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Synthesis and characterization of titanium alkyl, oxo, and diene complexes bearing a $SiMe_2$-bridged phenoxy-cyclopentadienyl ligand and their catalytic performance for copolymerization of ethylene and 1-hexene

Hidenori Hanaoka [a], Takahiro Hino [a], Masaaki Nabika [b], Tetsuya Kohno [c], Kazunori Yanagi [c], Yoshiaki Oda [a,*], Akio Imai [b], Kazushi Mashima [d,*]

[a] *Organic Synthesis Research Laboratory, Sumitomo Chemical Co. Ltd., 1-98, Kasugadenaka 3-chome, Konohana-ku, Osaka 554-8558, Japan*

[b] *Petrochemicals Research Laboratory, Sumitomo Chemical Co. Ltd., Kitasode, Sodegaura, Chiba 299-0295, Japan*

[c] *Genomic Science Laboratories, Dainippon Sumitomo Pharma Co. Ltd., 1-98, Kasugadenaka 3-chome, Konohana-ku, Osaka 554-0022, Japan*

[d] *Department of Chemistry, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan*

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Dedicated to Professor G. Erker on the occasion of his 60th birthday.

Abstract

A series of titanium complexes bearing a $SiMe_2$-bridged phenoxy-cyclopentadienyl ligand were synthesized and characterized, and their catalytic behavior for copolymerization of ethylene and 1-hexene was investigated. Treatment of dimethylsilyl(2,3,4,5-tetramethylcyclopentadienyl)(3-*tert*-butyl-5-methyl-2-phenoxy)-titanium dichloride (**1**) with appropriate nucleophiles afforded dimethoxy complex **2**, dimethyl complex **3**, and dibenzyl complex **4**. Standing a toluene solution of **2** in air afforded a dinuclear μ-oxo complex **5** as a single isomer. 1,3-Diene complexes **6**–**8** were prepared by reaction of **1** with the corresponding 1,3-dienes in the presence of 2 equiv. of *n*-BuLi. X-ray analysis of 1,4-diphenyl-1,3-butadiene complex **6** revealed that the diene ligand coordinates to titanium in *s-cis* fashion with a prone orientation. The newly prepared titanium complexes were applied to copolymerization of ethylene and 1-hexene upon activation with $Al^{i}Bu_3$ and $[C_6H_5NMe_2H][B(C_6F_5)_4]$. It was found that the alkyl complexes **3**–**4** and the diene complexes **6**–**8** showed higher activities than **1** at elevated temperature.

Keywords: Titanium complex; Cyclopentadiene; Phenolate; Diene; Polymerization

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1. Introduction

Alkene polymerization catalyst systems based on metallocene and half-metallocene complexes of early transition metals have attracted special interest in the past two decades because their homogeneous aspect enabled tunable ligand design of catalysts for precise control of polymer microstructure, copolymerization, and so on [1]. Among the developed catalysts, bridged cyclopentadienyl amide complexes (CGC: constrained geometry catalyst) [2] and bridged phenoxy complexes (PHENICS: phenoxy-induced complex of Sumitomo) [3] are two of the industrially important catalyst systems that produced new unpredicted elastomers starting from α-olefins.

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[*] Corresponding authors.
E-mail addresses: oday2@sc.sumitomo-chem.co.jp (Y. Oda), mashima@chem.es.osaka-u.ac.jp (K. Mashima).

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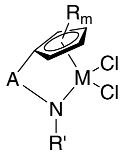
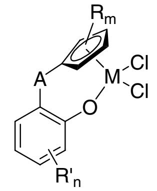
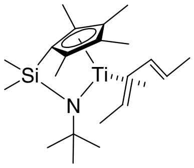


CGC

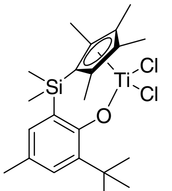


PHENICS

Alkyl groups have been reported as novel leaving substituents, leading to smooth generation of active species. Dimethyl and dibenzyl titanium complexes with $Me_2Si(\eta^5\text{-}C_5Me_4)(^tBuN)$ ligand showed higher activities than dichloro complex upon activation with borate cocatalyst [4]. 1,3-Butadiene derivatives are known to coordinate to early transition metals in various orientations [5], and diene ligand was readily activated to give catalytically active species [6–9]. Erker reported that 1,3-butadiene metallocene complexes readily reacted with $B(C_6F_5)_3$ to afford zwitterionic complexes which were applied to polymerization of α-olefin as well as detailed mechanistic study of olefin polymerization [7]. Marks and his coworkers synthesized a series of 1,3-butadiene CGC complexes in which the orientation of the diene moieties (prone/supine) was reported to depend on not only ligand architectures but also bulkiness of diene ligand [8]. They also reported that prone complex (**A**) showed high activity for copolymerization of ethylene and 1-octene upon activation with $B(C_6F_5)_3$. We report herein synthesis of alkyl, diene and methoxy derivatives of a $SiMe_2$-bridged PHENICS **1** and X-ray analyses of representative complexes. We also demonstrate copolymerization behavior of ethylene and 1-hexene using these newly prepared complexes.



A



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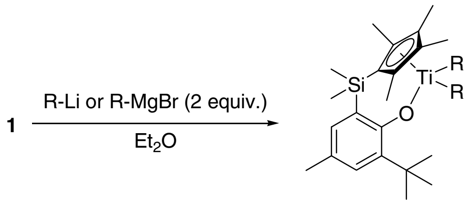
2. Results and discussion

Scheme 1 shows the synthesis of alkyl and methoxy titanium complexes **2**–**4**. A suspension of **1** in ether was treated with a solution of 2 equiv. of a nucleophile such as MeOLi, MeLi, or $PhCH_2MgBr$ in ether at −78 °C. After removal of inorganic materials at room temperature, crystallization from hexane gave the corresponding complexes **2** (70% yield), **3** (68% yield), and **4** (63% yield). Complexes **2**–**4** were characterized by NMR and elemental analysis. Structure of the dibenzyl complex **4** was further determined by X-ray analysis. Fig. 1 shows an ORTEP diagram, and selected bond parameters are summarized in Table 1. The dibenzyl complex **4** adopts three-legged piano stool geometry. Two angles of Ti–C–C(*ipso*) (112.13° and 130.0°) are much different: one of two benzyl groups coordinates in an η^1-fashion to the titanium atom, while the other in an η^2-fashion in order to compensate the coordinative unsaturation around the titanium atom Schemes 2–4.



2 : R = OMe
3 : R = Me
4 : R = CH_2Ph

Scheme 1.

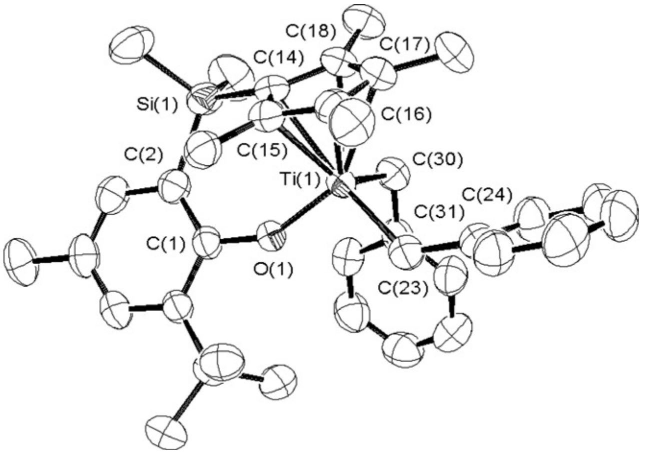
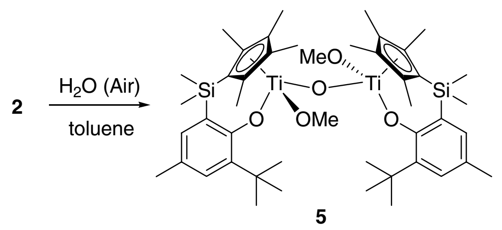


Fig. 1. ORTEP drawing of the molecular structure of **4**. All hydrogen atoms are omitted for clarity. Key atoms are labeled.

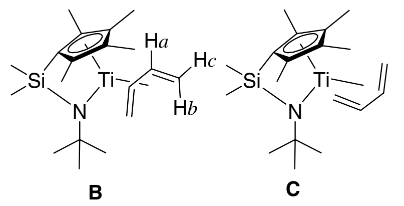
The dimethoxy complex **2** is moisture sensitive, and standing a toluene solution of **2** in air afforded a dinuclear μ-oxo complex **5** (76% yield), formed by hydrolysis of one

Table 1
Selected bond length (Å) and angles (°) for **4**

Bond lengths (Å)			
Ti(1)–C(30)	2.154(3)	Ti(1)–C(23)	2.135(3)
Ti(1)–O(1)	1.812(2)	Ti(1)–C(14)	2.287(2)
Ti(1)–C(15)	2.327(2)	Ti(1)–C(16)	2.421(3)
Ti(1)–C(17)	2.442(2)	Ti(1)–C(18)	2.384(2)
Bond angles (°)			
C(23)–Ti(1)–C(30)	102.5(1)	O(1)–Ti(1)–C(23)	102.5(1)
O(1)–Ti(1)–C(30)	102.2(1)	C(24)–C(23)-Ti(1)	130.0(2)
C(31)–C(30)–Ti(1)	112.1(2)	O(1)–Ti(1)–C(14)	90.80(9)
O(1)–Ti(1)–C(15)	89.83(9)	O(1)–Ti(1)–C(16)	120.1(1)
O(1)–Ti(1)–C(17)	146.33(8)	O(1)–Ti(1)–C(18)	123.9(1)
C(1)–O(1)–Ti(1)	150.3(2)	C(14)–Si(1)–C(2)	110.1(1)
Torsion angles (°)			
C(14)–Si(1)–C(2)–C(1)	−19.2(2)	Ti(1)–O(1)–C(1)–C(2)	11.8(5)



Scheme 2.



Scheme 4.

of the Ti–OMe bonds of **2**. Further hydrolysis did not occur in the reaction conditions. It is of interest that only one isomer, *cis* or *trans*, was obtained as evident from NMR analysis of **5**. Crystallization of **5** from methanol gave a single crystal suitable for X-ray analysis. An ORTEP drawing is shown in Fig. 2 and selected bond parameters are listed in Table 2. Two cyclopentadienyl moieties are located as *syn* geometry and two methoxy groups are placed as *anti* geometry. The torsion angles of ligand architectures [C(9)–Si(1)–C(1)–C(2), −29.7(2)°; C(32)–Si(2)–C(24)–C(25), −35.0(2)°] of **5** were larger than the value observed for **2** (−19.2(2)°), clearly indicating that the close position of the two ligands created a large strain on **5**.

1,3-Diene complexes **6**–**8** were synthesized by treating **1** with 2 equiv. of *n*-BuLi in the presence of the corresponding dienes in hexane [8,10]. After removal of the inorganic materials, recrystallization in hexane at −40 °C afforded the corresponding 1,3-diene complexes **6** (73% yield), **7** (52% yield), and **8** (34% yield). The lower yield of **8** was attributed to high solubility of **8** in hexane. There are two possible isomers (prone/supine) for *s-cis* diene complexes **6**–**8**, and their structures were characterized by ^{1}H NMR spectroscopy. Comparison of ^{1}H NMR spectral data obtained for these complexes with those reported for Ti(butadiene)($Me_4C_5SiMe_2NCMe_3$) (**B** and **C**) [11] suggested that coordination modes of 1,4-diphenylbutadiene of **6** and 2,5-hexadiene of **7** were prone, whereas that of 2,3-dimethyl-1,3-butadiene of **8** was revealed to be supine. Complex **B** displayed diene protons H*a*, H*b*, and H*c* at δ 4.15, 1.71, and 3.01, respectively, whereas **C** showed these protons at δ 6.33, 0.04 and 2.84, respectively. Chemical shifts of H*a* observed for **6** and **7** (**6**: δ 4.40, **7**: δ 3.83) corresponded to that of **B** (δ 4.15) rather than that of **C** (δ 6.33). On the other hand, chemical shifts of H*b* and H*c* for **8** were found at δ 0.49 and 2.77, respectively, and these values corresponded to those observed for **C** (δ 0.04 and 2.84). It was assumed that bulkiness of the two methyl groups at 2- and 3-positions of the diene moiety of **8** would cause steric repulsion against the methyl groups of tetramethylcyclopentadienyl moiety, and accordingly the diene coordinates in a supine form to the titanium atom.

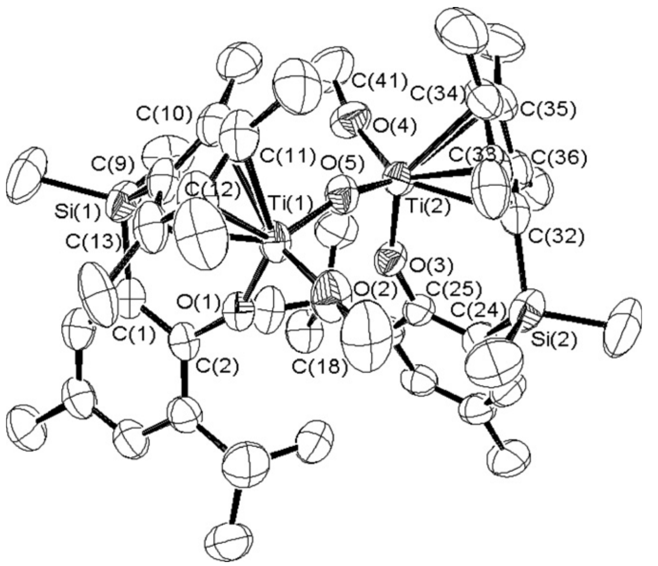
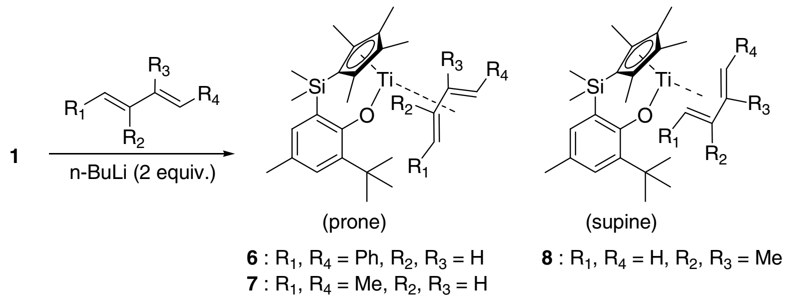


Fig. 2. ORTEP drawing of the molecular structure of **5**. All hydrogen atoms are omitted for clarity. Key atoms are labeled.

A single crystal of **6** suitable for X-ray analysis was obtained by recrystallization from hexane. Fig. 3 shows an ORTEP drawing, and selected bond parameters are



6 : R_1, R_4 = Ph, R_2, R_3 = H
7 : R_1, R_4 = Me, R_2, R_3 = H
8 : R_1, R_4 = H, R_2, R_3 = Me

Scheme 3.

Table 2
Selected bond length (Å) and angles (°) for **5**

Bond lengths (Å)			
Ti(1)–O(1)	1.846(2)	Ti(1)–O(2)	1.800(2)
Ti(1)–O(5)	1.829(2)	Ti(2)–O(3)	1.850(2)
Ti(2)–O(4)	1.798(2)	Ti(2)–O(5)	1.829(2)
Ti(1)–C(9)	2.322(3)	Ti(1)–C(10)	2.374(3)
Ti(1)–C(11)	2.402(3)	Ti(1)–C(12)	2.432(3)
Ti(1)–C(13)	2.377(3)	Ti(2)–C(32)	2.334(3)
Ti(2)–C(33)	2.380(3)	Ti(2)–C(34)	2.405(3)
Ti(2)–C(35)	2.436(3)	Ti(2)–C(36)	2.378(3)
Bond angles (°)			
Ti(1)–O(5)–Ti(2)	159.4(1)	O(2)–Ti(1)–O(1)	102.7(1)
O(5)–Ti(1)–O(1)	103.91(8)	O(2)–Ti(1)–O(5)	104.17(9)
O(4)–Ti(2)–O(3)	102.28(9)	O(5)–Ti(2)–O(3)	103.16(9)
O(4)–Ti(2)–O(5)	104.09(9)	O(1)–Ti(1)–C(9)	86.96(9)
O(1)–Ti(1)–C(10)	119.0(1)	O(2)–Ti(1)–C(11)	99.8(1)
O(1)–Ti(1)–C(12)	119.0(1)	O(1)–Ti(1)–C(13)	88.1(1)
O(3)–Ti(2)–C(32)	87.2(1)	O(3)–Ti(2)–C(33)	118.5(1)
O(3)–Ti(2)–C(34)	144.1(1)	O(3)–Ti(2)–C(35)	121.1(1)
O(3)–Ti(2)–C(36)	89.90(9)	C(2)–O(1)–Ti(1)	151.2(2)
C(25)–O(3)–Ti(2)	150.3(2)	C(9)–Si(1)–C(1)	108.6(1)
C(32)–Si(2)–C(24)	108.3(1)		
Torsion angles (°)			
C(9)–Si(1)–C(1)–C(2)	−29.7(2)	Ti(1)–O(1)–C(2)–C(1)	34.1(4)
C(32)–Si(2)–C(24)–C(25)	−35.0(2)	Ti(2)–O(3)–C(25)–C(24)	35.1(4)

Table 3
Selected bond length (Å) and angles (°) for **6**

Bond lengths (Å)			
Ti(1)–C(29)	2.216(2)	Ti(1)–C(30)	2.327(2)
Ti(1)–C(31)	2.324(2)	Ti(1)–C(32)	2.244(2)
Ti(1)–O(1)	1.874(2)	Ti(1)–C(14)	2.281(2)
Ti(1)–C(15)	2.310(2)	Ti(1)–C(16)	2.408(2)
Ti(1)–C(17)	2.452(2)	Ti(1)–C(18)	2.358(2)
C(29)–C(30)	1.411(3)	C(30)–C(31)	1.402(3)
C(31)–C(32)	1.419(3)		
Bond angles (°)			
C(29)–Ti(1)–C(32)	87.48(8)	O(1)–Ti(1)–C(14)	89.37(7)
O(1)–Ti(1)–C(15)	95.67(7)	O(1)–Ti(1)–C(16)	128.67(6)
O(1)–Ti(1)–C(17)	147.57(7)	O(1)–Ti(1)–C(18)	118.60(7)
C(6)–O(1)–Ti(1)	151.6(1)	C(14)–Si(1)–C(1)	111.2(1)
O(1)–Ti(1)–C(29)	93.83(7)	O(1)–Ti(1)–C(32)	100.52(5)
Torsion angles (°)			
C(14)–Si(1)–C(1)–C(6)	24.1(2)	Ti(1)–O(1)–C(6)–C(1)	−3.8(3)

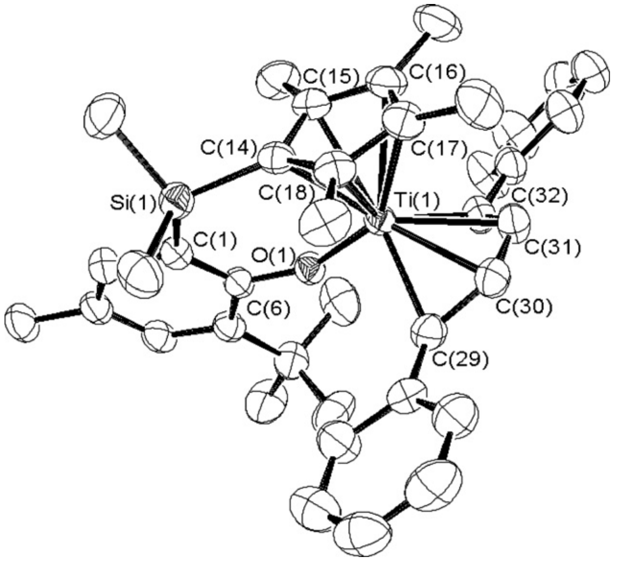


Fig. 3. ORTEP drawing of the molecular structure of **6**. All hydrogen atoms are omitted for clarity. Key atoms are labeled.

listed in Table 3. As expected from ^{1}H NMR analysis of **6**, the 1,4-diphenylbutadiene ligand coordinates in *s-cis*-diene fashion to the titanium atom with a prone orientation. The two Ti–C(terminal) diene distances (2.216(2) and 2.244(2) Å) differ by only 0.096 Å from the two Ti–C(internal) diene distances (2.324(2) and 2.327(2) Å), indicating that the diene moiety coordinates to the titanium atom with little contribution of σ^2,π form. The value of the difference is slightly smaller than that found for Ti(2,5-hexadiene)($Me_4C_5SiMe_2NCMe_3$) (0.112 Å) [7]. The torsion angle of the ligand architecture [24.1(2)° for C(14)–Si(1)–C(1)–C(6)] was smaller than that found for **5**.

Newly prepared complexes **2**–**8** along with **1** were applied as catalysts for copolymerization of ethylene and 1-hexene upon activation with Al^{i}Bu$_3$(TIBA) and [$C_6H_5NMe_2H$][$B(C_6F_5)_4$](AB) at different temperatures (40 and 130 °C). Results are listed in Table 4. All complexes showed similarly high activities at 40 °C ($>30\times10^6$ gmol(cat)$^{-1}$ h^{-1}) and gave high molecular weight copolymer (entries 1–8) with similar 1-hexene content. Molecular weight distribution (M_w/M_n) was found to be nearly 2.0, suggesting that single-site catalysts were generated through the polymerization systems. Activity of the dinuclear complex **5** was almost the same as that observed for the mononuclear methoxy complex **2**, suggesting that the reaction of **5** with cocatalyst resulted in the formation of the same mononuclear species (entries 2 and 5). This result seems reasonable, because both complexes [$(C_5H_5)_2ZrCl$]$_2$O and $(C_5H_5)_2ZrCl_2$ were reported to exhibit similar catalytic performance upon activation with MAO [12].

On the other hand, considerable differences among the tested complexes were found in the case of polymerization carried out at 130 °C (entries 9–16). Activities of the complexes were still high at the elevated temperature ($>5\times10^6$ gmol(cat)$^{-1}$ h^{-1}). Alkyl complexes **3** and **4** (entries 11 and 12) and diene complexes **6**–**8** (entries 14–16) showed higher activities than the chloro complex **1** (entry 9). Much higher activities were found for **7** and **8** (40.9×10^6 and 41.9×10^6 gmol(cat)$^{-1}$ h^{-1}, respectively), indicating that their 1,3-diene ligands dissociated readily under the reaction conditions to generate catalytically active species much faster and more effectively [7,8]. Worthy of note, the coordination mode (prone or supine) of the diene did not affect polymerization behavior (entries 15 and 16), indicating that both complexes gave the same active species. 1,3-Diphenylbutadiene complex **6** showed lower activity than **7** and **8**, indicating the

Table 4
Copolymerization of ethylene and 1-hexene catalyzed by **1**–**8** upon activation with TIBA/AB[a]

Entry	Complex	Temperature (°C)	Time (min)	Activity[b]	M_w[c]	M_w/M_n[c]	1-Hexene content[d]
1	**1**	40	5	61.6	635000	2.2	18
2	**2**	40	8	34.0	610700	2.0	14
3	**3**	40	8	51.3	502400	2.2	23
4	**4**	40	8	51.5	543400	2.1	15
5	**5**	40	8	38.4	770200	2.0	15
6	**6**	40	5	51.3	734600	1.9	17
7	**7**	40	5	43.6	759700	1.9	16
8	**8**	40	5	32.1	801800	1.9	17
9	**1**	130	3	6.6	198200	2.0	30
10	**2**	130	3	32.5	230300	2.5	20
11	**3**	130	3	27.0	235800	3.1	23
12	**4**	130	3	23.8	252700	2.5	24
13	**5**	130	3	9.1	318800	2.0	14
14	**6**	130	3	14.3	197300	2.8	33
15	**7**	130	3	40.9	245000	2.9	23
16	**8**	130	3	41.9	246300	2.3	21

[a] Conditions: toluene; 5 mL, 1-hexene; 60 μL (40 °C) and 40 μL (130 °C), ethylene; 0.6 MPa, complex; 0.1 μmol, TIBA; 40 μmol (40 °C) and 4 μmol (130 °C), AB; 0.3 μmol.

[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.

bulky diene ligand did not readily dissociate under the polymerization conditions. Polymerization activity observed for dinuclear complex **5** was lower than that found for mononuclear methoxy complex **2** (entries 10 and 13), indicating that breakage of the Ti–O–Ti bond sequence did not proceed smoothly at elevated temperature, resulting in a less reactive catalyst system. To confirm the efficiency of these new complexes, larger scale copolymerization of ethylene and 1-hexene with **7** was carried out in a 300 mL autoclave at 130 °C. The polymerization gave similarly high molecular weight copolymer ($M_w = 366{,}900$, Me branch = 26 per 1000 C) with high activity (67.2×10^6 gmol(cat)$^{-1}$ h^{-1}).

In conclusion, we prepared a series of PHENICS complexes by ligand exchange reaction, characterized them by X-ray analysis, and found that **1** was a novel starting material for preparing the complexes. Polymerization studies revealed that diene complexes **7** and **8** were useful precursors for the copolymerization of ethylene and 1-hexene at elevated temperature. More detailed polymerization behavior of these complexes will be reported elsewhere.

3. Experimental

3.1. General

All manipulations of air- and moisture-sensitive compounds were carried out 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. Complex **1** was prepared by a reported method [3a]. ^{1}H NMR (270 MHz) and ^{13}C NMR (68 MHz) were measured on a JEOL EX270 spectrometer. Mass spectra were recorded on a JEOL AX-505W. Elemental analyses were performed on 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 carried out at 160 °C using a Symyx RapidsGPC™, 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 vs. commercially available polystyrene standards (Polymer Laboratories).

3.2. *Dimethylsilyl(2,3,4,5-tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)-titanium dimethoxide (**2**)*

To a mixture of methanol (0.32 g, 10 mmol) and diethyl ether (40 mL) was added a 1.60 M solution of *n*-BuLi in hexane (4.1 mL, 6.6 mmol) at 0 °C. The reaction mixture was warmed to room temperature, and stirred for 30 min. Complex **1** (1.37 g, 3.0 mmol) was added to the reaction mixture cooled to 0 °C. After removal of the solvent, hexane (100 mL) was added to the mixture, and then insoluble materials were filtrated off. The solvent was removed and the crude product was recrystallized from hexane to give **2** as a yellow solid (0.95 g, 70% yield). Mp: 116–117 °C (dec). ^{1}H NMR (CD_2Cl_2) δ 0.46 (s, 6H, Si Me_2), 1.34 (s, 9H, *t-Bu*), 1.94 (s, 6H, C_5Me_4), 2.07 (s, 6H, C_5Me_4), 2.28 (s, 3H, Ar–*Me*), 4.09 (s, 6H, O*Me*), 7.05 (m, 2H, Ar–*H*); ^{13}C{^{1}H} NMR (CD_2Cl_2)δ −0.2 (Si Me_2), 10.5, 12.6, 20.4 (Ar–*Me*), 29.1 (Ar–C*Me*$_3$), 34.3 (Ar–*C*Me$_3$), 61.4 (O*Me*), 111.3, 126.4, 128.1, 128.5, 128.6, 130.4, 131.4, 135.5, 164.5. HRMS: *m*/*z* Calc. 450.5092, found 450.2086. Anal. Calc. for $C_{24}H_{38}O_3SiTi$: C, 63.98; H, 8.50. Found: C, 63.91; H, 8.53%.

3.3. Dimethylsilyl(2,3,4,5-tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)-titanium dimethyl (**3**)

To a mixture of **1** (2.30 g, 5.0 mmol) and diethyl ether (40 mL) was added a 1.0 M solution of MeLi in diethyl ether (10 mL) at −78 °C. The reaction mixture was warmed to room temperature, and stirred for 3 h. After removal of the solvent, hexane (100 mL) was added to the mixture and insoluble materials were filtrated off. The solvent was removed and the crude product was recrystallized from hexane to give **3** as a yellow solid (1.43 g, 68% yield). Mp: 136–137 °C (dec). ^{1}H NMR ($\mathrm{CD_2Cl_2}$)δ 0.33 (s, 6H, $\mathrm{Si}Me_2$), 0.39 (s, 6H, $\mathrm{Ti}Me_2$), 1.60 (s, 9H, *t-Bu*), 1.82 (s, 6H, C_5Me_4), 2.21 (s, 6H, C_5Me_4), 2.31 (s, 3H, Ar–*Me*), 7.01–7.05 (m, 1H, Ar–*H*), 7.13–7.18 (m, 2H, Ar–*H*); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$)δ −0.1 ($\mathrm{Si}Me_2$), 11.5, 12.8, 20.4 (Ar–*Me*), 29.3 (Ar–$\mathrm{C}Me_3$), 34.5 (Ar–$C\mathrm{Me_3}$), 52.4 (Ti–Me_2), 108.6, 128.4, 128.9, 130.0, 130.1, 130.2, 132.0, 135.2, 163.4. Anal. Calc. for $\mathrm{C_{24}H_{38}OSiTi}$: C, 68.88; H, 9.15. Found: C, 69.09; H, 8.75%.

3.4. Dimethylsilyl(2,3,4,5-tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)-titanium dibenzyl (**4**)

The same procedure as for **3** was followed except that benzyl magnesium bromide, prepared from benzyl bromide (1.71 g, 10 mmol) and magnesium (0.24 g, 10 mmol) in diethyl ether (25 mL), was used in place of MeLi to give **4** as an orange solid (1.80 g, 63% yield). Mp: 109–110 °C (dec). ^{1}H NMR ($\mathrm{CD_2Cl_2}$)δ 0.26 (s, 6H, $\mathrm{Si}Me_2$), 1.38 (s, 9H, *t-Bu*), 1.77 (s, 6H, C_5Me_4), 1.98 (s, 6H, C_5Me_4), 2.14–2.39 (m, 4H, $\mathrm{C}H_2\mathrm{Ph}\times 2$), 2.30 (s, 3H, Ar–*Me*), 6.77–6.90 (m, 5H, Ar–*H*), 6.98–7.09 (m, 5H, Ar–*H*), 7.12–7.16 (m, 1H, Ar–*H*); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$)δ −0.2 ($\mathrm{Si}Me_2$), 11.3, 12.7, 20.4 (Ar–*Me*), 29.7 (Ar–$\mathrm{C}Me_3$), 34.5 (Ar–$C\mathrm{Me_3}$), 82.5, 104.0, 121.9, 126.7, 127.5, 128.6, 130.1, 130.5, 130.7, 131.0, 132.4, 135.6, 148.5. Anal. Calc. for $\mathrm{C_{36}H_{46}OSiTi}$: C, 75.76; H, 8.12. Found: C, 75.98; H, 7.91%.

3.5. μ-Oxo complex (**5**)

A solution of **2** (0.90 g, 2.0 mmol) and toluene (10 mL) was stirred under air at room temperature for 20 h. After removal of the solvent, recrystallization from methanol gave **5** as a yellow solid (0.65 g, 76% yield). Mp: >250 °C. ^{1}H NMR ($\mathrm{CD_2Cl_2}$)δ 0.43 (s, 6H, $\mathrm{Si}Me\times 2$), 0.56 (s, 6H, $\mathrm{Si}Me\times 2$), 1.02 (s, 18H, *t-Bu*), 1.61 (s, 6H, C_5Me_4), 2.10 (s, 6H, C_5Me_4), 2.17 (s, 6H, C_5Me_4), 2.23 (s, 6H, C_5Me_4 or Ar–*Me*), 2.24 (s, 6H, C_5Me_4 or Ar–*Me*), 4.04 (s, 6H, O*Me*), 6.89 (d, 2H, $J = 2$ Hz, Ar–*H*), 6.96 (d, 2H, $J = 2$ Hz, Ar–*H*); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$)δ −1.3 (Si*Me*), 0.9 (Si*Me*), 10.8, 10.9, 11.6, 13.6, 20.4 (Ar–Me), 29.1 (Ar–$\mathrm{C}Me_3$), 34.0 (Ar–$C\mathrm{Me_3}$), 60.5, 111.5, 125.9, 126.2, 127.8, 127.9, 128.0, 130.0, 131.2, 132.0, 135.5, 165.8. Anal. Calc. for $\mathrm{C_{46}H_{70}O_5Si_2Ti_2}$: C, 64.62; H, 8.25. Found: C, 64.60; H, 8.10%.

3.6. Dimethylsilyl(2,3,4,5-tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)-titanium 1,4-diphenylbutadiene (**6**)

To a mixture of **1** (1.38 g, 3.0 mmol), *trans*,*trans*-1,4-diphenyl-1,3-butadiene (0.62 g, 3.0 mmol), and hexane (150 mL) was added a 1.6 M solution of *n*-BuLi in hexane (3.8 mL, 6.0 mmol) at −78 °C. The reaction mixture was warmed to room temperature, and stirred for 1 h. Afterwards, the mixture was heated to reflux for 1 h. After filtration of the insoluble materials, the solvent was removed under reduced pressure. Recrystallization from hexane gave **6** as a green solid (1.05 g, 73% yield). Mp: 126–127 °C (dec). ^{1}H NMR ($\mathrm{CD_2Cl_2}$)δ 0.25 (s, 6H, $\mathrm{Si}Me_2$), 1.29 (s, 9H, *t-Bu*), 1.44 (s, 6H, C_5Me_4), 1.52 (s, 6H, C_5Me_4), 2.30 (s, 3H, Ar–*Me*), 4.40 (m, 2H, diene), 4.70 (m, 2H, diene), 6.60–7.50 (m, 12H, Ar–*H*); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$)δ 0.1 ($\mathrm{Si}Me_2$), 10.7, 12.3, 22.0 (Ar–*Me*), 30.2 (Ar–$\mathrm{C}Me_3$), 37.0 (Ar–$C\mathrm{Me_3}$), 89.4, 105.0, 109.2, 123.7, 124.7, 127.5, 127.7, 128.4, 128.5, 136.7, 141.0, 166.9. Anal. Calc. for $\mathrm{C_{38}H_{46}OSiTi}$: C, 76.74; H, 7.80. Found: C, 76.98; H, 7.46%.

3.7. Dimethylsilyl(2,3,4,5-tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)-titanium 2,5-hexadiene (**7**)

The same procedure as for **6** was followed, except that 2,5-hexadiene (9.28 g, 9.0 mmol, a mixture of isomers) was used in place *trans*,*trans*-1,4-diphenyl-1,3-butadiene to give **7** as a green solid (0.73 g, 52% yield). Mp: 134–136 °C (dec). ^{1}H NMR ($\mathrm{CD_2Cl_2}$)δ 0.51 (s, 6H, $\mathrm{Si}Me_2$), 1.29 (s, 9H, *t-Bu*), 1.50 (s, 6H, C_5Me_4), 1.86 (s, 6H, C_5Me_4), 1.89 (d, $J = 5$ Hz, 6H, $\mathrm{C}H_3\mathrm{{-}CH{=}CH{-}CH{=}CH{-}C}H_3$), 2.36 (s, 3 H, Ar–*Me*), 2.48 (m, 2H, diene), 3.83 (m, 2H, diene), 6.96–6.97 (m, 2H, Ar–*H*), 7.03–7.04 (m, 2H, Ar–*H*); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$)δ −0.1 ($\mathrm{Si}Me_2$), 10.7, 12.5, 17.1, 20.3 (Ar–*Me*), 28.9 (Ar–$\mathrm{C}Me_3$), 33.9 (Ar–$C\mathrm{Me_3}$), 81.8, 110.8, 116.0, 120.8, 124.9, 127.7, 128.0, 128.2, 131.8, 136.3, 155.8 (Ar*C*–O). HRMS: *m*/*z* Calcd 470.2484. Found: 470.2470. Anal. Calc. for $\mathrm{C_{28}H_{42}OSiTi}$: C, 71.46; H, 9.00. Found: C, 71.61; H, 9.07%.

3.8. Dimethylsilyl(2,3,4,5-tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)-titanium 2,3-dimethylbutadiene (**8**)

The same procedure as for **6** was followed, except that 2,3-dimethyl-1,3-butadiene (9.28 g, 9.0 mmol) was used in place *trans*,*trans*-1,4-diphenyl-1,3-butadiene to give **8** as a purple solid(0.48 g, 34% yield). Mp: 128–130 °C (dec). ^{1}H NMR ($\mathrm{CD_2Cl_2}$)δ 0.48 (s, 6H, $\mathrm{Si}Me_2$), 0.49 (d, $J = 9$ Hz, 2H, $\mathrm{CH}H\mathrm{{=}CHMe{-}CHMe{=}CH}H$), 1.03 (s, 9H, *t-Bu*), 1.69 (s, 6H), 1.89 (s, 6H), 2.03 (s, 6H), 2.36 (s, 3H, Ar–*Me*), 2.77 (d, $J = 9$ Hz, 2H, $\mathrm{C}H\mathrm{H{=}CHMe{-}CHMe{=}C}H\mathrm{H}$), 6.97–7.03 (m, 2H, Ar–*H*), 7.07–7.13 (m, 2H, Ar–*H*); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$)δ −0.6 ($\mathrm{Si}Me_2$), 10.9, 12.8, 20.2

Table 5
Crystal data and data collection parameters for **4**–**6**

	4	**5**	**6**
Empirical formula	$C_{36}H_{46}OSiTi$	$C_{46}H_{70}O_5Si_2Ti_2$	$C_{38}H_{46}OSiTi$
Formula weight	570.74	855.03	594.77
Crystal dimensions	0.2 × 0.1 × 0.1 mm	0.4 × 0.2 × 0.2 mm	0.4 × 0.3 × 0.3 mm
Crystal system	Triclinic	Orthorhombic	Triclinic
a (Å)	9.6435(7)	19.0002(6)	11.8330(9)
b (Å)	9.9040(6)	20.5565(6)	11.8521(9)
c (Å)	18.390(1)	24.7946(7)	12.6002(9)
α (°)	79.442(4)	90	101.967(5)
β (°)	77.204(5)	90	103.097(5)
γ (°)	73.478(4)	90	99.170(5)
V (Å^3)	1628.4(2)	9684.2(5)	1643.8(2)
Space group	$P\bar{1}$(#2)	$Pbca$ (#61)	$P\bar{2}$(#2)
Z-value	2	8	2
D_{calc} (g/cm^3)	1.164	1.173	1.202
$2\theta_{max}$ (°)	143.2	143.6	136.4
Number of reflections measured	Total: 19069 Unique: 5611 ($R_{int} = 0.039$)	Total: 95329 Unique: 9271 ($R_{int} = 0.083$)	Total: 18114 Unique: 5818 ($R_{int} = 0.068$)
Residuals: R ($I > 2\sigma(I)$)	0.0558	0.0574	0.0418
Residuals: R (all refractions)	0.0606	0.0671	0.0507
Goodness-of-fit indicator	1.071	1.077	1.085

(Ar–*Me*), 23.1, 29.2 (Ar–C*Me*$_3$), 34.2 (Ar–*C*Me$_3$), 74.7, 123.8, 125.3, 126.7, 128.1, 128.9, 129.7, 131.9, 132.0, 166.3 (Ar*C*–O). HRMS: m/z calcd 470.2484, found 470.2488. Anal. Calc. for $C_{28}H_{42}OSiTi$: C, 71.46; H, 9.00. Found: C, 71.76; H, 8.96%.

3.9. Crystallographic analyses of **4**, **5** and **6**

Crystals of **4**–**6** suitable for the X-ray diffraction study were coated with paratone oil and mounted with nylon loop in cold nitrogen gas, and intensity data were collected at –180 °C on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Cu Kα radiation. The structure was solved by a direct method (SHELX97) and refined by the full-matrix least-squares method [13]. Crystal data and details of refinement are summarized in Table 5. All calculations were performed using the CrystalStructure crystallographic software package (Rigaku/MSC).

3.10. Copolymerization of ethylene with 1-hexene catalyzed by **1**–**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 TIBA (160 μL), 1-hexene (60 μL; 40 °C, 40 μL; 130 °C) 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 titanium 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 until 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.

3.11. Copolymerization of ethylene with 1-hexene catalyzed by 7 in 300 mL autoclave

An autoclave having an inner volume of 300 mL was dried under vacuum and purged with nitrogen. The vessel was then charged with toluene (150 mL) and 1-hexene (1.2 mL), and then heated to 130 °C. After ethylene was introduced (0.6 MPa), TIBA (0.05 mmol, 0.25 M toluene solution) was added. Subsequently, **7** (0.05 μmol, 1 mM toluene solution) and AB (0.3 μmol, 6 mM toluene solution) were added. Polymerization was carried out at 130 °C for 5 min, and 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 material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.06.012.

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