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ARTICLE

Synthesis and Characterization of Neutral and Cationic Aluminum Complexes Supported by Furfuryl-Containing Aminophenolate Ligand for Ring-Opening Polymerization of ε-Caprolactone

Jiraya Kiriratnikom,[a] Sucheewin Chotchatchawankul,[b] Setsiri Hesuwannakij,[b] Supavadee Kiatisevi [a] and Khamphee Phomphrai *[b]

The synthesis, structural characterization and reactivity of aluminum complexes supported by a novel tetradentate aminophenolate ligand containing furfuryl groups (LH), LAlMe$_2$ (**1**), LAlMeCl (**2**) and LAlMeO^{t}Bu (**3**) are described. The molecular structures of ligand LH and complexes **1**-**3** are determined by X-ray structural analysis. Complexes **1**-**3** contain four-coordinated mononuclear aluminum center. Activation of complex **1** with either B(C_6F_5)$_3$ or [Ph_3C][B(C_6F_5)$_4$] afforded the corresponding cationic complexes, [LAlMe][MeB(C_6F_5)$_3$] and [LAlMe][B(C_6F_5)$_4$], respectively. All cationic complexes were stable at room temperature in the absence of external Lewis base over a week. The cationic complex [LAlMe][MeB(C_6F_5)$_3$] decomposed upon heating at 70°C giving a neutral LAlMe(C_6F_5) complex. Complexes **1**-**3** were inactive for the ring-opening polymerization (ROP) of ε-caprolactone (CL) at room temperature. However, only cationic aluminum complex, [LAlMe][MeB(C_6F_5)$_3$], in the presence of benzyl alcohol was found to be active in the ROP of CL at room temperature in a well-behave manner giving a first-order reaction with respect to [CL].

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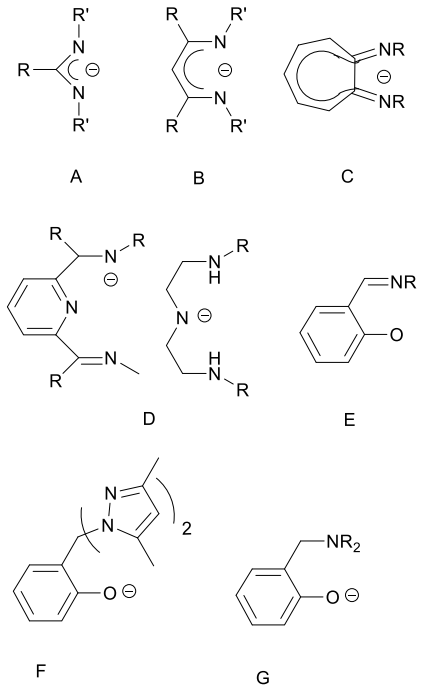
Introduction

Cationic aluminum complexes have been developed over the past decade as a catalysts for the polymerization reactions[1-10], particularly for olefin polymerization.[3, 11-14] The complexes have gained interests due to an electropositive charge on the aluminum center that enhances the Lewis acidity of the metal compared to the neutral analogues. The enhanced Lewis acidity of the complexes is anticipated to have greater catalytic activity making them suitable to be used as catalysts.[1, 11, 15-17] One of the typical methods to synthesize cationic aluminum complexes is via alkyl abstraction of neutral dialkyl aluminum precursors by a cationic activator[18, 19] such as B(C_6F_5)$_3$ or [Ph_3C][B(C_6F_5)$_4$].

Numerous ligand classes have been reported for supporting cationic aluminum complexes including *N,N*- or *N,O* based bi- and tri-dentate ligands.[20] Examples of the classes containing *N,N*-based bidentate ligands, e.g. amidinates,[12, 21, 22] β-diketiminate,[23-26] aminotroponiminate,[3, 27, 28] or *N,N,N*-based tridentate ligands[4, 13] are shown in Chart 1, structures A-D. Without an addition of an external Lewis base such as THF, many of the complexes either become dinuclear alkyl-bridged[12] or ligand-bridged cationic complexes[22, 29, 30] or undergo $C_6F_5^-$ transfer from boron to aluminum center leading to the formation of neutral decomposition products (Scheme 1).[22, 29, 31]

Chart 1 Schematic representation of various N,N-based and N,O-based ligands.



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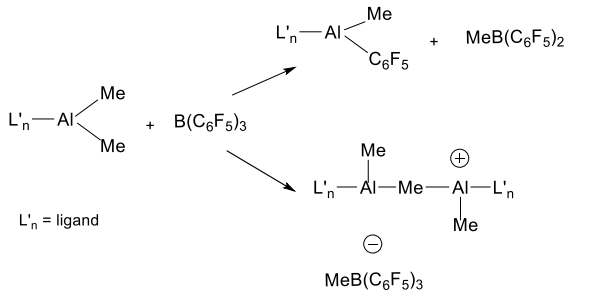
Electronic Supplementary Information (ESI) available: Crystallographic information of **1**-**2**, COSY experiments, DOSY experiment of **4**, and ESI mass spectra of PCL, CCDC 1551837, 1551838, 1553618, 1563972 for LH, complexes **1**-**3**, respectively. See DOI: 10.1039/x0xx00000x



Scheme 1 The activation and deactivation of alkyl aluminum complex with $B(C_6F_5)_3$.

Several studies revealed that the addition of external Lewis base increased the stability of the cationic complexes by forming a stable cation.[2, 6, 12, 32, 33] In addition, sterically hindered or chelating ligands have been shown to stabilize reactive complexes better than the less hindered or low coordinating ligands.[3, 6, 12, 23, 26, 32] An example was demonstrated by Bruce and co-workers who successfully synthesized a series of cationic aluminum complexes containing tridentate *N,N,N*-amidoiminopyridine ligand for ethylene polymerization.[11] In contrast, the previous attempt to produce a cation complex from bidentate *N,N*-β-ketiminato complex suffered from $C_6F_5^-$ transfer decomposition.[25]

Hence, we designed a new aminophenolate ligand to stabilize cationic aluminum complexes by incorporating furfuryl groups as additional chelating sites to the ligand backbone. It is known that an environment of the aluminum center affects the Lewis acidity of the metal, thus, affecting the catalytic activity mediated by aluminum complexes. Therefore, in order to maintain a good catalytic activity, it is important that the ligand is stabilizing but not blocking the active sites that may inhibit the coordination of the substrate to the metal.[20] In terms of the ligand of choice, we focus on *N,O*-based ligands which are relatively less explored than *N,N*-based ligands for their structures, reactivities, and catalytic activities.[6, 29, 30, 32, 34-41] The *N,O*-Schiff base ligands[34-37, 40], *N,O*- heteroscorpionate[38], and bi- or tridentate aminophenolate ligand[6, 29, 30, 32, 39, 41] (Chart 1, structures E-G, respectively), for example, are of great interests due to an excellent chelating ability of nitrogen and oxygen atoms to an oxophilic aluminum center. However, for ligands containing imine bond, variation of the ligands is limited because only a single substituent on the nitrogen atom is available for modification, allowing only linear multidentate ligand framework. To obtain a more variation especially in multipodal fashion, the reduced derivative aminophenolate ligand (Chart 1, structure G) is considered. Although a wide range of neutral aluminum complexes supported by aminophenolate ligand have been reported[42, 43] and some of them have been found to be active towards ring-opening polymerization (ROP) of cyclic esters,[43] the cationic complexes supported by this type of ligand remains relatively unexplored. The other advantage that makes phenolate ligands attractive is the tunability by changing the substituents on the phenyl ring. The phenolate ligands having bulky substituent groups on ortho-position have been shown to prevent the aggregation of the aluminum complex.[44, 45] Thus, the bulky ortho-substituent is part of the design for stable mononuclear aluminum complex.

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Herein, the aluminum complexes supported by novel furan-containing aminophenolate ligand have been synthesized and thoroughly characterized. They can be activated by Lewis acid and showed enhanced activity for ring-opening polymerization of ε-caprolactone in the presence of benzyl alcohol (BnOH) at room temperature.

Results and discussion

Synthesis and characterization of aluminum complexes

The novel aminophenolate ligand (LH) was synthesized via the condensation reaction of bis(furan-2-ylmethyl)amine, paraformaldehyde and 2,4-di-*tert*-butylphenol and isolated as a white solid in high yield. The two weakly coordinating furfuryl groups are chosen as additional coordination sites on pendent side arms of the ligand. They can provide more stabilization to the metal center if needed but are labile enough to dissociate from the metal for substrate coordination. Crystals suitable for X-ray crystallography were grown in benzene by slow evaporation at room temperature. The X-ray structure and crystallographic data of ligand LH are given in Fig. 1 and Table 1, respectively.

The synthesis of aluminum alkoxide complex, $LAl(OR)_2$, was first attempted through a standard method by reacting the ligand LH with $Al(O^iPr)_3$. Surprisingly, this method failed giving no reaction regardless of reaction temperature and time. The synthesis was then carried out through an aluminum methyl complex, $LAlMe_2$, by reacting LH with $AlMe_3$ at room temperature. The synthesis was successful giving the product $LAlMe_2$ (**1**) in high yield (Scheme 2). Subsequent addition of 1 equiv. of HO^tBu to complex **1**, however, gave a mixture of the product $LAlMeO^tBu$ (**3**) and a free ligand LH regardless of the addition temperature and conditions. This result is similar to the

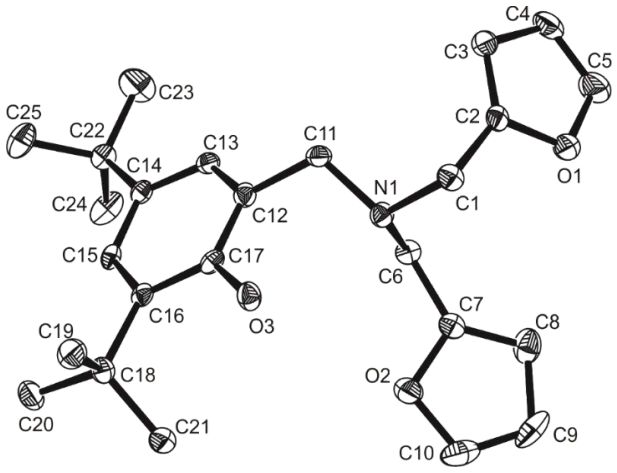
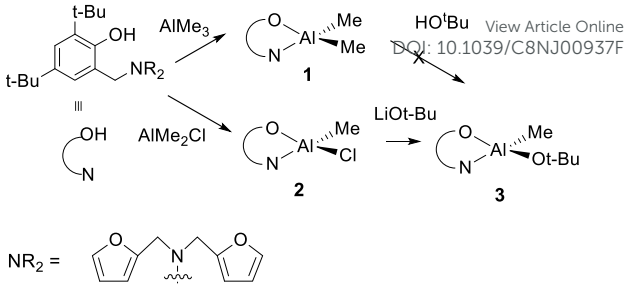


Fig. 1 X-ray crystal structure of ligand LH with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (°): O3–C17 1.370(3), N1–C1 1.482(4), N1–C6 1.478(4), N1–C11 1.478(4), C1–N1–C6 112.6(2), C1–N1–C11 111.7(2), C6–N1–C11 110.1(2).

report on the addition of various alcohols to methyl aluminum complexes based on 2,6-bis(hydroxyalkyl)-pyridines giving a mixture of the compound and the free ligand.[46] However, this was not the case when an alcohol was added to other alkyl aluminum complexes where the expected aluminum alkoxide was obtained without the generation of free ligand.[47-49] The result suggests that the anionic ligand is basic enough to compete with the methyl group on aluminum. It is possible that the two furfuryl groups may participate to abstract a proton from alcohol making the anionic ligand particularly basic. This result is in line with the observation that $Al(O^iPr)_3$ cannot abstract a proton from the ligand LH. An alternative synthesis route was then sought. The ligand LH was reacted with $AlMe_2Cl$ giving LAlMeCl (**2**) in high yield. Subsequent addition of 1 equiv. of LiO^tBu to complex **2** successfully gave complex **3** in high yield. The synthesis of complexes **1**-**3** are summarized in Scheme 2.

The complexes **1**-**3** were crystallized in hydrocarbon solvents and isolated as colorless crystals. All complexes are soluble in toluene, benzene and dichloromethane and stable under an inert atmosphere in both solution and solid state. The molecular structures of the aluminum complexes **1**-**3** were determined by X-ray crystallography and shown in Fig. 2-4, respectively, with the crystallographic data in Table 1 and selected bond distances and angles in Table 2. All X-ray structures establish the monomeric nature of the aluminum complexes with one ligand. The four-coordinated aluminum complexes are observed with phenolate oxygen and nitrogen atoms from the ligand and the corresponding methyl, chloride, or alkoxide groups binding to the aluminum center. The two oxygen atoms from furfuryl groups, however, do not coordinate to the metal center. The asymmetric units of the complexes **1** and **2** contain two fragments with slightly different bond angles and bond distances (see ESI, Fig. S1-S2 and Table S1).



Scheme 2 The synthesis of complexes **1**-**3**.

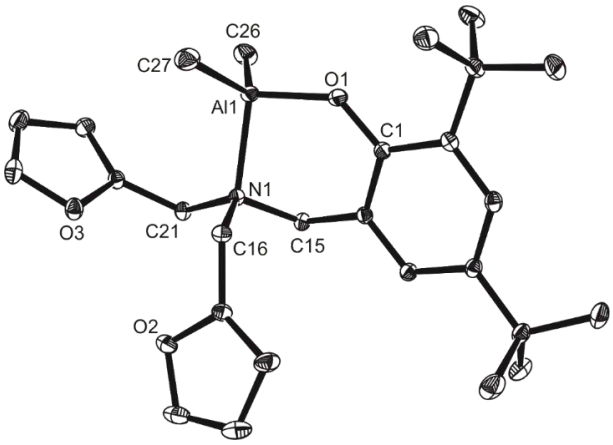


Fig. 2 X-ray crystal structure of $LAlMe_2$ (**1**) with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

Table 1 Crystallographic data for LH and complexes **1**-**3**

Compounds	LH	**1**	**2**	**3**
Formula	$C_{25}H_{33}NO_3$	$C_{54}H_{76}Al_2N_2O_6$	$C_{52}H_{70}Al_2Cl_2N_2O_6$	$C_{30}H_{44}AlNO_4$
F_w	395.52	903.12	943.96	509.64
Space group	$C_{2/}c$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a (Å)	18.34(2)	21.29(1)	21.13(2)	10.09(7)
b (Å)	6.446(6)	10.07(5)	10.01(8)	10.76(7)
c (Å)	38.25(3)	26.44(1)	26.32(2)	14.59(1)
α (deg)	90	90	90	105.77(2)
β (deg)	95.468(7)	112.81(2)	112.46(3)	97.25(2)
γ (deg)	90	90	90	96.59(2)
V (Å^3)	4501.7(7)	5225(4)	5146(6)	1492.4(2)
Z	8	4	4	2
T (K)	100	100	133	150
λ (Å)	0.71073	0.71073	0.71073	0.71073
D_{obsd} (g cm^{-3})	1.167	1.148	1.218	1.134
D_{calcd} (g cm^{-3})	1.167	1.148	1.218	1.134
μ (cm^{-1})	0.76	1.04	2.09	1.01
R	0.0785	0.0530	0.0581	0.0541
R_w	0.1634	0.1485	0.1631	0.1577

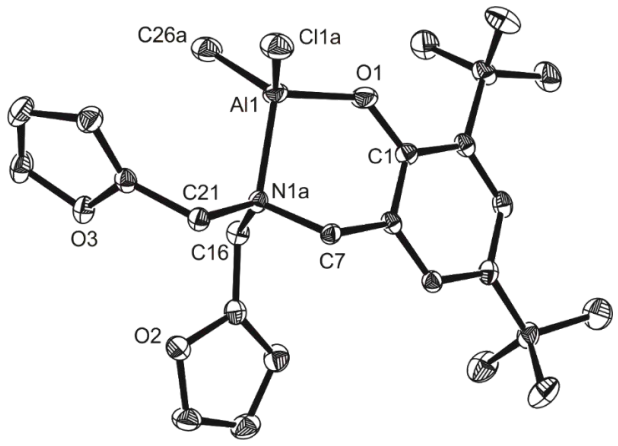


Fig. 3 X-ray crystal structure of LAlMeCl (**2**) with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

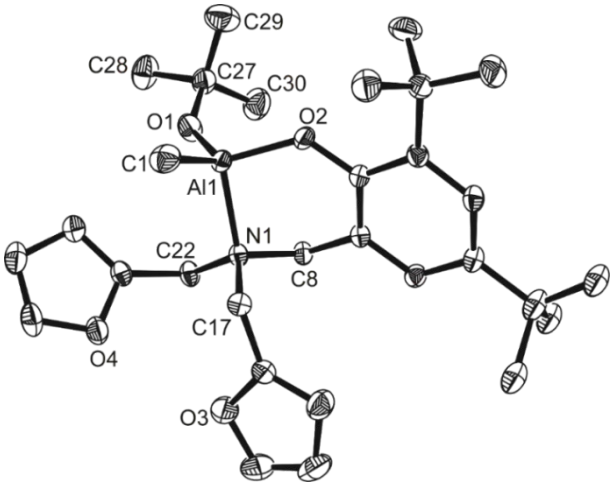


Fig. 4 X-ray crystal structure of LAlMeO^{t}Bu (**3**) with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

The geometries at aluminum center for all complexes are best described as distorted tetrahedral. The smallest angles for all complexes belong to the ligand bite angle, O_{Ph}-Al1-N1, ranging from 96.16(4) to 98.29(7)°, whereas the largest angles are the angles between the two monodentate ligands, C_{Me}-Al1-X; X= CH_3, Cl, or O^{t}Bu (Table 2). Other angles are close to the theoretical tetrahedral angle of 109.5°. The geometry and bond angles are similar to other related bidentate aminophenolate aluminum complexes reported by Dagorne and co-workers.[29] The Al1–O_{Ph} bond distances of complexes **1** and **3** are comparable to the reported value of 1.758(1) Å in $AlMe_2$ [29] except that of **2** which is slightly shorter. However, the bond distances of Al1-O_{Ph} for all complexes still lie in the typical range of Al–O_{Ph} bond distances of aluminum phenolate complexes (1.64–1.77 Å).[45, 50-53] The Al-N bond distances of all complexes range from 2.003(2) to 2.045(1) Å which lie in the normal range of Al-N dative bonds (1.96-2.24 Å).[45, 50]

The structure of **1** can also be compared to the related dimethyl aluminum complex having aminophenolate ligand

Table 2 Selected bond angles (deg) and bond distances (Å) of complexes **1**-**3**

Complexes	**1** (X= CH_3)	**2** (X =Cl)	**3** (X=O^{t}Bu)
O_{Ph}-Al1-C_{Me}	108.3(1)	116.2(1)	113.5(1)
O_{Ph}-Al1-N1	96.16(4)	98.29(7)	97.51(5)
C_{Me}-Al1-N1	108.2(1)	112.6(1)	109.9(1)
O_{Ph}-Al1-X	112.2(1)	107.4(1)	112.9(1)
C_{Me}-Al1-X	120.8(1)	115.4(1)	117.4(1)
N1-Al1-X	108.4(1)	105.3(1)	103.2(1)
Al1-O_{Ph}	1.764(1)	1.730(2)	1.755(1)
Al1-C_{Me}	1.973(1)	1.961(4)	1.955(2)
Al1-N1	2.045(1)	2.004(2)	2.032(1)
Al1-X	1.966(1)	2.139(1)	1.712(1)

containing pyridine moieties instead of the furfuryl groups.[42] The geometry of complex **1** is tetrahedral while that containing pyridyl groups is octahedral having the two pyridyl groups coordinated to the aluminum center. This is reasonable by the fact that pyridine is more basic than furan. Therefore, the pyridyl groups can coordinate to the metal center more strongly. This, in fact, is what was designed from the beginning where the furfuryl groups are labile and do not coordinate strongly to the metal center.

The ^{1}H and ^{13}C NMR spectra of complexes **1**- **3** agree with their solid-state structures. The ^{1}H NMR spectra of **1** in C_6D_6 clearly showed one PhCH_2N singlet (2H), two NCH_2 (4H) and one AlMe_2 (6H) resonances, reflecting the C_s symmetry of the complex (Fig. 5a). As expected, changing one methyl group on the aluminum center to chloride, LAlMeCl (**2**), or tert-butoxide group, LAlMeO^{t}Bu (**3**) makes the complexes asymmetric. Each proton in PhCH_2N resonance (2H) and NCH_2 resonance (4H) of their ^{1}H NMR spectra are magnetically inequivalent giving 6 different doublets (Fig. 5b-c). The symmetry of complexes **2** and **3** are consistent with C_1 symmetry. The ^{1}H NMR spectra of the NCH_2 region of complexes **1**–**3** are shown in Fig. 5 with the peak assignment according to the correlation in COSY NMR spectra (ESI, Fig. S3-S5).

Activation with Lewis acids

The neutral complex **1** can be activated immediately to a cationic species by an abstraction of methyl group at the aluminum center using 1 equiv. of $B(C_6F_5)_3$ in C_6D_6 or CD_2Cl_2 at room temperature (Scheme 3) giving [LAlMe][MeB$(C_6F_5)_3$] complex **4**. The ^{1}H, ^{13}C, and ^{19}F NMR spectra of complex **4** in CD_2Cl_2 confirmed the existence of the cationic complex with a free MeB$(C_6F_5)_3^-$ anion in solution. The characteristic signal of cationic Al–CH_3 was observed at -0.09 ppm in the ^{1}H NMR spectrum with a typical downfield shift from the signal of the original neutral complex [LAl(CH_3)$_2$] at -0.89 ppm. In addition, the B-CH_3 signal observed at 0.49 ppm was indicative of a free *Me*B$(C_6F_5)_3^-$ anion similar to the reported value at 0.50 ppm.[54] This value is different from the reported bridging Al-*Me*-B$(C_6F_5)_3^-$ resonance observed at 1.67 ppm.[12] The ^{13}C and ^{19}F

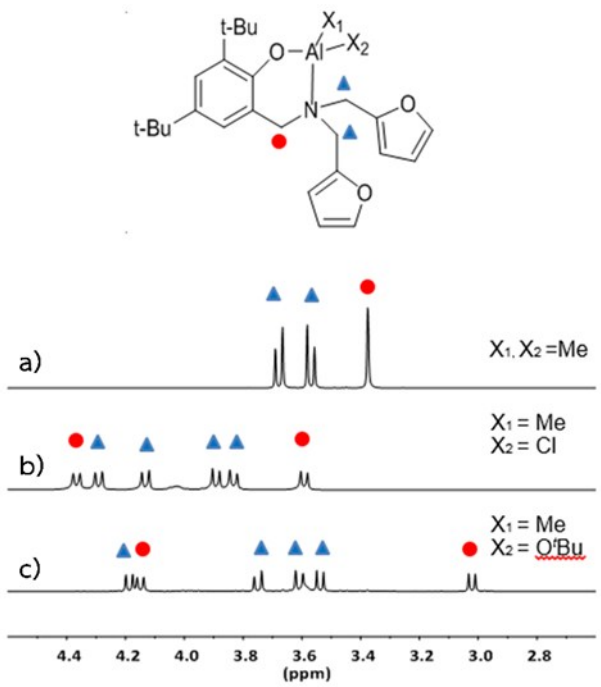
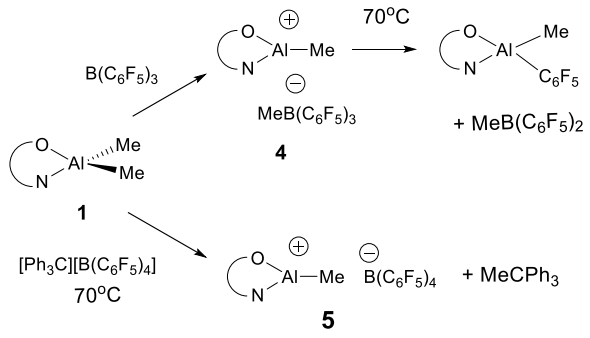


Fig. 5 ^{1}H NMR spectra of a) complex **1** in C_6D_6, b) complex **2** in $CDCl_3$ and c) complex **3** in C_6D_6.



Scheme 3 The activation of complex **1** with $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$.

NMR data also agree with the resonance of the reported free $MeB(C_6F_5)_3^-$ anion.[33] The overall NMR data for the cationic complex **4** is in agreement with C_s symmetry as confirmed by the presence of one PhC*H*$_2$N (2H) and two NC*H*$_2$ (4H) resonances in the ^{1}H NMR spectra. Unfortunately, all attempts to crystallize the cationic complex were unsuccessful. In order to determine the nuclearity of the aluminum cationic species, a diffusion-ordered spectroscopy (DOSY) experiment was performed in CD_2Cl_2 using benzene and $MeB(C_6F_5)_3^-$ as internal standard (ESI, Fig. S6). The molecular mass calculated from diffusion coefficient value[55, 56] is equal to 578 Da (ESI, Table S2) comparable to the molecular mass of the expected monomeric $[LAlMe]^+$ species at 436 Da, hence, supporting that the cationic species is monomeric rather than dimeric in solution.

The cationic complex **4** has good stability in organic solvent. There was no observable decomposition in the ^{1}H NMR spectrum when the complex was stored under inert atmosphere at room temperature for more than a week. However, the decomposition of complex **4** was observed when the solution was heated at 70 °C for 2 h where $C_6F_5^-$ transfer occurred from the anion to the cationic metal center giving the neutral complex $LAlMe(C_6F_5)$ and $MeB(C_6F_5)_2$ (Scheme 3). The ^{1}H NMR spectrum of the decomposition complex shows inequivalent protons in PhC*H*$_2$N (2H) and NC*H*$_2$ (4H) reflecting C_1 symmetry of the complex. The decomposition was confirmed by the ^{19}F NMR spectrum in C_6D_6 having the characteristic peaks of $MeB(C_6F_5)_2$ at -161.3, -147.0, and -130.0 ppm.[25] It is evident that the activated complex is monomeric with a free $[MeB(C_6F_5)_3]^-$ anion. We believe that the enhanced stability at room temperature along with the monomeric nature of the activated complex is a result of the two labile furfuryl groups added to the ligand system. This is further supported by comparison of complex **1** to the related dimethyl aluminum complex having aminophenolate ligand containing two non-coordinating methyl groups instead of two furfuryl groups where, in that case, the dimeric species was observed after activation with $B(C_6F_5)_3$.[29]

In addition to the activation with $B(C_6F_5)_3$, complex **1** can be converted to the cationic complex **5**, $[LAlMe][B(C_6F_5)_4]$, by the reaction with $[Ph_3C][B(C_6F_5)_4]$ in C_6D_6 at 70 °C (Scheme 3). The existence of the cationic species was confirmed by ^{1}H NMR spectroscopy showing the characteristic peak of Al*Me* resonance (3H) at -0.43 ppm in C_6D_6 which slightly shifted downfield compared to the Al*Me* resonance of the neutral complex at -0.47 ppm. Another key evidence is the presence of the characteristic peak of the by-product *Me*CPh$_3$ resonance (3H) at 2.04 ppm. The ^{1}H NMR signals of PhC*H*$_2$N (2H) and NC*H*$_2$ (4H) of complex **5** reflect C_s symmetry, similar to complex **4** described earlier. Complex **5** is also stable in C_6D_6 for more than a week at room temperature.

Polymerization of ε-caprolactone

Complex **1** was used as a catalyst for the ring-opening polymerization (ROP) of ε-caprolactone (CL) at room temperature using [CL]:[Al] ratio of 10:1. However, the catalyst was not active giving only a trace of poly(ε-caprolactone) (PCL) after 12 h. This is reasonable since complex **1** contains only the methyl groups not suitable to attack the monomers. Thus, complex **3** having alkoxide group was tested for the ROP of 10 equiv of CL at room temperature. Surprisingly, the reaction still gave only a trace of polymer even after 6 h. Addition of benzyl alcohol to complex **3** still gave similar polymerization result. We postulate that the sterically hindered four-coordinated complex **3** may have limited access preventing the coordination of the monomer.[57] If this is the case, the complex with less coordination and higher Lewis acidity may give rise to a better polymerization activity. Therefore, the cationic complex **4** was tested for the ROP of CL in the presence of benzyl alcohol as an initiator. Polymerization of CL using CL:**4**:BnOH ratio of 10:1:1 was carried out in CH_2Cl_2 at room temperature. The polymerization went to 88% completion in 15 min. An ESI mass spectrum reveals two major repeating mass series: as cyclic PCL

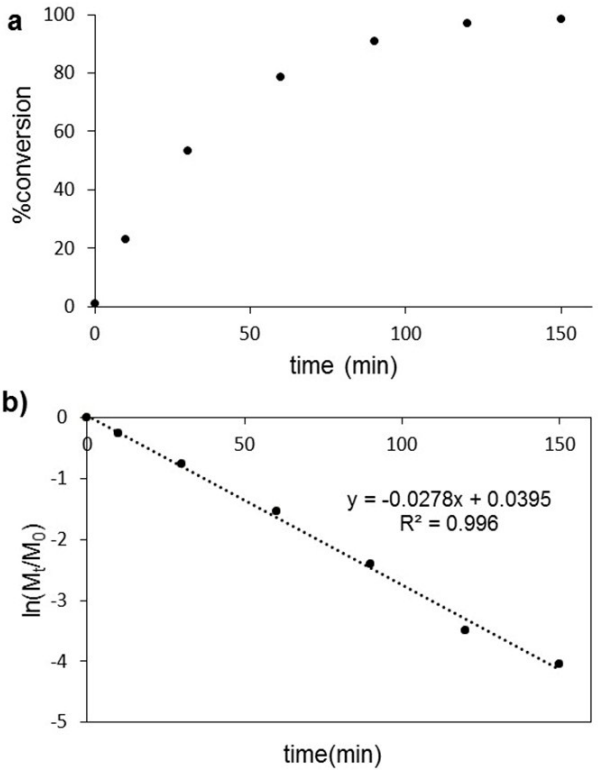
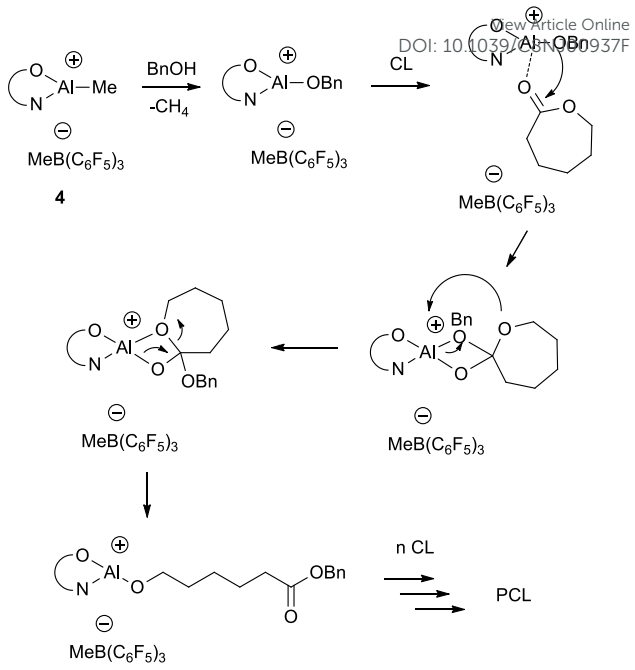


Fig. 6 (a) Plot of conversion vs time and (b) plot of $\ln([CL]/[CL]_0)$ vs time for the polymerization of 100 equiv of ε-CL using complex **4**/benzyl alcohol at room temperature.

$([CL]_n + H^+)$ from intramolecular transesterification and linear PCL ($BnO\text{-}[CL]_n\text{+}H^+$) having benzyl alcohol as an end group (ESI, Fig. S7). A similar procedure was carried for the polymerization of lactide as a monomer but unfortunately giving no polymerization. The polymerization mechanism is proposed in Scheme 4 starting from complex **4**. After BnOH addition, the cationic benzyloxide aluminum complex was generated and polymerized CL through a common coordination-insertion mechanism having benzyloxide as an initiator.

At higher monomer ratio, polymerization of 100 equiv of CL (0.5 M) at room temperature went to 97% completion in 2 h (Fig. 6a) giving PCL with M_n of 13,800 Daltons and a narrow dispersity of 1.21. The plot of $\ln([CL]/[CL]_0)$ vs time gave a first-order dependence on [CL] with a k_{obs} of 2.8 x 10^{-2} min^{-1} (Fig. 6b). The activity of complex **5** was tested for CL polymerization under the same condition as for complex **4**. The polymerization rate of **5** is slightly slower than that of **4** with k_{obs} of 2.1 x 10^{-2} min^{-1} (ESI, Fig. S8) possibly due to a larger counter ion $[B(C_6F_5)_4]^-$ blocking the active site. The activities of complexes **4** and **5** are comparable to that of the reported cationic *N*,*O*-chelate aluminum complexes.[30] However, the polymerization rates are faster than the rates reported in neutral *N*,*O*-chelate aluminium complexes.[30, 58, 59] It is important to note that the cationic nature of **4** and **5** enhances the catalytic activity of the complex. This is emphasized by the result that the neutral complex **3**, although bearing an alkoxide ligand capable of initiating the polymerization, did not polymerize ε-CL.



Scheme 4 Proposed mechanism for polymerization of ε-CL using complex **4**/benzyl alcohol as catalyst.

Conclusions

Several neutral and cationic alkyl, chloro and alkoxide aluminum complexes **1**-**5** supported by novel aminophenolate ligand containing two labile furfuryl groups have been synthesized. The ligand is suitable to support the aluminum center making all neutral aluminum complexes well-defined and monomeric in structure with four coordination as shown in the molecular structures determined by X-ray crystallographic analysis. The dimethyl complex **1** readily reacts with $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ giving the cationic complexes **4** and **5**. The ^1H NMR spectra of the cationic complexes are consistent with the monomeric structure with expected C_s symmetry. All cationic complexes are stable at room temperature over a week. Although the crystal structure cannot be obtained, we believe that the enhanced stability may arise from the reversible coordination of the two furfuryl groups on the ligand to the cationic aluminum center. The cationic species was found to be very efficient to polymerize CL at room temperature compared to the neutral analogue due to the enhanced Lewis acidity of the cationic metal center. Poly(ε-caprolactone) having molecular weight close to the expected value and a narrow dispersity was thus obtained. In addition, the polymerization was first-order with respect to [CL] indicating a well-behave catalytic species. To the best of our knowledge, the furfuryl moiety has not been used so far to stabilize ROP-active cationic species.[58] This is to emphasize the importance of cationic character that, once stabilized, can play an important role in term of enhanced catalytic activity that can be applied in other catalytic fields.

Experimental details

General Details.

All operations were carried out under dry nitrogen atmosphere using standard Schlenk-line and glovebox techniques. Benzene, n-hexane, toluene, dichloromethane and THF were dried using a PURE SOLV MD-5 solvent purification system from Innovative Technology Inc. Bis(furan-2-ylmethyl)amine[60] was synthesized following a literature procedure. $AlMe_3$, $AlMeCl_2$, $AlCl_3$, $[Ph_3C][B(C_6F_5)_4]$, $B(C_6F_5)_3$ were purchased from commercial supplier and were used as received. ε-Caprolactone (CL) was purified by distillation over calcium hydride under nitrogen and stored in a freezer in a glove box.

Measurements.

^1H and ^{13}C NMR spectra, including those in DOSY experiments, were recorded on a Bruker AVANCE III HD 600 MHz spectrometer or a Bruker Ascend™ 400 MHz spectrometer and referenced to protio impurity of commercial chloroform-*d* ($CDCl_3$, δ 7.26 ppm, 77.16 ppm) or benzene-d_6 (C_6D_6, δ 7.16 ppm, 128.06 ppm) as internal standards for ^1H and ^{13}C NMR, respectively. X-ray crystallography data was collected at 100 K, 133 K or 150 K on a Bruker D8 venture diffractometer using Mo κα radiation (λ = 0.71073 Å). Mass spectrometry were obtained from a compact QTOF Bruker mass spectrometer. High resolution mass spectra were carried out using atmospheric pressure compressed interface (APCI) mode. Gel permeation chromatography (GPC) analyses were carried out on a Malvern GPCmax VE-2001 instrument equipped with three 300 mm x 8.0 mm ID columns packed with porous styrene divinylbenzene copolymer. The GPC columns were eluted using tetrahydrofuran with a flow rate of 1.0 mL min^{-1} at 35 °C. Molecular weights and molecular weight distributions were calibrated with polystyrene standards ranging from 1,200 to 4,200,000 amu. Elemental analyses were performed on a TruSpec Micro CHNS.

X-ray crystallography

Data integration was performed with the *SAINT* software,[61] and intensity data were corrected based on the intensities symmetry-related reflections measured at different angular setting (*SADABS*).[62] The space group was determined with the *XPREP* software. The crystal structure was solved by intrinsic phasing method (*SHELXT*)[63] and refined by full-matrix least squares against F^2 using *SHELXL*[64] based on *ShelXle* engine or Olex2 software package.[65] All non-hydrogen atoms were refined anisotropically while the hydrogen atoms were placed in calculated positions and not refined. The crystallographic images were processed by Ortep3 program.[66]

2-((bis(furan-2-ylmethyl)amino)methyl)-4,6-di-tert-butylphenol, **LH.** Bis(furan-2-ylmethyl)amine (10.0 g, 56.5 mmol), paraformaldehyde (1.70 g, 56.5 mmol) and 2,4-di-*tert*-butylphenol (5.82 g, 28.2 mmol) were dissolved in 20 ml ethanol. The mixture was refluxed under N_2 overnight. The volatile components were removed under reduced pressure giving brown liquid as a crude product. The crude product was purified by column chromatography (9:1 hexane-EtOAc) giving colorless liquid which crystallize after standing at room temperature for a week (6.24 g, 56%). Crystals suitable for X-ray crystallography were grown by slow evaporation in methanol at room temperature. ^1H NMR (400 MHz, $CDCl_3$, 25°C): δ 10.45 (s, 1H, O*H*), 7.43 (dd, 2H, *J*=1.9, 0.8 Hz, Ar-*H*), 7.22 (d, 1H, *J*=2.5 Hz, Ph-*H*), 6.84 (d, 1H, *J*=2.5 Hz, Ph-*H*), 6.35 (dd, 2H, *J*=3.2, 1.8 Hz, Ar-*H*), 6.27 (d, 2H, *J*=3.2 Hz, Ar-*H*), 3.76 (s, 2H, PhCH_2N), 3.70 (s, 4H, NCH_2), 1.44 (s, 9H, CH_3), 1.28 (s, 9H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ 154.49 (Ph); 150.80, 142.66 (Ar); 140.65, 135.79 124.09, 123.11, 120.99 (Ph); 110.39, 109.97 (Ar); 57.45 (Ph*C*H_2N); 48.31(N*C*H_2); 35.06 (*C*CH_3); 31.84, 29.74 (*C*H_3). Anal. Calcd. for ($C_{25}H_{33}NO_3$): C, 75.91; H, 8.41; N, 3.54. Found: C, 76.18; H, 8.34; N, 3.41. ESI MS (*m/z*) 396.2539 ($C_{25}H_{33}NO_3 + H^+$). Found 396.2587.

LAlMe$_2$, 1. A solution of LH (0.550 g, 1.40 mmol) in toluene was added dropwise to $AlMe_3$ (0.700 mL, 2 M in toluene, 1.40 mmol) at room temperature. The mixture was stirred overnight. Volatile materials were removed under vacuum giving a white powder (0.580 g, 92%). Crystals suitable for X-ray crystallography were grown by slow evaporation in toluene at room temperature. ^1H NMR (600 MHz, C_6D_6, 30°C): δ 7.58 (d, J = 2.6 Hz, 1H, Ph-*H*), 7.09 – 6.92 (m, 2H, Ar-*H*), 6.78 (d, *J* = 2.5 Hz, 1H, Ph-*H*), 6.19 (d, *J* = 3.3 Hz, 2H, Ar-*H*), 6.00 (dd, *J* = 3.3, 1.9 Hz, 2H, Ar-*H*), 3.68 (d, *J* = 14.7 Hz, 2H, NCH_2), 3.57 (d, *J* = 14.8 Hz, 2H, NCH_2), 3.38 (s, 2H, PhCH_2N), 1.71 (s, 9H, CCH_3), 1.44 (s, 9H, CCH_3), -0.47 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6, 30°C): δ 157.35 (Ph); 146.92 (Ar); 143.52 (C_{Ar}H); 138.08 (Ph); 126.25, 124.45 (C_{Ph}H); 119.31 (Ph); 114.24, 110.69 (C_{Ar}H); 58.69 (N*C*H_2); 47.27 (Ph*C*H_2N); 35.54, 34.34 (*C*CH_3); 32.15, 30.00 (*C*H_3); -10.24 (Al-*C*H_3). Anal. Calcd. for ($C_{27}H_{38}AlNO_3$): C, 71.81; H, 8.48; N, 3.10. Found: C, 71.68; H, 8.33; N, 3.19. HRMS (*m/z*) 452.2740 ($C_{27}H_{38}NAlO_3 + H^+$). Found: 452.2731.

LAlMeCl, 2. A solution of LH (0.100 g, 0.260 mmol) in THF was added dropwise to $AlMe_2Cl$ (315 µL, 0.9 M in heptane, 0.280 mmol) at room temperature. The mixture was stirred overnight. Volatile materials were removed under vacuum giving a white powder (0.119 g, 97%). Crystals suitable for X-ray crystallography were grown by slow evaporation in toluene at room temperature. ^1H NMR (600 MHz, $CDCl_3$, 30°C): δ 7.55 (dd, *J* = 1.9, 0.8 Hz, 1H, Ar-*H*), 7.53 (dd, *J* = 1.9, 0.8 Hz, 1H, Ar-*H*), 7.30 (d, *J* = 2.5 Hz, 1H, Ph-*H*), 6.83 (d, *J* = 2.5 Hz, 1H, Ph-*H*), 6.74 (d, *J* = 3.3 Hz, 1H, Ar-*H*), 6.48 (d, *J* = 3.3 Hz, 1H, Ar-*H*), 6.47 – 6.44 (m, 1H, Ar-*H*), 6.44 – 6.43 (m, 1H, Ar-*H*), 4.37 (d, *J* = 13.7 Hz, 1H, PhCH_2N), 4.29 (d, *J* = 14.3 Hz, 1H, NCH_2), 4.13 (d, *J* = 14.8 Hz, 1H, NCH_2), 3.89 (d, *J* = 14.3 Hz, 1H, NCH_2), 3.83 (d, *J* = 14.8 Hz, 1H, NCH_2), 3.59 (d, *J* = 13.7 Hz, 1H, PhCH_2N), 1.40 (s, 9H, CCH_3), 1.31 (s, 9H, CCH_3), -0.87 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, 30°C): δ 155.20 (Ph); 146.42 (Ph); 145.28 (C_{Ar}H); 144.40 (C_{Ar}H); 139.34, 137.98 (Ar); 125.86 (C_{Ph}H); 124.63 (C_{Ph}H); 118.50 (Ph); 115.33 (C_{Ar}H); 111.12-110.79 (C_{Ar}H), 58.42 (Ph*C*H_2N); 49.19, 45.34 (N*C*H_2); 35.20, 34.29 (*C*CH_3); 31.86, 29.71 (*C*H_3); -12.85 (Al*C*H_3). Anal. Calcd. for ($C_{26}H_{35}AlClNO_3$): C, 66.16; H, 7.47; N, 2.97. Found: C, 65.89; H, 7.41; N, 2.80.

LAlMeO^{t}Bu, 3. A solution of LiO^t-Bu (41.6 mg, 0.520 mmol) in benzene was added dropwise to complex **2** (0.220 g, 0.460 mmol) at room temperature. The mixture was stirred for 1 h then filtered to remove LiCl salts. Volatile materials were removed under vacuum giving a white powder. The complex was purified by crystallization in hexane (0.21 g, 90%). Crystals suitable for X-ray crystallography were grown by placing a concentrated hexane solution in a freezer. ^{1}H NMR (600 MHz, C_6D_6, 30°C): δ 7.59 (d, J = 2.5 Hz, 1H, Ph-*H*), 7.09 (d, J = 1.1 Hz, 1H, Ar-*H*), 7.07 – 7.01 (m, 1H, Ar-*H*), 6.84 (d, J = 2.5 Hz, 1H, Ph-*H*), 6.80 (d, J = 3.3 Hz, 1H, Ar-*H*), 6.22 (d, J = 3.2 Hz, 1H, Ar-*H*), 6.08 (dd, J = 3.3, 1.9 Hz, 1H, Ar-*H*), 6.05 (dd, J = 3.3, 1.8 Hz, 1H, Ar-*H*), 4.19 (d, J = 13.8 Hz, 1H, NCH_2), 4.15 (d, J = 13.3 Hz, 1H, PhCH_2N), 3.61 (d, J = 15.2 Hz, 1H, NCH_2), 3.54 (d, J = 13.8 Hz, 1H, NCH_2), 3.02 (d, J = 13.3 Hz, 1H, PhCH_2N), 1.72 (s, 9H, CCH_3), 1.45 (s, 9H, CCH_3), 1.43 (s, 9H, OCCH_3), -0.70 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (150 MHz, C_6D_6, 30°C): δ 156.76, 148.07, 146.64 (Ph); 143.40 (C_{Ar}H); 138.26, 137.87 (Ar); 126.45, 124.45 (C_{Ph}H); 115.00, 114.62 (C_{Ar}H); 110.98, 110.54 (C_{Ar}H); 58.25 (PhCH$_2$N); 49.55, 44.55 (NCH$_2$); 35.48, 34.35(*C*CH$_3$); 34.20, 32.12, 30.10 (*C*H$_3$); -12.92 (AlCH$_3$). Anal. Calcd. for ($C_{30}H_{44}AlNO_4$): C, 70.70; H, 8.70; N, 2.75. Found: C, 70.51; H, 8.54; N, 2.70. HRMS (*m/z*) 510.3114 ($C_{30}H_{44}AlNO_4$ + H$^+$). Found: 510.3240.

NMR scale synthesis of [LAlMe][MeB(C_6F_5)$_3$], 4. An NMR tube was charged with a solution of complex **1** (5.0 mg, 1.1 µmol) in 0.3 mL CD_2Cl_2. A solution of B(C_6F_5)$_3$ (6.6 mg, 1.3 µmol) in 0.3 mL CD_2Cl_2 was added to the solution of complex **1** at room temperature giving 100% conversion to complex **4**. ^{1}H NMR (600 MHz, CD_2Cl_2, 30°C): δ 7.57 (d, J = 2.0 Hz, 2H, Ar-*H*), 7.18 (d, J = 2.5 Hz, 1H, Ph-*H*), 6.73 (d, J = 2.5 Hz, 1H, Ph-*H*), 6.51 (dd, J = 3.7, 2.0 Hz, 2H, Ar-*H*), 6.47 (d, J = 3.7 Hz, 2H, NCH_2), 4.50 (d, J = 15.0 Hz, 2H, NCH_2), 4.38 (d, J = 15.0 Hz, 2H, NCH_2), 3.91 (s, 2H, PhCH_2N), 1.38 (s, 9H, CCH_3), 1.18 (s, 9H, CCH_3), 0.49 (s, 3H, BCH_3), -0.09 (s, 3H, AlCH_3). ^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2, 30°C): δ 153.44 (Ph); 149.44 (*o*-C_6F_5); 148.00 (*p*-C_6F_5); 145.57 (Ar); 143.31(Ph); 142.12 (C_{Ar}H); 138.26 (Ph); 136.14 (*m*-C_6F_5); 126.48, 125.23 (C_{Ph}H); 118.62 (Ph); 114.71, 110.51(C_{Ar}H); 63.58 (NCH$_2$); 54.53 (PhCH$_2$N); 35.40, 34.44 (*C*CH$_3$); 31.55, 29.93 (*C*H$_3$); 10.55 (BCH$_3$); -12.80 (AlCH$_3$). ^{19}F NMR (565 MHz, CD_2Cl_2, 30°C): δ -133.18 (d, J = 19.4 Hz, 2F, *o*-C_6F_5), -143.79 (t, J = 20.2 Hz, 1F, *p*-C_6F_5), -167.86 (m, 2F, *m*-C_6F_5).

NMR scale synthesis of [LAlMe(C_6F_5)] An NMR tube was charged with a solution of complex **1** (7.0 mg, 16 µmol) in 0.3 mL C_6D_6. A solution of B(C_6F_5)$_3$ (9.3 mg, 18 µmol) in 0.3 mL C_6D_6 was added to the solution of **1** at room temperature. The solution was then heated to 70°C for 2 h giving a clean conversion to the decomposition product LAlMe(C_6F_5). ^{1}H NMR (600 MHz, C_6D_6, 30°C): δ 7.62 (d, J = 2.6 Hz, 1H, Ar-*H*), 6.99 (d, J = 1.8 Hz, 1H, Ph-*H*), 6.97 – 6.88 (m, 1H, Ph-*H*), 6.83 (d, J = 2.6 Hz, 1H, Ar-*H*), 6.11 (d, J = 3.3 Hz, 1H, Ar-*H*), 6.05 (d, J = 3.3 Hz, 1H, Ar-*H*), 5.93 (q, J = 2.5 Hz, 2H, Ar-*H*), 3.77 (d, J = 14.8 Hz, 1H, NCH_2), 3.68 (d, J = 14.5 Hz, 1H, NCH_2), 3.68 (d, J = 14.5 Hz, 1H, PhCH_2N), 3.59 (q, J = 14.7 Hz, 2H, NCH_2), 3.44 (d, J = 13.8 Hz, 1H, PhCH_2N), 1.67 (s, 9H, CCH_3), 1.43 (s, 9H, CCH_3), -0.25 (d, J = 1.9 Hz, 3H, AlCH_3). ^{13}C{^{1}H} NMR (150 MHz, C_6D_6, 30°C): δ 156.59 (Ph); 145.89 (Ar); 143.81, 143.70 (C_{Ph}H); 139.26, 138.64 (Ph); 126.18, 125.02 (C_{Ar}H); 119.12 (Ph); 114.72, 114.47, 110.72 (C_{Ar}H); 58.82 (PhCH$_2$N); 47.96, 47.70 (NCH$_2$); 35.53, 34.39 (*C*CH$_3$); 32.06, 30.03 (*C*H$_3$); -7.72 (AlCH$_3$). ^{19}F NMR (565 MHz, C_6D_6, 30°C): δ -128.76 (m, 2F, *o*-C_6F_5); -154.15 (m, 1F, *p*-C_6F_5), -159.98 (m, 2F, *m*-C_6F_5).

Spectroscopic data for by-product [MeB(C_6F_5)$_2$]. ^{1}H NMR (600 MHz, C_6D_6, 30°C): δ 1.33 (s, 3H, BCH_3). ^{13}C{^{1}H} NMR (150 MHz, C_6D_6, 30°C): δ 32.06 (BCH$_3$). ^{19}F NMR (565 MHz, C_6D_6, 30°C): δ -129.93 (m, 4F, *o*-(C_6F_5)$_2$); -146.95 (m, 2F, *p*-(C_6F_5)$_2$); -161.28 (m, 4F, *m*-(C_6F_5)$_2$).

NMR scale synthesis of [LAlMe][B(C_6F_5)$_4$], 5. An NMR tube was charged with a mixture of complex **1** (5.6 mg, 12 µmol) and [(Ph)$_3$C][B(C_6F_5)$_4$] (11 mg, 12 µmol) in 0.6 mL C_6D_6. The solution was then heated to 70°C for 30 min giving a clean conversion to complex **5**. ^{1}H NMR (600 MHz, C_6D_6, 30°C): δ 6.98 (t, J = 7.9 Hz, 2H, Ar-*H*), 6.49 (d, J = 2.0 Hz, 1H, Ph-*H*), 6.43 (d, J = 2.4 Hz, 1H, Ph-*H*), 5.60 (d, J = 3.9 Hz, 2H, Ar-*H*), 5.54 (dd, J = 3.7, 2.0 Hz, 2H, Ar-*H*), 3.30 (d, J = 15.0 Hz, 2H, NCH_2), 3.23 (d, J = 15.0 Hz, 2H, NCH_2), 2.77 (s, 2H, PhCH_2N), 1.37 (s, 9H, CCH_3), 1.20 (s, 9H, CCH_3), -0.43 (s, 3H, AlCH_3). ^{13}C{^{1}H} NMR (150 MHz, C_6D_6, 30°C): δ 145.16 (Ar), 140.88 (C_{Ph}H); 125.79, 125.20 (C_{Ar}H); 118.77 (Ph); 113.96, 109.30 (C_{Ar}H); 62.38 (NCH$_2$); 53.03 (PhCH$_2$N); 35.16, 34.19 (*C*CH$_3$); 31.49, 29.91(*C*H$_3$); -13.46 (AlCH$_3$). ^{19}F NMR (565 MHz, C_6D_6, 30°C): δ -131.90 (s, 2F, *o*-C_6F_5), -162.14 (t, J = 20.9 Hz, 1F, *p*-C_6F_5), -166.21 (s, 2F, *m*-C_6F_5).

Polymerization of ε-Caprolactone. The following representative polymerization is for ε-CL: **4** (generated *in situ*) mole ratio of 100: 1 with addition of one equiv of benzyl alcohol. The amount of ε-CL and catalysts can be adjusted accordingly for ε-CL: **4** mole ratio of 10: 1. A solution of complex **1** (21.7 mg, 48 µmol) and B(C_6F_5)$_3$ (25.4 mg, 48 µmol) in 5.0 mL CH_2Cl_2 was added to a Schlenk flask followed by the addition of ε-CL (0.560 g, 4.8 mmol) in 5.6 mL CH_2Cl_2. After that, benzyl alcohol (5.20 mg, 48 µmol) was added to the solution mixture. At a specific time, a small amount of sample was taken to determine conversion by NMR analysis. At the end of the reaction, the remaining solution was added a few drops of 10% acetic acid in CH_2Cl_2 solution, and then precipitated with excess cold methanol. The solid polymer was collected and dried under vacuum to constant weight. For a low ε-CL: **4** mole ratio of 10: 1, after quenching with a solution of 10% acetic acid in CH_2Cl_2, the polymer mixture was dried under vacuum and used as is for NMR and APCI-mass spectrometry analysis.

DOSY Experiments. Diffusion-ordered ^{1}H NMR data were acquired using pulsed gradient spin-echo (PGSE) NMR method, the Bruker pulse program ledbpgp2s. The gradient pulse duration (P30) was set to 1000 µs with a diffusion period of 48 ms (D20). The gradient strength was varied linearly for 16 gradient increment values from 2% to 95%. DOSY plots were generated by using mnova program. Diffusion coefficients (D_t) were calculated by fitting the intensity data to the Stejskal–Tanner expression.[60] The molecular masses in solution (m) were estimated using Graham's law of diffusion: D = K(T/m)$^{1/2}$, where the constant K depends on geometric factors

and temperature is 30°C. According to the equation, by plotting a calibration curve of m vs ($1/D^2$) of internal standards, the molecular mass can be determined.

Conflicts of Interest

There are no conflicts to declare.

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The mononuclear neutral and stable cationic aluminum complexes supported by novel furfuryl-containing aminophenolate ligand are reported along with ε-caprolactone polymerization.