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Synthesis and characterization of titanium and zirconium complexes with silicone-bridged phenoxycyclopentadienyl ligands

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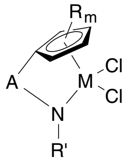
Abstract

Dimethylsilyl(2,3,4,5-tetramethylcyclopentadienyl)(3-*tert*-butyl-5-methyl-2-phenoxy)titanium dichloride (**1a**), a useful catalyst precursor for olefin copolymerization, was synthesized at high yield starting from allyl-protected phenolic ligand **3a**,which was first treated with 2 equiv. of *n*-BuLi to selectively give the dilithium salt of **3a** along with 1-heptene, a coupling product of a protected allyl ether moiety and butyl anion. Addition of $TiCl_4$ to the resulting dilithium salt of **3a** in toluene afforded **1a** in 50% isolated yield. This methodology could be applied to the preparation of related titanium and zirconoium complexes **1b**–**1d**, **8** with silicone-bridged Cp-phenoxy ligands, whereas the reaction starting from methyl-protected precursor **2a** did not produce the zirconium complex **8**. Copolymerization of ethylene and 1-hexene with the newly prepared complexes was also investigated.

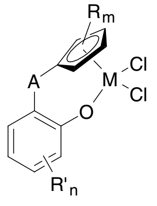
Keywords: Titanium; Silicone-bridged; Phenoxycyclopentadienyl ligand; Deallylation

1. Introduction

Metallocene catalysts of group 4 metals have been extensively studied for the past two decades and single-site catalysts have been used to control polyolefin micro-structures [1]. Bridged monocyclopentadienyl complexes with an appended heteroatom donor atom such as nitrogen [2,3], oxygen [4,5], and phosphorous [6] are highly active catalyst precursors. Bridged cyclopentadienyl amide complexes, namely "constrained geometry catalyst" (CGC) precursors, produce high molecular weight copolymer with high comonomer content in ethylene-α-olefin copolymerization [2a]. Recently, Lee reported that a bridged cyclopentadienyl-anilide complex produced higher molecular weight copolymer upon activation with activator [3a]. Many olefin polymerization catalysts with phenoxy moieties have also been studied [7], and metallocene catalysts with bridged [4] or non-bridged [8] phenoxy groups have been reported. Bridged phenoxy complexes, namely "phenoxy-induced complex of Sumitomo" (PHENICS) catalyst, have a notable feature in that they show high activities even at elevated temperatures, producing high molecular weight ethylene-α-olefin copolymer [4a–e].



CGC



PHENICS

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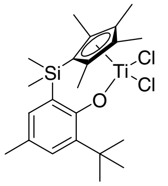
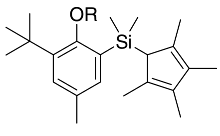
Silicone-bridged PHENICS complex **1a** was originally synthesized by reaction of the lithium salt of methyl-protected compound **2** with titanium tetrachloride, in which the titanium atom mediated the C–O bond cleavage and the subsequent formation of the Ti–O bond [4a,4f]. Because the O–Me bond is rather stable [9], this method has been limited. Our effort was directed to find a more easily removable protecting group to improve the chemical yield of **1a** [10]. Herein, we report an efficient synthesis of **1a** by reaction of a newly introduced allyl-protected precursor **3a** with *n*-BuLi, *in situ* preparation of the highly reactive dilithium salt of the ligand by deallylation, followed by subsequent treatment with titanium tetrachloride, and application of the synthetic method to preparation of related complexes.



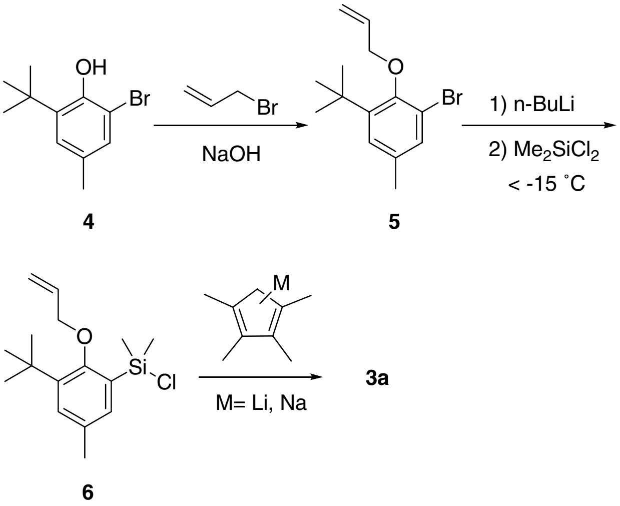
1a



2 : R = Me
3a : R = CH_2-CH=CH_2

2. Results and Discussion

The synthetic pathway to an allyl-protected ligand **3a** is depicted in Scheme 1. 2-Bromo-4-methyl-6-*tert*-butylphenol **4** was reacted with allyl bromide in the presence of NaOH to produce allyl ether compound **5** (92% yield). Treatment of **5** with *n*-BuLi in toluene at −20 °C followed by addition of dichlorodimethylsilane gave a chlorosilane compound **6** (85% yield). Since the lithiated derivative of **5** was thermally too unstable at room temperature and a dihydrobenzofurane compound **7** was resulted [11] (Scheme 2), the reaction was conducted below −15 °C. Treatment of **6** with the lithium or sodium salt of tetramethylcyclopentadienyl anion produced **3a** (lithium, 75% yield; sodium, 86% yield). The sodium tetramethylcyclopentadienilide was prepared using NaH. Since the reactivity of NaH toward tetramethylcyclopentadiene was low, a catalytic amount (5 mol%) of aniline was added to the reaction mixture to accelerate the reaction [12]. A sodium anilide species was assumed likely to play a key role in this reaction. Other cyclopentadiene derivatives **3b**–**3d** were prepared in the same manner (**3b**, 84% yield; **3c**, 86% yield; **3d**, 83% yield).



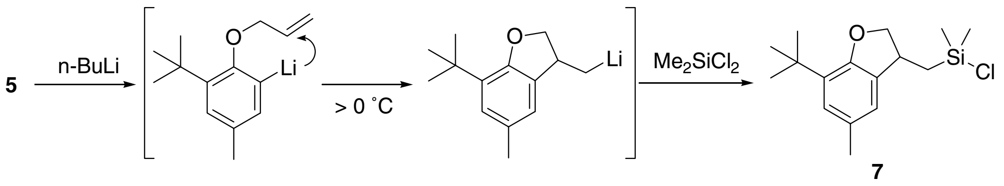
Scheme 1.

Treatment of **3a** under typical deallylation condition such as catalytic deprotection with palladium complexes [13] or stoichiometric reaction with trimethylsilyl iodide [14] did not afford any deprotected compounds but gave an unidentified mixture presumably due to instability of the desired product. Accordingly, complex **1a** was prepared by *in situ* deprotection of **3a** using *n*-BuLi followed by the reaction with $TiCl_4$. The synthesis of **1a** and corresponding zirconium complex **8** were conducted and results are listed in Table 1. The protective group of **3a** was removed more easily than that of **2**, producing **1a** in higher yield (entries 1 and 4). Interestingly, a high molar ratio of *n*-BuLi contributed to an increase in the yield of **1a**. Thus, treatment of **3** with 2.25 equiv. of *n*-BuLi in the presence of triethylamine, enhancing reactivity of lithium reagent, followed by addition of 1.5 equiv. of $TiCl_4$ produced **1a** in 50% isolated yield (entry 6). Zirconium complex **8** was also obtained in 43% yield by reaction of **3a** with zirconium tetrachloride under the same conditions (entry 7). In contrast, compound **2** did not produce **8** under the tested conditions, probably because the Lewis acidity of zirconium tetrachloride was too weak to cleavage of the strong C–O bond of Ar–OMe (entries 2 and 3) (Scheme 3).

Detection of 1-heptene in the reaction mixture suggested that phenoxy anion was formed by nucleophilic reaction of *n*-BuLi at the allyl group of **3a** (Scheme 4). The resulting dilithium salt apparently reacted with titanium tetrachloride to produce **1a**.

Compounds **3b**–**3d** could be treated in the same manner and produced **1b**–**1d** (**1b**, 36% yield; **1c**, 40% yield; **1d**, 45% yield). In these experiments, highly reactive dianion species were also generated under the reaction conditions. Allyl precursors are therefore regarded as useful reagents for the synthesis of silicone-bridged Cp-phenoxy complexes (Scheme 5).

A single crystal of **1c** suitable for X-ray diffraction study was grown from toluene at room temperature. Fig. 1 shows an ORTEP diagram and Table 2 lists selected bond parameters. It is of interest that the angle of Ti(1)–O(1)–C(18) (152.0(2)°) is smaller than that of the non-bridged Cp-phenoxy complexes (163.0–173.0°) [8], indicating the complex has a larger coordination site suitable for polymerization of bulky olefin. The angle of Cl(2)–Ti(1)–Cl(1) (104.55(4)°) is similar to that of related complexes. Torsion angles of C(1)–Si(1)–C(12)–C(18) (11.9(3)°) and



Scheme 2.

Table 1
Synthesis of silicone-bridged complexes by the reaction of aryl ether compounds with MCl_4^a

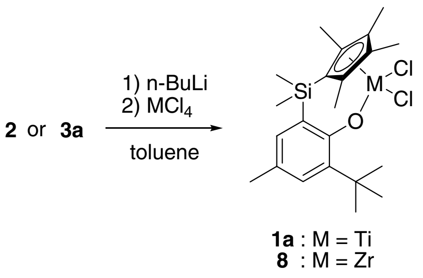
Entry	Aryl ether	*n*-BuLi, equiv.	MCl_4^b	Additive[b]	Complex	Yield, %[c]
1	**2**	1.0	$TiCl_4$(1.0)	–	**1a**	7
2	**2**	1.0	$ZrCl_4$(1.0)	–	**8**	0
3	**2**	1.0	$ZrCl_4$(1.5)	NEt_3(4.5)	**8**	0
4	**3a**	1.0	$TiCl_4$(1.0)	–	**1a**	25
5	**3a**	2.25	$TiCl_4$(1.5)	–	**1a**	34
6	**3a**	2.25	$TiCl_4$(1.5)	NEt_3(4.5)	**1a**	50(66)[d]
7	**3a**	2.25	$ZrCl_4$(1.5)	NEt_3(4.5)	**8**	43

[a] See Section 3.

[b] Parentheses indicate equivalence of the substrate.

[c] Isolated yield.

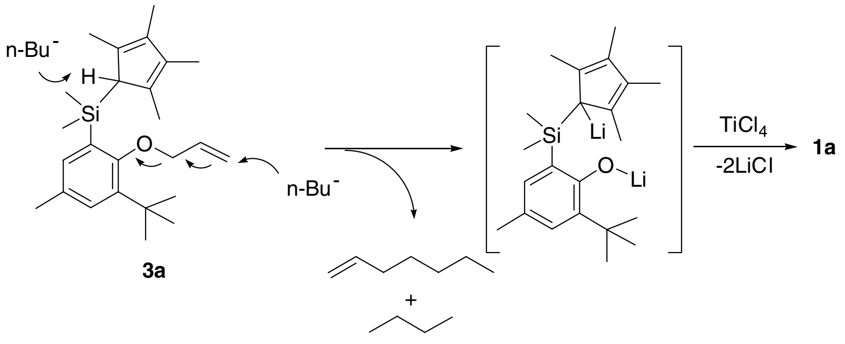
[d] Determined by ^1H NMR analysis of crude product.



Scheme 3.

Ti(1)–O(1)–C(18)–C(12) (7.3(5)°) indicate the complex has a slightly twisted structure. As the bridging group is expected to be flexible in solution, the structure could change appropriately to uptake bulky α-olefin during copolymerization.

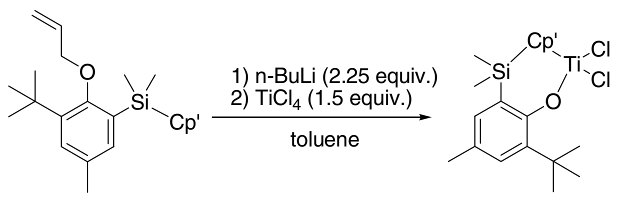
Newly prepared complexes **1b**–**1d**, **8** along with **1a** and CGC-Ti[(*tert*-$BuNSiMe_2C_5Me_4$)$TiCl_2$] were used as catalyst precursors for preliminary study of ethylene-1-hexene copolymerization upon activation with Al^iBu_3(TIBA) and $[PhNHMe_2][B(C_6F_5)_4]$ (AB) in toluene. The results are summarized in Table 3. Cp-phenoxy titanium complexes **1a**–**1d** showed efficiently high activity to afford ethylene-1-hexene high molecular weight copolymer with high 1-hexene content (entries 1–4), whereas zirconium complex **8** showed low activity (entry 5). Complex **1b**, which has the least hindered coordination site, gave copolymer with the highest 1-hexene content (entry 2). Indene complex **1c** afforded middle molecular weight polymer with moderately high comonomer content. It should be noted that all Cp-phenoxy titanium complexes **1a**–**1d** showed higher reactivity toward 1-hexene than CGC-Ti (entries 1–4 and 6). Desired copolymer would be obtained using **1a**–**1d** when an appropriate catalyst was chosen, because fine structural tuning of the catalyst controls molecular weight and comonomer content of resulting copolymer in wide range. To confirm the efficiency of newly prepared complexes, larger scale polymerization using **1c** was carried out in a 300 mL autoclave at 40 °C. The polymerization gave similarly high



Scheme 4.

molecular weight copolymer ($M_w = 293{,}000$; number of short chain branch = 23 per 1000 C) with high activity (223.8×10^6 g mol(cat)$^{-1}$ h^{-1}).

In conclusion, silicone-bridged cyclopentadienyl phenoxy titanium and zirconium complexes were synthesized by reaction of metal tetrachloride and the dilithium salt of the ligands, prepared by *in situ* deprotection of allyl ether precursors. More detailed catalytic study of these complexes for olefin polymerization will be described elsewhere.



3b : Cp' = C_5H_5
3c : Cp' = 1-Indenyl
3d : Cp' = 3-tert-Butyl-C_5H_4

1b : Cp'= C_5H_4
1c : Cp' = 1-Indenyl
1d : Cp' = 3-*tert*-Butyl-C_5H_3

Scheme 5.

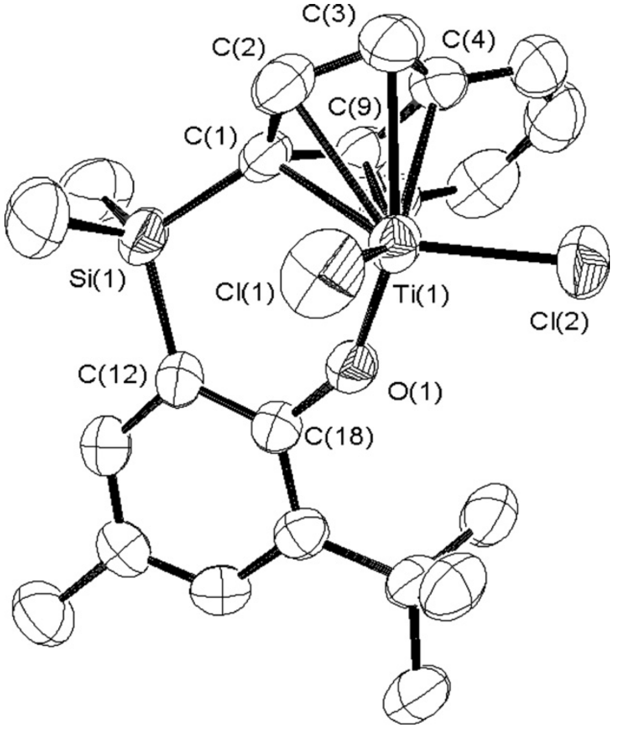


Fig. 1. ORTEP drawing of the molecular structure of **1c**. All hydrogen atoms are omitted for clarity. Key atoms are labeled.

Table 2
Selected bond lengths (Å) and angles (°) for **1c**

Bond lengths (Å)			
Ti(1)–Cl(1)	2.253(1)	Ti(1)–Cl(2)	2.252(1)
Ti(1)–O(1)	1.772(2)	Ti(1)–C(1)	2.266(3)
Ti(1)–C(2)	2.328(4)	Ti(1)–C(3)	2.407(4)
Ti(1)–C(4)	2.453(3)	Ti(1)–C(9)	2.344(3)
Bond angles (°)			
Cl(2)–Ti(1)–Cl(1)	104.55(4)	O(1)–Ti(1)–Cl(1)	99.38(7)
C(1)–Ti(1)–Cl(1)	107.12(9)	C(2)–Ti(1)–Cl(1)	86.5(1)
C(3)–Ti(1)–Cl(1)	100.5(1)	C(4)–Ti(1)–Cl(1)	134.41(9)
C(9)–Ti(1)–Cl(1)	142.51(9)	O(1)–Ti(1)–Cl(2)	104.55(7)
C(1)–Ti(1)–Cl(2)	143.12(9)	C(2)–Ti(1)–Cl(2)	130.5(1)
C(3)–Ti(1)–Cl(2)	96.81(9)	C(4)–Ti(1)–Cl(2)	85.11(8)
C(9)–Ti(1)–Cl(2)	107.92(8)	C(1)–Ti(1)–O(1)	88.51(9)
C(2)–Ti(1)–O(1)	121.3(1)	C(3)–Ti(1)–O(1)	146.0(1)
C(4)–Ti(1)–O(1)	121.5(1)	C(9)–Ti(1)–O(1)	90.22(9)
Ti(1)–O(1)–C(18)	152.0(2)	Ti(1)–C(1)–Si(1)	114.8(1)
Torsion angles (°)			
C(1)–Si(1)–C(12)–C(18)	11.9(3)	Ti(1)–O(1)–C(18)–C(12)	7.3(5)

3. Experimental

3.1. General

All manipulations of air- and moisture-sensitive compounds were performed under dry nitrogen using a Braun drybox or standard Schlenk line technique. Solvents were purchased from Kanto Chemicals Co., Ltd. (anhydrous grade) and stored in a drybox over molecular sieves. Toluene-d_8 was stored similarly. 2-Bromo-6-*tert*-butyl-4-methylphenol (**4**) was prepared according to a previously reported method [4a]. ^{1}H NMR (270 MHz) and ^{13}C NMR (68 MHz) were measured using a JEOL EX270 spectrometer. Mass spectra were recorded using a JEOL AX-505W. Elemental analyses were performed using an ELEMENTAR element analyzer at Sumika Chemical Analysis Service Ltd. All melting points were measured in sealed tubes under nitrogen atmosphere and were not corrected. Gel permeation chromatographic analyses were performed at 160 °C using a Symyx RapidsGPC™, equipped with three PLgel 10MICRO METER MIXED-B columns, and a Tosoh HLC-8121GPC/HT, equipped with a TSKgel GMHHR-H(S)HT. GPC columns were calibrated against commercially available polystyrene standards (Polymer Laboratories).

3.2. 2-(Allyloxy)-1-bromo-3-tert-butyl-5-methylbenzene (5)

A mixture of **4** (19.45 g, 80 mmol) and allylbromide (10.65 g, 88 mmol) in acetone (240 mL) was added to 20% NaOH (17.60 g, 88 mmol) dropwise at 25 °C. After the reaction mixture was stirred for 3 h, the aqueous layer was neutralized by addition of 5% H_2SO_4. After removal of acetone, the residue was extracted with toluene (200 mL). The organic layer was washed with saturated aqueous NaCl, then dried. Evaporation of the solvent followed by distillation (bp 74–75 °C, 0.08 Torr) gave **5** as a colorless oil (20.84 g, 92% yield). ^{1}H NMR ($CDCl_3$) δ 1.38 (s, 9H, *t*-Bu), 2.27 (s, 3H, *Me*), 4.57 (dt, 2H, $J = 5$, 2 Hz, $OCH_2CH{=}CH_2$), 5.29 (dq, 1H, $J = 11$, 2 Hz, $OCH_2CH{=}CH_2$), 5.49 (dq, 1H, $J = 17$, 2 Hz, $OCH_2CH{=}CH_2$), 6.13 (ddt, 1H, $J = 17$, 11, 5 Hz, $OCH_2CH{=}CH_2$), 7.07 (d, 1H, $J = 2$ Hz, Ar-*H*), 7.25 (d, 1H, $J = 2$ Hz, Ar-*H*); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 21.1 (Ar-CH_3), 31.3 (Ar-CMe_3), 35.9 (Ar-CMe_3), 73.8, 117.5, 118.4, 127.9, 132.6, 133.9, 134.6, 145.2, 153.2. HRMS: *m*/*z* calcd 282.0619, found 282.0614.

Table 3
Copolymerization of ethylene and 1-hexene catalyzed by **1a**–**1d** and **8** upon activation with TIBA/AB[a]

Entry	Complex	Activity[b]	M_w^c	M_w/M_n^c	1-Hexene content[d]
1	**1a**	61.6	635,000	2.2	18
2	**1b**	5.8	104,000	1.7	35
3	**1c**	52.2	265,000	1.9	20
4	**1d**	47.0	106,000	2.2	18
5	**8**	3.2	n.d.[e]	n.d.[e]	n.d.[e]
6	CGC-Ti	66.5	682,000	4.5	15

[a] Conditions: toluene; 5 mL, 1-hexene; 60 μL, ethylene; 0.6 MPa, complex; 0.1 μmol, TIBA; 40 μmol, AB; 0.3 μmol, temperature; 40 °C.

[b] In kg mmol(cat)$^{-1}$ h^{-1}.

[c] Determined by GPC against polystyrene standards.

[d] Number of methyl branches per 1000 carbon determined by FT-IR.

[e] Not determined.

*3.3. [2-(Allyloxy)-3-tert-butyl-5-methylphenyl](chloro)dimethylsilane (**6**)*

To a mixture of **5** (19.82 g, 70 mmol) and toluene (200 mL), 1.60 M hexane solution of *n*-BuLi (57 mL, 91 mmol) was added at −78 °C, and then the mixture was allowed to warm to −20 °C. After lithiation was completed, the mixture was transferred to a toluene (140 mL) solution of dichlorodimethylsilane (27.10 g, 210 mmol). The mixture was allowed to warm to room temperature and stirred for 5 h. After removal of inorganic materials by filtration, the solvent was evaporated. Distillation (129 °C, 0.1 Torr) gave **6** as a colorless oil (17.67 g, 85% yield). ^{1}H NMR (CDCl$_3$) δ 0.72 (s, 6H, SiMe_2), 1.39 (s, 9H, *t*-Bu), 2.32 (s, 3H, *Me*), 4.42 (dt, 2H, $J = 4$, 2 Hz, $OCH_2CH{=}CH_2$), 5.28 (dq, 1H, $J = 11$, 2 Hz, $OCH_2CH{=}CH_2$), 5.52 (dq, 1H, $J = 17$, 2 Hz, $OCH_2CH{=}CH_2$), 6.03 (ddt, 1H, $J = 17$, 11, 5 Hz, $OCH_2CH{=}CH_2$), 7.27 (d, 1H, $J = 2$ Hz, Ar-*H*), 7.25 (d, 1H, $J = 2$ Hz, Ar-*H*); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 3.8 (SiMe_2), 21.1 (Ar-CH_3), 31.3 (Ar-CMe_3), 35.2 (Ar-CMe$_3$), 76.4, 116.3, 129.8, 131.9, 132.9, 133.5, 134.6, 142.2, 161.0. HRMS: *m/z* calcd 296.1363, found 296.1363.

*3.4. [2-(Allyloxy)-3-tert-butyl-5-methylphenyl](dimethyl)(2,3,4,5-tetramethylcyclopenta-2,4-dien-1-yl)silane (**3a**)*

3.4.1. Method A

To a mixture of THF (80 mL) and 60% NaH (2.50 g, 62.5 mmol), aniline (0.23 g, 2.5 mmol) was added at room temperature, and the mixture was then stirred for 30 min. 1,2,3,4-Tetramethyl-1,3-cyclopentadiene (6.42 g, 52.5 mmol) was dropwise added to the mixture to 50 °C. The mixture was then stirred until evolution of hydrogen ceased. A toluene (10 mL) solution of **6** (14.85 g, 50 mmol) was added dropwise to the mixture cooled at 10 °C. The resulting mixture was allowed to warm to 20 °C, then stirred for 1 h. After the mixture was poured into water, the separated organic layer was washed with saturated aqueous NaCl and then dried over Na$_2$SO$_4$. Removal of the solvent followed by short column chromatography over silica (hexane/EtOAc, 20:1) gave **3a** as a pale yellow oil (16.45 g, 86% yield). ^{1}H NMR (CDCl$_3$) δ 0.13 (s, 6H, SiMe_2), 1.42 (s, 9H, *t*-Bu), 1.69 (s, 6H, C$_5$HMe_4), 1.79 (s, 6H, C$_5$HMe_4), 2.28 (s, 3H, Ar-*Me*), 3.42 (s, 1H, C$_5$*H*Me$_4$), 4.40 (dt, 2H, $J = 2$, 2 Hz, $OCH_2CH{=}CH_2$), 5.28 (dq, 1H, $J = 11$, 2 Hz, $OCH_2CH{=}CH_2$), 5.54 (dq, 1H, $J = 17$, 2 Hz, $OCH_2CH{=}CH_2$), 5.99 (ddt, 1H, $J = 17$, 11, 2 Hz, $OCH_2CH{=}CH_2$), 7.03 (d, 1H, $J = 2$ Hz, Ar-H), 7.17 (d, 1H, $J = 2$ Hz, Ar-H); ^{13}C{^{1}H} NMR (CDCl$_3$) δ −2.4 (SiMe_2), 11.1, 14.0, 21.1 (Ar-CH_3), 31.2 (Ar-CMe_3), 35.2 (Ar-CMe$_3$), 75.9, 116.0, 130.0, 132.1, 132.6, 133.4, 133.7, 133.9, 134.7, 135.8, 141.9, 161.3. HRMS: *m/z* calcd 382.2692, found 382.2686.

3.4.2. Method B

To a THF (400 mL) solution of 1,2,3,4-tetramethyl-1,3-cyclopentadiene (8.25 g, 67.5 mmol), 1.60 M hexane solution of *n*-BuLi (50 mmol) was added at −10 °C. The mixture was allowed to warm to 20 °C and then stirred for 3 h. THF (20 mL) solution of **6** (14.85 g, 50 mmol) was added to the mixture at −10 °C. The resulting mixture was allowed to warm to 20 °C, then stirred for 20 h. The same work-up as for Method A gave **3a** (14.35 g, 75% yield).

*3.5. Dimethylsilyl(2,3,4,5-tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)-titanium dichloride (**1a**)*

To a toluene (20 mL) solution of triethylamine (2.27 g, 22.6 mmol) and **3a** (1.91 g, 5 mmol), 1.60 M hexane solution of *n*-BuLi (7.0 mL, 11.3 mmol) was added at −78 °C. The mixture was allowed to warm to 20 °C, then stirred for 3 h. To the mixture cooled at −78 °C a toluene (5 mL) solution of TiCl$_4$ (0.82 mL, 7.5 mmol) was added dropwise. The resulting mixture was warmed to room temperature and then stirred for 1 h. Thereafter, the mixture was heated to 90 °C and stirred for a further 3 h. After cooling to room temperature, insoluble materials were filtered out. Removal of the solvent followed by recrystallization from hexane/toluene gave **1a** as a red solid (1.15 g, 50% yield). Mp: 228–230 °C (dec). ^{1}H NMR (C$_7$D$_8$) δ 0.41 (s, 6H, SiMe_2), 1.53 (s, 9H, *t*-Bu), 1.95 (s, 6H, C$_5$$Me_4$), 2.02 (s, 6H, C$_5$$Me_4$), 2.25 (s, 3H, Ar-*Me*), 7.12

(m, 1H, Ar-*H*), 7.19 (m, 1H, Ar-*H*); ^{13}C{^{1}H} NMR (C_7D_8) δ 0.0 (Si*Me*$_2$), 12.8, 14.8, 21.3 (Ar-*Me*), 30.2 (Ar-C*Me*$_3$), 35.2 (Ar-C*Me*$_3$), 117.7, 129.6, 129.9, 132.3, 133.8, 136.7, 138.6, 139.9, 166.8. Anal. Calc. for $C_{22}H_{32}Cl_2OSiTi$: C, 57.52; H, 7.02. Found C, 57.30; H, 7.00%.

*3.6. Dimethylsilyl(2,3,4,5-tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)-zirconium dichloride (**8**)*

A 1.60 M hexane solution of *n*-BuLi (7.0 mL, 11.3 mmol) was added to a toluene (20 mL) solution of triethylamine (2.27 g, 22.6 mmol) and **3a** (1.91 g, 5.0 mmol) cooled at −78 °C. The reaction mixture was gradually warmed to room temperature, then stirred for further 3 h. After the reaction mixture was again cooled to −78 °C, a suspension of toluene (20 mL) and $ZrCl_4$ (1.73 g, 7.5 mmol) was added dropwise. The resulting mixture was allowed to warm to room temperature and then stirred for 3 h. Insoluble materials were filtrated off, the filtrate was concentrated, and recrystallization from hexane/toluene gave **8** as a yellow solid (1.07 g, 43% yield). ^{1}H NMR (CD_2Cl_2) δ 0.54 (s, 6H, Si*Me*$_2$), 1.37 (s, 9H, *t*-Bu), 2.10 (s, 6H, C_5*Me*$_4$), 2.23 (s, 6H, C_5*Me*$_4$), 2.32 (s, 3H, Ar-*Me*), 7.11–7.18 (m, 2H, Ar-*H*); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ −0.3 (Si*Me*$_2$), 11.5, 13.4, 20.4, 29.5, 34.3, 116.5, 129.0, 131.8, 132.9, 134.2, 135.9, 136.9, 139.0, 161.2. HRMS: *m*/*z* calcd 500.0646, found 500.0645.

*3.7. [2-(Allyloxy)-3-tert-butyl-5-methylphenyl](cyclopentadienyl)(dimethyl) silane (**3b**)*

In a similar manner as described for preparation of **3a**, reaction of **6** with sodium cyclopentadienylide gave **3b** as a pale yellow oil (84% yield after short column chromatography over silica (hexane)). ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 6H, Si*Me*$_2$), 1.45 (s, 9H, *t*-Bu), 2.36 (s, 3H, Ar-*Me*), 3.11 (s, 1H, SiC_5*H*$_5$), 4.43 (m, 2H, OC*H*$_2$CH=CH$_2$), 5.31 (m, 1H, OCH$_2$CH=C*H*$_2$), 5.57 (m, 1H, OCH$_2$CH=C*H*$_2$), 6.07 (m, 1H, OCH$_2$C*H*=CH$_2$), 6.40–6.70 (m, 4H, SiC_5*H*$_5$), 7.16–7.22 (m, 2H, Ar-H); ^{13}C{^{1}H} NMR ($CDCl_3$, major isomer) δ −2.7 (Si*Me*$_2$), 21.1 (Ar-*C*H$_3$), 31.2 (Ar-C*Me*$_3$), 35.2 (Ar-*C*Me$_3$), 76.4, 116.1, 130.5, 132.1, 132.4, 133.6, 134.4, 135.1, 136.0, 138.2, 142.1, 161.3. HRMS: *m*/*z* calcd 326.2066, found 326.2073.

*3.8. Dimethylsilyl(cyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)-titanium dichloride (**1b**)*

Compound **1b** was prepared in a similar manner as **1a** (36% yield). Mp: 179–182 °C (dec). ^{1}H NMR (C_7D_8) δ 0.27 (s, 6H, Si*Me*$_2$), 1.57 (s, 9H, *t*-Bu), 2.22 (s, 3H, Ar-*Me*), 6.06 (t, 2H, *J* = 2 Hz, SiC_5H_4), 6.62 (t, 2H, *J* = 2 Hz, SiC_5H_4), 7.08(d, 1H, *J* = 2 Hz, Ar-H), 7.21 (d, 1H, *J* = 2 Hz, Ar-H); ^{13}C{^{1}H} NMR (C_7D_8) δ −2.1 (Si*Me*$_2$), 21.2 (Ar-*Me*), 30.5 (Ar-C*Me*$_3$), 35.2 (Ar-*C*Me$_3$), 121.5, 125.8, 126.5, 129.9, 133.1, 134.4, 136.6, 137.5, 168.5. Anal. Calc. for $C_{18}H_{24}Cl_2OSiTi$: C, 53.61; H, 6.00. Found C, 53.50; H, 6.00%.

*3.9. [2-(Allyloxy)-3-tert-butyl-5-methylphenyl](inden-1-yl)(dimethyl)silane (**3c**)*

In a similar manner as for **3a**, reaction of **6** with indene gave **3c** (Method B) (86% yield). ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 3H, Si*Me*$_2$), 0.12 (s, 3H, Si*Me*$_2$), 1.43 (s, 9H, *t*-Bu), 2.30 (s, 3H, Ar-*Me*), 4.05 (br, 1H, Ind-*H*), 4.41 (dt, 2H, *J* = 2, 2 Hz, OC*H*$_2$CH=CH$_2$), 5.27 (dq, 1H, *J* = 11, 2 Hz, OCH$_2$CH=C*H*$_2$), 5.54 (dq, 1H, *J* = 17, 2 Hz, OCH$_2$-CH=C*H*$_2$), 6.40 (ddt, 1H, *J* = 17, 11, 2 Hz, OCH$_2$C*H*=CH$_2$), 6.56 (dd, 1H, *J* = 5, 2 Hz, Ar-*H*), 6.88 (dd, 1H, *J* = 5, 1 Hz, Ar-*H*), 7.02–7.26 (m, 5H, Ar-*H*), 7.43 (d, 1H, *J* = 7 Hz, Ar-*H*); ^{13}C{^{1}H} NMR ($CDCl_3$) δ −3.2 (Si*Me*), −3.0 (Si*Me*), 21.1 (Ar-*Me*), 31.2 (Ar-C*Me*$_3$), 35.2 (Ar-*C*Me$_3$), 76.4, 116.1, 120.8, 123.0, 123.5, 124.8, 129.2, 130.6, 131.6, 132.5, 133.6, 134.9, 136.4, 142.1, 144.5, 145.3, 161.4. EI-MS: *m*/*z* 376 (M$^+$), 261, 205.

*3.10. Dimethylsilyl(inden-1-yl)(3-tert-butyl-5-methyl-2-phenoxy)-titanium dichloride (**1c**)*

Compound **1c** was prepared in a similar manner as for **1a**, but without triethylamine. 40% yield. Mp: 178–180 °C (dec). ^{1}H NMR (C_7D_8) δ 0.43 (s, 3H, Si*Me*$_2$), 0.50 (s, 3H, Si*Me*$_2$), 1.37 (s, 9H, *t*-Bu), 2.27 (s, 3H, Ar-*Me*), 6.60–6.71 (m, 2H, Ar-H), 6.73 (dt, 1H, *J* = 2, 4 Hz, Ar-*H*), 6.92 (ddd, 1H, *J* = 8, 7, 1 Hz, Ar-*H*), 7.12 (dq, 1H, *J* = 8, 1 Hz, Ar-*H*), 7.19 (ddd, 1H, *J* = 7, 2, 1 Hz, Ar-*H*), 7.52 (dt, 1H, *J* = 9, 1 Hz, Ar-*H*); ^{13}C{^{1}H} NMR (C_7D_8) δ −2.0 (Si*Me*), −1.8 (Si*Me*), 21.3 (Ar-*Me*), 30.1 (Ar-C*Me*$_3$), 35.0 (Ar-*C*Me$_3$), 113.4, 117.6, 125.0, 126.7, 128.1, 128.6, 128.7, 129.8, 131.9, 133.1, 134.3, 135.5, 136.9, 140.4, 168.1. Anal. Calc. for $C_{22}H_{26}Cl_2OSiTi$: C, 58.29; H, 5.78. Found C, 57.90; H, 5.80%.

*3.11. [2-(Allyloxy)-3-tert-butyl-5-methylphenyl](3-tert-butylcyclopentadienyl)(dimethyl)silane (**3d**)*

In a similar manner as for **3a**, reaction of **6** with *tert*-butylcyclopentadiene gave **3d** (Method B) (83% yield). ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 3H, Si*Me*$_2$), 0.17 (s, 3H, Si*Me*$_2$), 1.17 (s, 9H, *t*-Bu), 1.40 (s, 9H, *t*-Bu), 2.31 (s, 3H, Ar-*Me*), 3.70 (br, 1H, Cp-*H*), 4.18–4.41 (m, 2H, OC*H*$_2$CH=CH$_2$), 5.13–5.40 (m, 1H, OCH$_2$CH=C*H*$_2$), 5.42–5.58 (m, 1H, OCH$_2$CH=C*H*$_2$), 5.95–6.20 (m, 2H, OCH$_2$C*H*=CH$_2$ and Cp-H), 6.38–6.42 (m, 1H, Cp-*H*), 6.60–6.65 (m, 1H, Cp-*H*), 7.08–7.22 (m, 2H, Ar-*H*); ^{13}C{^{1}H} NMR ($CDCl_3$, major isomer) δ −2.9 (Si*Me*), −2.5 (Si*Me*), 21.1 (Ar-*C*H$_3$), 30.4 (C*Me*$_3$), 31.2 (C*Me*$_3$), 32.2 (*C*Me$_3$), 35.2 (*C*Me$_3$), 76.3, 116.1, 124.1, 130.4, 130.6, 132.3, 132.4, 133.7, 134.1, 134.4, 134.5, 142.0, 143.1, 161.3. HRMS: *m*/*z* calcd 382.26919, found 382.26430.

*3.12. Dimethylsilyl(3-tert-butylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)-titanium dichloride (**1d**)*

Compound **1d** was prepared in a similar manner as for **1a**. 45% yield. Mp: 170–172 °C (dec). ^{1}H NMR (C_7D_8), δ 0.32 (s, 3H, $SiMe_2$), 0.38 (s, 3H, $SiMe_2$), 1.34 (s, 9H, *t*-Bu), 1.57 (s, 9H, *t*-Bu), 2.23 (s, 3H, Ar-Me), 5.74 (dd, 1H, $J = 3$, 2 Hz, Cp-H), 6.74 (t, 1H, $J = 2$ Hz, Cp-H), 6.78 (dd, 1H, $J = 3$, 2 Hz, Cp-H), 7.10 (m, 1H, Ar-H), 7.20 (m, 1H, Ar-H). ^{13}C NMR (C_7D_8) δ −2.0 (Si*Me*), −1.9 (Si*Me*), 21.2 (Ar-CH_3), 30.4 (C*Me*$_3$), 31.1 (C*Me*$_3$), 33.9 (*C*Me$_3$), 35.2 (*C*Me$_3$), 121.7, 124.3, 125.5, 125.8, 129.9, 133.2, 134.3, 136.6, 154.4, 169.0. Anal. Calc. for $C_{25}H_{39}Cl_2OSiTi$(**1e** $\cdot$ $0.5C_6H_{14}$): C, 59.76; H, 7.82. Found C, 60.06; H, 7.50%.

*3.13. Crystallographic analysis of **1c***

A red block crystal of **1c** was mounted on glass, and intensity data were then collected using a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Cu Kα radiation. The structure was solved using a direct method (SIR92 [15]) and refined by the full-matrix least-squares methods. Crystal data and details of refinement are summarized in Table 4. The final discrepancy indices were R ($I > 3\sigma(I)$) = 0.029 and Rw ($I > 3\sigma(I)$) = 0.035. All calculations were performed using the CrystalStructure crystallographic software package (Rigaku/MSC).

Table 4
Crystal data and data collection parameters for **1c**

Empirical formula	$C_{22}H_{26}Cl_2OSiTi$
Formula weight	453.34
Crystal dimensions (mm)	0.1 × 0.2 × 0.2
Crystal system	Monoclinic
Detector position (mm)	127.40
Pixel size (mm)	0.100
a (Å)	10.073(2)
b (Å)	10.114(2)
c (Å)	22.788(5)
β (°)	95.54(1)
V (Å^3)	2310.9(8)
Space group	$P2_1/c$ (#14)
Z value	4
D_{calc} (g/cm^3)	1.303
Diffractometer	Rigaku RAXIS-RAPID
Radiation	Cu Kα ($l = 1.54187$ Å) Graphite, monochromated
$2\theta_{max}$ (°)	143.6
Number of reflections measured	Total: 27,638 Unique: 4229 ($R_{int} = 0.023$)
Structure solution	Direct methods (SIR92)
Refinement	Full-matrix least-squares on *F*
Number of observations ($I > 3\sigma(I)$)	2428
Residuals: R ($I > 3\sigma(I)$)	0.029
Residuals: Rw ($I > 3\sigma(I)$)	0.035
Goodness of fit indicator	1.008

*3.14. Polymerization of ethylene with 1-hexene catalyzed by **1a–1d** and **8** in 20 mL autoclave*

A pre-weighed glass vial insert and disposable stirring paddle were fitted to each reaction vessel of the reactor. The reactor was then closed, and 0.25 M triisobutylaluminium (160 μL), 1-hexene (60 μL) and toluene were injected into each reaction vessel through a valve. The total volume of reaction mixture was adjusted with toluene to 5 mL. The temperature was then set to the reaction temperature, the stirring speed was set to 800 rpm, and the mixture was pressurized to 0.6 MPa. Toluene solution of Cp-phenoxy complex (0.1 μmol, 1 mM toluene solution) was added followed by toluene solution of AB (0.3 μmol, 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 pre-set levels. After polymerization reaction, the temperature was allowed to drop 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.

*3.15. Polymerization of ethylene and 1-hexene catalyzed by **1c** in 300 mL autoclave*

An autoclave with an inner volume of 300 mL was dried under vacuum and purged with nitrogen. Toluene (150 mL) and 1-hexene (1.5 mL) were introduced into the vessel, which was then heated to 40 °C. After ethylene was introduced (0.6 MPa), triisobutylaluminum (0.60 mmol, 1.0 M toluene solution) was added. Subsequently, **1c** (1.0 μmol, 1 mM toluene solution) and TB (6.0 μmol, 6 mM toluene solution) were added. Polymerization was performed at 40 °C for 5 min, and then the reaction was then quenched by addition of methanol (5 mL). The reaction mixture was then poured into acidic methanol (500 mL with 1 mL of 5% 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.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.06.006.

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