (°C)	Al/M[b]	Activity[c] (×10^5)	1-Hexene content (mol%)[d]
1	**2**(CF_3,Zr)	60	1000	43.14	5.34
2	**3**(CF_3,Hf)	60	1000	1.198	–
3	**5**(F,Zr)	60	1000	11.85	5.27
4	**6**(F,Hf)	60	1000	0.029	–
5	**8**(Cl,Zr)	60	1000	30.81	6.53
6	**9**(Cl,Hf)	60	1000	0.263	–
7	**10**	60	1000	35.51	5.28

[a] Copolymerization conditions: [M] = 1 × 10^−4 mol/L, time = 30 min, 1-hexene 1 mL, 20 mL toluene, ethylene pressure 11 atm.
[b] Molar ratio of Al/Zr or Al/Hf.
[c] g Copolymer/(mol Zr h).
[d] 1-Hexene content in copolymer determined by ^{13}C NMR spectra.

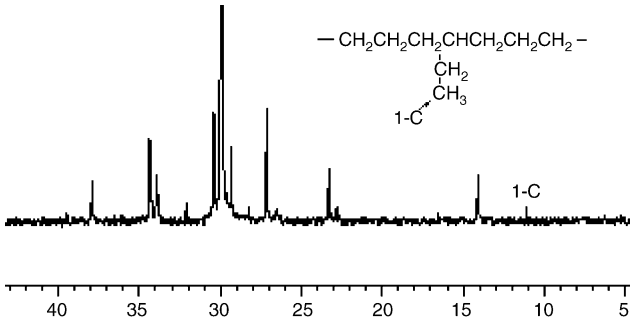


Fig. 3. ^{13}C NMR spectrum for copolymer of ethylene/1-hexene from complex **8**/MAO catalyst.

The differential scanning calorimetry (DSC) heating curves for E–H copolymers made by **2** or **8**/MAO are shown in Fig. 4. As expected, copolymer made by **2**/MAO exhibited the higher melting temperature (109 °C) than that (97.7 °C) made by **8**/MAO, which indicates that the copolymer made by **8**/MAO has the shorter ethylene sequences. This fact is consistent with what we can see from Table 2. Copolymer made by **8**/MAO showed the higher incorporation than copolymer made by **2**/MAO. Two copolymers showed the two or three peaks for melting point in the DSC spectra, The multi-melting-points were mainly due to the different lengths of ethylene sequence formed in the copolymer of ethylene and 1-hexene [21].

2.4. Copolymerization of ethylene and 1-octene by complexes (2, 3, 5, 6, 8, 9)/MAO catalyst systems

As shown in Table 3, zirconocene catalysts showed about 1000 times the catalytic activity of hafnocene catalysts in copolymerization of ethylene/1-octene. Complexes **2** and **8** showed the highest catalytic activity, which was the same as in ethylene polymerization. Complex **8** produced the copolymers with the highest octene incorporation. This was also the case in ethylene/1-hexene copolymerization. Fig. 5 shows the ^{13}C NMR spectrum for the ethylene/1-octene copolymer made by the complex **8**/MAO catalyst. We can also observe the signal arisen from the ethyl branch in the copolymer at about 11 ppm.

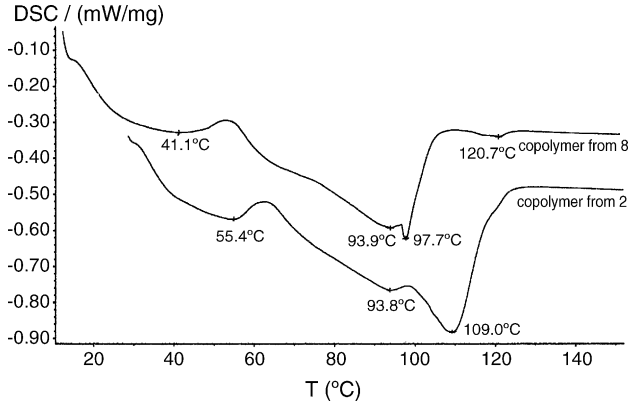


Fig. 4. DSC heating curves for ethylene/1-hexene copolymers made from **2**, **8**/MAO.

Table 3
Ethylene/1-octene copolymerization by complexes **2**, **3**, **5**, **6**, **8**, **9**/MAO catalyst systems[a]

Run	Complex	Temperature (°C)	Al/M[b]	Activity[c] /10^5	1-Octene content (mol%)[d]
1	**2**(CF_3,Zr)	60	1000	28.07	3.31
2	**3**(CF_3,Hf)	60	1000	0.029	–
3	**5**(F,Zr)	60	1000	6.01	3.58
4	**6**(F,Hf)	60	1000	0.013	–
5	**8**(Cl,Zr)	60	1000	26.60	5.29
6	**9**(Cl,Hf)	60	1000	0.025	–

[a] Copolymerization conditions: [M] = 1×10^{-4} mol/L, time = 30 min, 1-octene 1 mL, 20 mL toluene, ethylene pressure 11 atm.
[b] Molar ratio of Al/Zr or Al/Hf.
[c] g Copolymer/(mol Zr h).
[d] 1-Octene content in copolymer determined by ^{13}C NMR spectra.

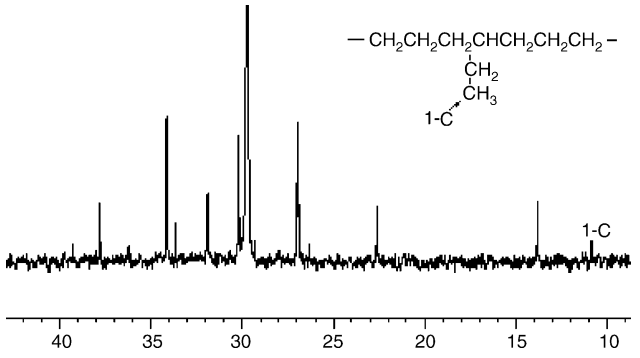


Fig. 5. ^{13}C NMR spectrum for copolymer of ethylene/1-octene from complex **8**/MAO catalyst.

3. Experimental

3.1. General procedures

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, from which they were distilled before use. Dichloromathane (CH_2Cl_2) was refluxed over phosphorus pentoxide (P_2O_5), and distilled prior to use. The cocatalyst 1.53 M methylaluminoxane (MAO) in toluene was purchased from Witco. 1-Hexene and 1-octene were distilled over sodium under argon and stored in the presence of activated 4 A molecular sieves. Ethylene for polymerization 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 analyses were carried out on an EA-1106 type analyzer. ^1H NMR spectra were recorded on a Bruker AVANCE 500-MHz spectrometer with TMS as internal standard. Mass spectrometry (MS) spectra 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.

3.2. Synthesis of 1,1′-(2,4-cyclopentadienylidenemethylene)bis-(3-trifluoromethylphenyl)

Synthesis of 1,1′-(2,4-cyclopentadien-ylidenemethylene) bis-(3-trifluoromethyl-phenyl) were conducted according to the previous report [13].

1,1′-(2,4-Cyclopentadien-ylidenemethylene)bis-(4-chlorophenyl) and 1,1′-(2,4-cyclopentadien-ylidenemethylene)bis-(4-fluorophenyl) were obtained by using a similar procedure.

3.3. Synthesis of (m-CF_3-Ph)$_2$C(C_5H_5)(C_9H_7) (ligand **1**)

Indenyl lithium (1.0 g, 8.2 mmol) in Et_2O (50 mL) was added to the solution of 1,1′-(2,4-cyclopentadienylidenemethylene)bis-(*m*-CF_3-phenyl) (3.0 g, 8.2 mmol) in Et_2O (30 mL) at 0 °C. 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 in vacuo to produce yellow viscous oil. The product was purified by chromatography on alumina (petroleum ether as a developer). A white solid powder (ligand **1**) 2.5g (yield 63%) was obtained.

The white powders (*p*-F-Ph)$_2$C(C_5H_5)(C_9H_7) (ligand **2**) (yield 75%) and (*p*-Cl-Ph)$_2$C(C_5H_5)(C_9H_7) (ligand **3**) (yield 79%) were obtained by using similar procedures.

3.4. Synthesis of complex (m-CF_3-Ph)$_2$C(C_5H_4)(C_9H_6)$TiCl_2$ (complex **1**)

A solution of *n*-butyllithium (1.66 mol/L, 1.75 mL, 2.90 mmol) in Et_2O (20 mL) was added to the solution of ligand **1** (0.70 g, 1.45 mmol) in Et_2O (30 mL) at 0 °C. The solution turned red with eventual solid precipitation. After removal of solvent in vacuo, dilithium salt of ligand was obtained as a white solid. The solution of dilithium salt in THF (50 mL) was dropped to the suspension of $TiCl_4$ ($TiCl_4$·2THF, 0.48 g, 1.45 mmol) in THF (30 mL) at 0 °C. After HCl gas was bubbled into the solution for 5 min, the solution became dark green. The mixture was stirred at room temperature overnight. Then solvent was removed in vacuo and Et_2O was added. The filtrate was reduced to 10mL in vacuo. Cooling to −20 °C overnight gave dark green crystals 70 mg (yield 8%). ^1H NMR (ppm, $CDCl_3$): $\delta = 7.64$ (s, 1H, Ph), 7.59 (d, $J = 7.8$ Hz, 1H, Ph), 7.51 (d, $J = 7.6$ Hz, 1H, Ind), 7.48 (d, $J = 7.8$ Hz, 1H, Ind), 7.4–7.38 (m, 2H, Ph), 7.26–7.25 (m, 3H, Ph), 7.21 (td, $J_1 = 0.9$ Hz, $J_2 = 7.6$ Hz, 1H, Ph), 6.93–6.89 (m, 2H, Ind), 6.51 (s, 2H, Ind, Cp), 6.49 (dt, $J_1 = 1.7$ Hz, $J_2 = 5.4$ Hz, 1H, Cp), 6.27 (d, $J = 5.6$ Hz, 1H, Ind), 6.22 (m, 1H, Cp), 6.17 (dt, $J_1 = 1.7$ Hz, $J_2 = 5.4$ Hz, 1H, Cp), 3.48 (q, $J = 7.0$ Hz, 0.8H, CH_3), 1.21 (t, $J = 7.0$ Hz, 1.2H, CH_2). MS (70 eV): $m/z = 480$ (100, M^+-$TiCl_2$), 411 (12, M^+-$TiCl_2$-CF_3), 335 (33, M^+-$TiCl_2$-$C_6H_4CF_3$), 266 (8, M^+-$TiCl_2$-$C_6H_4CF_3$-CF_3). IR (cm^{-1}, KBr): 3102w, 2960m, 2928m, 2869w, 1611w, 1593w, 1489w, 1458m, 1441m, 1366w, 1332s, 1289w, 1260m, 1251m, 1178s, 1165s, 1125s, 1097s, 1073s, 1024m, 981w, 958w,

915w, 862w, 802s, 778s, 714m, 699m, 665m, 630w, 432w. Anal. Calcd. for $C_{29}H_{18}Cl_2F_6Ti{\cdot}0.2C_4H_{10}O$: C, 58.29 H, 3.78; found: C, 58.88; H, 4.10%.

(*p*-F-Ph)$_2$C(C_5H_4)(C_9H_6)$TiCl_2$ (complex **4**) was obtained by using a similar procedure (yield 13%). ^{1}H NMR (ppm, $CDCl_3$): δ = 7.83–7.89 (m, 3H, Ph), 7.73 (m, 1H, Ind), 7.68 (d, J = 8.6 Hz, 1H, Ind), 7.47 (dd, J_1 = 8.9 Hz, J_2 = 6.4 Hz, 1H, Ph), 7.26 (d, J = 5.0 Hz, 1H, Ind), 7.08–7.19 (m, 4H, Ph), 6.83 (dd, J_1 = 5.6 Hz, J_2 = 3.4 Hz, 1H, Cp), 6.75–6.78 (m, 2H, Cp, Ind), 6.20 (d, J = 9.2 Hz, 1H, Ind), 5.81 (d, J = 3.4 Hz, 1H, Ind), 5.56 (dd, J_1 = 5.2 Hz, J_2 = 2.8 Hz, 1H, Cp), 5.49 (dd, J_1 = 5.2 Hz, J_2 = 2.8 Hz, 1H, Cp). MS (70 eV): m/z = 498 (12, M^+), 463 (69, M^+-Cl), 428 (4, M^+-2Cl), 380 (15, M^+-$TiCl_2$), 285 (12, M^+-$TiCl_2$-FPh). IR (cm^{-1}, KBr): 3130w, 3062w, 2865w, 1603m, 1506s, 1466w, 1444w, 1413w, 1381w, 1304w, 1223s, 1163s, 1108m, 1082w, 1016w, 816s, 747s, 700w, 578s, 546w, 471m. HRMS for $C_{27}H_{18}Cl_2F_2Ti$: 498.0233; found: 498.0250.

(*p*-Cl-Ph)$_2$C(C_5H_4)(C_9H_6)$TiCl_2$ (complex **7**) was obtained by using a similar procedure (yield 17%). ^{1}H NMR (ppm, $CDCl_3$): δ = 7.84 (dd, J_1 = 8.6 Hz, J_2 = 2.3 Hz, 1H, Ph), 7.82 (d, J = 8.6 Hz, 2H, Ph), 7.67–7.70 (m, 2H, Ind), 7.45–7.49 (m, 2H, Ph), 7.30 (d, J = 8.6 Hz, 2H, Ph), 7.25 (d, 1H, Ind), 7.37 (dd, J_1 = 8.4 Hz, J_2 = 2.2 Hz, 1H, Ph), 6.83 (dd, J_1 = 2.8 Hz, J_2 = 5.3 Hz, 1H, Cp), 6.79 (d, J = 8.8, 1H, Ind), 6.76 (dd, J_1 = 2.8 Hz, J_2 = 5.3 Hz, 1H, Cp), 6.23 (d, J = 8.8 Hz, 1H, Ind), 5.80 (d, J = 3.4 Hz, 1H, Ind), 5.54 (dd, J_1 = 2.8 Hz, J_2 = 5.3 Hz, 1H, Cp), 5.48 (dd, J_1 = 2.8 Hz, J_2 = 5.3 Hz, 1H, Cp). MS (70 eV): m/z = 530 (19, M^+), 495 (48, M^+-Cl), 494 (100, M^+-HCl), 460 (16, M^+-2Cl), 416 (4, M^+-Ind), 412 (13, M^+-$TiCl_2$), 300 (9, M^+-$TiCl_2$-C_6H_4Cl). IR (cm^{-1}, KBr): 3109m, 2958m, 2924m, 2853m, 1639w, 1590w, 1487s, 1469m, 1446m, 1405m, 1380w, 1261w, 1245w, 1158w, 1093s, 1047m, 1013s, 871w, 813s, 747s, 719w, 695w, 540s, 503m, 477m, 463w, 448w. HRMS for $C_{27}H_{18}Cl_4Ti$: 531.9613; found: 531.9529.

3.5. Synthesis of complex (*m*-CF_3-Ph)$_2$C(C_5H_4)(C_9H_6)$ZrCl_2$ (complex **2**)

A solution of *n*-butyllithium (0.77 mol/L, 5.10 mL, 4.00 mmol) in Et_2O (20 mL) was added to the solution of ligand **1** (0.96 g, 2.00 mmol) in Et_2O (50 mL) at 0 °C. The solution turned red with eventual solid precipitation. Then $ZrCl_4$ (0.46g, 2.00 mmol) was added into the reaction at −78 °C. The mixture was stirred at room temperature overnight. The solvent was removed in vacuo to yield a yellow solid which was dissolved in toluene leaving a precipitate of white LiCl. The filtrate was reduced to 10 mL in vacuo. Cooling to −20 °C overnight gave yellow crystals 530 mg (yield 34%). ^{1}H NMR (ppm, $CDCl_3$): δ = 8.18 (d, J = 9.3 Hz, 1H, Ph), 8.11–8.14 (m, 2H, Ph), 7.93 (d, J = 8.5 Hz, 1H, Ind), 7.70 (dd, J_1 = 8.5 Hz, J_2 = 2.8 Hz, 1H, Ind), 7.51–7.61 (m, 4H, Ph), 7.37 (t, J = 7.5 Hz, 1H, Ph), 7.16–7.21 (m, 7.5H, toluene), 6.98 (t, J = 3.6 Hz, 1H, Ind), 6.83 (t, J = 7.3 Hz, 1H, Ind), 6.64 (dd, J_1 = 15.5 Hz, J_2 = 2.3 Hz, 2H, Cp), 6.23 (dd, J_1 = 7.3 Hz, J_2 = 2.8 Hz, 1H, Ind), 6.21 (d, J = 3.6 Hz, 1H, Ind), 5.86 (dd, J_1 = 15.5 Hz, J_2 = 2.3 Hz, 1H, Cp), 5.70 (s, 1H, Cp), 2.36 (s, 4.5H, CH_3). MS (70 eV): m/z = 640 (87, M^+), 480 (51, M^+-$ZrCl_2$), 366 (7, M^+-$ZrCl_2$-Ind), 335 (13, M^+-$ZrCl_2$-$C_6H_4CF_3$), 297 (7, M^+-$ZrCl_2$-Ind-CF_3). IR (cm^{-1}, KBr): 3110w, 3085w, 3065w, 2922w, 2852w, 1612w, 1492w, 1461w, 1445m, 1407w, 1380w, 1330s, 1290m, 1234m, 1168s, 1124s, 1076s, 1001w, 956w, 872w, 807s, 778s, 747m, 714s, 699m, 675m. Anal. Calcd. for $C_{29}H_{18}Cl_2F_6Zr{\cdot}1.5C_6H_5CH_3$: C, 43.82, H, 5.01; found: C, 43.85, H, 5.29%.

3.6. Synthesis of complex (*p*-F-Ph)$_2$C(C_5H_4)(C_9H_6)$ZrCl_2$ (complex **5**)

A solution of *n*-butyllithium (0.77 mol/L, 6.80 mL, 5.22 mmol) in Et_2O (20 mL) was added to the solution of ligand **2** (1.00 g, 2.61 mmol) in Et_2O (50 mL) at 0 °C. The solution turned red with eventual solid precipitation. After removal of solvent in vacuo, dilithium salt of ligand was obtained as a white solid. The solution of dilithium salt in CH_2Cl_2 (50 mL) was dropped to the suspension of $ZrCl_4$ (0.61g, 2.61 mmol) in CH_2Cl_2 (30 mL) at 0 °C. The mixture was stirred at room temperature overnight. The solvent was removed in vacuo to yield a yellow solid which was dissolved in toluene leaving a precipitate of white LiCl. The filtrate was reduced to 10 mL in vacuo. Cooling to −20 °C overnight gave yellow crystals 790 mg (yield 56%). ^{1}H NMR (ppm, $CDCl_3$): δ = 7.82–7.88 (m, 3H, Ph), 7.68 (d, J = 8.61, 1H, Ind), 7.64 (m, 1H, Ind), 7.36 (dd, J_1 = 8.4 Hz, J_2 = 6.9 Hz, 1H, Ph), 7.04–7.14 (m, 4H, Ph), 6.93 (d, J = 3.5 Hz, 1H, Ind), 6.82 (t, J = 3.9 Hz, 1H, Ind), 6.60 (dd, J_1 = 5.9 Hz, J_2 = 3.1 Hz, 1H, Cp), 6.58 (dd, J_1 = 5.9 Hz, J_2 = 3.1 Hz, 1H, Cp), 6.35 (d, J = 9.0 Hz, 1H, Ind), 6.23 (d, J = 3.6 Hz, 1H, Ind), 5.86 (dd, J_1 = 5.5 Hz, J_2 = 2.8 Hz, 1H, Cp), 5.70 (dd, J_1 = 5.5 Hz, J_2 = 2.8 Hz, 1H, Cp). MS (70 eV): m/z = 540 (2, M^+), 380 (6, M^+-$ZrCl_2$), 316 (4, M^+-$ZrCl_2$-C_5H_4), 285 (4, M^+-$ZrCl_2$-C_6H_4F), 266 (9, M^+-$ZrCl_2$-C_9H_6), 221 (4, M^+-$ZrCl_2$-C_5H_4-C_6H_4F). IR (cm^{-1}, KBr): 3115m, 2958m, 2924m, 1627m, 1602s, 1506s, 1460m, 1409w, 1391w, 1231s, 1163s, 1104w, 1068w, 1015w, 832s, 813s, 801s, 783m, 763m, 732m, 696w, 662w, 627w, 580m, 518m, 468w, 420w, 406w. Anal. Calcd. for: $C_{27}H_{18}Cl_2F_2Zr$: C, 59.77, H, 3.34; found: C, 59.30, H, 3.56%.

(*p*-Cl-Ph)$_2$C(C_5H_4)(C_9H_6)$ZrCl_2$ (complex **8**) were obtained by using a similar procedure (yield 60%). ^{1}H NMR (ppm, $CDCl_3$): δ = 7.83 (m, 2H, Ph), 7.80 (dd, J_1 = 8.5 Hz, J_2 = 2.4 Hz, 1H, Ph), 7.68 (d, J = 8.6 Hz, 1H, Ind), 7.61 (dd, J_1 = 8.5 Hz, J_2 = 2.4 Hz, 1H, Ind), 7.43 (dd, J_1 = 8.4 Hz, J_2 = 2.3 Hz, 1H, Ph), 7.38–7.39 (d, J = 8.8 Hz, 2H, Ph), 7.32–7.36 (t, 2H, Ph), 6.93 (d, J = 3.4 Hz, 1H, Ind), 6.83 (t, 1H, Ind), 6.60 (dd, J_1 = 5.9 Hz, J_2 = 3.1 Hz, 1H, Cp), 6.58 (dd, J_1 = 5.9 Hz, J_2 = 3.1 Hz, 1H, Cp), 6.38 (d, J = 9.1 Hz, 1H, Ind), 6.21 (d, J = 3.4 Hz, 1H, Ind), 5.84 (dd, J_1 = 5.4 Hz, J_2 = 2.8 Hz, 1H, Cp), 5.69 (dd, J_1 = 5.4 Hz, J_2 = 2.8 Hz, 1H, Cp), 2.36 (s, 1.5H, CH_3). MS (70 eV): m/z = 574 (88, M^+), 461 (23, M^+-C_6H_4Cl), 412 (26, M^+-$ZrCl_2$), 301 (15, M^+-$ZrCl_2$-C_6H_4Cl). IR (cm^{-1}, KBr): 3099m, 3030m, 2956w, 2855w, 1634s, 1490s, 1461w, 1447w, 1405w, 1093s, 1043w, 1013s, 868w, 821s, 808s, 738s, 698m, 604m, 539s, 502m, 471m, 446w. Anal. Calcd. for $C_{27}H_{18}Cl_4Zr{\cdot}0.5C_6H_5CH_3$: C, 58.89, H, 3.58; found: C, 58.41, H, 4.32%.

3.7. Synthesis of complex $(m\text{-}CF_3\text{-}Ph)_2C(C_5H_4)(C_9H_6)HfCl_2$ (complex **3**)

A solution of *n*-butyllithium (1.64 mol/L, 2.50 mL, 4.12 mmol) in Et_2O (20 mL) solution was added to the solution of ligand **1** (1.00 g, 2.06 mmol) in Et_2O (50 mL) at 0 °C. The solution turned red with eventual solid precipitation. Then $HfCl_4$ (0.66g, 2.06 mmol) was added into the reaction at −78 °C. The mixture was stirred at room temperature overnight. The solvent was removed in vacuo to yield a yellow solid which was dissolved in toluene leaving a precipitate of white LiCl. The filtrate was reduced to 10 mL in vacuo. Cooling to −20 °C overnight gave yellow crystals 530 mg (yield 31%). ^{1}H NMR (ppm, $CDCl_3$): δ = 8.20–8.11 (m, 3H, Ph), 7.93 (d, J = 10.6 Hz, 1H, Ind), 7.67 (dd, J_1 = 3.19 Hz, J_2 = 8.8 Hz, 1H, Ind), 7.52–7.66 (m, 4H, Ph), 7.33 (t, J_1 = 7.1 Hz, J_2 = 8.2 Hz, 1H, Ph), 7.25–7.20 (m, 5H, toluene-Ph), 6.87 (t, J = 3.9 Hz, 1H, Ind), 6.81 (t, J = 7.0 Hz, 1H, Ind), 6.56 (m, 2H, Cp), 6.26 (m, 1H, Ind), 6.16 (d, J_1 = 3.9 Hz, 1H, Ind), 5.78 (dd, J_1 = 2.5 Hz, J_2 = 15.4 Hz, 1H, Cp), 5.64 (d, J = 2.0 Hz, 1H, Cp), 2.36 (s, 3H, CH_3). MS (70 eV): m/z = 730 (100, M^+), 480 (37, M^+-$HfCl_2$), 423 (25, M^+-$HfCl_2$-3F), 411 (7, M^+-$HfCl_2$-CF_3), 335 (18, M^+-$HfCl_2$-$C_6H_4CF_3$), 178 (15, M^+-$HfCl_2$-$2C_6H_4CF_3$). IR (cm^{-1}, KBr): 3024w, 2958m, 2924m, 2857w, 1629w, 1493m, 1461w, 1446m, 1407w, 1380w, 1329s, 1288m, 1235m, 1212w, 1166s, 1123s, 1075s, 1054m, 1043m, 1029w, 1000w, 969w, 957w, 929w, 913w, 872w, 829m, 816m, 779m, 736m, 714m, 698m, 675m, 651w, 465m, 427w. Anal. Calcd. for $C_{29}H_{18}Cl_2F_6Hf{\cdot}C_6H_5CH_3$: C, 52.60, H, 3.19; found: C, 53.12, H, 3.90%.

3.8. Synthesis of complex $(p\text{-}F\text{-}Ph)_2C(C_5H_4)(C_9H_6)HfCl_2$ (complex **6**)

A solution of *n*-butyllithium (1.64 mol/L, 3.20 mL, 5.22 mmol) in Et_2O (20 mL) solution was added to the solution of ligand **2** (1.00 g, 2.61 mmol) in Et_2O (50 mL) at 0 °C. The solution turned red with eventual solid precipitation. After removal of solvent in vacuo, dilithium salt of ligand was obtained as a white solid. The solution of dilithium salt in CH_2Cl_2 (50 mL) was dropped to the suspension of $HfCl_4$ (0.84 g, 2.61 mmol) in CH_2Cl_2 (30 mL) at 0 °C. The mixture was stirred at room temperature overnight. The solvent was removed in vacuo to yield a yellow solid which was dissolved in toluene leaving a precipitate of white LiCl. The filtrate was reduced to 10 mL in vacuo. Cooling to −20 °C overnight gave yellow crystals 881mg (yield 53%). ^{1}H NMR (ppm, $CDCl_3$): δ = 7.88 (m, 2H, Ph), 7.83 (m, 1H, Ph), 7.62–7.65 (m, 2H, Ind), 7.32 (dd, J_1 = 8.9 Hz, J_2 = 3.2 Hz, 1H, Ph), 7.03–7.15 (m, 4H, Ph), 6.82 (m, 1H, Ind), 6.79 (m, 1H, Ind), 6.52 (dd, J_1 = 5.7 Hz, J_2 = 3.3 Hz, 1H, Cp), 6.49 (dd, J_1 = 5.7 Hz, J_2 = 3.3 Hz, 1H, Cp), 6.37 (d, J = 8.3 Hz, 1H, Ind), 6.18 (d, J = 3.5 Hz, 1H, Ind), 5.78 (dd, J_1 = 5.5 Hz, J_2 = 2.9 Hz, 1H, Cp), 5.64 (dd, J_1 = 5.5 Hz, J_2 = 2.9 Hz, 1H, Cp). MS (70 eV): m/z = 630 (69, M^+), 535 (17, M^+-C_6H_4F), 380 (67, M^+-$HfCl_2$), 316 (15, M^+-$HfCl_2$-C_5H_4), 285 (26, M^+-$HfCl_2$-C_6H_4F), 266 (42, M^+-$HfCl_2$-Ind). IR (cm^{-1}, KBr): 3106w, 3089w, 3045w, 3029w, 2921w, 2854w, 1602m, 1505s, 1461w, 1449w, 1412w, 1379w, 1303w, 1225s, 1159s, 1105m, 1054w, 1014w, 866w, 826s, 808s, 739s, 712w, 699w, 578s, 543w, 465m, 402w. Anal. Calcd. for $C_{27}H_{18}Cl_2F_2Hf$: C, 51.49, H, 2.89; found: C, 51.91, H, 4.47%.

$(p\text{-Cl-Ph})_2C(C_5H_4)(C_9H_6)HfCl_2$ (complex **9**) was obtained by using a similar procedure (yield 33%). ^{1}H NMR (ppm, $CDCl_3$): δ = 7.84 (m, 2H, Ph), 7.80 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H, Ph), 7.64 (d, J = 9.0 Hz, 1H, Ind), 7.61 (dd, J_1 = 8.5 Hz, J_2 = 2.4 Hz, 1H, Ind), 7.43 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H, Ind), 7.39 (dd, J_1 = 11.3 Hz, J_2 = 2.4 Hz, 2H, Ph), 7.31–7.34 (m, 2H, Ph), 6.80–6.83 (m, 2H, Ind), 6.52 (dd, J_1 = 6.4 Hz, J_2 = 3.1 Hz, 1H, Cp), 6.49 (dd, J_1 = 6.4 Hz, J_2 = 3.1 Hz, 1H, Cp), 7.20–7.25 (m, 5H, toluene-Ph), 6.40 (d, J = 8.8 Hz, 1H, Ind), 6.16 (d, J = 3.5 Hz, 1H, Ind), 5.76 (dd, J_1 = 5.5 Hz, J_2 = 2.9 Hz, 1H, Cp), 5.63 (dd, J_1 = 5.5 Hz, J_2 = 2.9 Hz, 1H, Cp), 2.36 (d, 3H, CH_3). MS (70 eV): m/z = 662 (30, M^+), 551 (7, M^+-C_6H_4Cl), 548 (3, M^+-Ind), 412 (8, M^+-$HfCl_2$), 301 (4, M^+-$HfCl_2$-C_6H_4Cl), 187 (9, M^+-$HfCl_2$-C_6H_4Cl-Ind). IR (cm^{-1}, KBr): 3086m, 3026m, 2958m, 2923m, 2854m, 1627m, 1603m, 1591m, 1526w, 1491s, 1461m, 1404m, 1382w, 1350w, 1261w, 1237w, 1159w, 1094s, 1042m, 1017s, 871w, 818s, 781m, 735s, 697m, 538m, 517w, 504m, 469m, 440m, 416w. Anal. Calcd. For $C_{27}H_{18}Cl_4Hf{\cdot}1.0C_6H_5CH_3$: C, 54.10, H, 3.47; found: C, 53.76; H, 4.01%.

3.9. 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.

3.10. Ethylene/1-hexene copolymerization

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, and then 1 mL 1-hexene was added into the reaction with a syringe 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.

3.11. Ethylene/1-octene copolymerization

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, and

then 1 mL 1-octene was added into the reaction with a syringe 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.

The 1-hexene and 1-octene contents and monomer sequence distributions in the resultant copolymers were estimated by ^{13}C NMR spectra of copolymer.

Acknowledgments

We gratefully acknowledge the financial support from the Special Funds for Major State Basic Research Projects (2005 CB623801), the National Natural Science Foundation of China (NNSFC) (20372022) and Research Fund for the Doctoral Program of Higher Education (RFDP) (20020251002).

References

[1] W. Spaleck, F. Kuber, B. Bachmann, C. Fritze, A. Winter, J. Mol. Catal. A: Chem. 128 (1998) 279.
[2] G. Jany, M. Gustafsson, T. Repo, E. Aitola, J.A. Dobado, M. Klinga, M. Leskela, J. Organomet. Chem. 553 (1998) 173.
[3] H.G. Alt, M. Jung, J. Organomet. Chem. 568 (1998) 87.
[4] A. Koppl, A.I. Babel, H.G. Alt, J. Mol. Catal. A: Chem. 153 (2000) 109.
[5] J.J. Esteb, J.C.W. Chien, M.D. Rausch, J. Organomet. Chem. 688 (2003) 153.
[6] G. Melillo, L. Izzo, R. Centore, A. Tuzi, A.Z. Voskoboynikov, L. Oliva, J. Mol. Catal. A: Chem. 230 (2005) 29.
[7] J.A. Ewen, R.L. Jones, A. Razavi, J. Am. Chem. Soc. 110 (1988) 6255.
[8] A. Razavi, J.L. Atwood, J. Organomet. Chem. 459 (1993) 117.
[9] G.Y. Zhou, G.X. Jin, B.T. Huang, Chem. J. Chin. Univ. 21 (2000) 1489.
[10] W. Kaminsky, R. Engehausen, K. Zoumis, W. Spaleck, J. Rohrmann, Makromol. Chem. 193 (1992) 1643.
[11] T. Uozumi, K. Soga, Makromol. Chem. 193 (1992) 823.
[12] Malcolm, L.H. Green, N. Ishihara, J. Chem. Soc. Dalton Trans. (1994) 654.
[13] J.L. Huang, Y. Zhang, X.X. Yang, W. Chen, Y.L. Qian, J. Mol. Catal. A: Chem. 227 (2005) 147.
[14] A.R. Siedle, R.A. Newmark, B.F. Duerr, P.C. Leung, J. Mol. Catal. A: Chem. 214 (2004) 187.
[15] I.M. Lee, W.J. Gauthier, J.M. Ball, B. Iyengar, S. Collins, Organometallics 11 (1992) 2115.
[16] N. Piccolrovazzi, P. Pino, G. Consiglio, A. Sironi, M. Moret, Organometallics 9 (1990) 3098.
[17] L. Izzo, L. Caporaso, G. Senatore, L. Ollva, Macromolecules 32 (1999) 6913.
[18] L. Izzo, F.D. Riccardis, C. Alfano, L. Caporaso, G. Senatore, L. Ollva, Macromolecules 34 (2000) 2.
[19] G. Melillo, L. Izzo, M. Zinna, C. Tadesco, L. Oliva, Macromolecules 35 (2002) 9256.
[20] Y.L. Yuan, L. Wang, Y.X. Wang, L.X. Feng, Acta Chim. Sin. 57 (1999) 1174.
[21] J. Hung, A.P. Cole, R.M. Waymouth, Macromolecules 36 (2003) 2454.