

## Controlled Isospecific Polymerization of $\alpha$ -Olefins by Hafnium Complex Incorporating with a *trans*-Cyclooctanediyl-Bridged [OSSO]-Type Bis(phenolate) Ligand

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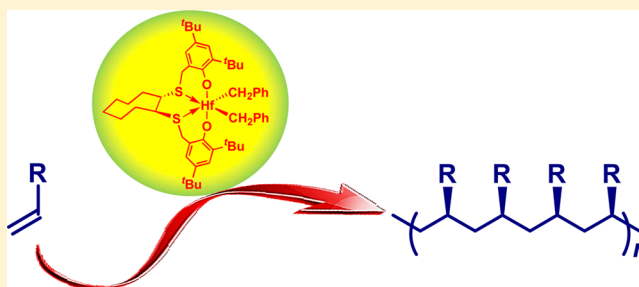
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### Supporting Information

**ABSTRACT:** Treatment of *trans*-cyclooctanediyl-bridged [OSSO]-type ligand **1** with  $\text{Hf}(\text{CH}_2\text{Ph})_4$  in toluene afforded the corresponding hafnium(IV) dibenzyl complex **5** as pale yellow crystals. X-ray crystallographic analysis of **5** revealed that the six-coordinated hafnium center incorporated in the [OSSO]-type ligand **1** adopted *cis*- $\alpha$  configuration, and two benzyl ligands were coordinated to hafnium center by  $\eta^1$ -fashion. In the polymerization of 1-hexene, the combination of hafnium complex **5** and  $\text{B}(\text{C}_6\text{F}_5)_3$ ,  $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$ , or dMAO (dried methylaluminoxane) as an activator provided poly(1-hexene)s with perfect isotacticity ( $[mmmm] > 95\%$ ) and high molecular weights ( $M_w = 74\,800\text{--}421\,000\text{ g mol}^{-1}$ ). The combination of **5**/dMAO catalyst system, in particular, exhibited fairly high activity of  $2100\text{ g mmol (S)}^{-1}\text{ h}^{-1}$ , which is quite higher than those of previously reported [OSSO]-type hafnium complexes. In addition, the polymerization of 4-methyl-1-pentene (4-MP) catalyzed by the **5**/ $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$  system at room temperature produced completely isotactic poly(4-MP)s with good activity ( $54\text{--}101\text{ g mmol (S)}^{-1}\text{ h}^{-1}$ ) and relatively narrow PDI ( $M_w/M_n = 1.3$ ). Furthermore, the propylene polymerization catalyzed by the **5**/dMAO system at different temperatures ( $0\text{--}70\text{ }^\circ\text{C}$ ) for 1 h afforded highly isotactic polypropylenes, where the catalyst activity and isotacticity depend on the polymerization temperature. Thus, the activity greatly increased from 500 to  $17\,000\text{ g mmol (S)}^{-1}\text{ h}^{-1}$  when the polymerization temperature was increased. In contrast, isotacticity and melting transition temperature ( $T_m$ ) were elevated by decreasing polymerization temperature (at  $0\text{ }^\circ\text{C}$ :  $[mmmm] = 93.7\%$ ,  $T_m = 156.2\text{ }^\circ\text{C}$ ; at  $70\text{ }^\circ\text{C}$ :  $[mmmm] = 86.8\%$ ,  $T_m = 140.9\text{ }^\circ\text{C}$ ).



## INTRODUCTION

During the past two decades, considerable attention has been paid to the development in so-called postmetallocene complexes as potent single-site catalysts for the  $\alpha$ -olefin polymerization to achieve high performance in terms of activity and stereocontrol.<sup>1,2</sup> In particular, [OSSO]-type bis(phenolate), in which the two phenoxide frameworks are linked to two sulfur donors in the ortho- or benzyl-positions, has been of great interest as the dianionic ancillary tetradentate ligands for group 4 metal centers.<sup>3,4</sup> Recently, we have succeeded in the development of a new [OSSO]-type bis(phenolate) ligand (**1**) based on a *trans*-1,2-cyclooctanediyl platform and syntheses of several zirconium<sup>5</sup> and titanium complexes.<sup>6</sup> Upon activation with  $\text{B}(\text{C}_6\text{F}_5)_3$  or  $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$ , zirconium(IV) dibenzyl complex **2** achieved highly active ( $1610\text{--}2500\text{ g mmol (2)}^{-1}\text{ h}^{-1}$ ) and completely isospecific polymerization of 1 hexene ( $[mmmm] > 95\%$ ).<sup>5a</sup> We have also presented that dMAO-activated titanium(IV) and -(III) complexes **3** and **4** incorporating with ligand **1**

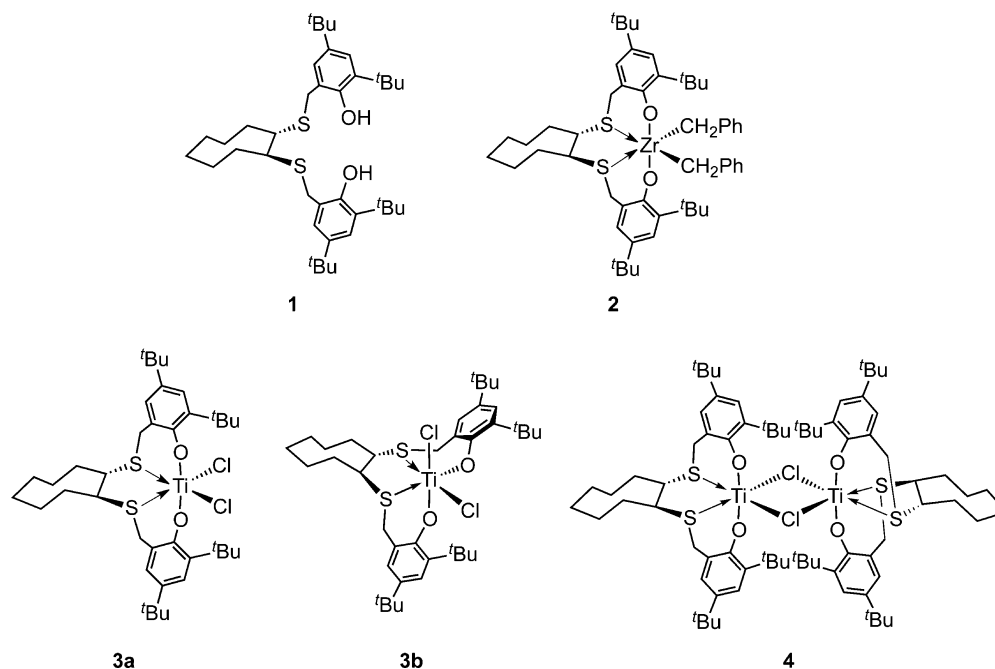
polymerized 1-hexene in an isotactic manner with monomodal molecular weight distributions ( $M_w = 22\,000\text{--}52\,000\text{ g mol}^{-1}$ ,  $M_w/M_n = 1.7\text{--}1.8$ ), albeit with quite low activity [ $0.27\text{--}1.0\text{ g mmol (cat)}^{-1}\text{ h}^{-1}$ ].<sup>6</sup> Despite interest for the postmetallocene complexes, until now there has been very limited achievements of both high activity and stereospecificity as a polymerization catalyst of hafnium complex bearing the [OSSO]-type ligand, due to the quite low reactivity compared with the corresponding titanium and zirconium complexes. For example, Okuda et al. have reported that a MAO-activated group 4 metal complexes with an 1,4-dithiabutanediyl linked [OSSO]-type bis(phenolate) ligand can be used for the isospecific polymerization of styrene.<sup>7</sup> In the case of hafnium complex, however, the formations of lower molecular weight polymers ( $M_n = 1000\text{--}4200\text{ g mol}^{-1}$ ) were observed with very low activities

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Chart 1

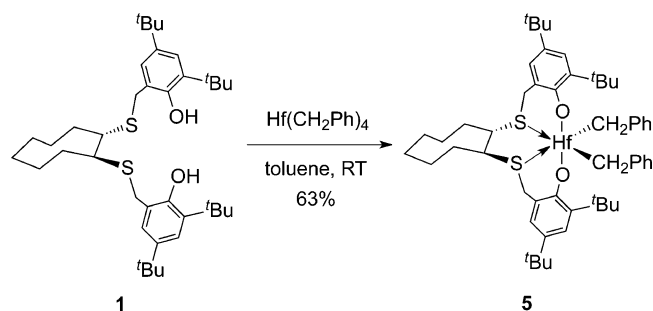


(0.6–9 g mmol (cat.)<sup>−1</sup> h<sup>−1</sup>). Miyatake et al. have reported that group 4 metal complexes except the hafnium complex, bearing a 1,2-dithioethanediyl-linked [OSSO]-type ligand, served as highly active precatalysts in polymerizations of  $\alpha$ -olefins such as 1-hexene, vinylcyclohexane, and propylene with stereoirregularity.<sup>8</sup> Recently, Jin et al. have introduced group 4 complexes that contain an *o*-carborane-bridged [OSSO]-type ligand.<sup>9</sup> While the zirconium complex exhibited good activity toward the ethylene polymerization, the hafnium complex was found to be almost inactive. On the other hand, quite recently, Kol et al. have developed a more bulky 1,2-dithioethanediyl-linked [OSSO]-type ligand including a bulky 1-adamantyl group on the *o*-phenolate moiety.<sup>10</sup> The hafnium complex activated by MAO at −10 °C polymerized propylene isospecifically ([*mmmm*] = 89%), albeit with low molecular weights ( $M_n$  = 4100–7800 g mol<sup>−1</sup>) and very low activities (3–22 g mmol (cat.)<sup>−1</sup> h<sup>−1</sup>). In this article, we present the synthesis and structure of hafnium(IV) dibenzyl complex (**5**) bearing the [OSSO]-type ligand **1** and its powerful performance in the polymerization of several  $\alpha$ -olefins, as a part of our investigation of [OSSO]-type ligand **1** in the single-site postmetallocene catalysis.

## RESULTS AND DISCUSSION

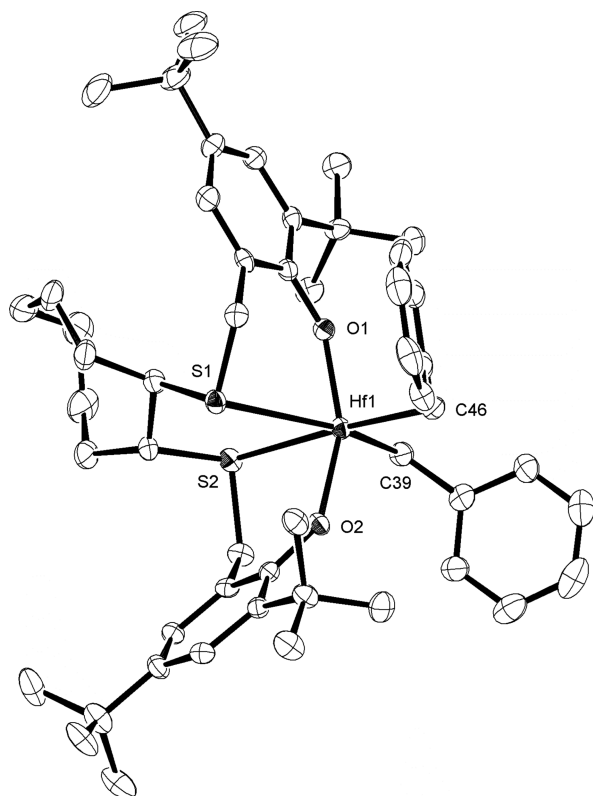
**Synthesis and Structure of Hafnium(IV) Dibenzyl Complex.** The reaction of [OSSO]-type ligand **1** with Hf(CH<sub>2</sub>Ph)<sub>4</sub> in toluene at room temperature gave the corresponding hafnium(IV) dibenzyl complex **5** as air- and moisture-sensitive pale yellow crystals in 76% yield (Scheme 1). In the <sup>1</sup>H NMR spectrum of **5**, the AB pattern due to the benzyl protons appeared at  $\delta$  3.13 and 3.41 as doublet signals ( $J$  = 14 Hz). The sulfur-bonded methine protons resonated at  $\delta$  2.35 as a broad singlet. Similar to the NMR observation of the related [OSSO]-type zirconium(IV) complex **2**, the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR data of **5** exhibited the magnetical equivalency of two phenolate moieties as well as the two benzyl ligands, indicating that **5** has a C<sub>2</sub>-symmetric *cis- $\alpha$*  structure in solution

Scheme 1



in the NMR time scale. The molecular structure of **5** was determined by X-ray crystallography as depicted in Figure 1. In the crystalline state, the hafnium core lies at the center of a distorted octahedral coordination sphere with *cis*-arranged two sulfur atoms and two benzyl groups, which adopts a *cis- $\alpha$* , ( $\Delta^*, R^*, R^*$ )-configuration as similar as [OSSO]-type zirconium(IV) dialkyl complexes. In contrast to zirconium(IV) complex **2**, which has  $\eta^2$ - and  $\eta^1$ -coordination fashion of the benzyl ligands,<sup>5</sup> two benzyl ligands of **5** were coordinated to hafnium center by  $\eta^1$ -mode with Hf–C<sub>benzyl</sub>–C<sub>ipso</sub> angles of 107.4(2)° and 118.5(3)°. The Hf–S bond lengths in **5** [Hf1–S1 = 2.7848(10), Hf1–S2 = 2.8361(10) Å] are comparable to those in a reported [OSSO]-type hafnium dibenzyl complex taking a similar *cis- $\alpha$*  coordination mode, [Hf{2,2'-(OC<sub>6</sub>H<sub>2</sub>-4,6-<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>Bn<sub>2</sub>}] [2.9222(9), 2.8269(8) Å].<sup>10</sup> The cyclooctane ring in **5** adopts a boat-chair conformation. The S–C–C–S dihedral angle [70.7(3)°] is somewhat deviated from the ideal 60° of the *gauche* conformation. Similar deviations, attributed to the conformation of cyclooctane rings, were observed in the starting [OSSO]-type bis(phenol) **1** [75.3(3)°] and zirconium complex **2** [67.2(2)°].<sup>5</sup>

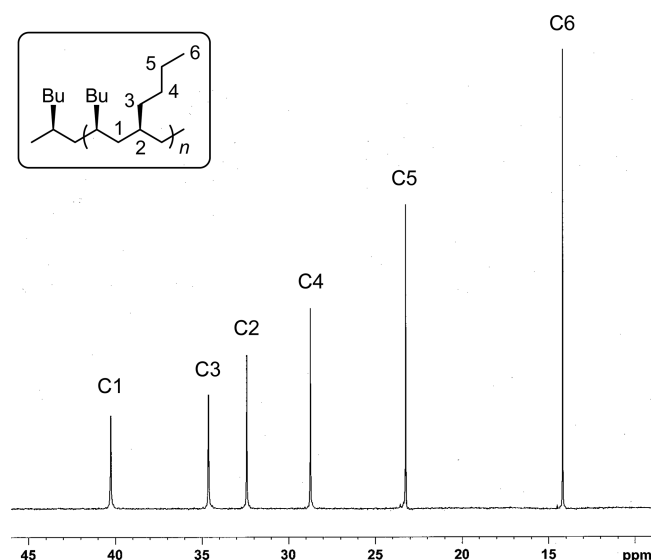
**Polymerization of 1-Hexene.** To evaluate the potential as a polymerization catalyst of  $\alpha$ -olefin, first of all, we tested 1-hexene polymerization with hafnium precatalyst **5**. The results



**Figure 1.** ORTEP drawing of dibenzyl hafnium(IV) complex **5** (50% thermal ellipsoids, hydrogen atoms and solvated benzenes and hexanes were omitted for clarity). Selected bond lengths [Å] and bond angles [deg]: Hf1–O1 = 1.968(3), Hf1–O2 = 1.980(3), Hf1–C39 = 2.274(4), Hf1–C46 = 2.263(4), Hf1–S1 = 2.7848(10), Hf1–S2 = 2.8361(10), O1–Hf1–O2 = 157.19(10), S1–Hf1–S2 = 71.19(3), C39–Hf1–C46 = 96.76(14), Hf1–C39–C40 = 107.4(2), Hf1–C46–C47 = 118.5(3), S1–C1–C2–S2 = 70.7(3).

are compiled in Table 1. The polymerization of 1-hexene (3.0 g) with **5** (0.020 mmol) upon activation with  $B(C_6F_5)_3$  (0.020 mmol) in the mixed solvent of benzene and hexane at 25 °C proceeded efficiently to yield poly(1-hexene)s (0.62–2.16 g) (runs 1–3). The GPC analyses of the resulting polymers revealed large molecular weights ( $M_w = 120\,000$ – $227\,000\text{ g mol}^{-1}$ ) and narrow polydispersities (PDI) ranging between 1.3 and 1.7, consistent with a single site behavior of the catalyst.

The molecular weight increases considerably with lengthening time in the range from 10 to 30 min. The microstructure of the polymers elucidated by  $^{13}C\{^1H\}$  NMR spectroscopy, which showed six sharp signals, were excellent isotacticity of more than 95% (Figure 2). In run 4, complex **5** activated with



**Figure 2.**  $^{13}C\{^1H\}$  NMR spectrum of poly(1-hexene) obtained by the  $5/B(C_6F_5)_3$  system (Table 1, run 1).

$B(C_6F_5)_3$  in benzene also furnished high isotactic polymer ( $[mmmm] > 95\%$ ) with a larger molecular weight ( $M_w = 191\,000\text{ g mol}^{-1}$ ) albeit with a nonliving character ( $M_w/M_n = 1.8$ ). Moreover, the combination of the  $S/(Ph_3C)[B(C_6F_5)_4]$  system at 0 °C afforded perfectly isotactic poly(1-hexene)s with extremely higher molecular weights ( $M_w = 256\,000$ – $421\,000\text{ g mol}^{-1}$ ) and narrower molecular weight distribution of 1.5–1.6 (runs 5 and 6). Interestingly, the complex **5** (0.0020 mmol) upon activation with  $dMAO^{11}$  ( $Al/Hf = 250$ ) could also be produce highly isotactic poly(1-hexene)s ( $M_w = 256\,000$ – $421\,000\text{ g mol}^{-1}$ ) with relatively narrow polydispersities of 1.2–1.4 at temperatures between 25 and 70 °C in toluene (runs 7–9). In particular, the productivity of up to  $2100\text{ g mmol (S)}^{-1}\text{ h}^{-1}$  at 70 °C in run 9 is comparable to that ( $4900\text{ g mmol (Hf)}^{-1}\text{ h}^{-1}$ ) reported by Waymouth for a MAO-activated hafnium(IV) complex based on a bis(phenolate) ether ligand ( $[mmmm] =$

**Table 1.** 1-Hexene Polymerization with Hafnium(IV) Dibenzyl Complex **5** upon Activation with  $B(C_6F_5)_3$ ,  $(Ph_3C)[B(C_6F_5)_4]$  or  $dMAO$

run	time [min]	temp [°C]	solvent	yield [g]	activity <sup>c</sup>	$M_w$ [g mol <sup>-1</sup> ]	PDI <sup>f</sup>	$[mmmm]^g$ [%]
1 <sup>a</sup>	10	25	benzene, hexane	0.62	186	120 000	1.3	>95
2 <sup>a</sup>	20	25	benzene, hexane	1.20	180	185 000	1.5	>95
3 <sup>a</sup>	30	25	benzene, hexane	2.16	216	227 000	1.7	>95
4 <sup>b</sup>	10	25	benzene	2.02	606	191 000	1.8	>95
5 <sup>c</sup>	15	0	toluene	0.76	152	256 000	1.5	>95
6 <sup>c</sup>	30	0	toluene	2.20	220	412 000	1.6	>95
7 <sup>d</sup>	10	25	toluene	0.14	420	102 600	1.2	>95
8 <sup>d</sup>	10	40	toluene	0.37	1110	149 800	1.4	>95
9 <sup>d</sup>	10	70	toluene	0.70	2100	74 800	1.7	>95

<sup>a</sup>Conditions: benzene (1 mL) and hexane (5 mL), **5**: 0.020 mmol,  $B(C_6F_5)_3$  0.020 mmol; 1-hexene 3.0 g (35.6 mmol). <sup>b</sup>Conditions: benzene (1 mL), **5**: 0.020 mmol,  $B(C_6F_5)_3$  0.020 mmol; 1-hexene 3.0 g (35.6 mmol). <sup>c</sup>Conditions: toluene (5 mL), **5**: 0.020 mmol,  $(Ph_3C)[B(C_6F_5)_4]$  0.020 mmol; 1-hexene 3.0 g (35.6 mmol). <sup>d</sup>Conditions: toluene (5 mL), **5**: 0.0020 mmol,  $dMAO$  0.50 mmol ( $Al/Hf = 250$ ); 1-hexene 3.0 g (35.6 mmol). <sup>e</sup>In g mmol ( $S$ )<sup>-1</sup> h<sup>-1</sup>. <sup>f</sup>PDI =  $M_w/M_n$ . Determined by HT-GPC. <sup>g</sup>Determined by  $^{13}C\{^1H\}$  NMR spectroscopy.

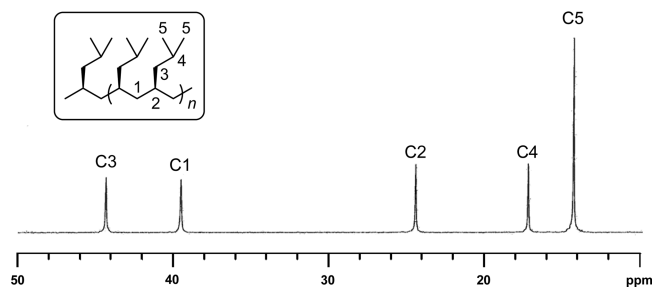
**Table 2.** 4-Methyl-1-pentene Polymerization with Hafnium(IV) Dibenzyl Complex **5** upon Activation with  $B(C_6F_5)_3$  and  $(Ph_3C)[B(C_6F_5)_4]$ 

run	time [min]	solvent	yield [g]	activity <sup>e</sup>	$M_w$ [g mol <sup>-1</sup> ]	PDI <sup>f</sup>	[ <i>mmmm</i> ] <sup>g</sup> [%]
1 <sup>a</sup>	5	benzene, hexane	0.090	54	51 000	1.5	>95
2 <sup>b</sup>	15	toluene	0.270	54	102 000	1.3	>95
3 <sup>c</sup>	10	CH <sub>2</sub> Cl <sub>2</sub>	0.336	101	44 000	2.0	>95
4 <sup>d</sup>	60	toluene	0.082	8	21 000	2.1	>95

<sup>a</sup>Conditions: benzene (1 mL) and hexane (5 mL), 25 °C, **5**: 0.02 mmol,  $B(C_6F_5)_3$ : 0.02 mmol; 4-methyl-1-pentene 1.0 g (11.9 mmol). <sup>b</sup>Conditions: toluene (5 mL), 25 °C, **5**: 0.02 mmol,  $(Ph_3C)[B(C_6F_5)_4]$  0.02 mmol; 4-methyl-1-pentene 1.0 g (11.9 mmol). <sup>c</sup>Conditions: CH<sub>2</sub>Cl<sub>2</sub> (5 mL), 25 °C, **5**: 0.02 mmol,  $(Ph_3C)[B(C_6F_5)_4]$  0.02 mmol; 4-methyl-1-pentene 1.0 g (11.9 mmol). <sup>d</sup>Conditions: toluene (10 mL), 25 °C, **5**: 0.01 mmol, dMAO 2.50 mmol (Al/Hf = 250); 4-methyl-1-pentene 1.0 g (11.9 mmol). <sup>e</sup>In g mmol(**5**)<sup>-1</sup> h<sup>-1</sup>. <sup>f</sup>PDI =  $M_w/M_n$ . Determined by HT-GPC. <sup>g</sup>Determined by <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy.

89%,  $M_w = 81\,600$  g mol<sup>-1</sup>,  $M_w/M_n = 2.04$ , at 50 °C).<sup>12</sup> Consequently, our hafnium catalyst systems exhibited remarkably good activity [152–2100 g mmol (**5**)<sup>-1</sup> h<sup>-1</sup>], which are quite higher than those of reported [OSSO]-type hafnium complexes [0.8–36.8 g mmol (cat.)<sup>-1</sup> h<sup>-1</sup>].<sup>8,10</sup> While the production of atactic and lower molecular weight poly(1-hexene)s with [OSSO]-type hafnium complexes was independently demonstrated by Miyatake<sup>8</sup> and Kol,<sup>10</sup> our catalytic system using **5** was able to provide poly(1-hexene)s with perfect isotacticity and high molecular weight. Furthermore, the catalytic activity in our [OSSO]-type group 4 metal complexes was found to be heavily dependent on the central metal. Thus, the hafnium complex **5** is slightly less active than the zirconium complex **2** [1610–2500 g mmol (**2**)<sup>-1</sup> h<sup>-1</sup>],<sup>5</sup> but obviously much more active than the titanium(IV) and -(III) complexes **3** and **4** [0.27–1.0 g mmol (cat.)<sup>-1</sup> h<sup>-1</sup>].<sup>6</sup>

**Polymerization of 4-Methyl-1-pentene.** Isotactic poly(4-methyl-1-pentene) is a semicrystalline polymer with different properties (high melting point, high clarity, good dielectric character, and chemical resistance) being suitable for many applications such as insulating sheaths of electrical wires and codes, food packaging, or optical components.<sup>13</sup> While a few group 4 postmetallocene complexes based on [ONNO]-type diamino bis(phenolate) ligands have been reported to polymerize 4-methyl-1-pentene (4-MP),<sup>14</sup> there is no attainment of both high activity and stereospecificity in the 4-MP polymerization. As a next catalytic application with hafnium complex **5**, we carried out the polymerization of a bulkier monomer, 4-methyl-1-pentene, at ambient temperature. The results are summarized in Table 2. The polymerization of 4-MP (1.0 g) employing the system consisting of **5** (0.020 mmol) and  $B(C_6F_5)_3$  (0.020 mmol) as an activator in benzene and hexane for 5 min yielded 90 mg of colorless solid polymer, corresponding to an activity of 54 g mmol (**5**)<sup>-1</sup> h<sup>-1</sup> (run 1). The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of the polymer showed five sharp signals indicating the formation of precisely isotactic poly(4-MP) ([*mmmm*] > 99%) (Figure 3). The GPC analysis exhibited that the obtained polymer has a monomodal molecular weight distribution ( $M_w = 51\,000$  g mol<sup>-1</sup>) and a narrow polydispersity of 1.5. In run 2, the **5**/ $(Ph_3C)[B(C_6F_5)_4]$  system in toluene the isotactic polymer obtained shows larger molecular weight ( $M_w = 102\,000$  g mol<sup>-1</sup>) and slightly narrower polydispersity ( $M_w/M_n = 1.3$ ). The catalytic activity was close to the polymerization condition of run 1. In the case of the **5**/ $(Ph_3C)[B(C_6F_5)_4]$  system in CH<sub>2</sub>Cl<sub>2</sub> led to slightly lower molecular weight of isotactic poly(4-MP) ( $M_w = 44\,000$  g mol<sup>-1</sup>,  $M_w/M_n = 2.0$ , [*mmmm*] > 99%) with higher activity of 101 g mmol (**3**)<sup>-1</sup> h<sup>-1</sup> (run 3). Meanwhile, the hafnium catalyst **5** activated by 100 equiv of dMAO at room temperature also

**Figure 3.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of poly(4-methyl-1-pentene) obtained by the **5**/ $B(C_6F_5)_3$  system (Table 2, run 1).

produced isotactic poly(4-MP) ( $M_w = 21\,000$  g mol<sup>-1</sup>,  $M_w/M_n = 2.1$ , [*mmmm*] > 99%), albeit with quite low activity (8 g mmol (**5**)<sup>-1</sup> h<sup>-1</sup>) compared with the polymerization conditions of runs 1–3. As a comparison for isospecific polymerization of 4-MP, the hafnium catalyst **5** exhibited considerably higher activity than those of reported single-site zirconium complexes having a [ONNO]-type tetradentate ligand (activity = 0.25 g mmol (cat.)<sup>-1</sup> h<sup>-1</sup>,  $M_w = 15\,000$  g mol<sup>-1</sup>)<sup>15</sup> or half-metallocene ligand (activity = 7.4 g mmol (cat.)<sup>-1</sup> h<sup>-1</sup>,  $M_w = 17\,700$  g mol<sup>-1</sup>),<sup>15</sup> and it afforded larger molecular weight poly(4-MP)s.

**Polymerization of Propylene.** Highly active and perfectly isospecific aptitude of complex **5** further encouraged us to investigate its catalytic behavior for the polymerization of propylene, which is the simplest  $\alpha$ -olefin. The results of propylene polymerization at varied temperatures with pre-catalyst **5** are collected in Table 3. The polymerization of propylene (80 g) employing the system consisting of **5**/dMAO (**5**: 1.0  $\mu$ mol, dMAO: 2.0 mmol, Al/Hf = 200) in toluene at 0 °C resulted in the formation of a crystalline isotactic polypropylene (0.50 g) (run 1). The microstructure of this polymer elucidated by <sup>13</sup>C{<sup>1</sup>H} NMR analysis indicated a [*mmmm*] pentad of 93.7% together with a small amount of [*mmmr*], [*mmrr*], and [*mrrm*] pentads in an approximately 2:2:1 ratio (Figure 4). In the same manner as an [OSSO]-type titanium complex for the styrene/ethylene copolymerization reported by Okuda and Proto,<sup>16</sup> this result shows that an enantiomorphic site control mechanism for stereospecific propagation is operating. In the DSC measurement, the higher melting temperature  $T_m$  of 156.2 °C was attributed to the presence of higher isotactic polypropylene. The molecular weight distribution of the polymer is a monomodal with the polydispersity index of 2.1 ( $M_w = 50\,400$  g mol<sup>-1</sup>), consistent with a single site behavior of the catalyst. This catalyst system showed an activity value of 500 g mmol (**5**)<sup>-1</sup> h<sup>-1</sup>. A similar propylene polymerization by the **5**/dMAO system was observed at 14 °C, producing isotactic polypropylene



Table 3. Propylene Polymerization with Hafnium(IV) Dibenzyl Complex **5** upon Activation with dMAO

run	time [min]	temp [°C]	yield [g]	activity <sup>b</sup>	$M_w$ [g mol <sup>-1</sup> ]	PDI <sup>c</sup>	[ <i>mmmm</i> ] <sup>d</sup> [%]	$T_m$ <sup>e</sup> [°C]
1 <sup>a</sup>	60	0	0.50	500	50 400	2.1	93.7	156.2
2 <sup>a</sup>	60	14	0.33	330	48 800	1.9	93.0	153.0
3 <sup>a</sup>	60	40	2.00	2000	27 000	2.0	91.0	149.3
4 <sup>a</sup>	60	70	16.90	17000	26 300	2.0	86.8	140.9

<sup>a</sup>Conditions: toluene (5 mL), **5**: 1.0  $\mu$ mol, dMAO 2.0 mmol, Al/Hf = 200; propylene 80 g (1.9 mol). <sup>b</sup>Activity = [g mmol (**5**)<sup>-1</sup> h<sup>-1</sup>]. <sup>c</sup>PDI =  $M_w/M_n$ . <sup>d</sup>Determined by <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy. <sup>e</sup>Determined by DSC.

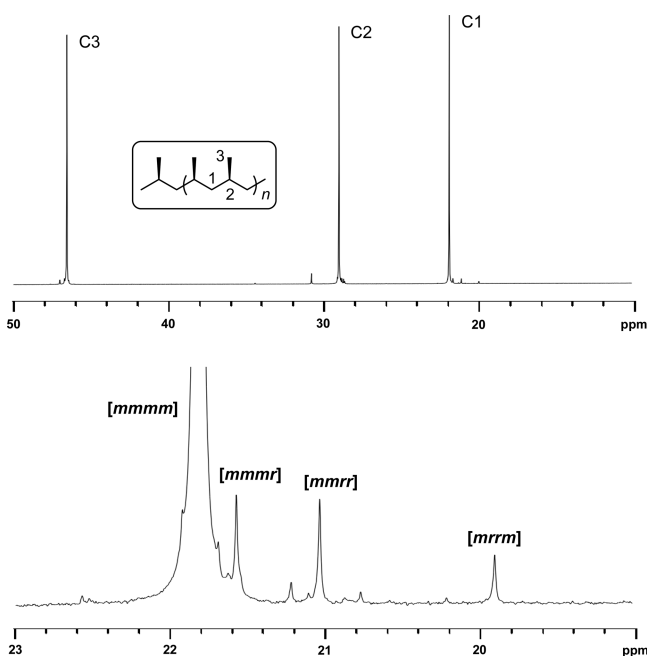


Figure 4. <sup>13</sup>C{<sup>1</sup>H} NMR spectra of polypropylene obtained by the **5**/dMAO system at 0 °C (Table 3, run 1).

([*mmmm*] = 93.0%) with the molecular weight of 48 800 g mol<sup>-1</sup> and the narrow polydispersity of 1.9 (run 2). At 40 °C, the **5**/dMAO system in the propylene polymerization displayed an increasing activity (2000 g mmol (**5**)<sup>-1</sup> h<sup>-1</sup>) (run 3) that is more than 4-fold larger than that at low temperature (runs 1 and 2). Even at 70 °C, moreover, the **5**/dMAO system recorded the highest activity of 17 000 g mmol (**5**)<sup>-1</sup> h<sup>-1</sup>, which is considerably more active by 2 orders of magnitude than those at lower temperature (run 4). Despite the higher polymerization temperature, the resulting polypropylene has a monomodal molecular weight distribution ( $M_w/M_n$  = 2.0). However, the isotacticity and  $T_m$  of the polypropylene at 70 °C reduced somewhat to 86.8% and 140.9 °C, respectively, compared with those of polymerization at 0 °C, and the molecular weight of the polymer diminished to 26 300 g mol<sup>-1</sup> from 50 400 g mol<sup>-1</sup> at 0 °C. Thus, whereas the previous [OSSO]-type precatalysts<sup>10</sup> accounted for the lack of stereospecificity during the propylene polymerization, the complex **5** could achieve highly isospecific polymerization together with excellent activity for the first time.<sup>17,18</sup>

## CONCLUSION

We have introduced a new powerful polymerization precatalyst, hafnium(IV) dibenzyl complex (**5**) supported by the [OSSO]-type bis(phenolate) ligand based on *trans*-cyclooctanediyl platform. In the presence of an activator, the hafnium precatalyst **5** was found to promote precisely isospecific

polymerizations of 1-hexene or 4-methyl-1-pentene involving good activity. Notably, the isotactic poly(1-hexene)s and poly(4-MP)s were produced by the **5**/activator system had significantly larger molecular weights than any polymers ever produced by group 4 metal complexes incorporating with the other [OSSO]-type ligands. Moreover, the complex **5** upon activation with dMAO led to the combination of high activity and controlled isotacticity in the polymerization of propylene at a range of temperatures (0–70 °C). The  $T_m$  values (140.9–156.2 °C) of obtained polypropylenes are proportional to the degree of isotacticity (125–160 °C). Especially, the highest isotacticity ([*mmmm*] = 93.7%) and melting transition temperature ( $T_m$  = 156.2 °C) were observed at 0 °C. These catalytic characteristics are an improvement over other postmetallocene catalysts for  $\alpha$ -olefin polymerization, making them an attractive option as the foundation for the development of general-purpose, new-generation industrial postmetallocene catalysts.

## EXPERIMENTAL SECTION

**General Procedures.** All manipulations of air- and/or moisture-sensitive compounds were performed either using standard Schlenk-line techniques or in an MBRAUM LABmaster Glovebox under an inert atmosphere of argon. Anhydrous hexane and toluene were further dried by passage through columns of activated alumina and supported copper catalyst supplied by Hansen & Co., Ltd. Deuterated benzene (benzene-*d*<sub>6</sub>) was dried and degassed over a potassium mirror by the freeze–thaw cycle prior to use. Other chemicals and gases were used as received. Melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. <sup>1</sup>H (400 or 500 MHz) and <sup>13</sup>C{<sup>1</sup>H} (100.5, 125.8, or 150.9 MHz) NMR spectra were obtained with Bruker DRX400, AVANCE500-T, AVANCE600, or JEOL JNM-ECS400 spectrometers. The <sup>13</sup>C{<sup>1</sup>H} NMR data of poly(1-hexene) were obtained in CDCl<sub>3</sub> at room temperature. The <sup>13</sup>C{<sup>1</sup>H} NMR data of poly(4-methyl-1-pentene) were obtained in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> at 130 °C. The <sup>13</sup>C{<sup>1</sup>H} NMR data of polypropylene were obtained in a mixture of *o*-dichlorobenzene-*d*<sub>4</sub> and *o*-dichlorobenzene (1/3) at 130 °C. The molecular weights and molecular weight distributions of polymers were determined against polystyrene standard by gel permeation chromatography on a SCL-10AVP/LC-10ATVP/DGU-14A/CTO-10ACVP/RID-10A apparatus (Shimadzu Corporation) using a GPC KF-804L (Shodex Corporation) column for poly(1-hexene)s, a HLC-8220 GPC apparatus (Tosoh Corporation) of the laboratory of Dr. Zhaomin Hou (Organometallic Chemistry Laboratory, RIKEN Advanced Science Institute) for poly(4-methyl-1-pentene)s, or a HLC-8121 GPC/HT apparatus (Tosoh Corporation) for polypropylene of Sumitomo Chemical Co. Ltd. X-ray crystallography was performed with a Rigaku Saturn724 diffractometer. Elemental analyses were performed by the Chemical Analysis Team of RIKEN Advanced Science Institute. *trans*-Cyclooctane-1,2-dithiol,<sup>19</sup> [OSSO]H<sub>2</sub> ligand **4**,<sup>5</sup> Hf(CH<sub>2</sub>Ph)<sub>4</sub>,<sup>20</sup> and dMAO<sup>11a</sup> were prepared by the literature procedures.

**Synthesis of Hafnium(IV) Dibenzyl Complex **5**.** A solution of **1** (192 mg, 0.313 mmol) in toluene (10 mL) was added to a solution of Hf(CH<sub>2</sub>Ph)<sub>4</sub> (170 mg, 0.313 mmol) in toluene (10 mL) at room temperature. The mixture was stirred for 1 h at room temperature, and

the solvent was removed under reduced pressure. The residue was recrystallized from hexane (2 mL) at room temperature. The pale yellow crystals were collected by filtration and dried in vacuo to give **5** (209 mg, 63%). **3**: mp 203–204 °C (dec.).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$ : 1.18–1.94 (m, 48 H), 2.35 (m, 2 H), 2.61 (d,  $^2J = 12$  Hz, 2 H), 2.88 (d,  $^2J = 12$  Hz, 2 H), 3.13 (d,  $^2J = 14$  Hz, 2 H), 3.41 (d,  $^2J = 14$  Hz, 2 H), 6.62 (d,  $^4J = 2$  Hz, 2 H), 6.78 (t,  $^3J = 8$  Hz, 2 H), 7.10 (t,  $^3J = 8$  Hz, 4 H), 7.29 (d,  $^3J = 8$  Hz, 4 H), 7.57 (d,  $^4J = 2$  Hz, 2 H).  $^{13}\text{C}$  NMR (100.4 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$ : 25.1, 26.2, 28.8, 30.5, 31.8, 32.1, 34.2, 35.6, 49.1, 77.2, 121.4, 121.8, 124.6, 125.6, 126.0, 129.3, 138.5, 141.1, 148.4, 157.9. Anal. Calcd for  $\text{C}_{52}\text{H}_{72}\text{HfO}_2\text{S}_2$ : C, 64.27; H, 7.47, Found: C, 63.87; H, 7.59.

**General Procedure for 1-Hexene Polymerization.** Method A: A 50 mL Schlenk flask was charged sequentially with catalyst precursor **5** (0.020 mmol), cocatalyst ( $\text{B}(\text{C}_6\text{F}_5)_3$  or  $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$ ), and toluene at room temperature. After stirring for 1 min at room temperature, 1-hexene (3.0 g, 35.6 mmol) was added to the reaction mixture. The mixture was stirred for 10–30 min at 0–70 °C. The reaction was quenched by addition of 2-propanol and concentrated hydrochloric acid. The mixture was extracted with toluene, and the organic layer was washed with methanol and dried over  $\text{MgSO}_4$ . The solvent was removed in vacuo at 70 °C during an overnight to leave poly(1-hexene). Method B: A 50 mL Schlenk flask was charged sequentially with 1-hexene (3.0 g, 35.6 mmol), dMAO, and toluene at room temperature. After stirring for 1 min at room temperature, toluene solution of catalyst precursor **5** (0.0020 mmol) was added to the reaction mixture. The mixture was stirred for 10–30 min at 0–70 °C. The reaction was quenched by addition of 2-propanol and concentrated hydrochloric acid. The mixture was extracted with toluene, and the organic layer was washed with methanol and dried over  $\text{MgSO}_4$ . The solvent was removed in vacuo at 70 °C during an overnight to leave poly(1-hexene).

**General Procedure for 4-Methyl-1-pentene Polymerization.** A 50 mL Schlenk flask was charged sequentially with 4-methyl-1-pentene (1.0 g, 11.9 mmol), cocatalyst ( $\text{B}(\text{C}_6\text{F}_5)_3$ ,  $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$ , or dMAO), and toluene at room temperature. After stirring for 1 min at room temperature, the toluene solution of catalyst precursor **5** was added to the reaction mixture. The mixture was stirred for 1 h at room temperature. The reaction was quenched by addition of 2-propanol and concentrated hydrochloric acid. The precipitate was filtered off and washed with methanol. The white solid was dried in vacuo at 70 °C overnight to leave poly(4-methyl-1-pentene).

**General Procedure for Propylene Polymerization.** A 400 mL autoclave was charged sequentially with propylene (80 g, 11.9 mmol) and toluene at room temperature. After setting at desired temperature, dMAO and toluene solution of catalyst precursor **5** was added to the reaction mixture. The mixture was stirred for 1 h at 0–70 °C. Then, the reaction was quenched by addition of methanol. After a few minutes the gas was vented, and the mixture was then poured into methanol (1.0 L) with hydrochloric acid (1 M, 10 mL). The polymer was isolated by filtration, washed with methanol, and dried in a high vacuum at 80 °C for 4 h.

**X-ray Crystallographic Analysis.** Pale yellow single crystals of **5** were grown by slow evaporation of its saturated hexane solution at –20 °C. The intensity data were collected at 100 K for **5** on a Rigaku AFC10 diffractometer equipped with a Saturn724+ CCD detector using graphite-monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073$  Å). The structure was solved by direct methods and refined by full-matrix least-squares procedures on  $F^2$  for all reflections (SHELX-97).<sup>21</sup> Hydrogen atoms of **5** were located by assuming ideal geometry and were included in the structure calculations without further refinement of the parameters. Crystallographic data and details of refinement for **5**:  $\text{C}_{49}\text{H}_{69}\text{HfO}_2\text{S}_2 \cdot 3\text{C}_6\text{H}_6 \cdot 0.5\text{C}_6\text{H}_{14}$ , MW = 1210.06, monoclinic, space group  $\text{P}2_1/n$ ,  $a = 10.5199(4)$  Å,  $b = 20.5400(7)$  Å,  $c = 29.3486(11)$  Å,  $\beta = 98.1250(10)^\circ$ ,  $V = 6278.0(7)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calc}} = 1.280$  g cm<sup>–3</sup>,  $R_1$  ( $I > 2\sigma$ ) = 0.0390,  $wR_2$  (all data) = 0.0896 for 11 684 reflections and 688 parameters, GOF = 1.003.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Crystallographic data for **5** as a CIF file and  $^{13}\text{C}\{^1\text{H}\}$  NMR charts of the produced polymers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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