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Synthesis and Structural Analysis of Titanatranes Bearing Terminal Substituted Aryloxo Ligands of the type [Ti(OAr){(O-2,4-$Me_2C_6H_2$-6-CH_2)$_2$(OCH_2CH_2)N}]$_n$ (n = 1, 2): Effect of Aryloxo Substituents in the Ethylene Polymerization[†]

Prabhuodeyara M. Gurubasavaraj and Kotohiro Nomura*

Graduate School of Materials Science, Nara Institute of Science and Technology (NAIST), 8916-5 Takayama, Ikoma, Nara 630-0101, Japan

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A series of titanatranes containing both chelate bis(aryloxo)-(alkoxo)amine and the terminal aryloxo ligands of type [Ti(OAr)(L)]$_n$ [n=1 or 2, Ar=2,6-$Me_2C_6H_3$ (**1**), 2,6-^{i}$Pr_2C_6H_3$ (**2**), 2,6-$Ph_2C_6H_3$ (**3**), 2-FC_6H_4 (**4**), 2,6-$F_2C_6H_3$ (**5**), C_6F_5 (**6**); L=(O-2,4-$Me_2C_6H_2$-6-CH_2)$_2$(OCH_2CH_2)N)] have been prepared, and their structures (**1**, **3**−**6**) were determined by X-ray crystallography. The *ortho*-substituents in the terminal aryloxo ligand directly affect the structure in the solid state; the structures of **1**−**3** possessed monomeric form and fold a distorted trigonal bipyramidal geometry around Ti, whereas the structure of **4**−**6** were of dimeric form and fold a distorted octahedral around Ti bridged with oxygen in the alkoxo arm expressed as [Ti(OAr){(O-2,4-$Me_2C_6H_2$-6-CH_2)$_2$(μ_2-OCH_2CH_2)N)}]$_2$. The Ti−O(Ar) bond distances and the Ti−O−C(Ar) bond angles are highly influenced by the terminal aryloxo substituents especially in the *ortho*-position. The 2,6-^{i}$Pr_2C_6H_3$ analogue (**2**), the C_6F_5 analogue (**6**), and the 2,6-$Me_2C_6H_3$ analogue (**1**) showed moderate/notable catalytic activities for ethylene polymerization in the presence of MAO especially at 80−100 °C, whereas both the 2,6-$Ph_2C_6H_3$ analogue (**3**) and 2-FC_6H_4 analogue (**4**) showed the negligible catalytic activities, clearly indicating that the activity was strongly affected by the terminal aryloxo substituents especially in the *ortho*-position.

Introduction

There has been immense research interest in designing various metal complexes containing tripodal trianionic donor (called "atrane") ligands, such as tris(amido)amine, tris(alkoxo)amine, and tris(aryloxo)amine.[1−12] These trianionic donor ligands, usually bind to a transition metal in a tetradentate manner and are capable of providing a range of stable steric and electronic environments for (catalytically active) metal centers. The perfect combination consisting of the exocylic axial group and a flexible transannular bond between an axial nitrogen atom (of the tripodal ligand) and a metal ion generates a pseudo 3-fold symmetric environment (like a specific pocket around the metal center).[1] There have been many reports for synthesis, structural analysis, and some reactions not only of main group atranes (silatranes, phosphatranes, etc.)[1a−c,4] but also of the transition metal complexes containing atrane ligands,[1d,e,3,5−12] especially titanatranes.[2c,d,3b,d,5−11] Some successful examples, such as

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[†] Dedicated to Professor Dr. Herbert W. Roesky (Göttingen University, Germany) on the occasion of his 75th birthday.

*To whom correspondence should be addressed. E-mail: nomurak@ms.naist.jp. Phone: +81-743-72-6041. Fax: +81-743-72-6049.

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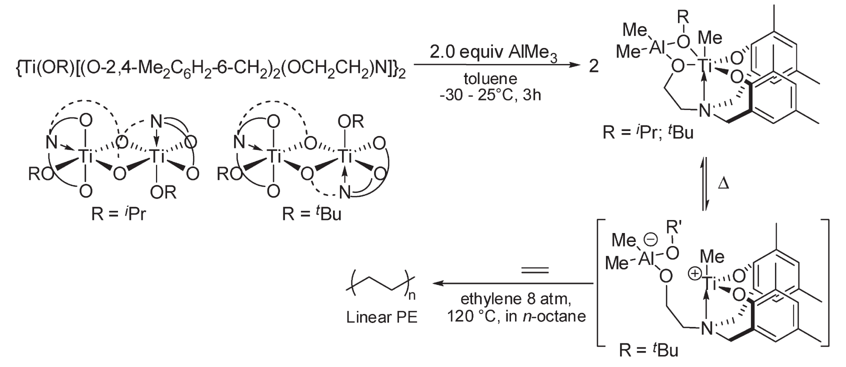
Scheme 1



Plausible Proposed Catalytically-Actie Species

applications as catalysts for organic synthesis by titanatranes[5,6h] and the catalytic dinitrogen activation by molybdenum complexes,[12] were well-known. Moreover, applications using titanatranes as the catalyst precursors for syndiospecific styrene polymerization[6e,7] and lactide polymerization[8] were known.

We reported that the titanium aryloxide/*iso*-propoxide complexes containing tris(aryloxo)amine ligand, $TiX[(O\text{-}2,4\text{-}R_2C_6H_2\text{-}6\text{-}CH_2)_3N]$ [R = Me, ^{t}Bu; X = O^{i}Pr, O-2,6-$^iPr_2C_6H_3$], were effective as catalysts precursor for ethylene polymerization in the presence of methylaluminoxane (MAO), and the activities remarkably increased at higher temperature even at 100−120 °C.[10] The activity also increased upon addition of small amount of $AlMe_3$. We thus focused on isolation of titanatranes containing bis(aryloxo)ethanolamine ligand of type $[Ti(OR')\{[(O\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_2(\mu_2\text{-}OCH_2CH_2)]N\}]_2$ [R′ = ^{i}Pr, ^{t}Bu] and reported that the dimeric titanatranes showed moderate catalytic activity for ethylene polymerization in the presence of MAO; the activity increased at higher temperature, as well as upon the addition of small amount of $AlMe_3$.[11a] The isolated Ti−Al heterobimetallic complex, $\{TiMe[(O\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_2(\mu_2\text{-}OCH_2CH_2)N]\}$-$[Me_2Al(\mu_2\text{-}O^tBu)]$, prepared by treatment with $AlMe_3$, showed moderate catalytic activity for ethylene polymerization without additional Al cocatalyst at 120 °C, affording high molecular weight polymer with unimodal distribution ($M_w = 1.00 \times 10^6$, $M_w/M_n = 2.58$). (Scheme 1).[11a] The result clearly suggests that the cationic species formed by cleavage of the Ti−O bonds play an important role as the active species for the polymerization. Later, we observed an improvement in the activity for the ethylene polymerization when the monomeric titanatrane containing a terminal aryloxo ligand, $Ti(O\text{-}2,6\text{-}^iPr_2C_6H_3)\{[(O\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_2(OCH_2CH_2)]N\}$,[6g] was used in place of the above titanatranes in the presence of MAO cocatalyst.[11b]

The above-mentioned results[10,11] prompted us to synthesize a series of titanatranes containing substituted aryloxo terminal ligands as the catalyst precursors for the olefin polymerization. Although considerable attention has been paid to modification of the atrane framework (e.g., variable ring size), however, detailed studies for synthesis and structural analysis for the titanatranes (bearing uniform ring size) containing various substituents on the aryloxo terminal ligand, including the effect of substituents on the aryloxo terminal ligands toward the crystal structures (monomeric/dimeric etc.) and the catalytic activities in the ethylene polymerization, have not so far been reported. In this paper, we thus explored syntheses and structural characterizations of titanatranes bearing substituted aryloxo ligands of the type $[Ti(OAr)\{(O\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_2(OCH_2CH_2)N\}]_n$ [n = 1,2; Ar = $2,6\text{-}Me_2C_6H_3$ (**1**), $2,6\text{-}^iPr_2C_6H_3$ (**2**), $2,6\text{-}Ph_2C_6H_3$ (**3**), $2\text{-}FC_6H_4$ (**4**), $2,6\text{-}F_2C_6H_3$ (**5**), C_6F_5 (**6**)] and their use in catalysis for ethylene polymerization in the presence of MAO cocatalyst (Chart 1).

Results and Discussion

1. Syntheses and Structural Analyses for Titanatranes Containing Substituted Aryloxo Terminal Ligands, $[Ti(OAr)\{(O\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_2(OCH_2CH_2)N\}]_n$ (n = 1, 2).

A series of titanatranes bearing substituted aryloxo ligands of the type $[Ti(OAr)(L)]_n$ [n = 1,2; Ar = $2,6\text{-}Me_2C_6H_3$ (**1**), $2,6\text{-}^iPr_2C_6H_3$ (**2**), $2,6\text{-}Ph_2C_6H_3$ (**3**), $2\text{-}FC_6H_4$ (**4**), 2,

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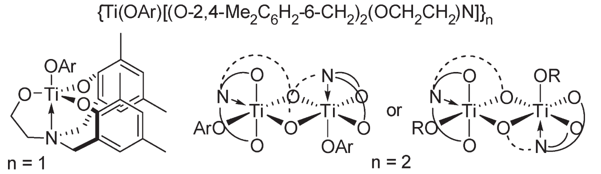
Chart 1



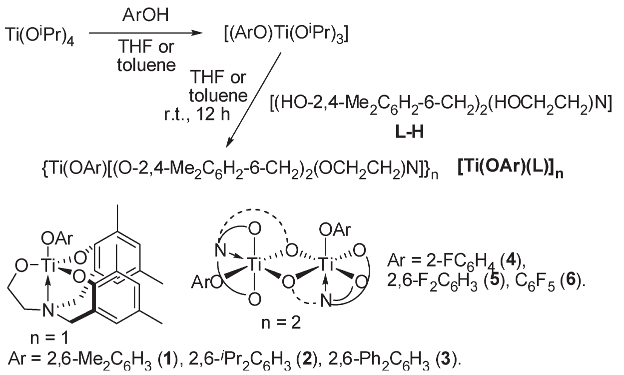
Ar = 2,6-Me$_2$C$_6$H$_3$ (**1**), 2,6-^{i}Pr$_2$C$_6$H$_3$ (**2**), 2,6-Ph$_2$C$_6$H$_3$ (**3**), 2-FC$_6$H$_4$ (**4**), 2,6-F$_2$C$_6$H$_3$ (**5**), C$_6$F$_5$ (**6**).

6-F$_2$C$_6$H$_3$ (**5**), C$_6$F$_5$ (**6**); L = (O-2,4-Me$_2$C$_6$H$_2$-6-CH$_2$)$_2$-(OCH$_2$CH$_2$)N}] have been prepared according to a modified method reported previously for synthesis of **2**.[6g] In situ formation of Ti(OAr)(O^{i}Pr)$_3$ by treatment of Ti(O^{i}Pr)$_4$ with 1 equiv of ArOH, followed by reaction with bis(2-hydroxy-3,5-dimethylbenzyl)ethanolamine (**L-H**) in THF or toluene at 25 °C (Scheme 2) afforded [Ti(OAr)(L)]$_n$ (**1**, **3**–**6**) as yellow-orange microcrystals in 69–86% yields after recrystallization from the chilled toluene solution (−18 °C). The resultant complexes were identified by NMR spectra and elemental analyses, and their structures were determined by X-ray crystallography, as described below.

The ^{1}H NMR spectra of **1** and **3** in C$_6$D$_6$ were analogous to that for **2**,[6g] and the non equivalent benzylic CH$_2$ protons of **1** and **3** appear as different resonances because a structure of the cage moiety of **1** and **3** is pseudo-C_s symmetric owing to the ring inversion.[13] Resonances ascribed to protons of both NCH_2-Ar and NCH_2-CH$_2$O groups in **1**–**3** were influenced by the substituent in the aryloxo terminal ligand (Me, ^{i}Pr, Ph) employed; the resonance in **1** was rather broad compared to that in **3**, probably because of the steric bulk of the phenyl group in **3** compared to that of the Me group in **1**.[13] The observed narrowing of these peaks would be assumed to be due to a difference in the rate of inversion of the terminal aryloxo group in the ^{1}H NMR time scale.

As shown in Figure 1, the ^{1}H NMR spectra in CDCl$_3$ for complexes **4**–**6** exhibit broad resonances at 25 °C, as observed in the titanatranes containing alkoxo terminal ligands, [Ti(OR′)(L)]$_2$ (R′ = ^{i}Pr, ^{t}Bu).[11a] Variable temperature (VT) NMR spectra of **4**–**6** showed a sharpening of each signal measured at 60 °C. As assumed in the case of titanatranes containing alkoxo terminal ligands, [Ti(OR′)(L)]$_2$,[11a] the observed broad resonances/temperature dependences might be due to several reasons such as (i) the cleavage of poly- or oligo-nuclear into monomeric species, (ii) an equilibrium between dimeric and monomeric species, (iii) the fluxional behavior of methylene units in these ligands. The third explanation, the fluxional nature of methylene units, may be most probably considered, because (1) the ^{1}H NMR spectrum of **4**–**6** even in THF-d_8 at 25 °C did not show any improvement in sharpening the resonances, although we assumed that THF may play a role to cleave the oligomeric (polymeric) or dimeric structure to monomeric by coordination of THF as a Lewis base adduct, (2) as described above, the observed resonances in the ^{1}H NMR spectra for (dimeric) complexes **4**–**6** were affected by the temperature measured (as shown in Figure 1), and similar temperature dependencies were observed in the ^{1}H NMR spectra for the monomeric titanatranes (**1**–**3**), (3) no significant changes in the chemical shifts of the methylene protons (especially for the alkoxo arm) were observed, and sharpening of the resonances was observed upon increasing the temperature, and (4) the same facts were seen in the similar titanatranes containing the alkoxo terminal ligand.[11a] The ^{19}F NMR spectra for **4**–**6** exhibit expected resonances.

Scheme 2



Structural Analysis for Complexes 1, 3–6. Suitable microcrystals of **1** and **3** for the X-ray crystallographic analysis were grown from a chilled toluene solution (−20 °C) for several days. Their structures are shown in Figure 2, and the selected bond distances and the angles for **1**–**3** determined by X-ray crystallography are summarized in Table 1.[14]

The structures indicate that these complexes possess a monomeric form as seen in the 2,6-^{i}Pr$_2$C$_6$H$_3$ analogue (**2**), which is in good agreement with the pattern in the ^{1}H NMR spectra, presumably because of the steric bulk of the axially located 2,6-dimethyl and 2,6-diphenyl phenolate ligands. As also seen in **2**, both **1** and **3** fold a distorted trigonal bipyramidal geometry around titanium and possess C_s symmetry; **1** crystallizes in orthorhombic space group $P2_12_12_1$ while complex **3** crystallizes in triclinic space group $P\bar{1}$. The coordination sphere of titanium consists of four oxygen atoms including three anionic oxygens from the atrane ligand, and the titanium atom in **1** and **3** is ligated via a transannular interaction stemming from the bridgehead amino nitrogen. The sum of the angles around the equatorial oxygens is 353.38(10)° and 353.56(9)° in **1** and **3**, respectively, both of which are in agreement with **2** [353.54(15)°]. As a consequence, the acute O$_{eq}$−Ti−N angles [av = 81.49(9)° for **1** and 81.60(8)° for **3**] and the obtuse O$_{eq}$−Ti−O$_{ax}$ angles [av = 98.67(11)° for **1** and 98.55(9)° for **3**] reflect a displacement of the titanium atom toward the axial oxygen, similar to the observation made in the case of **2**. Furthermore, the N$_{ax}$−Ti−O$_{ax}$ angle deviates from linearity by 6.84(10)° in **1** and by 7.44(7)° in **3**, compared to 9.62(13)° in **2**. These deviations are large compared with deviations of 0.20(8)−1.46(3)° reported for other mononuclear titanatranes,[5b,6f,7b] although values of 15.5(1)−51.05(8)° for this angle have been described for di- or multinuclear oxo-bridged titanatranes.[3b,6a−6d]

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[13] ^{1}H NMR spectra in CDCl$_3$ at various temperature for complexes **1** and **3** are shown in the Supporting Information.

[14] Detailed structural analysis results and structure reports including CIF files are shown in the Supporting Information.

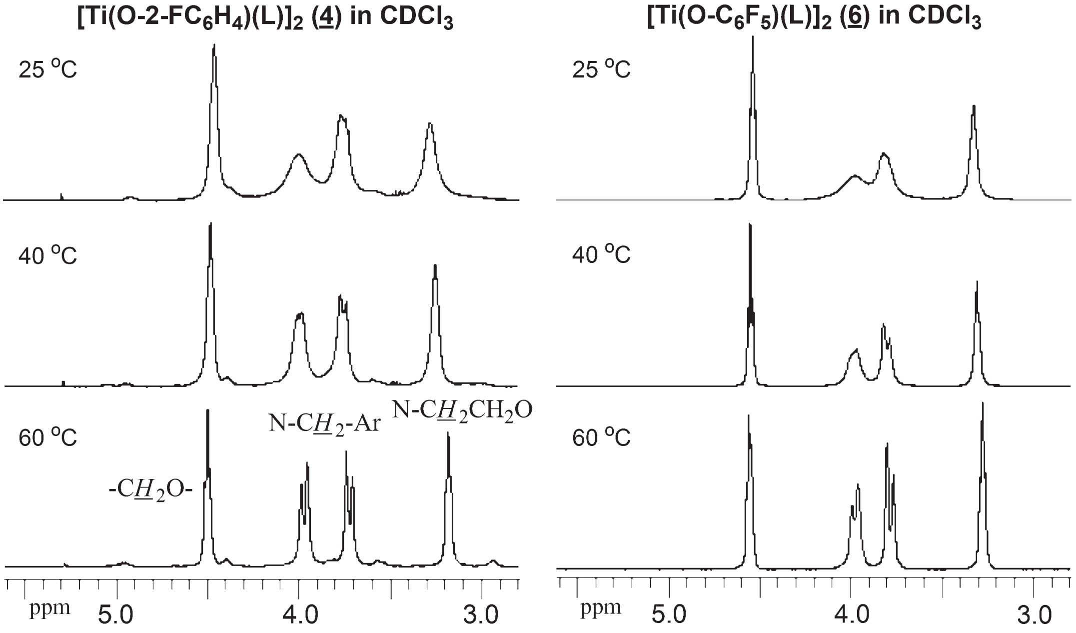

Figure 1. Variable temperature ^{1}H NMR spectra (in $CDCl_3$ extended at 3−5 ppm) of **4** (left) and **6** (right).

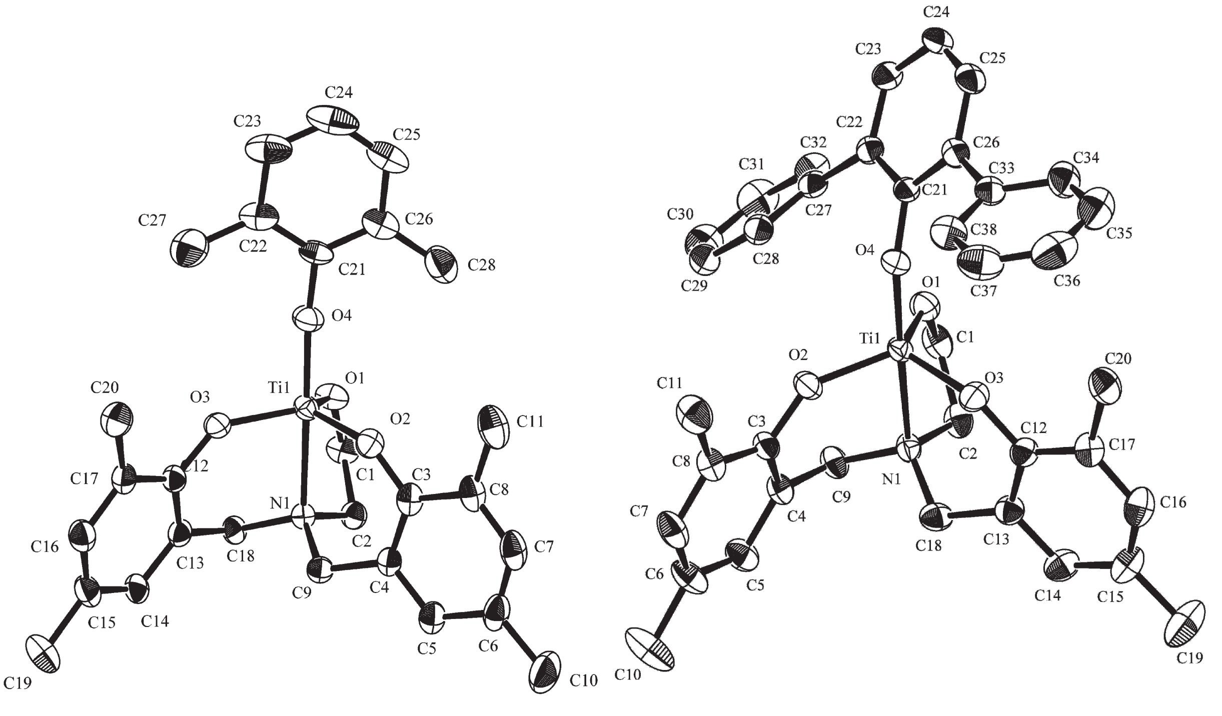

Figure 2. ORTEP Drawings of **1** (left) and **3** (right). Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.[14]

Note that both the bond lengths and the bond angles of **1**, **2**, and **3** are highly influenced by the ligands substituted at 2,6-positions on the terminal aryloxo ligand. The bond distance between the titanium and the terminal aryloxo oxygen in 2,6-$Me_2C_6H_3$ analogue (**1**) [Ti(1)−O(4) = 1.815(2) Å] is slightly shorter than that in the 2,6-$^iPr_2C_6H_3$ analogue (**2**) [1.825(3) Å],[6g] and apparently shorter than that in the 2,6-$Ph_2C_6H_3$ analogue (**3**) [Ti(1)−O(4) = 1.8576(19) Å].[15a] It is also noteworthy that the Ti−O−C(21) bond angle in **1** [174.0(2)°] is apparently different from those in **2** [145.7(3)°], **3** [141.12(15)°].[15c] The observed influence toward the Ti−O−C(Ar) bond angles is somewhat similar to the fact that the angles in Cp*$TiCl_2$(OAr) were influenced by the *ortho*-substituents in the aryloxo ligand,[15] and these would also be explained as an influence of (mostly) the steric bulk of the substituents in the *ortho*-position of the terminal aryloxo ligand. The

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(15) For example: (a) Nomura, K.; Tanaka, A.; Katao, S. *J. Mol. Catal. A* **2006**, *254*, 197–205; the Ti−O bond distance in Cp*$TiCl_2$(O-$R_2C_6H_3$) increased in the order: R=Ph [1.811(3) Å] > ^{t}Bu [1.804(2) Å] ≫ Me [1.785(2) Å], ^{i}Pr [1.772(3) Å]. (b) Nomura, K.; Liu, J.; Padmanabhan, S.; Kitiyanan, B. *J. Mol. Catal. A* **2007**, *267*, 1–29. (c) Nomura, K.; Naga, N.; Miki, M.; Yanagi, K. *Macromolecules* **1998**, *31*, 7588; the Ti−O−C(in Ar) in Cp$TiCl_n$(O-2,4,6-$Me_3C_6H_2)_{2-n}$ (n=0, 1) was highly influenced by the steric bulk around titanium. (d) Fenwick, A. E.; Phomphrai, K.; Thorn, M. G.; Vilardo, J. S.; Trefun, C. A.; Hanna, B.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **2004**, *23*, 2146.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for Ti(OAr)[(O-2,4-$Me_2C_6H_2$-6-$CH_2)_2(OCH_2CH_2)N$] [Ar = 2,6-$Me_2C_6H_3$ (**1**), 2,6-$Ph_2C_6H_3$ (**3**)][a]

Ar	2,6-$Me_2C_6H_3$ (**1**)	2,6-$^iPr_2C_6H_3$ (**2**)[b]	2,6-$Ph_2C_6H_3$ (**3**)
Selected Bond Distances (Å)			
Ti(1)−O(1)	1.839(2)	1.807(3)	1.8129(18)
Ti(1)−O(2)	1.846(2)	1.828(3)	1.834(2)
Ti(1)−O(3)	1.844(2)	1.829(3)	1.8257(17)
Ti(1)−O(4)	1.815(2)	1.825(3)	1.8576(19)
Ti(1)−N(1)	2.282(2)	2.287(4)	2.298(2)
O(1)−C(1)	1.426(4)	1.418(6)	1.429(3)
O(2)−C(3)	1.362(4)	1.361(5)	1.358(4)
O(3)−C(12)	1.361(4)	1.363(5)	1.371(2)
O(4)−C(21)	1.365(4)	1.350(5)	1.343(3)
N(1)−C(2)	1.488(4)	1.489(5)	1.505(3)
N(1)−C(9)	1.489(4)	1.418(5)	1.504(4)
N(1)−C(18)	1.492(3)	1.489(5)	1.481(3)
Selected Bond Angles (deg)			
O(1)−Ti(1)−O(2)	117.32(10)	117.91(15)	122.80(10)
O(1)−Ti(1)−O(3)	121.83(10)	121.16(15)	116.30(9)
O(1)−Ti(1)−O(4)	96.50(10)	93.68(14)	95.45(8)
O(1)−Ti(1)−N(1)	77.07(9)	76.87(14)	77.12(8)
O(2)−Ti(1)−O(3)	114.23(10)	114.47(14)	114.46(9)
O(2)−Ti(1)−O(4)	101.63(11)	102.43(13)	99.62(9)
O(2)−Ti(1)−N(1)	83.59(9)	83.89(13)	84.21(9)
O(3)−Ti(1)−O(4)	97.88(11)	99.66(14)	100.57(9)
O(3)−Ti(1)−N(1)	83.80(9)	84.01(13)	83.46(8)
O(4)−Ti(1)−N(1)	173.16(10)	170.38(13)	172.56(7)
Ti(1)−O(1)−C(1)	125.9(2)	127.5(3)	127.50(18)
Ti(1)−O(2)−C(3)	140.2(2)	140.8(3)	140.52(14)
Ti(1)−O(3)−C(12)	139.4(2)	140.0(3)	141.64(18)
Ti(1)−O(4)−C(21)	174.0(2)	145.7(3)	141.12(15)
Ti(1)−N(1)−C(2)	103.92(19)	103.2(3)	103.80(18)
Ti(1)−N(1)−C(9)	114.83(18)	113.5(3)	109.16(13)
Ti(1)−N(1)−C(18)	109.51(19)	109.7(3)	115.43(16)

[a] The details are shown in the Supporting Information.[14] [b] Corresponding bond distances and angles cited from reference .

Ti(1)−O(1) bond distance (titanium to oxygen of alkoxo arm) in **1** [1.839(2) Å] is longer than those in **2** [1.807(3) Å] and **3** [1.8129(18) Å]; the Ti(1)−O(3) bond lengths for the aryloxo bridged arm in **1** [1.846(2), 1.844(2) Å] are slightly longer than those in **2** [1.828(3), 1.829(3) Å] and **3** [1.834(2), 1.8257(17) Å]. These would also be due to an influence of the steric bulk of the substituents in the *ortho*-position of the terminal aryloxo ligand. In contrast, the Ti(1)−N(1) bond lengths in all the three complexes are similar [2.282(2)−2.298(2) Å] and fall near the short end of the range 2.264(3)−2.400(3) Å found in previously structurally characterized titanium tris(alkanol)amine derivatives.[6g]

Also note that the Ti−O(alkoxo) bond distances in **1**−**3** are shorter than those in the Ti−O(Ar in L) bond distances [**1**: 1.839(2) vs 1.846(2), 1.844(2) Å; **2**: 1.807(3) vs 1.828(3), 1.829(3) Å; **3**: 1.8129(18) vs 1.834(2), 1.8257(17) Å]. The fact clearly indicates that the alkoxo arm is more tightly bonded to the titanium than their aryloxo arms. All the Ti−O bond distances in **1** and **3** are shorter than Pauling's covalent radii,[16] and are also reasonably longer than the bridged bimetallic complexes [such as $Cp^*{}_2MeZr$-O-$TiMe_2Cp^*$ [1.816(4) Å];[17a] (L′)-MeAl-O-$TiMeCp_2$ [1.808(3) Å];[17b] (L′)MeAl-O-$TiMe_2$-Cp [1.764(1) Å],[17c] L′ = CH{N(2,6-$^iPr_2C_6H_3$)(CMe)}$_2$]. These aryloxo complexes (**1**, **2**, and **3**) have thus their titanium centers tightly bonded to the alkoxo arm of the atrane ligand (L), and the facts are an interesting contrast to those observed in the similar titanatranes containing alkoxo terminal ligands, $[Ti(OR')(L)]_2$[11a] and the titanatranes described below (**4**−**6**).

Suitable microcrystals for X-ray crystallographic analysis were grown from the chilled toluene solution containing **4**−**6** (at −20 °C). Their structures are shown in Figure 3 and the selected bond distances and angles are summarized in Table 2. These complexes fold dimeric structures bridged alkoxo ligands of the type [Ti(OAr){(O-2,4-$Me_2C_6H_2$-6-$CH_2)_2(\mu_2$-$OCH_2CH_2)N$}]$_2$ and the structure fold a rather distorted octahedral geometry around titanium: all compounds crystallize in monoclinic space group $P2_1/n$.[14] The facts (dimeric structures) observed here are in good correspondence to those observed in their ^{1}H NMR spectra, as described above, in which a broad resonances were seen and the spectra were dependent upon the temperature measured. The dimeric structures shown here (**4**−**6**) are a unique contrast to those in **1**−**3**, described above; the observed difference would be due to the lesser steric bulk in 2-FC_6H_4 (**4**), 2,6-$F_2C_6H_3$ (**5**), and C_6F_5 (**6**), especially the fluorine *ortho* substituent compared to 2,6-$R_2C_6H_3$ [R = Me (**1**), ^{i}Pr (**2**), Ph (**3**)] as the terminal aryloxo ligands, although we also have to take into consideration of the electronic effect (Me vs F). These results clearly indicate that the substituent in the terminal aryloxo ligand strongly influences their structures.

The bond distances between titanium and oxygen atoms indicate that the Ti−O bond lengths bound to the two titanium centers are influenced by the ligand in the *trans* position [e.g., Ti(1)−O(1) (*trans* to N), Ti(2)−O(1) (*trans* to O) = 2.032(3), 1.974(3) Å, for **4**; 2.019(5), 1.966(6) Å for **5**; 2.019(2), 2.014(2) Å for **6**, respectively]. These bond distances are similar to the titanatranes containing the alkoxo terminal complexes[11a] but are slightly longer than those in the terminal alkoxides [1.812(2), 1.778(3) Å] in $[Ti(OR')(L)]_2$,[11a] as well as in aryloxides [1.855(2)−1.922(2) Å]. The Ti−N bond distances are also influenced by the ligand coordinated in the *trans* position [e.g., Ti(1)−N(1) (*trans* to bridged oxygen), Ti(2)−N(2) (*trans* to terminal aryloxo group) = 2.295(4), 2.278(4) Å for **4**; 2.285(7), 2.285(7) Å for **5**; 2.290(3), 2.283(3) Å for **6**, respectively]. The Ti−O(Ar) bond distances are also influenced by the terminal aryloxo substituents [Ti−O: 1.849(3),1.881(3) Å for **4**; 1.860(6), 1.878(6) Å for **5**; 1.916(2),1.882(2) Å for **6**], and the bond distances are also influenced by the ligand in the *trans* position (bridged oxygen or nitrogen).

2. Ethylene Polymerization by 1−6−MAO Catalyst Systems. Ethylene polymerizations by **1**−**6** were conducted in *n*-octane in the presence of MAO cocatalyst. The white solid MAO, prepared by removing $AlMe_3$ and toluene from the commercially available MAO (PMAO-S, Tosoh Finechem Co.), was used because both titanatranes containing tris(aryloxo)amine ligand, TiX[(O-2,4-$R_2C_6H_2$-6-$CH_2)_3N$],[9] and titanatranes containing

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(16) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(17) (a) Gurubasavaraj, P. M.; Roesky, H. W.; Veeresha Sharma, P. M.; Oswald, R. B.; Dolle, V.; Herbst-Irmer, R.; Pal, A. *Organometallics* **2007**, *26*, 3346. (b) Gurubasavaraj, P. M.; Mandal, S. K.; Roesky, H. W.; Oswald, R. B.; Pal, A.; Noltemeyer, M. *Inorg. Chem.* **2007**, *46*, 1056. (c) Gurubasavaraj, P. M.; Roesky, H. W.; Nekouelsharaki, B.; Pal, A.; Herbst-Irmer, R. *Inorg. Chem.* **2008**, *47*, 5324.

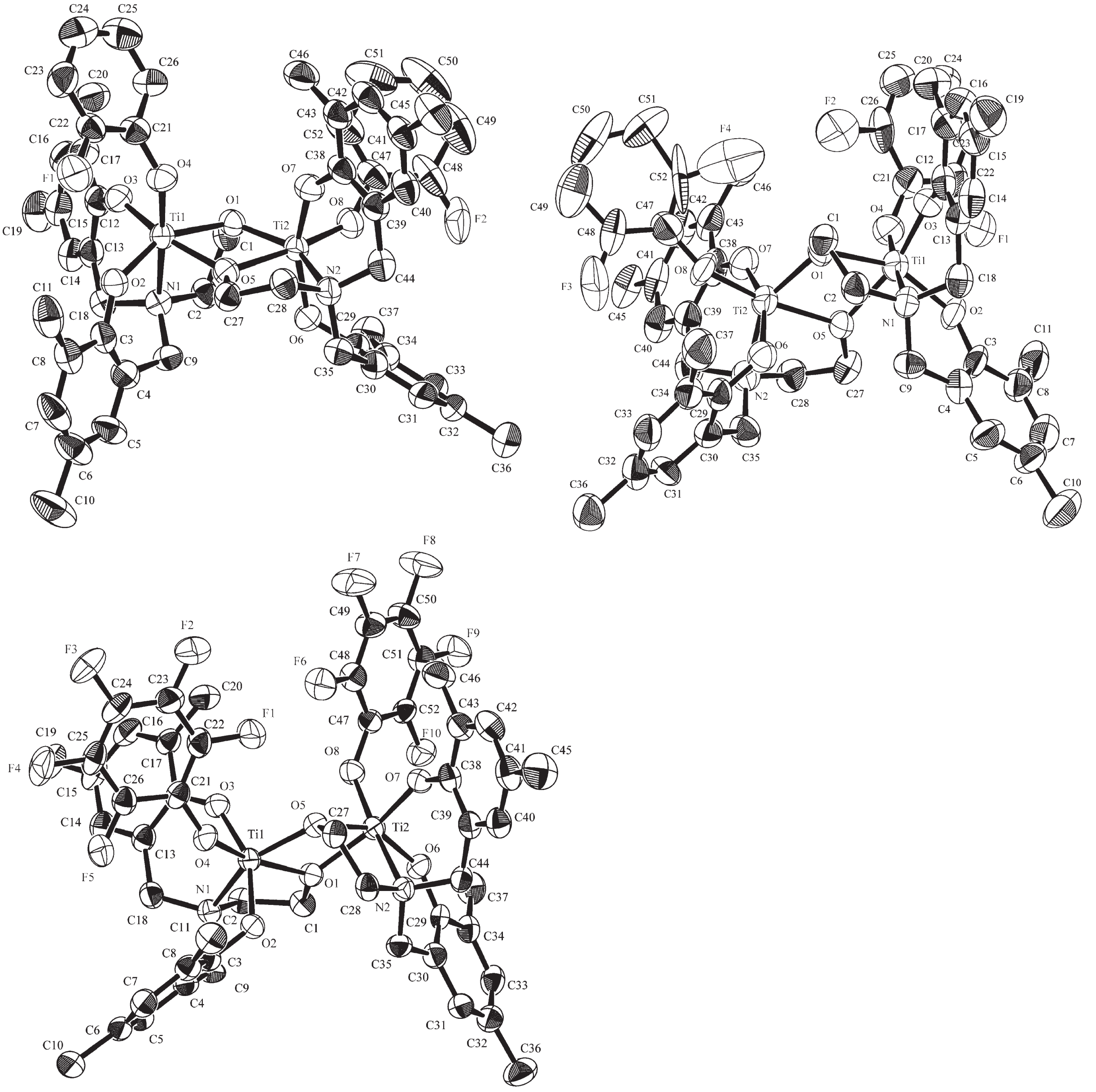

Figure 3. ORTEP drawings of **4** (top, left), **5** (top, right), and **6** (bottom, left). Thermal ellipsoids are drawn at the 50% probability level, and toluene molecules and H atoms are omitted for clarity.[14].

bis(aryloxo)-(alkoxo)amine and terminal alkoxo ligands, $[Ti(OR')(L)]_2$,[11a] were sensitive toward the amount of $AlMe_3$ into MAO. The results are summarized in Table 3.

The 2,6-$^iPr_2C_6H_3$ analogue (**2**) showed remarkable catalytic activity for ethylene polymerization at 100 °C (e.g., activity 1600−2000 kg-PE/mol-Ti·h),[11b] and the activity was affected by the Al/Ti molar ratio employed. The similar catalytic activity was observed even if the polymerizations were conducted at 80 °C (activity 1600−1860 kg-PE/mol-Ti·h), whereas the activity markedly decreased at 60 °C (activity 50 kg-PE/mol-Ti·h).[11b] The activities by the 2,6-$Me_2C_6H_3$ analogue (**1**) were lower than those by **2**, and similar effects toward the activity (Al/Ti molar ratios, temperature) were observed. The resultant polymers by **1**−**2** − MAO catalyst systems were linear polyethylene with relatively high molecular weights with unimodal molecular weight distributions in most cases; the distribution became broad if the polymerization was conducted in the presence of rather excess amount of MAO. The activities by **1**−**2**, [Ti(O-2,6-$R_2C_6H_3$)(L)] (R = Me, ^iPr), are higher than those by the titanatranes containing alkoxo terminal ligands, $[Ti(OR')(L)]_2$, under the same conditions.[11a]

Note that the activities by **1** and **2** decreased upon the addition of $AlMe_3$ (10 equiv to Ti), although the activity by titanatranes containing tris(aryloxo)amine ligand[9] and $[Ti(OR')(L)]_2$[11a] increased upon addition of small amounts of $AlMe_3$. As described below, the reaction of these titanatranes with $AlMe_3$ (2 equiv in *n*-hexane at 25 °C) did not take place, whereas the reactions with the titanatranes containing terminal alkoxo ligands exclusively afforded the heterobimetallic Ti−Al complexes,[11a] $\{TiMe[(O\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_2(\mu_2\text{-}OCH_2CH_2)N]\}\text{-}[Me_2Al(\mu_2\text{-}O^tBu)]$, which catalyze ethylene polymerization with/without assistance of an additional cocatalyst.[11a] The fact should be an interesting contrast

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for [Ti(OAr){(O-2,4-$Me_2C_6H_2$-6-CH_2)$_2$(μ_2-O CH_2CH_2)N}]$_2$ [Ar = 2-FC_6H_4 (**4**), 2,6-$F_2C_6H_3$ (**5**), C_6F_5 (**6**)][a]

Ar	2-FC_6H_4 (**4**)	2,6-$F_2C_6H_3$ (**5**)	C_6F_5 (**6**)
Selected Bond Distances (Å)			
Ti(1)−O(1)	2.032(3)	2.019(5)	2.019(2)
Ti(1)−O(2)	1.838(3)	1.830(5)	1.863(2)
Ti(1)−O(3)	1.849(3)	1.860(6)	1.830(2)
Ti(1)−O(4)	1.849(3)	1.860(6)	1.916(2)
Ti(1)−O(5)	2.007(3)	1.995(5)	1.964(2)
Ti(1)−N(1)	2.295(4)	2.285(7)	2.290(3)
Ti(2)−O(1)	1.974(3)	1.966(6)	2.014(2)
Ti(2)−O(5)	2.020(3)	2.017(5)	2.018(2)
Ti(2)−O(6)	1.875(3)	1.880(6)	1.828(2)
Ti(2)−O(7)	1.834(3)	1.823(6)	1.859(2)
Ti(2)−O(8)	1.881(3)	1.878(6)	1.882(2)
Ti(1)−N(2)	2.278(4)	2.285(7)	2.283(3)
Selected Bond Angles (deg)			
O(1)−Ti(1)−O(2)	150.59(15)	150.7(2)	96.33(11)
O(1)−Ti(1)−O(3)	92.84(14)	92.8(2)	96.69(12)
O(1)−Ti(1)−O(4)	103.33(15)	103.0(2)	165.63(12)
O(1)−Ti(1)−O(5)	71.47(13)	71.4(2)	72.15(11)
O(1)−Ti(1)−N(1)	76.45(14)	77.1(2)	76.51(11)
O(2)−Ti(1)−O(3)	104.64(16)	105.0(2)	155.26(13)
O(2)−Ti(1)−O(4)	99.34(16)	99.4(2)	84.29(12)
O(2)−Ti(1)−O(5)	89.58(15)	90.0(2)	99.89(11)
O(2)−Ti(1)−N(1)	82.68(15)	82.3(2)	82.47(11)
O(3)−Ti(1)−O(4)	92.64(16)	92.3(2)	88.22(12)
O(3)−Ti(1)−O(5)	164.30(14)	164.1(2)	104.10(11)
O(3)−Ti(1)−N(1)	82.07(15)	82.4(2)	80.24(11)
Ti(1)−O(4)−C(21)	139.2(3)	136.5(6)	139.8(2)
Ti(2)−O(8)−C(47)	138.0(3)	141.3(7)	134.4(2)

[a] The details are shown in the Supporting Information.[14]

between the alkoxo and the aryloxo terminal ligands,[18] although we do not have an appropriate explanation why the activity decreased upon addition of $AlMe_3$ in these catalyzes.

Importantly, the 2,6-$Ph_2C_6H_3$ analogue showed negligible catalytic activity even in the presence of excess amount of MAO. These results clearly indicate that the *ortho*-substituent in the terminal aryloxo ligand in the titanatranes directly affects the catalytic activity. Moreover, the 2-FC_6H_4 analogue (**4**) showed negligible catalytic activity, and low to moderate catalytic activities were observed if the 2,6-$F_2C_6H_3$ analogue (**5**) was used as the catalyst precursor. Note that the C_6F_5 analogue (**6**) showed high catalytic activities, and the activities by a series of titanatranes containing the aryloxo terminal ligands decreased in the order 2,6-$^i\mathrm{Pr}_2C_6H_3$ (**2**) > C_6F_5 (**6**) > 2,6-$Me_2C_6H_3$ (**1**) > 2,6-$F_2C_6H_3$ (**5**) ≫ 2,6-$Ph_2C_6H_3$ (**3**), 2-FC_6H_4 (**4**).[19] The activities by **5**, **6** decreased upon increasing the Al/Ti molar ratio, and the fact is somewhat different from those by **1**, **2**, probably because of difference in the stability of the catalytically active species under these conditions.

Concluding Remarks

We have prepared a series of titanatranes containing both chelate bis(aryloxo)-(alkoxo)amine and the terminal aryloxo ligands of type [Ti(OAr)(L)]$_n$ [n = 1 or 2, Ar = 2,6-$Me_2C_6H_3$ (**1**), 2,6-$^i\mathrm{Pr}_2C_6H_3$ (**2**),[6g] 2,6-$Ph_2C_6H_3$ (**3**), 2-FC_6H_4 (**4**), 2,6-$F_2C_6H_3$ (**5**), C_6F_5 (**6**); L = (O-2,4-$Me_2C_6H_2$-6-CH_2)$_2$(OCH_2CH_2)N], and their structures (**1**, **3**−**6**) were determined by X-ray crystallography. The *ortho*-substituents in the terminal aryloxo ligand directly affect the structure in the solid state; the structures of **1**−**3** were monomeric and fold a distorted trigonal bipyramidal around Ti, whereas the structure of **4**−**6** were of dimeric form and fold a distorted octahedral around Ti bridged with oxygen in the alkoxo arm expressed as [Ti(OAr){(O-2,4-$Me_2C_6H_2$-6-CH_2)$_2$(μ_2-OCH_2CH_2)N)}]$_2$. It turned out that the bond distances and Ti−O−C(Ar) bond angles are strongly influenced by the terminal aryloxo substituents especially in the *ortho*-position. Some of these complexes were effective as catalyst precursors for ethylene polymerization in the presence of MAO especially at 80−100 °C. The 2,6-$^i\mathrm{Pr}_2C_6H_3$ analogue (**2**), the C_6F_5 analogue (**6**), and the 2,6-$Me_2C_6H_3$ analogue (**1**) showed moderate/notable activities, whereas both the 2,6-$Ph_2C_6H_3$ analogue (**3**) and 2-FC_6H_4 analogue (**4**) showed the negligible catalytic activities. The facts clearly indicate that the activity was highly affected by the terminal aryloxo substituents especially in the *ortho*-position. The attempted reactions of these complexes (**1**−**3**) with 2 equiv of $AlMe_3$ in n-hexane did not take place at 25 °C, whereas the reaction of the titanatranes containing the alkoxo terminal ligand, [Ti(OR′)(L)]$_2$, afforded the heterobimetallic Ti−Al complexes, TiMe[(O-2,4-$Me_2C_6H_2$-6-CH_2)$_2$(μ_2-OCH_2CH_2)N)}[Me_2Al(μ_2-OR′)], which catalyze ethylene polymerization without any additional cocatalyst (R′ = ^{t}Bu).[11a,18] We believe the facts presented here should be important for designing efficient catalyst precursors for precise olefin polymerization, especially precise design of the terminal ligand as well as the chelate tetradentate donor ligand should be essential.

Experimental Section

General Procedures. All experimental manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques or using a glovebox unless otherwise specified. All chemicals used were of reagent grade and were purified by standard purification procedures. Toluene (anhydrous grade, Kanto Kagaku Co., Ltd.) and n-octane (anhydrous grade, Aldrich) for polymerization were stored in a bottle in the glovebox in the presence of molecular sieves. Polymerization grade ethylene was purchased (purity >99.9%, Sumitomo Seika Co. Ltd.) and used as received. Toluene and $AlMe_3$ from the commercially available MAO [PMAO-S, 9.5 wt % (Al) toluene solution, Tosoh Finechem Co.] were removed under reduced pressure (at ca. 50 °C for removing toluene and $AlMe_3$ and then heated at >100 °C for 1 h for completion) in the glovebox to give white solids. Bis(2-hydroxy-3,5-dimethylbenzyl)ethanolamine (L-H) was prepared according to a published procedure.[20] Molecular weights and molecular weight distributions

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(18) The fact would also suggest a possibility that the formation of catalytically active species in these titanatranes was different between [Ti(OR)(L)]$_2$ and Ti(OAr)(L). More recently, we observed cleanly the formation of another hetero bimetallic Ti−Al complex, {TiMe[(O-2,4-$Me_2C_6H_2$-6-CH_2)$_2$(μ_2-O-2,4-$Me_2C_6H_2$-6-CH_2)N][Me_2Al(μ_2-O^{i}Pr)], from the reaction of Ti(O^{i}Pr)[(O-2,4-$Me_2C_6H_2$-6-CH_2)$_3$N] with 1 equiv of $AlMe_3$ (G.M.P. unpublished result). Since the reaction of Ti(OAr)(L) even with 2 equiv of $AlMe_3$ in n-hexane did not take place at 25 °C, we may speculate that the reaction of the alkoxo arm (not the aryloxo terminal ligand) with MAO may first take place to generate the catalytically active species in the latter case.

(19) Although the polymerization results were highly reproducible (as shown in Table 3), we do not have any clear reasons why the 2-FC_6H_4 analogue (**4**) and 2,6-$Ph_2C_6H_3$ analogue (**3**) showed negligible catalytic activities under these conditions.

(20) Siegl, W. O.; Chattha, M. S. *Eur. Pat. Appl.* 276073, **1988**.

Table 3. Ethylene Polymerization by $[\mathrm{Ti(OAr)\{(O\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_2(OCH_2CH_2)N\}}]_n$ [n = 1, Ar = $2,6\text{-}\mathrm{Me_2C_6H_3}$ (**1**), $2,6\text{-}{}^i\mathrm{Pr_2C_6H_3}$ (**2**), $2,6\text{-}\mathrm{Ph_2C_6H_3}$ (**3**); n = 2, Ar = $2\text{-}\mathrm{FC_6H_4}$ (**4**), $2,6\text{-}\mathrm{F_2C_6H_3}$ (**5**), $\mathrm{C_6F_5}$ (**6**)]−MAO Catalyst Systems[a,b]

Ar (complex)	MAO/$\mathrm{AlMe_3}$/mmol (Al/Ti)[c]	temp/°C	yield/mg	activity[d]	M_{w}[e] $\times 10^{-4}$	M_{w}/M_n[e]
$2,6\text{-}\mathrm{Me_2C_6H_3}$ (**1**)	3.0 (60000)	80	41	820	24.7	1.31
$2,6\text{-}\mathrm{Me_2C_6H_3}$ (**1**)[f]	3.0 (60000)	80	41	820		
$2,6\text{-}\mathrm{Me_2C_6H_3}$ (**1**)	3.0/0.0005 (60000/10)	80	37	740	1.79	1.77
$2,6\text{-}\mathrm{Me_2C_6H_3}$ (**1**)[f]	3.0/0.0005 (60000/10)	80	38	760		
$2,6\text{-}\mathrm{Me_2C_6H_3}$ (**1**)	1.0 (20000)	100	11	220	23.5	1.32
$2,6\text{-}\mathrm{Me_2C_6H_3}$ (**1**)	2.0 (40000)	100	22	440	81.1	3.60
$2,6\text{-}\mathrm{Me_2C_6H_3}$ (**1**)	2.0/0.0005 (40000/10)	100	20	400	1.73	3.20
$2,6\text{-}\mathrm{Me_2C_6H_3}$ (**1**)	3.0 (60000)	100	28	560	39.0	1.69
$2,6\text{-}{}^i\mathrm{Pr_2C_6H_3}$ (**2**)	2.0 (40000)	80	85	1700	22.1	3.48
$2,6\text{-}{}^i\mathrm{Pr_2C_6H_3}$ (**2**)	2.0 (40000)	80	84	1680		
$2,6\text{-}{}^i\mathrm{Pr_2C_6H_3}$ (**2**)	3.0 (60000)	80	91	1820	32.6	3.08
$2,6\text{-}{}^i\mathrm{Pr_2C_6H_3}$ (**2**)[f]	3.0 (60000)	80	92	1840		
$2,6\text{-}{}^i\mathrm{Pr_2C_6H_3}$ (**2**)	3.0/0.0005 (60000/10)	80	80	1600	11.2	1.53
$2,6\text{-}{}^i\mathrm{Pr_2C_6H_3}$ (**2**)	4.0 (80000)	80	93	1860	16.5	3.28
$2,6\text{-}{}^i\mathrm{Pr_2C_6H_3}$ (**2**)	0.5 (10000)	100	55	1100	39.3	3.94
$2,6\text{-}{}^i\mathrm{Pr_2C_6H_3}$ (**2**)	1.0 (20000)	100	61	1220	32.3	2.45
$2,6\text{-}{}^i\mathrm{Pr_2C_6H_3}$ (**2**)[f]	1.0 (20000)	100	60	1200		
$2,6\text{-}{}^i\mathrm{Pr_2C_6H_3}$ (**2**)	2.0 (40000)	100	66	1320	33.7	2.96
$2,6\text{-}{}^i\mathrm{Pr_2C_6H_3}$ (**2**)[f]	2.0 (40000)	100	63	1280		
$2,6\text{-}{}^i\mathrm{Pr_2C_6H_3}$ (**2**)	2.0/0.0005 (40000/10)	100	58	1160	1.89	1.76
$2,6\text{-}{}^i\mathrm{Pr_2C_6H_3}$ (**2**)[f]	2.0/0.0005 (40000/10)	100	57	1140		
$2,6\text{-}{}^i\mathrm{Pr_2C_6H_3}$ (**2**)	3.0 (60000)	100	80	1600	35.1	4.90
$2,6\text{-}{}^i\mathrm{Pr_2C_6H_3}$ (**2**)[f]	3.0 (60000)	100	82	1640		
$2,6\text{-}{}^i\mathrm{Pr_2C_6H_3}$ (**2**)	3.0/0.0005 (60000/10)	100	70	1400	0.12	9.63
$2,6\text{-}{}^i\mathrm{Pr_2C_6H_3}$ (**2**)	4.0 (80000)	100	86	1720	22.3	3.06
$2,6\text{-}{}^i\mathrm{Pr_2C_6H_3}$ (**2**)	5.0 (100000)	100	100	2000	55.7	2.64
$2,6\text{-}\mathrm{Ph_2C_6H_3}$ (**3**)	3.0 (60000)	80	trace			
$2,6\text{-}\mathrm{Ph_2C_6H_3}$ (**3**)	3.0 (60000)	100	trace			
$2\text{-}\mathrm{FC_6H_4}$ (**4**)	3.0 (60000)	80	trace			
$2\text{-}\mathrm{FC_6H_4}$ (**4**)	3.0 (60000)	100	trace			
$2,6\text{-}\mathrm{F_2C_6H_3}$ (**5**)	3.0 (60000)	80	12	240	2.51	2.26
$2,6\text{-}\mathrm{F_2C_6H_3}$ (**5**)	0.5 (10000)	100	26	520	1.07	1.73
$2,6\text{-}\mathrm{F_2C_6H_3}$ (**5**)[f]	0.5 (10000)	100	26	520		
$2,6\text{-}\mathrm{F_2C_6H_3}$ (**5**)	1.0 (20000)	100	22	440	62.8	1.94
$2,6\text{-}\mathrm{F_2C_6H_3}$ (**5**)	2.0 (40000)	100	18	360	37.8	1.80
$2,6\text{-}\mathrm{F_2C_6H_3}$ (**5**)	3.0 (60000)	100	7	140		bimodal
$2,6\text{-}\mathrm{F_2C_6H_3}$ (**5**)	3.0 (60000)	120	trace			
$\mathrm{C_6F_5}$ (**6**)	3.0 (60000)	80	10	200	1.14	1.75
$\mathrm{C_6F_5}$ (**6**)	1.0 (20000)	100	22	440	78.04	2.29
$\mathrm{C_6F_5}$ (**6**)	2.0 (40000)	100	54	1080		bimodal
$\mathrm{C_6F_5}$ (**6**)[f]	2.0 (40000)	100	53	1060		
$\mathrm{C_6F_5}$ (**6**)	3.0 (60000)	100	65	1300	50.3	2.90
$\mathrm{C_6F_5}$ (**6**)[f]	3.0 (60000)	100	66	1320		
$\mathrm{C_6F_5}$ (**6**)	3.0/0.0005 (60000/10)	100	30	600	11.9	1.80
$\mathrm{C_6F_5}$ (**6**)	3.0 (60000)	120	31	620	38.2	1.91

[a] Conditions: Complex 0.05 μmol, *n*-octane 30 mL, ethylene 8 atm, MAO (prepared by removing $\mathrm{AlMe_3}$ and toluene from commercially available MAO), 60 min. [b] Ethylene polymerization results by **2** (under different conditions such as amount of catalyst, Al/Ti molar ratios) were also shown in reference. [c] Molar ratio of Al/Ti. [d] Activity = kg-PE/mol-Ti·h. [e] GPC data in *o*-dichlorobenzene vs polystyrene standards. [f] Polymerization results for reproducibility (independent experiments for this purpose).

for polyethylene were measured by gel permeation chromatography (Tosoh HLC- 8121GPC/HT) with a polystyrene gel column (TSK gel GMHHR-H HT × 2, 30 cm × 7.8 mm ø i.d.), ranging from $<10^2$ to $<2.8\times10^8$ MW) at 140 °C using *o*-dichlorobenzene containing 0.05 w/v % 2,6-di-*tert*-butyl-*p*-cresol as eluent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples. All ^{1}H and ^{19}F NMR spectra were recorded on a JEOL JNMLA 400 spectrometer (399.65 MHz for ^{1}H, 100.626 MHz for ^{13}C, 376.17 MHz for ^{19}F). All deuterated NMR solvents were stored over molecular sieves under a nitrogen atmosphere in the glovebox, and all chemical shifts are given in parts per million and referenced to tetramethyl silane (TMS). All spectra were obtained in the solvent indicated at 25 °C unless otherwise specified.

Syntheses of Titanatranes. The titanatranes containing phenoxy terminal ligands (**1**, **3**−**6**) were prepared by a modified procedure for **2** published previously.[6g] The typical procedure is as follows.

Synthesis of $\mathrm{Ti(O\text{-}2,6\text{-}Me_2C_6H_3)\{(O\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_2(OCH_2CH_2)N\}}$ (1). A toluene solution (10 mL) containing $2,6\text{-}\mathrm{Me_2C_6H_3OH}$ (0.244 g, 2.00 mmol) was added dropwise into a toluene solution (10 mL) containing $\mathrm{Ti(O^iPr)_4}$ (0.658 g, 2.00 mmol) at room temperature (25 °C). After 1 h, a toluene solution (10 mL) containing bis(2-hydroxy-3,5-dimethylbenzyl)ethanolamine (0.658 g, 2.00 mmol) was then added dropwise to the reaction vessel. The reaction mixture was stirred at room temperature overnight, and then the volatiles were evaporated under vacuum, leaving an orange-yellow solids. The resultant solids were added to 15 mL of toluene, and the orange solution was filtered through Celite pad. The filtrate was placed in vacuo to give the orange-yellow solids. The complex **1** was isolated as orange-yellow microcrystals from the chilled toluene solution (−15 °C). Yield (0.521 g, 78%). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 7.12 (d, 2H, J = 7.3 Hz, terminal aryl-*H*), 6.90 (t, 1H, J = 7.5 Hz, terminal aryl-*H*), 6.77 (br.s, 2H, aryl-*H*), 6.51 (br.s, 2H, aryl-*H*), 3.95 (br.t, 2H, $\mathrm{C}H_2\mathrm{O}$), 3.34 and 3.11 (br.d, 4H, $\mathrm{N}CH_2$-aryl), 2.81 (s, 6H, terminal aryl-$\mathrm{C}H_3$), 2.32 (s, 2H, $\mathrm{N}CH_2\mathrm{CH_2}$), 2.22 (s, 6H, aryl-*Me*), 2.16 (s, 6H,

Table 4. Crystallographic Data and Structure Refinement for Compounds **1**, **3**, **4**, **5**, and **6**[a]

	1	**3**	**4**[b]	**5**[b]	**6**[b]
empirical formula	$C_{28}H_{33}NO_4Ti$	$C_{38}H_{37}NO_4Ti$	$C_{131}H_{124}F_4N_4O_{16}Ti_4$	$C_{139.40}H_{124}F_8N_4O_{16}Ti_4$	$C_{135}H_{128}N_4O_{16}F_{20}Ti_4$
formula weight	495.47	619.61	2278.03	2454.92	2634.08
crystal system, space group	orthorhombic, $P2_12_12_1$	triclinic, $P\overline{1}$	monoclinic, $P2_1/n$	monoclinic, $P2_1/n$	monoclinic, $P2_1/n$
a [Å]	9.8007(3)	11.3277(5)	14.0275(7)	14.0922(8)	14.4822(6)
b [Å]	12.0225(5)	11.8376(5)	24.9336(11)	25.1053(13)	25.7823(8)
c [Å]	21.8908(8)	14.6005(7)	17.3094(7)	17.4834(11)	16.9356(6)
α [deg]		72.2383(16)			
β [deg]		69.0925(15)	93.3960(14)	93.0577(18)	94.8210(13)
γ [deg]		63.7256(11)			
V [Å^3]	2579.39(16)	1614.48(12)	6043.4(5)	6176.6(6)	6301.1(4)
Z	4	2	2	2	2
D_{calcd}	1.276	1.274	1.252	1.320	1.388
μ(Mo Kα) cm^{-1}	3.648	3.06	3.253	3.281	3.396
F (000)	1048.00	652.00	2380.00	2552.80	2724.00
2θmax [deg]	50.6	50.7	48.8	48.2	50.7
no. of reflections collected/unique	21447/2668 ($R_{\text{int}} = 0.044$)	13537/5898 ($R_{\text{int}} = 0.031$)	45019/9897 ($R_{\text{int}} = 0.077$)	44799/9796 ($R_{\text{int}} = 0.136$)	51321/11493 ($R_{\text{int}} = 0.071$)
observed reflections [$I > 2\sigma(I)$]	2333	4655	5028	3460	6559
gof	1.003	1.005	1.085	1.002	1.002
R_1, wR_2 [$I > 2\sigma(I)$]	0.0338, 0.0912	0.0425, 0.0803	0.0616, 0.0709	0.0642, 0.1612	0.0497, 0.1334
largest diff peak/hole [e Å^{-3}]	0.28/-0.30	0.40/-0.32	0.88/-0.45	0.41/-0.33	0.63/-0.37

[a] Detailed results are shown in the Supporting Information. [b] The crystal contained toluene in the formula (with certain ratio).

aryl-*Me*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 163.8, 159.1, 131.1, 129.5, 127.7, 127.6, 127.4, 124.8, 122.9, 120.4 (aryl), 72.0 (CH_2O), 57.2 (NCH_2-aryl), 56.8 (NCH_2CH_2), 20.5 (aryl-*Me*), 17.5 (terminal aryloxo-*Me*), 16.2 (aryl-*Me*). Anal. Calcd for $C_{28}H_{33}NO_4Ti$: C, 67.88; H, 6.71; N, 2.83. Found: C, 67.78; H, 6.90; N, 2.75.

Synthesis of Ti(O-2,6-$Ph_2C_6H_3$){(O-2,4-$Me_2C_6H_2$-6-CH_2)$_2$-(OCH_2CH_2)N} (3). The procedure for synthesis of **3** was conducted by the similar procedure for **1**, except that 2,6-$Ph_2C_6H_3OH$ was used in place of 2,6-$Me_2C_6H_3OH$. Yield 81%. ^1H NMR (C_6D_6): δ 7.92 (dd, 4H, $J = 7.7$ Hz, phenyl-*H*), 7.36 (d, $J = 7.7$ Hz, 2H, phenyl-*H*), 7.20 (t or dd, 4H, $J = 7.7$ Hz, phenyl-*H*), 7.04 (t, 2H, $J = 7.3$ Hz, phenyl-*H*), 6.93 (t, 1H, $J = 7.3$ Hz, phenyl-*H*), 6.76 (br.s, 2H aryl-H), 6.44 (br.s, 2H aryl-H), 3.59 (t, 2H, CH_2O), 3.06 and 2.97 (d, 4H, NCH_2-aryl), 2.14 (s, 8H, aryl-Me; NCH_2CH_2 peak merges with the aryl-*Me* peak), 1.95 (s, 6H, aryl-*Me*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 161.3, 159.4, 141.1, 133.4, 131.3, 130.8 130.4, 129.1, 127.8, 127.6, 126.4, 125.1, 123.1, 121.2 (aryl), 72.3 (CH_2O), 57.2 (NCH_2-aryl), 56.9 (NCH_2CH_2), 20.7 (aryl-*Me*), 16.1 (aryl-*Me*). Anal. Calcd for $C_{38}H_{37}NO_4Ti$: C, 73.66; H, 6.02; N, 2.26. Found: C, 73.06; H, 6.07; N, 2.06.

Synthesis of [Ti(O-2-FC_6H_4){(O-2,4-$Me_2C_6H_2$-6-CH_2)$_2$(μ_2-OCH_2CH_2)N}]$_2$ (4). The procedure for synthesis of **4** was conducted by the similar procedure for **1**, except that 2-FC_6H_4OH was used in place of 2,6-$Me_2C_6H_3OH$. Yield 69%. ^1H NMR ($CDCl_3$): δ 6.64−6.98 (m, 4H, terminal aryl-*H*), 6.88 (br.s, 2H, aryl-*H*), 6.70 (br.s, 2H, aryl-*H*), 4.47 (br.s, 2H, CH_2O), 4.00 and 3.76 (br, 4H, NCH_2-aryl), 3.30 (s, 2H, NCH_2CH_2), 2.21 (s, 6H, aryl-*Me*), 2.00 (s, 6H, aryl-*Me*). ^{19}F NMR ($CDCl_3$) δ 16.75 (s). Anal. Calcd for $C_{52}H_{56}F_2N_2O_8Ti_2 \cdot 4/3$ toluene: C, 67.35; H, 6.14; N, 2.56. Found: C, 67.02; H, 6.25; N, 2.72.

Synthesis of [Ti(O-2,6-$F_2C_6H_3$){(O-2,4-$Me_2C_6H_2$-6-CH_2)$_2$-(μ_2-OCH_2CH_2)N}]$_2$ (5). The procedure for synthesis of **5** was conducted by the similar procedure for **1**, except that 2,6-$F_2C_6H_3OH$ was used in place of 2,6-$Me_2C_6H_3OH$. Yield 82%. ^1H NMR ($CDCl_3$): δ. 6.81 (br.s, 2H, aryl-*H*), 6.70 (br.s, 2H, aryl-*H*), 6.64 (m, 2H, terminal aryl-*H*), 6.51 (m, 1H, terminal aryl-*H*), 4.55 (br.s, 2H, CH_2O), 3.99 and 3.83 (br, 4H, NCH_2-aryl), 3.30 (s, 2H, NCH_2CH_2), 2.21 (s, 6H, aryl-*Me*), 2.02 (s, 6H, aryl-*Me*). ^{19}F NMR ($CDCl_3$) δ −80.48 (b, s). Anal. Calcd for $C_{52}H_{54}F_4N_2O_8Ti_2 \cdot 8/5$ toluene: C, 65.77; H, 5.83; N, 2.43. Found: C, 65.75; H, 5.88; N, 2.35.

Synthesis of [Ti(OC_6F_5){(O-2,4-$Me_2C_6H_2$-6-CH_2)$_2$(μ_2-OCH_2CH_2)N}]$_2$ (6). The procedure for synthesis of **6** was conducted by the similar procedure for **1**, except that C_6H_5OH was used in place of 2,6-$Me_2C_6H_3OH$. Yield 86%. ^1H NMR ($CDCl_3$): δ 6.83 (br.s, 2H, aryl-*H*), 6.70 (br.s, 2H, aryl-*H*), 4.54 (t, 2H, CH_2O), 3.99 and 3.83 (br, 4H, NCH_2-aryl), 3.34 (s, 2H, NCH_2CH_2), 2.20 (s, 6H, aryl-*Me*), 2.00 (s, 6H, aryl-*Me*). ^{19}F NMR ($CDCl_3$): δ −10.48 (b, d, ortho*F*), −17.59 (b, t, para*F*), −22.85 (b, t, meta*F*). Anal. Calcd for $C_{52}H_{48}F_{10}N_2O_8Ti_2 \cdot 9/5$: C, 60.59; H, 4.91; N, 2.19. Found: C, 60.70; H, 4.94; N, 2.41.

Crystallographic Analysis. All measurements were made on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo Kα radiation. All structures were solved by direct methods and expanded using Fourier techniques,[21] and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations for complexes **1**, **3**−**6** were performed using the crystal structure crystallographic software package.[22] Selected crystal collection parameters are summarized in Table 4, and the detailed structure reports including their CIF files were shown in the Supporting Information.

Polymerization of Ethylene. Ethylene polymerizations were conducted in toluene or in *n*-octane by using a 100 mL scale autoclave. The typical procedure (run 1, Table 3) was performed as follows. Solvent (29.0 mL) and d-MAO (3.0 mmol) prepared by removing toluene and $AlMe_3$ from the commercially available MAO (PMAO-S, Tosoh Finechem Co.) were charged into an autoclave in the drybox, and the apparatus was placed under an ethylene atmosphere (1 atm). After the addition of toluene or *n*-octane solution (1.0 mL) containing catalyst via a syringe, the reaction apparatus was pressurized to 7 atm (total 8 atm), and the mixture was stirred magnetically for 10 or 60 min. After the above procedure, ethylene was purged, and the mixture was then poured into MeOH (150 mL) containing HCl (10 mL). The resultant polymer was collected on a filter paper by filtration and was adequately washed with MeOH and then dried under vacuum.

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Supporting Information Available: ^{1}H NMR spectra for complexes **1**−**6**, and X-ray crystallographic data and analysis reports including their CIF files for complexes **1** and **3**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.