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Ethylene and Ethylene/α-Olefin (Co)Polymerization Behavior of Bis(phenoxy−imine)Ti Catalysts: Significant Substituent Effects on Activity and Comonomer Incorporation

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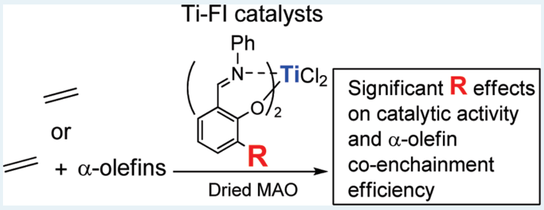
Supporting Information



ABSTRACT: The ethylene and ethylene/α-olefin (co)polymerization behavior of bis(phenoxy−imine)Ti complexes **1**−**7** possessing a series of substituents ortho to the phenoxy O's (ortho substituents **1**, ^{i}Pr; **2**, cyclohexyl; **3**, cyclooctyl; **4**, cyclododecyl; **5**, ^{t}Bu; **6**, CMe$_2$Ph; 7, Ph) with dried methylaluminoxane activation was investigated. At 50 °C, all complexes displayed some of the characteristics of living ethylene polymerization and produced polyethylenes (PEs) with very narrow molecular weight distributions (M_w/M_n 1.08−1.19, M_w 14 900−62 100), albeit under limited conditions. Generally, the Ti complexes with sterically bulkier ortho substituents exhibited higher activities [e.g., **6**: activity 93.2 kg of PE/(mol of cat. min)]; the ortho substituents with quaternary α-C atoms attached to the phenoxy rings, providing higher activities than those with tertiary α-C atoms on the basis of the steric bulk of the entire ortho substituent. To our surprise, complex **7** incorporating an ortho phenyl group displayed the highest activity and formed the highest-molecular-weight PE [activity 230 kg of PE/(mol of cat. min), M_w 456 000], demonstrating the beneficial effects of the ortho phenyl group. Conversely, as to ethylene/propylene copolymerization, an increase in the steric bulk of the ortho substituent resulted in reduced activity for complexes **5** and **6** having quaternary α-C atoms, although the increase led to enhanced activity for complexes **1**−**4** having tertiary α-C atoms. In addition, complexes **1**−**4** displayed far higher propylene incorporation (25.5−26.4 mol %) than complexes **5** and **6** (6.3 and 4.2 mol %). Again, complex **7** with the ortho phenyl group displayed exceptional behavior and had the highest copolymerization activity coupled with the highest propylene incorporation (38.8 mol %). It should be noted that a wide range of propylene incorporation (4.2−38.8 mol %) was achieved with complexes **1**−**7** under identical conditions. Moreover, for ethylene/1-hexene and ethylene/1-decene copolymerizations, complexes **4** (cyclododecyl) and **7** (phenyl) achieved high comonomer incorporation while maintaining high catalytic efficiency.

KEYWORDS: olefin (co)polymerization, group 4 transition metal complex, FI catalysts, X-ray crystallography, α-olefin copolymer, DFT calculations

INTRODUCTION

Ethylene-based polymers, as exemplified by ultrahigh-molecular-weight polyethylenes (PEs), high-density PEs, linear low-density PEs, amorphous ethylene/1-butene copolymers, and ethylene/propylene/diene elastomers, are today of great practical importance.[1−5] They are used in the manufacture of a large number of products, such as shopping bags, food and liquid packages, shampoo and detergent bottles, toys, athletic shoes, bullet-proof vests, and automotive interior and exterior parts (e.g., glass run channels and fuel tanks). Therefore, ethylene-based polymers are used in various fields and impact our daily lives in countless beneficial ways. In addition, new ethylene/α-olefin-based block copolymers or PE and ethylene/1-octene copolymer-based block copolymers have recently been commercialized, which is expanding the utility of ethylene-based polymers due to their unique material properties.[6−9]

The development of molecular catalysts for olefin polymerization, as represented by group 4 metallocene and other relevant catalysts, have offered new opportunities for the production of ethylene/α-olefin copolymers.[10−13] Prominent examples include *ansa*-monocyclopentadienylamide Ti complexes developed concurrently by Dow and Exxon. These Ti complexes, when activated, efficiently incorporate α-olefins into PE due to the sterically open nature of the active site, producing an array of ethylene/α-olefin copolymers with a wide range of α-olefin contents.[12]

The ligand environment of these molecular catalysts can be systematically varied to control the degree of α-olefin incorporation and, in some cases, the α-olefin distribution. Correlations between the catalyst structure and the microstructure of the resulting copolymer can bring about a tailoring of material properties. In addition, as demonstrated by the production of PE-based block copolymers using two kinds of molecular catalysts having different α-olefin coenchainment efficiency, control

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over α-olefin incorporation ability will allow for the formation of new copolymers with unprecedented architectures and associated properties.[6−9] Therefore, the development of molecular catalysts has made significant contributions to the creation of differentiated ethylene-based polymers.

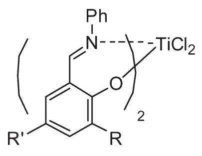
Recent studies of new molecular catalysts for olefin polymerization have led to the discovery of numerous high-performance catalysts based on both early and late transition metals supported by various ligand sets.[14−30] One of the notable additions to the collection of high-performance molecular catalysts is a family of bis(phenoxy−imine) and bis(phenoxy−ketimine) early transition metal complexes (now known as FI catalysts) developed by researchers at Mitsui Chemicals.[31−42] FI catalysts in association with appropriate activators exhibit a number of unique features, including exceptionally high ethylene insertion ability,[43−45] extremely high monomer selectivity (ethylene > α-olefins),[36,38,46,47] highly isospecific and syndiospecific polymerizations of both propylene and styrene,[48−60] high functional group tolerance,[61,62] and methylaluminoxane (MAO)- and borate-free polymerization catalysis (e.g., $MgCl_2$ or a heteropoly compound functions as a good activator/support).[63−67] Thus, there has been much academic and industrial interest in the development of phenoxy−imine and phenoxy−ketimine ligated early transition metal complexes for olefin insertion reactions, resulting in the further development of FI and related catalysts.[34−42,68−101]

As part of our investigations regarding catalyst structure and performance relationships within the family of FI catalysts, we have explored the catalytic properties of FI catalysts incorporating various substituents in close proximity to the active sites for the controlled (co)polymerization of olefinic monomers. These studies have revealed the significant effects of the substituent ortho to the phenoxy O on catalytic activity and comonomer enchainment efficiency regarding Ti-FI catalysts. Namely, we found that Ti-FI catalysts incorporating a cycloalkyl or a phenyl group ortho to the phenoxy O can produce high-molecular-weight polymers with high catalyst efficiency [ethylene and ethylene/α-olefin (co)polymerizations] and show high α-olefin incorporation [ethylene/α-olefin (co)polymerization].

In particular, the Ti-FI catalyst with the ortho phenyl group displayed remarkable catalytic properties, which is exceptional behavior considering the steric bulk of the phenyl group[62,102] and the molecular structure elucidated by X-ray diffraction. We therefore introduce herein the ethylene and ethylene/α-olefin (co)polymerization behavior of bis(phenoxy−imine)Ti complexes (Ti-FI catalysts) for a series of substituents of various steric bulk adjacent to the phenoxy O's in the presence of dried MAO (DMAO). The results provide a strategy for the development of Ti-FI catalysts with high ethylene insertion ability and controlled α-olefin reactivity.

RESULTS AND DISCUSSION

Synthesis of Bis(Phenoxy−Imine)Ti Complexes 2−4. Figure 1 displays the bis(phenoxy−imine)Ti complexes **1**−**7** that were used in this study. Complexes **1** and **5**−**7** were synthesized according to previously reported procedures.[31,39,102] Complexes **2**−**4** were prepared by reacting the lithium salts of the corresponding cycloalkylated phenoxy−imine ligands with $TiCl_4$ using a similar method (see the Experimental Section). In addition, complexes **2** and **3** were subject to single-crystal X-ray diffraction studies.



1-7

1: R = ^{i}Pr, R' = H
2: R = cyclohexyl, R' = H
3: R = cyclooctyl, R' = Me
4: R = cyclododecyl, R' = Me
5: R = ^{t}Bu, R' = H
6: R = CMe_2Ph, R' = Me
7: R = Ph, R' = H

Figure 1. Bis(phenoxy−imine)Ti complexes used in this study.

X-ray Crystallographic Analyses of Complexes 2 and 3. Single crystals of suitable quality for structural determination via X-ray diffraction were obtained for complexes **2** and **3** by a slow diffusion of a dried dichloromethane solution of complex **2** or **3** into an equal volume of dried diethylether. The molecular structures are depicted in Figure 2; selected bond distances and angles are summarized in Table 1, which also includes those for complexes **5**[103] and **7**[62] as a comparison. Complexes **2** and **3** in addition to complexes **5** and **7** possess an approximately octahedrally coordinated metal center, with a trans-O, cis-N, and cis-Cl disposition. These results further demonstrate the general preference of a bis(phenoxy−imine)Ti complex to adopt a trans-O, cis-N, and cis-Cl arrangement.[104−106]

Although these complexes possess the same spatial arrangement concerning the Ti, O, N, and Cl atoms, the cyclooctyl group of complex **3** assumes a fairly distorted structure, probably as a result of steric conflict (Figure 2). In addition, complexes **2**, **3**, and **7** exhibit narrower O−Ti−O angles [**2**, 165.75(5)°; **3**, 166.3(2)°; **7**, 165.05(8)°] and wider N−Ti−N angles [**2**, 80.35(5)°; **3**, 79.8(1)°; **7**: 81.35(8)°] than complex **5** [O−Ti−O, 171.6(2)°; N−Ti−N, 76.4(2)°]. Moreover, complexes **2**, **3**, and **7** display narrower Cl−Ti−Cl angles [**2**, 99.13(2)°; **3**, 100.36(7)°; **7**, 98.47(3)°] than complex **5** [103.10(8)°]. The reason for the differences in the bond angles for complexes **2**, **3**, **5**, and **7** is unclear at the current time.

It should be pointed out that the substituents on the imine N's and the substituents ortho to the phenoxy O's are in close proximity to the Cl−Ti−Cl moiety (which becomes a polymerization site after activation) (Figures 2 and 3). Namely, the substituents on the imine N's are located on a plane at the rear of the polymerization sites, whereas the substituents ortho to the phenoxy O's are situated above and below the polymerization sites. Thus, these substituents should have a significant effect on polymerization behavior. Although complexes **2**, **3**, **5**, and **7** display similar key bond distances (Ti−Cl, 2.276−2.305 Å; Ti−O, 1.835−1.860 Å; Ti−N, 2.208−2.243 Å), an inspection of the molecular structures of these complexes suggests that steric environments around the Cl-bound sites (polymerization sites) are considerably different among these complexes (Figure 3).

The distance between the Cl and its nearest C atom in the substituent on the imine N and the distance between the Cl and its nearest C atom in the substituent ortho to the phenoxy O (ortho substituent) are 3.63/4.53 Å (complex **2**), 3.58/4.20 Å (complex **3**), 3.60/3.97 Å (complex **5**), and 3.60/3.76 Å (complex **7**). It should be noted that complex **7** with an ortho phenyl group has the shortest distance between the Cl and its nearest C atom in the ortho substituent (3.76 Å) among these complexes because **7** has a small dihedral angle between the phenoxy moiety and the ortho phenyl group (almost coplanar structure, 16.9°).

For complexes **2**, **3**, **5**, and **7**, although the distance between the Cl and its nearest C atom in the substituent on the imine N (i.e., phenyl group) are similar to each other (3.58−3.63 Å), the distances between the Cl and its nearest C atom in the ortho substituent are considerably different from one another (3.76−4.53 Å).

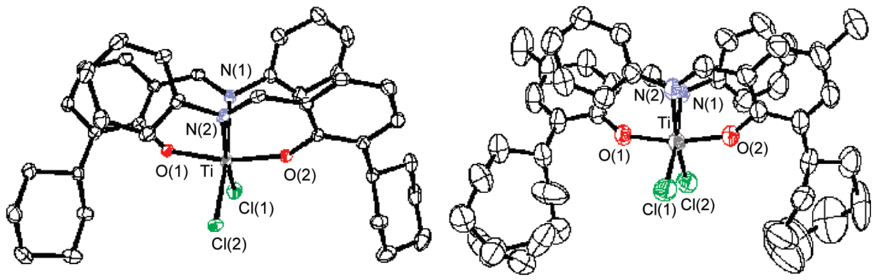


Figure 2. Molecular structures of complexes **2** (left) and **3** (right) (ORTEP illustration, 50% probability). Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (°) for Complexes 2, 3, 5,[103] and 7[62]

	2	3	5	7
		Distances		
Ti−Cl(1)	2.2924(5)	2.276(2)	2.305(2)	2.298(1)
Ti−Cl(2)	2.3032(5)	2.322(3)	2.296(2)	2.3005(8)
Ti−O(1)	1.843(1)	1.846(3)	1.852(4)	1.860(2)
Ti−O(2)	1.844(1)	1.835(3)	1.851(4)	1.845(2)
Ti−N(1)	2.222(1)	2.243(4)	2.236(4)	2.233(2)
Ti−N(2)	2.211(1)	2.208(5)	2.213(4)	2.213(2)
		Angles		
Cl(1)−Ti−Cl(2)	99.13(2)	100.36(7)	103.10(8)	98.47(3)
O(1)−Ti−O(2)	165.75(5)	166.3(2)	171.6(2)	165.05(8)
N(1)−Ti−N(2)	80.35(5)	79.8(1)	76.4(2)	81.35(8)

Table 2. Ethylene Polymerization Using Complexes 1−7 with DMAO[a]

entry	complex	yield/g	activity[b]	M_w[c]/10^3	M_w/M_n[c]
1	**1**	0.225	9.00	38.2	1.13
2	**2**	0.650	26.0	105	1.38
3	**3**	1.325	53.2	187	1.67
4	**4**	2.060	82.4	249	2.18
5	**5**	1.727	69.2	190	1.60
6	**6**	2.330	93.2	206	1.91
7	**7**[d]	1.150	230	456	3.26
8[e]	**2**[f]	0.125	31.3	27.7	1.11
9[e]	**3**[g]	0.143	71.5	53.5	1.19
10[h]	**4**	0.056	67	14.9	1.08
11[e]	**5**[g]	0.220	110	62.1	1.19
12[h]	**6**	0.127	152	33.4	1.10
13[h]	**7**[d]	0.037	220	36.8	1.19

[a] General conditions: toluene, 250 mL; complex, 5.0 μmol; DMAO, 1.25 mmol as Al; 50 °C; polymerization time, 5 min; ethylene feed, 100 L/h. [b] As kilograms of PE/(mol of cat. min). [c] Determined by GPC using PE calibration. [d] Complex 1.0 μmol. [f] 4.0 μmol. [g] 2.0 μmol. [e] Polymerization time, 1 min. [h] 10 s.

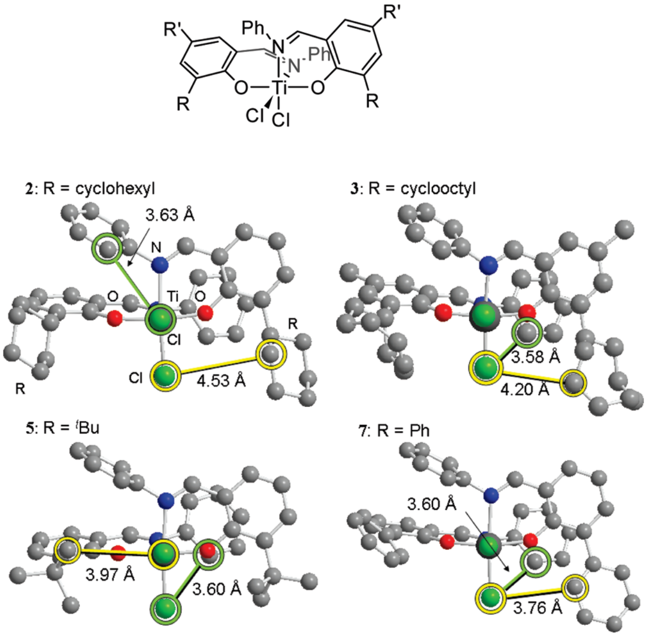


Figure 3. Steric environments around the Cl-bound sites of complexes **2**, **3**, **5**, and **7**. Hydrogen atoms are omitted for clarity.

Therefore, the polymerization behavior of these complexes may give useful information about the effects of the ortho substituents on polymerization catalysis.

Altogether, the molecular structures elucidated by X-ray analyses suggest that complex **7** presumably possesses the most sterically encumbered nature vis-à-vis polymerization, followed by complexes **5**, **3**, and **2**.

Ethylene Polymerization Behavior of Complexes 1−7/DMAO. Using DMAO as an activator, ethylene polymerizations with complexes **1**−**7** were carried out at 50 °C under ethylene at atmospheric pressure (complex **5** was evaluated as a comparison). Results are compiled in Table 2. For a 5 min polymerization, complex **1**/DMAO displayed some of the characteristics of living ethylene polymerization and generated PE with an extremely narrow molecular weight distribution (M_w/M_n 1.13; Table 2, entry 1).[39,102] In addition, complexes **2**−**7** with DMAO were able to produce very narrow molecular weight distribution PEs for a 1 min (complexes **2**, **3**, and **5**) or 10 s polymerization (complexes **4**, **6**, and **7**) (Table 2, entries 8−13). These results further demonstrate the high potential of bis(phenoxy−imine)Ti catalysts as living olefin polymerization catalysts.[39,102,107] Indeed, the incorporation of fluorine(s) ortho to the imine N turns bis(phenoxy−imine)Ti catalysts into unprecedented catalysts for living ethylene, propylene, and ethylene/α-olefin (co)polymerizations, allowing for the synthesis of a wide variety of unique polymers.[108−118]

The general trend observed is that an increase in the steric bulk of the ortho substituent (calculated R−H volume: ^{i}Pr, 69 Å^3; ^{t}Bu, 88 Å^3; cyclohexyl, 111 Å^3; cyclooctyl, 147 Å^3; CMe$_2$Ph, 170 Å^3; cyclododecyl, 220 Å^3)[119] resulted in enhanced catalytic activity (Figure 4; Table 2, entries 1−7). It is pertinent to think that the

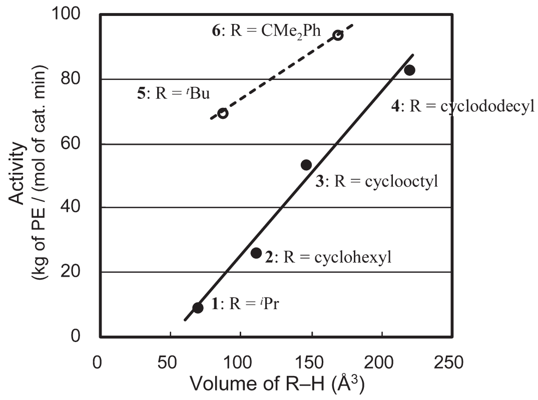


Figure 4. Plots of ethylene polymerization activity as a function of the calculated R—H volume for complexes **1**—**6** with DMAO (Table 2, entries 1—6).

bulky substituent gives better protection to the phenoxy O from electrophilic attack by Lewis acidic compounds (e.g., alkylaluminum, MAO) present in the reaction medium and, in addition, that it induces more effective ion separation between the cationic active species and an anionic activator.[120,121] In addition, the sterically more encumbered ortho substituents may shift the equilibrium to the mononuclear species from the dinuclear complexes that are inactive toward ethylene polymerization.[36]

It can be seen from Figure 4 that the Ti complexes with the ortho substituents having quaternary α-C atoms attached to the phenoxy rings (complexes **5** and **6**) exhibit higher catalytic activity than those having the tertiary α-C atoms (complexes **1**—**4**), on the basis of the steric bulk of the entire ortho substituent. These results may suggest that an ortho substituent with a quaternary α-C atom provides a more pronounced effect than an ortho substituent with a tertiary α-C atom, although the former evidently gives rise to a sterically more encumbered active site.

A striking feature observed is that complex **7** bearing the ortho phenyl group exhibited the highest catalytic activity and formed PE with the highest molecular weight [activity 230 kg of PE/(mol of cat. min), M_w 456 000, Table 2, entry 7] among the Ti complexes examined. The ortho phenyl group (calculated R—H volume: 99 Å^3)[119] is relatively unencumbered among the ortho substituents of the complexes investigated. In addition, the molecular structures of complexes **2**, **3**, **5**, and **7** elucidated by X-ray analyses suggested that complex **7** possesses the most sterically crowded environment around the Cl bound sites (polymerization sites). Therefore, the catalytic behavior of complex **7** with DMAO was unexpected.

DFT calculations[122—127] gave useful insight into the catalytic properties of the complex **7**/DMAO catalyst system. Figure 5 shows the DFT-optimized structures of the ethylene-coordinated cationic Ti species (model: cationic *n*-propyl Ti complex) derived from complexes **2**, **3**, **5**, and **7**. The distance between the C atom of the coordinated ethylene and its nearest C atom in the substituent on the imine N and the distance between the C atom of the coordinated ethylene and its nearest C atom in the ortho substituent are 3.573/4.824 Å (complex **2**), 3.752/5.133 Å (complex **3**), 3.996/4.347 Å (complex **5**), and 3.537/4.115 Å (complex **7**). The calculations also demonstrate that the distance between the Ti and its nearest C atom of the coordinated ethylene are 3.264 Å (complex **2**), 3.849 Å (complex **3**), 4.025 Å (complex **5**), and 3.010 Å (complex **7**), suggesting that the cationic Ti species derived from complex **7** has the shortest distance between the coordinated ethylene and the Ti metal, followed by those from complexes **2**, **3**, and **5**.

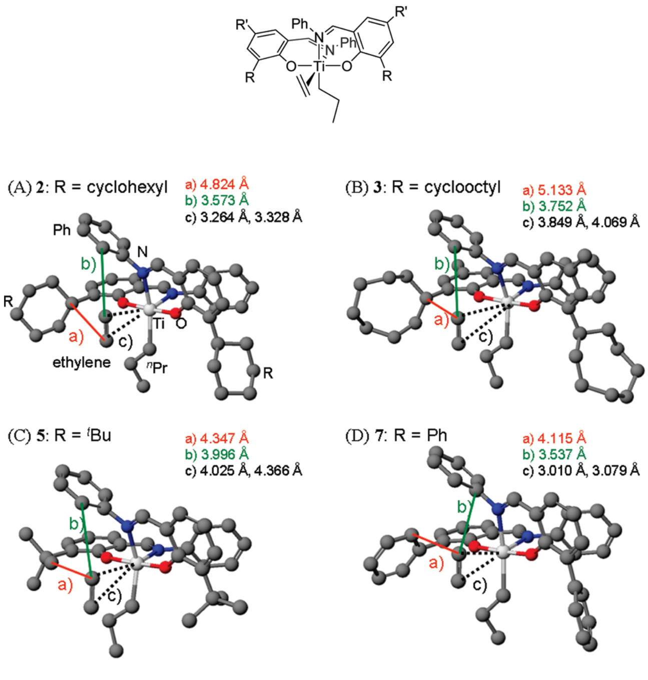


Figure 5. DFT-optimized structures of the ethylene-coordinated cationic Ti species (model: cationic *n*-propyl Ti complex) derived from complexes **2** (A), **3** (B), **5** (C), and **7** (D). Hydrogen atoms are omitted for clarity. (a—c) Distances between the C atoms of the coordinated ethylene and its nearest C atom in the ortho substituent (R) (a: red), its nearest C atom of the phenyl group on the imine N (b: green), or the Ti metal (c: black).

DFT calculations indicate that the cationic Ti species stemming from these complexes have similar electrophilicity (Mulliken charge of the Ti in atomic units: **2**, 1.757; **3**, 1.744; **5**, 1.741; **7**, 1.762). Therefore, we concluded that the cationic Ti species originating from complex **7** possesses the sterically most open nature vis-à-vis polymerization. Although complex **7** was suggested by the X-ray analysis to have the sterically most encumbered nature near the polymerization sites due to the ortho phenyl group, the ortho phenyl group can provide a sterically open active site as a result of its rotation to evade the steric hindrance between the coordinated ethylene and itself [dihedral angle between the phenoxy moiety and the ortho phenyl group: 53.6° (X-ray, 16.9°)] (Figure 5D).[128]

On the basis of the above facts, the sterically open nature (leading to a larger space for polymerization) presumably accounts for the high catalytic activity exhibited by **7**/DMAO. However, a comparison of the steric bulk of the ortho substituent and the distance from the coordinated ethylene and its nearest C in the ligand between structurally relevant complexes **2** (cyclohexyl) and **7** (phenyl) (**2**, 111 and 3.573 Å; **7**, 99 and 3.537 Å) leads us to postulate that the origin of the exceptionally high catalytic activity displayed by **7**/DMAO [**7**, 230 kg of PE/(mol of cat. min); **2**, 26.0 kg of PE/(mol of cat. min)] is derived not only from the steric nature but also from the electronic nature of the catalytically active species. We previously suggested that transition metal complexes with electronically more flexible ligands can form a catalyst displaying higher catalytic activity.[44,47,105,129] Therefore, the electronically flexible properties of the ligand of complex **7**, due to the more conjugated nature caused by the

Table 3. Ethylene/Propylene Copolymerization Using Complexes 1−7 with DMAO[a]

entry	complex	yield/g	activity[b]	M_w[c]/10^3	M_w/M_n[c]	P[d]/mol %	TOF for E[e]/min^{-1}	TOF for P[f]/min^{-1}
1	**1**	0.147	2.94	20.4	1.30	26.4	68	24
2	**2**	0.380	7.60	57.3	1.36	26.0	177	62
3	**3**	0.728	14.6	83.2	1.65	26.2	339	120
4	**4**	0.911	18.2	78.2	1.72	25.5	429	147
5	**5**	0.541	10.8	69.1	1.88	6.3	350	24
6	**6**	0.320	6.40	12.7	1.95	4.2	214	9
7	**7**	2.930	58.6	42.1	1.82	38.8	1071	679

[a] Conditions: toluene, 250 mL; complex, 5.0 μmol; dried MAO, 1.25 mmol as Al; 50 °C; 10 min; ethylene feed, 50 L/h; propylene feed, 150 L/h. [b] As kilograms of copolymer/(mol of cat. min). [c] Determined by GPC using polyethylene calibration. [d] Propylene content determined by means of ^{1}H NMR spectroscopic analysis. [e] Turnover frequency for ethylene. [f] Turnover frequency for propylene.

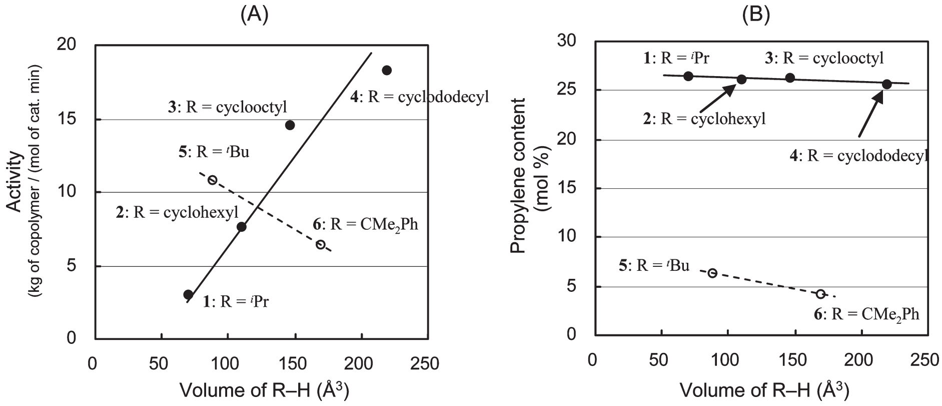


Figure 6. Plots of ethylene/propylene copolymerization activity (A) and those of propylene content (B) as a function of the calculated R−H volume for complexes **1**−**6** with DMAO.

presence of the ortho phenyl group, may also be responsible for the high activity observed.

Ethylene/α-Olefin Copolymerization Catalyzed by Complexes 1−7/DMAO. To gain further information about the polymerization catalysis of complexes **1**−**7**, ethylene/propylene copolymerizations were performed using these complexes with DMAO activation (complex **5** was examined as a comparison).[130−141] Table 3 summarizes copolymerization results. It is interesting to note that complexes **1**−**4** with ortho substituents with tertiary α-C atoms attached to the phenoxy rings and complexes **5** and **6** with ortho substituents with quaternary α-C atoms behaved differently for ethylene/propylene copolymerization, unlike the ethylene homopolymerization (Figures 4 and 6).

For complexes **1**−**4** with ortho substituents possessing tertiary α-C atoms, complexes bearing sterically bulkier ortho substituents displayed higher catalytic activities and formed copolymers with considerable propylene content (25.5−26.4 mol %) under the given conditions (Figure 6; Table 3, entries 1−4). As to these complexes, an increase in the steric bulk of the ortho substituent (an increase in the carbon number of the ortho substituent) led to enhanced turnover frequency (TOF) for both ethylene and propylene incorporation (Table 3, entries 1−4). These results probably indicate that the catalytically active species derived from complexes **1**−**4** possess enough space not only for ethylene insertion but also for propylene insertion.

Conversely, complexes **5** and **6** with ortho substituents having quaternary α-C atoms incorporated much lower amounts of propylene (**5**, 6.3 mol %; **6**, 4.2 mol %; Figure 6; Table 3, entries 5 and 6) than complexes **1**−**4**, the sterically larger ortho substituent leading to the lower propylene incorporation. In addition and importantly, for complexes **5** and **6**, an increase in the steric bulk of the ortho substituent resulted in reduced TOF for both ethylene and propylene incorporation, the TOF for propylene incorporation being more significantly reduced. Complexes **5** and **6**, after activation, evidently form sterically more crowded active sites than complexes **1**−**4** (whose active species probably have enough space for both ethylene and propylene insertion) due to the presence of the methyl group attached to the α-C atom. In addition, as previously described, bis(phenoxyimine)Ti catalysts generate more electrophilic cationic active species relative to group 4 metallocene and related catalysts due to the electron-withdrawing nature of the phenoxy−imine ligand.[36,102,142−146] Therefore, the strong affinity for propylene (leading to the prevailing coordination of propylene to the Ti metal) together with the sterically crowded nature of the active sites (resulting in the slow insertion of propylene into the Ti−C bond) is probably responsible for the ethylene/propylene copolymerization behavior of complexes **5** and **6** combined with DMAO.[129,147]

The above copolymerization results along with those obtained with ethylene polymerization (Table 2, Figure 4) give a clear demonstration that the ortho substituent is situated in a strategic position capable of affecting polymerization catalysis and that the steric bulk of the entire ortho substituent is fundamental to achieving high catalytic activity for ethylene polymerization. However, for ethylene/propylene copolymerization, the steric bulk of the ortho substituent near the α-C atom attached to the phenoxy ring is seen to play a key role in achieving high catalyst efficiency.

Table 4. Ethylene/1-Hexene and Ethylene/1-Decene Copolymerizations Using Complexes 2−5 and 7 with DMAO

	ethylene/1-hexene copolymerization[a]					ethylene/1-decene copolymerization[a]				
complex	yield/g	activity[b]	M_w[c]/10^3	M_w/M_n[c]	H[d]/mol %	yield/g	activity[b]	M_w[c]/10^3	M_w/M_n[c]	D[d]/mol %
2	0.177	14.2	48.3	1.16	5.6	0.333	26.6	55.9	1.17	4.0
3	0.218	17.4	56.1	1.18	8.4	0.502	40.2	65.3	1.26	7.2
4	0.279	22.3	42.8	1.27	12.6	0.616	49.3	56.6	1.39	9.6
5	0.148	11.8	41.7	1.29	1.5	0.164	13.1	55.3	1.32	1.0
7	1.754	140	126	1.92	12.0	2.270	182	145	1.97	8.7

[a] Conditions: toluene, 200 mL; complex, 2.5 μmol; dried MAO, 1.25 mmol as Al; 25 °C; 5 min; ethylene feed, 100 L/h; 1-hexene or 1-decene 50 mL. [b] As kilograms of copolymer/(mol of cat. min). [c] Determined by GPC using polyethylene calibration. [d] Comonomer content determined by means of ^{1}H NMR spectroscopic analysis

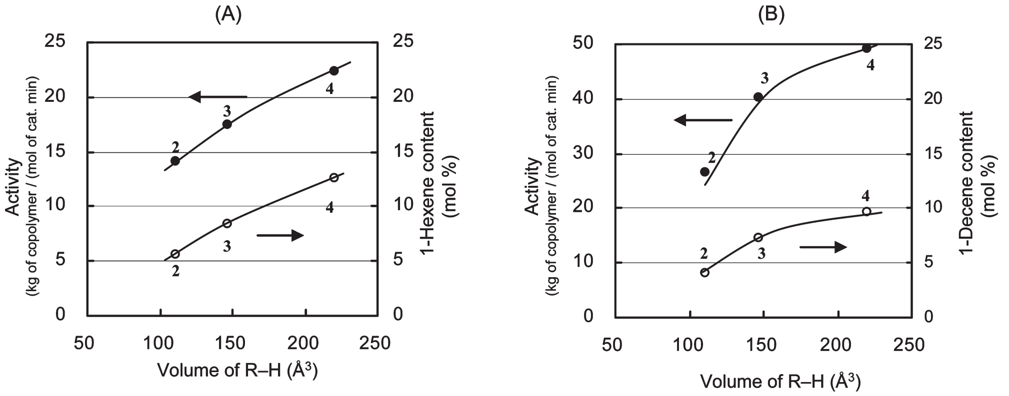


Figure 7. Plots of ethylene/1-hexene copolymerization activity and 1-hexene content (A) and those of ethylene/1-decene copolymerization activity and 1-decene content (B) as a function of the calculated R−H volume for complexes **2**−**4** with DMAO.

Again, complex **7**/DMAO displayed exceptional behavior, and this exhibited the highest catalytic activity and formed a copolymer with the highest propylene content (38.8 mol %). The sterically open nature of the active site together with the electronically flexible nature of the ligand may be responsible for this behavior. The largest TOF value for both ethylene and propylene incorporation obtained for the complex **7**/DMAO catalyst system (Table 3, entry 7) suggests the sterically most open nature of the active sites derived from complex **7**, which is consistent with DFT calculation results.

An inspection of the data in Table 3 suggests that the propylene content of the resulting copolymers can be controlled by selection of the ortho substituent. In fact, using complexes **1**−**7** with DMAO, ethylene/propylene copolymers having a wide range of propylene content (4.2−38.8 mol %, from high-density PE to amorphous ethylene/propylene copolymer) were successfully synthesized under identical conditions. The wide range of comonomer incorporation levels achieved by complexes **1**−**7**/DMAO is advantageous when considering the synthesis of block copolymers using a reversible chain transfer reaction.[6−9]

Ethylene/higher α-olefin (1-hexene, 1-decene) copolymerizations using complexes **2**−**4** and **7** with DMAO provided further insight into the catalysis of these complexes.[148−162] Copolymerization results are compiled in Table 4, which includes the results obtained with complex **5**/DMAO for comparison. As anticipated, complex **7** with DMAO exhibited the highest catalytic activity, producing the highest-molecular-weight copolymers with high comonomer content. The copolymerization results further demonstrated the beneficial effects of the ortho phenyl group on polymerization catalysis.[163]

Interestingly, DMAO-activated complexes **2**−**4** bearing the ortho cycloalkyl groups behaved differently for ethylene/higher α-olefin copolymerization than for ethylene/propylene copolymerization. For ethylene/propylene copolymerization, an increase in the steric bulk of the ortho cycloalkyl group resulted in about the same propylene content, although catalytic activity was enhanced (Table 3, entries 2−4; Figure 6), whereas for ethylene/1-hexene and ethylene/1-decene copolymerizations, an increase in the steric bulk of the ortho cycloalkyl group led to both enhanced catalytic activity and increased comonomer content (Table 4, Figure 7).

These facts suggest that the sterically more encumbered ortho cycloalkyl group having the tertiary α-C atom probably induces a more efficient ion separation between the cationic active species and an anionic activator species, which allows more space for the higher α-olefins to access and coordinate to the Ti metal. It should be emphasized that complex **4** having the ortho cyclododecyl group achieved higher 1-hexene and 1-decene incorporation than complex **7** with the ortho phenyl group.

The results obtained indicate that the introduction of the sterically encumbered ortho cycloalkyl group having a tertiary α-C atom may result in a catalyst that displays high catalytic activity and simultaneously high comonomer incorporation for ethylene/higher α-olefin copolymerization, which is of great significance because of the commercial importance of ethylene/higher α-olefin copolymers.

■ CONCLUSIONS

In summary, we studied the catalytic properties of bis(phenoxy−imine)Ti complexes (Ti-FI catalysts) bearing a series of substituents ortho to the phenoxy O's with DMAO activation for ethylene and ethylene/α-olefin (co)polymerizations. For ethylene polymerization, all of the DMAO-activated complexes showed some of the characteristics of living ethylene polymerization and could produce very narrow molecular-weight distribution PEs. An increase in the steric bulk of the ortho substituent led to enhanced catalytic activity for Ti complexes with the ortho substituents having both tertiary and quaternary α-C atoms attached to the phenoxy rings; the Ti complexes with the ortho substituents having the quaternary α-C atoms displayed higher catalytic activity. As to ethylene/α-olefin copolymerization, the Ti complexes with the ortho substituents having the tertiary α-C atoms and those with the ortho substituents having the quaternary α-C atoms behaved differently. For the Ti complexes possessing the quaternary α-C atoms, an increase in the steric bulk of the ortho substituent led to diminished activity and α-olefin incorporation, although for the Ti complexes with the tertiary α-C atoms, the increase resulted in enhanced catalytic activity and α-olefin incorporation.

We demonstrated the unique catalytic behavior of the Ti complexes with ortho cycloalkyl groups possessing tertiary α-C atoms. These Ti complexes achieved higher catalytic activity, together with far higher α-olefin incorporation than Ti complexes with ortho substituents possessing quaternary α-C atoms (^{t}Bu, CMe_2Ph). These facts suggest that for ethylene/α-olefin copolymerization, the steric bulk of the ortho substituent near the α-C atom plays a much more important role in the achievement of high catalytic activity and α-olefin incorporation than does the steric bulk of the entire ortho substituent. Notably, complex **4**, bearing the ortho cyclododecyl group, promoted the highest 1-hexene or 1-decene incorporation among the Ti complexes examined.

In addition and importantly, we revealed that Ti complex **7** bearing the ortho phenyl group exhibited exceptional behavior; namely, very high catalytic activity [ethylene and ethylene/α-olefin (co)polymerizations] and extremely high α-olefin incorporation (ethylene/α-olefin copolymerization). In our estimation, the electronically flexible properties of the phenoxy−imine ligand and the sterically open nature stemming from rotation of the ortho phenyl group may be responsible for the significant catalytic performance exhibited by complex **7**/DMAO.

The above polymerization results show that the ortho substituent is located at a strategic place vis-à-vis polymerization catalysis (i.e., catalytic activity and comonomer incorporation) and that control over the steric bulk of the ortho substituent near the α-C atom and the steric bulk of the entire ortho substituent gives rise to unique catalytic properties. The results described herein have further demonstrated the unique and versatile catalytic behavior of phenoxy−imine ligated early transition metal complexes (FI catalysts) for olefin insertion reactions, which may lead to the formation of additional value-added olefin-based compounds.[101]

EXPERIMENTAL SECTION

General Procedures and Materials. Dried solvents [diethyl ether (Et_2O), dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), and *n*-hexane] used for ligand and complex syntheses were purchased from Kanto Chemical Co., Inc. and Wako Pure Chemical Industries, Ltd. and used as received. Cyclooctene, cyclododecene, and ethyl magnesium bromide diethyl ether solution were obtained from Tokyo Kasei Kogyo Co., Ltd. 2-Cyclohexylphenol was purchased from Honshu Chemicals, Inc. *p*-Cresol and aniline for ligand syntheses were obtained from Wako Pure Chemical Industries, Ltd. *n*-Butyllithium hexane solution was purchased from Kanto Chemical Co., Inc. $TiCl_4$ as a 1.0 M toluene solution (Aldrich Chemical Co., Inc.) was used without further purification. The toluene used as a polymerization solvent (Wako Pure Chemical Industries, Ltd.) was dried over Al_2O_3 and degassed by the bubbling of dried nitrogen gas through it. Polymerization grade ethylene and propylene were obtained from Sumitomo Seika Co. and Mitsui Chemicals, Inc., respectively. Methylaluminoxane was purchased from Albemarle as a 1.2 M toluene solution, and the remaining trimethylaluminum was evaporated in vacuo, providing a solid white powder (DMAO). 1-Hexene and 1-decene (Wako Pure Chemical Industries, Ltd.) for copolymerization were dried over Al_2O_3 and degassed by the bubbling of dried nitrogen gas through them. All other chemicals were obtained commercially and used as supplied.

Ligand and Complex Analyses. ^1H NMR spectra were recorded on a JEOL 270 spectrometer (270 MHz) from Japan Electron Optics Laboratory Co. Ltd. in $CDCl_3$ with tetramethylsilane as the internal standard at ambient temperature (25 °C). Chemical shifts are reported in δ units. FD-MS spectra were recorded on a JMS-T100GC TOF mass spectrometer from Japan Electron Optics Laboratory Co. Ltd. Elemental analysis for C, H, and N was carried out using a CHNO-type instrument from Helaus Co.

Syntheses. Ligand syntheses were carried out under nitrogen in oven-dried glassware. All manipulations of complex syntheses were performed with the exclusion of oxygen and moisture under argon using standard Schlenk and cannula techniques in oven-dried glassware.

3-Cyclohexylsalicylaldehyde. A 3.0 M ethyl magnesium bromide diethyl ether solution (58.5 mL, 176 mmol) was added dropwise to a stirred solution of 2-cyclohexylphenol (29.5 g, 167 mmol) in THF (80 mL) at 0 °C. After the mixture was stirred at 0 °C for 2 h, a mixture of triethylamine (33.3 mL, 239 mmol) and paraformaldehyde [12.7 g (96% purity), 405 mmol] in toluene (100 mL) was added at room temperature. The resulting mixture was stirred for 2 h at 95 °C and was poured into 1 N HCl (250 mL) at 0 °C. The organic phase was separated, and the aqueous phase was extracted with diethyl ether (200 mL × 3). The combined organic phases were dried over $MgSO_4$ and evaporated in vacuo to give a yellow oil, which was purified by column chromatography on silica gel using *n*-hexane as eluent to give 3-cyclohexylsalicylaldehyde (18.0 g, 88.1 mmol) as a pale yellow oil in 53% yield. ^1H NMR ($CDCl_3$): δ 1.2−1.4 (m, 6H, cyclohexyl-CH_2), 1.74−1.92 (m, 4H, cyclohexyl-CH_2), 2.95−3.07 (m, 1H, cyclohexyl-CH), 6.98 (t, 1H, J = 7.3 Hz, aromatic H), 7.39 (dd, 1H, J = 7.3, 1.7 Hz, aromatic H), 7.45 (dd, 1H, J = 7.3, 1.7 Hz, aromatic H), 9.88 (s, 1H, CHO), 11.38 (s, 1H, OH).

N-(3-Cyclohexylsalicylidene)aniline. To a stirred solution of 3-cyclohexylsalicylaldehyde (3.11 g, 15.0 mmol) in ethanol (40 mL), aniline (1.54 g, 16.5 mmol) was added at room temperature. The resulting mixture was stirred at 80 °C for 17 h and then concentrated in vacuo to afford a crude imine compound. Purification by column chromatography on silica gel using *n*-hexane as eluent gave *N*-(3-cyclohexylsalicylidene)aniline (4.15 g, 14.4 mmol) as an orange oil in 96% yield. ^1H NMR ($CDCl_3$): δ 1.34−1.47 (m, 6H, cyclohexyl-CH_2), 1.74−1.93 (m, 4H, cyclohexyl-CH_2), 3.03−3.15 (m, 1H, cyclohexyl-CH), 6.90 (t, 1H, J = 7.6 Hz, aromatic H), 7.24−7.28 (m, 5H, aromatic H), 7.30−7.43 (m, 2H, aromatic H), 8.61 (s, 1H, CH=N), 13.68 (s, 1H, OH).

*Bis[N-(3-cyclohexylsalicylidene)anilinato]titanium(IV) Dichloride (**2**).* To a stirred solution of *N*-(3-cyclohexylsalicylidene)aniline (1.61 g, 5.60 mmol) in dried Et_2O (30 mL) at −78 °C, a 1.57 M *n*-butyllithium *n*-hexane solution (3.9 mL, 6.12 mmol) was added dropwise over a 10 min period. The solution was allowed to warm to room temperature and stirred for 7 h. The resulting mixture was added dropwise over a 25 min period to a 1.0 M solution of $TiCl_4$ in toluene (2.8 mL, 2.8 mmol) in dried Et_2O (30 mL) at −78 °C. The mixture was allowed to warm to room temperature and stirred for 18 h. Concentration of the reaction mixture in vacuo yielded a crude product. Dried CH_2Cl_2 (30 mL) was added to the crude product. The mixture was stirred for 15 min and then filtered. The solid residue was washed with dried CH_2Cl_2 (1 mL × 2), and the combined organic filtrates were concentrated in vacuo to afford a reddish brown solid. Dried Et_2O (20 mL) and dried *n*-hexane (10 mL) were added to the solid, and the mixture was stirred for 20 min. The resulting mixture was filtered and washed with dried *n*-hexane (2 mL × 2) and then dried in vacuo for 6 h to give complex **2** (0.65 g, 0.95 mmol) as a reddish brown powder in 34% yield. ^1H NMR ($CDCl_3$): δ 1.10−1.19 (m, 10H, cyclohexyl-CH_2), 2.62−2.74 (m, 2H, cyclohexyl-CH), 6.79 (t, 2H, J = 7.6 Hz, aromatic H), 6.94−7.12 (m, 14H, aromatic H), 8.05 (s, 2H, CH═N). FD-MS: 674 (M^+). Anal. Found: C, 68.09; H, 5.95; N, 3.83. Calcd. for $C_{38}H_{40}Cl_2N_2O_2Ti$: C, 67.56; H, 5.97; N, 4.15.

Complexes **3** and **4**, and their ligands were prepared by a route analogous to that outlined for complex **2** or its ligand synthesis.

4-Methyl-2-cyclooctylphenol. To a stirred mixture of *p*-cresol (44.4 g, 410 mmol), CH_2Cl_2 (500 mL), and cyclooctene (45.2 g, 410 mmol), concentrated sulfuric acid (24 mL) was added dropwise for 20 min while keeping the temperature below 0 °C. The reaction mixture was stirred for 30 min and then poured into a mixture of crushed ice and water. The resulting mixture was neutralized by adding a 3.0 N NaOH solution and then extracted with CH_2Cl_2 (250 mL × 3). The combined organic phases were washed with brine (200 mL), dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel using *n*-hexane/ethylacetate (20/1 v/v) as eluent to give 4-methyl-2-cyclooctylphenol (10.42 g, 47.7 mmol) as a colorless oil in 12% yield. ^1H NMR ($CDCl_3$): δ 1.50−1.90 (m, 15H, cyclooctyl-CH_2), 2.26 (s, 3H, Me), 2.97−3.09 (m, 1H, cyclooctyl-CH), 4.53 (br, 1H, OH), 6.63 (d, 1H, J = 7.2 Hz, aromatic H), 6.83 (dd, 1H, J = 7.2, 1.8 Hz, aromatic H), 6.96 (d, 1H, J = 1.8 Hz, aromatic H).

3-Cyclooctyl-5-methylsalicylaldehyde. 3-Cyclooctyl-5-methylsalicylaldehyde was obtained as a yellow oil in 71% yield from the reaction of 4-methyl-2-cyclooctylphenol using the same method as for 3-cyclohexylsalicylaldehyde synthesis. ^1H NMR ($CDCl_3$): δ 1.54−1.80 (m, 15H, cyclooctyl-CH_2), 2.31 (s, 3H, Me), 3.18−3.30 (m, 1H, cyclooctyl-CH), 7.13 (d, 1H, J = 2.3 Hz, aromatic H), 7.24 (d, 1H, J = 2.3 Hz, aromatic H), 9.80 (s, 1H, CHO), 11.18 (s, 1H, OH).

N-(3-Cyclooctyl-5-methylsalicylidene)aniline. *N*-(3-Cyclooctyl-5-methylsalicylidene)aniline was obtained as a yellow powder in 95% yield. ^1H NMR ($CDCl_3$): δ 1.60−1.80 (m, 15H, cyclooctyl-CH_2), 2.30 (s, 3H, Me), 3.25−3.37 (m, 1H, cyclooctyl-CH), 7.00 (d, 1H, J = 1.7 Hz, aromatic H), 7.10 (d, 1H, J = 1.7 Hz, aromatic H), 7.22−7.28 (m, 3H, aromatic H), 7.37−7.43 (m, 2H, aromatic H), 8.56 (s, 1H, CH═N), 13.38 (s, 1H, OH).

*Bis[N-(3-cyclooctyl-5-methylsalicylidene)anilinato]titanium(IV) Dichloride (**3**).* Compound **3** was obtained as a red powder in 45% yield. ^1H NMR ($CDCl_3$): δ 1.20−1.50 (m, 30H, cyclooctyl-CH_2), 2.22 (s, 6H, Me), 3.00−3.12 (m, 2H, cyclooctyl-CH), 6.79 (d, 2H, J = 1.6 Hz, aromatic H), 6.94−7.12 (m, 12H, aromatic H), 7.97 (s, 2H, CH═N). FD-MS: 758 (M^+). Anal. Found: C, 69.90; H, 5.85; N, 3.67. Calcd. for $C_{44}H_{52}Cl_2N_2O_2Ti$: C, 69.57; H, 6.90; N, 3.69.

4-Methyl-2-cyclododecylphenol. 4-Methyl-2-cyclododecylphenol was obtained as a white solid in 15% yield from the reaction of *p*-cresol and cyclododecene using the same method as for 4-methyl-2-cyclooctylphenol synthesis. ^1H NMR ($CDCl_3$): δ 1.20−1.65 (m, 22H, cyclododecyl-CH_2), 2.27 (s, 3H, Me), 3.07−3.19 (m, 1H, cyclooctyl-CH), 4.43 (br, 1H, OH), 6.75 (d, 1H, J = 1.7 Hz, aromatic H), 6.92 (dd, 1H, J = 7.3, 1.7 Hz, aromatic H), 7.00 (d, 1H, J = 1.7 Hz, aromatic H).

3-Cyclododecyl-5-methylsalicylaldehyde. 3-Cyclododecyl-5-methylsalicylaldehyde was obtained as a yellow solid in 61% yield. ^1H NMR ($CDCl_3$): δ 1.19−1.66 (m, 22H, cyclododecyl-CH_2), 2.32 (s, 3H, Me), 3.27−3.39 (m, 1H, cyclooctyl-CH), 7.15 (d, 1H, J = 1.6 Hz, aromatic H), 7.24 (d, 1H, J = 1.6 Hz, aromatic H), 9.82 (s, 1H, CHO), 11.14 (s, 1H, OH).

N-(3-Cyclododecyl-5-methylsalicylidene)aniline. *N*-(3-Cyclododecyl-5-methylsalicylidene)aniline was obtained as a yellow oil in 96% yield. ^1H NMR ($CDCl_3$): δ 1.50−1.90 (m, 22H, cyclododecyl-CH_2), 2.32 (s, 3H, Me), 3.34−3.46 (m, 1H, cyclododecyl-CH), 7.02 (d, 1H, J = 1.9 Hz, aromatic H), 7.10 (d, 1H, J = 1.9 Hz, aromatic H), 7.24−7.29 (m, 3H, aromatic H), 7.39−7.44 (m, 2H, aromatic H), 8.57 (s, 1H, CH═N), 13.24 (s, 1H, OH).

*Bis[N-(3-cyclododecyl-5-methylsalicylidene)anilinato]titanium(IV) Dichloride (**4**).* Compound **4** was obtained as a brown powder in 44% yield. ^1H NMR ($CDCl_3$): δ 1.20−1.50 (m, 44H, cyclododecyl-CH_2), 2.22 (s, 6H, Me), 3.17−3.29 (m, 2H, cyclododecyl-CH), 6.77 (d, 2H, J = 1.9 Hz, aromatic H), 6.99 (d, 2H, J = 1.9 Hz, aromatic H), 6.96−7.09 (m, 6H, aromatic H), 7.23−7.25 (m, 4H, aromatic H), 7.93 (s, 2H, CH═N). FD-MS: 870 (M^+). Anal. Found: C, 71.20; H, 7.81; N, 3.18. Calcd. for $C_{52}H_{68}Cl_2N_2O_2Ti$: C, 71.63; H, 7.86; N, 3.21.

X-ray Crystallography. The X-ray structure analysis data were collected using a Rigaku RAXIS-RAPID Imaging Plate (for complex **2**) or a Rigaku AFC7R diffractometer (for complex **3**). The structure was solved by direct method (SIR92)[164] and expanded using Fourier techniques.[165] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan crystallographic software package of the Rigaku/MSC and Rigaku Corporation.[166] Crystallographic data and the experimental details are summarized in Table 5.

Polymerization Procedures. *Ethylene Polymerization, Ethylene/Propylene Copolymerization.* Ethylene or ethylene/propylene (co)polymerization was carried out under atmospheric pressure in toluene using a 500 mL glass reactor equipped with a propeller-like mechanical stirrer and a condenser using a water/ethylene glycol mixture (below 0 °C) as a refrigerant. Toluene (250 mL) was introduced to the nitrogen-purged reactor and stirred vigorously (600 rpm). The toluene was kept at 50 °C, and the monomer gas feed was started (ethylene 100 L/h in ethylene polymerization; ethylene 50 L/h, propylene 150 L/h in ethylene/propylene copolymerization). After 10 min, (co)polymerization was initiated by adding 1.0 mL of DMAO solution in toluene (1.25 M, 1.25 mmol) followed by 1.0 mL of a prescribed concentration of complex solution in toluene (1.0−5.0 mM, 1.0−5.0 μmol) into the reactor with vigorous stirring (600 rpm).

Table 5. Summary of Crystallographic Data for Complexes **2** and **3**

complex	**2**	**3**
formula	$C_{38}H_{40}Cl_2N_2O_2Ti \cdot CH_2Cl_2$	$C_{44}H_{52}N_2O_2TiCl_2 \cdot (C_6H_{14})_{1/2}$
formula weight	760.42	801.75
crystal color, shape	red, prism	red, prism
crystal size/mm	0.45 × 0.30 × 0.25	0.25 × 0.20 × 0.20
crystal system	monoclinic	monoclinic
space group	$P2_1/c$ (#14)	$P2_1/c$ (#14)
a/Å	16.8818(5)	15.976(2)
b/Å	10.7967(3)	25.591(2)
c/Å	20.6102(6)	10.943(5)
β/deg	99.5901(7)	102.30(2)
V/Å^3	3704.1(2)	4371(2)
Z	4	4
D_{calcd}/g cm^{-3}	1.364	1.218
F_{000}	1584	1568
μ(Mo Kα)/mm^{-1}	0.556	0.357
λ (Mo Kα)/Å	0.71069	0.71069
T/°C	−173	−50
2θ max	61.0	55.0
no. of total reflns	70258	11985
no. of unique reflns	11305	10461
no. of observations	11298 ($F^2 > 2.00\sigma(F^2)$)	4593 ($I > 2.00\sigma(I)$)
no. of variables	433	478
refln/parameter ratio	26.1	9.61
residuals: R, R_w	0.0413, 0.1053	0.0635, 0.1676
goodness of fit indicator	0.87	1.01
max shift/error in final cycle	0.00	0.00
max and min peaks in final diff map/e$^-$ Å^{-3}	0.45, −0.47	0.36, −0.23

After a prescribed time, the (co)polymerization was quenched by the injection of isobutyl alcohol (3 mL), and the monomer gas feed was stopped. The resulting mixture was poured into acidified methanol (1 L containing 2 mL of conc HCl). The (co)polymer was collected by filtration, washed with methanol (200 mL × 2), and then dried in vacuo at 130 °C for 10 h.

Ethylene/Higher α-Olefin Copolymerization. Ethylene/higher α-olefin copolymerization was performed using the same type of equipment as the ethylene(/propylene) (co)polymerization described above. Toluene (200 mL) and a higher α-olefin (1-hexene or 1-decene, 50 mL) were introduced to the nitrogen-purged reactor and stirred vigorously (600 rpm). The solution was kept at 25 °C, and then the ethylene gas feed (100 L/h) was started. After 10 min, polymerization was initiated by adding 1.0 mL of DMAO solution in toluene (1.25 M, 1.25 mmol), followed by 1.0 mL of complex solution in toluene (2.5 mM, 2.5 μmol) into the reactor. After 5 min, the copolymerization was quenched by the injection of isobutyl alcohol (3 mL), and the ethylene gas feed was stopped. The resulting mixture was poured into acidified methanol (1 L containing 2 mL of conc HCl). The copolymer was collected by filtration, washed with methanol (200 mL × 2), and then dried in vacuo at 130 °C for 10 h.

Polymer Characterization. Molecular weights (M_w and M_n) and molecular weight distributions (M_w/M_n) were determined using a Waters GPC2000 gel permeation chromatograph equipped with four TSKgel columns (two sets of TSKgel GMH6-HT and two sets of TSKgel GMH6-HTL) at 140 °C using polyethylene calibration. *o*-Dichlorobenzene was employed as the solvent at a flow rate of 1.0 mL/min.

The comonomer (propylene, 1-hexene, and 1-decene) contents of the copolymers were determined by means of ^{1}H NMR analysis using an ECP500 spectrometer (500 MHz) from Japan Electron Optics Laboratory Co. Ltd.

DFT Calculations. DFT calculations were performed at the gradient-corrected density functional BLYP level[122−124] by means of the Amsterdam Density Functional program (ADF2006.01).[125−127] For geometry optimizations, we used a triple STO basis set on the titanium 3s, 3p, 3d, 4s, and 4p valence shells, and a double ζ STO basis set on the hydrogen (1s) and the remaining first row atoms (2s, 2p). The inner shells (except for the hydrogen atoms) were treated within the frozen-core approximation. For the energy calculations, the triple ζ STO basis set for the titanium and the double ζ plus polarization STO basis set for the other atoms were used, and the quasirelativistic correction was also added.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Crystallographic information files (CIF) for complexes **2** and **3** and ^{1}H NMR spectrum of complex **7** with a deuterated phenyl group (C_6D_5) on the imine N. This information is available free of charge via the Internet at http://pubs.acs.org/.

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