Supporting Information for

Substituent Effects on Silicon of Bridged Tetramethylcyclopentadienyl–Phenoxy Titanium Complexes for Controlling the Regiochemistry and Molecular Weight in 1-Olefin Polymerization

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Preparation of Complexes. A series of bridged cyclopentadienyl-phenoxy titanium complexes (PHENICS) bearing different bridging groups $R_1R_2Si(C_5Me_4)(3\text{-}^t\text{Bu-5-Me-2-C}_6\text{H}_2\text{O})TiCl_2$ (**1b–f**) were prepared following a similar procedure previously described for $Me_2Si(C_5Me_4)(3\text{-}^t\text{Bu-5-Me-2-C}_6\text{H}_2\text{O})TiCl_2$ (**1a**) (Scheme S1).^{S1-1} Low to moderate yields of complexes (5–33%) are the results of difficulty of purification of intermediate chlorosilane derivatives **4b–f** and ligands **5b–f**. These materials were used without purification (See experimental section).

Scheme S1

Figure S1. The methyl region of the ^{13}C NMR spectrum obtained by **1b**.

Figure S2. The olefin region of the ^1H NMR spectrum obtained by **1b**.

Molecular Structures and Crystal Data of Complexes. The structures of the PHENICS-Ti **1b**, **1c**, and **1f** were determined by X-ray analysis.^{SI-2} Selected bond lengths and angles of these complexes are summarized in Table S1. The crystal data and data collection parameters are listed in Table S2. Figure S3 shows the crystal structure of **1b**, **1c**, and **1f**, each of which adopts a three-legged piano-stool geometry. Two perspective views of the complexes are shown in Figure S4. The space of the left coordination sites (site 1) of these complexes have almost the same environment, whereas that of the right coordination sites (site 2) are quite different. In the case of **1b**, a large torsion angle around the bridging group generates a small coordination site (Figure S4a). Rotation of the Si–C(23) bond also contributes to restrict 2,1-insertion of monomer. On the contrary, **1c** possess a relatively large monomer coordination sites on both sides, because the bridging substituent is fixed upward by the cyclic structure (Figure S4b). The high ratio of 2,1-insertion observed through the polymerization with **1c** is probably due to the large coordination site derived from the *constrained* structure of the cyclic silylene moiety. In the case of **1f**, the bulky Cy group is located at the backside of site 2, suggesting 2,1-insertion of monomer is highly restricted by steric repulsion (Figure S4c).

Figure S3. Molecular structures of the complexes (a) **1b**, (b) **1c**, and (c) **1f**. All hydrogen atoms are omitted for clarity. Key atoms are labeled.

Table S1. Selected Bond Lengths (Å) and Angles (deg) for **1b**, **1c**, and **1f**

complex	1b	1c	1f
bridging group	SiEt ₂	Si(CH ₂) ₄	SiCyMe
Bond Lengths			
Ti–Cl(1)	2.2741(6)	2.2758(9)	2.2718(4)
Ti–Cl(2)	2.2642(7)	2.2595(10)	2.2609(4)
Ti–Cp _{cent}	2.015	2.015	2.011
Ti–O	1.804(2)	1.7923(16)	1.7958(9)
Si–C(1)	1.888(2)	1.870(2)	1.889(1)
Si–C(10)	1.879(2)	1.879(2)	1.882(1)
Bond Angles			
O–Ti–C(1)	87.94(7)	86.61(8)	87.34(4)
Cl(1)–Ti–Cl(2)	102.59(3)	102.22(3)	101.83(1)
Torsion Angles			
C(1)–Si–C(10)–C(11)	40.3(2)	8.9(2)	19.4(1)
Ti–O–C(11)–C(10)	31.6(3)	7.5(5)	8.8(3)
Dihedral Angle			
θ^a	58.20	68.52	68.36

^a θ denotes the dihedral angle between the best plane of cyclopentadienyl ring carbons and that of phenyl ring carbons.

Table S2. Crystal Data and Data Collection Parameters of 1b, 1c, and 1f

	1b	1c	1f
empirical formula	C ₂₄ H ₃₆ Cl ₂ OSiTi	C ₂₄ H ₃₄ Cl ₂ OSiTi	C ₂₇ H ₄₀ Cl ₂ OSiTi
formula weight	487.42	485.40	527.48
crystal system	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ /c (No. 14)	<i>P</i> 2 ₁ /n (No. 14)	<i>P</i> 2 ₁ /c (No. 14)
<i>a</i> , Å	10.0351(3)	10.275(2)	9.9973(2)
<i>b</i> , Å	13.4187(4)	22.990(5)	26.2911(7)
<i>c</i> , Å	19.0746(6)	10.374(2)	10.3204(3)
α, deg	-	-	-
β, deg	100.762(1)	97.662(4)	94.849(1)
γ, deg	-	-	-
<i>V</i> , Å ³	2523.37(13)	2428.9(9)	2702.91(12)
<i>Z</i>	4	4	4
<i>D</i> _{calcd} , g/cm ⁻³	1.283	1.327	1.296
<i>F</i> (000)	1032.0	1024.0	1120.0
μ [Mo Kα], mm ⁻¹	0.611	0.635	0.576
<i>T</i> , K	113(1)	113(2)	113(1)
crystal size, mm	0.31 x 0.05 x 0.05	0.32 x 0.20 x 0.08	0.50 x 0.50 x 0.35
θ _{max} , deg	30.460	27.620	30.480
no. of reflections measured	50884	18386	54201
unique data (<i>R</i> _{int})	49721 (0.051)	5359 (0.039)	53555 (0.034)
data / restraints / parameters	7644 / 0 / 267	5359 / 0 / 263	8199 / 0 / 409
<i>R</i> ₁ ^a (<i>I</i> > 2.0σ(<i>I</i>))	0.0506	0.0452	0.0352
<i>wR</i> ₂ ^a (<i>I</i> > 2.0σ(<i>I</i>))	0.1118	0.1129	0.0858
<i>R</i> ₁ ^a (all data)	0.0749	0.0630	0.0409
<i>wR</i> ₂ ^a (all data)	0.1248	0.1297	0.0917
GOF on <i>F</i> ²	1.062	1.097	1.058
Δρ, e ⁻ /Å ³	0.51, -0.53	0.38, -0.47	0.53, -0.56

$$^a R_1 = (\sum ||F_o| - |F_c||) / (\sum |F_o|); wR_2 = [\{\sum w(F_o^2 - F_c^2)^2\} / \{\sum (wF_o^4)\}]^{1/2}$$

Figure S4. Two perspective views of the molecular structures of (a) **1b**, (b) **1c**, and (c) **1f**.

Table S3. Polymerization of Ethylene and 1-Hexene Using 1a–f and 2 Catalyst Systems with TIBA/TB^a

entry	complex	act ^b	M_w^c (x10 ³)	M_w/M_n^c	1-hexene (mol %) ^d
1	1a	2 730	913	1.5	7.9
2	1b	2 810	1 330	1.6	8.1
3	1c	195	629	1.6	6.7
4	1e	885	1 410	1.5	8.4
5	1f	2 090	1 740	1.5	6.9
6	2	2 070	1 750	1.5	4.0

^a Conditions: toluene 149 mL, 1-hexene 1.5 mL, ethylene 0.6 MPa, complex 0.02 μmol, TIBA 60 μmol, TB 0.1 μmol, initial polymerization temperature 70 °C, polymerization time 2 min. ^b kg of copolymer/(mmol of Ti·h). ^c Determined by GPC with polystyrene standards. ^d Determined by ¹³C NMR.

Experimental Section

General. All manipulations of air- and moisture-sensitive materials were performed under dry nitrogen using a glovebox or standard Schlenk line technique. Solvents were purchased from Kanto Chemical Co., Inc. (anhydrous grade) and used as received. Complex **1a** was prepared by a reported method.^{SI-1} Dichlorodiethylsilane, dichloromethylphenylsilane and dichlorocyclohexylmethylsilane were purchased from TCI (Tokyo Chemical Industry Co., Ltd.). Dichloroethylmethylsilane was purchased from Sigma-Aldrich, Inc. Cyclotetramethylenedichlorosilane was purchased from Gelest, Inc. Aniline and ⁿBuLi (1.6 M in hexane) were purchased from Kanto Chemical Co., Inc. NaH and triethylamine were purchased from Nacalai Tesque Co., Inc. TiCl₄ and Me₂Si(C₅Me₄)(^tBuN)TiCl₂ (**2**) were purchased from Wako Pure Chemical Industries, Ltd. ^tBu₃Al (TIBA) (1M in toluene) was purchased from Tosoh Finechem. Co., Ltd. [Ph₃C][B(C₆F₅)₄] (TB) was purchased from Asahi Glass Co., Ltd. All melting points were measured in sealed aluminum pans under nitrogen atmosphere by differential scanning calorimeter (DSC) on a TA instrument Q2000 at a heating rate of 10 °C/min. ¹H NMR (270 MHz) and ¹³C NMR (68 MHz) were measured on a JEOL EX270 spectrometer. Chemical shifts for ¹H and ¹³C NMR spectra were referenced using internal solvent resonances and are reported relative to tetramethylsilane. High-resolution mass spectra were recorded using a JEOL JMS-T100GC spectrometer, and elemental analyses were performed using an ELEMENTAR element analyzer at Sumika Chemical Analysis Service, Ltd. 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 °C using a Symyx Rapid GPC™, equipped with three Plgel 10MICRO METER MIXED B columns, and a Tosoh HLC-8121GPC/HT, equipped with TSKgel GMHHR-H(S)HT. GPC columns were calibrated using commercially available polystyrene standards (Polymer Laboratories).

Synthesis of (2-Allyloxy-3-*tert*-butyl-5-methylphenyl)chlorodiethylsilane (4b). A typical procedure for the preparation of **4b** is given below. To a mixture of 2-(allyloxy)-1-bromo-3-*tert*-butyl-5-

methylbenzene (**3**) (60.00 g, 211.9 mmol) and toluene (700 mL) at $-78\text{ }^{\circ}\text{C}$, was added a hexane solution of $n\text{-BuLi}$ (1.58 M, 174.32 mL, 275.42 mmol), and then the reaction mixture was allowed to gradually warm to $-15\text{ }^{\circ}\text{C}$. After lithiation was completed, the mixture was cooled to $-78\text{ }^{\circ}\text{C}$, and then dichlorodiethylsilane (99.86 g, 635.59 mmol) was added quickly. The mixture was allowed to warm to room temperature, and then heated at $50\text{ }^{\circ}\text{C}$ for 1 h. After the solvent was evaporated, inorganic materials was removed by filtration with hexane. Evaporation of solvent and further vacuum concentration ($70\text{ }^{\circ}\text{C}$, 0.1 Torr) for 3 h gave **4b** as a pale yellow oil (38.56 g, 56% yield, determined by GC analysis). Obtained **4b** was used for next step without further purification. ^1H NMR (CDCl_3): δ 0.99–1.19 (m, 10H, Si- Et_2), 1.38 (s, 9H, Ar- $t\text{-Bu}$), 2.32 (s, 3H, Ar- Me), 4.36 (dt, $J = 4.3, 2.0\text{ Hz}$, 2H, OCH_2), 5.29 (dq, $J = 10.7, 1.8\text{ Hz}$, 1H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 5.51 (dq, $J = 17.1, 1.8\text{ Hz}$, 1H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 6.03 (ddt, $J = 17.2, 10.7, 4.3\text{ Hz}$, 1H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 7.24 (d, $J = 2.1\text{ Hz}$, 1H, Ar- H), 7.32 (d, $J = 2.3\text{ Hz}$, 1H, Ar- H). ^{13}C NMR (CDCl_3): δ 6.92 (Si- Et), 9.19 (Si- Et), 21.09 (Ar- Me), 31.21 (Ar- CMe_3), 35.14 (Ar- CMe_3), 76.53 (OCH_2), 116.10, 127.62, 131.75, 132.95, 133.50, 135.53, 141.99, 161.01. EI-HRMS: m/z calcd 324.16762, found 324.16851.

(2-Allyloxy-3-*tert*-butyl-5-methylphenyl)chloro(cyclotetramethylene)silane (4c): 68% yield. ^1H NMR (CDCl_3): δ 0.80–0.96 (m, 2H, Si- CH_2), 1.12–1.30 (m, 2H, Si CH_2), 1.38 (s, 9H, Ar- $t\text{-Bu}$), 1.54–1.88 (m, 4H, Si CH_2CH_2), 2.34 (s, 3H, Ar- Me), 4.50 (dt, $J = 4.6, 1.8\text{ Hz}$, 2H, OCH_2), 5.27 (dq, $J = 10.7, 1.6\text{ Hz}$, 1H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 5.49 (dq, $J = 17.3, 1.8\text{ Hz}$, 1H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 6.04 (ddt, $J = 17.1, 10.5, 4.6\text{ Hz}$, 1H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 7.22–7.28 (m, 2H, Ar- H). ^{13}C NMR (CDCl_3): δ 16.23 (Si- CH_2), 20.98 (Ar- Me), 25.79 (Si CH_2CH_2), 30.96 (Ar- CMe_3), 35.13 (Ar- CMe_3), 76.07 (OCH_2), 116.34, 128.74, 131.68, 132.84, 133.61, 135.06, 142.33, 160.67. EI-HRMS: m/z calcd 322.15197, found 322.15160.

(2-Allyloxy-3-*tert*-butyl-5-methylphenyl)chloromethylphenylsilane (4d): 71% yield ^1H NMR (CDCl_3): δ 1.00 (s, 3H, Si- Me), 1.37 (s, 9H, Ar- $t\text{-Bu}$), 2.32 (s, 3H, Ar- Me), 4.06 (ddt, $J = 13.3, 4.4, 1.8\text{ Hz}$, 1H, OCH_2), 4.21 (ddt, $J = 13.5, 4.3, 1.8\text{ Hz}$, 1H, OCH_2), 5.14 (dq, $J = 10.7, 1.8\text{ Hz}$, 1H,

OCH₂CH=CH₂), 5.25 (dq, *J* = 17.3, 1.8 Hz, 1H, OCH₂CH=CH₂), 5.76 (ddt, *J* = 17.3, 10.7, 4.3 Hz, 1H, OCH₂CH=CH₂), 7.29 (d, *J* = 2.3 Hz, 1H, Ar-*H*), 7.33–7.45 (m, 4H, Ar-*H*), 7.59–7.68 (m, 2H, Ar-*H*). ¹³C NMR (CDCl₃): δ 2.01 (Si-*Me*), 21.09 (Ar-*Me*), 31.23 (Ar-CMe₃), 35.20 (Ar-CMe₃), 76.19 (OCH₂), 116.07, 127.95, 128.04, 130.23, 132.18, 132.92, 133.30, 133.87, 135.83, 136.32, 142.27, 161.22. EI-HRMS: *m/z* calcd 358.15197, found 358.15222.

(2-Allyloxy-3-*tert*-butyl-5-methylphenyl)chloroethylmethylsilane (4e): 68% yield. ¹H NMR (CDCl₃): δ 0.70 (s, 3H, Si-*Me*), 0.98–1.19 (m, 5H, Si-*Et*), 1.38 (s, 9H, Ar-*t*Bu), 2.32 (s, 3H, Ar-*Me*), 4.40 (sext, *J* = 2.1 Hz, 2H, OCH₂), 5.29 (dq, *J* = 10.7, 1.8 Hz, 1H, OCH₂CH=CH₂), 5.51 (dq, *J* = 17.3, 1.8 Hz, 1H, OCH₂CH=CH₂), 6.03 (ddt, *J* = 17.1, 10.7, 4.4 Hz, 1H, OCH₂CH=CH₂), 7.26 (d, *J* = 2.3 Hz, 1H, Ar-*H*), 7.31 (d, *J* = 2.3 Hz, 1H, Ar-*H*). ¹³C NMR (CDCl₃): δ 1.44 (Si-*Me*), 6.87 (Si-*Et*), 10.95 (Si-*Et*), 21.08 (Ar-*Me*), 31.23 (Ar-CMe₃), 35.17 (Ar-CMe₃), 76.49 (OCH₂), 116.19, 128.79, 131.84, 132.94, 133.54, 134.98, 142.16, 161.01. EI-HRMS: *m/z* calcd 310.15197, found 310.15301.

(2-Allyloxy-3-*tert*-butyl-5-methylphenyl)chlorocyclohexylmethylsilane (4f): 70% yield. ¹H NMR (CDCl₃): δ 0.66 (s, 3H, Si-*Me*), 1.10–1.35 (br, 5H, Si-*Cy*), 1.37 (s, 9H, Ar-*t*Bu), 1.63–1.80 (br, 6H, Si-*Cy*), 2.32 (s, 3H, Ar-*Me*), 4.30 (ddt, *J* = 13.8, 4.3, 1.8 Hz, 1H, OCH₂), 4.42 (ddt, *J* = 13.8, 4.1, 2.1 Hz, 1H, OCH₂), 5.30 (dq, *J* = 10.7, 1.8 Hz, 1H, OCH₂CH=CH₂), 5.52 (dq, *J* = 17.3, 2.0 Hz, 1H, OCH₂CH=CH₂), 6.03 (ddt, *J* = 17.1, 10.7, 4.3 Hz, 1H, OCH₂CH=CH₂), 7.24 (d, *J* = 2.1 Hz, 1H, Ar-*H*), 7.30 (d, *J* = 2.1 Hz, 1H, Ar-*H*). ¹³C NMR (CDCl₃): δ –0.08 (Si-*Me*), 21.11 (Ar-*Me*), 26.60 (Si-*Cy*), 26.69 (Si-*Cy*), 27.68 (Si-*Cy*), 29.33 (Si-*Cy*), 31.21 (Ar-CMe₃), 35.16 (Ar-CMe₃), 76.50 (OCH₂), 116.08, 128.14, 131.70, 132.91, 133.56, 135.29, 142.04, 160.96. EI-HRMS: *m/z* calcd 364.19892, found 364.19930.

Synthesis of (2-Allyloxy-3-*tert*-butyl-5-methylphenyl)(2,3,4,5-tetramethylcyclopenta-2,4-dien-1-yl)diethylsilane (5b). A typical procedure for the preparation of **5b** is given below. To a mixture of THF (102 mL) and 60% NaH (3.00 g, 125.19 mmol), aniline (0.53 g, 5.69 mmol) was added at room

temperature, and the mixture was stirred at 50 °C for 1 h. A THF (26 mL) solution of 1,2,3,4-tetramethyl-1,3-cyclopentadiene (12.75 g, 104.33 mmol) was added dropwise to the mixture. The mixture was stirred until evolution of hydrogen ceased. A toluene (26 mL) solution of **4b** (30.82 g, 94.84 mmol) was added dropwise to the mixture at 0 °C. The resulting mixture was allowed to warm to room temperature, then stirred for 3 h. After the mixture was poured into the mixture of 10% aqueous NaHCO₃ and 10% aqueous Na₂CO₃, the organic layer was extracted with toluene. Removal of the solvent gave **5b** as a yellow oil (34.67 g, 89% yield, determined by GC analysis). Obtained **5b** was used for next step without further purification. ¹H NMR (CDCl₃, major isomer): δ 0.65–1.04 (m, 10H, Si-Et₂), 1.38 (s, 9H, Ar-^{*t*}Bu), 1.72 (s, 6H, Cp-Me), 1.75 (s, 6H, Cp-Me), 2.29 (s, 3H, Ar-Me), 3.51 (s, 1H, Cp-H), 4.37 (dt, *J* = 4.3, 1.8 Hz, 2H, OCH₂CH=CH₂), 5.27 (dq, *J* = 10.7, 2.0 Hz, 1H, OCH₂CH=CH₂), 5.53 (dq, *J* = 17.1, 2.0 Hz, 1H, OCH₂CH=CH₂), 6.04 (ddt, *J* = 17.1, 10.7, 4.3 Hz, 1H, OCH₂CH=CH₂), 6.99 (d, *J* = 2.1 Hz, 1H, Ar-H), 7.17 (d, *J* = 2.1 Hz, 1H, Ar-H). ¹³C NMR (CDCl₃, major isomer): δ 3.98 (Si-Et), 8.01 (Si-Et), 11.18 (Cp-Me), 14.24 (Cp-Me), 21.16 (Ar-Me), 31.19 (Ar-CMe₃), 35.14 (Ar-CMe₃), 53.04, 75.69 (OCH₂), 115.87, 129.95, 130.04, 131.77, 133.74, 133.84, 135.32, 135.58, 141.75, 161.69. EI-HRMS: *m/z* calcd 410.30049, found 410.30314.

(2-Allyloxy-3-*tert*-butyl-5-methylphenyl)(2,3,4,5-tetramethylcyclopenta-2,4-dien-1-yl)(cyclotetramethylene)silane (5c): 88% yield. ¹H NMR (CDCl₃, major isomer): δ 0.75–1.00 (m, 4H, Si-CH₂), 1.39 (s, 9H, Ar-^{*t*}Bu), 1.45–1.90 (m, 4H, Si-CH₂CH₂), 1.68 (s, 6H, Cp-Me), 1.77 (s, 6H, Cp-Me), 2.34 (s, 3H, Ar-Me), 3.80 (s, 1H, Cp-H), 4.45 (dt, *J* = 4.7, 1.8 Hz, 2H, OCH₂CH=CH₂), 5.31 (dq, *J* = 10.5, 1.7 Hz, 1H, OCH₂CH=CH₂), 5.52 (dq, *J* = 17.3, 1.7 Hz, 1H, OCH₂CH=CH₂), 6.09 (ddt, *J* = 17.3, 10.5, 4.7 Hz, 1H, OCH₂CH=CH₂), 7.09 (d, *J* = 2.1 Hz, 1H, Ar-H), 7.21 (d, *J* = 2.1 Hz, 1H, Ar-H). ¹³C NMR (CDCl₃, major isomer): δ 11.12 (Cp-Me), 13.64 (Si-CH₂), 14.57 (Cp-Me), 21.07 (Ar-Me), 26.42 (Si-CH₂CH₂), 31.05 (Ar-CMe₃), 35.06 (Ar-CMe₃), 52.01, 75.94 (OCH₂), 116.90, 129.76, 130.64, 132.10, 132.96, 133.58, 133.65, 135.94, 142.11, 160.88. EI-HRMS: *m/z* calcd 408.28484, found 408.28499.

(2-Allyloxy-3-*tert*-butyl-5-methylphenyl)(2,3,4,5-tetramethylcyclopenta-2,4-dien-1-

yl)methylphenylsilane (5d): 89% yield. ^1H NMR (CDCl_3 , major isomer): δ 0.63 (s, 3H, Si-*Me*), 1.38 (s, 9H, Ar-*t*Bu), 1.46 (s, 3H, Cp-*Me*), 1.53 (s, 3H, Cp-*Me*), 1.68 (s, 6H, Cp-*Me*), 2.32 (s, 3H, Ar-*Me*), 3.51 (s, 1H, Cp-*H*), 4.18–4.23 (m, 2H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 5.21 (dq, $J = 10.7, 1.8$ Hz, 1H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 5.36 (dq, $J = 17.3, 1.8$ Hz, 1H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 5.87 (ddt, $J = 17.3, 10.7, 4.3$ Hz, 1H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 7.16–7.41 (m, 5H, Ar-*H*), 7.42–7.56 (m, 1H, Ar-*H*), 7.59–7.68 (m, 1H, Ar-*H*). ^{13}C NMR (CDCl_3 , major isomer): δ 0.29 (Si-*Me*), 11.01 (Cp-*Me*), 11.12 (Cp-*Me*), 14.10 (Cp-*Me*), 14.18 (Cp-*Me*), 21.11 (Ar-*Me*), 30.99 (Ar- CMe_3), 35.13 (Ar- CMe_3), 53.36, 76.01 (OCH_2), 116.43, 127.20, 127.83, 128.88, 129.58, 130.09, 130.96, 133.23, 133.60, 134.81, 135.75, 136.47, 137.21, 138.85, 141.98, 161.59. EI-HRMS: m/z calcd 444.28484, found 444.27554.

(2-Allyloxy-3-*tert*-butyl-5-methylphenyl)(2,3,4,5-tetramethylcyclopenta-2,4-dien-1-

yl)ethylmethylsilane (5e): 92% yield. ^1H NMR (CDCl_3 , major isomer): δ 0.00 (s, 3H, Si-*Me*), 0.82–0.96 (m, 5H, Si-*Et*), 1.39 (s, 9H, Ar-*t*Bu), 1.57 (s, 3H, Cp-*Me*), 1.60 (s, 3H, Cp-*Me*), 1.77 (s, 3H, Cp-*Me*), 1.80 (s, 3H, Cp-*Me*), 2.30 (s, 3H, Ar-*Me*), 3.47 (s, 1H, Cp-*H*), 4.40 (dt, $J = 4.1, 2.0$ Hz, 2H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 5.29 (dq, $J = 10.7, 2.0$ Hz, 1H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 5.55 (dq, $J = 17.3, 2.0$ Hz, 1H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 6.06 (ddt, $J = 17.3, 10.7, 4.3$ Hz, 1H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 7.01 (d, $J = 2.1$ Hz, 1H, Ar-*H*), 7.18 (d, $J = 2.1$ Hz, 1H, Ar-*H*). ^{13}C NMR (CDCl_3 , major isomer): δ -6.13 (Si-*Me*), 6.58 (Si-*Et*), 7.99 (Si-*Et*), 11.07 (Cp-*Me*), 11.18 (Cp-*Me*), 13.92 (Cp-*Me*), 14.27 (Cp-*Me*), 21.14 (Ar-*Me*), 31.17 (Ar- CMe_3), 35.15 (Ar- CMe_3), 53.60, 75.75 (OCH_2), 115.92, 129.12, 129.95, 130.92, 131.94, 133.32, 133.74, 135.26, 135.58, 135.93, 141.79, 161.59. EI-HRMS: m/z calcd 396.28484, found 396.28183.

(2-Allyloxy-3-*tert*-butyl-5-methylphenyl)(2,3,4,5-tetramethylcyclopenta-2,4-dien-1-

yl)cyclohexylmethylsilane (5f): 93% yield. ^1H NMR (CDCl_3 , major isomer): δ 0.37 (s, 3H, Si-*Me*), 1.11–1.41 (m, 5H, Si-*Cy*), 1.40 (s, 9H, Ar-*t*Bu), 1.58–2.02 (m, 6H, Si-*Cy*), 1.62 (s, 3H, Cp-*Me*), 1.67 (s, 3H, Cp-*Me*), 1.79 (s, 3H, Cp-*Me*), 1.92 (s, 3H, Cp-*Me*), 2.32 (s, 3H, Ar-*Me*), 3.40 (s, 1H, Cp-*H*), 4.41

(dt, $J = 3.1, 2.0$ Hz, 2H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 5.32 (dq, $J = 10.7, 1.8$ Hz, 1H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 5.57 (dq, $J = 17.1, 1.8$ Hz, 1H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 6.09 (ddt, $J = 17.1, 10.7, 4.4$ Hz, 1H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 7.06 (d, $J = 1.6$ Hz, 1H, Ar- H), 7.20 (d, $J = 1.6$ Hz, 1H, Ar- H). ^{13}C NMR (CDCl_3 , major isomer): δ -6.69 (Si- Me), -2.33 (Si- CH), 11.03 (Cp- Me), 11.16 (Cp- Me), 14.10 (Cp- Me), 14.20 (Cp- Me), 21.13 (Ar- Me), 26.84 (Si- Cy), 27.91 (Si- Cy), 29.33 (Si- Cy), 31.20 (Ar- CMe_3), 35.09 (Ar- CMe_3), 52.74, 76.63 (OCH_2), 116.34, 129.53, 130.41, 130.92, 131.27, 132.69, 133.88, 134.06, 134.92, 135.87, 141.98, 161.13. EI-HRMS: m/z calcd 450.33179, found 450.32764.

Synthesis of Diethylsilylene(2,3,4,5-tetramethylcyclopentadienyl)(3-*tert*-butyl-5-methyl-2-phenoxy)titanium dichloride (1b). A typical procedure for the preparation of **1b** is given below. To a toluene (206 mL) solution of triethylamine (16.63 g, 164.35 mmol) and **5b** (13.35 g, 32.50 mmol) at -78 °C, was added a hexane solution of $n\text{BuLi}$ (1.60 M, 51.36 mL, 82.17 mmol). The mixture was allowed to warm to room temperature, and then stirred for 3 h. To the mixture at -78 °C, was added a toluene (55 mL) solution of TiCl_4 (10.39 g, 54.78 mmol) dropwise. The resulting mixture was warmed to room temperature and then heated to 90 °C and stirred for 2 h. After cooling to room temperature, solvent was evaporated. Heptane was added and insoluble materials were removed by filtration. Removal of the solvent followed by recrystallization from pentane gave **1b** as orange solids (2.94 g, 19% yield: 3 steps from **3**). Mp: 214–218 °C (dec). ^1H NMR (CDCl_3): δ 0.92–1.16 (m, 10H, Si- Et_2), 1.39 (s, 9H, Ar- tBu), 2.11 (s, 6H, Cp- Me), 2.32 (s, 6H, Cp- Me), 2.36 (s, 3H, Ar- Me), 7.08 (d, $J = 2.1$ Hz, 1H, Ar- H), 7.16 (d, $J = 2.1$ Hz, 1H, Ar- H). ^{13}C NMR (CDCl_3): δ 4.89 (Si- Et), 7.47 (Si- Et), 13.20 (Cp- Me), 14.81 (Cp- Me), 21.31 (Ar- Me), 29.92 (Ar- CMe_3), 34.82 (Ar- CMe_3), 117.55, 127.54, 129.01, 132.92, 133.26, 136.05, 139.01, 140.68, 166.86. Anal. Calcd for $\text{C}_{24}\text{H}_{36}\text{Cl}_2\text{OSiTi}$: C, 59.14; H, 7.44. Found: C, 59.14; H, 7.44.

Cyclotetramethylenesilylene(2,3,4,5-tetramethylcyclopentadienyl)(3-*tert*-butyl-5-methyl-2-phenoxy)titanium dichloride (1c): 5% yield. Mp: 224–227 °C (dec). ^1H NMR (CDCl_3): δ 1.04–1.19 (m, 2H, Si- CH_2), 1.20–1.34 (m, 2H, Si- CH_2), 1.41 (s, 9H, Ar- tBu), 1.71–2.02 (m, 4H, Si- CH_2CH_2), 2.14

(s, 6H, Cp-*Me*), 2.35 (s, 3H, Ar-*Me*), 2.36 (s, 6H, Cp-*Me*), 7.08 (d, $J = 2.0$ Hz, 1H, Ar-*H*), 7.16 (d, $J = 2.0$ Hz, 1H, Ar-*H*). ^{13}C NMR (CDCl_3): δ 13.27 (Cp-*Me*), 14.72 (Cp-*Me*), 15.65 (Si- CH_2), 21.25 (Ar-*Me*), 27.75 (Si- CH_2CH_2), 30.08 (Ar- CMe_3), 34.89 (Ar- CMe_3), 117.07, 128.01, 129.46, 132.67, 133.68, 136.24, 138.85, 140.27, 166.71. Anal. Calcd for $\text{C}_{24}\text{H}_{34}\text{Cl}_2\text{OSiTi}$: C, 59.39; H, 7.06. Found: C, 59.40; H, 7.13.

Methylphenylsilylene(2,3,4,5-tetramethylcyclopentadienyl)(3-*tert*-butyl-5-methyl-2-phenoxy)titanium dichloride (1d): 19% yield. Mp: 201–204 °C (dec). ^1H NMR (CDCl_3): δ 0.87 (s, 3H, Si-*Me*), 1.44 (s, 9H, Ar-*tBu*), 1.66 (s, 3H, Cp-*Me*), 2.17 (s, 3H, Cp-*Me*), 2.26 (s, 3H, Cp-*Me*), 2.30 (s, 3H, Cp-*Me*), 2.34 (s, 3H, Ar-*Me*), 7.09 (d, $J = 1.8$ Hz, 1H, Ar-*H*), 7.20 (d, $J = 1.8$ Hz, 1H, Ar-*H*), 7.32–7.46 (m, 3H, Si-*Ph*), 7.50–7.57 (m, 2H, Si-*Ph*). ^{13}C NMR (CDCl_3): δ –1.71 (Si-*Me*), 13.03 (Cp-*Me*), 13.27 (Cp-*Me*), 14.74 (Cp-*Me*), 15.09 (Cp-*Me*), 21.21 (Ar-*Me*), 30.00 (Ar- CMe_3), 34.92 (Ar- CMe_3), 117.12, 127.18, 128.24, 129.61, 130.03, 133.13, 133.74, 134.82, 135.22, 136.35, 138.92, 139.18, 140.22, 141.15, 167.02. Anal. Calcd for $\text{C}_{27}\text{H}_{34}\text{Cl}_2\text{OSiTi}$: C, 62.19; H, 6.57. Found: C, 62.57; H, 6.65.

Ethylmethylsilylene(2,3,4,5-tetramethylcyclopentadienyl)(3-*tert*-butyl-5-methyl-2-phenoxy)titanium dichloride (1e): 33% yield. Mp: 174–176 °C (dec). ^1H NMR (CDCl_3): δ 0.51 (s, 3H, Si-*Me*), 0.98–1.12 (m, 5H, Si-*Et*), 1.39 (s, 9H, Ar-*tBu*), 2.06 (s, 3H, Cp-*Me*), 2.18 (s, 3H, Cp-*Me*), 2.32 (s, 6H, Cp-*Me*), 2.36 (s, 3H, Ar-*Me*), 7.11 (d, $J = 2.1$ Hz, 1H, Ar-*H*), 7.16 (d, $J = 2.1$ Hz, 1H, Ar-*H*). ^{13}C NMR (CDCl_3): δ –1.99 (Si-*Me*), 7.07 (Si-*Et*), 7.60 (Si-*Et*), 13.02 (Cp-*Me*), 13.28 (Cp-*Me*), 14.42 (Cp-*Me*), 15.26 (Cp-*Me*), 21.27 (Ar-*Me*), 29.89 (Ar- CMe_3), 34.84 (Ar- CMe_3), 117.92, 128.97, 129.07, 132.40, 133.54, 136.08, 138.84, 139.08, 140.12, 140.85, 166.49. Anal. Calcd for $\text{C}_{23}\text{H}_{34}\text{Cl}_2\text{OSiTi}$: C, 58.36; H, 7.24. Found: C, 58.61; H, 7.29.

Cyclohexylmethylsilylene(2,3,4,5-tetramethylcyclopentadienyl)(3-*tert*-butyl-5-methyl-2-phenoxy)titanium dichloride (1f): 14% yield. Mp: 208–211 °C (dec). ^1H NMR (CDCl_3): δ 0.43 (s, 3H, Si-*Me*), 1.08–1.42 (m, 6H, Si-*Cy*), 1.38 (s, 9H, Ar-*tBu*), 1.69–1.83 (m, 3H, Si-*Cy*), 1.85–2.02 (m, 2H, Si-

Cy), 1.93 (s, 3H, Cp-*Me*), 2.03 (s, 3H, Cp-*Me*), 2.31 (s, 6H, Cp-*Me*), 2.37 (s, 3H, Ar-*Me*), 7.13 (d, $J = 2.0$ Hz, 1H, Ar-*H*), 7.16 (d, $J = 2.0$ Hz, 1H, Ar-*H*). ^{13}C NMR (CDCl_3): δ -1.95 (Si-*Me*), 12.79 (Cp-*Me*), 13.61 (Cp-*Me*), 13.92 (Cp-*Me*), 16.18 (Cp-*Me*), 21.35 (Ar-*Me*), 24.79 (Si-Cy), 26.65 (Si-Cy), 27.90 (Si-Cy), 27.96 (Si-Cy), 28.08 (Si-Cy), 28.28 (Si-Cy), 29.86 (Ar- CMe_3), 34.83 (Ar- CMe_3), 118.14, 128.83, 129.02, 132.13, 133.45, 136.16, 138.57, 139.56, 139.97, 141.50, 167.04. Anal. Calcd for $\text{C}_{27}\text{H}_{40}\text{Cl}_2\text{OSiTi}$: C, 61.48; H, 7.64. Found: C, 61.36; H, 7.68.

Polymerization of Propylene. Polymerization of propylene was performed by using an autoclave and the typical reaction procedure is as follows. An autoclave having an inner volume of 300 mL was dried under vacuum and purged with nitrogen. The vessel was then charged with toluene (145 mL), and then heated to 40 °C. After propylene was introduced (0.2 MPa), $i\text{Bu}_3\text{Al}$ (TIBA) (60 μmol , 0.06 M toluene solution) was added. Subsequently, complex (0.05 μmol , 0.05 mM toluene solution) and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (TB) (0.5 μmol , 0.5mM toluene solution) were added. Polymerization was performed at 40 °C for 5 min, and then the reaction was quenched by addition of methanol (5 mL). The reaction mixture was poured into acidic methanol (500 mL with 1 mL of 5% aqueous HCl). The polymer was collected by filtration, washed with methanol, and then dried in a high vacuum oven at 80 °C for 2 h to constant weight.

Copolymerization of Ethylene and 1-Hexene. Copolymerization of ethylene and 1-hexene was performed by using an autoclave and the typical reaction procedure is as follows. An autoclave having an inner volume of 300 mL was dried under vacuum and purged with nitrogen. The vessel was then charged with toluene (144 mL) and 1-hexene (1.5 mL), and then heated to 70 °C. After ethylene was introduced (0.6 MPa), TIBA (60 μmol , 0.06 M toluene solution) was added. Subsequently, complex (0.02 μmol , 0.02 mM toluene solution) and TB (0.1 μmol , 0.1mM toluene solution) were added. Polymerization was performed at 70 °C for 2 min, and then the reaction was quenched by addition of methanol (5 mL). The reaction mixture was poured into acidic methanol (500 mL with 1 mL of 5% aqueous HCl). The polymer

was collected by filtration, washed with methanol, and then dried in a high vacuum oven at 80 °C for 2 h to constant weight.

Polymer Characterization. Carbon and proton NMR spectra of polymers were recorded on a Bruker AV-600 spectrometer operating at 150.91 MHz in the Fourier transform mode, at 130 °C. The samples were prepared by dissolving 40 mg of polymer in 0.6 mL of a mixture of *o*-dichlorobenzene and *o*-dichlorobenzene-*d*₄ (7/1) at 130 °C. Chemical shifts were referenced to the solvent (132.43 ppm for ¹³C and 6.93 ppm for ¹H). Each carbon NMR spectrum was acquired with 90° pulse, 10 s of delay between pulses and CPD (waltz 16) to remove ¹H-¹³C coupling. About 4000 transients were stored in 65K data points. Each proton spectrum was acquired with a 30° pulse, 3 s of delay between pulses. About 256 of transients were stored in 65K data points. The calculations of 1-hexene content were conducted according to the literature.^{SI-3}

X-Ray Crystallographic Analysis. 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(1) K. Data were collected using Rigaku RAXIS RAPID imaging plate area detector (**1b** and **1f**) or Rigaku AFC7R/Mercury CCD detector (**1c**) with graphite monochromated Mo-Kα (0.71075 Å) radiation. Crystal data and structure refinement parameters were summarized in Table S2. The structures were solved by direct methods (SIR 92)^{SI-4} and refined on F^2 by the full-matrix least-squares methods (SHELXL-97).^{SI-5} Non-hydrogen atoms were anisotropically refined. 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 function 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^{SI-6} was used to draw the molecule.

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