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Synthesis and characterization of phosphorous-bridged bisphenoxy titanium complexes and their application to ethylene polymerization

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Abstract

Phosphorous-bridged bisphenoxy titanium complexes were synthesized and their ethylene polymerization behavior was investigated. Bis[3-*tert*-butyl-5-methyl-2-phenoxy](phenyl)phosphine tetrahydrofuran titanium dichloride (**4a**) was obtained by treatment of 3 equiv of *n*-BuLi with bis[3-*tert*-butyl-2-hydroxy-5-methylphenyl](phenyl)phosphine hydrochloride salt (**3a**) followed by $TiCl_4(THF)_2$ in THF. THF-free complexes **5a**–**5d** were synthesized more conveniently by the direct reaction of MOM-protected ligands (**2a**–**2d**) with $TiCl_4$ in toluene. X-ray analysis of **4a** revealed that the ligand is bonded to the octahedral titanium (IV) center in a facial fashion and two chlorine atoms possess *cis*-geometry. Complexes **4a** and **5a**–**5d** were utilized as catalyst precursors for ethylene polymerization. Complex **5c** gave high molecular weight polyethylene ($M_w = 1,170,000$, $M_w/M_n = 2.0$) upon activation with $Al(^iBu)_3/[Ph_3C][B(C_6F_5)_4]$ (TB). Ethylene polymerization activity of **5d** activated with $Al(^iBu)_3$/TB reached 49.0×10^6 g mol (cat) $^{-1}$ h^{-1}.
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Keywords: Titanium; Phosphorous-bridged bisphenoxy ligand; Polymerization catalyst

1. Introduction

Olefin polymerization by metallocene [1] and post metallocene catalysis [2] has attracted much interest in the past two decades. Among these catalyst systems, early transition metal complexes with phenoxy ligands have been one of the most attractive and extensively studied target catalysts in polymerization chemistry [3]. Titanium complexes with bridged bis(aryloxo) ligands also have been studied due to their unique polymerization behavior: Kakugo and Miyatake reported pioneering work in this field using Ti(tbmp)Cl$_2$ (**A**), tbmp = 2,2′-thiobis(2-*tert*-butyl-4-methylphenoxy), which is a highly active catalyst for not only homo polymerization but also copolymerization of α-olefins, resulting in high molecular weight polyethylene and polypropylene, syndiotactic polystyrene and isotactic poly(ethylene-*alt*-styrene) [4]. A variety of bridging groups, such as SO$_2$ [5], tellurium [6], *N*-heterocyclic carbine [7], ethylene [8], 1,4-dithiabutane [9] have been studied. Okuda recently reported 1,4-dithiabutane-bridged bisphenoxy complex **B** is an excellent catalyst for isospecific styrene polymerization [9]. Kol and his group reported that bisphenoxyamine zirconium complex **C**, which has a side-arm donor, is highly active for polymerization of 1-hexene [10], and also reported bisphenoxy zirconium complex **D**, which has two nitrogen atoms in the bridging group, catalyzes the isoselective living polymerization of 1-hexene [11]. Non-bridged phenoxy complexes have been attractive catalyst precursors: Fujita and coworkers reported that phenoxy-imine zirconium complexes show very high activity for ethylene polymerization [12]. Moreover, Fujita and Coates independently reported that fluorine substituted phenoxy-imine titanium complexes catalyze syndiospecific living polymerization of propylene [13].

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A

B

C

D
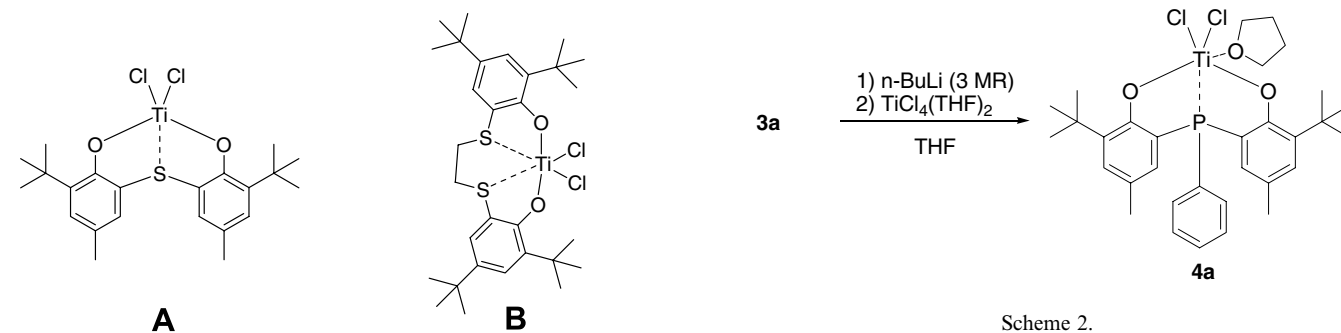
Scheme 2.
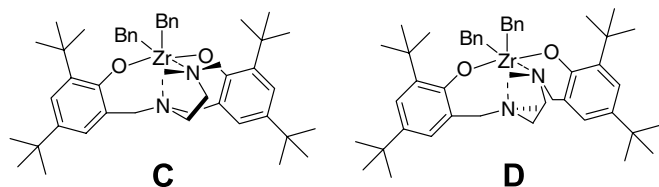
We have been interested in phosphorous incorporated complexes, whose unique properties are recently reported for phenoxyimine [14] and half-metallocenes of group 4 metals [15] as well as rare earth metals [16]. Herein we report the synthesis of phosphorous-bridged bisphenoxy titanium complexes and their catalytic behavior for ethylene polymerization. Additionally, we found an efficient synthesis of the complexes and the effect of a side-arm donor on the phosphorus atom on polymerization behavior.

2. Results and discussion

Scheme 1 shows the synthesis of a new ligand bis[3-*tert*-butyl-2-hydroxy-5-methylphenyl](phenyl)phosphine hydrochloride salt (**3a**) from 2-*tert*-butyl-1-(methoxymethoxy)-4-methylbenzene (**1**). Lithiation of **1** using *n*-BuLi at −78 °C followed by addition of a half equivalent of dichlorophenylphosphine afforded bis[3-*tert*-butyl-2-methoxymethoxy-5-methylphenyl](phenyl)phosphine (**2a**) as a
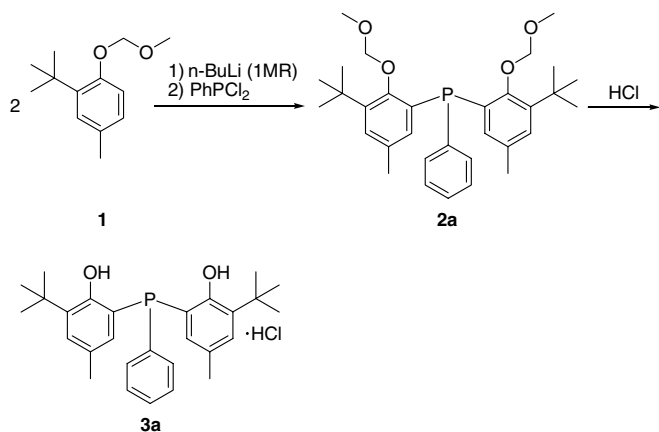
white solid (65% yield). The lithiation proceeded selectively at *ortho* position due to the MOM protected group [17]. Treatment of **2a** with HCl in methanol deprotected the MOM group to give an HCl salt of phenol derivative **3a** in 90% yield. It is notable that the formation of the salt **3a** caused phosphorous moiety to be stable in air, leading to easy handling on a large scale.

We prepared a titanium complex **4a** by reaction of the dilithium salt of **3a**, which was obtained by treating with 3 equiv of *n*-BuLi and TiCl$_4$(THF)$_2$ in THF (Scheme 2). Compound **4a** was characterized by NMR and mass spectroscopy, together with X-ray analysis. The ^{1}H NMR spectrum of **4a** displayed signals due to diphenolic phosphine ligand and THF in an exact 1:1 ratio, indicating that one THF coordinated to the titanium center. In the ^{31}P{^{1}H} NMR spectrum of **4a**, a singlet signal was observed at 18.5 ppm. The chemical shift value was shifted downfield, typically indicating that the phosphorous atom coordinated to the titanium atom [14,18]. It is assumed likely that the titanium atom adopted octahedral geometry with two oxygen atoms and a phosphine atom in a facial geometry and two chlorines and one oxygen of THF occupying the remaining three coordination sites. Thus, two chloride
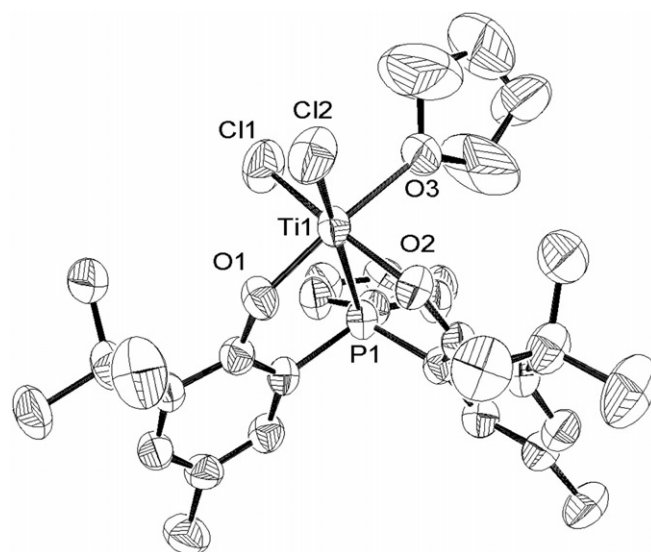

Scheme 1.

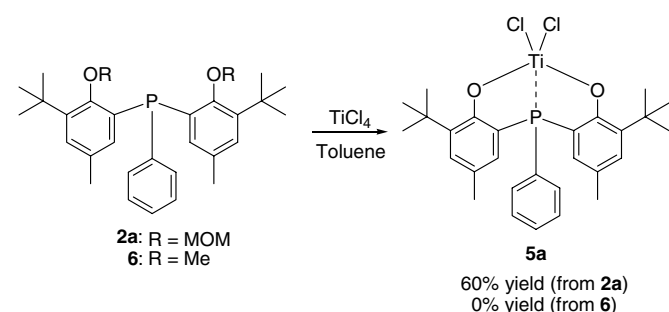Fig. 1. ORTEP drawing of the molecular structure of **4a**. All hydrogen atoms are omitted for clarity. Key atoms are labeled.

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

Bond lengths (Å)			
Ti(1)–Cl(1)	2.321(2)	Ti(1)–Cl(2)	2.281(2)
Ti(1)–P(1)	2.620(2)	Ti(1)–O(1)	1.822(3)
Ti(1)–O(2)	1.864(4)	Ti(1)–O(3)	2.143(4)
Bond angles (°)			
Cl(1)–Ti(1)–Cl(2)	103.18(7)	Cl(1)–Ti(1)–P(1)	86.53(6)
Cl(1)–Ti(1)–O(1)	89.7(1)	Cl(1)–Ti(1)–O(2)	157.1(1)
Cl(1)–Ti(1)–O(3)	84.7(1)	Cl(2)–Ti(1)–P(1)	169.38(7)
Cl(2)–Ti(1)–O(1)	100.0(1)	Cl(2)–Ti(1)–O(2)	97.5(1)
Cl(2)–Ti(1)–O(3)	93.4(1)	P(1)–Ti(1)–O(1)	75.4(1)
P(1)–Ti(1)–O(2)	73.8(1)	P(1)–Ti(1)–O(3)	91.8(1)
O(1)–Ti(1)–O(2)	96.3(2)	O(1)–Ti(1)–O(3)	166.4(2)

2b: R = *tert*-Bu
2c: R = C$_6$H$_4$-2-CH$_2$NMe$_2$
2d: R = C$_6$F$_5$

5b: R = *tert*-Bu
5c: R = C$_6$H$_4$-2-CH$_2$NMe$_2$
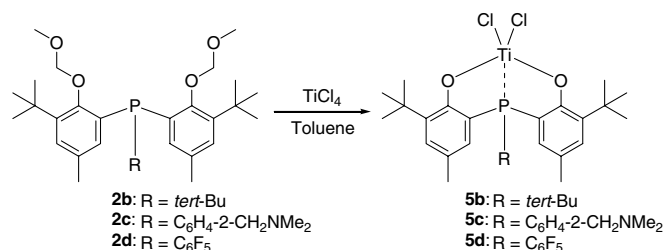**5d**: R = C$_6$F$_5$

Scheme 4.

atoms possessed *cis*-geometry, required as a polymerization catalyst. These structural features were revealed by X-ray analysis of **4a** (Fig. 1).

A single crystal of **4a** suitable for X-ray diffraction study was grown from toluene at room temperature. Fig. 1 shows an ORTEP diagram, and Table 1 lists selected bond parameters. The ligand is bonded to the octahedral titanium (IV) center in a facial fashion with titanium–phosophine distance 2.620 Å, a value comparable to that found for TiCl$_4$(dppe) (average 2.650 Å) [18]. The titanium–oxygen bond distances (1.822 and 1.864 Å) are slightly shorter than those (average 1.888 Å) observed for [Ti(tbmp)(O*i*Pr)$_2$]$_2$ [19]. The angle of O(1)–Ti(1)–O(2) is 96.3°, a value which is a little larger than that observed for [Ti(tbmp)(O*i*Pr)$_2$]$_2$ (92.5°) [19]. Titanium–chlorine bond distances lie in a range of 2.281–2.321 Å, and the angle of Cl(1)–Ti(1)–Cl(2) is 103.18°.

THF-free titanium complex **5a** was prepared by the reaction of **2a** with TiCl$_4$ in toluene in 60% yield. This reaction was more convenient and economical because the deprotection process, forming **3a**, was eliminated. Methoxymethylchloride was observed in the reaction mixture by ^{1}H NMR analysis, indicating C–O cleavage selectively occurred at the aryl methoxymethyl ether position. The same treatment for the methyl ether derivative, bis(3-*tert*-butyl-2-methoxy-5-methylphenyl)(phenyl)phosphine (**6**), did not give **5a**, but an unidentified mixture, which is probably due to the strong C–O bond strength of Ar–OMe (Scheme 3). Complex **5a** is expected to exist as a dimer sim-

ilar to thiobisphenoxy titanium complex [19]. It is notable that TiCl$_4$ induced the C–O cleavage and selective Ti–O bond formation when an appropriate protecting group was chosen [20].

We assumed that other bisphenoxy titanium complexes with different substituents could be synthesized by this method (Scheme 4). Compounds **2b**–**2d**, prepared in the same manner as for **2a** (68%, 42% and 62% yield, respectively), were applied to the tandem deprotection and Ti–O bond formation reaction, giving a *tert*-butylphosphine complex **5b** (62% yield), a 2-(dimethylaminomethyl)-phenylphosphine complex **5c** (56% yield), and a pentafluorophenyl complex **5d** (69% yield), respectively. In the ^{31}P{^{1}H} NMR spectra of these complexes, **5b**–**5d**, the chemical shift values were shifted downfield, indicating that the phosphorous atom also coordinated to the titanium atom. Complex **5c** is expected to show unique properties, because it has a nitrogen atom as a side-arm donor. Methyl groups on the nitrogen atom of **5c** are observed as two singlet peaks in its ^{1}H NMR spectrum, suggesting the coordination of the nitrogen atom to the titanium atom.

The complexes obtained were utilized as catalyst precursors for ethylene polymerization. The polymerization experiments were carried out in a 20 mL autoclave. MMAO or Al(*i*-Bu)$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] (TB) was employed as an activator. The results of ethylene homo polymerization reaction with **4a** and **5a**–**d** are summarized in Table 2. The

Table 2
Polymerization of ethylene catalyzed by phosphorous-bridged bisphenoxytitanium complexes with co-catalysts[a]

Entry	Catalyst	Co-catalyst[b]	Activity[c]	M_w[d]$\times10^{-3}$	M_w/M_n[d]
1	**4a**	I	1.0	–	–
2	**5a**		1.3	–	–
3	**5b**		1.2	–	–
4	**5c**		36.2	1700	6.2
5	**5d**		59.9	166	7.0
6	**4a**	II	1.3	–	–
7	**5a**		1.9	–	–
8	**5b**		3.7	–	–
9	**5c**		8.8	1170	2.0
10	**5d**		49.0	34	2.7

[a] Conditions: toluene; 5 mL, ethylene; 0.6 MPa, temperature; 40 °C.
[b] I: catalyst; 0.1 μmol, MMAO; 100 μmol. II: catalyst; 0.1 μmol, TIBA; 40 μmol, TB; 0.3 μmol.
[c] In kg mmol (cat)$^{-1}$ h^{-1}.
[d] Determined by GPC against polystyrene standards.

2a: R = MOM
6: R = Me

5a
60% yield (from **2a**)
0% yield (from **6**)

Scheme 3.

ethylene polymerization activities were found to be quite excellent in all cases and comparable to those observed in Ti(tbmp)Cl$_2$ [4,5] and phosphinophenoxyimine titanium [14] systems. THF seemed to be liberated from **4a** when it was activated by aluminium co-catalyst, as the activity of **4a** was almost the same as that of THF free complex **5a**. It is of interest that fluorophenyl-substituted complex **5c** and dimethylaminobenzyl-substituted complex **5d** showed greater activities than hydrocarbon-substituted complexes **5a** and **5b** (entries 4, 5, 9, and 10). We assumed that a heteroatom of the aromatic ring attached to phosphorus coordinated to the active titanium cation species, resulting in the stabilization of catalytically active species. Polymers with narrow molecular distribution ($M_w/M_n = 2.0$ and 2.7) were obtained when **5c** and **5d** were activated with TB (entries 9 and 10), showing single site catalysts were generated through the polymerization systems. Molecular weight of polyethylene obtained with **5c** was very high (>1,000,000), indicating that β-elimination of active species derived from **5c** was thought to be restrained by side-arm nitrogen atom. To confirm the efficiency of **5c**, larger scale polymerization was carried out in a 300 mL autoclave. The polymerization gave similarly high molecular weight polyethylene ($M_w = 1,129,000$, $M_w/M_n = 2.0$) with high activity (28.8×10^6 gmol (cat)$^{-1}$ h^{-1}). Further application of the phosphorous-bridged bisphenoxy titanium complexes and combinations of these ligands with other metals are currently in progress.

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. 2-*tert*-Butyl-1-(methoxymethoxy)-4-methylbenze (**1**) [21] and dichloro-(pentafluorophenyl)phosphine [22] were synthesized by published methods. Dichloro(2-dimethylaminomethylphenyl)phosphine was prepared by the reaction of phosphorus trichloride and the lithium salt of *N*,*N*-dimethylbenzylamine [23]. Solvents were purchased from Kanto Chemicals Co., Ltd. as anhydrous grade and stored in a drybox over molecular sieves. Dichloromethane-*d*$_2$ was purchased from Aldrich and stored in a drybox over molecular sieves. ^{1}H NMR (270 MHz), ^{13}C NMR (68 MHz) and ^{31}P NMR (109 MHz) spectra were measured on a JEOL EX270 spectrometer. Mass spectra were recorded on a JEOL AX-505 W. Elemental analyses were performed on an ELEMENTAR element analyzer at Sumika Chemical Analysis Service Ltd. 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 against commercially available polystyrene standards (Polymer Laboratories).

3.2. Bis[3-tert-butyl-2-methoxymethoxy-5-methylphenyl](phenyl)phosphine (2a)

To a solution of 2-*tert*-butyl-1-(methoxymethoxy)-4-methylbenze (10.41 g, 50.0 mmol) in THF (100 mL) was added a 1.60 M hexane solution of *n*-BuLi (31.3 mL, 50.0 mmol) at −78 °C. The mixture was allowed to warm to 20 °C and additionally stirred for 12 h. Dichlorophenylphosphine (4.47 g, 25.0 mmol) was added to the reaction mixture cooled at −78 °C. The mixture was allowed to warm to 20 °C and stirred for 2 h. Water and toluene were added to the mixture, and the organic layer was separated. The organic layer was washed with saturated aqueous NaCl and dried over Na$_2$SO$_4$. Removal of the solvent followed by chromatography on silica (hexane/EtOAc) gave **1a** as white solid (8.50 g, 65% yield).

^{1}H NMR (CDCl$_3$) δ 1.40 (s, 18H, Ar–*t*-Bu), 2.13 (s, 6H, Ar–C*H*$_3$), 3.51 (s, 6H, O*Me*), 5.14–5.23 (m, 4H, ArO–C*H*$_2$–OMe), 6.39 (dd, 2H, *J* = 4, 2 Hz, Ar–*H*), 7.14 (d, 2H, *J* = 2 Hz, Ar–*H*), 7.23–7.31 (m, 5H, Ar–*H*); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 21.1 (Ar–*C*H$_3$), 30.8 (Ar–*C*Me$_3$), 35.1 (Ar–*C*Me$_3$), 57.3 (ArO*C*H$_2$O*Me*), 99.5 (ArO*C*H$_2$OMe), 128.2 (Ar*C*–H), 129.5 (Ar*C*–H), 131.7, 133.1, 133.2 (Ar*C*–H), 133.6 (Ar*C*–H), 142.8 (Ar*C*–P), 156.2 (Ar*C*–OCH$_2$OMe); ^{31}P{^{1}H} NMR (CDCl$_3$) δ −18.6. Anal. Calc. for C$_{32}$H$_{43}$O$_4$P: C, 73.54; H, 8.29. Found: C, 73.33; H, 8.27%.

3.3. Bis[3-tert-butyl-2-methoxymethoxy-5-methylphenyl](tert-butyl)phosphine (2b)

Reaction of 2-*tert*-butyl-1-(methoxymethoxy)-4-methylbenze with *tert*-butyldichlorophosphine produced **2b** as white solid (8.54 g, 68% yield).

^{1}H NMR (CDCl$_3$) δ 1.11 (d, 9H, *J*$_{P–H}$ = 13 Hz, P–*t*-Bu), 1.42 (s, 18H, Ar–*t*-Bu), 2.25 (s, 6H, Ar–C*H*$_3$), 3.62 (s, 6H, O*Me*), 5.12–5.18 (m, 2H, ArO–C*H*$_2$–OMe), 5.48–5.54 (m, 2H, ArO–C*H*$_2$–OMe), 7.01 (t, 2H, *J* = 2 Hz, Ar–*H*), 7.14 (d, 2H, *J* = 2 Hz, Ar–*H*); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 21.3 (Ar–*C*H$_3$), 29.6 (d, *J*$_{P–C}$ = 15 Hz, P–*C*Me$_3$), 30.9 (Ar–*C*Me$_3$), 32.6 (d, *J*$_{P–C}$ = 18 Hz, P–*C*Me$_3$), 35.1 (Ar–*C*Me$_3$), 57.4 (ArO*C*H$_2$O*Me*), 99.7 (ArO*C*H$_2$OMe), 129.1 (Ar*C*–H), 130.9, 132.0, 133.5 (Ar*C*–H), 143.0, 157.0 (Ar*C*–O); ^{31}P{^{1}H} NMR (CDCl$_3$) δ −4.7. Anal. Calc. for C$_{30}$H$_{47}$O$_4$P: C, 71.68; H, 9.42. Found: C, 71.65; H, 9.40%.

3.4. Bis[3-tert-butyl-2-methoxymethoxy-5-methylphenyl]-[2-(dimethylaminomethyl)-phenyl]phosphine (2c)

Reaction of 2-*tert*-butyl-1-(methoxymethoxy)-4-methylbenze with dichloro(2-dimethylaminomethylphenyl)phosphine produced **2c** as white solid (6.08 g, 42% yield).

^{1}H NMR (CDCl$_3$) δ 1.40 (s, 18H, Ar–*t*-Bu), 2.09 (s, 6H, Ar–C*H*$_3$ or N*Me*$_2$), 2.11 (s, 6H, Ar–C*H*$_3$ or N*Me*$_2$), 3.50 (s, 6H, ArO*C*H$_2$O*Me*), 3.56 (s, 2H, C*H*$_2$NMe$_2$), 5.10–5.28 (m, 4H, ArO–C*H*$_2$–OMe), 6.36 (dd, 2H, *J* = 4, 3 Hz, Ar–*H*), 6.88 (ddd, 1H, *J* = 8, 4, 1 Hz, Ar–*H*), 7.08–7.16 (m, 3H,

Ar–*H*), 7.24–7.34 (m, 1H, Ar–*H*), 7.44–7.52 (m, 1H, Ar–*H*); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 21.2 (Ar–*C*H$_3$), 30.8 (Ar–*CMe*$_3$), 35.1 (Ar–*C*Me$_3$), 45.1 (N*Me*$_2$), 57.3 (ArO-CH$_2$O*Me*), 62.3 (*C*H$_2$NMe$_2$), 99.2 (ArO*C*H$_2$OMe), 126.9 (Ar*C*–H), 128.4 (Ar*C*–H), 128.6 (Ar*C*–H), 129.1 (Ar*C*–H), 131.5, 132.9, 133.5 (Ar*C*–H), 142.6, 155.9 (Ar*C*–O); ^{31}P{^{1}H} NMR (CDCl$_3$) δ −27.1. Anal. Calc. for C$_{35}$H$_{50}$NO$_4$P: C, 72.51; H, 8.69; N, 2.42. Found: C, 72.58; H, 8.68; N, 2.21%.

3.5. Bis[3-tert-butyl-2-methoxymethoxy-5-methylphenyl](pentafluorophenyl)phosphine (2d)

Reaction of 2-*tert*-butyl-1-(methoxymethoxy)-4-methyl-benze with dichloro(pentafluorophenyl)phosphine produced **2d** as white solid (9.50 g, 62% yield).

^{1}H NMR (CDCl$_3$) δ 1.40 (s, 18H, Ar–*t-Bu*), 2.18 (s, 6H, Ar–C*H*$_3$), 3.50 (s, 6H, ArOCH$_2$O*Me*), 5.15–5.28 (m, 4H, ArO–C*H*$_2$–OMe), 6.50–6.55 (m, 2H, Ar–*H*), 7.16–7.20 (m, 2H, Ar–*H*); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 21.2 (Ar–*C*H$_3$), 30.9 (Ar–*CMe*$_3$), 35.1 (Ar–*C*Me$_3$), 57.3 (ArO-CH$_2$O*Me*), 99.5 (ArO*C*H$_2$OMe), 127.9, 128.2, 130.4 (Ar*C*–H), 132.1 (Ar*C*–H), 133.6, 143.1, 155.7 (Ar*C*–O); ^{31}P{^{1}H} NMR (CDCl$_3$) δ −31.0. Anal. Calc. for C$_{32}$H$_{38}$F$_5$O$_4$P: C, 62.74; H, 6.25. Found: C, 62.74; H, 6.23%.

3.6. Bis[3-tert-butyl-2-hydroxy-5-methylphenyl](phenyl)-phosphine hydrochloride salt (3a) by deprotection of 2a

To the solution of **2a** (3.62 g, 6.9 mmol) in a mixture of methanol (40 mL) and EtOAc (40 mL) was added acetyl chloride (2.72 g, 34.6 mmol) at 0 °C. The mixture was allowed to warm to 20 °C and additionally stirred for 12 h. Removal of the solvent followed by recrystallization from toluene gave **3a** as white solid (2.72 g, 90% yield).

^{1}H NMR (CDCl$_3$) δ 1.42 (s, 18H, Ar–*t-Bu*), 2.23 (s, 6H, Ar–C*H*$_3$), 6.63 (dd, 2H, *J* = 13, 2 Hz, Ar–*H*), 7.41 (d, 2H, *J* = 2 Hz, Ar–*H*), 7.46–7.61 (m, 4H, Ar–*H*), 7.64–7.73 (m, 1H, Ar–*H*), 8.40 (br, 2H, ArO–*H*), 13.18 (br, 1H, *H*Cl); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 20.0 (Ar–*C*H$_3$), 29.8 (Ar–*CMe*$_3$), 35.2 (Ar–*C*Me$_3$), 129.8 (Ar*C*–H), 130.8 (Ar*C*–H), 131.6, 133.4 (Ar*C*–H), 133.6, 133.7 (Ar*C*-H), 134.9 (Ar*C*–H), 142.2, 157.1 (2 C, Ar*C*–O); ^{31}P{^{1}H} NMR (CDCl$_3$) δ −14.9. Anal. Calc. for C$_{28}$H$_{36}$ClO$_2$P: C, 71.40; H, 7.70. Found: C, 71.52; H, 7.76%.

3.7. Bis[3-tert-butyl-5-methyl-2-phenoxy](phenyl)-phosphine tetrahydrofuran titanium dichloride (4a)

To a solution of **3a** (0.25 g, 0.5 mmol) in tetrahydrofuran (10 mL) was added a 1.60 M hexane solution of *n*-BuLi (0.63 mL, 1.0 mmol) at −78 °C. The mixture was stirred for 12 h at 20 °C then cooled again to −78 °C. To the mixture was added a solution of titanium tetrachloride tetrahydrofuran complex (0.18 g, 0.5 mmol) in tetrahydrofuran (5 mL) then warmed to 20 °C. After the mixture was stirred

for 12 h, the solvent was removed under reduced pressure. Toluene was added to the residue, subsequently the insoluble material was filtrated off. Evaporation of solvent followed by crystallization from toluene gave **4a** as red crystals (0.15 g, 45% yield).

^{1}H NMR (CD$_2$Cl$_2$) δ 1.32 (s, 18H, Ar–*t-Bu*), 1.71–1.78 (m, 4H, THF), 2.14 (s, 3H, Ar–C*H*$_3$), 4.04–4.14 (m, 4H, THF), 6.78–6.88 (m, 2H, Ar–*H*), 7.02–7.12 (m, 2H, Ar–*H*), 7.35–7.52 (m, 3H, Ar–*H*), 7.58–7.68 (m, 2H, Ar–*H*); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 23.0 (Ar–*Me*), 25.7 (THF), 29.5 (Ar–*CMe*$_3$), 35.2 (Ar–*C*Me$_3$), 74.7 (THF), 129.4 (Ar*C*–H), 130.5 (Ar*C*–H), 131.3 (Ar*C*–H), 131.9 (Ar*C*–H), 132.7 (Ar*C*–H), 132.9, 133.9, 136.7, 139.5, 170.8 (Ar*C*–O); ^{31}P NMR (CDCl$_3$) δ 18.5. EI-MS: *m/z* 550 (M$^+$−THF), 515 (M$^+$−THF−Cl). Anal. Calc. for C$_{32}$H$_{41}$Cl$_2$O$_3$PTi: C, 61.65; H, 6.63. Found: C, 61.40; H, 6.37%.

3.8. Bis[3-tert-butyl-5-methyl-2-phenoxy](phenyl)-phosphine titanium dichloride (5a)

To a solution of **2a** (0.52 g, 1.0 mmol) and toluene (20 mL) was added a solution of titanium tetrachloride (0.23 g, 1.2 mmol) in toluene (20 mL) at −78 °C. The mixture was allowed to warm to 20 °C and was stirred for 20 h. After removal of the solvent by evaporation to 5 mL, complex deposited was collected by filtration. Recrystallization from toluene gave **5a** (0.33 g, 60% yield) as red solid.

^{1}H NMR (CD$_2$Cl$_2$) δ 1.36 (s, 18H, Ar–*t-Bu*), 2.25 (s, 6H, Ar–C*H*$_3$), 6.98–7.06 (m, 2H, Ar–*H*), 7.10–7.62 (m, 7H, Ar–*H*); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 20.4 (Ar–*C*H$_3$), 28.8 (Ar–*CMe*$_3$), 34.5 (Ar–*C*Me$_3$), 128.6 (Ar*C*–H), 130.4 (Ar*C*–H), 130.7 (Ar*C*–H), 131.9 (Ar*C*–H), 132.3 (Ar*C*–H), 133.9, 136.1, 137.1, 167.0 (Ar*C*–O); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ 13.3. HRMS: *m/z* calcd 550.1074, found 550.1089. Anal. Calc. for C$_{28}$H$_{33}$Cl$_2$O$_2$PTi: C, 61.00; H, 6.03. Found: C, 60.90; H, 5.93%.

3.9. Bis[3-tert-butyl-5-methyl-2-phenoxy](tert-butyl)-phosphine titanium dichloride (5b)

Yield (62%). ^{1}H NMR (CD$_2$Cl$_2$) δ 1.37 (s, 18H, Ar–*t-Bu*), 1.43 (d, 9H, J_{P-H} = 17 Hz, P–*t-Bu*), 2.34 (s, 6H, Ar–C*H*$_3$), 7.26–7.29 (m, 2H, Ar–*H*), 7.33–7.37 (m, 2H, Ar–*H*); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 20.5 (Ar–*C*H$_3$), 26.6 (d, J_{P-C} = 6 Hz, P–*CMe*$_3$), 28.9 (Ar–*CMe*$_3$), 31.3 (Ar–*C*Me$_3$), 34.6 (d, J_{P-C} = 2 Hz, P–*C*Me$_3$), 130.8 (Ar*C*–H), 132.3 (Ar*C*–H), 133.8, 136.2, 138.6, 168.3 (Ar*C*–O); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ 31.0. HRMS: *m/z* calcd 530.1388, found 530.1409. Anal. Calc. for C$_{26}$H$_{37}$Cl$_2$O$_2$PTi: C, 58.77; H, 7.02. Found: C, 59.16; H, 7.03%.

3.10. Bis[3-tert-butyl-5-methyl-2-phenoxy][2-(dimethyl-aminomethyl)-phenyl] phosphine titanium dichloride (5c)

Yield (56%). ^{1}H NMR (CD$_2$Cl$_2$) δ 1.38 (s, 18H, Ar–*t-Bu*), 2.21 (s, 6H, Ar–C*H*$_3$), 2.68 (s, 3H, N*Me*), 2.70 (s, 3H, N*Me*), 4.32 (m, 2H, Ar–C*H*$_2$–NMe$_2$), 6.73–6.77 (m,

2H, Ar–H), 7.10–7.12 (m, 2H, Ar–H), 7.45–7.63 (m, 3H, Ar–H), 7.98–8.02 (m, 1H, Ar–H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 20.5 (Ar–CH_3), 28.8 (Ar–CMe_3), 34.5 (Ar–CMe_3), 43.8 (NMe_2), 62.7 (ArCH_2N), 126.9 (ArC–H), 127.8 (ArC–H), 127.9 (ArC–H), 128.6 (ArC–H), 128.9 (ArC–H), 130.6, 130.7 (ArC–H), 131.5, 135.9, 137.3, 171.8 (ArC–O); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 16.4. HRMS: m/z calcd 607.1653, found 607.1659.

3.11. Bis[3-tert-butyl-5-methyl-2-phenoxy](pentafluoro-phenyl)phosphine titanium dichloride (5d)

Yield (69%). ^1H NMR (CD_2Cl_2) δ 1.33 (s, 18H, Ar–t-Bu), 2.26 (s, 6H, Ar–CH_3), 6.95–7.05 (m, 2H, Ar–H), 7.13–7.21 (m, 2H, Ar–H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 20.5 (Ar–CH_3), 28.7 (Ar–CMe_3), 34.6 (Ar–CMe_3), 121.5, 122.5, 128.4, 129.5 (ArC–H), 131.7 (ArC–H), 134.0, 136.4, 145.6, 146.1, 167.0 (ArC–O); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 2.2. HRMS: m/z calcd 640.0604, found 640.0582.

3.12. Crystallographic analysis of 4a

A red block crystal of **4a** was mounted in glass and the intensity data were collected 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 methods [24]. Crystal data and details of refinement are summarized in Table 3. The final discrepancy indices are $R = 0.069$ and $Rw = 0.086$. All calculations were performed using the CrystalStructure crystallographic software package (Rigaku/MSC).

3.13. Polymerization of ethylene catalyzed by titanium complexes 4a and 5a–5d 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) and toluene were injected into each reaction vessel through a valve. The total volume of reaction mixture was adjusted to 5 mL with toluene. The temperature was then set to 40 °C, 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 TB (0.3 µmol, 1 mM toluene solution). When MMAO was used as a co-catalyst, MMAO (100 µmol, 0.25 M toluene solution) and a catalyst precursor (0.1 µmoL, 1 mM toluene solution) were added. 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 temperature was allowed to drop to room temperature and the ethylene

Table 3
Crystal data and data collection parameters of **4a**

Empirical formula	$C_{32}H_{41}Cl_2O_3PTi$
Formula weight	623.45
Crystal system	Triclinic
a (Å)	9.0430(5)
b (Å)	9.7206(4)
c (Å)	19.1903(9)
α (°)	101.701(1)
β (°)	94.308(1)
γ (°)	89.917(3)
V (Å^3)	1647.0(1)
Space group	$P\bar{1}$ (#2)
Z value	2
D_{calc} (g/cm^3)	1.257
Diffractometer	Rigaku RAXIS-RAPID
Radiation	Cu Kα ($\lambda = 1.54178$ Å)
	Graphite monochromated
$2\theta_{max}$ (°)	136.3
No. of reflections measured	Total: 34,762
	Unique: 5499 ($R_{int} = 0.037$)
Structure solution	Direct methods (SHELX97)
Refinement	Full-matrix least-squares on F
No. observations ($I > 3.00\sigma(I)$)	3929
Residuals: R ($I > 3.00\sigma(I)$)	0.069
Residuals: Rw ($I > 3.00\sigma(I)$)	0.086

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.

3.14. Polymerization of ethylene catalyzed by titanium complexes 5c 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 heated to 40 °C. After ethylene was introduced (0.6 MPa), tri-isobutylaluminium (0.60 mmol, 1.0 M toluene solution) was added. Subsequently, a catalyst precursor (1.0 µmol, 1 mM toluene solution) and TB (6.0 µmol, 6 mM toluene solution) were added. Polymerization was carried out at 40 °C for 5 min, and the reaction was quenched by adding 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 and washed with methanol, and dried in a high vacuum oven at 80 °C for 2 h to constant weight.

Appendix A. Supplementary data

References

[1] H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem., Int. Ed. 34 (1995) 1143.

[2] (a) V.C. Gibson, S.K. Spitzmesser, Chem. Rev. 103 (2003) 283;
(b) G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem., Int. Ed. 38 (1999) 428;
(c) S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169.

[3] (a) Y. Suzuki, H. Terao, T. Fujita, Bull. Chem. Soc. Jpn. 76 (2003) 1493;
(b) U. Siemeling, Chem. Rev. 100 (2000) 1495.

[4] (a) T. Miyatake, K. Mizunuma, Y. Seki, M. Kakugo, Makromol. Chem., Rapid Commun. 10 (1989) 349;
(b) T. Miyatake, K. Mizunuma, M. Kakugo, Makromol. Chem., Macromol. Symp. 66 (1993) 203.

[5] K. Takaoki, T. Miyatake, Macromol. Symp. 157 (2000) 251.

[6] Y. Nakayama, K. Watanabe, N. Ueyama, A. Nakamura, A. Harada, J. Okuda, Organometallics 19 (2000) 2498.

[7] H. Aihara, T. Matsuo, H. Kawaguchi, Chem. Commun. (2003) 2204.

[8] S. Fokken, T.P. Spaniol, J. Okuda, Organometallics 16 (1997) 4240.

[9] C. Capacchione, A. Proto, H. Ebeling, R. Mülhaupt, K. Möller, T.P. Spaniol, J. Okuda, J. Am. Chem. Soc. 125 (2003) 4964.

[10] E.Y. Tshuva, I. Goldberg, M. Kol, H. Weitmanb, Z. Goldschmidt, Chem. Commun. (2000) 379.

[11] E.Y. Tshuva, I. Goldberg, M. Kol, J. Am. Chem. Soc. 122 (2000) 10706.

[12] S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, N. Matsukawa, Y. Takagi, K. Tsuru, M. Nitabaru, T. Nakano, H. Tanaka, N. Kashiwa, T. Fujita, J. Am. Chem. Soc. 123 (2001) 6847.

[13] (a) M. Mitani, R. Furuyama, J. Mohri, J. Saito, S. Ishii, H. Terao, N. Kashiwa, T. Fujita, J. Am. Chem. Soc. 124 (2002) 7888;
(b) J. Tian, P.D. Hustad, G.W. Coates, J. Am. Chem. Soc. 123 (2001) 5134.

[14] W. Hu, X. Sun, C. Wang, Y. Gao, Y. Tang, L. Shi, W. Xia, J. Sun, H. Dai, X. Li, X. Yao, X. Wang, Organometallics 23 (2004) 1684.

[15] K. Kunz, G. Erker, S. Döring, R. Fröhlich, G. Kehr, J. Am. Chem. Soc. 123 (2001) 6181.

[16] L. Zhang, Y. Luo, Z. Hou, J. Am. Chem. Soc. 127 (2005) 14562.

[17] C.A. Townsend, L.M. Bloom, Tetrahedron Lett. 22 (1981) 5925.

[18] C.S. Blackman, C.J. Carmalt, I.P. Parkin, L. Apostolico, K.C. Molloy, A.J.P. White, D.J. Williams, J. Chem. Soc., Dalton Trans. (2002) 2702.

[19] L. Porri, A. Ripa, P. Colombo, E. Miano, S. Capelli, S.V. Meille, J. Organomet. Chem. 514 (1996) 213.

[20] A. Rau, S. Schmitz, G. Luft, J. Organomet. Chem. 608 (2000) 71.

[21] A.F. Kluge, K.G. Untch, J.H. Fried, J. Am. Chem. Soc. 94 (1972) 7827.

[22] D.D. Magnelli, G. Tesi, J.U. Lowe, W.E. McQuistion, Inorg. Chem. 5 (1966) 457.

[23] L. Brammer, J.C. Mareque Rivas, C.D. Spilling, J. Organomet. Chem. 609 (2000) 36.

[24] G.M. Sheldrick, T.R. Schneider, Methods Enzymol. 277 (1997) 319.