

Ethylene polymerization and ethylene/styrene copolymerization with secondary phosphine-pendant and phosphide-pendant complexes of Zr and Hf

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Abstract

Ethylene and styrene polymerizations and ethylene/styrene copolymerization have been examined with a catalytic system obtained by a combination of zirconium or hafnium complexes bearing a secondary phosphine-pendant cyclopentadienyl ligand $\{\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{P}(\text{H})\text{R}\}$ (R = 2,4,6-trimethylphenyl (Mes), 2,4,6-tri(*i*-propyl)phenyl (Tip)) or a phosphide-pendant cyclopentadienyl ligand $\{\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{PR-}\kappa\text{P}\}$ with modified methylaluminoxane (MMAO) or a mixture of methylaluminoxane (MAO) and tri-*i*-butylaluminum (TIBA) as a cocatalyst. These systems show moderate activity in ethylene polymerization (8–316 g mmol⁻¹ h⁻¹) but show inactivity in styrene polymerization. In ethylene/styrene copolymerization, these systems afford ethylene/styrene copolymers with a relatively high styrene content (35–87%).

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1. Introduction

Since the discovery of the homogeneous zirconocene/methylaluminoxane (MAO) catalyst system [1–4] achieved a breakthrough in the heterogeneous Ziegler-Natta catalysts, studies on homogeneous olefin polymerization catalysts have been extended to a variety of non-metallocene complexes, some of which have exhibited excellent catalytic reactivities [5–18]. Among them, titanium complexes with an amide-pendant cyclopentadienyl (Cp) ligand, $[(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^i\text{Bu-}\kappa\text{N})\text{TiL}_2]$ (L = Cl, alkyl group) called constrained-geometry catalysts (CGC), have been reported to be effective in olefin copolymerization [10–16]. The great catalytic activity of group 4 transition-metal complexes with the amide-pendant Cp ligand has been stimulating the researchers to prepare analogous phosphide-pendant Cp complexes and examine their catalytic activities. However,

due to preparative difficulties, the first report of preparation of a phosphide-pendant Cp complex [19] was published about 10 years after the report of amide-pendant Cp complexes. Several complexes with a phosphide-pendant Cp ligand have been isolated and characterized to date [20–25]. However, few studies have been reported on the catalytic activity in olefin polymerization of the phosphide complexes. This paper presents the results of ethylene and styrene polymerizations, and ethylene/styrene copolymerization promoted by secondary phosphine-pendant and phosphide-pendant complexes of Zr and Hf, which we recently reported. These complexes are listed in Chart 1.

2. Experimental

2.1. General remarks

All experiments were performed under a nitrogen atmosphere using Schlenk, glovebox, and vacuum line techniques.

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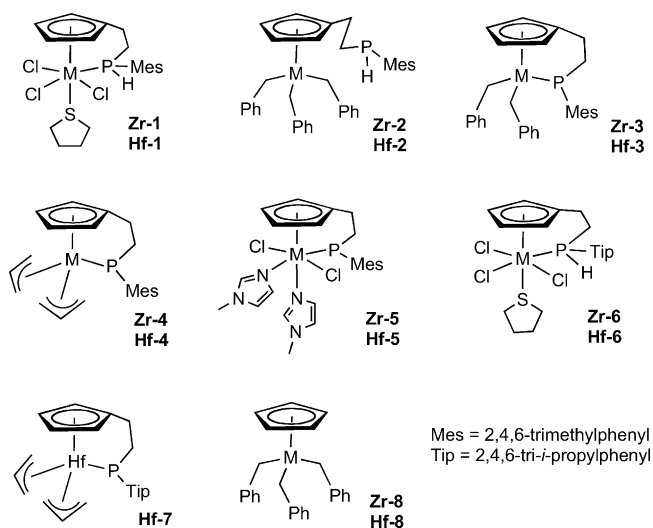


Chart 1.

All solvents used were dried over Na/K alloy or CaH₂, and distilled before use. Modified methylaluminoxane (MMAO), which is an alkylaluminoxane containing mainly methyl groups and partly *i*-butyl groups as alkyl groups, methylaluminoxane, and (Allyl)MgCl were obtained from common commercial sources and used without further purification. ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were recorded on a JEOL LA-300 or a JNM-AL400 multinuclear spectrometer. ¹H and ¹³C{¹H} NMR data were referenced to SiMe₄, and ³¹P{¹H} NMR data were referenced to 85% H₃PO₄. The following complexes were synthesized according to literature methods: the trichloride complexes with secondary phosphine-pendant ligands (**Zr-1**, **Hf-1**, **Zr-6**, **Hf-6**) [26], the tribenzyl complexes having secondary phosphine-pendant ligands (**Zr-2**, **Hf-2**) [25], the phosphide complexes (**Zr-4**, **Hf-4**, **Zr-5**, **Hf-5**) [25], the monocyclopentadienyl tribenzyl complex **Zr-8** [27,28]. **Zr-3** and **Hf-3** were prepared via thermolysis of **Zr-2** and **Hf-2** in toluene, respectively [25], and their toluene solutions were used directly without isolation of products in the subsequent polymerization reactions.

2.2. Synthesis of [η^5 -C₅H₄(CH₂)₂P*Tip*-κ*P*]Hf(*allyl*)₂ (**Hf-7**)

The synthetic procedure was similar to that for **Hf-4** [25]. A solution of (allyl)MgCl (3.75 mmol) in 4 mL of THF was added to a suspension of **Hf-1** (0.88 g, 1.25 mmol) in 20 mL of ether at room temperature. After stirring overnight, the volatile compounds were evaporated in vacuo. The orange residue obtained was extracted with ether/hexane = 2/1 and then filtered. Removal of the solvents gave a brown powder of **Hf-7** (0.43 g, 59%). ¹H NMR (300 MHz, C₆D₆): δ 7.23 (d, *J*_{HH} = 2.0 Hz, 2H, *m*-H in tri(*i*-propyl)phenyl (*Tip*)), 5.57–5.49 (m, 2H, 2-H in allyl), 5.35 (m, 2H, Cp), 5.28 (m, 2H, Cp), 4.39 (m, 2H, *o*-CHMe₂ in *Tip*), 3.28 (m, 1H,

p-CHMe₂ in *Tip*), 3.06–2.63 (m, 12H, 1,3-H in allyl and CH₂CH₂), 1.42 (br, 12H, *o*-CHMe₂ in *Tip*), 1.32–1.25 (m, 6H, *p*-CHMe₂ in *Tip*). ¹³C{¹H} NMR (75.5 MHz, C₆D₆): δ 154.0 (d, *J*_{PC} = 4.3 Hz, aromatic-C in *Tip*), 149.7 (d, *J*_{PC} = 1.8 Hz, aromatic-C in *Tip*), 137.5 (d, *J*_{PC} = 8.7 Hz, aromatic-C in *Tip*), 132.4 (d, *J*_{PC} = 4.3 Hz, aromatic-C in *Tip*), 129.2 (m, 1-C in Cp), 121.7 (d, *J*_{PC} = 5.6 Hz, 2-C in allyl), 103.4 (s, 2,5- or 3, 4-C in Cp), 101.1 (s, 2,5- or 3, 4-C in Cp), 62.9 (s, 1, 3-C in allyl), 39.7 (s, CpCH₂), 34.7 (s, *p*-CHMe₂ in *Tip*), 33.9 (d, *J*_{PC} = 8.7 Hz, *o*-CHMe₂ in *Tip*), 27.3 (d, *J*_{PC} = 14.9 Hz, PCH₂), 25.6 (br-m, *o*-CHMe₂ in *Tip*), 24.2 (s, *p*-CHMe₂ in *Tip*). ³¹P{¹H} NMR (121.5 MHz, C₆D₆): δ 126.73 (s).

2.3. Synthesis of [η^5 -CpHf(CH₂Ph)₃] (**Hf-8**)

The procedure followed is a modification of that for [η^5 -CpZr(CH₂Ph)₃] [27,28]. A solution of (CH₂Ph)MgCl (1.17 mmol) in 7 mL of THF was added slowly to a solution of [η^5 -CpHfCl₃(dme)] [29] (0.17 g, 0.39 mmol) in 20 mL of ether at room temperature. The reaction mixture was stirred for 1 h, and then the volatile compounds were evaporated in vacuo. The yellow residue obtained was extracted with ether/hexane = 2/1 and then filtered. Removal of the solvents gave yellow wax of **Hf-8** (0.14 g, 71%). ¹H NMR (300 MHz, C₆D₆): δ 7.20–7.15 (m, 9H, Ph), 6.67–6.65 (m, 6H, Ph), 5.60 (s, 5H, Cp), 1.60 (s, 6H, CH₂Ph). ¹³C{¹H} NMR (75.5 MHz, C₆D₆): δ 144.1 (s, Ph); 129.3 (s, Ph); 127.6 (s, Ph); 123.2 (s, Ph); 113.0 (s, Cp); 77.2 (s, CH₂Ph).

2.4. Ethylene polymerization

MMAO (10.00 mmol) and ca. 180 mL of toluene were placed in a 500 mL separable reactor under nitrogen atmosphere, and then the reactor was saturated with ethylene. A toluene solution containing transition-metal precatalyst (0.01 mmol) was added to the reactor to give 200 mL of toluene in total. The reaction mixture thus formed was stirred at 40 °C for 1 h with the passage of ethylene (1000 mL/min) under atmospheric pressure. Then, EtOH and HCl were added to terminate the polymerization.

2.5. Styrene polymerization

MAO (2.00 mmol), tri-*i*-butylaluminum (TIBA) (2.00 mmol), and 10 mL of styrene were placed in a 40 mL ampoule sealed with a septum cap under nitrogen atmosphere in a glovebox. After the ampoule was warmed up to a set temperature, a toluene solution containing transition-metal precatalyst (0.01 mmol) was added to the reaction mixture. The reaction mixture was stirred for 1 h, and then polymerization was terminated by adding MeOH.

2.6. Ethylene/styrene copolymerization

TIBA (1.00 mmol), 200 mL of styrene, and toluene were placed in a 1500 mL stainless steel autoclave reactor, and

then the reactor was saturated with ethylene. A toluene solution containing transition-metal precatalyst (0.01 mmol) and MAO (10.00 mmol) was added to the reactor to give 200 mL of toluene in total. The reaction mixture was stirred at a set temperature for 1 h under ethylene pressure at 3 bar. Then, polymerization was terminated by adding MeOH.

Molecular weights (M_w and M_n) of polymers were determined by the GPC analysis using *o*-dichlorobenzene or 1,2,4-trichlorobenzene as a solvent and polystyrene as a standard. The percentage of styrene components in the ethylene/styrene copolymer (St (%)) was determined by GPC/FTIR measurement [30].

3. Results and discussion

The phosphorus-pendant cyclopentadienyl Zr and Hf complexes in Chart 1 were inactive by themselves in the polymerization of ethylene and styrene. However, these complexes in combination with a cocatalyst such as an alkylaluminumoxane exhibited catalytic activity towards ethylene polymerization and ethylene/styrene copolymerization, but almost none towards styrene polymerization. Modified methylaluminumoxane is widely used as an olefin polymerization cocatalyst, and has generally greater stability and greater solubility in a hydrocarbon solution than methylaluminumoxane [31]. Therefore, MMAO or a mixture of MAO and tri-*i*-butylaluminum was used as a cocatalyst in this study.

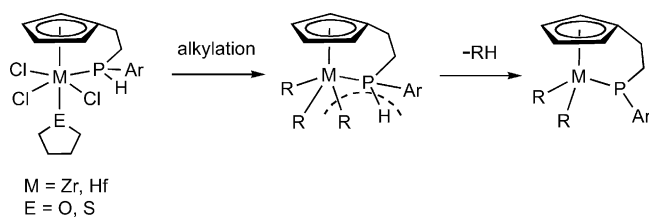
3.1. Ethylene polymerization

Ethylene polymerization was conducted with the phosphorus-pendant Zr and Hf complexes under atmospheric pressure of ethylene at 40 °C. The results of the Zr and Hf complexes having a 2,4,6-trimethylphenyl (Mes) group are summarized in Table 1. For comparison, the results ob-

Table 1
Results of ethylene polymerization with phosphorus-pendant complexes having a Mes group

	Yield (g)	Activity (g mmol ⁻¹ h ⁻¹)	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	M_w/M_n
Zr-1	0.21	21	31.87	0.65	48.95
Hf-1	1.80	180	7.76	1.18	6.60
Zr-2	0.08	8	112.88	1.69	66.89
Hf-2	0.80	80	2.95	0.62	4.75
Zr-3	0.21	21	22.66	0.77	29.34
Hf-3	1.48	148	2.94	0.57	5.14
Zr-4	0.43	43	20.48	0.63	32.31
Hf-4	3.05	305	6.17	0.76	8.12
Zr-5	0.30	30	10.20	0.55	18.66
Hf-5	3.16	316	8.86	1.06	8.39
Zr-8	0.35	35	8.43	0.61	13.82
Hf-8	0.29	29	5.41	0.59	9.17

Polymerization conditions: polym. time, 1 h; amount of catalyst, 0.01 mmol; amount of MMAO, 10.00 mmol; atmospheric pressure of ethylene; 200 mL of toluene; temperature, 40 °C.



Scheme 1.

Table 2
Results of ethylene polymerization with phosphorus-pendant complexes having a Tip group

	Yield (g)	Activity (g mmol ⁻¹ h ⁻¹)	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	M_w/M_n
Zr-6	0.64	64	18.34	0.62	29.41
Hf-6	0.29	29	20.51	0.75	27.52
Hf-7	0.12	12	41.23	1.87	22.10

Polymerization conditions: polym. time, 1 h; amount of catalyst, 0.01 mmol; amount of MMAO, 10.00 mmol; atmospheric pressure of ethylene; 200 mL of toluene; temperature, 40 °C.

tained using [η^5 -CpM(CH₂Ph)₃] (**Zr-8**, **Hf-8**) are also listed in Table 1.

For the Zr complexes, the catalytic activities of the secondary phosphine complexes (21, for **Zr-1**, 8 for **Zr-2**) and those of the phosphide complexes (21 for **Zr-3**, 43 for **Zr-4**, 30 for **Zr-5**) are almost the same and these values are also close to that of the phosphorus-pendant free **Zr-8** (35). For the Hf complexes, the catalytic activities of the secondary phosphine complex (180 for **Hf-1**, 80 for **Hf-2**) and those of the phosphide complexes (148 for **Hf-3**, 305 for **Hf-4**, and 316 for **Hf-5**) are almost the same, but these values are greater than those for the phosphorus-pendant Zr complexes (8–43) and that for the phosphorus-pendant free **Hf-8** (29). Since the phosphide complex was reported to be formed through alkylation of the secondary phosphine trichloride complex in our previous papers (Scheme 1) [24,25], it is likely that the precursor secondary phosphine complexes would be first converted into phosphide com-

Table 3
Results of styrene polymerization

	Temperature (°C)	Yield (g)	Activity (g mmol ⁻¹ h ⁻¹)
Zr-2	50	0.01	1
	80	0.13	13
Hf-2	50	0.04	4
	80	0.03	3
Zr-3	50	trace	–
	80	0.05	5
Hf-3	50	0.09	9
	80	0.03	3
Blank	50	0.03	–
	80	0.07	–

Polymerization conditions: polym. time, 1 h; amount of catalyst, 0.01 mmol; amount of MAO, 2.00 mmol; amount of TIBA, 2.00 mmol; amount of styrene, 10 mL.

Table 4
Results of ethylene/styrene polymerization

	Temperature (°C)	Yield (g)	Activity (g mmol ⁻¹ h ⁻¹)	Mw × 10 ⁻⁴	Mn × 10 ⁻⁴	Mw/Mn	St (%)
Zr-2	50	0.46	46	30.97	2.00	15.50	35
	80	0.60	60	7.68	0.89	8.70	64
Hf-2	50	0.32	32	15.21	0.79	19.30	78
	80	0.93	93	5.99	0.83	7.20	87
Zr-3	50	0.43	43	33.08	1.85	17.90	31
	80	1.08	108	9.14	1.08	8.50	62
Hf-3	80	0.79	79	269	0.58	4.60	75

Polymerization conditions: polym. time, 1 h; amount of catalyst, 0.01 mmol; amount of MAO, 10.00 mmol; amount of TIBA, 1.00 mmol; ethylene pressure, 3 bar; amount of styrene, 200 mL; amount of toluene, 200 mL.

plexes in combination with MMAO, and then into a real active species. Although it is hard, at present, to specify the real active species in the catalytic system, we presume that a cationic phosphide monoalkyl complex formulated as $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PMes-}\kappa\text{P})\text{MR}]^+$ would serve as an active species, because analogous cationic amide monoalkyl complexes $[(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^i\text{Bu-}\kappa\text{N})\text{MR}]^+$ (M = Ti, Zr) have been proposed as an active species in the polymerization reaction [10,31–39]. One of the reasons for the low activity with Zr catalyst may come from the short life time of the Zr active species, since complexes of the second row transition-metals in the periodic table are less stable than those of the third row transition-metals. The large polydispersity in the case of Zr system may stem from the presence of a few active species in this system.

Table 2 presents the results of ethylene polymerization with the complexes having a 2,4,6-tri-*i*-propylphenyl group under the same conditions. It is remarkable that the Tip Hf complexes show much lower activities (29 for **Hf-6** versus 180 for **Hf-1** and 12 for **Hf-7** versus 305 for **Hf-4**) and larger Mw/Mn values (22.10–27.52) than the Mes Hf complexes (6.60–8.12). It is highly probable that the bulky Tip group would interfere with coordination of ethylene to the metal, causing the low activities. The reason for the large Mw/Mn values is not clear now.

3.2. Ethylene/styrene copolymerization

Whether a catalyst has copolymerization activity or not is one of the interesting subjects in the olefin polymerization field [40–44]. Therefore, we examined catalytic activities in ethylene/styrene copolymerization with the phosphorus-pendant complexes.

The results of styrene polymerization are listed in Table 3. For comparison, the results of a blank experiment are also added in Table 3. On the basis of the results of the blank experiment, it was found that the systems based on these phosphorus-pendant complexes are almost inactive in styrene single-polymerization, similarly in the case of $[(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^i\text{Bu-}\kappa\text{N})\text{ML}_2]$ (M = Ti, Zr; L = Cl, alkyl group) [10,16].

Table 4 presents the results of ethylene/styrene copolymerization at 50 and 80 °C. These systems based on the phosphorus-pendant Cp complexes showed activities. However, the activities were relatively low compared with those reported to date [10,42,44]. The polymers obtained were analyzed by GPC/FTIR measurement [30], which revealed that the polymers contain styrene components. St (%) in Table 4 shows the percentage of styrene components in the polymer. It should be noted that the polymers are not mixtures of polyethylene and polystyrene but ethylene–styrene copolymers, since these phosphorus-pendant complex systems did not show activity in styrene polymerization (Table 3). At higher temperature (80 °C), all phosphorus-pendant complex systems exhibited higher activities and higher St (%) values, which suggests the possibility that these catalysts can control the ratio of the ethylene/styrene content in the formed copolymer through thermal conditions. It should be noted that the catalytic system obtained by combining phosphorus-pendant complexes and alkylaluminum affords ethylene/styrene copolymers with a high styrene content, in contrast with CGC bearing an amide ligand; CGC-type Ti complexes give the copolymers with styrene contents limited to maximum 50% [10,44], and CGC-type Zr complexes afford no copolymer but polyethylene even under ethylene/styrene copolymerization conditions [16].

4. Conclusions

Catalytic activities in the polymerization of ethylene and styrene and copolymerization of ethylene/styrene were examined for the systems obtained by combination of secondary phosphine-pendant and phosphide-pendant complexes of Zr and Hf with alkylaluminum co-catalysts. The systems of both Zr and Hf complexes exhibit activity in ethylene polymerization and catalysts based on the Hf complexes are more active. In contrast, these systems are inactive in styrene polymerization. It should be noted that these systems are active in the copolymerization of ethylene/styrene and the copolymers obtained have a relatively high styrene content. Such behavior has not been observed in copolymerizations with the corresponding amido-pendant Cp complexes.

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Appendix A. Supplementary data

Supplementary data associated with this item can be found at doi:10.1016/j.molcata.2004.06.024.

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