# ORGANOMETALLICS

# Effect of Terminal Aryloxo Ligands in Ethylene Polymerization Using Titanatranes of the Type, $[Ti(OAr){(O-2,4-R_2C_6H_2)-6-CH_2}_3N]$ : Synthesis and Structural Analysis of the Heterobimetallic Complexes of Titanatranes with AlMe<sub>3</sub>

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**Supporting Information** 

ABSTRACT: Effects of aryloxo terminal ligands and AlMe<sub>3</sub> in ethylene polymerization using a series of Ti(OAr)[{(O-2,4- $R_{2}C_{6}H_{2}$ -6-CH<sub>2</sub> $_{3}N$  [R = Me (1), <sup>t</sup>Bu (2); Ar = 2,6-Me\_{2}C\_{6}H\_{3} (a),  $2_{,6}$ -<sup>*i*</sup> $Pr_2C_6H_3$  (b),  $2_{,6}$ - $Ph_2C_6H_3$  (c),  $2_{,6}$ - $F_2C_6H_3$  (d),  $C_6F_5$  (e)] (1a-1e, 2d, 2e) in the presence of methylaluminoxane (MAO) have been explored. Reactions of 1b,1d,1e, which showed an increase in the activity upon addition of a small amount of AlMe<sub>3</sub>, with 1.0 equiv of AlMe3 afforded heterobimetallic Ti-Al complexes,  $TiMe(O-2,6^{-i}Pr_{2}C_{6}H_{3})[(O-2,4-Me_{2}C_{6}H_{2}-6-CH_{2})(\mu_{2}-6-CH_{2})]$  $O-2,4-Me_2C_6H_2-6-CH_2)(Me_2Al-\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)N$ (3b) and  $[TiMe{(O-2,4-Me_2C_6H_2-6-CH_2)_2(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)_2(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)_2(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)_2(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)_2(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)_2(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)_2(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)_2(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)_2(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)_2(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)_2(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)_2(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)_2(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)_2(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)_2(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)_2(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)_2(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)_2(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)_2(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)_2(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)_2(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)_2(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)_2(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)_2(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)_2(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_2-2)_2(\mu_$  $6-CH_2)N\}][Me_2Al(\mu_2-OAr)] [Ar = 2,6-F_2C_6H_3 (3d), C_6F_5 (3e)],$ in moderate yields, and their structures were determined by X-ray crystallography. In contrast, the similar reaction of 1a (which



showed a decrease in the activity upon addition of AlMe<sub>3</sub>) yielded  $[Al(\mu_2-O-2,6-C_6H_3)Me_2]_2$  and  $TiMe[{(O-2,4-Me_2C_6H_2)-6-C_6H_3}Me_2]_2$  $(CH_2)_3N$  as isolated forms:  $[Al(\mu_2-OC_6F_5)Me_2]_2$  was isolated from the mixture in the reactions of 1c,2d,2e. The isolated heterobimetallic complexes (3b,3d,3e) exhibited high catalytic activities for ethylene polymerization in the presence of MAO, suggesting that these bimetallic species play a role in this catalysis.

# INTRODUCTION

The design of efficient molecular catalysts for precise olefin polymerization has been one of the most attractive research fields since the discovery of Ziegler-Natta catalysts.<sup>1-7</sup> In the typical polymerization process, transition-metal complexes are activated by different types of cocatalysts to form cationic species, which are proposed to be an active species in this catalysis.<sup>2d,8,9</sup> Al reagents, such as Al alkyl methylaluminoxane (MAO), play an important role as cocatalysts,<sup>10</sup> and these Al complexes are also involved in the catalysis by forming heterobimetallic complexes or counteranions with titanium complexes.<sup>8,11,12</sup> These bimetallic complexes exhibit high catalytic activity to produce polymers with different microstructures. The activation of metal complexes is usually associated with a decrease in complex stability due to the electronic deficiency of the metal center,<sup>8,9</sup> but this would be improved/tuned by ligand modifications with several donor atoms.

Atrane ligands contain a neutral nitrogen atom that facilitates coordination in a chelate fashion when necessary by providing the metal with additional electronic density. There have been many reports for the synthesis of complexes containing the

atrane ligands,<sup>13,14</sup> including main group metals to transitionmetal complexes. Titanatranes among group 4 metals have been utilized in organic synthesis,<sup>14a-f</sup> and syndiospecific styrene polymerization.<sup>14g-k</sup> We have focused on titanatranes that feature two or three aryloxo arms as the catalyst precursors for olefin polymerization.<sup>15,16</sup> We first demonstrated that  $Ti(O^{i}Pr)[(O-2,4-R_{2}C_{6}H_{2}-6-CH_{2})_{3}N]$  (R = Me, <sup>t</sup>Bu) were effective as catalyst precursors for ethylene polymerization in the presence of MAO, and the activities remarkably increased at higher temperature even at 100-120 °C.<sup>15a</sup> The activity also increased upon addition of a small amount of AlMe<sub>3</sub>.<sup>15a</sup> Recently, we isolated heterobimetallic Ti-Al complexes of the type,  $[TiMe{(\mu_2-O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-CH_2)(O-2,4-R_2C_6H_2-CH_2)(O-2,4-R_2C_6H_2-CH_2)(O-2,4-R_2C_6H_2-CH_2)(O-2,4-R_2C_6H_2-CH_2)(O-2,4-R_2C_6H_2-CH_2)(O-2,4-R_2C_6H_2-CH_2)(O-2,4-R_2C_6H_2-CH_2)(O-2,4-R_2C_6H_2-CH_2)(O-2,4-R_2C_6H_2-CH_2)(O-2,4-R_2C_6H_2-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,4-CH_2)(O-2,CH_2)(O-2,4-CH_2)(O-2,CH_2)(O-2,CH_2)(O-2,CH_2)(O-2,CH_2)(O-2,CH_$  $CH_2$ \_N}][R'\_Al( $\mu_2$ -O'Pr)], and demonstrated that these are effective as catalyst precursors for ethylene polymerization.

Recently, we isolated heterobimetallic Ti-Al complexes containing a tris(aryloxo)amine ligand of the type, [TiMe{( $\mu_2$ - $O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)_2N$ ][Me<sub>2</sub>Al( $\mu_2$ -O'Pr)], which exhibited moderate catalytic activities for

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Scheme 1



Scheme 2

ethylene polymerization in toluene in the presence of MAO at 80–120 °C.<sup>15e</sup> In particular, [TiMe{( $\mu_2$ -O-2,4-<sup>t</sup>Bu<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)<sub>2</sub>N}][Me<sub>2</sub>Al( $\mu_2$ -O<sup>t</sup>Pr)] itself polymerizes ethylene without cocatalysts to afford a high-molecular-weight polymer with a uniform distribution.<sup>15e</sup> We also reported that the isolated Ti–Al heterobimetallic complex, [TiMe{(O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)<sub>2</sub>( $\mu_2$ -OCH<sub>2</sub>CH<sub>2</sub>)N}][Me<sub>2</sub>Al-( $\mu_2$ -O<sup>t</sup>Bu)], showed moderate catalytic activity for ethylene polymerization without cocatalysts at 120 °C, affording a high-molecular-weight polymer with a uniform distribution.<sup>15b</sup> These results clearly suggest a hypothesis that the cationic species generated by cleavage of the Ti–O bonds play an important role as the active species in this catalysis (Scheme 1).

Later, we reported that the activity in ethylene polymerization using  $[Ti(OAr){(O-2,4-Me_2C_6H_2-6 (CH_2)_2(OCH_2CH_2)N]_n$  (*n* = 1, 2) was strongly affected by the terminal aryloxo substituents especially in the ortho position. The facts thus suggested that the type of aryloxo ligand presumably affects the equilibrium process in generation of the catalytically active species shown in Scheme 1. In this paper, we describe the preparation and characterization of a series of titanatranes bearing substituted aryloxo ligands of the type,  $Ti(OAr)[\{(O-2,4-Me_2C_6H_2)-6-CH_2\}_3N]$  [Ar = 2,6- $Me_2C_6H_3$  (1a), 2,6-Ph<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (1c), 2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (1d), C<sub>6</sub>F<sub>5</sub> (1e)], and their use as the catalyst precursors for ethylene polymerization in the presence of MAO. We also explored the effect of AlMe<sub>3</sub> on the catalytic activity and isolated several heterobimetallic Ti-Al complexes that may provide insight into the nature of the catalytic species that may be involved in the ethylene polymerization process.<sup>17</sup>

# RESULTS AND DISCUSSION

Synthesis of Ti(OAr)[{(O-2,4- $R_2C_6H_2$ )-6-CH<sub>2</sub>}<sub>3</sub>N] [R = Me (1a-1e), <sup>t</sup>Bu (2d,2e); Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (a), 2,6-<sup>t</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (b), 2,6-Ph<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (c), 2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (d), C<sub>6</sub>F<sub>5</sub> (e)]. A series of titanatranes bearing substituted aryloxo ligands of the type,  $Ti(OAr)[{(O-2,4-Me_2C_6H_2)-6-CH_2}_3N] [Ar = 2,6-Me_2C_6H_3]$ (1a), 2,6-Ph<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (1c), 2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (1d), C<sub>6</sub>F<sub>5</sub> (1e)], were prepared according to a modified procedure for the synthesis of the 2,6-<sup>*i*</sup> $Pr_2C_6H_3$  analogue (1b, Scheme 2).<sup>18</sup> In situ formation of Ti(OAr)(O<sup>i</sup>Pr)<sub>3</sub> by treatment of Ti(O<sup>i</sup>Pr)<sub>4</sub> with 1 equiv of ArOH and subsequent reaction with tris(2-hydroxy-3,5dimethylbenzyl)amine in toluene at 25 °C afforded 1a,1c-1e in 62.1-93.4% yields as yellow-orange microcrystals. The resultant complexes were identified by <sup>1</sup>H and <sup>13</sup>C NMR spectra and elemental analysis, and complexes 1d,1e were also identified by <sup>19</sup>F NMR spectra. According to our previous report as well as that in the 2,6-diisopropyl phenoxy analogue (1b),<sup>18</sup> the resultant complexes should have monomeric structures, and no significant changes in the <sup>1</sup>H NMR spectra were observed by varying the measurement temperature.

The similar reaction of  $Ti(O^{i}Pr)_{4}$  with 2,6- $F_2C_6H_3OH$  or  $C_6F_5OH$  and subsequent reaction with tris(2-hydroxy-3,5-ditert-butylbenzyl)amine in toluene afforded the other aryloxo modified titanatranes,  $Ti(OAr)[\{(O-2,4^{-t}Bu_2C_6H_2)-6-CH_2\}_3N]$ [Ar = 2,6- $F_2C_6H_3$  (2d),  $C_6F_5$  (2e)]. Complexes 2d,2e were also identified by <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectra and elemental analysis. However, the reactions with 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OH, 2,6- $^{i}Pr_2C_6H_3OH$ , and 2,6- $Ph_2C_6H_3OH$  in place of 2,6- $F_2C_6H_3OH$  afforded  $Ti(O^{i}Pr)[\{(O-2,4^{-t}Bu_2C_6H_2)-6-CH_2\}_3N]$ (2f) (Scheme 2). Since the reaction products of  $Ti(O^{i}Pr)_3(O-2,6^{-i}Pr_2C_6H_3)^{18}$  with [ $\{(HO-2,4^{-t}Bu_2C_6H_2)-6-CH_2\}_3N$ ] afforded the isopropoxy analogue (2f),<sup>19</sup> it thus seems likely

Table 1. Ethylene Polymerization by $Ti(OAr)[\{(O-2,4-R_2C_6H_2)-6-CH_2\}_3N]$ [R = Me (1), <sup>t</sup> Bu	(2); Ar = $2,6-Me_2C_6H_3$ (a),
$2,6^{-i}Pr_2C_6H_3$ (b), $2,6$ -Ph $_2C_6H_3$ (c), $2,6$ -F $_2C_6H_3$ (d), $C_6F_5$ (e)] (1a-1e, 2d,2e)-MAO (MAO/A	lMe <sub>3</sub> ) Catalyst Systems <sup><i>a</i></sup>

run	Ar (complex)	d-MAO/mmol (Al/Ti) <sup>b</sup>	$AlMe_3/\mu mol (Al/Ti)^b$	temp/°C	yield/mg	activity <sup>c</sup>	$M_{\rm w}^{\ d} \times 10^{-5}$	$M_{\rm w}/M_{\rm n}^{\ d}$
1	2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (1a)	3.0 (30 000)		100	97.8	978	7.88	3.09
2	2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (1a)	3.0 (30 000)	1.0 (10)	100	88.5	885	6.86	2.66
3	$2,6^{-i}Pr_2C_6H_3$ (1b)	3.0 (30 000)		100	103.7	1040	8.14	2.51
4	$2,6^{-i}Pr_2C_6H_3$ (1b)	3.0 (30 000)	1.0 (10)	100	150.2	1500	9.02	2.07
5	$2,6^{-i}Pr_2C_6H_3$ (1b)	4.0 (40 000)		100	78.7	787	7.46	2.58
6 <sup>e</sup>	$2,6^{-i}Pr_2C_6H_3$ (1b)	4.0 (40 000)		120	97.1	971		
7	$2,6^{-i}Pr_2C_6H_3$ (1b)	4.0 (40 000)	1.0 (10)	100	134.9	1350	8.01	2.35
8 <sup>e</sup>	$2,6^{-i}Pr_2C_6H_3$ (1b)	4.0 (40 000)	1.0 (10)	120	474.0	4740	1.91	2.1
9	$2,6-Ph_2C_6H_3$ (1c)	3.0 (30 000)		100	242.9	2430	8.94	3.11
10	$2,6-Ph_2C_6H_3$ (1c)	3.0 (30 000)	1.0 (10)	100	159.2	1590	6.05	2.32
11	$2,6-Ph_2C_6H_3$ (1c)	4.0 (40 000)		100	231.4	2310	7.14	2.14
12	$2,6-F_2C_6H_3$ (1d)	3.0 (30 000)		100	74.6	746	7.70	2.80
13	$2,6-F_2C_6H_3$ (1d)	3.0 (30 000)	1.0 (10)	100	104.3	1040	8.16	2.22
14	$C_6F_5$ (1e)	2.0 (20 000)		100	97.3	973	9.10	2.82
15	$C_6F_5$ (1e)	2.0 (20 000)	1.0 (10)	100	143.3	1430	9.42	2.74
16	$C_6F_5$ (1e)	3.0 (30 000)		100	109.3	1090	7.60	2.46
17	$C_6F_5$ (1e)	3.0 (30 000)	1.0 (10)	100	153.2	1530	8.40	2.21
18	$2,6-F_2C_6H_3$ (2d)	2.0 (20 000)		100	93.9	939	9.05	2.72
19	$2,6-F_2C_6H_3$ (2d)	2.0 (20 000)	1.0 (10)	100	89.1	891	7.07	2.11
20	$2,6-F_2C_6H_3$ (2d)	3.0 (30 000)		100	92.6	926	7.59	2.56
21	$2,6-F_2C_6H_3$ (2d)	3.0 (30 000)	1.0 (10)	100	75.1	751	6.28	2.35
22	$C_6F_5$ (2e)	2.0 (20 000)		100	113.5	1140	7.94	2.40
23	$C_{6}F_{5}(2e)$	2.0 (20 000)	1.0 (10)	100	81.9	819	6.38	2.18
24	$C_6F_5$ (2e)	3.0 (30 000)		100	108.6	1090	6.62	2.46
25	$C_6F_5$ (2e)	3.0 (30 000)	1.0 (10)	100	73.0	730	5.70	2.37

<sup>*a*</sup>Conditions: catalyst, 0.1  $\mu$ mol; n-octane, 30 mL; ethylene, 8 atm; 100 °C; 60 min; d-MAO (prepared by removing AlMe<sub>3</sub> and toluene from commercially available MAO). <sup>*b*</sup>Al/Ti molar ratio. <sup>*c*</sup>Activity in kg-PE/mol-Ti·h. <sup>*d*</sup>GPC data in *o*-dichlorobenzene vs polystyrene standards. <sup>*e*</sup>Cited from ref 15a.

that the ligand exchange between aryloxide and isopropoxide occurred in the reaction mixture probably due to a steric effect.<sup>20</sup> The reaction of **2f** with 1 equiv of  $2,6-Me_2C_6H_3OH$  in  $C_6D_6$  at 25 °C did not take place even after 24 h.

Ethylene Polymerization by Ti(OAr)[{(O-2,4-R<sub>2</sub>C<sub>6</sub>H<sub>2</sub>)-6- $CH_{2}_{3}N$ ] (R = Me, <sup>t</sup>Bu) in the Presence of Al Cocatalysts. Ethylene polymerizations by  $Ti(OAr)[\{(O-2,4-R_2C_6H_2)-6 [CH_2]_3N$  [R = Me, Ar = 2,6-Me\_2C\_6H\_3 (1a), 2,6-Ph\_2C\_6H\_3 (1c),  $2_{,6}F_{2}C_{6}H_{3}$  (1d),  $C_{6}F_{5}$  (1e);  $R = {}^{t}Bu$  (2d,2e)] were conducted in *n*-octane (ethylene, 8 atm; 100 °C; 60 min) in the presence of methylaluminoxane (MAO). MAO white solid (d-MAO), prepared by removing AlMe<sub>3</sub> and toluene from the commercially available samples (PMAO-S, 6.8 wt % in toluene, Tosoh Finechem Co.), was chosen, because it was generally effective in the preparation of high-molecular-weight ethylene/  $\alpha$ -olefin copolymers with unimodal molecular weight distributions exemplified by using catalysts based on Cp\*TiCl2(O- $2,6^{-i}Pr_2C_6H_3$ ) and  $[Me_2Si(C_5Me_4)(N'Bu)]TiCl_2.^{21}$  This is also because, as reported previously,<sup>15</sup> we also conducted these ethylene polymerizations in the copresence of a small amount of AlMe<sub>3</sub> (10 equiv to Ti). The results are summarized in Table 1.

As reported previously in ethylene polymerization using the  $Ti(O^{i}Pr)[\{(O-2,4-Me_2C_6H_2)-6-CH_2\}_3N]$  (1f)–MAO catalyst system,<sup>15e</sup> the catalytic activity by the 1b–MAO catalyst system increased at high temperature (100  $\rightarrow$  120 °C, runs 5 and 6) and the activities increased upon addition of AlMe<sub>3</sub> in a small amount (10 equiv to Ti, runs 5–8). The resultant polymers prepared by the 1b–MAO catalyst system possessed relatively high molecular weights with unimodal molecular weight

distributions. As reported previouly,<sup>15a</sup> the activities by 1b,1f in toluene instead of *n*-octane showed low activity, and we assumed that this would be due to coordination of toluene to the proposed catalytically active species.<sup>22</sup>

Observed activities in the ethylene polymerizations by  $Ti(OAr)[\{(O-2,4-Me_2C_6H_2)-6-CH_2\}_3N]$  [Ar = 2,6-Me\_2C\_6H\_3 (1a), 2,6-Ph<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (1c), 2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (1d), C<sub>6</sub>F<sub>5</sub> (1e)]-MAO catalyst systems (under optimized Al/Ti molar ratios) increased in the order: Ar =  $2,6-F_2C_6H_3$  (1d, 746 kg-PE/mol-Ti·h, run 12) < 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (1a, 978, run 1) < 2,6-<sup>*i*</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>  $(1b, 1037, run 3) < C_6F_5$   $(1e, 1093, run 16) < 2,6-Ph_2C_6H_3$ (1c, 2429, run 9). The results thus suggest that the activity was influenced by the terminal aryloxide ligand employed. It should be noted that the catalytic activities displayed by 1b,1d,1e-MAO catalyst systems increased upon addition of a small amount of AlMe<sub>3</sub> (runs 4, 7, 8, 13, 15, 17), whereas those for 1a,1c-MAO catalyst systems decreased (runs 2 and 10). We believe that these are in unique contrast in these catalysts, because the observed effect is highly influenced by the terminal aryloxide ligand employed. In all cases, the resultant polymers (prepared at 100 °C) possessed relatively high molecular weights with unimodal molecular weight distributions  $(M_w =$  $(6.05-9.42) \times 10^5$ ,  $M_w/M_n = 2.07-3.11$ , and significant decreases/increases in the  $M_w$  values were not observed under these conditions. These results also suggest that these ethylene polymerizations proceeded with uniform catalytically active species irrespective of the kind of terminal aryloxide ligand (OAr) employed.

The catalytic activities by  $Ti(OAr)[\{(O-2,4-{}^tBu_2C_6H_2)-6-CH_2\}_3N]$  [Ar = 2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**2d**), C<sub>6</sub>F<sub>5</sub> (**2e**)] were somewhat



Figure 1. ORTEP drawings for TiMe(O-2,6<sup>-i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)[( $\mu_2$ -O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)(Me<sub>2</sub>Al- $\mu_2$ -O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)(O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)N] (3b, left) and [TiMe{( $\mu_2$ -O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)(O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)]N][Me<sub>2</sub>Al( $\mu_2$ -OAr)] [Ar = 2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (3d, middle), C<sub>6</sub>F<sub>5</sub> (3e, right)]. Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.<sup>23</sup>

higher than those by the methyl analogues (1d,1e) under the same conditions [activity: 939 kg-PE/mol-Ti·h (by 2d, run 18) vs 746 kg-PE/mol-Ti·h (by 1d, run 12); 1135 kg-PE/mol-Ti·h (by 2e, run 22) vs 1093 kg-PE/mol-Ti·h (by 1e, run 16)]. In contrast to the above results by 1d,1e (runs 13, 15, 17), the activities by 2d,2e decreased upon addition of AlMe<sub>3</sub> (runs 19, 21, 23, 25). The observed difference may be explained as due to a steric bulk of the <sup>t</sup>Bu substituent compared to Me on the chelate phenoxy ligand in titanatranes. The resultant polymers possessed relatively high molecular weights with unimodal distributions ( $M_w = (5.70-9.05) \times 10^5$ ,  $M_w/M_n = 2.11-2.72$ ), and significant decreases/increases in the molecular weights were not observed under these conditions. These results also suggest that these ethylene polymerizations proceeded with uniform catalytically active species.

Reaction of Ti(OAr)[{(O-2,4-R<sub>2</sub>C<sub>6</sub>H<sub>2</sub>)-6-CH<sub>2</sub>}<sub>3</sub>N] with AlMe<sub>3</sub>, and Structural Analysis of the Heterobimetallic Ti–Al Complexes. We previously reported that heterobimetallic Ti–Al complexes containing a tris(aryloxo)amine ligand of the type, [TiMe{( $\mu_2$ -O-2,4-R<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)(O-2,4-R<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)<sub>2</sub>N}][Me<sub>2</sub>Al( $\mu_2$ -O<sup>i</sup>Pr)] (R = Me, <sup>t</sup>Bu), prepared by reacting Ti(O<sup>i</sup>Pr)[(O-2,4-R<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)<sub>3</sub>N] (1f, 2f) with 1.0 equiv of AlMe<sub>3</sub> in toluene, exhibited moderate catalytic activities for ethylene polymerization in toluene in the presence of MAO, and the observed activities were relatively close to those observed by the tris(aryoloxo)amine analogues (1f, 2f) in the presence of MAO upon addition of AlMe<sub>3</sub>.<sup>15e</sup> Moreover, the *tert*-butyl analogue itself polymerizes ethylene, affording a high-molecular-weight polymer with a uniform distribution.<sup>15e</sup> Therefore, we explored reactions of Ti(OAr)[{(O-2,4-R<sub>2</sub>C<sub>6</sub>H<sub>2</sub>)-6-CH<sub>2</sub>}<sub>3</sub>N] [R = Me (1a-1e), 'Bu (2d,2e); Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (a), 2,6-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (b), 2,6-Ph<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (c), 2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (d), C<sub>6</sub>F<sub>5</sub> (e)] with AlMe<sub>3</sub> to clarify reasons for the observed results in Table 1.

The reactions of **1b**,1**d**,1**e**, which showed an increase in the activity upon addition of a small amount of AlMe<sub>3</sub>, with 1.0 equiv of AlMe<sub>3</sub> afforded the corresponding heterobimetallic Ti–Al complexes (**3b**,**3d**,**3e**) in moderate yields (50.6-76.1%; Scheme 3). The resultant complexes were identified by <sup>1</sup>H and <sup>13</sup>C (and <sup>19</sup>F) NMR spectra and elemental analyses, and their structures were determined by X-ray crystallography (Figure 1), as described below.<sup>23</sup> These complexes are soluble in toluene, THF, hexane, and chloroform and were very stable as microcrystals that can be stored for long periods in the drybox without partial decomposition (at room temperature or in the freezer at -30 °C).

a

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for  $TiMe[(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)_2N][Me_2Al(\mu_2-OAr)]$  [Ar = 2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (3d), C<sub>6</sub>F<sub>5</sub> (3e)] and TiMe(O-2,6-<sup>*i*</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)[(\mu\_2-O-2,4-Me\_2C\_6H\_2-6-CH\_2)(Me\_2Al-\mu\_2-O-2,4-Me\_2C\_6H\_2-6-CH\_2)N] (3b)<sup>*a*</sup>

		3b	3d	3e
			selected bond distances (Å)	
	$T_{i}(1) - O(1)$	2.115(3)	2.1766(12)	2.2136(16)
	Ti(1) - O(2)	2.102(3)	2.0656(13)	2.0532(17)
	Ti(1) - O(3)	1.810(3)	1.8090(11)	1.8049(16)
	Ti(1) - O(4)	1.806(2)	1.8238(11)	1.8262(17)
	Ti(1) - N(1)	2.334(4)	2.4263(12)	2.4270(14)
	Ti(1) - C(1)	2.082(5)	2.0881(15)	2.0984(17) Ti(1)-C(7)
	Al(1) - O(1)	1.829(3)	1.8411(13)	1.8534(17)
	Al(1) - O(2)	1.872(3)	1.8355(13)	1.8368(17)
	Al(1)-C(2)	1.947(6)	1.953(2)	1.9526(19) Al $(1)-C(8)$
	Al(1) - C(3)	1.950(5)	1.955(2)	1.953(3)  Al(1) - C(9)
			selected bond angles (deg)	
	O(1) - Ti(1) - O(2)	71.06(12)	69.03(4)	68.56(6)
	O(1) - Ti(1) - O(3)	167.30(15)	164.17(5)	164.96(8)
	O(1) - Ti(1) - O(4)	90.64(13)	85.93(5)	84.21(7)
	O(1)-Ti(1)-N(1)	83.19(13)	92.14(5)	91.80(6)
	O(2) - Ti(1) - O(3)	96.33(14)	95.89(5)	97.26(7)
	O(2) - Ti(1) - O(4)	157.71(13)	150.85(5)	148.71(7)
	O(2)-Ti(1)-N(1)	80.65(14)	82.36(5)	81.68(6)
	O(3) - Ti(1) - O(4)	101.29(15)	107.16(6)	107.85(8)
	O(3)-Ti(1)-N(1)	84.71(15)	80.71(5)	80.83(6)
	O(1)-Ti(1)-C(1)	87.96(16)	93.95(6)	93.26(7) O(1)-Ti(1)-C(7)
	O(2)-Ti(1)-C(1)	92.32(19)	92.38(6)	93.21(8) O(2)-Ti(1)-C(7)
	O(3)-Ti(1)-C(1)	99.85(19)	91.38(6)	92.50(8) O(3)-Ti(1)-C(7)
	N(1)-Ti(1)-C(1)	170.11(19)	169.96(5)	170.96(8) N(1)-Ti(1)-C(7)
	Ti(1) - O(1) - Al(1)	101.23(13)	100.74(5)	100.30(7)
	Ti(1) - O(2) - Al(1)	100.26(14)	105.17(5)	107.07(8)
	O(1)-Al(1)-O(2)	82.92(15)	81.73(6)	81.42(8)
	C(2)-Al(1)-C(3)	117.5(2)	116.79(10)	118.40(11) C(8)-Al(1)-C(9)
Гhe d	letails are shown in the Supporting Ini	formation. <sup>23</sup>		

Microcrystals of 3b,3d,3e suitable for their crystallographic analyses were grown from a hot toluene solution upon cooling, and their structures are shown in Figure 1. The selected bond distances and angles are summarized in Table 2.23 These complexes fold a distorted octahedral geometry around titanium consisting of a C-Ti-N axis  $[170.11(19)^{\circ}$  for 3b;  $169.96(5)^{\circ}$  for 3d;  $170.96(8)^{\circ}$  for 3e] and a distorted plane of one terminal aryloxo ligand and three aryloxo chelate ligands [total bond angles of the O(1)-Ti(1)-O(2), O(2)-Ti(1)-O(3), O(3)-Ti(1)-O(4), and O(1)-Ti(1)-O(4) for 3d,3e were 358.01° and 357.88°, respectively; the total bond angle for **3b** was 359.32°]. The coordination sphere of titanium consists of one methyl and four oxygen atoms, including three oxygens from the atrane ligand, and the titanium atoms in 3b,3d,3e are ligated via a transannular interaction stemming from the bridgehead amino nitrogen. The average O-Ti-N bond angles for 3b, 3d, and 3e are 85.52, 84.80, and 84.62°, respectively, suggesting a displacement of the titanium atom toward the axial oxygen, similar to the observation made in the case of the other heterobimetallic Ti-Al complexes.<sup>15b,e</sup>

Note that Al atoms in 3d,3e are ligated through oxygen atoms in the terminal aryloxo ligand and the atrane ligand, whereas Al atoms in 3b are ligated through two oxygen atoms in the atrane ligand. Therefore, Ti–O (in  $\mu_2$ -O) bond distances in 3b,3d,3e [2.0532(17)–2.2136(16) Å, corresponding to Ti–O(1) and Ti–O(2) distances] are longer than the other Ti–O distances in the aryloxo ligands [1.8049(16)–1.8262(17) Å,

corresponding to Ti–O(3) and Ti–O(4) distances]: these distances are also longer than those in Al–O bond distances [1.829(3)–1.872(3) Å, corresponding to Al–O(1) and Al–O(2) distances]. These are a similar observation to that in the [TiMe{( $\mu_2$ -O-2,4-R<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)(O-2,4-R<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)<sub>2</sub>N}][Me<sub>2</sub>Al( $\mu_2$ -O<sup>i</sup>Pr)], reported previously.<sup>15e</sup> The results in **3d**,**3e** thus clearly indicate that the resultant complexes possess Ti–Me bonds by replacement of the OAr group with AlMe<sub>3</sub>, and the structure of **3b** would be formed by rearrangement as a stable form after the alkylation (replacement).

These complexes also fold a distorted tetrahedral geometry around Al, and the C(2)–Al(1)–C(3) bond angles in these complexes [C(8)-Al-C(9) in 3e] were 116.79(10)–118.40(11)°, although the O(1)–Al(1)–O(2) bond angles were small [81.42(8)° and 82.92(15)°]. As described above, Al–O bond distances [1.829(3)–1.872(3) Å] are shorter than the Ti–O (in  $\mu_2$ -O) bond distances [2.0532(17)–2.2136(16) Å].

Moreover, Ti–O(1) and Ti–O(2) bond distances in **3b**,3**d**,3**e** [2.0532(17)–2.2136(16) Å] are relatively longer than those in [TiMe{( $\mu_2$ -O-2,4-R<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)(O-2,4-R<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)<sub>2</sub>N}][Me<sub>2</sub>Al( $\mu_2$ -O'Pr)] [2.071(13), 2.072(11) Å in R = Me; 2.0673(19), 2.095(2) Å in R = 'Bu], reported previously.<sup>15e</sup> These are probably due to a steric bulk of the aryloxo fragment. It is assumed that longer (rather weak) Ti–O bond distances would be probably more suited in terms of

# Scheme 4



Scheme 5



Scheme 6



generation of the assumed catalytically active species from  $[TiMe{(\mu_2-O-2,4-{}^tBu_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)_2N}][Me_2Al(\mu_2-O^{i}Pr)],^{15e}$  generated by dissociation of two Ti–O bonds bridged to the Al atom.

In contrast to the results in the reactions of 1b,1d,1e, isolated compounds (crystals) from a reaction mixture of Ti(O-2,6- $Me_2C_6H_3$  [{(O-2,4-Me\_2C\_6H\_2)-6-CH\_2}\_3N] (1a) with AlMe\_3 were  $[Al(\mu_2-O-2,6-Me_2C_6H_3)Me_2]_2$  (5, 38.2%) and TiMe- $[\{(O-2,4-Me_2C_6H_2)-6-CH_2\}_3N]$  (4) identified by X-ray crystallographic analysis (Scheme 4).<sup>24</sup> Formation of 4 could only be confirmed by isolation after careful repetitive recrystallization (shown in the Experimental Section). The result may suggest that, once formed, the heterobimetallic Ti-Al complex was converted to the methyl species (4) and aluminum phenoxide (5) by dissociation, although the reaction in 1b afforded thermally stable 3b in relatively high yield (76.1%). The attempted reaction of the diphenyl analogue (1c)with AlMe<sub>3</sub> in toluene afforded complex mixtures, and no complexes could be isolated cleanly from the reaction mixture. These results by 1a,1c were thus in unique contrast to those by 1b,1d,1e, affording the heterobimetallic Ti-Al complexes (3b,3d,3e), but the results also corresponded well to the experimental facts in the above ethylene polymerization, especially the effect of AlMe<sub>3</sub> toward the activity.

Moreover,  $[Al(\mu_2 - OC_6F_5)Me_2]_2$  (6) was an only isolated product from the reaction mixture of  $Ti(OC_6F_5)[\{(O-F_5)\}]$  $2_{4}$ -<sup>t</sup>Bu<sub>2</sub>C<sub>6</sub>H<sub>2</sub>)-6-CH<sub>2</sub> $_{3}N$  (2e) with AlMe<sub>3</sub>, and 6 was identified by NMR spectra and X-ray crystallographic analysis (Scheme 5).<sup>24</sup> The isolated compound (white microcrystals) in the reaction of 2d with AlMe<sub>3</sub> conducted under the same conditions showed similar resonances assumed as [Al( $\mu_2$ -O-2,6- $F_2C_6H_3$ )Me<sub>2</sub>]<sub>2</sub> on the basis of the <sup>1</sup>H and <sup>19</sup>F NMR spectra. Because these reactions did not afford the heterobimetallic Ti-Al complexes, the results were also compatible with the experimental results that the activities in ethylene polymerization decreased upon the addition of AlMe<sub>3</sub>. Taking into account these experimental results, it is thus highly suggested that formation of the heterobimetallic Ti-Al complexes plays an important role toward the catalytic activities in the presence of AlMe<sub>3</sub>.

As an another approach for modification of Al in  $[TiMe{(\mu_2 - O^2A^+Bu_2C_6H_2-6-CH_2)(O^-2,4^+Bu_2C_6H_2-6-CH_2)_2N}][Me_2Al-(\mu_2-O^{i}Pr)]$ , which showed catalytic activity for ethylene polymerization without additional cocatalysts, we conducted a reaction of  $Ti(O^{i}Pr)[{(O^-2,4^+Bu_2C_6H_2)-6-CH_2}_3N]$  (2f) with 1 equiv of Me\_2AlCl. The isolated crystalline material from this reaction was identified as  $TiCl[{(O^-2,4^+Bu_2C_6H_2)-6-CH_2}_3N]$  on the basis of NMR measurements and elemental analysis (Scheme 6).<sup>25</sup> Moreover, the reaction of 2f with  $[Al(\mu_2 - D^{i}Pr)]$ 

Table 3. Ethylene Polymerization by TiMe[(O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)<sub>2</sub>( $\mu_2$ -O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)N][Me<sub>2</sub>Al( $\mu_2$ -OAr)] [Ar = 2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (3d), C<sub>6</sub>F<sub>5</sub> (3e)]-MAO and TiMe(O-2,6-<sup>*i*</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)[(O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)( $\mu_2$ -O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)(Me<sub>2</sub>Al- $\mu_2$ -O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)N] (3b)-MAO Catalyst Systems<sup>*a*</sup>

run	complex (µmol)	temp/°C	d-MAO/mmol (Al/Ti) <sup>b</sup>	AlMe <sub>3</sub> / $\mu$ mol	yield/mg	activity <sup>c</sup>	$M_{\rm w}^{d}  imes 10^{-5}$	$M_{\rm w}/M_{\rm n}^{\ d}$
26	<b>3b</b> (1.0)	80			trace	trace		
27	<b>3b</b> (1.0)	100			trace	trace		
28	<b>3b</b> (1.0)	120			trace	trace		
29	<b>3b</b> (0.1)	80	3.0 (30 000)		140.0	1400	11.4	2.02
30	<b>3b</b> (0.1)	100	3.0 (30 000)		158.7	1590	8.76	2.06
31	<b>3b</b> (0.1)	120	3.0 (30 000)		85.0	850	5.50	2.13
32	<b>3b</b> (0.1)	100	2.0 (20 000)		125.3	1250	9.15	2.28
33	<b>3b</b> (0.1)	100	4.0 (40 000)		142.2	1420	7.65	2.11
4	1b (0.1)	100	3.0 (30 000)	1.0	150.2	1500	9.02	2.07
7	1b (0.1)	100	4.0 (40 000)	1.0	134.9	1350	8.01	2.35
34	<b>3d</b> (1.0)	80			trace	trace		
35	<b>3d</b> (1.0)	100			trace	trace		
36	<b>3d</b> (1.0)	120			trace	trace		
37	<b>3d</b> (0.1)	80	3.0 (30 000)		95.6	956	11.0	2.17
38	<b>3d</b> (0.1)	100	3.0 (30 000)		143.8	1440	7.96	2.20
39	3d (0.1)	120	3.0 (30 000)		76.0	760	4.07	2.15
40	<b>3d</b> (0.1)	100	2.0 (20 000)		126.6	1270	8.95	2.14
41	3d (0.1)	100	4.0 (40 000)		122.2	1220	7.17	2.19
13	1d (0.1)	100	4.0 (40 000)	1.0	104.3	1040	8.16	2.22
42	<b>3e</b> (1.0)	80			trace	trace		
43	<b>3e</b> (1.0)	100			trace	trace		
44	<b>3e</b> (1.0)	120			trace	trace		
45	<b>3e</b> (0.1)	80	3.0 (30 000)		123.0	1230	insoluble	insoluble
46	<b>3e</b> (0.1)	100	3.0 (30 000)		170.6	1710	7.99	2.38
47	<b>3e</b> (0.1)	120	3.0 (30 000)		56.0	560	3.51	2.31
48	<b>3e</b> (0.1)	100	2.0 (20 000)		138.8	1390	8.55	2.27
49	<b>3e</b> (0.1)	100	4.0 (40 000)		101.7	1020	7.18	2.08
15	1e (0.1)	100	3.0 (30 000)	1.0	143.3	1430	9.42	2.74
17	1e (0.1)	100	4.0 (40 000)	1.0	153.2	1530	8.40	2.21

"Conditions: *n*-octane, 30 mL; ethylene, 8 atm; 60 min; d-MAO. <sup>b</sup>Al/Ti molar ratio. <sup>c</sup>Activity in kg-PE/mol-Ti·h. <sup>d</sup>GPC data in *o*-dichlorobenzene vs polystyrene standards.

 $OC_6F_5)Me_2]_2$  (6) in  $CDCl_3$  afforded a simple mixture of 2f and  $Ti(OC_6F_5)[\{(O-2,4-^tBu_2C_6H_2)-6-CH_2\}_3N]$  (2) after the ligand exchange (Scheme 6).<sup>26</sup> These results thus suggest that a careful design of both titanatranes and Al reagents should be required for the efficient synthesis of Ti–Al heterobimetallic complexes.

Ethylene Polymerization by TiMe(O-2,6<sup>-*i*</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)[( $\mu_2$ -O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)(Me<sub>2</sub>Al- $\mu_2$ -O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)-(O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>) N] (3b) and TiMe[( $\mu_2$ -O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)(O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)<sub>2</sub>N][Me<sub>2</sub>Al( $\mu_2$ -OAr)] [Ar = 2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (3d), C<sub>6</sub>F<sub>5</sub> (3e)] in the Presence of MAO. Ethylene polymerization by the isolated heterobimetallic Ti-Al complexes, TiMe(O-2,6<sup>-</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)[( $\mu_2$ -O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)(Me<sub>2</sub>Al- $\mu_2$ -O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)(O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)(O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)(O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)( $\mu_2$ -O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)( $\mu_2$ -O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)( $\mu_2$ -O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)( $\mu_2$ -O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (3d), C<sub>6</sub>F<sub>5</sub> (3e)], was conducted in *n*-octane for 1 h in the presence of MAO. The results are summarized in Table 3.

The catalytic activities by **3b** at 100 °C were slightly higher than those by **1b** in the presence of MAO/AlMe<sub>3</sub> under the similar conditions (runs 4, 7 vs runs 30, 33). The relatively high catalytic activity was observed even at 80 °C (run 29). The resultant polymers prepared by **1b** and **3b** (at 100 °C) possessed high molecular weights with unimodal molecular weight distributions, and no significant differences in the  $M_w$ values were observed. The  $M_w$  values decreased at high temperature (runs 29–31). These results thus suggest that, as assumed in the previous report in  $[TiMe{(\mu_2-O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)_2N}][R'_2Al(\mu_2-O'Pr)]$ ,<sup>15e</sup> the bimetallic complexes, first formed in the reaction mixture containing the precursors of **1b** in the presence of MAO and a small amount of AlMe<sub>3</sub>, play a role in this catalysis. We assume that a decrease in the activity by **3b** at 120 °C would be probably due to a stability of the catalytically active species under these conditions.

The activities by the 2,6- $F_2C_6H_3$  analogue (3d) were higher than that by 1d under the similar conditions: moderate activity was observed at 80 °C, and the activity decreased at 120 °C, as observed in the polymerization by 3b. Moreover, the activities by the  $C_6F_5$  analogue (3e) were higher than that by 1e under similar conditions, although the activity by 3e was highly affected by MAO concentration conditions employed (runs 46, 48, 49). The resultant polymers possessed high molecular weights with unimodal molecular weight distributions, and significant differences in  $M_w$  values were observed between the resultant polymers prepared by 1d,1e and 3d,3e. These results also suggest that, as proposed previously,<sup>15b,e</sup> the bimetallic complexes, first formed in the reaction mixture containing the precursors of 1d,1e in the presence of MAO and a small amount of AlMe<sub>3</sub>, play a role in these catalyses.

As described above, Ti-O(1) and Ti-O(2) bond distances in **3b**,**3d**,**3e** [2.0533(19)-2.2137(17) Å] are relatively longer Scheme 7



than those in  $[TiMe{(\mu_2-O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-6-CH_2)(O-2,4-R_2C_6H_2-2)(O-2,4-R_2C_6H_2-2)(O-2,4-R_2C_6H_2-2)(O-2,4-R_2C_6H_2-2)(O-2,4-R_2C_6H_2-2)(O-2,4-R_2C_6H_2-2)(O-2,4-R_2C_6H_2-2)(O-2,4-R_2C_6H_2-2)(O-2,4-R_2C_6H_2-2)(O-2,4-R_2C_6H_2-2)(O-2,4-R_2C_6H_2-2)(O-2,4-R_2C_6H_2-2)(O-2,4-R_2C_6H_2-2)(O-2,4-R_2C_6H_2-2)(O-2,4-R_2C_6H_2-2)(O-2,4-R_2C_6H_2-2)(O-2,4-R_2C_6H_2-2)(O-2,4-R_2C_6H_2-2)(O-2,4-R_2C_6H_2-2)(O-2,4-R_2C_6H_2-2)(O-2,4-R_2C_6H_2-2)(O-2,4-R_2C_6H_2-2)(O-2,4-R_2C_6H_2-2)(O-2,4-R_2C_6H_2-2)(O-2,4-R_2C_6H_2-2))$  $R_2C_6H_2$ -6-CH<sub>2</sub>)<sub>2</sub>N}][Me<sub>2</sub>Al( $\mu_2$ -O<sup>i</sup>Pr)] [2.071(13), 2.072(11) Å in R = Me; 2.0673(19), 2.095(2) Å in R =  ${}^{t}Bu$ ], reported previously.<sup>15e</sup> We expected that longer (rather weak) Ti-O bond distances would be more suited in terms of generation of the assumed catalytically active species,<sup>15e</sup> generated by dissociation of two Ti-O bonds bridged to the Al atom. However, these complexes (3b, 3d, 3e) showed negligible catalytic activities (trace amount of polymers) in the absence of MAO at 100 °C (Table 3): the activities were negligible at 80 and 120 °C. To understand why 3d,3e showed negligible activities, we examined their thermal stabilities in n-octane at 100 °C (under polymerization conditions). Although previously isolated Ti-Al [TiMe{( $\mu_2$ -O-2,4-R<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)(O- $2_{4}-R_{2}C_{6}H_{2}-6-CH_{2}N_{2}N_{1}[Me_{2}Al(\mu_{2}-O'Pr)] (R = Me_{1}^{t}Bu) were$ thermally stable in toluene- $d_8$  at various temperatures,<sup>15e</sup> we observed that 3d,3e decomposed gradually at 100 °C in noctane even after 30 min (monitored by both <sup>1</sup>H and <sup>19</sup>F NMR spectra).<sup>27</sup> These results clearly indicate that MAO helps stabilize the catalytically active species derived from 3d,3e during the ethylene polymerization process.

#### CONCLUDING REMARKS

A series of titanatranes containing a tris(phenoxy)amine ligand of the type,  $Ti(OAr)[\{(O-2,4-R_2C_6H_2)-6-CH_2\}_3N]$  [R = Me (1), <sup>t</sup>Bu (2); Ar = 2,6-Me\_2C\_6H\_3 (a), 2,6-Pr\_2C\_6H\_3 (b), 2,6-Ph\_2C\_6H\_3 (c), 2,6-F\_2C\_6H\_3 (d), C\_6F\_5 (e)] (1a-1e, 2d,2e), have been employed as the catalyst precursors for ethylene polymerization in the presence of methylaluminoxane (MAO). Reactions of 1b,1d,1e, which showed increases in

the activity upon addition of a small amount of AlMe<sub>3</sub>, with 1.0 equiv of AlMe<sub>3</sub> afforded the corresponding heterobimetallic Ti–Al complexes, TiMe $(O-2,6^{-i}Pr_2C_6H_3)[(\mu_2-O-2,4-Me_2C_6H_2 6-CH_2$ )(Me<sub>2</sub>Al- $\mu_2$ -O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)(O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6- $(CH_2)N$  (3b) and  $TiMe[(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2))$  $Me_2C_6H_2-6-CH_2)_2N$  [Me<sub>2</sub>Al( $\mu_2$ -OAr)] [Ar = 2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (3d),  $C_6F_5$  (3e)], in moderate yields. In contrast, TiMe[{(O-2,4- $Me_2C_6H_2$ )-6-CH<sub>2</sub> $_3N$  (4) and  $[Al(\mu_2-O-2,6-Me_2C_6H_3)Me_2]_2$ (5) were isolated from the reaction mixture of 1a (showed a decrease in the activity upon addition of AlMe<sub>3</sub>) with AlMe<sub>3</sub> conducted under the same conditions: the reactions of 1c, **2d**,**2e** afforded complex mixtures except an isolation of  $[Al(\mu_2 - \mu_2)]$  $OC_6F_5)Me_2_2$ . The isolated heterobimetallic complexes (3b,3d,3e) exhibited high catalytic activities for ethylene polymerization in the presence of MAO, suggesting that the present bimetallic species play a role in this catalysis (Scheme 7). However, unfortunately, these heterobimetallic complexes (3b,3d,3e) showed negligible catalytic activities for ethylene polymerization in the absence of MAO, because these complexes decomposed gradually in n-octane at 100 °C. These observations thus clearly suggest that MAO would play a role for stabilization of the catalytically active species in this catalysis.

Taking into account these results, it becomes clear that we have to consider steric bulk of both bridged ligands (ligand substituent in the atrane ligand and/or terminal ligand) for designing efficient catalysts for the desired purpose (to exhibit activity without cocatalyst). We highly believe that these facts should be potentially important for designing more efficient catalysts in precise olefin polymerization, especially catalysts without the presence of excess Al cocatalysts, and we are now preparing various titanatranes: these results will be introduced in the future as our subsequent contribution.

# EXPERIMENTAL SECTION

General Procedures. All experimental procedures were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques or using a Vacuum Atmospheres drybox unless otherwise specified. All chemicals used were of reagent grade and were purified by standard purification procedures. Toluene (anhydrous grade, Kanto Kagaku Co., Ltd.) for polymerization was stored in a bottle in the drybox in the presence of molecular sieves (a mixture of 3A 1/16, 4A 1/8, and 13X 1/16). Polymerization grade ethylene (purity > 99.9%, Sumitomo Seika Co. Ltd.) was used as received. Toluene and AlMe<sub>3</sub> from commercially available methylaluminoxane [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<sub>3</sub> and then heated at >100 °C for 1 h for completion) in the drybox to give white solids. Tris(2-hydroxy-3,5-dimethylbenzyl)amine and tris(2hydroxy-3,5-di-tert-butylbenzyl)amine were prepared according to a published procedure.<sup>28</sup> Ti $(O-2,6^{-i}Pr_2C_6H_3)$ [{ $(O-2,4-Me_2C_6H_2)-6 CH_2$ <sub>3</sub>N] (1b) was prepared according to a published method.

Molecular weights and molecular weight distributions 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 ×m7.8 mm $\varphi$ , ranging from <10<sup>2</sup> to <2.8 × 10<sup>8</sup> 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.

Elemental analyses were performed by using an EAI CE-440 CHN/ O/S elemental analyzer (Exeter Analytical, Inc.). All <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectra were recorded on a Bruker AV500 spectrometer (500.13 MHz for <sup>1</sup>H, 125.77 MHz for <sup>13</sup>C). All spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. Chemical shifts are given in parts per million and are referenced to SiMe<sub>4</sub> ( $\delta$  0.00 ppm, <sup>1</sup>H, <sup>13</sup>C), CFCl<sub>3</sub> ( $\delta$  0.00, <sup>19</sup>F). Coupling constants are given in hertz.

Synthesis of Ti(O-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)[{(O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>)-6-CH<sub>2</sub>}<sub>3</sub>N] (1a). Into a toluene solution (10 mL) containing  $2,6-Me_2C_6H_3OH$ (0.244 g, 2.00 mmol) was added dropwise into a toluene solution (10 mL) containing  $Ti(O^{i}Pr)_{4}$  (0.568 g, 2.00 mmol) at room temperature. After 1 h, a toluene solution (10 mL) containing tris(2-hydroxy-3,5dimethylbenzyl)amine (0.839 g, 2.00 mmol) was then added dropwise into the above reaction mixture (containing titanium and phenol). The reaction mixture was stirred at room temperature overnight, and then the volatiles were evaporated under vacuum, leaving yellow solids. The resultant solids were added to 20 mL of toluene, and the yellow solution was filtered through a Celite pad. The filtrate was placed in vacuo to give a yellow solid. The complex 1a was isolated as orangeyellow crystals from the chilled  $CH_2Cl_2/n$ -hexane solution (-30 °C). Yield: 0.723 g (62.1%). <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  2.15 (s, 9H, Ar-C $H_3$ ), 2.19 (s, 9H, Ar-CH<sub>3</sub>), 2.47 (br.d, 2H, N-CH<sub>2</sub>), 2.80 (s, 6H, terminal Ar-CH<sub>3</sub>), 3.94 (br.d, 2H, N-CH<sub>2</sub>), 6.45 (br.s, 3H, Ar-H), 6.73 (br.s, 3H, Ar-H), 6.94 (t, 1H, J = 7.4 Hz, terminal Ar-H), 7.14 (d, 2H, J = 7.4 Hz, terminal Ar-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  16.1 (Ar-CH<sub>3</sub>), 18.0 (terminal Ar-CH<sub>3</sub>), 20.7 (Ar-CH<sub>3</sub>), 58.7 (N-CH<sub>2</sub>), 120.7, 123.4, 124.4, 127.2, 127.4, 127.7, 130.1, 131.0, 159.3, 165.5 (aromatic carbon resonances). Anal. Calcd for C<sub>35</sub>H<sub>39</sub>NO<sub>4</sub>Ti: C, 71.79 (69.74 + Ti – C); H, 6.71; N, 2.39. Found: C, 69.82; H, 6.71; N, 2.50.

**Synthesis of Ti(O-2,6-Ph<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)[{(O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>)-6-CH<sub>2</sub>}<sub>3</sub>N] (1c).** The procedure for the synthesis of 1c was conducted by the similar procedure for 1a, except that 2,6-Ph<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OH was used in place of 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OH. Yield: 0.888 g (62.6%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.76 (s, 9H, Ar-CH<sub>3</sub>), 2.21 (s, 9H, Ar-CH<sub>3</sub>), 2.87 and 3.87 (br.s, 6H, NCH<sub>2</sub>), 6.64 (br.s, 3H, Ar-H), 6.78 (br.s, 3H, aryl-H), 7.00 (t, 2H, *J* = 7.4 Hz, Ar-H), 7.04 (t, 1H, *J* = 7.6 Hz, Ar-H), 7.14 (t, 4H, *J* = 7.6 Hz, Ar-H), 7.28 (d, 2H, *J* = 7.5 Hz, Ar-H), 7.80 (d, 4H, *J* = 7.2 Hz, Ar-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  15.9 (Ar-CH<sub>3</sub>), 20.7 (Ar-CH<sub>3</sub>), 58.6 (NCH<sub>2</sub>), 120.8, 123.2, 124.3, 126.5, 127.0, 127.9, 129.8, 130.0, 130.8, 133.3,

140.6 (aromatic carbon resonances). Anal. Calcd for  $C_{45}H_{43}NO_4Ti$ : C, 76.16; H, 6.11; N, 1.97. Found: C, 75.83; H, 6.03; N, 2.19.

**Synthesis of Ti(O-2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)[{(O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>)-6-CH<sub>2</sub>}<sub>3</sub>N] (1d).** The procedure for the synthesis of 1d was conducted by the similar procedure for 1a, except that 2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OH was used in place of 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OH. Yield: 0.897 g (75.6%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.13 (s, 9H, Ar-CH<sub>3</sub>), 2.26 (s, 9H, Ar-CH<sub>3</sub>), 2.44 and 3.89 (br.s, 6H, NCH<sub>2</sub>), 6.34 (m, 1H, terminal Ar-H), 6.42 (br.s, 3H, Ar-H), 6.77 (m, 2H, terminal Ar-H), 7.00 (br.s, 3H, Ar-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  15.7 (Ar-CH<sub>3</sub>), 20.7 (Ar-CH<sub>3</sub>), 58.8 (NCH<sub>2</sub>), 123.3, 124.4, 127.3, 130.5, 131.0, 160.1 (aromatic carbon resonances). <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  –130.5 (br. s). Anal. Calcd for C<sub>33</sub>H<sub>33</sub>F<sub>2</sub>NO<sub>4</sub>Ti·CH<sub>2</sub>Cl<sub>2</sub>: C, 60.19; H, 5.20; N, 2.06. Found: C, 59.83; H, 4.84; N, 2.03.

**Synthesis of Ti(OC<sub>6</sub>F<sub>5</sub>)[{(O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>)-6-CH<sub>2</sub>}<sub>3</sub>N] (1e).** The procedure for the synthesis of 1e was conducted by the similar procedure for 1a, except that C<sub>6</sub>F<sub>5</sub>OH was used in place of 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OH. Yield: 1.210 g (93.4%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  2.12 (s, 9H, Ar-CH<sub>3</sub>), 2.20 (s, 9H, Ar-CH<sub>3</sub>), 2.42 amd 3.82 (br.s, 6H, NCH<sub>2</sub>), 6.41 (br.s, 3H, Ar-H), 6.68 (br.s, 3H, Ar-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  15.7 (Ar-CH<sub>3</sub>), 20.7 (Ar-CH<sub>3</sub>), 58.8 (NCH<sub>2</sub>), 123.2, 124.2, 127.4, 131.0, 131.2, 160.1 (aromatic carbon resonances). <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  –171.7 (br. t, *para-F*), –166.8 (br. d, *meta-F*), –160.7 (br. d, *ortho-F*). Anal. Calcd for C<sub>33</sub>H<sub>30</sub>F<sub>5</sub>NO<sub>4</sub>Ti: C, 61.22; H, 4.67; N, 2.16. Found: C, 60.97; H, 4.67; N, 2.16.

**Synthesis of Ti(O-2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)[{(O-2,4-<sup>t</sup>Bu<sub>2</sub>C<sub>6</sub>H<sub>2</sub>)-6-CH<sub>2</sub>]<sub>3</sub>N] (2d).** The procedure for the synthesis of 2d was conducted by the similar procedure for 1a, except that 2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OH and tris(2-hydroxy-3,5-di-*tert*-butylbenzyl)amine were used in place of 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OH and tris(2-hydroxy-3,5-dimethylbenzyl)amine. Yield: 1.131 g (66.8%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.33 (s, 27H, C(CH<sub>3</sub>)<sub>3</sub>), 1.59 (s, 27H, C(CH<sub>3</sub>)<sub>3</sub>), 2.68 (br.d, 3H, NCH<sub>2</sub>), 4.13 (br.d, 3H, NCH<sub>2</sub>), 6.40 (m, 1H, terminal Ar-H), 6.76 (m, 2H, terminal Ar-H), 6.80 (br.d, 3H, Ar-H), 7.43 (br.d, 3H, Ar-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  29.7 ((CH<sub>3</sub>)<sub>3</sub>C), 31.8 ((CH<sub>3</sub>)<sub>3</sub>C), 34.6 ((CH<sub>3</sub>)<sub>3</sub>C), 35.0 ((CH<sub>3</sub>)<sub>3</sub>C), 59.1 (NCH<sub>2</sub>), 111.3, 118.1, 123.5, 124.0, 135.8, 143.5, 160.9 (aromatic carbon resonances). <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  -127.5 (br. s). Anal. Calcd for C<sub>51</sub>H<sub>69</sub>F<sub>2</sub>NO<sub>4</sub>Ti-*n*-hexane: C, 73.45; H, 8.97; N, 1.50. Found: C, 72.83; H, 8.95; N, 1.68.

**Synthesis of Ti(OC<sub>6</sub>F<sub>5</sub>)[{(O-2,4-<sup>t</sup>Bu<sub>2</sub>C<sub>6</sub>H<sub>2</sub>)-6-CH<sub>2</sub>}<sub>3</sub>N] (2e).** The procedure for the synthesis of 2e was conducted by the similar procedure for 2d, except that C<sub>6</sub>F<sub>5</sub>OH was used in place of 2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OH. Yield: 1.357 g (75.4%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.32 (s, 27H, C(CH<sub>3</sub>)<sub>3</sub>), 1.52 (s, 27H, C(CH<sub>3</sub>)<sub>3</sub>), 2.64 (br.d, 3H, NCH<sub>2</sub>), 4.05 (br.d, 3H, NCH<sub>2</sub>), 6.78 (br.d, 3H, Ar-H), 7.41 (br.d, 3H, Ar-H). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  29.8 ((CH<sub>3</sub>)<sub>3</sub>C), 31.8 ((CH<sub>3</sub>)<sub>3</sub>C), 34.6 ((CH<sub>3</sub>)<sub>3</sub>C), 35.2 ((CH<sub>3</sub>)<sub>3</sub>C), 60.0 (NCH<sub>2</sub>), 123.9, 124.3, 136.1, 144.2, 161.4 (aromatic carbon resonances). <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  –171.9 (br. t, *para*-F), –167.1 (br. d, *meta*-F), –158.1 (br. d, *ortho*-F). Anal. Calcd for C<sub>51</sub>H<sub>66</sub>F<sub>3</sub>NO<sub>4</sub>Ti·*n*-hexane: C, 69.43; H, 8.18; N, 1.42. Found: C, 69.40; H, 7.95; N, 1.56.

Synthesis of TiMe(O-2,6-<sup>*i*</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)[( $\mu_2$ -O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)- $(Me_{2}AI - \mu_{2} - O - 2, 4 - Me_{2}C_{6}H_{2} - 6 - CH_{2})(O - 2, 4 - Me_{2}C_{6}H_{2} - 6 - CH_{2})N]$  (3b). Into a toluene solution (10 mL) containing Ti(O-2,6-<sup>*i*</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)[{(O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>)-6-CH<sub>2</sub>}<sub>3</sub>N] (0.642 g, 1.0 mmol) was added slowly AlMe<sub>3</sub> (1.0 mL, of 1.0 M *n*-hexane solution) at room temperature. The reaction mixture was then stirred at room temperature for 2 h. The volatiles were evaporated under vacuum, and to the resultant orange solid was added 15 mL of toluene. The orange solution was then filtered through a Celite pad. The filtrate was removed under vacuum to obtain orange solids. The complex was isolated as orange microcrystals from the hot toluene solution. Yield: 0.543 g (76.1%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  –1.35 (s, 3H, Al-CH<sub>3</sub>), –0.41 (s, 3H, Al-CH<sub>3</sub>) 1.02 (br.s, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.43 (s, 3H, Ti-CH<sub>3</sub>) 1.98 (s, 3H, Ar-CH<sub>3</sub>), 2.01 (s, 3H, Ar-CH<sub>3</sub>), 2.16 (s, 3H, Ar-CH<sub>3</sub>), 2.22 (s, 3H, Ar- $CH_3$ ), 2.37 (s, 3H, Ar- $CH_3$ ), 2.45 (s, 3H, Ar- $CH_3$ ), 2.81 (d, J = 13 Hz, 1H, N-CH), 3.20 (d, J = 13 Hz, 1H, N-CH), 3.31 (d, J = 13 Hz, 1H, N-CH), 3.74 (br.s, 2H,  $CH(CH_3)_2$ ), 3.91 (d, J = 13 Hz, 1H, N-CH), 4.18 (d, J = 13 Hz, 1H, N-CH), 4.30 (d, J = 13 Hz, 1H, N-CH), 6.22 (s, 1H, Ar-H), 6.50 (s, 1H, Ar-H), 6.55 (s, 1H, Ar-H), 6.62 (s, 1H, Ar-H), 6.66 (s, 1H, Ar-H), 6.88 (s, 1H, Ar-H), 6.90 (t, J = 7 Hz, 1H,

Table 4. Crystal Data and Structure Refinement Parameters for Complexes,  $TiMe(O-2,6^{-i}Pr_2C_6H_3)[(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)(Me_2Al+\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)N]$  (3b),  $[TiMe\{(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)N]$  (3b),  $[TiMe\{(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)N]$  (3c), and  $[TiMe\{(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)N]]$  (3c), and  $[TiMe\{(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)N]$  (3c), and  $[TiMe\{(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)N]]$  (3c), and  $[TiMe\{(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)N]]$  (3c), and  $[TiMe\{(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)N]]$  (3c), and  $[TiMe\{(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)(O-2,4-Me_2C_6H_2-6-CH_2)N]]$  (3c), and  $[TiMe\{(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)N]$  (3c), and  $[TiMe\{(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)N]]$  (3c), and  $[TiMe\{(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)N]$  (3c), and  $[TiMe\{(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)N]]$  (3c), and  $[TiMe\{(\mu_2-O-2,4-Me_2C_6H_2-6-CH_2)N]$  (3c), and [Ti

	3b	3d	3e <sup>b</sup>
empirical formula	$C_{91}H_{112}Al_2N_2O_8Ti_2$	$C_{36}H_{42}AlF_2NO_4Ti$	$C_{37}H_{41}AlCl_2F_5NO_4Ti$
fw	1511.66	665.61	804.51
cryst color, habit	orange, needle	orange, block	orange, block
cryst size (mm)	$0.05 \times 0.02 \times 0.01$	$0.190 \times 0.120 \times 0.09$	$0.180 \times 0.170 \times 0.100$
cryst syst	triclinic	triclinic	triclinic
space group	P1 (No. 2)	P1 (No. 2)	$P\overline{1}$ (No. 2)
a (Å)	9.5175(7)	10.0973(3)	11.6357(3)
b (Å)	12.2092(10)	11.9776(3)	11.9512(3)
c (Å)	18.6971(17)	15.2802(3)	15.3879(3)
$\alpha$ (deg)	104.352(3)	68.0736(7)	109.5937(7)
$\beta$ (deg)	97.765(2)	78.2313(7)	99.5987(7)
γ (deg)	93.793(2)	83.2675(7)	106.3486(7)
V (Å <sup>3</sup> )	2074.3(3)	1676.73(6)	1851.96(7)
Z	1	2	2
$D_{ m calcd}$	1.210	1.318	1.443
$\mu$ (Mo K $\alpha$ ) cm <sup>-1</sup>	2.697	3.318	4.645
$F_{000}$	806.00	700.00	832.00
$2\theta \max (\deg)$	48.8	54.9	54.9
no. of defins collected/unique	$15548/6790~(R_{\rm int}=0.0104)$	$16760/7639~(R_{\rm int}=0.0194)$	$18599/8454 (R_{int} = 0.0173)$
observed reflns $[I > 2\sigma(I)]$	6790	7639	8454
GOF	1.032	1.058	1.092
$R_1, wR_2 [I > 2\sigma(I)]$	0.0742, 0.1812	0.0397, 0.1145	0.0483, 0.1396
largest diff peak/hole [e Å <sup>-3</sup> ]	0.36/-0.43	0.58/-0.30	0.73/-0.61

<sup>a</sup>Detailed results are shown in the Supporting Information.<sup>23</sup> <sup>b</sup>The crystal contained CH<sub>2</sub>Cl<sub>2</sub> in the formula (with certain ratio).

terminal Ar-H), 7.00 (br.d, 3H, Ar-H).  $^{13}\mathrm{C}$  NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  14.3 (Al-CH<sub>3</sub>), 15.6 (Al-CH<sub>3</sub>), 17.1 (Ar-CH<sub>3</sub>), 18.7 (Ar-CH<sub>3</sub>), 20.4 (Ar-CH<sub>3</sub>), 20.5 (Ar-CH<sub>3</sub>), 20.7 (Ar-CH<sub>3</sub>), 26.0 ((CH<sub>3</sub>)<sub>2</sub>CH), 22.8 ((CH<sub>3</sub>)<sub>2</sub>CH), 31.7 ((CH<sub>3</sub>)<sub>2</sub>CH), 60.2 (N-CH<sub>2</sub>), 64.0 (N-CH<sub>2</sub>), 64.5 (N-CH<sub>2</sub>), 65.61 (Ti-CH<sub>3</sub>), 122.4, 122.7, 123.4, 123.8, 125.7, 126.6, 128.2, 128.6, 129.1, 130.3, 130.7, 130.9, 131.2, 131.4, 132.1, 151.6, 158.2, 161.2 (aromatic carbon resonances). Anal. Calcd for C<sub>42</sub>H<sub>56</sub>AlNO<sub>4</sub>Ti: C, 70.68; H, 7.91; N, 1.96. Found: C, 70.22; H, 8.36; N, 1.96.

Synthesis of [TiMe{( $\mu_2$ -O-2,4-Me\_2C\_6H\_2-6-CH\_2)(O-2,4- $Me_2C_6H_2-6-CH_2)_2N[Me_2Al(\mu_2-O-2,6-F_2C_6H_3)]$  (3d). The procedure for the synthesis of 3d was conducted by the similar procedure for 3b, except that  $Ti(O-2,6-F_2C_6H_3)[\{(O-2,4-Me_2C_6H_2)-6-CH_2\}_3N]$  was used in place of  $Ti(O-2,6^{-i}Pr_2C_6H_3)\{(O-2,4-Me_2C_6H_2-6-CH_2)_3N\}$ . Yield: 0.377 g (50.6%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  –0.82 (s, 3H, Al-CH<sub>3</sub>), -0.56 (s, 3H, Al-CH<sub>3</sub>), 1.94 (s, 3H, Ar-CH<sub>3</sub>), 1.98 (s, 3H, Ar-CH<sub>3</sub>), 2.01 (s, 3H, Ar-CH<sub>3</sub>), 2.14 (s, 6H, Ar-CH<sub>3</sub>), 2.16 (s, 3H, Ar-CH<sub>3</sub>), 2.44 (s, 3H, Ti-CH<sub>3</sub>), 2.71 (d, J = 13 Hz, 1H, N-CH), 2.92 (d, J = 13 Hz, 1H, N-CH), 3.03 (d, J = 13 Hz, 1H, N-CH), 3.66 (d, J = 13 Hz, 1H, N-CH), 4.10 (d, J = 13 Hz, 1H, N-CH), 4.41 (d, J = 13 Hz, 1H, N-CH), 6.14 (s, 1H, Ar-H), 6.44 (s, 1H, Ar-H), 6.48 (s, 1H, Ar-H), 6.60 (s, 1H, Ar-H), 6.69 (s, 2H, Ar-H), 6.79 (br.d, 2H, terminal Ar-H), 6.99 (m, 1H, terminal Ar-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  15.85 (Al-CH<sub>3</sub>), 15.92 (Al-CH<sub>3</sub>), 17.14 (Ar-CH<sub>3</sub>), 20.38 (Ar-CH<sub>3</sub>), 20.70 (Ar-CH<sub>3</sub>), 60.61 (N-CH), 62.04 (N-CH), 62.94 (N-CH), 67.28 (Ti-CH<sub>3</sub>), 111.98, 112.40, 122.00, 124.24, 126.72, 127.56, 129.59, 130.13, 130.41, 131.39, 131.96, 150.30, 158.49, 159.26 (aromatic carbon resonances). <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -122.17 (br. s). Anal. Calcd for C36H42AlF2NO4Ti: C, 64.96; H, 6.36; N, 2.10. Found: C, 63.93; H, 6.57; N, 2.09.

[TiMe{( $\mu_2$ -O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)(O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)<sub>2</sub>N]]-[Me<sub>2</sub>Al( $\mu_2$ -O-C<sub>6</sub>F<sub>5</sub>)] (3e). The procedure for the synthesis of 3e was conducted by the similar procedure for 3b, except that Ti(OC<sub>6</sub>F<sub>5</sub>)-[{(O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>)-6-CH<sub>2</sub>]<sub>3</sub>N] was used in place of Ti(O-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)[{(O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>)-6-CH<sub>2</sub>]<sub>3</sub>N]. Yield: 0.534 g (74.2%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  -0.81 (s, 3H, Al-CH<sub>3</sub>), -0.56 (s, 3H, Al-CH<sub>3</sub>), 1.93 (s, 3H, Ar-CH<sub>3</sub>), 1.98 (s, 3H, Ar-CH<sub>3</sub>), 2.00 (s, 3H, Ar-CH<sub>3</sub>), 2.15 (s, 6H, Ar-CH<sub>3</sub>), 2.19 (s, 3H, Ar-CH<sub>3</sub>), 2.43 (s, 3H, Ti-CH<sub>3</sub>), 2.72 (d, J = 13 Hz, 1H, N-CH), 2.93 (d, J = 13 Hz, 1H, N-CH), 3.09 (d, J = 13 Hz, 1H, N-CH), 3.66 (d, J = 13 Hz, 1H, N-CH), 4.05 (d, J = 13 Hz, 1H, N-CH), 4.27 (d, J = 13 Hz, 1H, N-CH), 6.13 (s, 1H, Ar-H), 6.46 (s, 1H, Ar-H), 6.49 (s, 1H, Ar-H), 6.62 (s, 1H, Ar-H), 6.71 (s, 1H, Ar-H), 6.75 (s, 1H, Ar-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  15.77 (Al-CH<sub>3</sub>), 15.80 (Al-CH<sub>3</sub>), 17.07 (Ar-CH<sub>3</sub>), 20.36 (Ar-CH<sub>3</sub>), 20.66 (Ar-CH<sub>3</sub>), 20.69 (Ar-CH<sub>3</sub>), 60.64 (N-CH), 61.98 (N-CH), 62.96 (N-CH), 67.56 (Ti-CH<sub>3</sub>), 124.09, 124.54, 124.61, 125.80, 126.72, 126.80, 127.18, 127.65, 129.53, 130.14, 130.30, 130.38, 130.79, 131.56, 132.32, 150.03, 158.09, 159.38 (aromatic carbon resonances). <sup>19</sup>F-NMR (CDCl<sub>3</sub>):  $\delta$  -151.40 (br. d, *ortho*-F), -164.29 (br. t, *meta*-F), -164.70 (br. t, *para*-F). Anal. Calcd for C<sub>36</sub>H<sub>39</sub>AlF<sub>5</sub>NO<sub>4</sub>Ti-CH<sub>2</sub>Cl<sub>2</sub>: C, 55.24; H, 5.14; N, 1.74. Found: C, 55.22; H, 5.05; N, 1.89.

Reaction of Ti(O-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)[{(O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>)-6-CH<sub>2</sub>}<sub>3</sub>N] (1a) with AlMe<sub>3</sub>. Into a cold toluene solution (20 mL) containing 1a (0.293 g, 0.50 mmol) chilled at -30 °C was added slowly a cold toluene solution containing AlMe3 (1.05 M n-hexane solution, 0.50 mmol). The reaction mixture was then warmed to room temperature with stirring, which was continued for 1 h. The volatiles were evaporated under vacuum, and to the resultant orange-brown oil was added 15 mL of toluene. The solution was then filtered through a Celite pad. The filtrate was removed under vacuum to obtain an orange sticky solid; the solid was then dissolved in *n*-hexane and placed in the freezer chilled at -30 °C (for ca. 1 month). A mixture of white and orange microcrystals were obtained, and the mixture was dissolved with cold toluene for separation (extracted with cold toluene). The white microcrystals were then isolated after removing toluene and recrystallized from a minimum amount of n-hexane (at -30 °C). The white microcrystals were identified as  $[Al(\mu_2-O-2,6-Me_2C_6H_3)Me_2]_2$  (5) determined by X-ray crystallography.<sup>24</sup> Yield: 0.068 g (38.2%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  -0.41 (s, 12H, Al-CH<sub>3</sub>), 2.40 (s, 12H, Ar-CH<sub>3</sub>), 6.80 (t, 2H, Ar-H), 6.86 (d, 4H, Ar-H). The orange brown solid, which was insoluble with cold toluene in the mixture of crystals, was dissolved in a minimum amount of CH<sub>2</sub>Cl<sub>2</sub>

and layered with *n*-hexane. Careful repetitive recrystallization from the chilled  $CH_2Cl_2/n$ -hexane eventually afforded pure orange microcrystals of TiMe[{(O-2,4-Me\_2C\_6H\_2)-6-CH\_2}\_3N] (4) only determined by X-ray crystallography.

**Reaction of Ti(OC<sub>6</sub>F<sub>5</sub>)[{(O-2,4-<sup>t</sup>Bu<sub>2</sub>C<sub>6</sub>H<sub>2</sub>)-6-CH<sub>2</sub>]<sub>3</sub>N] (2e) with AlMe<sub>3</sub>. Into a cold toluene solution (20 mL) containing 2e (0.423 g, 0.50 mmol) chilled at -30 °C was added slowly a cold toluene solution containing AlMe<sub>3</sub> (1.05 M** *n***-hexane solution, 0.50 mmol). The reaction mixture was then warmed to room temperature with stirring, which was continued for 2 h. The volatiles were evaporated under vacuum, and to the resultant yellow oil was added 15 mL of toluene. The solution was then filtered through Celite pad. The filtrate was removed under vacuum; the oil was then dissolved in** *n***-hexane and placed in the freezer chilled at -30 °C. White microcrystals determined as [Al(\mu\_2 \cdot OC\_6F\_5)Me\_2]\_2 (6) by X-ray crystallographic analysis<sup>24</sup> were collected from the chilled solution (after ca. 2 weeks). Yield: 0.051 g (42.2%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C): \delta -0.56 (s, 12H, Al-CH<sub>3</sub>). <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C): \delta -154.4 (br. d,** *ortho-F***), -161.0 (br. t,** *meta-F***), -162.5 (br., t,** *para-F***).** 

Reaction of Ti(O-2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>){(O-2,4-<sup>1</sup>Bu<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)<sub>3</sub>N} (2d) with AlMe<sub>3</sub> was conducted according to the analogous procedure for 2f. White microcrystals assumed as  $[Al(\mu_2$ -O-2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)Me<sub>2</sub>]<sub>2</sub> by NMR spectra were collected from the chilled solution. Yield: 0.045 g (48.0%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  –0.16 (s, 12H, Al-CH<sub>3</sub>), 6.16 (t, 2H, Ar-H), 6.37 (d, 4H, Ar-H). <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  –126.0 (br. s).

Reaction of  $Ti(O'Pr)[\{(O-2,4-{}^{t}Bu_{2}C_{6}H_{2})-6-CH_{2}\}_{3}N]$  (2f) with Me<sub>2</sub>AlCl. A cold toluene solution (10 mL) containing Me<sub>2</sub>AlCl (1.08 M in n-hexane, 0.50 mmol) chilled at -20 °C was added dropwise into a cold toluene solution (10 mL, chilled at -20 °C) containing  $Ti(O'Pr)[(O-2_{1}6^{-t}Bu_{2}-C_{6}H_{3})_{3}N]$  (2f, 0.388 g, 0.50 mmol) at room temperature. The reaction mixture was then stirred at room temperature for 2 h. The volatiles were evaporated in vacuo, and to the resultant orange solid was added 15 mL of toluene. The orange solution was then filtered through a Celite pad. The filtrate was removed under vacuum to obtain orange solids. The complex was isolated as orange microcrystals from CH<sub>2</sub>Cl<sub>2</sub>/n-hexane solution. Yield: 0.208 g (63.8%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 1.32 (s, 27H, CH(CH<sub>3</sub>)<sub>3</sub>), 1.66 (s, 27H, CH(CH<sub>3</sub>)<sub>3</sub>), 2.55 (d, J = 13.8 Hz, 3H, N-CH), 3.95 (d, J= 13.8 Hz, 3H, N-CH), 6.76 (d, J = 2.35 Hz, 3H, Ar-H), 7.43 (d, J = 2.35 Hz, 3H, Ar-H). The spectral data were highly analogous to those reported previously.<sup>25</sup> Anal. Calcd for  $C_{45}H_{66}ClNO_3Ti \cdot n$ -hexane: C, 73.05; H, 9.62; N, 1.67. Found: C, 73.61; H, 9.56; N, 1.73. The microcrystals were then dissolved in benzene and placed in vacuum to give another solid containing benzene. Anal. Calcd for C45H66ClNO3Ti-1.5C6H6: C, 74.59; H, 8.69; N, 1.61. Found: C, 74.62; H, 8.66; N, 1.63.

**Crystallographic Analysis.** All measurements were made on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo K $\alpha$  radiation. All structures were solved by direct methods<sup>29</sup> and expanded using Fourier techniques, and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included, but not refined. All calculations were performed using the CrystalStructure<sup>30</sup> crystallographic software package except for refinement, which was performed using SHELXL-97.<sup>31</sup> Table 4 summarizes selected crystal collection parameters, and the detailed structure reports, including their CIF files, are shown in the Supporting Information.<sup>23</sup>

**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 1) was performed as follows. Toluene (29.0 mL) and d-MAO (3.0 mmol) prepared by removing toluene and AlMe<sub>3</sub> 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 *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 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.

#### ASSOCIATED CONTENT

#### **Supporting Information**

<sup>1</sup>H NMR spectra for monitoring the reaction of Ti(O<sup>i</sup>Pr)<sub>3</sub>(O- $2_{6}^{+i}Pr_{2}C_{6}H_{3}$  with [{(HO-2\_{4}^{+i}Bu\_{2}C\_{6}H\_{2})-6-CH\_{2}}\_{3}N]; ^{1}H and <sup>19</sup>F NMR spectra for the reaction mixture of Ti(O<sup>i</sup>Pr)[{(O- $2_{4} + Bu_{2}C_{6}H_{2} - 6 - CH_{2}_{3}N$  (2f) with  $[Al(\mu_{2} - OC_{6}F_{5})Me_{2}]_{2}$  (6) in CDCl<sub>3</sub>; <sup>1</sup>H and <sup>19</sup>F NMR spectra after heating of  $(CH_2)_2N$  [Me<sub>2</sub>Al( $\mu_2$ -OAr)] [Ar = 2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (3d), C<sub>6</sub>F<sub>5</sub> (3e)] in *n*-octane at 100 °C; and a table summarizing crystal data and structure refinement parameters, including structure reports and CIF files, for TiMe[ $\{(O-2, 4-Me_2C_6H_2)-6-CH_2\}_3N$ ] (4),  $[Al(\mu_2-O-2,6-Me_2C_6H_3)Me_2]_2$  (5), and  $[Al(\mu_2-OC_6F_5) Me_2$ , (6) and structure reports, including CIF files, for  $TiMe(O-2,6-{}^{i}Pr_{2}C_{6}H_{3})[(\mu_{2}-O-2,4-Me_{2}C_{6}H_{2}-6-CH_{2})(Me_{2}Al \mu_2$ -O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>)(O-2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-6-CH<sub>2</sub>) N] (3b) and 3d,3e. This material is available free of charge via the Internet at http://pubs.acs.org.

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# Notes

The authors declare no competing financial interest.

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