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Communication

Synthesis of New Phenoxide Modified Half-Titanocenes for Ethylene Polymerization

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Abstract

A series of half-titanocenes containing different trialkylsilyl *para*-phenoxy substituents, $Cp^{*}TiCl_2(O\text{-}2,6\text{-}{}^{i}Pr_2\text{-}4\text{-}R\text{-}C_6H_2)$ [$Cp^{*} = C_5Me_5$; R = $Si(n\text{-}Bu)_3$ (**5**), $SiMe_2(n\text{-}C_8H_{17})$ (**6**), $SiMe_2(t\text{-}Bu)$ (**7**)], have been prepared and identified. The catalytic activity in the ethylene polymerization by $Cp^{*}TiCl_2(O\text{-}2,6\text{-}{}^{i}Pr_2\text{-}4\text{-}R\text{-}C_6H_2)$ [R = H (**1**), $SiMe_3$ (**2**), $SiEt_3$ (**3**), $Si(i\text{-}Pr)_3$ (**4**), **5-7**]—MAO (methylaluminoxane) catalysts increased in the order (in toluene at 25 °C, ethylene 4 atm): R = H (**1**) < $SiMe_3$ (**2**), $SiEt_3$ (**3**), $Si(i\text{-}Pr)_3$ (**4**) < $SiMe_2(t\text{-}Bu)$ (**7**) < $SiMe_2(n\text{-}C_8H_{17})$ (**6**) < $Si(n\text{-}Bu)_3$ (**5**, activity = 6.56×10^4 kg-PE/mol-Ti·h). The results thus suggest that the introduction of alkyl group into the silyl substituent led to an increase in activity. The activities by **5** were affected by Al/Ti molar ratio (amount of MAO charged), and the highest activity (7.00×10^5 kg-PE/mol-Ti·h) was observed under the optimized conditions at 50 °C; the activity decreased at 80 °C. In ethylene copolymerization with 1-dodecene, the $Si(n\text{-}Bu)_3$ analogue (**5**) exhibited the remarkable catalytic activity (4.32×10^6 kg-polymer/moil-Ti·h at 25 °C), which was higher than those by the reported catalysts (**1-3**), affording poly(ethylene-*co*-1-dodecene)s with efficient comonomer incorporation as observed by **3** [r_E = 3.77 (**5**) *vs* 3.58 (**3**)].

Keywords: titanium catalyst; homogeneous catalysis; polymerization; polyethylene; ligand effect; copolymerization; methylaluminoxane; phenoxide ligand

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1. Introduction

Polyolefins [exemplified as high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), isotactic polypropylene (PP), ethylene propylene diene terpolymer (EPDM) etc.] are commodity plastics in our daily life, and transition metal catalyzed olefin polymerization is the core technology. Development of new polymers exhibiting specified properties has been an important subject in the field of catalysis, polymer chemistry [1–16]. The copolymerization approach by incorporation of monomers, that cannot be incorporated by conventional catalysts (Ziegler-Natta, metallocene catalysts), has been employed as an efficient approach, because their material properties (physical, mechanical, chemical etc.) can be modified by individual components (contents of two, three monomers) [2–5,7–9,12]. Design of the molecular catalysts especially exhibiting high catalytic activities with better comonomer incorporations, thus attracts considerable attention in the field of catalysis as well as polymer chemistry [1–16].

It has been demonstrated that *nonbridged* half-titanocenes (half-sandwich titanium complexes) modified with anionic ancillary donor ligands (Y) of type, $Cp'TiX_2(Y)$ (Cp′ = cyclopentadienyl, X = halogen or alkyl, Scheme 1), display as promising catalysts for synthesis of the new copolymers by incorporations of various olefins (sterically encumbered olefins, cyclic olefins, aromatic vinyl monomers, the others) [7–9,16]. The phenoxide (**1**,**3**, **A**) [7–9,17–19], the ketimide (**B**) [7–9,20–22] and phosphinimide (**C**) [7–9,23–25] analogues have been the known successful examples [26–28], and the η^1-amidinate analogue (**D**) later demonstrated an industrial production of chlorine-free synthetic

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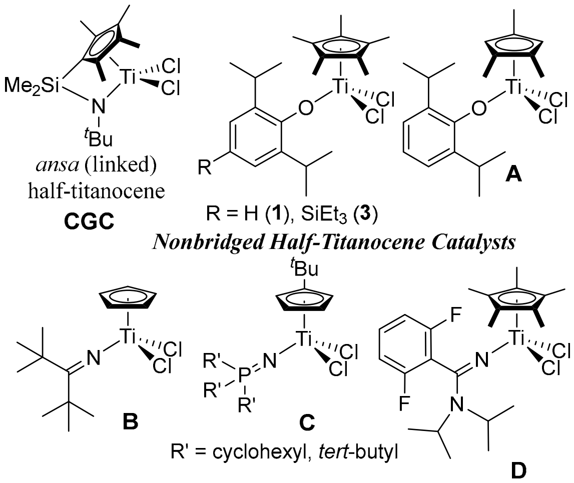
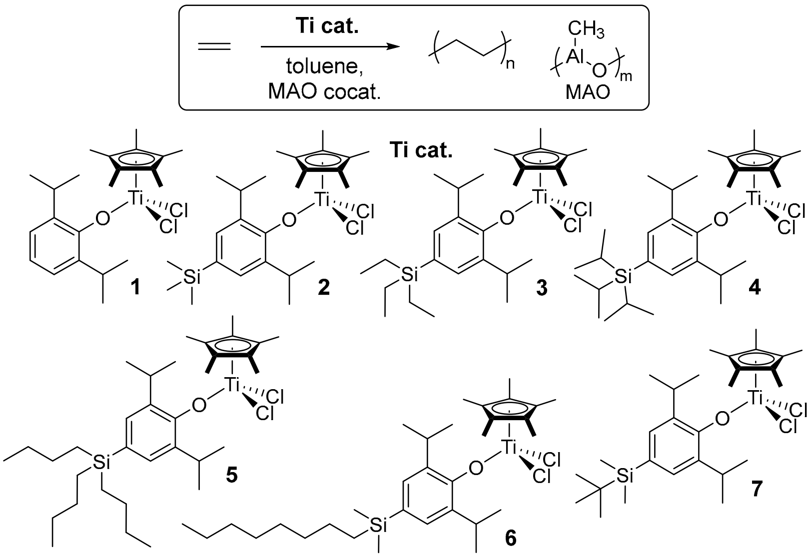
EPDM rubber without deep cooling, commonly employed in the conventional (Ziegler type) catalyst systems in industry [12].



Scheme 1. Selected Examples for Half-Titanocene Catalysts for Olefin Polymerization [7–9,12,16].

Recently, we communicated that the phenoxide modified half-titanocenes containing $SiEt_3$ *para*-substituent, $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2\text{-}4\text{-}SiEt_3\text{-}C_6H_2)$ (**3**, Cp* = C_5Me_5), exhibited the remarkable increase in the catalytic activities compared to the original **1** in ethylene copolymerizations with 2-methyl-1-pentene, 1-decene, 1-dodecene (DD) at 50 °C in the presence of methylaluminoxane (MAO) cocatalyst. The efficient synthesis of high molecular weight ethylene copolymers containing 9-decene-1-ol could also be demonstrated in this catalysis with high catalytic activities [17]. Moreover, we reported later that both the $SiEt_3$ (**3**) and $Si(i\text{-}Pr)_3$ (**4**) catalysts were effective for synthesis of ethylene copolymers with 2-allylpohenol [29]. In order to explore the effect of trialkyl substituent on the *para*-phenoxide ligand in the ethylene polymerization, we prepared and identified various half-titanocenes containing different *para*-phenoxy substituents, $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2\text{-}4\text{-}R\text{-}C_6H_2)$ [R = $Si(n\text{-}Bu)_3$ (**5**), $SiMe_2(n\text{-}C_8H_{17})$ (**6**), $SiMe_2(t\text{-}Bu)$ (**7**)], and studied the ligand effect in ethylene polymerization and ethylene copolymerization with 1-dodecene by using **1**-**7**—MAO catalysts (Scheme 2). We thus wish to present our preliminary data that the $Si(n\text{-}Bu)_3$ (**5**) displays promising capability in term of the activities and the comonomer incorporation.



Scheme 2. Effect of trialkysilyl *para*-phenoxy substituents in ethylene (co)polymerization using $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2\text{-}4\text{-}R\text{-}C_6H_2)$—MAO catalysts.

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2. Results and Discussion

*2.1. Synthesis of Half-Titanocenes Containing Different Trialkylsilyl Para-Phenoxy Substituents, $Cp^*TiCl_2(O-2,6-{}^iPr_2-4-R-C_6H_2)$ (**5**-**7**)*

A series of phenoxide modified half-titanocenes containing different trialkylsilyl *para*-phenoxy substituent, $Cp^*TiCl_2(O-2,6-{}^iPr_2-4-R-C_6H_2)$ [R = $Si(n-Bu)_3$ (**5**), $SiMe_2(n-C_8H_{17})$ (**6**), $SiMe_2(t-Bu)$ (**7**)], were prepared by treating Cp^*TiCl_3 with the corresponding phenol, $2,6-{}^iPr_2-4-R-C_6H_2OH$, in toluene in the presence of NEt_3 according to synthesis of the $SiEt_3$ analogue (**3**) [17]. The reaction conditions for synthesis of $2,6-{}^iPr_2-4-R-C_6H_2OH$ had to be optimized, as conducted in the synthesis of $2,6-{}^iPr_2-4-Si(i-Pr)_3-C_6H_2OH$ [28], especially ratio of solvent and the reaction temperature and time, these phenols could be obtained as moderate yields (51-86 %). The resultant titanium complexes were identified by NMR spectra and elemental analysis (shown below in the Experimental section).

*2.2. Ethylene Polymerization by $Cp^*TiCl_2(O-2,6-{}^iPr_2-4-R-C_6H_2)$ (**1**-**7**)*

Ethylene polymerizations using $Cp^*TiCl_2(O-2,6-{}^iPr_2-4-R-C_6H_2)$ [**1**-**7**; R = H (**1**), $SiMe_3$ (**2**), $SiEt_3$ (**3**), $Si(i-Pr)_3$ (**4**), $Si(n-Bu)_3$ (**5**), $SiMe_2(n-C_8H_{17})$ (**6**), $SiMe_2(t-Bu)$ (**7**)] were conducted in toluene (30 mL scale) in the presence of MAO cocatalyst at 25 or 50 °C, and the selected results conducted under the same conditions (catalyst 0.015 μmol, MAO 3.0 mmol, ethylene 4 atm, 10 min) are summarized in Table 1. MAO employed in this study was used as white solids (expressed as dried MAO) after removal of $AlMe_3$ and toluene from the commercially available MAO [TMAO-S, 9.5 wt% (Al) toluene solution, Tosoh Finechem Co.], since the use of this MAO was effective to afford the ethylene copolymers with uniform compositions [7–9,17–20,22].

It was revealed that the catalytic activities were affected by the trialkylsilyl *para*-phenoxy substituent employed, and the activity by $Cp^*TiCl_2(O-2,6-{}^iPr_2-4-R-C_6H_2)$ (**1**-**7**)—MAO catalysts increased in the order (25 °C, ethylene 4 atm): R = H (**1,** activity 49600 kg-PE/mol-Ti·h, run 1) < $SiMe_3$ (**2**, 54400, run 3), $SiEt_3$ (**3**, 55600, run 5), $Si(i-Pr)_3$ (**4**, 56400, run 7) < $SiMe_2(t-Bu)$ (**7**, 58800, run 15) < $SiMe_2(n-C_8H_{17})$ (**6**, 62800, run 13) < $Si(n-Bu)_3$ (**5**, 65600, run 9). It seems likely that the introduction of alkyl group into the silyl group led to an increase in activity, probably due to better π-donation to titanium, as discussed previously [7-9.17]. It was also revealed that the activities at 50 °C by **1**, **4**, **5** were low compared to those conducted at 25 °C, whereas the activities by **2**, **3**, **6**, **7** increased at 50 °C. The resultant polymers prepared at 25 °C possessed ultrahigh molecular weights ($M_n = 0.78-1.64\times10^6$) with unimodal molecular weight distributions ($M_w/M_n = 2.43-3.84$) although the PDI (M_w/M_n) values are rather high. The M_n values in the resultant polymers prepared at 50 °C became low (M_n = $4.3-6.7\times10^5$) with low PDI values ($M_w/M_n = 2.31-2.96$) compared to those prepared at 25 °C, suggesting that certain degree of chain-transfer increased with an increase of the polymerization temperature.

Table 1. Ethylene polymerization by $Cp^*TiCl_2(O-2,6-{}^iPr_2-4-R-C_6H_2)$ [R = H (**1**), $SiMe_3$ (**2**), $SiEt_3$ (**3**), $Si(i-Pr)_3$ (**4**), $Si(n-Bu)_3$ (**5**), $SiMe_2(n-C_8H_{17})$ (**6**), $SiMe_2(t-Bu)$ (**7**)]–MAO catalysts (in toluene, ethylene 4 atm, 10 min).[1]

run	cat.	temp / °C	yield / mg	activity / kg-PE/mol-Ti·h	M_n[2] ×10^{-6}	M_w/M_n[2]
1	**1**	25	124	49600	1.06	3.18
2	**1**	50	120	48000	0.67	2.41
3	**2**	25	136	54400		
4	**2**	50	147	58800		
5	**3**	25	139	55600	1.64	3.84
6	**3**	50	161	64400	0.55	2.96
7	**4**	25	141	56400	1.17	2.67
8	**4**	50	127	50800	0.43	2.31
9	**5**	25	164	65600	0.88	2.84
10	**5**	25	170	68000	1.21	2.78
11	**5**	50	157	62800	0.53	2.44

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12	**6**	25	154	61600	0.78	2.89
13	**6**	25	157	62800	0.67	2.49
14	**6**	50	179	71600		
15	**7**	25	147	58800	1.06	2.43
16	**7**	50	157	62800	0.44	2.72

[1] Conditions: Catalyst 0.015 μmol, toluene total 30 mL, ethylene 4 atm, d-MAO 3.0 mmol, 10 min. [2] GPC data in *o*-dichlorobenzene *vs*. polystyrene standards.

Table 2 summarizes the results for effect of MAO (Al/Ti molar ratio) toward the catalytic activities in the ethylene polymerization by the Si(*i*-Pr)$_3$ (**4**) and the Si(*n*-Bu)$_3$ (**5**) analogues at 25-80 °C, since the activity by the SiEt$_3$ analogue (**3**) was affected by the amount of MAO charged at various temperature [17]. It was revealed that, as observed in the ethylene polymerization by **2**,**3**–MAO catalysts (under the same conditions), the activities by **4**,**5** conducted at 25 °C increased upon increase in the amount of MAO charged (runs 17-22). Moreover, the activity by **5** at 50 °C initially increased upon increasing the MAO charged (runs 23-25) but decreased upon further addition (run 26); the similar trend was seen by **5** conducted at 80 °C (runs 27-31). Since the M_n values decreased upon increasing the MAO charged as well as increase in the polymerization temperature, it thus seems likely that certain degree of the chain-transfer to Al occurred in this catalysis especially at 50-80 °C.

Table 2. Ethylene polymerization by Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$-4-R-C$_6$H$_2$) [R = Si(*i*-Pr)$_3$ (**4**), Si^{n}Bu$_3$ (**5**)]–MAO catalysts (in toluene, ethylene 4 atm): Effect of MAO and temperature.[1]

run	cat. / μmol	temp / °C	MAO / mmol	yield / mg	activity / kg-PE/mol-Ti·h	M_n[2] ×10^{-6}	M_w/ M_n[2]
17	**4** (0.005)	25	2.0	40	48000	1.23	2.98
18	**4** (0.005)	25	3.0	60	72000		
19	**4** (0.005)	25	4.0	73	87600	0.65	2.18
20	**5** (0.005)	25	2.0	80	96000	0.65	2.81
21	**5** (0.005)	25	3.0	108	129600		
22	**5** (0.005)	25	4.0	120	144000	0.55	2.20
23	**5** (0.015)	50	3.0	157	628000	0.53	2.44
24	**5** (0.015)	50	4.0	161	644000	0.37	1.95
25	**5** (0.015)	50	5.0	175	700000	0.29	1.75
26	**5** (0.015)	50	6.0	161	644000	0.24	2.28
27	**5** (0.015)	80	2.0	107	428000	0.28	2.85
28	**5** (0.015)	80	3.0	124	496000	0.27	1.87
29	**5** (0.015)	80	4.0	132	528000	0.23	2.14
30	**5** (0.015)	80	5.0	151	604000	0.17	2.05
31	**5** (0.015)	80	6.0	144	576000	0.15	2.22

[1] Conditions: Catalyst 0.005 or 0.015 μmol, toluene total 30 mL, ethylene 4 atm, 10 min. [2] GPC data in *o*-dichlorobenzene *vs*. polystyrene standards.

*2.3. Ethylene Copolymerization with 1-Dodecene by Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$-4-R-C$_6$H$_2$) (**4**-**7**)*

Ethylene copolymerizations with 1-dodecene (DD) by Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$-4-R-C$_6$H$_2$) [R = Si(*i*-Pr)$_3$ (**4**), Si(*n*-Bu)$_3$ (**5**), SiMe$_2$(*n*-C$_8$H$_{17}$) (**6**), SiMe$_2$(*t*-Bu) (**7**)] were conducted at 25 or 50 °C in the presence of MAO cocatalyst [ethylene 6 atm, DD 5.0 mL, 0.75 M in toluene (total 30 mL), 6 min, Scheme 3] in order to study the effect of trialkylsilyl *para*-phenoxy substituent toward the activity and the DD incorporation. The results are summarized in Table 3, and the results conducted by **1**-**3** are also placed for comparison.

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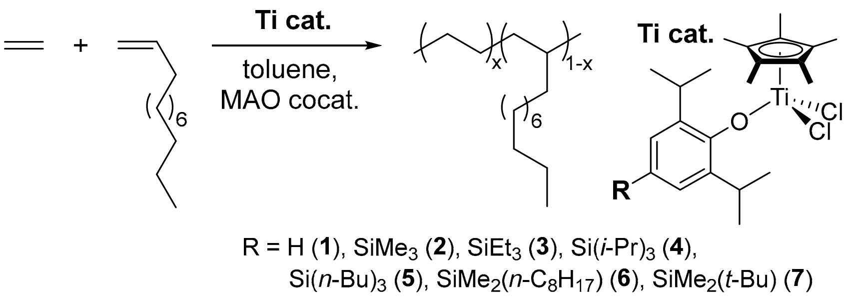

Scheme 3. Effect of trialkysilyl *para*-phenoxy substituents in ethylene copolymerization with 1-dodecene (DD) using $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2\text{-}4\text{-}R\text{-}C_6H_2)$—MAO catalysts.

It was revealed that the catalytic activities in the copolymerizations conducted at 25 °C increased in the order: **1** (activity = 1.60×10^5 kg-polymer/mol-Ti·h, run 32) < **2** (8.50×10^5, run 34) < **3** (1.09×10^6, run 36) < **7** (1.56×10^6, run 52) < **4** (2.07×10^6, run 38) < **6** (3.10×10^6, run 46) < **5** (3.40×10^6, run 41; 4.32×10^6, run 42); the Si(*n*-Bu)$_3$ analogue (**5**) thus showed the highest activity conducted under the same conditions. The resultant polymers were poly(ethylene-*co*-DD)s possessing rather high molecular weights (M_n = 1.50-2.54×10^5) with unimodal molecular weight distributions (M_w/M_n = 1.54-1.90); no significant differences in the DD content in the resultant copolymers were seen. It should be noted that the activities by **1-3** increased at 50 °C (with increases in the DD contents), whereas no significant differences in the activities were seen by **5**,**6** conducted under the optimized amount of MAO charged (runs 44,45,50); the activities, in contrast decreased by **4** and **7** (runs 39,40,53,54). Among these catalysts, the Si(*n*-Bu)$_3$ analogue (**5**) showed the highest catalytic activities (runs 44,45). The M_n values in the resultant copolymers prepared at 50 °C (M_n = 1.31-1.68×10^5) were somewhat low compared to those prepared at 25 °C (M_n = 1.50-2.54×10^5); no significant differences in the DD contents were seen, as observed reported by **1-3** [17]. This probably presumes that the trialkylsilyl substituent would only contribute to increase the catalytic activity (through π-donation to the catalytically active Ti) leading to the higher catalytic activity [7–9].

Table 3. Ethylene copolymerization with 1-dodecene (DD) by $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2\text{-}4\text{-}R\text{-}C_6H_2)$ [R = H (**1**), SiMe$_3$ (**2**), SiEt$_3$ (**3**), Si(*i*-Pr)$_3$ (**4**), Si(*n*-Bu)$_3$ (**5**), SiMe$_2$(*n*-C_8H_{17}) (**6**), SiMe$_2$(*t*-Bu) (**7**)]–MAO catalysts (in toluene, DD 0.75 M, ethylene 6 atm, 6 min).[1.]

run	cat.	temp / °C	MAO / mmol	yield / mg	activity[2] / kg-polymer/mol-Ti·h	M_n[3] ×10^{-5}	M_w/ M_n[3]	cont.[4] / mol%
32	**1**	25	2.0	16	160000	2.54	1.90	
33	**1**	50	2.0	89	890000			
34	**2**	25	2.0	85	850000	1.50	1.54	
35	**2**	50	2.0	105	1050000			
36	**3**	25	2.0	109	1090000	1.67	1.62	
37	**3**	50	2.0	155	1550000			
38	**4**	25	2.0	207	2070000	1.95	1.86	19.8
39	**4**	50	2.0	60	600000			
40	**4**	50	3.5	72	720000	1.59	2.03	25.2
41	**5**	25	2.0	340	3400000	2.29	1.72	18.9
42[5]	**5**	25	2.0	108	4320000			
43	**5**	50	2.0	298	2980000			
44	**5**	50	3.5	350	3500000	1.46	2.07	25.9
45	**5**	50	3.5	355	3550000			
46	**6**	25	2.0	310	3100000	1.99	1.84	19.8
47	**6**	50	2.0	40	400000			
48	**6**	50	2.5	75	750000			
49	**6**	50	3.0	309	3090000			

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50	**6**	50	3.5	328	3280000	1.31	2.01	21.8
51	**6**	50	4.0	225	2250000			
52	**7**	25	2.0	156	1560000	1.96	1.84	18.3
53	**7**	50	2.0	90	900000			
54	**7**	50	3.5	120	1200000	1.68	2.07	23.2

[1] Conditions: Catalyst 0.001 μmol (run 42, 0.00025 μmol), toluene and 1-dodecene (5.0 mL, DD 0.75 M) total 30.0 mL, ethylene 6 atm, 6 min. [2] Activity in kg-polymer/mol-Ti·h. [3] GPC data in *o*-dichlorobenzene vs polystyrene standards. [4] 1-Dodecene (DD) content (mol%) estimated by ^{13}C NMR spectra. [5] Catalyst 0.00025 μmol.

Table 4 summarizes the triad sequence distribution, the dyads, r_E, r_D, and $r_E \cdot r_D$ values [E = ethylene, D = 1-dodecene (DD)] by microstructural analysis of poly(ethylene-*co*-1-dodecene)s prepared by **4**-**7**–MAO catalysts estimated by the ^{13}C NMR spectra (shown in Supplementary Materials) [30,31]. The $r_E \cdot r_D$ values are 0.44-0.57, clearly suggesting that these copolymerizations proceeded in a random manner (DD incorporation is random), whereas the DD incorporation was rather alternating. The monomer reactivity ratios, defined as r_E, for **4**-**7** are 3.34-4.40, and these values were not affected by the polymerization temperature employed, whereas it has been known that the r_E value is affected by the polymerization temperature in the ethylene copolymerization using ordinary metallocene catalysts [32,33]. As commented previously [7–9], this is one of the unique characteristics in this catalysis. The r_E values are close to those by original catalyst **1** (r_E= 3.92) [34] and the $SiEt_3$ analogue (**3**, r_E = 3.58) [35]. The values by the Si(*n*-Bu)$_3$ analogue **5** (3.77, 4.09), exhibited the highest catalytic activity with efficient DD incorporation, are rather small compared to that by the linked half-titanocene (called constrained geometry catalysis), $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (CGC, r_E = 4.31) [34], known as the efficient catalyst for ethylene copolymerization [4,5].

Table 4. Microstructural Analysis for Poly(ethylene-1-dodecene) by ^{13}C NMR spectra.[1]

run	cat.	temp. / °C	DD[2] / mol%	triad sequence distribution[3]/ % EEE	EED+DEE	DED	EDE	DDE+EDD	DDD	dyads[4]/ % EE	ED+DE	DD	r_E[5]	r_D[5]	$r_E \cdot r_D$[6]	$r_E \cdot r_D$[7]
38	**4**	25	19.8	46.4	27.5	6.2	15.3	3.6	0.9	60.1	37.1	2.7	3.34	0.14	0.48	0.48
40	**4**	50	25.2	48.1	20.6	6.0	19.6	5.6	trace	58.5	38.7	2.8	4.05	0.11	0.44	0.44
41	**5**	25	18.9	52.5	25.3	3.3	15.4	2.8	0.7	65.1	32.8	2.1	4.09	0.12	0.50	0.50
44	**5**	50	25.9	42.9	26.7	4.4	20.4	3.6	1.9	56.3	40.0	3.7	3.77	0.14	0.51	0.51
46	**6**	25	19.7	47.3	28.7	4.3	16.3	1.1	2.3	61.6	35.5	2.9	3.57	0.16	0.56	0.57
50	**6**	50	21.8	46.7	27.7	3.7	17.3	4.0	0.5	60.6	36.9	2.5	4.40	0.10	0.44	0.45
52	**7**	25	18.3	54.5	23.9	3.2	15.4	2.4	0.5	66.5	31.7	1.7	4.32	0.11	0.46	0.46
54	**7**	50	23.2	48.2	22.9	5.6	17.3	5.4	0.5	59.7	37.1	3.2	4.31	0.13	0.55	0.56

[1] Detailed polymerization data, see Table 3. [2] 1-Dodecene (DD or D) contents estimated by ^{13}C NMR spectra, [DD] = [EDE]+[DDE+EDD]+[DDD]. [3] Estimated by ^{13}C NMR spectra, E = ethylene, D = 1-dodecene. [4] [EE] = [EEE] + 1/2[EED+DEE], [ED+DE] = [DED]+[EDE]+1/2{[EED+DEE]+[DDE+EDD]}, [DD] = [DDD]+1/2[DDE+EDD]. [5] $r_E = [D]_0/[E]_0 \times 2[EE]/[ED+DE]$, $r_C = [E]_0/[C]_0 \times 2[DD]/[ED+DE]$, $[E]_0$, $[D]_0$ corresponds to the initial concentration. [6] $r_E \cdot r_D = 4[EE][DD]/[ED+DE]^2$. [7] $r_E \cdot r_D = r_E \times r_D$.

3. Conclusions

In this study, effect of trialkylsilyl *para*-phenoxy substituent in ethylene polymerization and ethylene/1-dodecene copolymerization using $Cp^*TiCl_2(O\text{-}2,6\text{-}^iPr_2\text{-}4\text{-}R\text{-}C_6H_2)$ [**1**-**7**; R = H (**1**), $SiMe_3$ (**2**), $SiEt_3$ (**3**), Si(*i*-Pr)$_3$ (**4**), Si(*n*-Bu)$_3$ (**5**), $SiMe_2$(*n*-C_8H_{17}) (**6**), $SiMe_2$(*t*-Bu) (**7**)] have been studied. For this purpose, complexes **4**-**7** have been prepared and identified by NMR spectra and elemental analysis. The activity in ethylene polymerization by a series of complexes (**1**-**7**)—MAO catalysts increased in the order (25 °C, ethylene 4 atm): R = H (**1,** activity 49600 kg-PE/mol-Ti·h, run 1) < $SiMe_3$ (**2**, 54400, run 3), $SiEt_3$ (**3**, 55600, run 5), Si(*i*-Pr)$_3$ (**4**, 56400, run 7) < $SiMe_2$(*t*-Bu) (**7**, 58800, run 15) < $SiMe_2$(*n*-C_8H_{17}) (**6**, 62800, run 13) < Si(*n*-Bu)$_3$ (**5**, 65600, run 9). And the activity was also affected by the amount of MAO charged, whereas increase in the activity was observed when the polymerizations by **5** were conducted at 50 °C. Moreover, the catalytic activities in the ethylene/1-dodecene copolymerizations (ethylene 6 atm, DD 0.75M, 25 °C) increased in the order: **1** (activity = 1.60×10^5 kg-polymer/mol-Ti·h, run 32) < **2** (8.50×10^5,

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run 34) < **3** (1.09×10^6, run 36) < **7** (1.56×10^6, run 52) < **4** (2.07×10^6, run 38) < **6** (3.10×10^6, run 46) < **5** (3.40×10^6, run 41; 4.32×10^6, run 42); the Si(*n*-Bu)$_3$ analogue (**5**) thus showed the highest activity conducted under the same conditions. The microstructural analysis revealed that the r_E values by **5** (3.77, 4.09) are close to those by original catalyst **1** (r_E= 3.92) [34] and the SiEt$_3$ analogue (**3**, r_E = 3.58) [35]. The values by the Si(*n*-Bu)$_3$ analogue (**5**), clearly suggesting the copolymerization proceeds with efficient comonomer incorporation. It is clear that the present catalyst, especially **5**, displays promising capability as the catalyst for ethylene copolymerization; further studies including copolymerizations with sterically sterically encumbered olefins, alken-1-ol [17] will be introduced in the future.

4. Materials and Methods

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox unless otherwise specified. All chemicals including 1-dodecene (DD, Tokyo Chemical Industry Co., Ltd.) used were of reagent grade and were purified by the standard purification procedures. Anhydrous grade of toluene (Kanto Kagaku Co. Ltd) was transferred into a bottle containing molecular sieves (mixture of 3A, 4A 1/16, and 13X) in the drybox and used without further purification. Ethylene for polymerization was of polymerization grade (purity >99.9%; Sumitomo Seika Co., Ltd.) and was used as received. Toluene and AlMe$_3$ in the commercially available methylaluminoxane (MAO) [TMAO-S, 9.5 wt% (Al) toluene solution, Tosoh Finechem Co.] were taken to dryness under reduced pressure (at ca. 50 °C for removing toluene, Me$_3$Al, and then heated at >100 °C for 1 h for completion) in the drybox to give d-MAO white solids [17–20,22]. Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**) [36], Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$-4-SiMe$_3$-C$_6$H$_2$) (**2**) [17], Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$-4-SiEt$_3$-C$_6$H$_2$) (**3**) [17], and Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$-4-Si(*i*-Pr)$_3$-C$_6$H$_2$) (**4**) [29] were prepared according to the reported procedure.

All ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV500 spectrometer (500.13 MHz, ^{1}H; 125.77 MHz, ^{13}C), and all spectra were obtained in the solvent indicated at 25 ℃ unless otherwise noted. Chemical shifts are given in ppm and are referenced to SiMe$_4$ (δ 0.00 ppm, ^{1}H, ^{13}C). Elemental analyses were performed by using EAI CE-440 CHN/O/S Elemental Analyzer (Exeter Analytical, Inc.). Molecular weights and molecular weight distributions for the resultant polymers were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) using a RI-8022 detector (for high temperature; Tosoh Co.) with a polystyrene gel column (TSK gel GMHHR-H HT × 2, 30 cm × 7.8 mm i.d.), ranging from $<10^2$ to $< 2.8 \times 10^8$ M_W) at 140 °C using *o*-dichlorobenzene containing 0.05 wt/v% 2,6-di-*tert*-butyl*p*-cresol as the solvent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples.

*Synthesis of Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$-4-SiBu$_3$-C$_6$H$_2$) (**5**).* (i) Synthesis of 4-SiBu$_3$-2,6-^{i}Pr$_2$C$_6$H$_2$OH. To a solution of 4-Br-2,6-^{i}Pr$_2$C$_6$H$_2$OH (2.57 g, 10 mmol) in 15 mL of Et$_2$O was added TMSCl (1.35 g, 12 mmol) and Et$_3$N (1262 mg, 12 mmol) at -30 ℃. The mixture was then warmed to room temperature and stirred overnight. The reaction mixture was filtered through the Celite pad and washed with Et$_2$O. The filtrate was dried under reduced pressure to give a yellow liquid product (4-Br-2,6-^{i}Pr$_2$C$_6$H$_2$OTMS, 3.0 g). Yield: 92%. 4.0 mL *n*-BuLi (1.6 M, 6.2 mmol) was added at -78 ℃ to a solution of 4-Br-2,6-^{i}Pr$_2$C$_6$H$_2$OTMS (1.66 g, 5.0 mmol) in 6.0 mL hexane, and 10 mL THF was added at -78 ℃. The mixture was stirred for 1.5 h at -78 ℃, and Bu$_3$SiCl (5.87 g, 25 mmol) was then added. The mixture was stirred for 6 h at -78 ℃. The reaction mixture was then warmed consecutively to 0 ℃ and stirred for 18 h, and to room temperature and stirred for 2 h. The reaction mixture was filtered through the Celite pad and washed with hexane. The filtrate was dried under reduced pressure to give a green oily product. 10 wt% HCl aq. (10 mL) was added to the solution of the green oily product in dissolved in 10 mL of THF, and then stirred for 20 min at 0ºC. Water was added to quench the reaction, and extracted with hexane. The organic phase was collected and dried over MgSO$_4$. The mixture was filtered to remove the MgSO$_4$, and the organic layer was collected and dried under reduced pressure to give a liquid crude product. The crude product was purified by silica gel column chromatography (hexane/EtOAc = 30:2) to give a slight orange liquid product (1.25 g, yield: 66%). ^{1}H NMR (CDCl$_3$): δ 7.15 (s, 2H), 4.82 (s, 1H), 3.11-3.19 (m, 2H), 1.32-1.33 (m, 12H), 1.28 (d, J = 8.2 Hz, 12H), 0.88 (t, J = 7.5 Hz, 9H), 0.74-0.77 (m, 6H). ^{13}C NMR (CDCl$_3$): δ 151.7, 133.5, 130.4, 129.5, 28.1, 27.8, 27.1, 23.8, 14.8, 13.4.

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(ii) Synthesis of Cp^*TiCl_2(O-4-$SiBu_3$-2,6-$^iPr_2C_6H_2$) (**5**). A solution of 4-$SiBu_3$-2,6-$^iPr_2C_6H_2OH$ (412 mg, 1.1 mmol) in 10 mL of toluene and Et_3N (0.15 g, 1.5 mmol) was added at -30°C to a solution of Cp^*TiCl_3 (289 mg, 1.0 mmol) in toluene (20 mL). The mixture was warmed to room temperature and stirred overnight. The reaction mixture was filtered through the Celite pad and washed with toluene. The filtrate was dried under reduced pressure to give a red oily product. The oily product was then dissolved in hexane and placed in the freezer (-30 °C) to give red crystals. Yield: 497 mg (81.3%). ^{1}H NMR ($CDCl_3$): δ 7.16 (s, 2H), 3.15-3.19 (m, 2H), 2.18 (s, 15H), 1.31-1.33 (m, 12H), 1.21 (d, J = 8.2 Hz, 12H), 0.88 (t, J = 7.5 Hz, 9H), 0.74-0.78 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 161.1, 138.9, 133.5, 133.3, 129.9, 27.7, 27.5, 27.2, 25.0, 14.8, 13.9, 13.3. Anal. Calcd. $C_{34}H_{58}Cl_2OSiTi$: C, 64.85; H, 9.28; found: C, 64.84; H, 9.20.

Synthesis of Cp^*TiCl_2*(O-2,6-*$^iPr_2$*-4-*$SiMe_2$*(n-*C_8H_{17}*)-*C_6H_2*) (***6***).* (i) Synthesis of 4-$SiMe_2$(*n*-C_8H_{17})-2,6-$^iPr_2C_6H_2OH$. NaH (150 mg, 6.2 mmol) was added a -30 °C to a solution of 4-Br-2,6-$^iPr_2C_6H_2OH$ (1290 mg, 5.0 mmol) in 6.0 mL hexane and 10 mL THF. The mixture was warmed to room temperature and stirred for 1 h. Then it cooled down to -78 °C. 4.0 mL *n*-BuLi (1.6 M, 6.2 mmol) was added to the reaction mixture and stirred for 1.5 h at -78 °C. $SiMe_2$(*n*-C_8H_{17})Cl (5.15 g, 25 mmol) was then added and stirred for 4 h at -78 °C. The reaction mixture was then warmed consecutively to 0 °C and stirred for 14 h, and to room temperature and stirred for 2 h. The reaction mixture was filtered through the Celite pad and washed with hexane. The filtrate was dried under reduced pressure to give a green oily product. 10 mL of 10 wt% HCl aq. was added to the solution of green oily product in 10 mL of THF, and the mixture was then stirred for 20 min at 0 °C. Water was added to quench the reaction and extracted with hexane. The organic phase was collected and dried over $MgSO_4$. The mixture was filtered to remove the $MgSO_4$, and the organic layer was collected and dried under reduced pressure to give a liquid crude product. The crude product was purified by silica gel column chromatography (hexane/EtOAc = 30:2) to give an orange liquid product (0.93 g, yield: 51.2%). ^{1}H NMR ($CDCl_3$): δ 7.15 (s, 2H), 4.82 (s, 1H), 3.09-3.15 (m, 2H), 1.22-1.35 (m, 24H), 0.84 (t, J = 2.7 Hz, 3H), 0.69 (t, J = 7.5 Hz, 2H), 0.20 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 151.9, 133.6, 131.2, 129.8, 34.6, 32.9, 30.3, 30.2, 28.3, 24.9, 23.7, 23.6, 16.9, 15.1.

(ii) Synthesis of Cp^*TiCl_2(O-4-$SiMe_2$(*n*-C_8H_{17})-2,6-$^iPr_2C_6H_2$) (**6**). The procedure for the synthesis of **6** was conducted using the same procedure for the synthesis of catalyst **5** using 4-$SiMe_2$(*n*-C_8H_{17})-2,6-$^iPr_2C_6H_2OH$ (381.7 mg, 1.1 mmol). Yield: 573 mg (89.3%). ^{1}H NMR ($CDCl_3$): δ 7.18 (s, 2H), 3.13-3.20 (m, 2H), 2.18 (s, 15H), 1.24-1.30 (m, 12H), 1.21 (d, J = 8.2 Hz, 12H), 0.85-0.90 (m, 3H), 0.71 (d, J = 6.9 Hz, 2H), 0.24 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 161.2, 139.0, 135.0, 133.3, 129.3, 34.5, 32.9, 30.3, 30.2, 27.5, 25.0, 24.9, 23.7, 16.9, 15.1, 13.9, 13.9. Anal. Calcd. $C_{32}H_{54}Cl_2OSiTi$: C, 63.88; H, 9.05; found: C, 64.10; H, 9.08.

Synthesis of Cp^*TiCl_2*(O-2,6-*$^iPr_2$*-4-*$SiMe_2$*(t-Bu)-*C_6H_2*) (***7***).* (i) Synthesis of 4-$SiMe_2$(*t*-Bu)-2,6-$^iPr_2C_6H_2OH$. NaH (150 mg, 6.2 mmol) was added a -30 °C to a solution of 4-Br-2,6-$^iPr_2C_6H_2OH$ (1.29 g, 5.0 mmol) in 6.0 mL hexane and 10 mL THF. The mixture was warmed to room temperature and stirred for 1 h. Then it cooled down to -78 °C. 4.0 mL *n*-BuLi (1.6 M, 6.2 mmol) was added to the reaction mixture and stirred for 1.5 h at -78 °C. $SiMe_2$(*t*-Bu)Cl (5.25 g, 35 mmol) was added and stirred for 3 h at -78 °C. The reaction mixture was then warmed consecutively to 0 °C and stirred for 10 h and to room temperature for 2 h. The reaction mixture was filtered through the Celite pad and washed with hexane. The filtrate was dried under reduced pressure to give a green oily product. 10 mL of 10 wt% HCl aq. was added to the solution of the green oily product in 10 mL of THF and stirred for 20 min at 0 °C. Water was added to quench the reaction and extracted with hexane. The organic phase was collected and dried over $MgSO_4$. The mixture was filtered to remove the $MgSO_4$, and the organic layer was collected and dried under reduced pressure to give a liquid crude product. The crude product was purified by silica gel column chromatography (hexane/EtOAc = 30:2) to give an orange liquid product (1.0 g, yield: 86%). ^{1}H NMR ($CDCl_3$): δ 7.19 (s, 2H), 4.85 (s, 1H), 3.12-3.19 (m, 2H), 1.28 (d, J = 6.9 Hz, 12H), 0.86 (s, 9H), 0.25 (s, 6H). ^{13}C NMR ($CDCl_3$): δ .151.9, 133.4, 130.7, 129.1, 28.2, 27.5, 23.7, 17.8, 15.1.

(ii) Synthesis of Cp^*TiCl_2(O-4-$SiMe_2$(*t*-Bu)-2,6-$^iPr_2C_6H_2$) (**7**). The procedure for the synthesis of **5** was conducted using the same procedure for the synthesis of catalyst **4,** using 4-$SiMe_2$(*t*-Bu)-2,6-$^iPr_2C_6H_2OH$ (320.1 mg, 1.1 mmol). Yield: 448 mg (65.0%). ^{1}H NMR ($CDCl_3$): δ 7.19 (s, 2H), 3.12-3.23

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(m, 2H), 2.18 (s, 15H), 1.21 (d, *J* = 6.9 Hz, 12H), 0.84 (s, 9H), 0.27 (s, 6H). ^{13}C NMR (CDCl$_3$): δ 160.2, 137.9, 133.7, 132.5, 129.5, 35.0, 26.6, 24.2, 24.1, 21.5, 18.8, 13.05. Anal. Calcd. $C_{32}H_{54}Cl_2OSiTi$: C, 61.65; H, 8.50; found: C, 61.65; H, 8.46.

Ethylene Polymerization. Reactions with ethylene were conducted as follows. In the drybox, Toluene (29.0 mL) and the prescribed amount of MAO were charged to a 100 mL scale stainless steel autoclave. The reaction apparatus was then filled with ethylene (1 atm), and the prescribed amount of complex in 1.0 mL of toluene was added. The autoclave was then pressurized with ethylene to 3 atm (total ethylene pressure is 4 atm), and the mixture was stirred for 5 or 10 min with constant ethylene pressure. The resultant polymers were collected as white precipitates by precipitation in HCl acidified MeOH and by filtration and were adequately washed with MeOH. The resultant polymer was then dried *in vacuo* at 60°C for 2 h.

Ethylene copolymerization with 1-dodecene (DD). The copolymerization reactions were conducted as follows. In the drybox, the prescribed amounts of 1-hexene or 1-dodecene, MAO, and toluene (total 29 mL) were added into the 100 mL scale stainless steel autoclave. Ethylene (1 atm), and a toluene solution containing a prescribed amount of complex (1.0 mL) were added to the reaction apparatus. The autoclave was then immediately pressurized with ethylene to 5 atm (total pressure is 6 atm), and the mixture was stirred for 6 min with constant ethylene pressure at the prescribed temperature. After the reaction, the autoclave was placed in an ice bath to release the unreacted ethylene. The resultant polymers were collected as white precipitates by precipitation in HCl acidified MeOH and by filtration and were adequately washed with MeOH. The resultant polymer was then dried *in vacuo* at 60 °C for 6 h.

Supplementary Materials: The following supporting information can be downloaded at: Preprints.org, Selected NMR spectra of the ligands and catalysts, selected ^{13}C NMR spectra for resultant ethylene/1-dodecene copolymers, and GPC charts of the resultant polymers.

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Data Availability Statement: The data are contained within the article and the Supplementary Material (NMR spectra, GPC traces).

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