Novel Monocyclopentadienyl Zirconium and Hafnium Trialkoxide Complexes: Syntheses and Catalytic Properties for Olefin Polymerization

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ABSTRACT: Monocyclopentadienyl trialkoxy compounds of zirconium and hafnium [$CpZr(OR)_3$ and $CpHf(OR)_3$], which cannot be prepared by earlier methods, are synthesized *in situ* by reacting bis(cyclopentadienyl) magnesium with zirconium tetraalkoxides [$Zr(OR)_4$] and with hafnium tetraalkoxides [$Hf(OR)_4$], respectively. The generation of $CpZr(OR)_3$ and $CpHf(OR)_3$ compounds involves a highly effective cyclopentadienyl ligand (Cp) transfer reaction from the Cp ligand of bis(cyclopentadienyl) magnesium to Group 4 metal alkoxides. The utilization of $CpZr(OR)_3$ and $CpHf(OR)_3$ compounds as catalyst precursors for mediating α-olefin polymerizations was carefully investigated. Results show that highly active catalysts can be generated by reacting these mono-Cp Zr and Hf alkoxides with methylaluminoxane. The resulting active $CpZr(OR)_3$/MAO and $CpHf$ $(OR)_3$/MAO catalysts induce ethylene polymerization and ethylene/propylene copolymerization with high activity (e.g., 1820 kg PE/mole of catalyst-h). © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 2040–2049, 2010

Key words: metallocene catalysts; α-olefin polymerization; ethylene/propylene copolymerization

INTRODUCTION

Cyclopentadienyl (Cp) ligands containing Group 4 metal compounds, also known as metallocene complexes, have been the subject of intensive investigation over the past two decades because of their industrial applications in mediating olefin polymerizations.[1-3] Utilization of various structures of Group 4 metal catalysts to provide effective polymer architectural control (e.g., molecular weight,[4,5] molecular weight distribution,[6,7] regiochemistry,[8-10] stereochemistry,[11-14] branching,[15-17] and chain end functionalization[18-23]) has led to significant advancement in polymer chemistry. Studies have demonstrated that employing different structures of Group 4 metal catalysts in olefin polymerizations drastically affects the chain reaction pathways;[24,25] thus, specific polymer architectures can be obtained by the proper selection of Group 4 metal catalysts. Developing new catalyst systems is an important area of research because they may lead to new polymer technologies.[26-28]

To date, Cp-containing Group 4 metal complexes can be prepared via a reaction between cyclopentadienylides and Group 4 metal halides; this synthetic route provides Cp-containing Group 4 metal halides,[29-31] which can be structurally further modified by replacing the labile halides with other ligands. Jordan and Lappert demonstrated that the combination of Group 4 metal amide complexes and various structures of cyclopentadiene led to *in situ* preparations of Cp-containing Group 4 metal amide compounds (Scheme 1).[32-34] In a recent study, the authors demonstrated that the reaction between one equiv of bis-Cp magnesium (Cp_2Mg) with two equiv of titanium alkoxides [$Ti(OR)_4$] led to the quantitative production of two equiv of monocyclopentadienyl (mono-Cp) titanium trialkoxides (Scheme 2), which can serve as the precursor of highly active catalysts to mediate syndiospecific styrene polymerization.[35] The successful generation of mono-Cp titanium alkoxides involves an effective Cp transfer reaction (from bis-Cp magnesium to titanium alkoxides) that leads to the *in situ* generation of mono-Cp titanium trialkoxides with a quantitative yield.[35] The new Cp transfer route offers a unique and highly effective method for the preparations of mono-Cp Ti alkoxides, which are difficult to prepare using other methods. In this study, we investigate whether mono-Cp tialkoxide compounds of Zr and Hf, which cannot be prepared by earlier methods, can be synthesized using the unique Cp transfer route. We demonstrate that by reacting one equiv of bis-Cp magnesium with two equiv of $Zr(OR)_4$ and with two
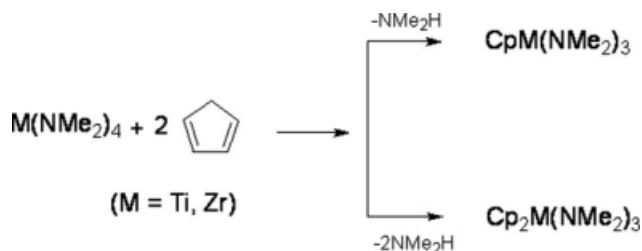
Scheme 1 Preparations of Cp-containing Group 4 metal amide complexes by the reaction between Group 4 metal amides and cyclopentadiene.

equiv of $Hf(OR)_4$, mono-Cp zirconium trialkoxides and mono-Cp hafnium trialkoxides can be prepared, respectively, in high yields. The utilization of the obtained mono-Cp Group 4 metal (Zr and Hf) alkoxides as catalyst precursor for mediating α-olefin polymerization was carefully investigated. Results show that mono-Cp zirconium and hafnium alkoxides exhibit high catalytic activity for ethylene polymerization and ethylene/propylene copolymerization after activated with methylaluminoxane (MAO). Moreover, catalytic activity comparisons show that the catalytic activity of the obtained mono-Cp Zr and Hf trialkoxides is higher than that of the known mono-Cp Zr and Hf halides.

EXPERIMENTAL

All reactions and manipulations were conducted under a nitrogen atmosphere using the standard Schlenk line or drybox techniques. Solvents and common reagents were obtained commercially and used as received or purified by distillation with sodium/benzophenone. Ethylene and propylene (purity > 99.9%) were obtained from Matheson and were used as received. Tetravalent Group 4 metal alkoxide complounds, including titanium tetra-t-butoxide [$Ti(O^tBu)_4$], titanium tetraethoxide [$Ti(OEt)_4$], zirconium tetraethoxide [$Zr(OEt)_4$], zirconium tetra-t-butoxide [$Zr(O^tBu)_4$], hafnium tetraethoxide [$Hf(OEt)_4$], and hafnium tetra-t-butoxide [$Hf(O^tBu)_4$], were purchased from Strem Chemical (purity > 97%) and were used as received. Bis-Cp magnesium compounds, including bis(pentamethylcyclopentadienyl) magnesium [$(Me_5Cp)_2Mg$], bis(cyclopentadienyl) magnesium (Cp_2Mg), and bis(n-propylcyclopentadienyl) magnesium [$(^nPrCp)_2Mg$], were commercially obtained from Strem Chemical (purity > 98%) and were used as received. Methylaluminoxane (MAO; 14% in toluene), which was purchased from Albemarle, was dried under vacuum to remove trimethylaluminum (TMA).[36] The resulting

TMA-free MAO was diluted in toluene to the desired concentration before use.

In situ ^{1}H-NMR studies for the syntheses of mono-Cp trialkoxide compounds of zirconium and hafnium

Representative experiment (for entry 3 of Table I): Cp_2Mg (0.01 g; 6.47×10^{-2} mmol) and $Zr(O^tBu)_4$ (0.05 g, 1.29×10^{-1} mmol) were allowed to dissolve in 2 mL of benzene-d_6 within a sealable NMR tube. The Cp transfer reaction was monitored using ^{1}H-NMR. The conversion ratio was determined by comparing the decrease of the $(C_5H_5)_2Mg$ resonance at 6.02 ppm (s, 10H) with the increase of the $(C_5H_5)Zr(O^tBu)_3$ resonance at 6.24 ppm (s, 5H). After allowing the reaction to proceed at 60°C for 6 h, a complete consumption of both $(C_5H_5)_2Mg$ and $Zr(O^tBu)_4$ and the formation of $(C_5H_5)Zr(O^tBu)_3$ as the only detectable reaction product were observed. ^{1}H-NMR (300 MHz; C_6D_6): 6.24 ppm [s, 5H; $(C_5H_5)Zr(O^tBu)_3$], 1.16 ppm {s, 27H; $(C_5H_5Zr[OC(CH_3)_3]_3$}. Anal. Calcd (%) for $C_{17}H_{32}O_3Zr$ (375.66): C, 54.35%; H, 8.59%. Found: C, 54.23; H, 8.50.

Ethylene polymerization

Representative Experiment (for entry 5 of Table II): A 1-L stainless steel reactor, equipped with a magnetic stirrer, was allowed to dry at 80°C under vacuum. After being refilled with nitrogen, the reactor was charged sequentially with 100 mL of toluene, 15 mmol of MAO, and 5.0 μmol of $CpZr(O^tBu)_3$. After being allowed to stir at 80°C for 5 min, the reactor was charged with ethylene (2 atm) to initiate polymerization. The polymerization was conducted under 2 atm of ethylene at 80°C for 20 min. The polymerization solution was then quenched with excess (15 mL) acidic methanol (1N HCl solution in methanol), which led to the deposition of ethylene polymer as a white precipitate. The crude polymer was collected by filtration and then purified by extracting it with boiling hexane in a Soxhlet extractor. The resulting insoluble fraction of the polymer was collected and dried under vacuum to provide
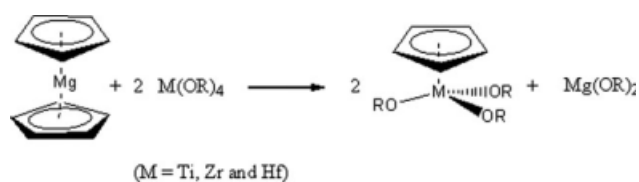
Scheme 2 Preparations of Group 4 metal mono-(cyclopentadienyl) trialkoxide complexes by the reaction between bis-Cp magnesium and Group 4 metal alkoxides.

TABLE I
In Situ ^{1}H-NMR Studies of the Reaction Between Bis-Cp Magnesium and Group 4 Metal Alkoxides

Entries	Group 4 metal alkoxides	Bis-Cp Mg complexes	Reaction conditions[a]	Reaction products	Product conversion[b]
1	$Zr(OEt)_4$	Cp_2Mg	100°C, 12 h	$CpZr(OEt)_3$	74%
2	$Zr(OEt)_4$	Cp_2Mg	100°C, 24 h	$CpZr(OEt)_3$	99%
3	$Zr(O^tBu)_4$	Cp_2Mg	60°C, 6 h	$CpZr(O^tBu)_3$	99%
4	$Hf(OEt)_4$	Cp_2Mg	100°C, 72 h	$CpHf(OEt)_3$	68%
5	$Hf(O^tBu)_4$	Cp_2Mg	60°C, 6 h	$CpHf(O^tBu)_3$	99%
6	$Zr(OEt)_4$	$(^nPrCp)_2Mg$	100°C, 12 h	$(^nPrCp)Zr(OEt)_3$	68%
7	$Zr(O^tBu)_4$	$(^nPrCp)_2Mg$	100°C, 12 h	$(^nPrCp)Zr(O^tBu)_3$	99%
8	$Hf(OEt)_4$	$(^nPrCp)_2Mg$	100°C, 72 h	$(^nPrCp)Hf(OEt)_3$	72%
9	$Hf(O^tBu)_4$	$(^nPrCp)_2Mg$	100°C, 12 h	$(^nPrCp)Hf(O^tBu)_3$	99%
10	$Zr(OEt)_4$	$(Me_5Cp)_2Mg$	100°C, 24 h	$Me_5CpZr(OEt)_3$	82%
11	$Zr(O^tBu)_4$	$(Me_5Cp)_2Mg$	100°C, 16 h	$Me_5CpZr(O^tBu)_3$	99%
12	$Hf(O^tBu)_4$	$(Me_5Cp)_2Mg$	100°C, 16 h	$Me_5CpHf(O^tBu)_3$	99%
13	$Ti(OEt)_4$	Cp_2Mg	Room temp, 5 min	$CpTi(OEt)_3$	99%
14	$Ti(O^tBu)_4$	Cp_2Mg	60°C, 2 h	$CpTi(O^tBu)_3$	99%
15	$Ti(O^tBu)_4$	$(^nPrCp)_2Mg$	60°C, 6 h	$(^nPrCp)Ti(O^tBu)_3$	99%
16	$Ti(O^tBu)_4$	$(Me_5Cp)_2Mg$	60°C, 24 h	$Me_5CpTi(O^tBu)_3$	99%

[a] Reactions were conducted in a high pressure sealable NMR tube in benzene-d_6 by mixing 1 equiv of magnesium compounds with 2 equiv of Group 4 metal alkoxides.
[b] The conversion ratio was determined using ^{1}H-NMR analyses.

TABLE II
Ethylene Polymerization Studies Using Various Mono-Cp Zr and Hf Alkoxides as Catalysts[a]

Entries	Catalyst[b]	$T(°C)$	Al/cata[c]	Activity[d]	T_m[e] (°C)	M_w[f] ($\times 10^{-3}$)	M_w/M_n
1	I	40	1000	–	–	–	–
2	I	60	1000	220	141	50.3	2.75
3	I	60	3000	550	137	48.2	2.61
4	I	80	1000	396	129	41.9	2.72
5	I	80	3000	1308	130	39.2	2.84
6	I	100	1000	470	124	28.2	3.10
7	I	100	3000	1650	123	25.4	2.98
8	II	60	1000	105	140	63.5	2.83
9	II	60	3000	151	137	61.3	2.87
10	II	80	1000	158	133	54.2	2.88
11	II	80	3000	184	133	51.2	2.76
12	II	100	1000	345	130	42.0	2.95
13	II	100	3000	525	131	38.8	3.03
14	III	40	1000	214	139	57.2	3.12
15	III	60	1000	430	142	56.3	2.95
16	III	60	3000	1030	141	55.0	2.81
17	III	80	1000	685	136	46.3	2.91
18	III	80	3000	1660	136	44.0	2.83
19	III	100	1000	802	133	35.1	2.92
20	III	100	3000	1820	133	33.2	2.91
21	IV	60	3000	1440	140	53.7	2.84
22	IV	80	3000	1870	137	47.8	2.76
23	IV	100	3000	2120	134	34.8	2.93
24	V	80	1000	263	135	26.8	2.98
25	VI	80	1000	65	138	63.6	3.42

[a] Polymerization conditions: 50 mL of toluene, 2 atm of ethylene, 5 μmol of mono-Cp catalysts, reaction time = 20 min.
[b] Catalyst I = $CpZr(O^tBu)_3$, Catalyst II = $CpHf(O^tBu)_3$, Catalyst III = $CpZr(OEt)_3$, Catalyst IV = $Me_5CpZr(OEt)_3$, Catalyst V = $CpZrCl_3$, and Catalyst VI = $CpHfCl_3$
[c] [MAO]/[catalyst] ratio
[d] Activity = kg of polymer/(mole of catalyst-h).
[e] T_m (melting temperature) was determined by DSC.
[f] M_w (weight-average molecular weight) and M_w/M_n (molecular weight distribution) were determined by high-temperature GPC (solvent 1,2,4-trichlorobenzene; temperature 135°C).

TABLE III
Ethylene–Propylene Copolymerization Studies Using Various Mono-Cp Zr and Hf Alkoxides as Catalysts[a]

Entries	E/P ratio	Catalyst[b]	Activity[c]	T_m[d] (°C)	T_g[d] (°C)	M_w[e] ($\times 10^{-3}$)	M_w/M_n[e]	f_{PP}[f]
1	1 : 1	I	269	110	–	58	2.90	16%
2	1 : 1	II	83	115	–	92	2.71	12%
3	1 : 1	III	396	105	–	76	2.71	22%
4	1 : 1	IV	467	107	–	81	2.82	18%
5	1 : 2	I	202	89	−48	37	2.85	23%
6	1 : 2	III	352	50	−45	56	3.11	32%
7	1 : 2	IV	389	54	−45	58	2.92	31%
8	1 : 4	I	151	–	−43	33	2.75	35%
9	1 : 4	III	227	–	−42	52	2.89	42%
10	1 : 4	IV	265	–	−42	54	2.80	42%
11	1 : 4	V	72	64	−47	62	3.34	26%

[a] Polymerization conditions: 50 mL of toluene, total pressure = 3 atm, 5 μmol of mono-Cp Zr or Hf catalysts, 15 mmole of MAO, reaction temperature = 80°C.
[b] Catalyst I = $CpZr(O^tBu)_3$, Catalyst II = $CpHf(O^tBu)_3$, Catalyst III = and $CpZr(OEt)_3$, and Catalyst IV = $Me_5CpZr(OEt)_3$, Catalyst V = $CpZrCl_3$.
[c] Activity = kg of polymer/(mole of catalyst-h).
[d] T_m (melting temperature) and T_g (glass transition temperature) were determined by DSC.
[e] M_w (weight-average molecular weight) and M_w/M_n (molecular weight distribution) were determined by high-temperature GPC (solvent 1,2,4-trichlorobenzene; temperature 135°C).
[f] f_{PP} (propylene incorporation ratio) was determined by ^{13}C-NMR analyses.

6.5 g of polyethylene as an off-white powder. M_w = 39,200, M_w/M_n = 2.84 by GPC (in 1,2,4-trichlorobenzene at 135°C).

Ethylene/propylene copolymerization

Representative Experiment (for entry 5 of Table III): A 1-L stainless steel reactor, equipped with a magnetic stirrer, was allowed to dry at 100°C under vacuum. After being refilled with nitrogen, the reactor was charged sequentially with 100 mL of toluene, 15 mmol of MAO, and 5.0 μmol of mono-Cp $CpZr(O^tBu)_3$. After being allowed to stir at 100°C for 5 min, the reactor was charged with a premix gas mixture containing 1 atm of ethylene and 2 atm of propylene from a 10-L stainless steel reservoir to initiate copolymerization. The copolymerization was conducted at 100°C for 20 min. The resulting solution was then quenched with excess (15 mL) acidic methanol (1N HCl solution in methanol), which led to the deposition of the polymerization product as a white precipitate. The copolymer was isolated by filtration and then dried under vacuum to provide 1.58 g of ethylene/propylene copolymer as an off-white powder. M_w = 37,000, M_w/M_n = 2.85 by GPC (in 1,2,4-trichlorobenzene at 135°C).

Analysis

Elemental analyses were run in a Heraeus VarioEL-III CHNS elemental analyzer. The molecular weight and molecular weight distribution (M_w/M_n) of polymers (PE and E/P copolymer) were determined using a high-temperature gel permeation chromatog-raphy (Waters 150-CALAC/GPC) with a refractive index (RI) detector and a set of U-Styragel HT columns with po sizes of 10^6, 10^5, 10^4, and 10^3 in series. The measurements were taken at 135°C using 1, 2, 4-trichlorobenzene as solvent. Polystyrene samples with narrow MWDs were used as the standards for calibration. The standards were in the range of absolute molecular weight, which is from 980 to 2,110,000; the R square of the ideal calibrated line was limited to up to 0.999. The melting temperatures and glass transition temperatures were measured by Differential Scanning Calorimeter (DSC) using a Perkin Elmer DSC-7. The DSC thermograms were recorded during the second heating cycle with a heating rate of 20°C /min. ^{1}H-NMR spectra were recorded on a Varian Gemini 300-MHz spectrometer using $CDCl_3$ or benzene-d_6 as the solvent.

RESULTS AND DISCUSSION

The *in situ* ^{1}H-NMR monitoring of the reactions between bis-Cp magnesium and Group 4 metal alkoxides

To investigate the Cp transfer processes, reactions between various bis-Cp magnesium compounds and Group 4 metal (Zr and Hf) tetraalkoxides were conducted in benzene-d_6 (within a sealable NMR tube), and monitored using ^{1}H-NMR spectroscopy. The experimental results are summarized in Table I. As shown in entries 1–12 of Table I, reactions between various bis-Cp magnesium compounds [e.g. Cp_2Mg, $(Me_5Cp)_2Mg$ and $(^nPrCp)_2Mg$] and various zirconium and hafnium alkoxides [e.g. $Zr(OEt)_4$, $Zr(O^tBu)_4$, $Hf(OEt)_4$, and $Hf(O^tBu)_4$] led to the
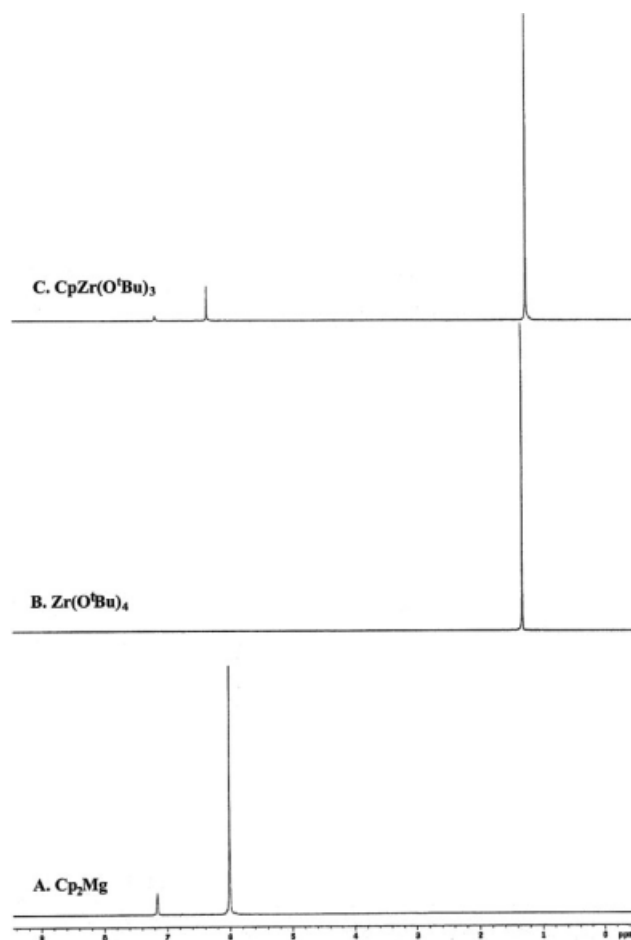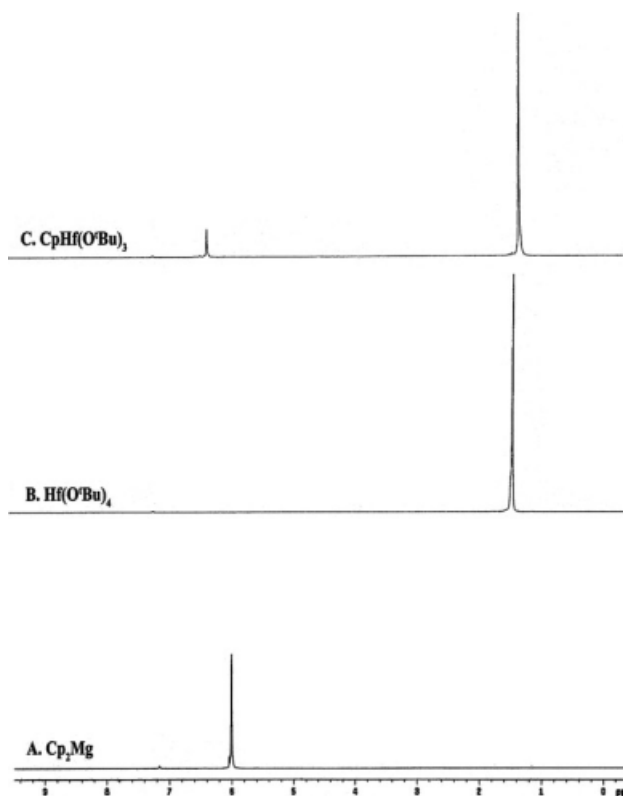
Figure 1 ^{1}H-NMR (300 MHz) monitoring of the reaction between Cp$_2$Mg and Zr(O^{t}Bu)$_4$: (A) Cp$_2$Mg, (B) Zr(O^{t}Bu)$_4$, (C) a mixture of one equiv of Cp$_2$Mg and two equiv of Zr(O^{t}Bu)$_4$ at 60°C for 6 h. (solvent, benzene-d_6).

generation of various mono-Cp zirconium and hafnium trialkoxides with high conversion ratios. ^{1}H-NMR monitoring of the reaction between one equiv of Cp$_2$Mg [Fig. 1(a)] and two equiv of Zr(O^{t}Bu)$_4$ [Fig. 1(b)] shows a decrease of the ^{1}H resonances at 6.02 and 1.38 ppm, which correspond to [(C$_5$H$_5$)$_2$Mg, s, 10H] and {Zr[OC(CH$_3$)$_3$]$_4$, s, 36H}, respectively, and an increase of two resonances at 6.24 and 1.16 ppm, which correspond to the ^{1}H resonances of [(C$_5$H$_5$)Zr(O^{t}Bu)$_3$, s 5H] and {CpZr[OC(CH$_3$)$_3$]$_3$, s, 27H}, respectively. After the reaction was allowed to proceed at 60°C for 6 h, a complete conversion of both reactants and the generation of the pure Cp Zr(O^{t}Bu)$_3$ as the only reaction product were observed [Fig. 1(c)]. Figure 2 shows the results for the reaction between one equiv of Cp$_2$Mg [Fig. 2(a)] and two equiv of Hf(O^{t}Bu)$_4$ [Fig. 2(b)]. Similarly, after the reaction was allowed to proceed at 60°C for 6 h, a complete conversion of both reactants and the generation of CpHf(O^{t}Bu)$_3$ as the only Cp transfer product were observed [Fig. 2(c)]. These results

clearly indicate that bis-Cp magnesium complexes are capable of inducing the Cp transfer reaction not only to titanium alkoxides[35] (entries 13–16) but also to various structures of zirconium and hafnium alkoxides (entries 1–12).

The results given in Table I show that the Cp transfer reaction is highly dependent on the steric bulkiness of the Cp ligands as evidenced by the fact that increasing the steric bulkiness of the bis-Cp magnesium complexes from Cp$_2$Mg to (Me$_5$Cp)$_2$Mg leads to a drastic Cp transferring rate reduction (entries 1–12). It should be noted that increasing the steric bulkiness of the metal alkoxides from Zr(OEt)$_4$ to Zr(O^{t}Bu)$_4$ and from Hf(OEt)$_4$ to Hf(O^{t}Bu)$_4$, respectively, led to the contradictory rate enhancing effects as revealed by comparing results between entries 2 and 3, entries 4 and 5, entries 6 and 7, entries 8 and 9, and entries 10 and 11. Of note, an increase in the steric bulkiness of the bis-Cp magnesium complexes resulting in a retardation of the Cp transferring rate is consistent with an earlier report on the production of mono-Cp titanium alkoxide complexes (entries 14–16).[35] However, the enhancement of the Cp transferring rate obtained by increasing the steric bulkiness of Zr and Hf alkoxide complexes contradicts our previous report, in which a

Figure 2 ^{1}H-NMR (300 MHz) monitoring of the reaction between Cp$_2$Mg and Hf(O^{t}Bu)$_4$: (A) Cp$_2$Mg, (B) Hf(O^{t}Bu)$_4$, (C) a mixture of one equiv of Cp$_2$Mg and two equiv of Hf(O^{t}Bu)$_4$ at 60°C for 6 h. (solvent, benzene-d_6).

bulky titanium alkoxide complex was found to display a slower Cp transferring rate (entries 13 and 14 of Table I).[35] These contradictory results can be explained by the solubility differences between Zr$(OEt)_4$ and $Zr(O^tBu)_4$ complexes and between $Hf(OEt)_4$ and $Hf(O^tBu)_4$ complexes, respectively. It should be noted that these Zr and Hf alkoxides are polymetallic cluster complexes[10a] and are only slightly soluble in benzene-d_6 at low temperature. Although the bulky $Zr(O^tBu)_4$ and $Hf(O^tBu)_4$ complexes also show poor solubility at room temperature, they are partially soluble in benzene-d_6 at high temperatures ($>60°C$). In contrast, the less bulky $Zr(OEt)_4$ and $Hf(OEt)_4$ cluster complexes were found to remain insoluble in benzene-d_6 even at 100°C. Evidently, the solubility differences enable the bulky $Zr(O^tBu)_4$ and $Hf(O^tBu)_4$ to interact with the bis-Cp magnesium compounds for initiating the Cp transferring reaction at a lower temperature and therefore lead to much higher Cp transfer rates than those of the corresponding less bulky $Zr(OEt)_4$ and $Hf(OEt)_4$.

The results listed in Table I clearly demonstrate that various mono-Cp Zr and Hf alkoxides can be prepared with high yields using the Cp transferring route. Of note, these mono-Cp Zr and Hf alkoxide complexes have never been prepared before. Thus, the unique Cp transfer synthetic route offers the opportunity for preparing these new Group 4 metal mono-Cp alkoxides (Scheme 2) for use in α-olefin polymerization studies.

Ethylene polymerization

Mono-Cp Zr and Hf alkoxide complexes can be activated by treating with MAO for the generation of active catalysts. Our results show that both $CpZr(OR)_3$/MAO and $CpHf(OR)_3$/MAO were unable to mediate the syndiospecific styrene polymerization despite structurally similar mono-Cp titanium alkoxide compounds being able to mediate the syndiospecific styrene polymerization with high catalytic activity.

The ethylene polymerizations were examined using various mono-Cp Zr and Hf alkoxides, including $CpZr(O^tBu)_3$ (I), $CpHf(O^tBu)_3$ (II), $CpZr(OEt)_3$ (III), and $Me_5CpZr(OEt)_3$ (IV). The experimental results are summarized in Table II. The comparison between entries 2–7 and 8–13 clearly demonstrates that Zr catalyst (I) [$CpZr(O^tBu)_3$] exhibits drastically higher catalytic activity for mediating ethylene polymerization than that of the corresponding catalyst (II) [$CpHf(O^tBu)_3$] despite ethylene polymers prepared by the Hf catalyst (II) typically having higher molecular weight than that of ethylene polymers prepared by catalyst (I). Of note, bis-Cp Zr compounds have been demonstrated to display higher catalytic activity but producing lower molecular
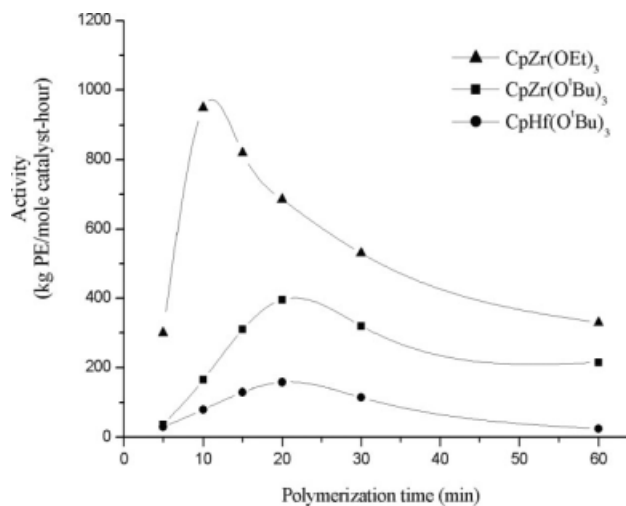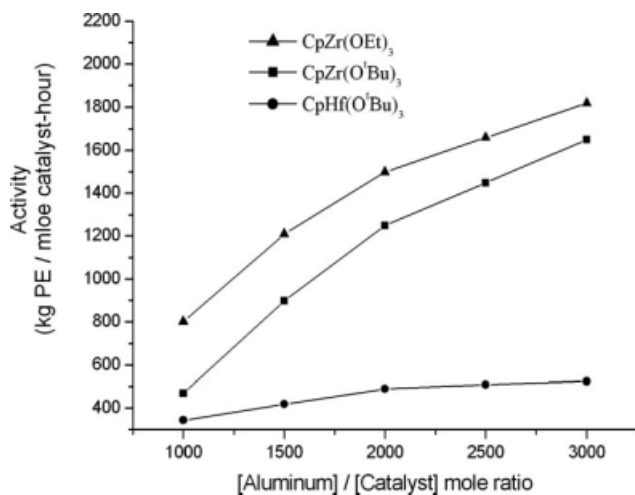

Figure 3 Dependence of the catalyst activity on reaction time in the presence of different catalysts (reaction temperature = 80°C, MAO/catalyst = 1000).

weight polyethylene than the corresponding bis-Cp Hf complexes. Mono-Cp Hf catalyst (II) produces olefin polymers with higher molecular weight but at a lower catalytic activity compared with those of Zr catalysts (I) is consistent with published results.[37–40]

Comparisons between entries 1–7 and 14–20 show that the bulky $CpZr(O^tBu)_3$ (I) exhibits drastically lower ethylene polymerization activity than that of $CpZr(OEt)_3$ (III). These catalytic activity differences have two possible explanations. First, the bulky *tert*-butoxyl ligands in catalyst (I) may retard the catalyst activation processes (by removing the *tert*-butoxyl ligand) for the generation of active catalysts. Second, after catalyst activation, the bulky *tert*-butoxyl ligand may inhibit monomer coordination through its unfavorable steric effect. To verify the cause of the polymerization rate retardation, the dependence of catalyst activity versus reaction time was carefully investigated; the experimental results are shown in Figure 3. As shown in the Figure, catalyst (III) reaches its highest activity at a much faster rate than those of the corresponding *tert*-butoxid containing catalysts (I) and (II). These results clearly indicate that catalyst (III) can be activated by reacting it with MAO to produce the active catalyst at a faster rate than those of corresponding catalysts (I) and (II). In addition, a comparison between entries 1 and 14 of Table II shows that catalyst (III) can undergo the ethylene polymerization at a lower temperature) (40°C) than catalyst (I). These results clearly reveal that the bulky *tert*-butoxide containing catalysts (I) and (II) require a longer activation time for generating active catalysts.

It should be noted that the efficiency for catalysts activation was found to be highly dependent on [MAO] as well as on the activation temperature.[35]

Figure 4 Dependence of catalyst activity on the MAO/catalyst ratio in the presence of different catalysts (reaction time = 20 min, reaction temperature = 100°C).

Accordingly, the dependence of catalyst activity versus [MAO] and versus the polymerization temperature were also examined; the results are shown in Figures 4 and 5, respectively. Figure 4, shows the plot of catalyst activity versus [MAO]/[catalyst] ratios for ethylene polymerization conducted in the presence of various Group 4 mono-Cp alkoxides. As shown in the Figure, an increase in the [MAO]/[catalyst] ratio typically leads to the activity enhancement for catalysts (I), (II), and (III). The extent of activity enhancement for Hf catalyst (II) is relatively insignificant compared with Zr catalysts (I) and (III), which can be attributed to the low activity nature of the Hf catalyst. Of note, the activity difference between catalyst (I) and catalyst (III) can be reduced by increasing the [MAO]/[catalyst] ratio (Fig. 4). Since the increase in the [MAO]/[catalyst] ratio increase the catalyst activation efficiency (it generates more active catalyst at a higher [MAO]/[catalyst] ratio), the reduction in the catalyst activity difference between catalysts (III) and (I) at a higher [MAO]/[catalyst] ratio indicates that catalyst (III) can be more effectively activated by MAO to form active catalyst than the corresponding bulky *tert*-butoxide catalysts (I).
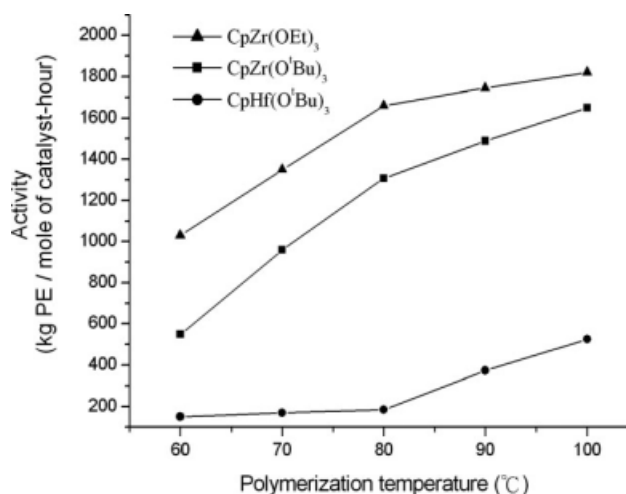
Figure 5 shows the dependence of catalyst activity on the polymerization temperature in the presence of various catalysts. As shown in the Figure, an increase in the polymerization temperature also leads to a reduction in the catalytic activity difference between catalysts (I) and (III). An increase in the polymerization temperature accelerate the catalyst activation processes (enhances the catalyst activation efficiency),[35] so the reduction in catalytic activity difference between catalysts (I) and (III) at a higher temperature further supports that the higher

activity in catalyst (III) is mainly due to the slower activation processes for the bulky *tert*-butoxid catalyst (I).

Entries 21–23 of Table II show the results of ethylene polymerization at different MAO/catalyst ratios using Me$_5$CpZr(OEt)$_3$ (IV) as the polymerization catalyst. The comparison between entries 14–20 and entries 21–23 clearly demonstrates that catalyst (IV) has a slightly higher activity than that of the corresponding catalyst (III). The experimental results showing that the presence of electron donating alkyl groups on the Cp ligand can enhance the catalyst activity are consistent with results reported by Collins and coworkers.[41] Finally, ethylene polymerization studies using the known CpZrCl$_3$ (V) and CpHfCl$_3$ (VI) were examined; the experimental results are listed in Table II (entries 24 and 25). Comparisons between entries 4, 17, 22, and 24 and between entries 12 and 25 clearly demonstrate that the mono-Cp Zr and Hf alkoxides exhibit higher catalytic activity than those of the corresponding known mono-Cp Zr and Hf halides. Evidently, the new Cp transferring route not only offers the first preparation method for mono-Cp Zr and Hf alkoxides, but also leads to the generation of highly active catalysts for use in α-olefin polymerization studies.[42–44]

Ethylene–propylene copolymerization studies

The ethylene/propylene (EP) copolymerizations were conducted at various ethylene/propylene ratios using different mono-Cp zirconium and hafnium compounds (I, II, III, IV, and V) as catalysts. The results of EP copolymerization are summarized in Table III. Comparisons between entries 1, 5, and 8, between entries 3, 6, and 9, and between entries 4, 7,

Figure 5 Dependence of the catalyst activity on polymerization temperature in the presence of different catalysts (reaction time = 20 min, MAO/catalyst = 3000).
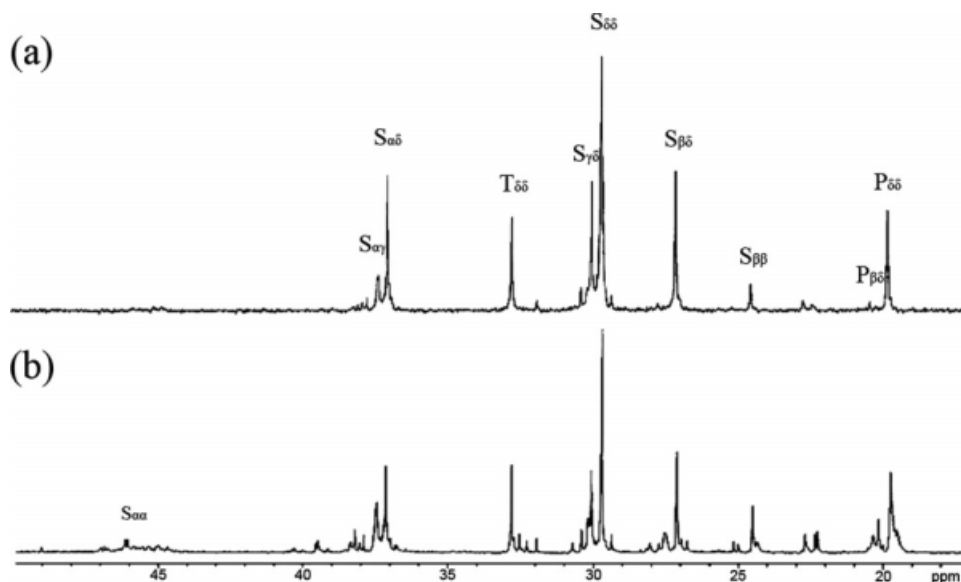
Figure 6 The ^{13}C-NMR (75 MHz) spectra of EP copolymers prepared by CpZr(OEt)$_3$/MAO: (a) entry 3 of Table III, M_w = 76,000, M_w / M_n = 2.71, propylene content = 22 mol %, and (b) entry 9 of Table III, M_w = 52,000, M_w/M_n = 2.89, propylene content = 42 mol % (solvent, CDCl$_3$; temperature 60°C).

and 10 show an increase in the propylene pressure typically results in a reduction in the catalytic activity and decrease in both the melting temperatures (T_m of PE domain) and the molecular weight of resulting EP copolymers (EPs). The reductions in molecular weight and in the catalytic activity can be explained by the fact that a higher propylene pressure leads to the production of EPs containing a higher propylene incorporation ratio. As propylene monomer has a slower chain propagating rate than ethylene, the incorporation of a higher concentration of propylene units into the polymer backbone reduces both catalytic activity and the molecular weight of the resulting EPs. Similarly, the decrease in T_m in the resulting EPs can also be explained by the fact that the increase in the propylene pressure produces EPs containing a higher propylene incorporation ratio. The incorporation of higher concentration of propylene units interrupts the ethylene homopolymerization sequences and reduces the size of the polyethylene domain in the resulting EPs; thus, a reduction in the PE-based crystalline melting temperature can be observed for EPs prepared at a higher propylene pressure.

Comparisons between entries 1 and 3, between entries 5 and 6, and between entries 8 and 9 clearly indicate that EPs prepared using catalyst (III) have a higher molecular chain length and a higher propylene incorporation ratio than those of EPs prepared using catalyst (I). The presence of bulky *tert*-butoxide ligands in catalyst (I) retards the insertion rates for both ethylene and propylene monomers. However, the effect on propylene is more significant than that on ethylene because of the larger molecular size of propylene. Thus, employing catalyst (I) to mediate EP copolymerization produces EPs with a lower propylene incorporation ratio and at a lower catalytic activity than those of EPs prepared using catalyst (III).

Comparisons between entries 3 and 4, between entries 6 and 7, and between entries 9 and 10 indicate that EPs prepared using catalysts (III) and (IV) have a similar propylene incorporation ratio. However, catalyst (IV) typically has a higher catalytic activity for EP copolymerization than catalyst (III). These results clearly indicate that the presence of electron donating bulky pentamethyl-Cp ligand in catalyst (IV) can enhance the catalyst activity for EP copolymerization (electron donating effect) but it is unable to retard the propylene insertion rate (steric effect).

A comparison between entries 9, 10, and 11 reveals that mono-Cp Zr alkoxide compounds display much higher catalytic activity for E/P copolymerization than the corresponding known CpZrCl$_3$. Moreover, EPs prepared by mono-Cp Zr alkoxides (catalysts III and IV) have a higher propylene incorporation ratio than that of EPs prepared using the mono-Cp Zr halide (catalyst V). Evidently, employing mono-Cp Zr alkoxide/MAO catalysts to mediate the E/P copolymerization can drastically enhance the propylene incorporation ratio. Figure 6 shows the ^{13}C-NMR spectrum of EPs prepared using CpZr(OEt)$_3$/MAO (entries 3 and 9 of Table III). The detailed chemical assignments (Scheme 3) are based on the structural information revealed in the ^{13}C-NMR spectra, and form comparisons with previous NMR analyses of EPs. The propylene incorporation ratio was determined using ^{13}C-NMR analyses with
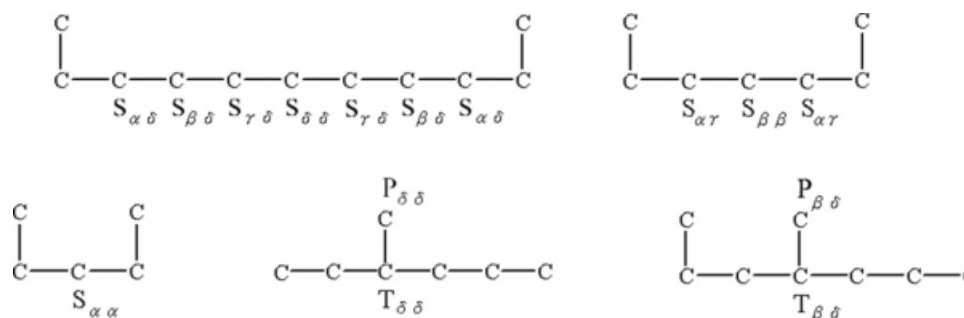
Scheme 3 Nomenclature used for methyl (primary), methylene (secondary), and methine (tertiary) carbons of ethylene–propylene copolymers.

methods described in the literature.[45–47] Detailed microstructural analyses using ^{13}C-NMR spectroscopy (Fig. 6) reveal that EPs prepared using mono-Cp Zr alkoxide have a very low level of propylene–propylene repeating units ($S_{\alpha\alpha}$) comparing with EPs prepared using other metallocene catalysts.[16] The extremely low level of propylene–propylene repeating units indicates that EPs prepared by these new catalyst systems have a unique microstructure, which is characterized by its highly random EP distribution. This unique microstructure is highly desirable for EP rubber. Our results also show that EPs with a high propylene incorporation ratio can be obtained form using these mono-Cp Zr alkoxide compounds (catalysts III and IV) as the catalysts. Thus, EPs with a high propylene incorporation ratio and with highly random ethylene–propylene distribution can be prepared by conducting EP copolymerization in the presence of these new catalyst systems.

CONCLUSIONS

Our results show that various mono-Cp alkoxide compounds of zirconium and hafnium can be quantitatively prepared by reacting one equiv of bis-Cp magnesium with two equiv of Zr(OR)$_4$ and with two equiv of Hf(OR)$_4$, respectively. The resulting mono-Cp zirconium and hafnium alkoxides can be activated by reacting them with MAO. The resulting active catalyst systems [CpZr(OR)$_3$/MAO and CpHf(OR)$_3$/MAO] can mediate ethylene polymerization and ethylene/propylene copolymerization with good catalytic activity. Efforts to use these mono-Cp Zr and Hf alkoxides for mediating the polymerization of other olefin monomers and to apply the Cp transfer reaction route for the synthesis of new Cp-containing catalysts are currently underway.

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