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Preparation of half-titanocenes of thiophene-fused trimethylcyclopentadienyl ligands and their ethylene copolymerization reactivity

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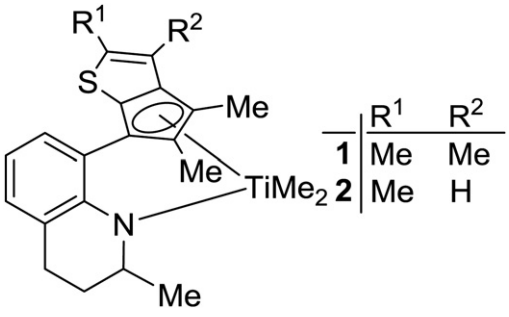
ABSTRACT

Methylthiophene-fused or dimethylthiophene-fused trimethylcyclopentadienyltitanium trichloride complexes, (η^5-Me_4RC_7S)$TiCl_3$ (R = Me or H), are prepared, from which a chloride ligand is replaced with 2,6-diisopropylphenoxy, di(*tert*-butyl)ketimide, or tri(*tert*-butyl)phosphinimide ligand to yield (η^5-Me_4RC_7S)$TiXCl_2$ (**11**, R = Me, X = $iPr_2C_6H_3O$–; **12**, R = H, X = $iPr_2C_6H_3O$–; **13**, R = Me, X = tBu_2C = N–; **14**, R = H, X = tBu_2C = N–; **15**, R = Me, X = tBu_3P = N–; **16**, R = H, X = tBu_3P = N–). The molecular structures of **11**, **14**, and **16** are confirmed by X-ray crystallography. The Cp(centroid)–Ti–N angles of **11**, **14**, and **16** (119.83°, 111.98°, and 125.34°, respectively) are significantly larger than the corresponding angle observed for the related thiophene-fused and tetrahydroquinaldine-linked cyclopentadienyl complex (**1**), [(η^5-(Me_4C_7S)-(2-MeC_9H_9N-κ*N*)]$TiMe_2$ (106.6°). The phenoxy complexes **11** and **12** show negligible activity, while the ketimido and phosphinimido complexes **13**–**16** exhibit good activities (5–20 × 10^6 g/molTi h) for ethylene/1-octene copolymerization. The ketimido-complexes **13** and **14** are able to incorporate a high amount of 1-octene (15–16 mol%), while the phosphinimido-complexes **15** and **16** are not as capable (8 mol % 1-octene) under the identical polymerization conditions. The catalytic performance of **13**–**16** is inferior to **1** in terms of activity and comonomer incorporation.

1. Introduction

Metallocene and bridged half-metallocene complexes constructed using thiophene-fused cyclopentadienyl ligands have been reported to exhibit enhanced polymerization activities, especially with a high molecular-weight polymer [1–5]. Recently, we also observed some advantageous catalytic performances for half-titanocenes of thiophene-fused and tetrahydroquinaldine-linked cyclopentadienyl ligands (**1**, **2**) [6]. Complex **1** exhibits higher activity with production of higher molecular-weight polymer than the tetramethylcyclopentadienyl analogue.

Nonbridged half-titanocene complexes have drawn much attention as a homogeneous Ziegler catalyst in olefin polymerization [7]. They are simply prepared from $TiCl_4$ through the successive replacement of two chlorides with η^5-cyclopentadienyl-type π-donor ligand and anionic ancillary donor ligand such as aryloxo [8,9], ketimide [10,11], or phosphinimide ligand [12,13]. They are advantageous in terms of simplicity of preparation over the analogous bridged half-titanocene complexes. For the bridged complexes, the ligand is elaborately prepared and the metalation conditions are costly in some cases. The advantageous performances of the metallocene and bridged half-metallocene complexes that are constructed using thiophene-fused cyclopentadienyl ligands prompted us to prepare nonbridged half-titanocene analogues.



	R^1	R^2
1	Me	Me
2	Me	H

2. Results and discussion

2.1. Synthesis and characterization

A thiophene-fused cyclopentenones (**3** and **4**) are atom-economically synthesizable in large scale (50-g scale) using the

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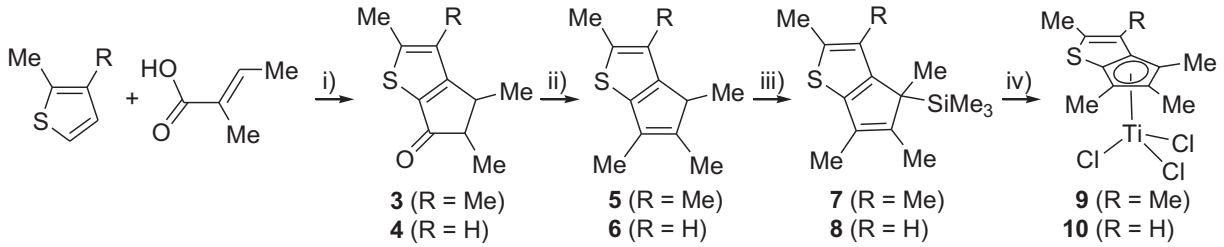
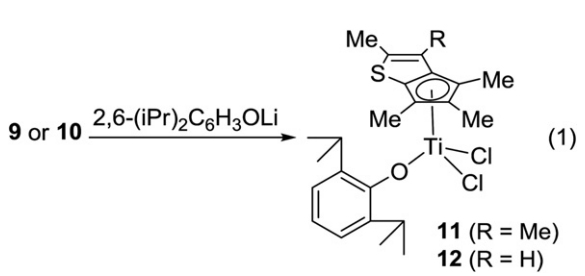
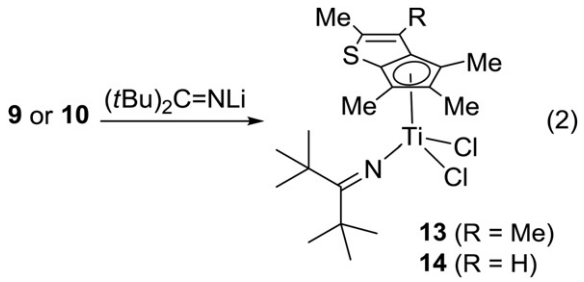


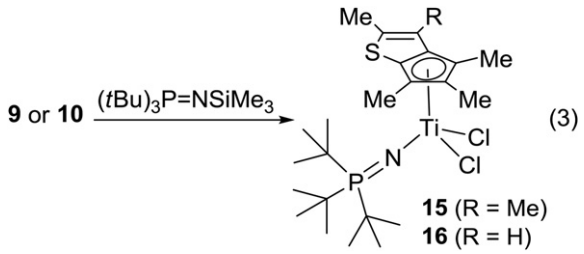
Scheme 1. i) polyphosphoric acid; ii) MeLi then HCl (2 N); iii) nBuLi then Me_3SiCl; iv) $TiCl_4$.

inexpensive starting materials, tiglic acid and the corresponding thiophene (Scheme 1). Dissolving two components in polyphosphoric acid successively triggers the Friedel–Craft acylation and the Nazarov-cyclization to generate **3** and **4** in one pot. The Nazarov-cyclization is one of the best tools to construct a cyclopentadiene or cyclopentenone system [14–16]. In case of **3**, an amount of uncyclized compound (~30%) is concomitantly obtained that is removed through chromatography. In case of **4**, the desired product is obtained almost quantitatively and can be isolated through vacuum distillation. Addition of MeLi to **3** or **4** in diethyl ether and subsequent acidic work-up affords the desired thiophene-fused cyclopentadienes **5** and **6** in 74%–76% yield. The 1,5-sigmatropic rearrangement is facile in the substituted cyclopentadiene system, causing isomerism and, consequently, producing complicated and broad NMR signals. However, in the case of **5** and **6**, the 1,5-sigmatropic rearrangement is not allowed due to the aromacity of thiophene ring. Hence, a single set of sharp signals are observed in the ^1H and ^{13}C NMR spectra. After substitution of a proton on **5** or **6** with a trimethylsilyl group, addition of $TiCl_4$ in methylene chloride yields the corresponding cyclopentadienyl-$TiCl_3$ complexes **9** or **10** in 63%–64% yield. In the ^1H NMR spectrum of **9**, just five singlet methyl signals are observed at 1.9–2.2 ppm. In the ^1H NMR spectrum of **10**, four singlet methyl signals are observed at the same region along with a vinyl signal at 6.22 ppm.

Addition of 2,6-diisopropylphenoxy lithium to **9** or **10** in toluene gives a nonbridged aryloxo half-titanocene complex **11** or **12** in 46%–68% yield (equation (1)). A single septet signal is observed at 3.2 ppm, indicating the two isopropyl groups are equivalent. Addition of $(t\text{Bu})_2C{=}NLi$ to **9** or **10** in toluene gives the corresponding nonbridged ketimido half-titanocene complex **13** or **14** in 71%–97% yield (equation (2)). The two *tert*-butyl units are equivalent in these complexes and a single signal is observed at 1.14 ppm for the *tert*-butyl-CH_3 protons in the ^1H NMR spectrum and at 31.2 ppm for the *tert*-butyl-CH_3 carbon in the ^{13}C NMR spectrum. Addition of $(t\text{Bu})_3P{=}NLi$ to **9** or **10** in toluene also gives the corresponding nonbridged phosphinimido half-titanocene complex **15** or **16** in 96%–97% yield (equation (3)). The *tert*-butyl proton signal is observed at 1.22 ppm as a doublet (J = 13 Hz) coupled with a phosphorus atom. A phosphorous signal is observed at 47 ppm in the ^{31}P NMR spectrum.







2.2. X-ray crystallographic studies

The molecular structures of **11**, **14**, and **16** were determined by X-ray crystallography (Figs. 1–3). The metrical parameters are summarized in Table 1 compared with those observed in the bridged complex **1**. The Cp(centroid)–Ti–N angles, which have been used as a qualitative measure for the openness of the reaction site, are 119.83°, 111.98°, and 125.34° for **11**, **14**, and **16** respectively. The angles are significantly larger than those observed for the related bridged complexes such as **1** (106.62°) and the CGC, [Me_2Si(η^5-Me_4C_5)(N*t*Bu)]$TiCl_2$ (107.6°), indicating that the reaction sites in the nonbridged complexes **11**, **14**, and **16** are not so widely opened as in the bridged complexes **1** and the CGC. Among the nonbridged three complexes, the angle of the ketimido-complex **14** is the smallest (111.98°), suggesting the highest capability for comonomer incorporation. The Ti–O–C angle in **11** is 163.32(18)°, indicating a geometry between the trigonal and the linear arrangement, which is attributed to the significant amount of π-donation from oxygen to titanium. Deviation of the Ti–N–C and Ti–N–P angles in **14** and **16** (165.5(2)° and 169.19(16)°, respectively) from the ideal trigonal angle (120°) also indicate π-donation from nitrogen to titanium. The larger Ti–N–C angle in the phosphinimido-complex **16** than in ketimido-complex **14** implies the increased π-donation in the phosphinimido-complex **16**. Due to this increased π-donation, the Ti–N distance in phosphinimido-complex **16** (1.773(2) Å) is shorter than in ketimido-complex **14** (1.844(2) Å). The Ti–N distances in both ketimido-complexes **14** and phosphinimido-complex **16** are shorter than that of the amido-complex **1** (1.934 (3) Å). While the Ti–N distance is shorter in **16** than in **14**, the Ti–Cp (cent) and Ti–Cl distances are longer in **16** than in **14**. The Ti–Cp

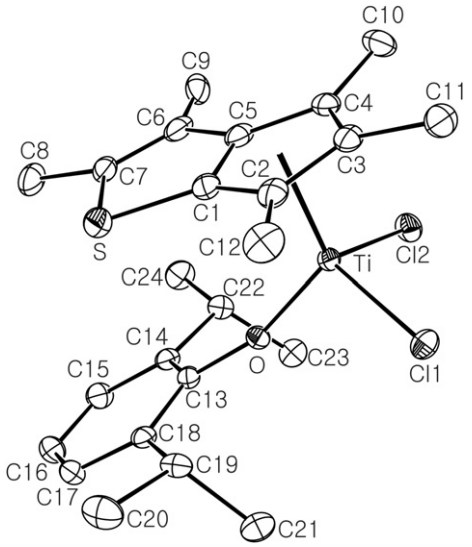


Fig. 1. Thermal ellipsoid plot (30% probability level) of **11**.

(cent) distances in both **14** and **16** are longer (2.052 and 2.099 Å, respectively) than that in **1** (2.041 Å). In **14**, the thiophene ring is positioned at the opposite side of the $(t\text{Bu})_2\text{C}{=}\text{N}$ ligand, passing through the Ti center. In contrast, the thiophene ring in **16** is situated close to the $(t\text{Bu})_3\text{P}{=}\text{N}$ ligand.

2.3. Polymerization studies

The newly prepared complexes **11**–**16** were screened for ethylene/1-octene copolymerization after activation with $(Ph_3C)[B(C_6F_5)_4]$ and iBu_3Al. Triisobutylaluminum is added both as a scavenger and as an alkylating agent. The polymerization results are summarized in Table 2 compared with those of the related complexes of $Cp^*Ti[NC(t\text{Bu})_2]Cl_2$ (Cp*, pentamethylcyclopentadienyl), $Cp^*Ti[NP(t\text{Bu})_3]Cl_2$, and **1**. The phenoxy complexes, **11** and **12** show negligible activity in the polymerization conditions, while the ketimido- and phosphinimido-complexes **13**–**16** exhibit good activities ($5–20 \times 10^6$ g/molTi h). The phosphinimido-complexes **15** and **16** are more active than the ketimido-complexes **13** and **14** under the identical polymerization conditions (entries 3 and 5 versus entries 7 and 8). Activities of the ketimido-complexes **13** and **14** are almost the same with that of $Cp^*Ti[NC(t\text{Bu})_2]Cl_2$ (entries 3 and 5 versus 9), while activities of the phosphinimido-complexes **13** and **14** are almost half of that of $Cp^*Ti[NP(t\text{Bu})_3]Cl_2$ (entry 7 and 8 versus 11). All the complexes screened in this study displays significantly lower activity than the bridged complex **1** (67×10^6 g/molTi h, entry 12). Higher activities are attained when the ketimido-complexes **13** and **14** are activated with MMAO instead of $[Ph_3C][B(C_6F_5)_4]$ (19–20 g/molTi h, entries 4 and 6).

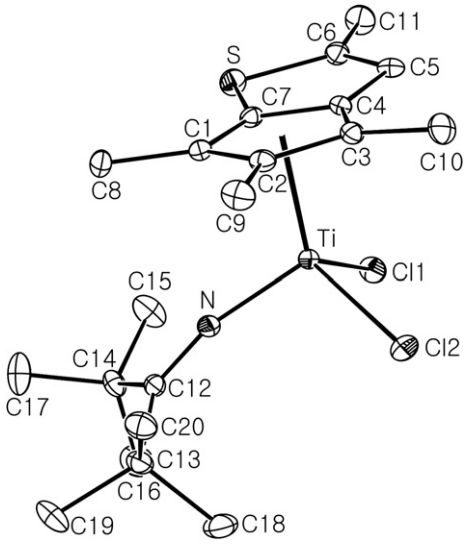


Fig. 2. Thermal ellipsoid plot (30% probability level) of **14**.

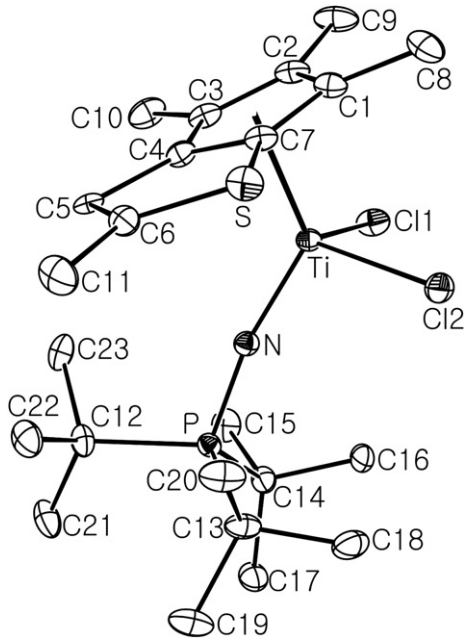


Fig. 3. Thermal ellipsoid plot (30% probability level) of **16**.

The ketimido-complexes **13** and **14**, when activated with $[Ph_3C][B(C_6F_5)_4]$, are able to incorporate fairly high amount of 1-octene (15–16 mol%) while the phosphinimido-complexes **13** and **14** are not so capable (8 mol% 1-octene). This trend agrees with the Cp (centroid)–Ti–N angles observed in X-ray crystallography. The angle of the ketimido-complex **14** is smaller (111.98°) than that of the phosphinimido-complex **16** (125.34°), indicating that the reaction site of **14** is more widely opened and, hence, that **14** is capable of incorporating a higher amount of 1-octene. Almost the same trend is observed for the Cp*-complexes (entries 9 and 11; 18 mol% for $Cp^*Ti[NC(t\text{Bu})_2]Cl_2$, 5 mol% for $Cp^*Ti[NP(t\text{Bu})_3]Cl_2$). Attachment of one more methyl group on the thiophene ring does not influence the activity and the 1-octene incorporation capability when the complexes are activated with $[Ph_3C][B(C_6F_5)_4]$. When activated with MAO, compound **13**, bearing two methyl substituent

Table 1
Selected bond distances (Å) and angles (°) in **11**, **14**, **16**, and **1**.

	11	**14**	**16**	**1**
Ti–Cp(cent)	2.042	2.052	2.099	2.041
Ti–N or Ti–O	1.7858(19)	1.844(2)	1.773(2)	1.934(3)
Ti–Cl(1)	2.2617(9)	2.2772(8)	2.3032(8)	
Ti–Cl(2)	2.2608(9)	2.2931(8)	2.3108(8)	
S–C(Cp)	1.739(3)	1.719(3)	1.728(3)	1.730(3)
S–C	1.786(4)	1.755(3)	1.727(3)	1.769(3)
O–C, N–C, or N–P	1.368(3)	1.268(3)	1.611(2)	
Cp(cent)–Ti–N (or O)	119.83	111.98	125.34	106.62
Cl(1)–Ti–Cl(2)	102.38(3)	100.36(3)	100.60(3)	
Cl(1)–Ti–N (or O)	102.65(7)	104.73(7)	102.96(8)	
Cl(2)–Ti–N (or O)	102.07(7)	103.80(7)	102.25(8)	
Ti–O–C, Ti–N–C, or Ti–N–P	163.32(18)	165.5(2)	169.19(16)	

Table 2
Ethylene/1-octene copolymerization results.[a]

Entry	Catalyst	Yield (g)	Activity[b]	[Oct][c] (mol%)	M_w ($\times 10^{-3}$)	M_w/M_n
1	**11**	~0				
2	**12**	~0				
3	**13**	0.25	5.0	15	464	2.81
4[d]	**13**	0.64	19	19	27	2.25
5	**14**	0.23	4.6	16	288	2.78
6[d]	**14**	0.66	20	13	39	2.49
7	**15**	0.45	9.0	8	543	2.44
8	**16**	0.40	8.0	8	752	2.17
9	Cp*Ti[NC(*t*Bu)$_2$]Cl$_2$	0.31	6.1	18	522	2.82
10[d]	Cp*Ti[NC(*t*Bu)$_2$]Cl$_2$	0.55	17	13	90	2.69
11	Cp*Ti[NP(*t*Bu)$_3$]Cl$_2$	1.1	23	5	204	3.32
12[e]	**1**	0.84	67	21	295	1.73

[a] Polymerization conditions: 30 mL toluene solution of 1-octene (0.30 M, 1.0 g), 1.0 μmol Ti, 4.0 μmol [Ph_3C][$B(C_6F_5)_4$], 0.20 mmol Al(*i*Bu)$_3$, 60 psig ethylene, 3 min, 80 °C initial temperature.
[b] Activity in unit of 10^6 g/molTi h.
[c] 1-Octene content in the copolymer determined by the ^{1}H NMR.
[d] MMAO (Al/Ti = 3000) and 2 min of reaction time are employed.
[e] 0.25 μmol of **1** and 1.0 μmol of $[Ph_3C]+[B(C_6F_5)_4]^-$ is employed (data from reference [10]).

on the thiophene ring, shows a high 1-octene incorporation (entry 4, 19 mol%), but compound **14**, bearing one methyl substituent on the thiophene ring, shows a significantly lower 1-octene incorporation (entry 6; 13 mol%). All the complexes are inferior in terms of 1-octene incorporation capability to the bridged complex **1** (entry 12; 21 mol%), which can also be inferred from small Cp(centroid)–Ti–N angle of **1** (106.6°).

In the case of ketimido-complexes, **13**, bearing two methyl substituent on the thiophene ring, provides higher molecular-weight polymer than **14** [M_w, 4 64 000 (entry 3) versus M_w, 2 88 000 (entry 5)]. These molecular weights are lower than that of polymer obtained with Cp*Ti[NC(*t*Bu)$_2$]Cl$_2$ [M_w, 5 22 000 (entry 9)]. This trend is reversed in cases of phosphinimido complexes. The complex **15** bearing two methyl substituents on the thiophene ring provides a lower molecular-weight polymer than **16**, bearing one methyl substituent on the thiophene ring [M_w, 5 43 000 (entry 7) versus M_w, 7 52 000 (entry 8)]. These molecular weights are higher than that of the polymer obtained with Cp*Ti[NP(*t*Bu)$_3$]Cl$_2$ [M_w, 2 04 000 (entry 11)]. When the complexes are activated with MMAO, significantly lower molecular-weight polymers are obtained (M_w, 27 000–90 000), probably due to a chain transfer reaction to MMAO (entries 4, 6, and 10). The molecular weight distributions are narrow in all cases (M_w/M_n, 2.2–3.3), indicating a single active site.

3. Experimental section

3.1. General remarks

All manipulations were performed under an inert atmosphere using standard glove box and Schlenk techniques. Toluene, hexane, THF, diethyl ether, and CH_2Cl_2 were distilled from benzophenone ketyl. Me_3SiCl was dried over CaH_2 and transferred under the vacuum to reservoirs. The NMR spectra were recorded on a Varian Mercury plus 400. Elemental analyses were carried out at the Analytical Center, Kyunghee University. Mass spectra were obtained on a Micromass VG Autospec. Gel permeation chromatograms (GPC) were obtained at 140 °C in trichlorobenzene using a Waters Model 150-C+ GPC and the data were analyzed using a polystyrene analyzing curve. Compounds **3**, **4**, and (*t*Bu)$_3$PSiMe$_3$ were prepared according to the procedure and conditions reported in the literature [6,17].

3.2. Compound **5**

MeLi (29.7 mL, 47.6 mmol, 1.6 M in diethyl ether) was added dropwise to a stirred solution of **3** (7.71 g, 39.7 mmol) in diethyl ether (77 mL) at −78 °C. The solution was stirred overnight at room temperature. Water (40 mL), ethyl acetate (40 mL), and aqueous HCl (2 N, 80 mL) were successively added. After the two phase solution was stirred for 10 min, the organic phase was collected and then washed with saturated aqueous Na_2CO_3 solution (80 mL). The product was extracted with additional ethyl acetate (3 × 100 mL). The combined organic phase was dried over anhydrous $MgSO_4$. Removal of the solvent with a rotary evaporator gave a residue that was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 20:1). The product was obtained as a yellowish oil (5.62 g, 74%). ^{1}H NMR (C_6D_6): δ 3.03 (q, J = 7.2 Hz, 1H, CH), 2.41 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 1.96 (s, 3H, CH_3), 1.27 (d, J = 7.6 Hz, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 11.99, 12.36, 14.01, 14.31, 45.22, 128.06, 128.38, 131.03, 141.50, 142.07, 149.97 ppm. HRMS (EI): m/z calcd ($[M]^+$ $C_{12}H_{16}S$) 192.0973. Found: 192.0974.

3.3. Compound **6**

The compound was synthesized from **4** using the same conditions and procedure as those for **5**. It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 20:1). The product was obtained as a yellowish oil (76%). ^{1}H NMR (C_6D_6): δ 6.69 (s, 1H, C═CH), 3.01 (q, J = 7.6 Hz, 1H, CH), 2.53 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 1.93 (s, 3H, CH_3), 1.21 (d, J = 8 Hz, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 12.09, 12.36, 15.63, 16.32, 45.23, 119.88, 128.13, 137.91, 141.66, 144.73, 149.79 ppm. HRMS (EI): m/z calcd ($[M]^+$ $C_{11}H_{14}S$) 178.0816. Found: 178.0815.

3.4. Complex **7**

To a solution of **5** (5.62 g, 29.2 mmol) in hexane (56 mL) was added *n*BuLi (42.8 mmol) at −30 °C. After the solution was stirred for 4 days at room temperature, the precipitates were collected by filtration and washed with hexane. Drying at a reduced pressure gave a yellowish solid (4.78 g, 83%). The collected solids (5.77 g, 29.1 mmol) were dissolved in THF (75 mL) and the solution was cooled to −78 °C. Trimethylsilyl chloride (4.07 mL, 32.0 mmol) was added with a syringe. After the solution was stirred overnight at room temperature, the solvent was removed using a vacuum line. Pentane was added to the residue and the solution was filtered over Celite. The filtrate was dried using a vacuum line to give a yellowish oil (5.96 g, 77%). ^{1}H NMR spectrum indicated a mixture of two isomers in a 2:1 ratio. ^{1}H NMR (C_6D_6): δ 2.22 (s, 1H, CH_3), 2.20 (s, 2H, CH_3), 2.17 (s, 2H, CH_3), 2.08 (s, 2H, CH_3), 2.08 (s, 1H, CH_3), 1.95 (s, 1H, CH_3), 1.84 (s, 2H, CH_3), 1.81 (s, 1H, CH_3), 1.40 (s, 1H, CH_3), 1.35 (s, 2H, CH_3), −0.04 (s, 6H, $Si(CH_3)_3$), −0.11 (s, 3H, $Si(CH_3)_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ −3.09, −1.32, 12.37, 12.90, 13.05, 14.08, 14.28, 14.34, 14.74, 18.08, 48.84, 50.26, 125.44, 128.06, 129.81, 131.52, 133.41, 142.05, 142.49, 143.36, 143.79, 148.84, 151.00 ppm. HRMS (EI): m/z calcd ($[M]^+$ $C_{15}H_{24}SSi$) 264.1368. Found: 264.1369.

3.5. Compound **8**

The compound was synthesized from **6** using the same conditions and procedure as those for **7**. The product was obtained as a yellowish oil (98%). ^{1}H NMR spectrum indicated a mixture of two isomers in a 2:1 ratio. ^{1}H NMR (C_6D_6): δ 6.58 (s, 0.66H, C═CH), 6.54 (s, 0.33H, C═CH), 2.34 (s, 2H, CH_3), 2.32 (s, 1H, CH_3), 1.99 (s, 1H, CH_3), 1.96 (s, 2H, CH_3), 1.83 (s, 1H, CH_3), 1.81 (s, 2H, CH_3), 1.34 (s, 1H, CH_3), 1.32 (s, 2H, CH_3), −0.07 (s, 3H, $Si(CH_3)_3$), −0.12 (s, 6H, Si

$(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ −3.12, −2.61, 12.50, 13.11, 13.23, 15.94, 16.69, 16.84, 17.84, 48.85, 49.60, 116.83, 120.40, 128.51, 128.96, 137.61, 140.30, 142.62, 143.35, 144.00, 145.31, 149.76, 151.31 ppm. HRMS (EI): *m*/*z* calcd ($[M]^+$ $C_{14}H_{22}SSi$) 250.1211. Found: 250.1211.

3.6. Complex **9**

To a solution of **7** (5.96 g, 22.5 mmol) in dichloromethane (110 mL) was added $TiCl_4$ (30.75 g, 22.53 mmol, 1 M in dichloromethane) at −78 °C. After stirring for 5 h at room temperature, the solvent was removed using a vacuum line. The residue was dissolved in toluene (80 mL) and the solution was filtered over Celite. Removal of the solvent gave a dark black solid (4.92 g, 64%). ^1H NMR (C_6D_6): δ 2.19 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 1.96 (s, 3H, CH_3), 1.94 (s, 3H, CH_3), 1.90 (s, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 13.04, 14.62, 15.20, 15.36, 15.90, 127.72, 127.98, 138.56, 139.77, 144.32, 145.41 ppm. Anal. Calc. ($C_{12}H_{15}Cl_3STi$): C, 41.71; H, 4.38. Found: C, 41.53; H, 4.12%.

3.7. Complex **10**

It was synthesized from **8** using the same conditions and procedure as those for **10**. The product was obtained as a dark black solid (63%). ^1H NMR (C_6D_6): δ 6.23 (s, 1H, C═CH), 2.18 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 1.93 (s, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 15.40, 15.94, 16.03, 17.19, 118.74, 127.84, 139.47, 139.83, 144.84, 153.72 ppm. Anal. Calc. ($C_{11}H_{13}Cl_3STi$): C, 39.85; H, 3.95. Found: C, 39.67; H, 3.71%.

3.8. Complex **11**

A solution of (2,6-$iPr_2C_6H_3$)OLi in toluene was prepared by mixing *tert*-BuLi (0.333 g, 0.868 mmol, 1.7 M in solution in pentane) and (2,6-$iPr_2C_6H_3$)OH in toluene (1.2 mL). The prepared solution was added to a solution of **9** (0.300 g, 0.868 mmol) in toluene (4.2 mL) at −30 °C. After the mixed solution was stirred at room temperature for 12 h, it was filtered over Celite. Solvent was removed using a vacuum line. The compound was purified by recrystallizion in hexane at −30 °C (0.197 g, 46%). ^1H NMR (C_6D_6): δ 7.01 (d, *J* = 7.6 Hz, 2H, *meta*), 6.93 (t, *J* = 7.4 Hz, 1H, *para*), 3.20 (septet, *J* = 6.8 Hz, Ph−CH), 2.33 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 1.90 (s, 3H, CH_3), 1.74 (s, 3H, CH_3), 1.29 (d, *J* = 6.8 Hz, 6H, $CH(CH_3)_2$), 1.24 (d, *J* = 6.8 Hz, 6H, $CH(CH_3)_2$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 12.95, 13.71, 14.53, 14.76, 15.02, 24.63, 24.82, 27.99, 122.58, 123.59, 123.91, 124.23, 126.19, 132.78, 135.78, 139.86, 140.95, 143.02, 160.27 ppm. Anal. Calc. ($C_{24}H_{32}Cl_2OSTi$): C, 59.15; H, 6.62. Found: C, 59.42; H, 6.53%.

3.9. Complex **12**

It was synthesized from **10** using the same conditions and procedure as those for **11**. It was purified by recrystallization in hexane at −30 °C (68%). ^1H NMR (C_6D_6): δ 6.99 (d, *J* = 7.2 Hz, 2H, *meta*), 6.90 (t, *J* = 7.4 Hz, 1H, *para*), 6.04 (s, 1H, C═CH_3), 3.18 (septet, *J* = 6.8 Hz, CH), 2.25 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 1.70 (s, 3H, CH_3), 1.27 (d, *J* = 6.8 Hz, 6H, $CH(CH_3)_2$), 1.25 (d, *J* = 6.8 Hz, 6H, $CH(CH_3)_2$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 13.80, 15.42, 15.57, 16.79, 24.55, 24.70, 28.07, 115.99, 123.07, 123.76, 123.85, 124.23, 134.31, 135.54, 139.52, 139.74, 151.20, 159.89 ppm. Anal. Calc. ($C_{23}H_{30}Cl_2OSTi$): C, 58.36; H, 6.39. Found: C, 58.67; H, 6.43%.

3.10. Complex **13**

A solution of LiN═C(*t*-Bu)$_2$ in toluene was prepared by mixing *tert*-BuLi (0.333 g, 0.868 mmol, 1.7 M solution in pentane) and HN═C(*t*-Bu)$_2$ (0.123 g, 0.868 mmol) in toluene (1.2 mL) at −30 °C. The prepared solution was added to a solution of **9** (0.300 g, 0.868 mmol) in toluene (4.2 mL). After the mixed solution was stirred at room temperature for 12 h, it was filtered over Celite. The solvent was removed under vacuum. The compound was purified by recrystallization in hexane at −30 °C (0.273 g, 71%). ^1H NMR (C_6D_6): δ 2.38 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 1.14 (s, 18H, $C(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 13.18, 14.36, 14.75, 14.96, 15.15, 31.16, 47.71, 117.62, 120.77, 126.82, 130.74, 132.69, 139.62, 140.49, 203.49 ppm. Anal. Calc. ($C_{21}H_{33}Cl_2NSTi$): C, 56.01; H, 7.39; N, 3.11. Found: C, 56.30; H, 7.61; N, 3.48%.

3.11. Complex **14**

It was synthesized from **10** using the same conditions and procedure as those for **13**. It was purified by recrystallization in hexane at −30 °C (97%). ^1H NMR (C_6D_6): δ 6.39 (s, 1H, C═CH), 2.27 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 1.14 (s, 18H, $C(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 14.47, 15.34, 15.41, 17.31, 31.17, 47.75, 117.67, 118.85, 119.13, 132.49, 132.59, 139.23, 148.63, 203.40 ppm. Anal. Calc. ($C_{20}H_{31}Cl_2NSTi$): C, 55.06; H, 7.16; N, 3.21. Found: C, 55.23; H, 7.35; N, 3.51%.

3.12. Complex **15**

A solution of (tBu)$_3$PSiMe$_3$ (0.251 g, 0.868 mmol) in toluene (1.2 mL) was added to a solution of **9** (0.300 g, 0.868 mmol) in toluene (3 mL) at −30 °C. After the mixed solution was stirred for 5 h at 80 °C, volatiles were removed under vacuum. The compound was purified by recrystallization in hexane at −30 °C (0.440 g, 96%). ^1H NMR (C_6D_6): δ 2.46 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 1.21 (d, J_{PH} = 13.2 Hz, 27H, $PC(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 13.68, 13.92, 14.12, 14.87, 15.24, 30.32, 42.46, 42.90, 114.65, 117.87, 126.66, 126.91, 131.04, 136.86, 138.04 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 46.64 ppm. Anal. Calc. ($C_{24}H_{42}Cl_2NPSTi$): C, 54.76; H, 8.04; N, 2.66. Found: C, 54.98; H, 8.22; N, 2.87%.

3.13. Complex **16**

It was synthesized from **10** using the same conditions and procedure as those for **15**. It was purified by recrystallization in hexane at −30 °C. Yield was 97%. ^1H NMR (C_6D_6): δ 6.49 (s, 1H, C]CH), 2.37 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 1.19 (d, J_{PH} = 13.2 Hz, 27H, $PC(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 14.15, 14.64, 14.90, 17.52, 30.25, 42.49, 42.92, 115.72, 117.23, 117.99, 129.51, 131.50, 135.66, 144.26 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 46.98 ppm. Anal. Calc. ($C_{23}H_{40}Cl_2NPSTi$): C, 53.91; H, 7.87; N, 2.73. Found: C, 53.72; H, 7.80; N, 2.49%.

3.14. Ethylene/1-octene copolymerization

In a glove box, 30 mL of toluene solution of 1-octene (1.0 g, 0.30 M) was added to a dried 60 mL glass reactor. The reactor was assembled, brought out from the glove box, and heated to 80 °C using a mantle. An activated catalyst was prepared by mixing the complex (1.0 μmol), (iBu)$_3$Al (0.20 mmol), and $[C(C_6H_5)_3]$+$[B(C_6F_5)_4]^-$ (4.0 μmol) or MMAO-4 (Akzo, 7.0 wt% Al in toluene, Al/Ti = 3000) for 5 min. After the activated catalyst was added with a syringe, the ethylene gas (60 psig) was fed immediately. After polymerization was conducted for 2 or 3 min, the ethylene gas was vented. Methanol (10 mL) was added immediately. Concentrated aqueous HCl (10 mL) was added and the two-phase solution was stirred for 1 h. With the ketimido-complexes, the toluene phase was collected and solvent was removed using a rotary evaporator to

Table 3
Crystallographic parameters of **11**, **14**, and **16**[a].

	11	**14**	**16**
Formula	$C_{24}H_{32}Cl_2OSTi$	$C_{20}H_{31}Cl_2NSTi$	$C_{23}H_{40}Cl_2NPSTi$
Fw	487.36	436.31	512.39
a, Å	9.8772(6)	8.5606(4)	17.2415(10)
b, Å	14.1347(9)	11.6136(4)	8.7086(4)
c, Å	18.2093(13)	12.0684(5)	19.1042(10)
α, deg	90	78.6898(11)	90
β, deg	107.1329(19)	69.0316(13)	13.5458(15)
γ, deg	90	82.9022(14)	90
V, Å^3	2429.4(3)	1096.75(8)	2629.6(2)
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	P-1	$P2_1/n$
D(calc), g cm^{-1}	1.332	1.321	1.294
Z	4	2	4
μ, mm^{-1}	0.671	0.732	0.679
No. of data collected	18091	15660	24147
No. of unique data [R(int)]	4280[0.0279]	4996[0.0310]	6008[0.0620]
No. of variables	262	350	418
R(%)	0.0469	0.0460	0.0593
R_w(%)	0.1225	0.1496	0.1681
Goodness of fit	1.041	1.117	1.053

[a]Data collected at 150(2) K with Mo Kα radiation (λ(Kα) = 0.7107 Å), R $(F) = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ with $F_o > 2.0\sigma(I)$, $R_w = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o)^2]^2]]^{1/2}$ with $F_o > 2.0\sigma(I)$.

isolate polymers. In cases of phosphinimido-complexes, the polymer was isolated by filtration. The isolated polymers were dried under vacuum at 150 °C for several hours. The 1-octene contents were calculated by the analysis of the ^{1}H NMR spectra of the copolymers. In the ^{1}H NMR spectra, the methyl (CH_3) signal (0.93–1.02 ppm) is well isolated from the methine (CH) and methylene (CH_2) signals (1.30–1.50 ppm), and the 1-octene content can be calculated from the integration values of the two regions. ^{1}H NMR spectra of the polymers (5 mg) were obtained at 90 °C after dissolving in a cosolvent of 1,2,4-trichlorobenzene and C_6D_6 (v/v, 1:3).

3.15. X-ray crystallography

Crystals of **11**, **14**, and **16** coated with grease (Apiezon N) were mounted onto a thin glass fiber with epoxy glue and placed in a cold nitrogen stream at 150(2) K on Rigaku single crystal X-ray diffractometer. The structures were solved by direct methods (SHELXL-97) and refined against all F^2 data (SHELXL-97). All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were treated as idealized contributions. The crystal data and refinement results are summarized in Table 3.

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Appendix. Supplementary material

CCDC Nos. 796171 (**11**); 800660 (**14**); 802055 (**16**) contain the supplementary crystallographic data for this paper. Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center . Copies of this information may be obtained free of charge form The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033: e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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