# Notable Effect of Fluoro Substituents in the Imino Group in Ring-Opening Polymerization of $\varepsilon$ -Caprolactone by Al Complexes Containing Phenoxyimine Ligands

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A series of Al complexes containing phenoxyimine ligands of the types  $R^1(R^2)Al[O-2-Bu-6{(C_6F_5)N=CH}C_6H_3]$  [ $R^1$ ,  $R^2 = Me$ , Me (1a); Et, Et (1b); Me, Cl (1c)] and Me<sub>2</sub>Al[O-2-'Bu-6-(ArN=CH)C\_6H\_3] [Ar = 2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (2a), 2,4-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (3a), 3,4-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (4a)] have been prepared and identified on the basis of NMR spectra and elemental analyses. Their structures were determined by X-ray crystallography, and these complexes fold a distorted tetrahedral geometry around Al. The ring-opening polymerizations (ROPs) of  $\varepsilon$ -caprolactone (CL) using 1a-c in the presence of PhCH<sub>2</sub>OH proceeded efficiently in a living manner, and the propagation rates were somewhat influenced by the anionic donor ligand employed (Me, Et, or Cl). The catalytic activity by 1a-6a [ $Ar = C_6H_5$  (5a), 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (6a)]-PhCH<sub>2</sub>OH catalyst systems was strongly affected by the aromatic substituent (Ar) in the imino group, and placement of fluorine substituents especially in the *ortho*-position strongly affected the catalytic activity. The ROPs by 2a-6a were accompanied by a certain degree of side reactions (transesterification), whereas the living polymerization systems can be accomplished using the C<sub>6</sub>F<sub>5</sub> analogues (1a-c). Therefore, the C<sub>6</sub>F<sub>5</sub> substituent in the imino group plays an essential key role in the ROP of CL in terms of both the catalytic activity and maintaining a living manner.

## Introduction

Certain aliphatic polyesters are known to possess promising characteristics as biodegradable and bioassimilable materials not only due to their practical biodegradability, but also due to their biocompatibility for medical and pharmaceutical applications.<sup>1</sup> Aluminum alkoxides are known to be one of the important reagents employed as initiators for ring-opening polymerization (ROP) of cyclic esters<sup>2</sup> such as lactides<sup>3,4c</sup> and lactones,<sup>3j,n,4,5</sup> and considerable attention has thus been paid to the synthesis and structural determinations of monomeric/dimeric Al complexes.<sup>6</sup>

We recently demonstrated that Me<sub>2</sub>Al[O-2-<sup>*t*</sup>Bu-6-{(C<sub>6</sub>F<sub>5</sub>) N=CH}C<sub>6</sub>H<sub>3</sub>] (**1a**) exhibits unique characteristics for a rapid living ROP of  $\varepsilon$ -caprolactone (CL) and  $\delta$ -valerolactone (VL) in the presence of "BuOH (1.0 equiv).<sup>4</sup> We also demonstrated

that the imino substituent (R) in Me<sub>2</sub>Al[O-2-'Bu-6-(RN= CH)C<sub>6</sub>H<sub>3</sub>] plays a crucial role in efficient ROP; the catalytic activity (turnover number, TON) in the ROP increased in the order R = C<sub>6</sub>F<sub>5</sub>  $\gg$  R = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> > R = 2,6-'Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> > R = C<sub>6</sub>H<sub>5</sub> > R = cyclohexyl > R = 'Bu > R = adamantyl (negligible activity).<sup>4a,b</sup> Moreover, the PDI value ( $M_w/M_n$ ) increased without a notable increase in the  $M_n$  values at high CL conversion (ca. 80%) in the ROP by Me<sub>2</sub>Al[O-2-'Bu-6-{(cyclohexyl)N=CH}C<sub>6</sub>H<sub>3</sub>]-"BuOH catalyst, whereas the  $M_w/M_n$  values remained constant ( $M_w/M_n = 1.17-1.19$ ) in the ROP by the C<sub>6</sub>F<sub>5</sub> analogue-"BuOH catalyst under the same conditions (at 60 °C).<sup>4b</sup>

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Scheme 1



It has been generally proposed that the ROP proceeds via coordination and insertion of CL,<sup>7</sup> and the presence of two types

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of side reactions, intra- and intermolecular transesterifications, is also known (Scheme 1).8 Therefore, this fact (broadening of the molecular weight distributions in the ROP by the cyclohexyl analogue) would suggest a possibility of (probably intramolecular) transesterification accompanying the catalytic ROP as a side reaction.4b However, there is no detailed information concerning a ligand effect toward the polymerization behavior especially for the precise control in the ROP without a side reaction such as transesterification.

In this study, we thus investigated synthesis and structural analysis of a series of four-coordinate R<sup>1</sup>(R<sup>2</sup>)Al[O-2-<sup>*t*</sup>Bu- $6{-}(C_6F_5)N=CH C_6H_3 [R^1, R^2 = Et, Et (1b); Me, Cl (1c)] and$ conducted the ROPs of CL by 1a-c in the presence of 1 equiv of PhCH<sub>2</sub>OH. Through this research, we explored the effect of an anionic (alkyl or chloro) ligand ( $\mathbb{R}^1$ ,  $\mathbb{R}^2$ ) on both the catalytic activity (propagation rate) and the polymerization behavior. We also investigated synthesis and structural analysis of the series  $Me_2Al[O-2-^tBu-6-(ArN=CH)C_6H_3]$  [Ar = 2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (2a), 2,4- $F_2C_6H_3$  (3a), 3,4- $F_2C_6H_3$  (4a)] and explored the effect of the imino substituent on both the activity and the polymerization behavior in the ROPs of CL using a series of 1a-6a-PhCH<sub>2</sub>OH catalyst systems [Ar =  $C_6H_5$  (5a), 2,6-Me<sub>2</sub> $C_6H_3$  (6a)]. Through this project, we present important factors to establish the fast, controlled ring-opening polymerization of the cyclic esters exemplified as CL.

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**Results and Discussion** 

Synthesis and Structural Analysis of  $R^1(R^2)Al[O-2-Bu-6-{(C_6F_5)N=CH}C_6H_3]$  ( $R^1$ ,  $R^2 = Et$ , Et; Me, Cl) and  $Me_2Al[O-2-Bu-6-(ArN=CH)C_6H_3]$  ( $Ar = 2,6-F_2C_6H_3$ ,  $2,4-F_2C_6H_3$ , 3,4-

**F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>).** Various Al complexes containing different anionic (alkyl, halogen) ligands, R<sup>1</sup>(R<sup>2</sup>)Al[O-2-'Bu-6-{(C<sub>6</sub>F<sub>5</sub>)N=CH} C<sub>6</sub>H<sub>3</sub>] [R<sup>1</sup>, R<sup>2</sup> = Et, Et (**1b**); Me, Cl (**1c**)], have been prepared by treatment of AlEt<sub>3</sub> or Me<sub>2</sub>AlCl with 1 equiv of 2-'Bu-6-(ArN=CH)C<sub>6</sub>H<sub>3</sub>OH in *n*-hexane (Scheme 2).<sup>9</sup> The synthetic procedures are analogous to that for Me<sub>2</sub>Al[O-2-'Bu-6-{(C<sub>6</sub>F<sub>5</sub>)N=CH}C<sub>6</sub>H<sub>3</sub>] (**1a**), and the complexes were identified on the basis of their <sup>1</sup>H and <sup>13</sup>C NMR spectra and elemental analyses. The structures of **1b** and **1c** were determined by X-ray crystallography (Figure 1), and the selected bond distances and angles are summarized in Table 1.<sup>10</sup>

Complexes 1b and 1c have a distorted tetrahedral geometry around the Al, as seen in 1a.4b The Al-O bond distances in 1b,c [1.753(2) and 1.7479(11) Å, respectively] are shorter than that in **1a** [1.7737(16) Å], and the Al-N bond distance in **1c** [1.9429(12) Å] is shorter than those in **1a**,**b** [1.9780(19) and 1.986(2) Å, respectively]. One Al-carbon bond distance in 1b [2.127(10) Å] is apparently longer than the Al–C bond distances in 1a,c [1.9304(17)-1.951(2) Å]; this can probably be explained as due to the steric bulk of two ethyl groups in 1b. The Al-Cl bond distance [2.1547(6) Å] in 1c seems similar to the reported values [ca. 2.1238–2.1239 Å in (TTP)AlCl<sub>2</sub>, TTPH =  $2-(p-1)^{-1}$ tolylamino)-4-(p-tolylimino)-2-pentene].<sup>6b</sup> The bond angle C(in Me or Et)-Al-C(Me, Et) or C-Al-Cl is influenced by the anionic ligand (Me, Et, or Cl) employed, and the angle increases in the order C(12)-Al-C(14) [127.0(2)°] (1b) > C(1)-Al-C(2) $[118.12(12)^{\circ}]$  (1a) > Cl(1)-Al-C(8)  $[113.88(6)^{\circ}]$  (1c). The O-Al-N angle in 1c [95.45(5)°] is somewhat larger than those



**Figure 1.** ORTEP drawings of  $Et_2Al[O-2-'Bu-6-{(C_6F_5)N=CH}C_6H_3]$  (**1b**; left) and  $Me(Cl)Al[O-2-'Bu-6-{(C_6F_5)N=CH}C_6H_3]$  (**1c**; right). Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.<sup>10</sup>

Table 1. Selected Bond Distances (A	) and Angles (deg) for $Me_2Al[O-2-^{t}Bu-6-\{(C_6F_5)N=CH\}C_6H_3]$ (1a), $Et_2Al[O-2-^{t}Bu-6-\{(C_6F_5)N=CH\}C_6H_3]$	<b>H</b> 3]
	(1b), and Me(Cl)Al[O-2-'Bu-6-{ $(C_6F_5)N=CH$ }C <sub>6</sub> H <sub>3</sub> ] (1c) <sup>a</sup>	

la		1b		lc		
Bond Distances (Å)						
Al(1) - O(1)	1.7737(16)	Al(1) - O(1)	1.753(2)	Al(1) - O(1)	1.7479(11)	
Al(1) - N(1)	1.9780(19)	Al(1) - N(1)	1.986(2)	Al(1)-N(1)	1.9429(12)	
Al(1)-C(1)	1.951(2)	Al(1) - C(12)	1.920(4)	Al(1)-C(8)	1.9304(17)	
Al(1) - C(2)	1.941(2)	Al(1) - C(14)	2.127(10)	Al(1)-Cl(1)	2.1547(6)	
N(1) - C(3)	1.300(2)	N(1)-C(7)	1.308(4)	N(1) - C(7)	1.3104(19)	
N(1) - C(10)	1.436(2)	N(1)-C(16)	1.423(3)	N(1) - C(13)	1.4344(19)	
		Bond Angles	(deg)			
O(1) - Al(1) - N(1)	93.17(7)	O(1) - Al(1) - N(1)	93.26(10)	O(1) - Al(1) - N(1)	95.45(5)	
C(1) - Al(1) - C(2)	118.12(12)	C(12) - Al(1) - C(14)	127.0(2)	Cl(1) - Al(1) - C(8)	113.88(6)	
Al(1) - O(1) - C(9)	133.89(14)	Al(1) - O(1) - C(1)	132.06(15)	Al(1) - O(1) - C(1)	131.10(9)	
Al(1) - N(1) - C(3)	122.97(14)	Al(1) - N(1) - C(7)	121.32(18)	Al(1) - N(1) - C(7)	120.78(10)	
Al(1) - N(1) - C(10)	120.55(14)	Al(1) - N(1) - C(16)	120.8(2)	Al(1) - N(1) - C(13)	121.82(9)	
O(1) - Al(1) - C(1)	113.73(10)	O(1) - Al(1) - C(12)	109.72(18)	O(1) - Al(1) - C(8)	116.16(7)	
O(1) - Al(1) - C(2)	113.71(10)	O(1) - Al(1) - C(14)	106.67(16)	Cl(1) - Al(1) - O(1)	110.01(3)	
N(1) - Al(1) - C(1)	105.34(9)	N(1) - Al(1) - C(12)	110.75(16)	N(1) - Al(1) - C(8)	117.86(7)	
N(1) - Al(1) - C(2)	109.26(10)	N(1) - Al(1) - C(14)	104.2(2)	Cl(1) - Al(1) - N(1)	101.22(4)	

<sup>a</sup> For detailed analysis conditions, see the Supporting Information.<sup>10</sup>



**Figure 2.** ORTEP drawings of Me<sub>2</sub>Al[O-2-'Bu-6-{( $2,6-F_2C_6H_3$ ) N=CH}C<sub>6</sub>H<sub>3</sub>] (**2a**; top), Me<sub>2</sub>Al[O-2-'Bu-6-{( $2,4-F_2C_6H_3$ )N=CH}C<sub>6</sub>H<sub>3</sub>] (**3a**; middle), and Me<sub>2</sub>Al[O-2-'Bu-6-{( $3,4-F_2C_6H_3$ )N=CH}C<sub>6</sub>H<sub>3</sub>] (**4a**; bottom). Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.<sup>10</sup>

in **1a,b** [93.17(7) and 93.26(10), respectively], and the other angles are also influenced by the anionic donor ligands employed

(Me, Et, or Cl). These results may be important in considering the influences of the anionic donor ligands.

Al complexes containing phenoxyimine ligands with a series of fluorinated aromatic substituents in the imino group, Me<sub>2</sub>Al[O-2-'Bu-6-(ArN=CH)C<sub>6</sub>H<sub>3</sub>] [Ar = 2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**2a**), 2,4-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**3a**), 3,4-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**4a**)], were prepared by treating AlMe<sub>3</sub> with the corresponding iminophenols<sup>9</sup> in *n*-hexane, and their synthetic procedures are also analogous to that for **1a**.<sup>4b</sup> The resultant complexes were identified on the basis of the <sup>1</sup>H and <sup>13</sup>C NMR spectra and elemental analyses. The structures of **2a**, **3a**, and **4a** were also determined by X-ray crystallography (Figure 2), and the selected bond distances and angles are summarized in Table 2.<sup>10</sup>

The structures of 2a-4a indicate that these complexes fold a distorted tetrahedral geometry around Al. The Al–N bond distances are not strongly influenced by the imino substituent [1.968(3)-1.9692(14) Å], and the Al–O bond distance in 4a [1.759(2) Å] is somewhat shorter than those in 1a-3a[1.7680(15)-1.7737(16) Å]. The Al–C(in Me) bond distances in 4a [1.921(4) and 1.930(4) Å] are shorter than those in 1a and 3a [1.941(2)-1.956(2) Å] and are apparently shorter than those in 2a [1.963(2) and 1.973(2) Å]. The C–Al–C bond angles increase in the order 3a  $[119.29(11)^\circ] > 1a$ , 2a  $[118.12(12)^\circ$  and  $118.00(10)^\circ$ , respectively]  $> 4a [117.51(19)^\circ]$ , and some bond angles are also influenced by the imino substituent.

Attempted reaction of Me<sub>2</sub>Al[O-2-'Bu-6-{(C<sub>6</sub>F<sub>5</sub>)N=CH} C<sub>6</sub>H<sub>3</sub>] (**1a**) with 1.0 equiv of PhCH<sub>2</sub>OH in C<sub>6</sub>D<sub>6</sub> at 25 °C afforded a mixture of products that seemed difficult for their identifications.<sup>11</sup> The reaction of Me<sub>2</sub>Al(OCH<sub>2</sub>Ph) with 2-'Bu-6-{(C<sub>6</sub>F<sub>5</sub>)N=CH}C<sub>6</sub>H<sub>3</sub>OH in C<sub>6</sub>D<sub>6</sub> also afforded a mixture of products, and a trimetallic Al complex, [Me<sub>2</sub>Al( $\mu_2$ -OCH<sub>2</sub>Ph)]<sub>2</sub> [Al{O-2-'Bu-6-{(C<sub>6</sub>F<sub>5</sub>)N=CH}C<sub>6</sub>H<sub>3</sub>}( $\mu_2$ -OCH<sub>2</sub>Ph)<sub>2</sub>] (**7**), determined by X-ray crystallography, was isolated from the chilled *n*-hexane solution (53% yield).<sup>11</sup> The results suggest that both the PhCH<sub>2</sub>OH and CL should be required for generating the actual catalytically active species (assumed by the chain-end analysis<sup>4</sup>) from **1a** in this catalysis.

Effect of a Ligand on the Ring-Opening Polymerization of  $\varepsilon$ -Caprolactone Using R<sup>1</sup>(R<sup>2</sup>)Al[O-2-'Bu-6-(ArN=CH) C<sub>6</sub>H<sub>3</sub>]-PhCH<sub>2</sub>OH Catalyst Systems. We recently demonstrated that rapid living ROPs of both CL and VL were achieved with high catalyst (initiation) efficiencies by using Me<sub>2</sub>Al[O-2-'Bu-6-{(C<sub>6</sub>F<sub>5</sub>)N=CH}C<sub>6</sub>H<sub>3</sub>] (1a) in the presence of "BuOH (1.0 equiv).<sup>4</sup> We also reported that the imino

Table 2. Selected Bond Distances (Å) and Angles (deg) for  $Me_2Al[O-2-'Bu-6-\{(2,6-F_2C_6F_3)N=CH\}C_6H_3]$  (2a),  $Me_2Al[O-2-'Bu-6-\{(2,4-F_2C_6H_3)N=CH\}C_6H_3]$  (3a), and  $Me_2Al[O-2-'Bu-6-\{(3,4-F_2C_6H_3)N=CH\}C_6H_3]$  (4a)<sup>*a*</sup>

2a		3a		4a		
Bond Distances (Å)						
Al(1) - O(1)	1.7680(15)	Al(1) - O(1)	1.7713(19)	Al(1) - O(1)	1.759(2)	
Al(1) - N(1)	1.9692(14)	Al(1)-N(1)	1.9692(16)	Al(1) - N(1)	1.968(3)	
Al(1)-C(8)	1.963(2)	Al(1)-C(8)	1.956(2)	Al(1)-C(8)	1.930(4)	
Al(1)-C(9)	1.973(2)	Al(1)-C(9)	1.954(3)	Al(1)-C(9)	1.921(4)	
N(1) - C(7)	1.300(2)	N(1)-C(7)	1.302(2)	N(1)-C(7)	1.312(5)	
N(1)-C(14)	1.435(2)	N(1) - C(14)	1.436(2)	N(1) - C(14)	1.427(4)	
		Bond Angles	(deg)			
O(1) - Al(1) - N(1)	93.15(6)	O(1) - Al(1) - N(1)	93.01(7)	O(1) - Al(1) - N(1)	93.28(13)	
C(8) - Al(1) - C(9)	118.00(10)	C(8) - Al(1) - C(9)	119.29(11)	C(8) - Al(1) - C(9)	117.51(19)	
Al(1) - O(1) - C(1)	133.60(11)	Al(1) - O(1) - C(1)	134.54(14)	Al(1) - O(1) - C(1)	133.4(2)	
Al(1) - N(1) - C(7)	122.84(12)	Al(1) - N(1) - C(7)	123.09(14)	Al(1) - N(1) - C(7)	122.0(2)	
Al(1)-N(1)-C(14)	119.56(11)	Al(1) - N(1) - C(14)	119.52(12)	Al(1) - N(1) - C(14)	120.0(2)	
O(1) - Al(1) - C(8)	112.97(8)	O(1) - Al(1) - C(8)	113.02(10)	O(1) - Al(1) - C(8)	111.57(17)	
O(1) - Al(1) - C(9)	112.13(9)	O(1) - Al(1) - C(9)	110.79(10)	O(1) - Al(1) - C(9)	110.47(16)	
N(1) - Al(1) - C(8)	109.06(8)	N(1) - Al(1) - C(8)	107.91(9)	N(1) - Al(1) - C(8)	112.64(16)	
N(1) - Al(1) - C(9)	108.54(8)	N(1) - Al(1) - C(9)	109.52(9)	N(1) - Al(1) - C(9)	108.74(15)	

<sup>a</sup> For detailed analysis conditions, see the Supporting Information.<sup>10</sup>



Table 3. Living Ring-Opening Polymerization of CL Initiated by  $R^1(R^2)Al[O-2-'Bu-6-\{(C_6F_5)N=CH\}C_6H_4] [R^1, R^2 = Me, Me (1a); Et, Et (1b); Me, Cl (1c)]-PhCH_2OH Catalyst Systems<sup>a</sup>$ 

complex R <sup>1</sup> , R <sup>2</sup>	time/min	conversion <sup>b</sup> /%	$\frac{M_{\rm n(GPC)}}{10^{-4}}^c \times$	$M_{\rm w}/M_{\rm n}^{\ c}$	N <sup>d</sup> /µmol
Me, Me (1a)	15	48	3.15	1.19	31
Me, Me (1a)	30	81	4.87	1.21	33
Me, Me (1a)	45	94	5.53	1.22	34
Et, Et (1b)	15	48	2.32	1.24	41
Et, Et (1b)	30	78	3.50	1.23	45
Et, Et (1b)	45	91	4.12	1.21	44
Me, Cl (1c)	15	53	2.46	1.12	43
Me, Cl (1c)	30	83	3.57	1.14	47
Me, Cl (1c)	45	93	3.96	1.12	47

<sup>*a*</sup> Conditions: Al (40  $\mu$ mol), PhCH<sub>2</sub>OH (40  $\mu$ mol), CL (10.0 mmol) (CL/Al = 250), toluene, [CL]<sub>0</sub> = 1.0 mmol/mL, 50 °C. <sup>*b*</sup> Estimated by <sup>1</sup>H NMR spectra. <sup>*c*</sup> By gel permeation chromatography (GPC) in THF vs polystyrene standards. <sup>*d*</sup> Estimated number of polymer chains ( $\mu$ mol) = mass of CL reacted (mg) based on conversion/{ $M_{n(GPC)} \times 0.56$ }.<sup>12</sup>

 Table 4. Summary of the Rate Constants in Living Ring-Opening

 Polymerization of CL Initiated by

 $R^{1}(R^{2})Al[O-2-Bu-6-{(C_{6}F_{5})N=CH}C_{6}H_{4}] [R^{1}, R^{2} = Me, Me (1a); Et, Et (1b); Me, Cl (1c)]-PhCH_{2}OH Catalyst Systems<sup>a</sup>$ 

complex R <sup>1</sup> , R <sup>2</sup>	$k_{\text{obsd}}^{\ b} \times 10^{-2} \text{ min}^{-1}$	N <sup>c</sup> /µmol	relative efficiency <sup>d</sup>	$k_{\rm rcor}^{e} \times 10^{-2}  {\rm min}^{-1}$
Me, Me (1a)	2.8	34	0.72	3.9
Et, Et (1b)	2.4	44	0.94	2.6
Me, Cl (1c)	2.6	47	1.0	2.6

<sup>*a*</sup> Polymerization conditions are shown in Table3. <sup>*b*</sup> Estimated on the basis of Figure4 (slope). <sup>*c*</sup> Estimated number of polymer chains ( $\mu$ mol) = mass of CL reacted (mg) based on conversion/{ $M_{n(GPC)} \times 0.56$ }, cited from Table3 (after 45 min).<sup>12</sup> <sup>*d*</sup> Relative efficiency on the basis of *N* ( $\mu$ mol) by **1c** [= $N_{(by 1a or 1b)}/N_{(by 1c)}$ ]. <sup>*e*</sup> Corrected relative *k* value based on  $k_{obsd}$  and the relative efficiency.

substituent strongly affects both the catalytic activity and the catalyst efficiency. As described above, to explore the details concerning major roles of the anionic donor ligand (Me, Et, Cl) and the imino substituents (Ar) in both the catalytic activity and the polymerization behavior (including a possibility of accompanying side reactions such as transesterification), we thus conducted the ROPs of CL using the series  $R^{1}(R^{2})Al[O-2^{-t}Bu-6-{(C_{6}F_{5})N=CH}C_{6}H_{3}] [R^{1}, R^{2} = Me, Me$ (1a); Et, Et (1b); Me, Cl (1c)] in the presence of PhCH<sub>2</sub>OH. We also conducted the ROPs of CL using the series Me<sub>2</sub>Al[O- $2^{-t}Bu-6-(ArN=CH)C_6H_3$  [Ar =  $C_6F_5$  (1a), 2,6- $F_2C_6H_3$  (2a), 2,4-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (3a), 3,4-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (4a), C<sub>6</sub>H<sub>5</sub> (5a), 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (6a)] in the presence of PhCH<sub>2</sub>OH, especially to explore the role of the fluorinated substituent in the imino group (Scheme 3). PhCH<sub>2</sub>OH was chosen in place of <sup>n</sup>BuOH, because the ROP (conversion of monomers) can be easily monitored by <sup>1</sup>H NMR spectra as references to the benzyl protons.<sup>12</sup> The results are summarized in Tables 3-5.12

It turned out that the ROPs of CL using the  $C_6F_5$  derivatives (**1a**-**c**) were almost completed after 45 min (conversion 91–94%, Table 3), indicating that **1b**,**c** are also effective in

Table 5. Ring-Opening Polymerization of CL Initiated by
$Me_2Al[O-2-Bu-6-(ArN=CH)C_6H_4]$ [Ar = C <sub>6</sub> F <sub>5</sub> (1a), 2,6-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (2a)
2,4-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (3a), 3,4-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (4a), C <sub>6</sub> H <sub>5</sub> (5a), 2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>
(6a)]-PhCH <sub>2</sub> OH Catalyst Systems <sup>a</sup>

			-		
			$M_{n(GPC)}^{c} \times$	$M_{\rm w}/$	
complex Ar	time/min	conversion <sup>b</sup> /%	$10^{-4}$	$M_n^c$	N <sup>d</sup> /µmol
$C_{6}F_{5}(1a)$	15	48	3.15	1.19	31
$C_{6}F_{5}(1a)$	30	81	4.87	1.21	33
$C_{6}F_{5}(1a)$	45	94	5.53	1.22	34.
$2,6-F_2C_6H_3(2a)$	30	21	1.06	1.12	39
$2,6-F_2C_6H_3(2a)$	60	49	2.16	1.24	46
$2,6-F_2C_6H_3(2a)$	90	73	2.99	1.42	49
$2,6-F_2C_6H_3(2a)$	120	89	3.35	1.50	51
$2,4-F_2C_6H_3$ (3a)	60	25	1.20	1.11	41
$2,4-F_2C_6H_3$ (3a)	120	59	2.45	1.18	48
$2,4-F_2C_6H_3$ (3a)	180	87	3.47	1.32	50
$2,4-F_2C_6H_3$ (3a)	240	97	3.94	1.48	49
$3,4-F_2C_6H_3$ (4a)	60	19	0.95	1.13	40
$3,4-F_2C_6H_3$ (4a)	120	46	1.92	1.17	47
$3,4-F_2C_6H_3$ (4a)	180	73	2.82	1.41	51
$3,4-F_2C_6H_3$ (4a)	240	89	3.24	1.58	55
$C_{6}H_{5}(5a)$	60	14	0.67	1.11	40
$C_{6}H_{5}(5a)$	120	31	1.37	1.16	45
$C_{6}H_{5}(5a)$	180	50	1.93	1.28	52
$C_{6}H_{5}(5a)$	240	69	2.55	1.43	54
$C_{6}H_{5}(5a)$	300	82	2.79	1.78	59
$C_{6}H_{5}(5a)$	360	91	2.99	1.98	61
$2,6-Me_2C_6H_3$ (6a)	60	14	0.79	1.11	36
$2,6-Me_2C_6H_3$ (6a)	120	35	1.74	1.14	41
$2,6-Me_2C_6H_3$ (6a)	180	55	2.61	1.14	42
$2,6-Me_2C_6H_3$ (6a)	240	72	3.19	1.21	45
$2,6-Me_2C_6H_3$ (6a)	300	83	3.53	1.31	47
$2.6-Me_2C_6H_3$ (6a)	360	90	3.74	1.42	48

<sup>*a*</sup> Conditions: Al (40  $\mu$ mol), PhCH<sub>2</sub>OH (40  $\mu$ mol), CL (10.0 mmol) (CL/Al = 250), toluene, [CL]<sub>0</sub> = 1.0 mmol/mL, 50 °C. <sup>*b*</sup> Estimated by <sup>1</sup>H NMR spectra. <sup>*c*</sup> By GPC in THF vs polystyrene standards. <sup>*d*</sup> Estimated number of polymer chains ( $\mu$ mol) = mass of CL reacted (mg) based on conversion/{ $M_{n(GPC)} \times 0.56$ }.<sup>12</sup>



**Figure 3.**  $M_n$  and  $M_w/M_n$  vs monomer conversion in the ringopening polymerization of  $\varepsilon$ -caprolactone initiated by R<sup>1</sup>(R<sup>2</sup>)Al[O-2-'Bu-6-{(C<sub>6</sub>F<sub>5</sub>)N=CH}C<sub>6</sub>H<sub>4</sub>] [R<sup>1</sup>, R<sup>2</sup> = Me, Me (**1a**;  $\blacklozenge$ ,  $\diamondsuit$ ); Et, Et (**1b**;  $\blacklozenge$ ,  $\bigcirc$ ); Me, Cl (**1c**;  $\blacksquare$ ,  $\Box$ )]-PhCH<sub>2</sub>OH catalyst systems. The detailed conditions are summarized in Table 3.

the ROP of CL in terms of the activity as seen in the ROP by **1a** reported previously.<sup>4</sup> The PDI values  $(M_w/M_n)$  of **1c** were somewhat lower than those of **1a,b**. As shown in Figure 3, linear relationships between the monomer conversions and  $M_n$  values were observed in these ROPs consistently with narrow molecular weight distributions, and no significant differences were observed in the *N* values [number of polymer chains estimated by the  $M_{n(GPC)}$  values and the conversions] during the time course.<sup>13</sup> These results thus clearly indicate that these ROPs by **1b,c** proceeded in a living manner as demonstrated by **1a**.<sup>4</sup>

<sup>(9) (</sup>a) Syntheses of various salicylaldimine ligands: Fujita, T.; Tohi, Y.; Mitani, M. European Patent EP 0874005A1, 1998. (b) Use of this ligand for synthesis of group 4 transition-metal complexes for highly active olefin polymerization catalysts was also reported by the same authors (Fujita, T.; Mitani, M.; et al.), as introduced previously.<sup>3</sup>

<sup>(10)</sup> The detailed structural results including the CIF file are shown in the Supporting Information.



**Figure 4.** log[[CL]/[CL]<sub>0</sub>] vs time in the ring-opening polymerization of  $\varepsilon$ -caprolactone initiated by R<sup>1</sup>(R<sup>2</sup>)Al[O-2-'Bu-6-{(C<sub>6</sub>F<sub>5</sub>)N=CH}C<sub>6</sub>H<sub>4</sub>] [R<sup>1</sup>, R<sup>2</sup> = Me, Me (**1a**;  $\diamond$ ); Et, Et (**1b**;  $\bigcirc$ ); Me, Cl (**1c**;  $\Box$ )]-PhCH<sub>2</sub>OH catalyst systems.

As shown in Figure 4, the propagation rates in the ROPs by 1a-c were first-order-dependent upon the monomer concentration, suggesting that the ROPs proceeded without catalyst deactivation. The observed rates  $(k_{obsd})$  by 1a-c seemed to be close  $(k_{obsd} =$  $(2.4-2.8) \times 10^{-2} \text{ min}^{-1}$ , Table 4); however, the estimated N value of 1a was lower than those of 1b,c, due to their different catalyst efficiencies.<sup>13</sup> Therefore, the actual k value (propagation rate constant) of **1a** should be higher than those of **1b**,**c** (Table 4). We assume that the observed difference between 1a and 1c would probably be due to a different electronic nature of the propagating Al species between Me and Cl, and the methyl group in 1c would be reacted with PhCH<sub>2</sub>OH to generate the initiating species. We also speculate that the observed difference between the methyl (1a) and ethyl (1b) analogues would be due to the steric bulk around the propagating Al center, as seen in the unique Al-C bond angle in both Figure 1 and Table 1, although we do not have any clear evidence to explain this speculation.

It also turned out that the catalytic activity in the ROPs of CL using a series of Al complexes containing phenoxyimine ligands (with different fluorinated aromatic substituents in the imino group), Me<sub>2</sub>Al[O-2-'Bu-6-(ArN=CH)C<sub>6</sub>H<sub>3</sub>], increased in the order Ar = C<sub>6</sub>F<sub>5</sub> (**1a**)  $\gg$  Ar = 2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**2a**) > Ar = 2,4-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**3a**) > Ar = 3,4-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**4a**) > Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**6a**) > Ar = C<sub>6</sub>H<sub>5</sub> (**5a**) (Table 5). The results clearly indicate that substitution of the *ortho*-position, especially the fluorine substituent, strongly affects the catalytic activity. As described above, the ROP by the C<sub>6</sub>F<sub>5</sub> analogue (**1a**) proceeded in a living manner; a linear relationship between the monomer conversions and the  $M_n$  values consistently with low  $M_w/M_n$  values was observed (Figure 5, plotted as  $\blacklozenge,\diamondsuit$ ).

In contrast, as shown in Figure 5 (right), the molecular weight distributions ( $M_w/M_n$  values) in the resultant polymers prepared by the C<sub>6</sub>H<sub>5</sub> analogue (**5a**, plotted as  $\Box$ ) became broad after certain

monomer conversions [e.g.,  $M_w/M_n = 1.16$  (conversion 31%), 1.78 (conversion 82%), 1.98 (conversion 91%), Table 5], and an increase in the N value (number of polymer chains) was also seen at high CL conversion. The results strongly suggest that a certain degree of transesterification (shown in Scheme 1)<sup>8</sup> accompanied the propagation in the ROP of CL. Similarly, increases in both the  $M_{\rm w}/M_{\rm n}$  and the N values at high monomer conversion were observed in the ROPs of CL using the above Al complexes (2a-6a, Figure 5), whereas no significant changes in both the  $M_w/$  $M_{\rm n}$  and the N values were seen in the ROP using the C<sub>6</sub>F<sub>5</sub> analogue (1a). The results also suggest that a certain degree of transesterification would be present in the ROPs under these conditions, although the degree of the transesterification seemed to decrease in the presence of an ortho-substituent [5a (C<sub>6</sub>H<sub>5</sub>) vs 6a (2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), **5a** (C<sub>6</sub>H<sub>5</sub>) vs **2a** (2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), **3a** (2,4-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) vs **4a**  $(3,4-F_2C_6H_3)$ , Table 5]. We thus assume that the presence of a rather strong electron-withdrawing group (C<sub>6</sub>F<sub>5</sub>) would be required to prohibit the transesterification from accompanying the propagation in the ROP, probably by a weak H-F interaction as well as better stabilization of the propagating species.<sup>14,15</sup> Taking into account these results, use of the C<sub>6</sub>F<sub>5</sub> substituent in the imino group is thus essential in terms of both the catalytic activity and the ROP proceeding in the living manner.

### **Concluding Remarks**

A series of Al complexes containing phenoxyimine ligands of the types  $R^{1}(R^{2})AI[O-2^{-t}Bu-6-\{(C_{6}F_{5})N=CH\}C_{6}H_{3}]$  [R<sup>1</sup>, R<sup>2</sup> = Et, Et (1b); Me, Cl (1c)] and Me<sub>2</sub>Al[O-2- $^{t}$ Bu-6-(ArN= CH)C<sub>6</sub>H<sub>3</sub>] [Ar = 2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**2a**), 2,4-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**3a**), 3,4-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (4a)] have been prepared and identified on the basis of NMR spectra and elemental analyses, and their structures were determined by X-ray crystallography. The ROPs of CL using 1a-c in the presence of PhCH<sub>2</sub>OH proceeded efficiently in a living manner, and the propagation rates were affected by the anionic donor ligand employed (Me, Et, or Cl). The catalytic activity using 1a-6a [Ar = C<sub>6</sub>H<sub>5</sub> (5a), 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (6a)]-PhCH<sub>2</sub>OH catalyst systems was highly affected by the aromatic substituent in the imino group, and fluorinated substituents especially in the *ortho*-position affected the catalytic activity. The ROPs using  $2a-6a-PhCH_2OH$  catalyst systems were accompanied by a certain degree of side reactions such as transesterification, whereas the living polymerization systems can be accomplished using the  $C_6F_5$  analogues (1a-c). Although we could not find a more efficient catalyst than 1a reported previously,<sup>4</sup> these results clearly indicate that the  $C_6F_5$  substituent in the imino group plays an essential key role in the ROP of CL in terms of both the catalytic activity and the ROP proceeding in a living manner.



**Figure 5.**  $M_n$  and  $M_w/M_n$  vs monomer conversion in the ring-opening polymerization of  $\varepsilon$ -caprolactone initiated by Me<sub>2</sub>Al[O-2-'Bu-6-(ArN=CH)C<sub>6</sub>H<sub>4</sub>]-PhCH<sub>2</sub>OH catalyst systems: (left) Ar = C<sub>6</sub>F<sub>5</sub> (1a), 2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (2a), 2,4-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (3a), 3,4-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (4a); (right) Ar = C<sub>6</sub>F<sub>5</sub> (1a), C<sub>6</sub>H<sub>5</sub> (5a), 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (6a). The detailed conditions are summarized in Table 5.

Table 6. Crystal Data and Structure Refinement Parameters for Et <sub>2</sub> Al[O-2-'Bu-6-{(C <sub>6</sub> F <sub>5</sub> )N=CH}C <sub>6</sub> H <sub>3</sub> ] (1b),	
Me(Cl)Al[O-2-'Bu-6-{(C <sub>6</sub> F <sub>5</sub> )N=CH}C <sub>6</sub> H <sub>3</sub> ] (1c), and Me <sub>2</sub> Al[O-2-'Bu-6-(ArN=CH)C <sub>6</sub> H <sub>3</sub> ] [Ar = 2,6-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (2a), 2,4-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (3a), 3,4-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (4a), 2,4-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (4a), 2,4-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (4a), 3,4-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	$[a]^a$

	1b	1c	2a	3a	4a
empirical formula	C <sub>21</sub> H <sub>23</sub> AlF <sub>5</sub> NO	C <sub>18</sub> H <sub>16</sub> AlClF <sub>5</sub> NO	C <sub>19</sub> H <sub>22</sub> AlF <sub>2</sub> NO	C <sub>19</sub> H <sub>22</sub> AlF <sub>2</sub> NO	C19H22AlF2NO
fw	427.39	419.76	345.37	345.37	345.37
cryst color, habit	yellow, block	colorless, block	colorless, block	colorless, block	yellow, block
cryst size (mm)	$0.62 \times 0.44 \times 0.24$	$0.32 \times 0.20 \times 0.15$	$0.22 \times 0.20 \times 0.18$	$0.54 \times 0.42 \times 0.35$	$0.30 \times 0.18 \times 0.15$
cryst syst	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	<i>C</i> 2/ <i>c</i> (No. 15)	$P2_1/a$ (No. 14)	<i>P</i> 1 (No. 2)	<i>P</i> 1 (No. 2)	$P2_1/c$ (No. 14)
a (Å)	32.263(3)	12.4278(6)	7.5473(4)	7.7061(4)	7.0439(3)
b (Å)	7.9795(5)	12.3734(6)	9.8452(7)	9.7853(6)	20.8564(11)
<i>c</i> (Å)	20.2578(16)	12.7793(7)	12.7096(7)	12.7343(8)	26.5114(13)
$\beta$ (deg)	124.982(2)	91.7271(17)	74.8131(14)	105.4480(18)	93.2474(13)
$V(Å^3)$	4272.9(6)	1964.24(17)	906.84(9)	915.65(10)	3888.5(3)
Ζ	8	4	2	2	8
$D_{\text{calcd}}$ (g/cm <sup>3</sup> )	1.329	1.419	1.265	1.253	1.180
$F_{000}$	1776.00	856.00	364.00	364.00	1456.00
no. of reflns measd	19796	19089	9121	9074	31362
no. of observations	2862	3467	3214	3460	3306
no. of variables	285	260	239	239	485
R1	0.0554	0.0319	0.0433	0.0681	0.0456
wR2	0.0921	0.0948	0.1619	0.2190	0.1167
goodness of fit	1.004	1.007	1.000	1.000	1.006

<sup>*a*</sup> Detailed conditions are shown in the Supporting Information.<sup>10</sup>

On the basis of simple PM3 calculations for energy evaluations for stabilization in the model propagating species (R<sup>2</sup>)Al[O-2-'Bu-6-(ArN=CH)C<sub>6</sub>H<sub>3</sub>][O(CH<sub>2</sub>)<sub>5</sub>C(O)OMe] [R<sup>2</sup> = Me and Ar = Ph, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2,4-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 3,4-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>; R<sup>2</sup> = Me, Et, Cl and Ar = C<sub>6</sub>F<sub>5</sub>], after geometry optimization, an introduction of fluorine into the aryl group (Ar) drastically increases the stability of the catalytically active species; the C<sub>6</sub>F<sub>5</sub> analogue was the most suited among these aryl substituents.<sup>14</sup>Moreover, weak H–F interactions were observed when C<sub>6</sub>F<sub>5</sub> and 2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub> were used as the aryl substituent, which would form a favored geometry for subsequent CL coordination and insertion (without coordination of CL from the other site forming a dormant species).<sup>14,15</sup> Although more precise calculations are necessary, we would assume that

(13) On the basis of the results for estimation of the number of polymer chains (*N* value), *N* values by **1b**,**c** were slightly larger than the Al complex charged. We assume that this would be due to the accuracy of the  $M_n$  values corrected, because the corrected  $M_n$  values used for the estimation were based on the  $M_n$  value measured by GPC in THF vs polystyrene standards. Since the number of polymer chains (*N* values) did not change during the time course, we assume that the ROPs by **1b**,**c** proceeded with quantitative initiation efficiencies. The catalyst efficiency by **1a** estimated on the basis of the *N* value by **1c** is 72%, and the value is relatively close to that estimated previously by <sup>1</sup>H NMR spectra (68%).<sup>4b,c</sup>

this fact should provide appropriate explanations of why the  $C_6F_5$  analogue is the most suited in terms of both the activity and efficiency. We believe that the results obtained here should be highly promising for designing more efficient catalysts of living ROP of cyclic esters.

#### **Experimental Section**

General Procedures. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques. Anhydrous-grade n-hexane and toluene (Kanto Kagaku Co., Ltd.) were transferred into a bottle containing molecular sieves (a mixture of 3A 1/16, 4A 1/8, and 13X 1/16) in the drybox under a N<sub>2</sub> stream and were passed through a short alumina column under a N2 stream before use. All chemicals used were of reagent grade and were purified by the standard purification procedures. Reagent-grade AlMe3, AlEt3, and Me2AlCl in n-hexane (Kanto Kagaku Co. Ltd.) were stored in the drybox and were used as received. Various salicylaldimines (iminophenols) containing different substituents on the imino groups, 2-'Bu-6- $(RN=CH)C_6H_3OH [R = Ph, 2,6-Me_2C_6H_3, C_6F_5, 2,6-F_2C_6H_3, 2,4-$ F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 3,4-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>] were prepared according to the reported procedures.<sup>9</sup> Syntheses of Al complexes (1, 5, 6a) were as described in our previous papers.<sup>4a,b</sup> Elemental analyses were performed by using a PE2400II series (Perkin-Elmer Co.) instrument. All <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz for <sup>1</sup>H, 100.40 MHz for <sup>13</sup>C). All spectra were obtained in the solvent indicated at 25 °C unless otherwise noted, and their chemical shifts are given in parts per million and are referenced to SiMe<sub>4</sub> ( $\delta$  0.00, <sup>1</sup>H, <sup>13</sup>C). The molecular weights and molecular weight distributions of the resultant polymers were measured by GPC. GPC was performed at 40 °C on a Shimadzu SCL-10A using an RID-10A detector (Shimadzu Co. Ltd.) in THF (containing 0.03 wt % 2,6-di-tert-butyl-p-cresol, flow rate 1.0 mL/ min). GPC columns (ShimPAC GPC-806,- 804, and -802, 30 cm  $\times$  8.0 mm Ø, spherical porous gel made of styrene/divinylbenzene copolymer, ranging from MW <  $10^2$  to MW = 2 ×  $10^7$ ) were calibrated versus polystyrene standard samples.

Synthesis of 2-'Bu-6-{(2,4-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)N=CH}C<sub>6</sub>H<sub>3</sub>OH. A mixture of 2,4-difluoroaniline (1.42 g, 11.0 mmol), 3-*tert*-butyl-2-hydroxybenzaldehyde (1.78 g, 10.0 mmol), and *p*-toluenesulfonic acid (3 mg, 17  $\mu$ mol) in toluene (25 mL) was refluxed for 17 h. Removal of the solvent from the reaction mixture by a rotary evaporator in vacuo gave a dark yellow oil, and purification by silica gel column chromatography using *n*-hexane afforded a yellow oil (2.87 g, 99%)

<sup>(11)</sup> Attempted reaction of Me<sub>2</sub>Al[O-2-'Bu-6-{(C<sub>6</sub>F<sub>5</sub>)N=CH}C<sub>6</sub>H<sub>3</sub>] with 1.0 equiv of PhCH<sub>2</sub>OH in C<sub>6</sub>D<sub>6</sub> and Me<sub>2</sub>Al(OCH<sub>2</sub>Ph) with 2-'Bu-6-{(C<sub>6</sub>F<sub>5</sub>)N=CH}C<sub>6</sub>H<sub>3</sub>OH in C<sub>6</sub>D<sub>6</sub> afforded a mixture of products including [Me<sub>2</sub>Al( $\mu_2$ -OCH<sub>2</sub>Ph)]<sub>2</sub>[Al{O-2-'Bu-6-{(C<sub>6</sub>F<sub>5</sub>)N=CH}C<sub>6</sub>H<sub>3</sub>] ( $\mu_2$ -OCH<sub>2</sub>Ph)<sub>2</sub>] (7) determined by X-ray crystallography. On the basis of the above reaction results and the fact that the living polymerization was initiated by the AlOCH<sub>2</sub>Ph species (by the chain end analysis), it is thus clear that both PhCH<sub>2</sub>OH and CL should be required to generate the assumed initiating species from Me<sub>2</sub>Al[O-2-'Bu-6-{(C<sub>6</sub>F<sub>5</sub>)N=CH}C<sub>6</sub>H<sub>3</sub>]. Details on attempted experiments including isolation and analysis results for 7 are shown in the Supporting Information.

<sup>(12)</sup> We estimated conversions of CL by <sup>1</sup>H NMR spectra, and most of the spectra are shown in the Supporting Information. Moreover, the exact  $M_n$  values for ring-opened poly(CL)s were corrected from the  $M_n$  values by GPC vs polystyrene standards according to the equation  $M_n(PCL) =$  $0.56M_n(GPC vs polystyrene standards)$  according to the following reference: (a) Save, M.; Schappacher, M.; Soum, A. *Macromol. Chem. Phys.* **2002**, *203*, 889. (b) Duda, A.; Kowalski, A.; Penczek, S. *Macromolecules* **1998**, *31*, 2114. We did not estimate the  $M_n$  values from the <sup>1</sup>H NMR spectra, because the spectra were a mixture of the reaction products [CL, poly(CL), toluene, etc.] and seemed to be lacking accuracy. As demonstrated previously,<sup>4</sup> PhCH<sub>2</sub>OH (1.0 equiv relative to Al) was prerequisite for generating the aluminum alkoxide (as proposed initiating species for the ROP), and the polymerization did not take place in the absence of PhCH<sub>2</sub>OH. Addition of more than 1 equiv of PhCH<sub>2</sub>OH will afford a mixture of mono- and bisalkoxide, and this is not suited for the precise control in this catalysis.

yield). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.58 (s, 9H, 'Bu), 6.30–6.48 (m, 3H, aromatic), 6.77 (t, 1H, J = 8 Hz, aromatic), 6.88 (d, 1H, J = 7 Hz, aromatic), 7.36 (d, 1H, J = 7 Hz, aromatic), 7.95 (s, 1H, CH=N), 14.01 (s, 1H, OH). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  29.6, 35.2, 104.8 (dd,  $J_1 = 3$  Hz,  $J_2 = 2$  Hz), 111.5 (dd,  $J_1 = 22$  Hz,  $J_2 = 4$  Hz), 118.7, 119.3, 121.9 (dd,  $J_1 = 10$  Hz,  $J_2 = 2$  Hz), 131.2, 132.9 (dd,  $J_1 = 11$  Hz,  $J_2 = 4$  Hz), 138.1, 156.0 (dd,  $J_1 = 252$  Hz,  $J_2 = 12$  Hz), 161.2 (dd,  $J_1 = 247$  Hz,  $J_2 = 11$  Hz), 161.3, 165.0. Anal. Calcd for C<sub>17</sub>H<sub>17</sub>F<sub>2</sub>NO: C, 70.58; H, 5.92; N, 4.84. Found: C, 70.20; H, 6.10; N, 4.80.

**Synthesis of 2-'Bu-6-{(3,4-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)N=CH}C<sub>6</sub>H<sub>3</sub>OH.** A mixture of 3,4-difluoroaniline (1.42 g, 11.0 mmol), 3-*tert*-butyl-2-hydroxybenzaldehyde (1.78 g, 10.0 mmol), and *p*-toluenesulfonic acid (3 mg, 17  $\mu$ mol) in toluene (25 mL) was refluxed for 18 h. The solution was then concentrated in vacuo, and purification by silica gel column chromatography using *n*-hexane afforded a yellow oil (2.81 g, 97% yield). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.61 (s, 9H, 'Bu), 6.23–6.60 (m, 3H, aromatic), 6.79 (t, 1H, J = 8 Hz, aromatic), 6.89 (d, 1H, J = 7 Hz, aromatic), 7.37 (d, 1H, J = 7 Hz, aromatic), 7.75 (s, 1H, *CH*=N), 13.79 (s, 1H, OH). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  29.6, 35.2, 110.1 (d, J = 190 Hz), 117.5 (d, J = 18 Hz), 117.8 (dd,  $J_1 = 5$  Hz,  $J_2 = 3$  Hz), 118.8, 119.1, 131.1, 131.2, 145.0 (dd,  $J_1 = 6$  Hz,  $J_2 = 3$  Hz), 149.4 (dd,  $J_1 = 246$  Hz,  $J_2 = 13$  Hz), 150.8 (dd,  $J_1 = 248$  Hz,  $J_2 = 14$  Hz), 161.0, 164.0. Anal. Calcd for C<sub>17</sub>H<sub>17</sub>F<sub>2</sub>NO: C, 70.58; H, 5.92; N, 4.84. Found: C, 70.81.; H, 6.27; N, 4.73.

Synthesis of  $Et_2Al[O-2-^tBu-6-\{(C_6F_5)N=CH\}C_6H_3]$  (1b). To a stirred solution containing 2-'Bu-6-{(C<sub>6</sub>F<sub>5</sub>)N=CH}C<sub>6</sub>H<sub>3</sub>OH (1.37 g, 4.00 mmol) in n-hexane (5.0 mL) was added AlEt<sub>3</sub> (0.90 M n-hexane solution, 4.67 mL, 4.20 mmol of Al) dropwise over a 10 min period at -20 °C. The solution was allowed to warm to room temperature slowly and was stirred for 3 h. The mixture was then concentrated in vacuo, and the chilled solution (-20 °C) afforded yellow microcrystals of **1b** (1.26 g, 74% yield). <sup>1</sup>H NMR ( $C_6D_6$ ): δ 0.33 (s, 4H, AlCH2CH3), 1.36 (s, 6H, AlCH2CH3), 1.49 (s, 9H,'Bu), 6.52 (br, 1H, aromatic), 6.64 (br, 1H, aromatic), 7.33 (s, 1H, CH=N), 7.40 (br, 1H, aromatic). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.3, 9.1, 29.3, 35.3, 118.0, 119.3, 121.6-121.9 (m), 134.7, 136.7-137.0 (m), 137.3, 138.8-139.5 (m), 140.4-140.6 (m), 141.4-141.7 (m), 142.3, 143.0-143.1 (m), 167.0, 177.3. Anal. Calcd for C<sub>21</sub>H<sub>23</sub>F<sub>5</sub>AlNO: C, 59.02; H, 5.42; N, 3.28. Found: C, 58.71; H, 5.18; N, 3.12.

Synthesis of Me(Cl)Al[O-2-<sup>t</sup>Bu-6-{(C<sub>6</sub>F<sub>5</sub>)N=CH}C<sub>6</sub>H<sub>3</sub>] (1c). To a stirred solution containing  $2^{-t}Bu-6-\{(C_6F_5)N=CH\}C_6H_3OH$ (0.87 g, 3.00 mmol) in a mixture of *n*-hexane (10.0 mL) and toluene (4 mL) was added Me<sub>2</sub>AlCl (0.46 M *n*-hexane solution, 6.90 mL, 3.15 mmol of Al) dropwise over a 10 min period at -20 °C. The solution was allowed to warm to room temperature and was stirred for 3 h (Scheme 2). The mixture was then concentrated in vacuo, and the chilled solution (-20 °C) afforded colorless microcrystals of 1c (939 mg, 78% yield). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  -0.06 (t, J = 2Hz, 3H, Me), 1.44 (s, 9H, <sup>t</sup>Bu), 6.52 (t, J = 8 Hz, 3H, aromatic), 6.60 (dd,  $J_1 = 8$  Hz,  $J_2 = 2$  Hz, aromatic), 7.26 (s, 1H, N=CH), 7.39 (dd,  $J_1 = 7$  Hz,  $J_2 = 2$  Hz, 1H, aromatic). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  -11.1, 29.3, 35.3, 119.2, 119.2, 120.1-120.5 (m), 134.9, 136.6-137.0 (m), 138.1, 139.1-139.5 (m), 140.5-140.7 (m), 141.9-142.1 (m), 142.5, 142.9-143.2 (m), 165.4, 177.91. Anal. Calcd for C<sub>18</sub>H<sub>16</sub>F<sub>5</sub>AlClNO: C, 51.50; H, 3.84; N, 3.34. Found: C, 51.38; H, 3.79; N, 3.23.

Synthesis of Me<sub>2</sub>Al[O-2-'Bu-6-{(2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)N=CH}C<sub>6</sub>H<sub>3</sub>] (2a). To a stirred solution containing 2-'Bu-6-{(2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) N=CH}C<sub>6</sub>H<sub>3</sub>OH (0.87 g, 3.00 mmol) in *n*-hexane (7.5 mL) was added AlMe<sub>3</sub> (0.47 M *n*-hexane solution, 6.67 mL, 3.15 mmol of Al) dropwise over a 10 min period at -20 °C. The solution was allowed to warm to room temperature and was stirred for 3 h (Scheme 2). The mixture was then concentrated in vacuo, and the resultant solid was dissolved in a minimum amount of toluene. The chilled solution (-20 °C) afforded colorless microcrystals of 2a (878 mg, 85% yield). <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  -0.21 (t, J = 1 Hz, 6H, Al $Me_2$ ), 1.49 (s, 9H, 'Bu), 6.38–6.49 (m, 3H, aromatic), 6.53 (t, J = 8 Hz, 1H, aromatic), 6.59 (dd,  $J_1 = 8$  Hz,  $J_2 = 2$  Hz, 1H, aromatic), 7.37 (m, 2H, aromatic, CH=N). <sup>13</sup>C NMR ( $C_6D_6$ ):  $\delta$  -10.0, 29.4, 35.3, 112.1–112.3 (m), 117.5, 119.6, 124.1 (t, J = 2 Hz), 134.5, 136.0, 142.0, 156.5 (dd,  $J_1 = 250$  Hz,  $J_2 = 4$  Hz), 165.8, 176.1–176.2 (m). Anal. Calcd for C<sub>19</sub>H<sub>22</sub>AlNO: C, 66.08; H, 6.42; N, 4.06. Found: C, 66.06; H, 6.12; N, 4.04.

Synthesis of Me<sub>2</sub>Al[O-2-<sup>t</sup>Bu-6-{ $(2,4-F_2C_6H_3)N=CH$ }C<sub>6</sub>H<sub>3</sub>] (3a). To a stirred solution containing  $2^{-1}Bu-6-\{(2,4-F_2C_6H_3)\}$  $N=CHC_6H_3OH$  (1.16 g, 4.00 mmol) in *n*-hexane (10.0 mL) was added AlMe<sub>3</sub> (0.43 M n-hexane solution, 9.67 mL, 4.20 mmol of Al) dropwise over a 10 min period at -20 °C. The solution was allowed to warm to room temperature and was stirred for 3 h (Scheme 2). The mixture was then concentrated in vacuo, and the chilled solution (-20 °C) afforded colorless microcrystals of 3a (1.28 g, 93% yield). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  -0.26 (s, 6H, AlMe<sub>2</sub>), 1.52 (s, 9H, 'Bu), 6.26-6.36 (m, 2H, aromatic), 6.50-6.64 (m, 3H, aromatic), 7.34 (s, 1H, CH=N), 7.40 (d, J = 7 Hz, 1H, aromatic). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  -9.6, 29.4, 35.3, 105.3 (t, J = 25Hz), 111.9 (dd,  $J_1 = 22$  Hz,  $J_2 = 3$  Hz), 117.6, 119.7, 126.0 (d, J = 10 Hz), 130.9 (dd,  $J_1$  = 11 Hz,  $J_2$  = 3 Hz), 134.3, 135.7, 141.9, 155.5 (dd,  $J_1 = 251$  Hz,  $J_2 = 12$  Hz), 161.6 (dd,  $J_1 = 248$  Hz,  $J_2$ = 11 Hz), 165.3, 173.5. Anal. Calcd for  $C_{19}H_{22}F_2AINO$ : C, 66.08; H, 6.42; N, 4.06. Found: C, 66.16; H, 6.54; N, 4.08.

Synthesis of Me<sub>2</sub>Al[O-2-<sup>t</sup>Bu-6-{ $(3,4-F_2C_6H_3)N=CH$ }C<sub>6</sub>H<sub>3</sub>] (4a). To a stirred solution containing  $2^{-1}Bu-6-\{(3,4-F_2C_6H_3)\}$  $N=CHC_6H_3OH$  (1.16 g, 4.00 mmol) in *n*-hexane (10.0 mL) was added AlMe<sub>3</sub> (1.09 M n-hexane solution, 4.67 mL, 4.20 mmol of Al) dropwise over a 10 min period at -20 °C. The solution was allowed to warm to room temperature and was stirred for 3 h (Scheme 2). The mixture was then concentrated in vacuo, and the chilled solution (-20 °C) afforded colorless microcrystals of 4a (1.12 g, 87% yield). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  -0.28 (s, 6H, AlMe<sub>2</sub>), 1.53 (s, 9H, 'Bu), 6.40–6.46 (m, 3H, aromatic), 6.61 (t, J = 8 Hz, 1H, aromatic), 6.66 (dd,  $J_1 = 8$  Hz,  $J_2 = 2$  Hz, 1H, aromatic), 7.19 (s, 1H, CH=N), 7.42 (dd,  $J_1 = 7$  Hz,  $J_2 = 2$  Hz, 1H, aromatic). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  -8.9, 29.4, 35.3, 117.59, 118.12 (dd,  $J_1$  = 18 Hz,  $J_2 = 2$  Hz), 118.74 (dd,  $J_1 = 6$  Hz,  $J_2 = 3$  Hz), 119.74, 134.24, 135.56, 141.84, 143.19 (dd,  $J_1 = 7$  Hz,  $J_2 = 4$  Hz), 149.90 (dd,  $J_1$ = 249 Hz,  $J_2$  = 13 Hz), 150.78 (dd,  $J_1$  = 250 Hz,  $J_2$  = 14 Hz), 164.89, 170.72. Anal. Calcd for C<sub>19</sub>H<sub>22</sub>F<sub>2</sub>AlNO: C, 66.08; H, 6.42; N, 4.06. Found: C, 66.28; H, 6.59; N, 4.03.

**ROP of CL.** Typical polymerization procedures (Table 3) are as follows. To a sealed Schlenk tube containing a toluene solution of **1a** (40  $\mu$ mol/0.100 mL of toluene) was added PhCH<sub>2</sub>OH (0.040 mmol/0.096 mL of toluene) in the drybox at room temperature. The solution was stirred for 10 min, and then toluene (8.76 mL) and  $\varepsilon$ -caprolactone (5.0 mmol) were added. The reaction mixture was then placed into an oil bath preheated at 50 °C, and the solution was stirred for the prescribed time (15 min). A small amount of the reaction mixture was partly taken out from the mixture for a certain period to monitor the reaction, especially to analyze the

<sup>(14)</sup> The results for geometry optimizations for proposed catalytically active species ( $R^2$ )Al[O-2-<sup>*t*</sup>Bu-6-(ArN=CH)C<sub>6</sub>H<sub>3</sub>][O(CH<sub>2</sub>)<sub>5</sub>C(O)OMe] [ $R^2$  = Me and Ar = Ph, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2,4-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, C<sub>6</sub>F<sub>5</sub>;  $R^2$  = Me, Et, Cl and Ar = C<sub>6</sub>F<sub>5</sub>] and energy evaluations [equilibrium geometry at the ground state with semiempirical PM3, geometry optimization, RHF/ PM3D Spartan '06 for Windows (Wavefunction Inc.)] are shown in the Supporting Information. Geometry optimizations (for confirmation of the results in PM3 calculations) were also explored with the DFT B3LYP/6-31G\* method (initial PM3 data). These results are shown in the Supporting Information.

<sup>(15)</sup> Previous report which introduces that weak H–F interaction in the  $C_6F_5$  group plays a role in the living polymerization of ethylene: Mitani, M.; Mohri, J.; Yoshida, Y.; Saito, J.; Ishii, S.; Tsuru, K.; Matsui, S.; Furuyama, R.; Nakano, T.; Tanaka, H.; Kojoh, S.; Matsugi, T.; Kashiwa, N; Fujita, T. J. Am. Chem. Soc. **2002**, 124, 3327.

# ROP by Al Complexes with Phenoxyimine Ligands

monomer conversion [by <sup>1</sup>H NMR (400 MHz)] and  $M_n$  and  $M_w/M_n$  (by GPC).

**Crystallographic Analysis.** All measurements were made on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphitemonochromated Mo K $\alpha$  radiation. The selected crystal collection parameters are summarized in Table 6, and the detailed results are described in the Supporting Information.<sup>10</sup> All structures were solved by direct methods and expanded using Fourier techniques,<sup>16</sup> and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations for complexes **1b,c** and and **2a–4a** were performed using the Crystal Structure<sup>17,18</sup> crystallographic software package. Acknowledgment. N.I. and K.N. express their thanks to Daiso Co., Ltd. for support, and J.L. thanks the JSPS (Japan Society for the Promotion of Science) for a postdoctoral fellowship (Grant P05397).

**Supporting Information Available:** Text giving (i) detailed polymerization results including <sup>1</sup>H NMR spectra in the ringopening polymerization of CL by **1a**–**c** and **2a**–**6a** in the presence of PhCH<sub>2</sub>OH, (ii) attempted reaction of Me<sub>2</sub>Al[O-2-'Bu-6-{(C<sub>6</sub>F<sub>5</sub>)N=CH}C<sub>6</sub>H<sub>3</sub>] with 1.0 equiv of PhCH<sub>2</sub>OH in C<sub>6</sub>D<sub>6</sub> and Me<sub>2</sub>Al(OCH<sub>2</sub>Ph) with HO-2-'Bu-6-{(C<sub>6</sub>F<sub>5</sub>)N=CH}C<sub>6</sub>H<sub>3</sub> in C<sub>6</sub>D<sub>6</sub> including the structure of [Me<sub>2</sub>Al( $\mu_2$ -OCH<sub>2</sub>Ph)]<sub>2</sub>[Al{O-2-'Bu-6-{(C<sub>6</sub>F<sub>5</sub>)N=CH}C<sub>6</sub>H<sub>3</sub>}( $\mu_2$ -OCH<sub>2</sub>Ph)<sub>2</sub>] (7), (iii) results for geometry optimizations for proposed catalytically active species and energy evaluations (by PM3 and DFT), and (iv) CIF files and structure reports for **1b,c**, **2a**–**4a**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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<sup>(16)</sup> Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Delder, R.; Israel, R.; Smits, J. M. M. *The DIRDIF94 Program System*; Technical Report of Crystallography Laboratory; University of Nijmegen: Nijmegen, The Netherlands, 1994.

<sup>(17)</sup> Crystal Structure 3.6.0: Crystal Structure Analysis Package; Rigaku and Rigaku/MSC: The Woodlands, TX, 2000–2004.

<sup>(18)</sup> Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS Issue 10*; Chemical Crystallography Laboratory: Oxford, U.K., 1996.