

# Rational Design of Silicon-Bridged Fluorenyl–Phenoxy Group 4 Metal Complexes as Catalysts for Producing High Molecular Weight Copolymers of Ethylene and 1-Hexene at Elevated Temperature

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**ABSTRACT:** For producing high molecular weight copolymers of ethylene and 1-hexene, a series of silicon-bridged fluorenyl–phenoxy group 4 complexes  $R_2Si(Flu)(3\text{-}^iBu\text{-}5\text{-}Me\text{-}2\text{-}C_6H_5O)MCl_2$  (**4a**: M = Ti; R = Me; Flu = fluorenyl-9-yl; **4b**: M = Ti; R = Et; Flu = fluorenyl-9-yl; **4c**: M = Ti; R = Me; Flu = 2,7-<sup>i</sup>Bu<sub>2</sub>-fluorenyl-9-yl; **4d**: M = Ti; R = Et; Flu = 2,7-<sup>i</sup>Bu<sub>2</sub>-fluorenyl-9-yl; **8**: M = Zr; R = Me; Flu = 2,7-<sup>i</sup>Bu<sub>2</sub>-fluorenyl-9-yl; **9**: M = Hf; R = Me; Flu = 2,7-<sup>i</sup>Bu<sub>2</sub>-fluorenyl-9-yl) were prepared by two methods. One was a reaction of  $MCl_4$  (M = Ti, Zr, and Hf) with the dilithium salts generated by treating corresponding ligands **1a–d** with <sup>i</sup>BuLi in the presence of Et<sub>3</sub>N in toluene and the other used  $MCl_2(NR'_2)_2$  (**6a**: M = Ti; R' = Me, **6b**: M = Zr; R' = Et, **6c**: M = Hf; R' = Me) instead of  $MCl_4$  followed by successive chlorination with Me<sub>3</sub>SiCl. X-ray crystallographic study of **4d** indicated that the cyclopentadienyl moiety of the fluorenyl ligand is bound to the titanium atom in a fashion between  $\eta^3$  and  $\eta^5$ . The newly prepared titanium complexes **4a–d** exhibited high catalytic activities for copolymerization of ethylene and 1-hexene in the presence of <sup>i</sup>Bu<sub>3</sub>Al/[Me<sub>2</sub>NHPh][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and afforded higher molecular weight copolymers than the parent tetramethyl-substituted cyclopentadienyl titanium complex Me<sub>2</sub>Si( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>)(3-<sup>i</sup>Bu-5-Me-2-C<sub>6</sub>H<sub>5</sub>O)TiCl<sub>2</sub> (**10**). In particular, the active species generated from complex **4d** was thermally stable and exhibited high polymerization activities even at 210 °C and produced high molecular weight copolymers with good 1-hexene content.

## Introduction

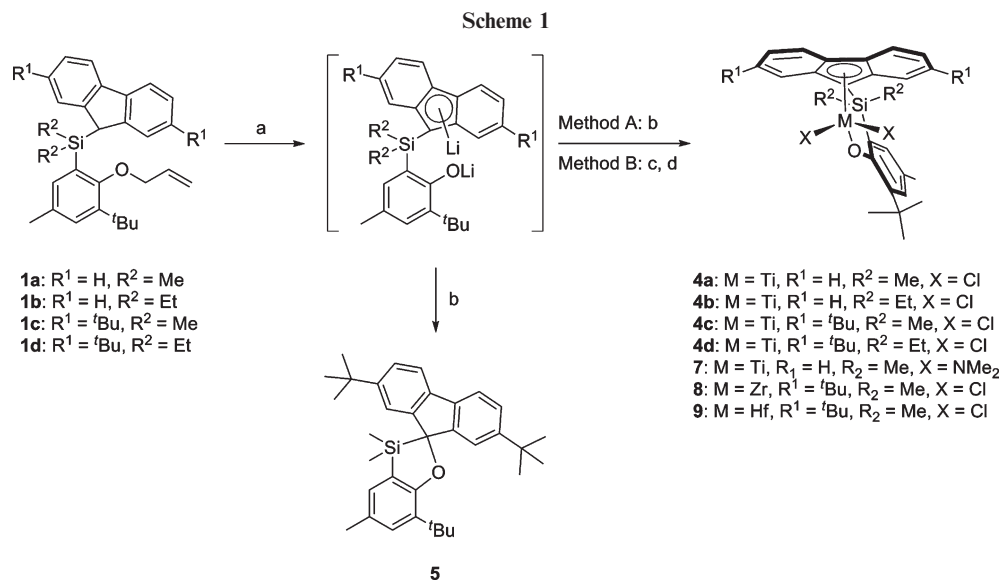
Fluorene compounds have been widely investigated as alternatives to cyclopentadienyl moiety in group 4 metallocene chemistry.<sup>1</sup> Particularly, symmetrically substituted fluorenyl moiety is useful to synthesize C<sub>s</sub>-symmetrical metallocene complexes, which enable us to produce syndiotactic polyolefins by a mechanism of stereocontrol consisting of a regularly alternating insertion of olefins at the enantiotopic sites derived from the C<sub>s</sub>-symmetry.<sup>2–4</sup> Bridged fluorenyl–amido group 4 complexes, for which the molecular structures were first characterized by Okuda as their zirconium complexes, have also attracted great attention because of their C<sub>s</sub>-symmetric structure.<sup>5</sup> The fluorenyl–amido systems have been further investigated by Shiono<sup>6</sup> and Razavi<sup>7</sup> as their titanium derivatives. Attractive features of these titanium complexes include not only capability for production of syndiotactic polymers but also the living nature of the polymerization of propylene and 1-hexene, while the parent tetramethyl-substituted cyclopentadienyl–amido titanium complex gives almost atactic polymers accompanied by chain transfer reactions. The fluorenyl–amido titanium catalyst systems are also applicable for (co)polymerization of bulky comonomer such as norbornene,<sup>8</sup> indicating that the ligand architecture possesses large coordination sites for bulky comonomer insertion along with stereoselective coordination sites for syndiospecific polymerization of 1-olefins.

In the course of our investigation on production of high molecular weight polyolefins catalyzed by PHENICS

(phenoxy-induced complex of Sumitomo) system,<sup>9</sup> we found that molecular weight of the polyolefins produced by titanium-based PHENICS (PHENICS-Ti) was efficiently controlled by the bulkiness of the cyclopentadienyl moiety,<sup>9a</sup> the substituent at the *ortho* position of the phenoxy group,<sup>9c</sup> and the choice of substituents at the silicon bridge.<sup>9d</sup> These findings suggest that steric protection around the active metal center and suppression of 2,1-insertion of 1-olefins are crucial factors for the PHENICS systems to produce high molecular weight copolymers; however, largely open coordination sites of PHENICS systems present the unavoidable problem of irregularity in the 1-olefin insertion. An advantageous feature of PHENICS is that catalytically active species are thermally stable at high temperature, though high-temperature processes usually lower molecular weight of copolymers due to chain termination. Thus, to develop catalyst systems capable of achieving high catalytic activity and copolymers of high molecular weight with high 1-olefin incorporation upon polymerization operated at elevated temperature is a challenging target.<sup>10</sup>

To attain this goal, we have been interested in the results reported for silicon-bridged fluorenyl–amido catalyst systems.<sup>11</sup> The stereoselectivity of 1-olefin insertion generated by the fluorenyl ligand architecture definitely contributes to regioselectivity of 1-olefin insertion for PHENICS systems. Herein, we report the syntheses and characterizations of a series of group 4 metal complexes, PHENICS-M (M = Ti, Zr, Hf), bearing fluorenyl ligands. To introduce a fluorenyl framework to the PHENICS system, we have developed improved metalation reaction by use of  $MCl_2(NR'_2)_2$  (M = Ti, Zr, Hf; R' = Me, Et) precursors.

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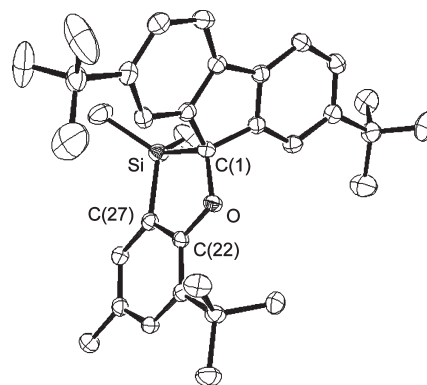


<sup>a</sup> Conditions and reagents: (a) *n*-BuLi/Et<sub>3</sub>N/toluene, -78 °C to rt; (b) TiCl<sub>4</sub>, -78 °C to 90 °C; (c) MCl<sub>2</sub>(NR<sup>3</sup>)<sub>2</sub> (**6a**: M = Ti, R<sup>3</sup> = Me; **6b**: M = Zr, R<sup>3</sup> = Et; **6c**: M = Hf, R<sup>3</sup> = Me), -78 °C to 90 °C; (d) Me<sub>3</sub>SiCl, 0 °C to 35 °C.

Among these newly prepared complexes, PHENICS-Ti with sterically modified fluorenyl systems are highly active even at 210 °C, maintaining high molecular weight copolymers (up to  $M_w = 86\,000$ ) with high 1-hexene content.

## Results and Discussion

**Synthesis of Silicon-Bridged Fluorenyl–Phenoxy Group 4 Complexes.** Silicon-bridged fluorenyl–phenoxy ligands (**1a–d**) were prepared by treatment of fluorene compounds (**2a**: fluorene; **2b**: 2,7-*t*Bu<sub>2</sub>-fluorene) with <sup>*n*</sup>BuLi followed by reaction with [2-(OCH<sub>2</sub>CH=CH<sub>2</sub>)-3-*t*Bu-5-Me-C<sub>6</sub>H<sub>3</sub>]*SiR*<sup>2</sup><sub>2</sub>Cl (**3a**: R<sup>2</sup> = Me; **3b**: R<sup>2</sup> = Et) (see Experimental Section). To begin our studies, syntheses of corresponding silicon-bridged fluorenyl–phenoxy titanium complexes **4a,b** were tried following the previously described procedure for cyclopentadienyl and indenyl complexes (Scheme 1, method A).<sup>9a</sup> The salt metathesis route, however, generally afforded a complicated mixture. It was difficult to isolate desired fluorenyl titanium complexes **4a,b** from the reaction mixture due to both low yield and existence of significant amount of unknown byproducts.<sup>12</sup> The reaction starting from **1c,d**, in which bulky *t*Bu groups on the 2,7-position of fluorene aimed to improve the crystallinity of the resulting complex and to hinder undesired formation of *spiro*-metallocene, afforded corresponding titanium complexes **4c,d** in low isolated yields (12–24%). Detailed investigation of the reaction using **1c** as a ligand precursor revealed that an unexpected *spiro* compound **5** bearing fluorenyl–oxygen bond was formed along with **4c**. The structure of **5** was determined by X-ray crystallography (Figure 1). Although the mechanism of generation of the byproduct **5** was unclear, we concluded that strong Lewis acidity of TiCl<sub>4</sub> and use of excess amounts of <sup>*n*</sup>BuLi (2.25 equiv) and TiCl<sub>4</sub> (1.50 equiv) hampered clean metalation reaction.<sup>13</sup> To avoid further reaction of produced dichlorotitanium complex with unreacted dilithium salt or excess <sup>*n*</sup>BuLi,<sup>14</sup> it was found that use of TiCl<sub>2</sub>(NMe<sub>2</sub>)<sub>2</sub> (**6a**)<sup>15</sup> as a titanium source (method B) significantly improved selectivity of the reaction. Thus, treatment of **1a** with <sup>*n*</sup>BuLi (2.25 equiv) in the presence of Et<sub>3</sub>N (4.50 equiv) in toluene followed by reaction with **6a** (1.20 equiv) afforded the corresponding diamidotitanium complex **7**. Because isolation of **7** was



**Figure 1.** Molecular structure of **5**. All hydrogen atoms are omitted for clarity. Key atoms are labeled. Selected bond distances (Å) and angles (deg) are as follows: C(1)–O = 1.4550(18), C(22)–O = 1.3886(19), C(22)–C(27) = 1.397(2), C(27)–Si = 1.8441(17), C(1)–Si = 1.9432(17), C(1)–O–C(22) = 115.38(11), C(1)–Si–C(27) = 89.90(7), O–C(1)–Si = 106.22(10), Cp'–Ph = 89.35.

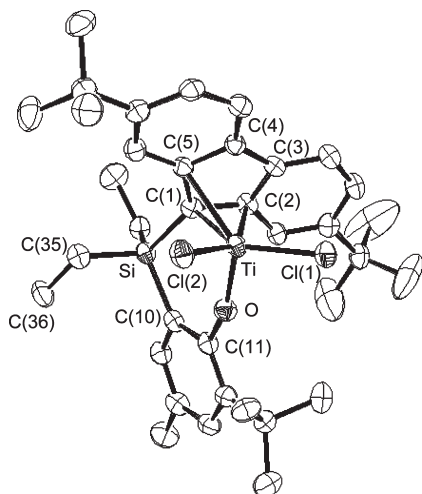
difficult due to high solubility toward solvents such as pentane, successive chlorination of the reaction mixture by addition of excess amount of Me<sub>3</sub>SiCl (10 equiv) was conducted in toluene to afford corresponding dichlorotitanium complex **4a** in good isolated yield (75% yield based on three steps from **2a**).<sup>16</sup> Zirconium complex **8** (78% yield) and hafnium **9** (58% yield) were also prepared by a similar procedure, using ZrCl<sub>2</sub>(NEt<sub>2</sub>)<sub>2</sub> and HfCl<sub>2</sub>(NMe<sub>2</sub>)<sub>2</sub> as metal sources.<sup>17</sup>

**Crystal Structure.** The structure of the fluorenyl complex **4d** was determined by X-ray analysis. A single crystal suitable for X-ray analysis was grown by slow evaporation of toluene solution at room temperature. It was found that there was 0.5 equiv of toluene in the crystal. Selected bond lengths and angles of **4d** are summarized in Table 1. The crystal data and data collection parameters are provided in Table S1 (see Supporting Information). Figure 2 shows the crystal structure of **4d**, which adopts a three-legged piano-stool geometry. The bond distances of Ti–C(1), Ti–C(2), Ti–C(3), Ti–C(4), and Ti–C(5) are found to lie in the range of 2.246–2.487 Å. The difference in bond length between

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **4d**

bond lengths			
Ti–Cl(1)	2.2632(15)	Ti–Cl(2)	2.2566(16)
Ti–C(1)	2.246(4)	Ti–C(2)	2.334(4)
Ti–C(3)	2.487(4)	Ti–C(4)	2.470(4)
Ti–C(5)	2.408(4)	Ti–C <sub>pcent</sub>	2.036
Ti–O	1.771(3)	Si–C(1)	1.878(4)
bond angles			
O–Ti–C(1)	88.97(15)	Cl(1)–Ti–Cl(2)	104.41(5)
C(1)–C <sub>pcent</sub> –Ti	81.88	C <sub>pcent</sub> –C(1)–Ti	64.70
torsion angles			
C(1)–Si–C(10)–C(11)	29.3(4)	Ti–O–C(11)–C(10)	13.9(8)
dihedral angle			
$\theta^a$	66.03		

<sup>a</sup>  $\theta$  denotes the dihedral angle between the best plane of cyclopentadienyl ring and that of phenyl ring carbons.



**Figure 2.** ORTEP drawing of **4d**. All hydrogen atoms and solvent molecule are omitted for clarity. Key atoms are labeled.

Ti–C(1) and Ti–C(3) is 0.241 Å, suggesting that the coordination of cyclopentadienyl moiety of fluorenyl ligand to titanium atom is contributed in somewhat of an  $\eta^3$ -manner. A similar finding was previously reported for the crystal structure of bridged fluorenyl–amide complex  $\text{Me}_2\text{Si}(\text{Flu})(^t\text{BuN})\text{TiMe}_2$  (Flu = substituted fluorene-1-yl).<sup>6f,h</sup> The bond angle C(1)–C<sub>pcent</sub>–Ti of **4d** ( $\alpha = 81.88^\circ$ ) is close to the corresponding angle of  $\text{Me}_2\text{Si}(\text{Flu})(^t\text{BuN})\text{TiMe}_2$  (Flu = fluorene-1-yl:  $\alpha = 79.20^\circ$ ; Flu = 2,7- $^t\text{Bu}_2$ -fluorene-1-yl:  $\alpha = 77.11^\circ$ ; Flu = 3,6- $^t\text{Bu}_2$ -fluorene-1-yl:  $\alpha = 78.19^\circ$ ). The large torsion angles of C(1)–Si–C(10)–C(11) ( $29.31^\circ$ ) and Ti–O–C(11)–C(10) ( $13.87^\circ$ ) and the small dihedral angle ( $\theta$ ) between the best plane of cyclopentadienyl ring carbons and that of phenyl ring carbons ( $66.03^\circ$ ) indicate that **4d** has a vastly distorted bridging backbone. The highly twisted structure is characteristic of  $\text{Et}_2\text{Si}$ -bridged PHENICS and is effective for controlling 2,1-insertion of 1-olefin (vide infra).<sup>9d</sup> From the viewpoint of the coordination mode tendency toward  $\eta^3$ -fashion, the molecular structure of **4d** is similar to those of silicon-bridged dithiophene-fused cyclopentadienyl–phenoxy complexes.<sup>10</sup>

**Copolymerization of Ethylene and 1-Hexene.** Fluorenyl-titanium complexes **4a–d**, zirconium complex **8**, hafnium complex **9**, and a tetramethyl-substituted cyclopentadienyl complex  $\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{Me}_4)(3\text{-}^t\text{Bu-5-Me-2-C}_6\text{H}_4\text{O})\text{TiCl}_2$  (**10**) were preliminarily evaluated as catalyst precursors for copolymerization of ethylene and 1-hexene in the presence of  $^t\text{Bu}_3\text{Al}$  (TIBA) and  $[\text{Me}_2\text{NHPH}][\text{B}(\text{C}_6\text{F}_5)_4]$  (AB) at various temperatures (70 and 130 °C) using a Symyx parallel pressure reactor (PPR) system. Polymerization results are summarized

Table 2. Copolymerization of Ethylene and 1-Hexene<sup>a</sup>

entry	complex	temp (°C)	activity <sup>b</sup>	$M_w^c$ ( $\times 10^4$ )	$M_w/M_n^c$	1-hexene content <sup>d</sup>
1	<b>4a</b>	70	48.4	26.7	1.8	19
2		130	7.8	29.6	1.6	16
3	<b>4b</b>	70	15.7	38.7	2.0	20
4		130	8.1	34.3	1.6	17
5	<b>4c</b>	70	16.8	58.4	2.2	20
6		130	8.4	36.6	1.8	16
7	<b>4d</b>	70	18.5	73.6	2.1	17
8		130	16.5	44.1	2.1	17
9	<b>8</b>	70	6.2	2.0	1.8	14
10		130	0.4	n.d. <sup>e</sup>	n.d. <sup>e</sup>	n.d. <sup>e</sup>
11	<b>9</b>	70	1.2	112.0	27.0 <sup>f</sup>	11
12		130	0.1	n.d. <sup>e</sup>	n.d. <sup>e</sup>	n.d. <sup>e</sup>
13	<b>10</b>	70	41.1	23.6	2.2	16
14		130	10.6	25.4	1.5	14

<sup>a</sup> All data except for **8** and **9** are average of two runs using a Symyx PPR system. Conditions: toluene 5 mL (total volume), 1-hexene 50  $\mu\text{L}$  (70 °C) or 40  $\mu\text{L}$  (130 °C), ethylene 0.6 MPa, complex 0.1  $\mu\text{mol}$ , TIBA 40  $\mu\text{mol}$  (70 °C) or 4  $\mu\text{mol}$  (130 °C), AB 0.3  $\mu\text{mol}$ , 20 min or until consumption of ethylene reached preset levels. <sup>b</sup> In kg of copolymer/[mmol of complex]·h. <sup>c</sup> Determined by GPC with polystyrene standards. <sup>d</sup> Number of short chain branches per 1000 carbons determined by FT-IR.<sup>18</sup> <sup>e</sup> Not determined due to low yield. <sup>f</sup> Bimodal distribution was observed.

in Table 2. All data listed in Table 2 are taken as the average of two runs except for a single run each for complexes **8** and **9**. Fluorenyl complexes of titanium **4a–d** exhibited high polymerization activity and moderate 1-hexene incorporation (up to SCB/1000C = 20) (entries 1–8). The  $M_w$  values of copolymer obtained by **4a–d** were higher than those of **10**. The tendency of  $M_w$  values of the copolymer was influenced by both 2,7-substituents of fluorenyl ligand and bridging structure. It was obvious that introduction of  $^t\text{Bu}$  substituents on the 2,7-positions of fluorene enhanced  $M_w$  of the copolymers and contributed to stability at 130 °C (entries 1–4 vs 5–8). Our recent study on a series of tetramethyl-substituted cyclopentadienyl PHENICS through investigation of regio- and stereochemistry of propylene polymerization using various complexes with different bridging structures revealed that  $\text{Et}_2\text{Si}$ -bridged complex is one of the best complexes to afford high  $M_w$  value,<sup>9d</sup> and the same tendency was found for **4a–d**. Copolymerization using zirconium complex **8** at 70 °C gave low- $M_w$  copolymer ( $M_w = 20\,000$ ) (entry 9). The results are comparable to those obtained by zirconium complexes with bridged fluorenyl–amido ligands.<sup>5c,7</sup> Hafnium complex **9** also less active under our tested conditions and gave high- $M_w$  copolymer with bimodal MWD at 70 °C (entry 11). Almost no polymers were obtained using **8** or **9** at 130 °C (entries 10 and 12), indicating the active species derived from **8** and **9** are unstable under high temperature.

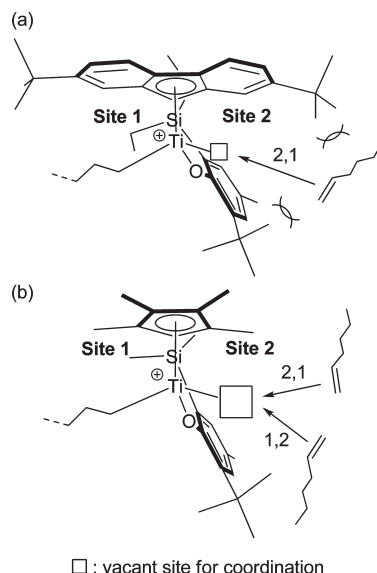
**High-Temperature Copolymerization of Ethylene and 1-Hexene.** High-temperature tolerance is an important factor for industrial use in terms of productivity of a commercial process. To investigate the scale-up polymerization performance of silicon-bridged fluorenyl–phenoxy complexes **4c,d** at elevated temperatures in detail, copolymerization experiments of ethylene and 1-hexene were carried out under modified polymerization conditions, and the results are summarized in Table 3. These complexes were highly active polymerization catalysts at 180 °C. Here again, the  $\text{Et}_2\text{Si}$ -bridged complex **4d** gave higher  $M_w$  copolymer than the  $\text{Me}_2\text{Si}$ -bridged **4c** (entries 1 vs 2). Content of 1-hexene in the copolymer obtained from **4d** increased when the amount of 1-hexene was increased, and it was found that the  $M_w$  value of the copolymer given by **4d** was still about 2 times higher



**Table 3.** High-Temperature Copolymerization of Ethylene and 1-Hexene<sup>a</sup>

entry	complex	temp (°C)	yield (g)	activity <sup>b</sup>	$M_w^c (\times 10^4)$	$M_w/M_n^c$	1-hexene content <sup>d</sup>
1	<b>4b</b>	180	2.96	177	9.9	1.8	22
2	<b>4d</b>	180	3.39	204	13.8	2.1	23
3 <sup>e</sup>	<b>4d</b>	180	3.20	192	12.0	2.0	27
4 <sup>f</sup>	<b>4d</b>	180	2.60	156	10.0	1.9	31
5	<b>4d</b>	210	1.45	87	8.6	2.1	20
6 <sup>f</sup>	<b>4d</b>	210	1.40	84	5.9	2.3	34
7 <sup>g</sup>	<b>10</b>	180	2.75	165	6.3	2.1	32

<sup>a</sup> Conditions: toluene 185 mL, 1-hexene 15 mL, ethylene 2.5 MPa, complex 0.5  $\mu$ mol, TIBA 0.3 mmol, AB 3.0  $\mu$ mol, 2 min. <sup>b</sup> In kg of copolymer/(mmol of Ti  $\cdot$  h). <sup>c</sup> Determined by GPC with polystyrene standards. <sup>d</sup> Number of short chain branches per 1000 carbons determined by FT-IR. <sup>e</sup> Toluene 180 mL, 1-hexene 20 mL. <sup>f</sup> Toluene 175 mL, 1-hexene 25 mL. <sup>g</sup> Cyclohexane 185 mL, 1-hexene 15 mL.

**Figure 3.** Control of 2,1-insertion of 1-hexene by the size of vacant site for coordination of (a) **4d** and (b) **10**.

than that produced by parent tetramethyl-substituted cyclopentadienyl complex **10** under the high 1-hexene conditions (entries 3 and 4 vs 7). It is noteworthy that **4d** showed moderate polymerization activity even at 210 °C, while maintaining high degree of  $M_w$  (entries 5 and 6).

The distinct polymerization behavior observed in these bridged fluorenyl-phenoxy titanium complexes, giving high- $M_w$  copolymer, is attributable to steric effects of the fluorenyl ligands. The planar structure of fluorene moiety is capable of protecting the active titanium center from the upper side without hindering the approach of 1-hexene. The protection by the planar structure is profitable to reduce chain transfer to monomer<sup>19</sup> and aluminum compound.<sup>20</sup> The fluorenyl ligand architecture is also important for controlling regiochemistry of 1-olefin insertion. The regioselective insertion is crucial for high  $M_w$  because 2,1-insertion of 1-olefin tends to terminate the chain growth via a facile  $\beta$ -hydride elimination.<sup>21</sup> The ability to give high  $M_w$  may be explained by the size of the vacant coordination site for approaching monomers. A plausible mechanism for controlling 2,1-insertion is illustrated in Figure 3. Two coordination sites of active species derived from **4d** are differentiated due to steric repulsion between bridging ethyl groups and fluorenyl moiety.<sup>9d</sup> The polymer main chain is probably situated on the more open side during polymerization (site 1) (Figure 3a). The highly twisted structure acts to keep the small coordination site (site 2), which is effective for restriction of 2,1-insertion. On the other hand, the methyl group labeled C(36) shown in Figure 2 at the end position of bridging moiety plays an important role in interrupting 1-hexene approach from behind of open coordination site

(site 1). The backside protection mechanism is provided only by bridging ethyl substituents and is not observed in dimethyl-substituted complexes. The bulky <sup>t</sup>Bu substituents on the fluorenyl 2,7-positions are also preferable for restricting 2,1-insertion of 1-hexene. Tetramethyl-substituted cyclopentadienyl complex **10** has relatively large coordination sites on both sides (Figure 3b), resulting in frequent 2,1-insertion of 1-hexene leading to lower  $M_w$ . Another possibility of the origin of high  $M_w$  observed for **4d** is that conformation leading to  $\beta$ -hydrogen elimination is unfavorable for the fluorenyl-phenoxy ligand architecture.<sup>22</sup> The observed  $M_w$  values of copolymer from **4d** are higher than those from related dithiophene-fused cyclopentadienyl-phenoxy derivatives,<sup>10</sup> indicating steric protection of active metal center by bulky <sup>t</sup>Bu substituents is more important for producing high- $M_w$  copolymer of ethylene and 1-hexene. The results are comparable to results observed in related carbon-bridged metallocenes with fluorenyl and dithiophene-fused cyclopentadienyl, where dithiophene-fused cyclopentadienyl complex afforded lower syndiospecificity than the fluorenyl analogue: the fluorenyl ligand system endows active species with more stereoselective and regioselective coordination sites.<sup>23</sup>

## Conclusion

We demonstrated that introduction of fluorene moieties to a PHENICS-Ti system greatly increased the molecular weight of the copolymers of ethylene and 1-hexene. On the basis of the crystal structure analysis of **4d**, we proposed that a design that produces smaller vacant sites for coordination of 1-hexene is quite important for producing high molecular weight copolymer. In particular, the 2,7-<sup>t</sup>Bu<sub>2</sub>-fluorenyl complex **4d** exhibited the highest  $M_w$  value in the copolymerization under elevated temperature and was highly active even at 210 °C, while maintaining a high degree of high molecular weight and high 1-hexene content.

## Experimental Section

**General Procedures.** All manipulations of air- and moisture-sensitive materials were performed under dry nitrogen using a glovebox or standard Schlenk line techniques. Solvents (heptane, hexane, pentane, toluene, and THF) were purchased from Kanto Chemical Co., Inc. (anhydrous grade), and used as received. <sup>n</sup>BuLi was purchased from Kanto Chemical Co., Inc. Fluorene (**2a**) and Me<sub>3</sub>SiCl were purchased from TCI (Tokyo Chemical Industry Co., Ltd.). 2,7-Di-<sup>t</sup>-butylfluorene (**2b**), HfCl<sub>4</sub>, Hf(NMe<sub>2</sub>)<sub>4</sub>, and Ti(NMe<sub>2</sub>)<sub>4</sub> were purchased from Sigma-Aldrich. ZrCl<sub>4</sub> and Et<sub>3</sub>N were purchased from Nacalai Tesque Co., Inc. Zr(NMe<sub>2</sub>)<sub>4</sub> was purchased from Strem Chemicals, Inc. TiCl<sub>4</sub> was purchased from Wako Pure Chemical Industries, Ltd. <sup>t</sup>Bu<sub>3</sub>Al (TIBA) (1 M in toluene) was purchased from Tosoh Finechem. Co., Ltd. [Me<sub>2</sub>NHPh][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (AB) was purchased from Asahi Glass Co., Ltd. Chlorosilane compounds **3a**<sup>9a</sup> and **3b**,<sup>9d</sup> TiCl<sub>2</sub>(NMe<sub>2</sub>)<sub>2</sub> (**6a**),<sup>15</sup> and titanium complex **10**<sup>9a</sup> were

prepared by reported methods.  $^1\text{H}$  NMR (270 MHz) and  $^{13}\text{C}$  NMR (68 MHz) were measured on a JEOL EX270 spectrometer. Chemical shifts for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were referenced using internal solvent resonances and are reported relative to tetramethylsilane. When toluene- $d_8$  was used as the solvent, the spectra were referenced to the resonance of the residual solvent proton at  $\delta$  2.09 in the  $^1\text{H}$  NMR spectra. Mass spectra were recorded on JEOL JMS-T100GC (EI) and JMS-700 (FD) mass spectrometers. High-resolution mass spectra were recorded using a JEOL JMS-T100GC mass spectrometer, and elemental analyses were performed using an Elementar element analyzer at Sumika Chemical Analysis Service, Ltd. All melting points were measured in sealed aluminum pans under a nitrogen atmosphere by differential scanning calorimetry (DSC) on a TA Instruments Q2000 at a heating rate of  $10^\circ\text{C}/\text{min}$ . Molecular weights ( $M_w$  and  $M_n$ ) and molecular weight distributions ( $M_w/M_n$ ) were determined by high-temperature gel permeation chromatography (GPC). GPC analyses were carried out at  $160^\circ\text{C}$  using a Symyx Rapid GPC, equipped with three Plgel  $10\ \mu\text{m}$  mixed-B columns, and a Tosoh HLC-8121GPC/HT gel permeation chromatograph, equipped with TSKgel GMHHR-H(S)HT mixed bed columns. GPC columns were calibrated using commercially available polystyrene standards (Polymer Laboratories). FT-IR measurements were performed on a Bruker Equinox 55 + PIKE Mapp IR spectrometer to determine 1-hexene content in the copolymer.

**Synthesis of  $\text{Zr}(\text{NEt}_2)_2\text{Cl}_2$  (6b) and  $\text{HfCl}_2(\text{NMe}_2)_2$  (6c).**  $\text{ZrCl}_2(\text{NEt}_2)_2$  (6b) and  $\text{HfCl}_2(\text{NMe}_2)_2$  (6c) were prepared according to the literature for corresponding THF adducts by equimolar reactions of  $\text{M}(\text{NR}_2)_4$  with  $\text{MCl}_4$  ( $\text{M} = \text{Zr}, \text{Hf}$ ) in toluene, respectively.<sup>17</sup>

**$\text{ZrCl}_2(\text{NEt}_2)_2$  (6b).**  $^1\text{H}$  NMR (THF- $d_8$ ):  $\delta$  1.02 (t,  $J = 6.9$  Hz, 12H,  $\text{NCH}_2\text{CH}_3$ ), 3.48 (q,  $J = 6.9$  Hz, 8H,  $\text{NCH}_2\text{CH}_3$ ).  $^{13}\text{C}$  NMR (THF- $d_8$ ):  $\delta$  12.56 ( $\text{NCH}_2\text{CH}_3$ ), 42.87 ( $\text{NCH}_2\text{CH}_3$ ).

**$\text{HfCl}_2(\text{NMe}_2)_2$  (6c).**  $^1\text{H}$  NMR (THF- $d_8$ ):  $\delta$  3.05 (s, 12H,  $\text{NCH}_3$ ).  $^{13}\text{C}$  NMR (THF- $d_8$ ):  $\delta$  43.87 ( $\text{NCH}_3$ ).

**Synthesis of (2-Allyloxy-3-*tert*-butyl-5-methylphenyl)(fluoren-9-yl)dimethylsilane (1a).** A typical procedure for the preparation of **1a** is given below. To a THF (112 mL) solution of fluorene (**2a**) (5.00 g, 30.08 mmol) at  $0^\circ\text{C}$  was added a hexane solution of  $n\text{-BuLi}$  (1.61 M, 19.6 mL, 31.58 mmol). The reaction mixture was allowed to warm to  $35^\circ\text{C}$  and then stirred for 2 h. To the mixture cooled at  $-78^\circ\text{C}$  was added dropwise a toluene (14 mL) solution of (2-allyloxy-3-*tert*-butyl-5-methylphenyl)chlorodimethylsilane (**3a**) (9.82 g, 33.09 mmol). The resulting mixture was allowed to warm to  $35^\circ\text{C}$  and then stirred for 3 h. After the reaction mixture was poured into a mixture of 10% aqueous  $\text{NaHCO}_3$  and 10% aqueous  $\text{Na}_2\text{CO}_3$ , and the organic layer was extracted with toluene and dried over  $\text{Na}_2\text{SO}_4$ . Removal of the solvent gave **1a** as a yellow oil. Obtained **1a** was used in the next step without further purification (as quantitative yield). Analytically pure sample was prepared by the recrystallization from methanol; mp:  $84\text{--}85^\circ\text{C}$  (dec).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$   $-0.02$  (s, 6H, Si- $\text{Me}_2$ ), 1.44 (s, 9H, Ar- $t\text{-Bu}$ ), 2.28 (s, 3H, Ar- $\text{Me}$ ), 4.38–4.42 (m, 3H), 5.25 (dq,  $J = 10.7, 1.8$  Hz, 1H,  $\text{OCH}_2\text{CH}=\text{CH}_2$ ), 5.52 (dq,  $J = 17.3, 1.8$  Hz, 1H,  $\text{OCH}_2\text{CH}=\text{CH}_2$ ), 6.03 (ddt,  $J = 17.3, 10.7, 4.1$  Hz, 1H,  $\text{OCH}_2\text{CH}=\text{CH}_2$ ), 6.96 (d,  $J = 1.6$  Hz, 1H, Ar- $H$ ), 7.05–7.19 (m, 4H), 7.24–7.33 (m, 3H), 7.80 (d,  $J = 7.6$  Hz, 2H, Flu- $H_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$   $-3.16$  (Si- $\text{Me}_2$ ), 21.10 (Ar- $\text{Me}$ ), 31.31 (Ar- $\text{CMe}_3$ ), 35.26 (Ar- $\text{CMe}_3$ ), 41.52, 76.33 ( $\text{OCH}_2$ ), 116.06, 119.65, 124.32, 125.16, 125.83, 130.66, 131.10, 132.52, 133.58, 135.36, 140.64, 142.15, 145.52, 161.55. FD-MS:  $m/z$  426 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{29}\text{H}_{34}\text{OSi}$ : C, 81.64; H, 8.03. Found: C, 81.31; H, 8.38.

**(2-Allyloxy-3-*tert*-butyl-5-methylphenyl)(fluoren-9-yl)diethylsilane (1b).** Mp:  $110\text{--}113^\circ\text{C}$  (dec).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.43–0.64 (m, 6H, Si- $\text{Et}_2$ ), 0.73–1.05 (m, 4H, Si- $\text{Et}_2$ ), 1.43 (s, 9H, Ar- $t\text{-Bu}$ ), 2.27 (s, 3H, Ar- $\text{Me}$ ), 4.36–4.41 (m, 2H), 4.49 (s, 1H, Cp'- $H$ ), 5.26 (dq,  $J = 10.9, 1.8$  Hz, 1H,  $\text{OCH}_2\text{CH}=\text{CH}_2$ ), 5.54 (dq,  $J = 17.1, 2.0$  Hz, 1H,  $\text{OCH}_2\text{CH}=\text{CH}_2$ ), 6.03 (ddt,  $J =$

17.1, 10.9, 4.0 Hz, 1H,  $\text{OCH}_2\text{CH}=\text{CH}_2$ ), 6.89 (d,  $J = 2.3$  Hz, 1H, Ar- $H$ ), 7.04–7.40 (m, 7H), 7.81 (d,  $J = 7.6$  Hz, 2H, Flu- $H_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.59 (Si- $\text{CH}_2\text{CH}_3$ ), 7.45 (Si- $\text{CH}_2\text{CH}_3$ ), 21.12 (Ar- $\text{Me}$ ), 31.27 (Ar- $\text{CMe}_3$ ), 35.23 (Ar- $\text{CMe}_3$ ), 40.73, 76.19 ( $\text{OCH}_2$ ), 115.88, 119.69, 124.53, 125.16, 125.78, 130.42, 130.53, 132.21, 133.61, 136.10, 140.69, 142.08, 145.84, 161.84. FD-MS:  $m/z$  454 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{31}\text{H}_{38}\text{OSi}$ : C, 81.88; H, 8.42. Found: C, 81.53; H, 8.38.

**(2-Allyloxy-3-*tert*-butyl-5-methylphenyl)(2,7-di-*tert*-butylfluoren-9-yl)dimethylsilane (1c).** Mp:  $80\text{--}83^\circ\text{C}$  (dec).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$   $-0.02$  (s, 6H, Si- $\text{Me}_2$ ), 1.23 (s, 18H, Flu- $t\text{-Bu}_2$ ), 1.45 (s, 9H, Ar- $t\text{-Bu}$ ), 2.28 (s, 3H, Ar- $\text{Me}$ ), 4.40 (s, 1H, Cp'- $H$ ), 4.43 (dt,  $J = 4.1, 1.8$  Hz, 2H,  $\text{OCH}_2\text{CH}=\text{CH}_2$ ), 5.33 (dq,  $J = 10.7, 1.8$  Hz, 1H,  $\text{OCH}_2\text{CH}=\text{CH}_2$ ), 5.60 (dq,  $J = 17.3, 1.8$  Hz, 1H,  $\text{OCH}_2\text{CH}=\text{CH}_2$ ), 6.09 (ddt,  $J = 17.3, 10.7, 4.0$  Hz, 1H,  $\text{OCH}_2\text{CH}=\text{CH}_2$ ), 6.97 (d,  $J = 2.1$  Hz, 1H, Ar- $H$ ), 7.05 (s, 2H, Flu- $H_2$ ), 7.26–7.32 (m, 3H), 7.70 (d,  $J = 8.1$  Hz, 2H, Flu- $H_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$   $-3.16$  (Si- $\text{Me}_2$ ), 21.07 (Ar- $\text{Me}$ ), 31.51 (Flu- $\text{CMe}_3$ ), 31.56 (Ar- $\text{CMe}_3$ ), 34.62 (Flu- $\text{CMe}_3$ ), 35.31 (Ar- $\text{CMe}_3$ ), 41.23, 76.19 ( $\text{OCH}_2$ ), 115.90, 118.74, 121.29, 122.15, 131.00, 131.53, 132.45, 133.79, 135.53, 138.05, 142.24, 145.50, 148.41, 161.57. FD-MS:  $m/z$  538 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{37}\text{H}_{50}\text{OSi}$ : C, 82.47; H, 9.35. Found: C, 82.30; H, 9.32.

**(2-Allyloxy-3-*tert*-butyl-5-methylphenyl)(2,7-di-*tert*-butylfluoren-9-yl)diethylsilane (1d).** Mp:  $100\text{--}105^\circ\text{C}$  (dec).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.40–0.66 (m, 6H, Si- $\text{Et}_2$ ), 0.72–1.04 (m, 4H, Si- $\text{Et}_2$ ), 1.24 (s, 18H, Flu- $t\text{-Bu}_2$ ), 1.43 (s, 9H, Ar- $t\text{-Bu}$ ), 2.28 (s, 3H, Ar- $\text{Me}$ ), 4.39 (dt,  $J = 4.0, 1.8$  Hz, 2H,  $\text{OCH}_2\text{CH}=\text{CH}_2$ ), 4.47 (s, 1H, Cp'- $H$ ), 5.30 (dd,  $J = 10.9, 1.8$  Hz, 1H,  $\text{OCH}_2\text{CH}=\text{CH}_2$ ), 5.57 (dd,  $J = 17.3, 1.8$  Hz, 1H,  $\text{OCH}_2\text{CH}=\text{CH}_2$ ), 6.06 (ddt,  $J = 17.3, 10.9, 3.8$  Hz, 1H,  $\text{OCH}_2\text{CH}=\text{CH}_2$ ), 6.96 (d,  $J = 2.1$  Hz, 1H, Ar- $H$ ), 7.11 (s, 2H, Flu- $H_2$ ), 7.27 (d,  $J = 8.1$  Hz, 2H, Flu- $H_2$ ), 7.30 (d,  $J = 1.8$  Hz, 1H, Ar- $H$ ), 7.67 (d,  $J = 8.1$  Hz, 2H, Flu- $H_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.44 (Si- $\text{CH}_2\text{CH}_3$ ), 7.44 (Si- $\text{CH}_2\text{CH}_3$ ), 21.13 (Ar- $\text{Me}$ ), 31.46 (Ar- $\text{CMe}_3$ ), 31.51 (Flu- $\text{CMe}_3$ ), 34.64 (Flu- $\text{CMe}_3$ ), 35.26 (Ar- $\text{CMe}_3$ ), 40.44, 76.01 ( $\text{OCH}_2$ ), 115.71, 118.79, 121.52, 122.15, 129.47, 130.78, 132.21, 133.81, 136.24, 138.10, 142.20, 145.78, 148.34, 161.75. FD-MS:  $m/z$  566 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{39}\text{H}_{54}\text{OSi}$ : C, 82.62; H, 9.60. Found: C, 82.68; H, 9.58.

**Synthesis of Dimethylsilylene(fluoren-9-yl)(3-*tert*-butyl-5-methyl-2-phenoxy)titanium Dichloride (4a).** Method B: To a toluene (20 mL) solution of  $\text{Et}_3\text{N}$  (5.34 g, 52.73 mmol) and **1a** (5.00 g, 11.72 mmol) at  $-78^\circ\text{C}$  was added a hexane solution of  $n\text{-BuLi}$  (1.61 M, 16.38 mL, 26.37 mmol). The mixture was allowed to warm to room temperature and then stirred for 2 h. To the mixture at  $-78^\circ\text{C}$  was added dropwise a toluene (15 mL) solution of  $\text{TiCl}_2(\text{NMe}_2)_2$  (**6a**) (2.91 g, 14.06 mmol). The resulting mixture was warmed to room temperature and then heated to  $90^\circ\text{C}$  and stirred for 3 h. After cooling to room temperature, the solvent was evaporated. Heptane was added, and insoluble materials were removed by filtration. Removal of the solvent gave [bis(dimethylamido)][dimethylsilylene(fluoren-9-yl)(3-*tert*-butyl-5-methyl-2-phenoxy)]titanium (**7**) as a yellow oil (4.79 g). Elemental analysis of **7** was failed due to the difficulty of the purification, and the composition was determined by EI-HRMS.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.16 (s, 6H, Si- $\text{Me}_2$ ), 1.39 (s, 9H, Ar- $t\text{-Bu}$ ), 2.32 (s, 3H, Ar- $\text{Me}$ ), 2.58 (s, 12H, N- $\text{Me}_2$ ), 7.05–7.27 (m, 6H), 7.47 (d,  $J = 7.8$  Hz, 2H, Flu- $H_2$ ), 7.92 (d,  $J = 7.8$  Hz, 2H, Flu- $H_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$   $-0.31$  (Si- $\text{Me}_2$ ), 21.21 (Ar- $\text{Me}$ ), 30.02 (Ar- $\text{CMe}_3$ ), 34.93 (Ar- $\text{CMe}_3$ ), 44.95 (N- $\text{Me}_2$ ), 92.18, 119.34, 121.11, 122.46, 124.94, 129.05, 130.63, 133.97, 134.34, 135.29, 136.79, 143.61, 165.00. EI-HRMS:  $m/z$  Calcd 520.23894. Found 520.23809.

The above-obtained **7** (2.63 g) was dissolved in toluene (58 mL) and cooled to  $0^\circ\text{C}$ . To the mixture  $\text{Me}_3\text{SiCl}$  (6.99 g, 64.35 mmol) was added dropwise. The resulting mixture was warmed to  $35^\circ\text{C}$  and then stirred for 3 h. After cooling to room temperature, solvent was evaporated. Recrystallization from pentane gave **4a** as a brown solid (2.42 g, 75% yield, three steps

from **2a**); mp: 224–232 °C (dec).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.84 (s, 6H, Si– $\text{Me}_2$ ), 1.18 (s, 9H, Ar– $t\text{Bu}$ ), 2.44 (s, 3H, Ar– $\text{Me}$ ), 7.18 (s, 1H, Ar– $H$ ), 7.33 (s, 1H, Ar– $H$ ), 7.49 (dd,  $J$  = 8.4, 7.5 Hz, 2H, Flu– $H_2$ ), 7.60 (dd,  $J$  = 8.4, 7.5 Hz, 2H, Flu– $H_2$ ), 7.66 (d,  $J$  = 8.4 Hz, 2H, Flu– $H_2$ ), 8.32 (d,  $J$  = 8.4 Hz, 2H, Flu– $H_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  –0.02 (Si– $\text{Me}_2$ ), 21.36 (Ar– $\text{Me}$ ), 29.76 (Ar– $\text{CMe}_3$ ), 34.74 (Ar– $\text{CMe}_3$ ), 108.51, 124.21, 128.06, 128.32, 129.26, 130.19, 131.21, 132.21, 132.35, 132.81, 134.32, 136.38, 168.32. Anal. Calcd for  $\text{C}_{26}\text{H}_{28}\text{Cl}_2\text{OSiTi}$ : C, 62.04; H, 5.61. Found: C, 61.75; H, 5.64.

**Diethylsilylene(fluoren-9-yl)(3-*tert*-butyl-5-methyl-2-phenoxy)-titanium Dichloride (4b).** Method B (0.94 g, 29% yield, three steps from **2a**). Brown solid; mp: 190–198 °C (dec).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.07 (t,  $J$  = 7.7 Hz, 6H, Si– $\text{Et}_2$ ), 1.18 (s, 9H, Ar– $t\text{Bu}$ ), 1.28–1.50 (m, 4H, Si– $\text{Et}_2$ ), 2.44 (s, 3H, Ar– $\text{Me}$ ), 7.18 (d,  $J$  = 1.8 Hz, 1H, Ar– $H$ ), 7.28 (d,  $J$  = 1.8 Hz, 1H, Ar– $H$ ), 7.43–7.52 (m, 2H), 7.56–7.67 (m, 4H), 8.28 (d,  $J$  = 8.4 Hz, 2H, Flu– $H_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  5.35 (Si– $\text{CH}_2\text{CH}_3$ ), 7.60 (Si– $\text{CH}_2\text{CH}_3$ ), 21.42 (Ar– $\text{Me}$ ), 29.80 (Ar– $\text{CMe}_3$ ), 34.72 (Ar– $\text{CMe}_3$ ), 107.47, 124.22, 128.25, 128.28, 129.25, 129.63, 130.29, 131.22, 132.57, 133.56, 133.87, 136.47, 168.91. Anal. Calcd for  $\text{C}_{28}\text{H}_{32}\text{Cl}_2\text{OSiTi}$ : C, 63.28; H, 6.07. Found: C, 63.40; H, 6.13.

**Synthesis of Dimethylsilylene(2,7-di-*tert*-butylfluoren-9-yl)(3-*tert*-butyl-5-methyl-2-phenoxy)titanium Dichloride (4c).** Method A: To a toluene (48 mL) solution of  $\text{Et}_3\text{N}$  (1.84 g, 18.23 mmol) and **1c** (2.18 g, 4.05 mmol) at –78 °C, was added a hexane solution of  $n\text{BuLi}$  (1.58 M, 5.77 mL, 9.11 mmol). The mixture was allowed to warm to room temperature and then stirred for 2 h. To the mixture at –78 °C was added dropwise a toluene (6 mL) solution of  $\text{TiCl}_4$  (1.15 g, 6.08 mmol). The resulting mixture was warmed to room temperature and then heated to 90 °C and stirred for 3 h. After cooling to room temperature, the solvent was evaporated. Hexane was added, and insoluble materials were removed by filtration. Removal of the solvent and addition of pentane gave **5** as colorless solids (0.371 g, 18% yield, two steps from **2b**). **4c** was obtained as brown solids by recrystallization from pentane soluble part after removal of **5** (0.300 g, 12% yield, two steps from **2b**).

**Dimethylsilylene(2,7-di-*tert*-butylfluoren-9-yl)(3-*tert*-butyl-5-methyl-2-phenoxy)titanium Dichloride (4c).** Mp: 217–218 °C (dec).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.84 (s, 6H, Si– $\text{Me}_2$ ), 1.18 (s, 9H, Ar– $t\text{Bu}$ ), 1.26 (s, 18H, Flu– $t\text{Bu}_2$ ), 2.43 (s, 3H, Ar– $\text{Me}$ ), 7.16 (d,  $J$  = 2.0 Hz, 1H, Ar– $H$ ), 7.34 (d,  $J$  = 2.0 Hz, 1H, Ar– $H$ ), 7.57 (s, 2H, Flu– $H_2$ ), 7.65 (d,  $J$  = 8.9 Hz, 1H, Flu– $H$ ), 7.65 (d,  $J$  = 8.9 Hz, 1H, Flu– $H$ ), 8.19 (d,  $J$  = 8.9 Hz, 2H, Flu– $H_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  –0.12 (Si– $\text{Me}_2$ ), 21.35 (Ar– $\text{Me}$ ), 29.98 (Ar– $\text{CMe}_3$ ), 30.81 (Flu– $\text{CMe}_3$ ), 34.75 (Ar– $\text{CMe}_3$ ), 35.33 (Flu– $\text{CMe}_3$ ), 107.92, 122.73, 123.70, 127.59, 128.86, 129.12, 132.13, 132.50, 133.19, 133.91, 136.15, 153.64, 167.99. Anal. Calcd for  $\text{C}_{34}\text{H}_{44}\text{Cl}_2\text{OSiTi}$ : C, 66.34; H, 7.20. Found: C, 65.86; H, 7.19.

**Compound 5.** Mp: 254–258 °C (dec).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.03 (s, 6H, Si– $\text{Me}_2$ ), 1.27 (s, 18H, Flu– $t\text{Bu}_2$ ), 1.33 (s, 9H, Ar– $t\text{Bu}$ ), 2.39 (s, 3H, Ar– $\text{Me}$ ), 7.18–7.22 (m, 2H, Ar– $H_2$ ), 7.29 (s, 2H, Flu– $H_2$ ), 7.32 (d,  $J$  = 7.9 Hz, 1H, Flu– $H$ ), 7.33 (d,  $J$  = 7.9 Hz, 1H, Flu– $H$ ), 7.61 (d,  $J$  = 7.9 Hz, 2H, Flu– $H_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  –2.02 (Si– $\text{Me}_2$ ), 20.87 (Ar– $\text{Me}$ ), 29.41 (Ar– $\text{CMe}_3$ ), 31.43 (Flu– $\text{CMe}_3$ ), 34.66 (Ar– $\text{CMe}_3$ ), 34.74 (Flu– $\text{CMe}_3$ ), 86.35, 119.36, 121.17, 121.50, 123.89, 129.39, 130.11, 130.70, 135.02, 136.04, 147.49, 149.53, 164.55. FD-MS:  $m/z$  496 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{34}\text{H}_{44}\text{OSi}$ : C, 82.20; H, 8.93. Found: C, 81.84; H, 9.00.

**Diethylsilylene(2,7-di-*tert*-butylfluoren-9-yl)(3-*tert*-butyl-5-methyl-2-phenoxy)titanium Dichloride (4d).** Elemental analysis indicated that **4d** contained 0.5 equiv of toluene, and the existence of 0.5 equiv of toluene in crystal was also confirmed by X-ray analysis. Method A (6.73 g, 24% yield, two steps from **2b**). Brown solid; mp: 119–127 °C (dec).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.09 (t,  $J$  = 7.7 Hz, 6H, Si– $\text{Et}_2$ ), 1.18 (s, 9H, Ar– $t\text{Bu}$ ), 1.25 (s, 18H, Flu– $t\text{Bu}_2$ ), 1.26–1.48 (m, 4H, Si– $\text{Et}_2$ ), 2.43 (s, 3H, Ar– $\text{Me}$ ),

7.16 (s, 1H, Ar– $H$ ), 7.29 (s, 1H, Ar– $H$ ), 7.56 (s, 2H, Flu– $H_2$ ), 7.64 (d,  $J$  = 8.9 Hz, 2H, Flu– $H_2$ ), 8.18 (d,  $J$  = 8.9 Hz, 2H, Flu– $H_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  5.55 (Si– $\text{CH}_2\text{CH}_3$ ), 7.76 (Si– $\text{CH}_2\text{CH}_3$ ), 21.39 (Ar– $\text{Me}$ ), 30.04 (Ar– $\text{CMe}_3$ ), 30.81 (Flu– $\text{CMe}_3$ ), 34.71 (Ar– $\text{CMe}_3$ ), 35.33 (Flu– $\text{CMe}_3$ ), 106.80, 123.00, 123.67, 127.54, 128.92, 129.07, 129.45, 133.09, 133.50, 133.56, 136.21, 153.68, 168.60. Anal. Calcd for  $\text{C}_{36}\text{H}_{48}\text{Cl}_2\text{OSiTi}$ : C, 68.79; H, 7.60. Found: C, 68.54; H, 7.97.

**Dimethylsilylene(2,7-di-*tert*-butylfluoren-9-yl)(3-*tert*-butyl-5-methyl-2-phenoxy)zirconium Dichloride (8).** The zirconium complex was prepared analogously using  $\text{ZrCl}_4$  instead of  $\text{TiCl}_4$  (method A) or  $\text{ZrCl}_2(\text{NMe}_2)_2$  (**6b**) instead of  $\text{TiCl}_2(\text{NMe}_2)_2$  (**6a**) (method B). Method A: (0.58 g, 22% yield, two steps from **2b**). Method B: (1.92 g, 78% yield, three steps from **2b**). Elemental analysis indicated that **8** contained 0.5 equiv of  $\text{LiCl}$ , and the  $\text{LiCl}$  free composition was determined by EI-HRMS. Yellow solid; mp: 244–253 °C (dec).  $^1\text{H}$  NMR (toluene- $d_8$ ):  $\delta$  0.80 (s, 6H, Si– $\text{Me}_2$ ), 1.19 (s, 18H, Flu– $t\text{Bu}_2$ ), 1.33 (s, 9H, Ar– $t\text{Bu}$ ), 2.30 (s, 3H, Ar– $\text{Me}$ ), 7.21 (d,  $J$  = 1.9 Hz, 1H, Ar– $H$ ), 7.36 (dd,  $J$  = 8.9 Hz, 1.6 Hz, 2H, Flu– $H_2$ ), 7.38 (d,  $J$  = 1.9 Hz, 1H, Ar– $H$ ), 7.76 (s, 2H, Flu– $H_2$ ), 7.89 (d,  $J$  = 8.9, 2H, Flu– $H_2$ ).  $^{13}\text{C}$  NMR (toluene- $d_8$ ):  $\delta$  0.06 (Si– $\text{Me}_2$ ), 21.25 (Ar– $\text{Me}$ ), 30.28 (Ar– $\text{CMe}_3$ ), 30.85 (Flu– $\text{CMe}_3$ ), 34.90 (Ar– $\text{CMe}_3$ ), 35.36 (Flu– $\text{CMe}_3$ ), 89.16, 120.84, 123.73, 124.12, 125.39, 128.99, 130.02, 132.42, 132.56, 134.93, 137.45, 153.45, 162.91. Anal. Calcd for  $\text{C}_{34}\text{H}_{44}\text{Cl}_2\text{OSiZr}$ : 0.5( $\text{LiCl}$ ): C, 60.04; H, 6.52. Found: C, 60.20; H, 6.82. EI-HRMS:  $m/z$  Calcd 656.15855. Found 656.15771.

**Dimethylsilylene(2,7-di-*tert*-butylfluoren-9-yl)(3-*tert*-butyl-5-methyl-2-phenoxy)hafnium Dichloride (9).** The hafnium complex was prepared analogously using  $\text{HfCl}_4$  instead of  $\text{TiCl}_4$  (method A) or  $\text{HfCl}_2(\text{NMe}_2)_2$  (**6c**) instead of  $\text{TiCl}_2(\text{NMe}_2)_2$  (**6a**) (method B). Method A: (0.16 g, 5% yield, two steps from **2b**). Method B: (1.60 g, 58% yield, three steps from **2b**). Pale yellow solid; mp: 220–229 °C (dec).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  0.83 (s, 6H, Si– $\text{Me}_2$ ), 1.18 (s, 9H, Ar– $t\text{Bu}$ ), 1.25 (s, 18H, Flu– $t\text{Bu}_2$ ), 2.40 (s, 3H, Ar– $\text{Me}$ ), 7.20 (d,  $J$  = 1.6 Hz, 1H, Ar– $H$ ), 7.35 (d,  $J$  = 1.6 Hz, 1H, Ar– $H$ ), 7.59 (dd,  $J$  = 8.9 Hz, 1.6 Hz, 2H, Flu– $H_2$ ), 7.65 (br s, 2H, Flu– $H_2$ ), 8.19 (d,  $J$  = 8.9 Hz, 2H, Flu– $H_2$ ).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  0.22 (Si– $\text{Me}_2$ ), 21.13 (Ar– $\text{Me}$ ), 30.12 (Ar– $\text{CMe}_3$ ), 30.95 (Flu– $\text{CMe}_3$ ), 34.72 (Ar– $\text{CMe}_3$ ), 35.55 (Flu– $\text{CMe}_3$ ), 85.95, 120.64, 121.93, 123.97, 125.32, 129.06, 129.97, 132.41, 132.80, 134.53, 137.28, 153.56, 161.77. Anal. Calcd for  $\text{C}_{34}\text{H}_{44}\text{Cl}_2\text{HfOSi}$ : C, 54.73; H, 5.94. Found: C, 54.34; H, 6.09.

**Crystallographic Analyses of 4d and 5.** All crystals were handled similarly. The crystals were mounted on the CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 113(2) K. All measurements were made on a Rigaku AFC7R/Mercury CCD detector with graphite-monochromated Mo  $\text{K}\alpha$  (0.710 75 Å) radiation. Crystal data and structure refinement parameters are summarized in Table S1. The structures were solved by direct methods (SIR 92)<sup>24</sup> and refined on  $F^2$  using a full-matrix least-squares methods (SHELXL-97).<sup>25</sup> Non-hydrogen atoms were anisotropically refined for **5**. In the case of **4d**, non-hydrogen atoms were anisotropically refined except for a disordered solvent molecule, which was refined isotropically. H atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was  $[\sum w(F_o^2 - F_c^2)^2]$  ( $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ ), where  $P = (\text{Max}(F_o^{2,0}) + 2F_c^2)/3$  with  $\sigma^2(F_o^2)$  from counting statistics. The functions  $R_1$  and  $wR_2$  were  $(\sum ||F_o| - |F_c||)/(\sum |F_o|)$  and  $\{[\sum w(F_o^2 - F_c^2)^2]/[\sum (wF_o^4)]\}^{1/2}$ , respectively. The ORTEP-3 program (for Windows, version 2.02)<sup>26</sup> was used to draw the molecule.

**Primary Screening Procedure.** A Symyx PPR system was used for primary screening experiments. A typical procedure for the copolymerization of ethylene and 1-hexene at 70 °C is given as follows: Other polymerizations at 130 °C were carried out analogously. A prewashed glass vial insert and disposable stirring paddle were fitted to each reaction vessel of the reactor. The reactor was then closed, and TIBA (40  $\mu\text{mol}$ , 160  $\mu\text{L}$ , 0.25 M



toluene solution), 1-hexene (50  $\mu\text{L}$ ), and toluene were injected into each reaction vessel through a valve. The total volume of the reaction mixture was adjusted with toluene to 5 mL. The temperature was then set to 70 °C, the stirring speed was set to 800 rpm, and the mixture was pressurized with ethylene to 0.6 MPa. Polymerization was started by addition of a toluene solution of complex (0.1  $\mu\text{mol}$ , 1 mM toluene solution) followed by a toluene solution of AB (0.3  $\mu\text{mol}$ , 1 mM toluene solution). Ethylene pressure in the cell and the temperature setting were maintained by computer control until the end of the polymerization experiment. The polymerization reactions were allowed to continue for 20 min unless consumption of ethylene reached preset levels. After polymerization reaction, the reaction mixture was allowed to cool to room temperature and the ethylene pressure in the cell was slowly vented. The glass vial insert was then removed from the pressure cell, and the volatile components were removed using a centrifuge vacuum evaporator to give polymer product.

**Copolymerization of Ethylene and 1-Hexene at High Temperature.** An autoclave with an inner volume of 400 mL was dried under vacuum and purged with argon. After charging with toluene (185 mL) and 1-hexene (15 mL), the autoclave was heated to 180 °C. Ethylene was introduced to the vessel, and the pressure was adjusted at 2.5 MPa. After the system was stabilized TIBA (0.3 mmol) was added to the mixture. Subsequently, titanium complex (0.5  $\mu\text{mol}$ ) and AB (3.0  $\mu\text{mol}$ ) were added. Polymerization was performed at 180 °C for 2 min, and then the reaction was quenched with ethanol/methanol (9:1) (5 mL). The reaction mixture was poured into acidic ethanol/methanol (9:1) (500 mL with 1 mL of 5% HCl). The polymer was collected by filtration, washed with methanol, and dried under high vacuum at 80 °C for 2 h to constant weight.

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**Supporting Information Available:** Figures showing NMR spectra of **7** and **8** and table of crystal data for **4d** and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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