DOI: 10.1002/ejic.200900158

# Aluminum Complexes with Bidentate *N*,*N*-Dialkylaniline–arylamido Ligands: Synthesis, Structures, and Catalytic Properties for Efficient Ring-Opening Polymerization of ε-Caprolactone

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**Keywords:** Aluminum / Ring-opening polymerization / N ligands

A number of Al complexes bearing bidentate *N*,*N*-dialkylaniline–arylamido ligands, *ortho*-$(ArNCH_2)C_6H_4NR_2AlMe_2$ (R = Me, Ar = 2,6-*i*$Pr_2C_6H_3$, **3a**; 2,6-$Et_2C_6H_3$, **3b**; 2,6-$Me_2C_6H_3$, **3c**; 4-$MeC_6H_4$, **3d**; Ph, **3e**; and R = Et, Ar = 2,6-*i*$Pr_2C_6H_3$, **3f**; 2,6-$Me_2C_6H_3$, **3g**; Ph, **3h**), have been synthesized from the reaction of the corresponding free ligands, *ortho*-$(ArNHCH_2)C_6H_4NR_2$ (R = Me, Ar = 2,6-*i*$Pr_2C_6H_3$, **2a**; 2,6-$Et_2C_6H_3$, **2b**; 2,6-$Me_2C_6H_3$, **2c**; 4-$MeC_6H_4$, **2d**; Ph, **2e**; and R = Et, Ar = 2,6-*i*$Pr_2C_6H_3$, **2f**; 2,6-$Me_2C_6H_3$, **2g**; Ph, **2h**), with $AlMe_3$ (1 equiv.). All complexes were characterized by $^1H$ and $^{13}C$ NMR spectroscopy and elemental analysis. Single-crystal X-ray diffraction analysis of complexes **3c** and **3e** revealed that these Al complexes have a distorted tetrahedral geometry around the metal center. All complexes were found to be efficient catalysts for the ring-opening polymerization of ε-caprolactone (CL) in the presence of benzyl alcohol, and complexes **3a**–**h** catalyze the polymerization of CL in a living fashion.


## Introduction

The synthesis of poly(ε-caprolactone) (PCL) and poly(lactide) (PLA) as well as their copolymers have received considerable attention because of their potential applications in medicine, pharmaceutics, and tissue engineering such as delivery medium for the controlled release of drugs, scaffolds, and the delivery of antibodies and genes.[1] The signal-site metal complex catalyzed ring-opening polymerization (ROP) of ε-caprolactone (CL) is the major method used to synthesize PCL due to its good control over the molecular weight of the polymerization product.[2] A number of main-group and transition-metal complexes, including magnesium,[3] calcium,[4] aluminum,[5] titanium,[6] iron,[7] zinc,[8] tin,[9] and rare-earth metal[10] complexes supported by various ligands have been reported to be efficient catalysts for the ROP of CL. Among these catalysts, Al complexes are the most intensely studied catalysts due to their high Lewis acidity. A series of salicylaldimine–aluminum complexes have been reported by Nomura and coworkers that are efficient catalysts for the ROP of CL, and the catalytic activity of this type of complexes was found to increase with increasing steric bulk of their ligands.[11] Recently, our group reported a similar type of Al catalysts with *N*-arylanilido–arylimine ligands.[12] The catalytic activity of this type of catalysts was found to decrease with an increase in the steric hindrance of the ligands. To further modify the ligand and examine the steric effect of the ligand, we have developed a number of new Al complexes bearing bidentate *N*,*N*-dialkylaniline–arylamido ligands. From a structural point of view, the steric hindrance of the new ligands should be moderate in comparison to those of the salicylaldimine ligands and the *N*-arylanilido–arylimine ligands. The new Al complexes were found to be efficient catalysts for the ROP of CL in the presence of benzyl alcohol (BnOH). In this paper, we wish to report the synthesis of the Al complexes *ortho*-$(ArNCH_2)C_6H_4NR_2AlMe_2$ (R = Me, Ar = 2,6-*i*$Pr_2C_6H_3$, **3a**; 2,6-$Et_2C_6H_3$, **3b**; 2,6-$Me_2C_6H_3$, **3c**; 4-$MeC_6H_4$, **3d**; Ph, **3e**; and R = Et, Ar = 2,6-*i*$Pr_2C_6H_3$, **3f**; 2,6-$Me_2C_6H_3$, **3g**; Ph, **3h**) as well as their catalytic properties for the ROP of CL.

## Results and Discussion

### Synthesis and Spectroscopic Characterization of the Free Ligands and Their Al Complexes

Al complexes **3a**–**h** were synthesized from the reaction of corresponding free ligands *ortho*-$(ArNHCH_2)C_6H_4NR_2$ (R = Me, Ar = 2,6-*i*$Pr_2C_6H_3$, **2a**; 2,6-$Et_2C_6H_3$, **2b**; 2,6-$Me_2C_6H_3$, **2c**; 4-$MeC_6H_4$, **2d**; Ph, **2e**; and R = Et, Ar = 2,6-*i*$Pr_2C_6H_3$, **2f**; 2,6-$Me_2C_6H_3$, **2g**; Ph, **2h**) with $AlMe_3$ (1 equiv.), as shown in Scheme 1. *ortho*-Dimethylaminobenzaldehyde (**A**) and *ortho*-diethylaminobenzaldehyde (**B**) were prepared by treatment of *N*,*N*-dimethylaniline and *N*,*N*-diethylaniline with *n*BuLi (1 equiv.), followed by reac-

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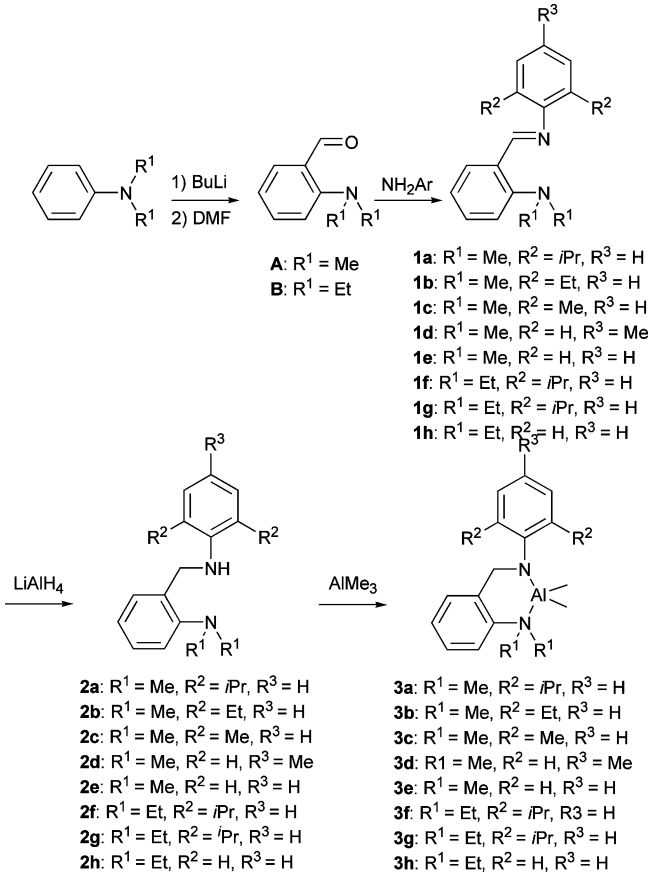
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.200900158.

tion with DMF. Preligands **1a**–**h** were synthesized by condensation between **A** or **B** and a substituted aniline in methanol. Reduction of preligands **1a**–**h** with $LiAlH_4$ in ethyl ether gave free ligands **2a**–**h**. Among these compounds, **1d**, **1e**, **1h**, and **2e** have been reported previously.[13] All new compounds were characterized by $^1H$ and $^{13}C$ NMR spectroscopy along with elemental analyses. The $^1H$ NMR spectra of preligands **1a**–**c** and **1f**–**g** exhibit a resonance in the range of $\delta$ = 8.50–8.80 ppm for the imino N=CH proton, with the corresponding $^{13}C$ NMR resonance around $\delta$ = 160 ppm. The NH resonance in free ligands **2a**–**d** and **2f**–**h** appears at characteristically middle field about $\delta$ = 3.90 ppm.




Scheme 1. Synthetic procedure of ligands **2a**–**h** and complexes **3a**–**h**.

Al complexes **3a**–**h** were obtained in good yields by alkane elimination reaction as shown in Scheme 1. The reaction of free ligands **2a**–**h** with $AlMe_3$ (1.0 equiv.) affords Al complexes **3a**–**h**. The disappearance of the N–H signal of the free ligands and the appearance of the resonances for the protons of $AlMe_2$ ($\delta$ = –0.60 to –1.04 ppm) for complexes **3a**–**h** in high-field regions in the $^1H$ NMR spectra demonstrate the formation of the desired complexes. Complexes **3a**–**h** were all characterized by $^1H$ and $^{13}C$ NMR spectroscopy and elemental analyses. As mentioned above, the $^1H$ NMR spectra of complexes **3a**–**h** all exhibit characteristic resonances for the protons of $AlMe_2$, with the corresponding $^{13}C$ NMR resonances for the carbon atoms of the $AlMe_2$ group in the regions of $\delta$ = –9.78 to –10.51 ppm for **3a**–**h**.

## X-ray Crystallographic Analysis

The molecular structure of complex **3c** is shown in Figure 1. Selected bond lengths and angles for **3c** are given in Table 1. X-ray analysis revealed that the Al center of complex **3c** adopts a distorted tetrahedral geometry with the metal center chelated by the amine and amido nitrogen atoms of the bidentate ligand. The six-membered chelating ring has a legless chair geometry and the aluminum atom occupies the top position of the backrest. The torsion angle between the plane of N1–Al–N2 and the plane of C6–C7–N1 is 57.6°, which is an indication of how far the Al atom is out of the plane of the aniline backbone. The N1–Al–N2 angle [94.23(12)°] in the complex is close to those in related known Al complexes.[14] The Al–N2 (amido) distance [1.809(3) Å] is shorter than the Al–N1 (amine) distance [2.027(3) Å], which indicates the Al–N (amine) coordination bond character.

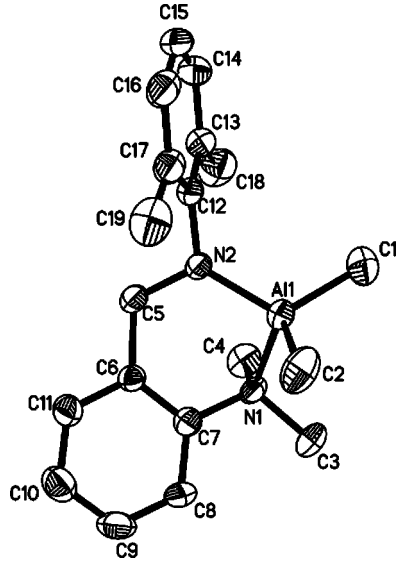



Figure 1. The molecular structure of complex **3c**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Complex **3e** crystallizes with two independent molecules (assigned as **3e1** and **3e2**) in an asymmetric unit cell. The structure of molecule **3e1** is shown in Figure 2, and the structures of both molecules **3e1** and **3e2** are given in Figure S1 (Supporting Information). The two molecules have similar conformation and structural parameters. Selected bond lengths and angles for **3e** are given in Table 1. The structural feature around the Al atom in **3e** is similar to that in **3c**, adopting a distorted tetrahedral geometry with the four-coordinate metal center chelated by the amine and amido nitrogen atoms of the bidentate ligand. The torsion angles between the plane of N1–Al–N2 and the plane of C6–C7–N1 are 55.5 and 57.2° for **3e1** and **3e2**, respectively.

Table 1. Selected bond lengths [Å] and angles [°] for **3c** and **3e**.

| Complex **3c** | | | |
|---|---|---|---|
| Al–N1 | 2.027(3) | N2–Al–C1 | 114.52(16) |
| Al–N2 | 1.809(3) | C1–Al–C2 | 113.7(2) |
| Al–C2 | 1.959(4) | N1–Al–N2 | 94.23(12) |
| Al–C1 | 1.952(4) | N1–Al–C2 | 103.22(15) |
| C5–N2 | 1.450(4) | N1–Al–C1 | 108.94(16) |
| N2–Al–C1 | 119.06(16) | | |
| Complex **3e1** | | Complex **3e2** | |
| Al1–N1 | 2.032(2) | Al2–N3 | 2.035(2) |
| Al1–N2 | 1.863(2) | Al2–N4 | 1.860(2) |
| Al1–C16 | 1.963(2) | Al2–C33 | 1.961(2) |
| Al1–C17 | 1.968(2) | Al2–C34 | 1.965(2) |
| C9–N2 | 1.459(3) | C26–N4 | 1.464(3) |
| N2–Al1–C16 | 114.77(10) | N4–Al2–C33 | 114.31(10) |
| N2–Al1–C17 | 115.25(10) | N4–Al2–C34 | 114.81(10) |
| C16–Al1–C17 | 115.98(11) | C33–Al2–34 | 116.74(11) |
| N1–Al1–N2 | 95.82(8) | N3–Al2–N4 | 96.46(8) |
| N1–Al1–C16 | 106.43(10) | N3–Al2–C33 | 106.97(10) |
| N1–Al1–C17 | 105.52(10) | N3–Al2–C34 | 104.47(10) |

The N1–Al–N2 bond angles [95.82(8) and 96.46(8)° for **3e1** and **3e2**, respectively] are slightly larger than that in **3c**. As seen in **3c**, the Al–N2 (amido) distances [1.863(2) and 1.860(2) Å] are also shorter than the Al–N1 (amine) distances [2.032(2) and 2.035(2) Å] in **3e**. Both the Al–N1 and Al–N2 distances in **3e** are longer than those in **3c**. The observed differences in the bond lengths and angles between **3c** and **3e** may simply result from the packing force, as it cannot be reasonably explained otherwise.

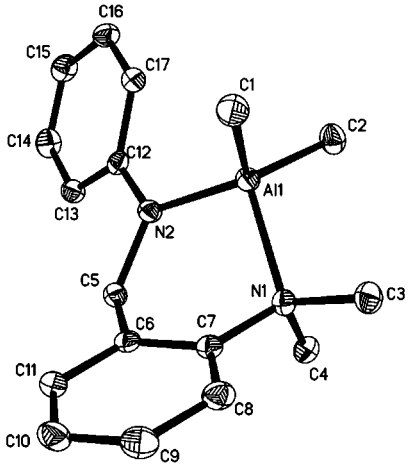



Figure 2. The molecular structure of one (**3e1**) of the two independent complexes present in the crystals of **3e**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

## Ring-Opening Polymerization of ε-Caprolactone Initiated by 3a–e

Complexes **3a**–**h** were systematically investigated for the ROP of CL. Representative experimental results are summarized in Table 2. Complexes **3a**–**h** all show high reactivity for catalyzing the ROP of CL in the presence of BnOH, whereas no reaction takes place in the absence of BnOH (Table 2, Entries 1–5). The *ortho*-$(ArNCH_2)C_6H_4NMe_2$-$AlMe_2$ complexes **3a**–**e** were synthesized and studied as catalysts for the ROP of CL first and it was found that their catalytic activity under the same conditions is in the order of **3a** > **3b** > **3c** > **3d** > **3e** (Table 2, Entries 6–10). These results indicate that increasing the steric hindrance of the aryl group at the amido N atom in the ligands of these complexes can considerably increase their catalytic activity. A similar phenomenon has been observed in the salicylaldimine–aluminum catalyst system.[11] However, reverse results were obtained with the bulky *N*-arylanilido–arylimine Al catalyst system.[12] To systematically examine and correctly understand the steric effect of the ligands on the catalytic activity of the new type of complexes, *ortho*-$(ArNCH_2)$-$C_6H_4NEt_2AlMe_2$ complexes **3f**–**h** were then synthesized and their catalytic properties for the ROP of CL was studied. It is interesting to find that the catalytic activities of these complexes increases first and then decreases with an increase in the steric hindrance of the aryl group at the amido N atom in their ligands (Table 2, Entries 25–27). These results indicate that catalysts of this type require their ligands with adequate steric hindrance to show the highest catalytic activity. A too-bulky ligand may block the coordination and insertion of the monomer, whereas a less-bulky ligand might allow the coordination of the ester linkages in the polymer chain. For complexes **3a**–**e**, the $NMe_2$ group is small in size, which results in these complexes requiring a bulky aryl group at the amido N atom in their ligands to demonstrate good catalytic activity. To examine the effect of reaction conditions on the catalytic activity of the new catalyst system, polymerization experiments under different conditions were conducted with complex **3a** in the presence of BnOH. The role of BnOH in the ROP of CL has been studied and reported previously.[12,15] Under similar conditions, the catalytic activity of **3a** was observed to change obviously with the change in the BnOH/Al molar ratio, and the highest catalytic activity was obtained with a BnOH/Al molar ratio of 2:1. It was found that the number-averaged degree of polymerization ($DP_n$) of the obtained polymers (calculated by $^1H$ NMR) is close to the CL/BnOH molar ratio, and the molecular weight ($M_n$) of the polymers determined by gel permeation chromatography is proportional to the CL/BnOH molar ratio (Figure 3). Similar results have previously been reported for other initiator systems,[12,16] which have been described as "immortal" polymerization. The polymerization reaction was also examined at different reaction temperatures and the reactivity of complex **3a** was found to increase noticeably from 20 to 70 °C. When the polymerization reaction was carried out at 20 °C for different times, it was found that the $DP_n$ and $M_n$ values of the obtained polymers increase linearly with an increase in polymer yields. These results demonstrate the "living" character of the polymerization process with BnOH as a co-initiator. In comparison with related known initiator systems, the reactivity of the present system is similar to that of the *N*-arylanilido–arylimine Al catalyst system.[12] The $^1H$ NMR spectrum of a typical PCL sample shows the pres-

Table 2. Ring-opening polymerization of ε-caprolactone initiated by complexes **3a**–**h**.[a]

| Entry | Cat. | [BnOH]/[Al]/[CL] | Temp. [°C] | Time | Yield [%][b] | TOF[c] | $DP_n$[d] | $M_n$[e] × $10^3$ | $M_n$(SEC)[f] × $10^3$ | $M_n$(theor)[g] × $10^3$ | $M_w/M_n$[e] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **3a** | 0:1:100 | 70 | 24 h | 0 | – | – | – | – | – | – |
| 2 | **3b** | 0:1:100 | 70 | 24 h | 0 | – | – | – | – | – | – |
| 3 | **3c** | 0:1:100 | 70 | 24 h | 0 | – | – | – | – | – | – |
| 4 | **3d** | 0:1:100 | 70 | 24 h | 0 | – | – | – | – | – | – |
| 5 | **3e** | 0:1:100 | 70 | 24 h | 0 | – | – | – | – | – | – |
| 6 | **3a** | 2:1:100 | 70 | 3 min | 96.5 | 1930 | 49 | 11.8 | 6.6 | 5.6 | 1.24 |
| 7 | **3b** | 2:1:100 | 70 | 4 min | 94.3 | 1414 | 53 | 12.7 | 7.1 | 5.5 | 1.18 |
| 8 | **3c** | 2:1:100 | 70 | 4.7 min | 95.1 | 1214 | 56 | 13.4 | 7.5 | 5.5 | 1.25 |
| 9 | **3d** | 2:1:100 | 70 | 6.5 min | 96.7 | 892 | 47 | 11.4 | 6.3 | 5.6 | 1.20 |
| 10 | **3e** | 2:1:100 | 70 | 7 min | 95.8 | 821 | 51 | 12.3 | 6.9 | 5.4 | 1.12 |
| 11 | **3a** | 0.5:1:100 | 70 | 18 min | 93.2 | 311 | 197 | 37.9 | 21.2 | 21.4 | 1.35 |
| 12 | **3a** | 1:1:100 | 70 | 14 min | 95.7 | 409 | 97 | 19.1 | 10.7 | 11.0 | 1.41 |
| 13 | **3a** | 4:1:100 | 70 | 10 min | 92.6 | 556 | 27 | 7.51 | 4.2 | 2.7 | 1.56 |
| 14 | **3a** | 2:1:100 | 50 | 7 min | 94.9 | 813 | 55 | 13.2 | 7.4 | 5.5 | 1.32 |
| 15 | **3a** | 2:1:100 | 20 | 12 min | 93.4 | 467 | 48 | 11.6 | 6.5 | 5.4 | 1.28 |
| 16 | **3a** | 2:1:200 | 70 | 5 min | 96.2 | 2308 | 99 | 21.4 | 12.0 | 11.1 | 1.35 |
| 17 | **3a** | 2:1:300 | 70 | 7 min | 98.1 | 2522 | 159 | 26.0 | 14.6 | 16.9 | 1.72 |
| 18 | **3a** | 2:1:400 | 70 | 9.3 min | 96.3 | 2485 | 203 | 39.7 | 22.2 | 22.1 | 1.51 |
| 19 | **3a** | 2:1:450 | 70 | 12.7 min | 95.3 | 2026 | 225 | 43.7 | 24.5 | 24.6 | 1.74 |
| 20 | **3a** | 2:1:400 | 20 | 9 min | 46.5 | 1240 | 95 | 20.3 | 11.4 | 10.7 | 1.16 |
| 21 | **3a** | 2:1:400 | 20 | 18 min | 70.2 | 936 | 146 | 28.5 | 16.0 | 16.1 | 1.18 |
| 22 | **3a** | 2:1:400 | 20 | 27 min | 85.0 | 755 | 175 | 33.8 | 18.9 | 19.5 | 1.19 |
| 23 | **3a** | 2:1:400 | 20 | 36 min | 92.4 | 616 | 187 | 35.2 | 19.7 | 21.2 | 1.24 |
| 24 | **4** | 0:1:100 | 70 | 3 min | 97.1 | 1942 | 50 | 11.4 | 6.4 | 5.6 | 1.36 |
| 25 | **3f** | 2:1:100 | 70 | 5.5 min | 92.1 | 1005 | 46 | 11.1 | 6.2 | 5.4 | 1.27 |
| 26 | **3g** | 2:1:100 | 70 | 5 min | 94.6 | 1135 | 52 | 12.5 | 7.0 | 5.5 | 1.19 |
| 27 | **3h** | 2:1:100 | 70 | 8 min | 95.2 | 714 | 54 | 12.9 | 7.2 | 5.5 | 1.26 |

[a] Polymerization conditions: catalyst (0.19 mmol), [CL] = 1 M in toluene. [b] Isolated yield. [c] Mole of CL consumed per mol of catalyst per hour. [d] The number-averaged degree of polymerization calculated by $^1$H NMR spectroscopy. [e] The molecular weight obtained from GPC analysis. [f] SEC values of precipitated polymer samples corrected with the coefficient 0.56. [g] Calculated for one growing polymer chain with $M_n$(theor) = {[ε-CL]$_0$/[BnOH]$_0$ × 114 × (conversion)+ 108}.

ence of a benzyl ester group at $\delta$ = 5.12 ppm (singlet, C$H_2$Ph) as the initiating chain end. These results suggest that BnOH reacts first with the alkyl Al complexes to form the LAl–OBn complexes as the catalytic active species. To further confirm that the benzyloxyaluminum complex acts as the active catalyst, benzyloxyaluminum complex **4** was synthesized by reaction of **3a** with BnOH (2 equiv.) and used as catalyst for the ROP of CL (Figure 4A). It was found that complex **4** shows similar catalytic activity to the catalyst system of **3a**/BnOH (1:2). The formation of Al-[O(C$H_2$)$_5$C=O]$_n$OC$H_2$Ph intermediates during the polymerization was confirmed by $^1$H NMR spectroscopy (Figure 4B), in which the signals of the methylene protons (c, d, e, and f) of the polymer appear at $\delta$ = 4.22, 2.46, 1.81, 1.54 ppm, and the sharp signal at $\delta$ = 5.27 ppm arises from the ending benzyl C$H_2$ group.

On the basis of the above results, a mechanism for the present polymerization system, similar to the one proposed previously for the *N*-arylanilido–arylimine Al catalyst system,[12] can be proposed as shown in Scheme 2. The benzyloxyaluminum complexes are the active catalysts that are produced by the reaction of the alkylaluminum complexes with BnOH. The polymerization reaction takes place by repeated coordination of the CL monomer to the metal center and insertion into the Al–O bond to form the polymerization intermediates LAl–OP (where P refers to the polymer chain). Free polymers can be released by the addition of

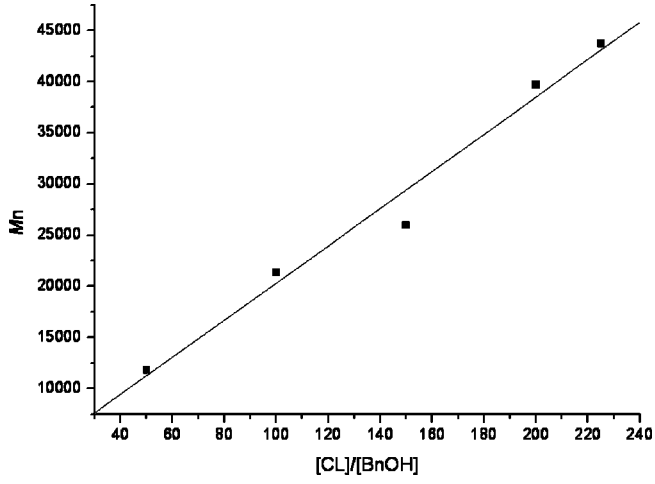



Figure 3. Plot of Mn vs. [CL]/[BnOH] for the ROP of CL catalyzed by complex **3a**/BnOH in toluene at 70 °C.

BnOH or acetic acid. BnOH acts as a chain initiator as well as a chain transfer reagent in the polymerization procedure. During the polymerization, excess BnOH (if any) would react with the polymerization intermediates LAl–OP to replace the –OP groups and form the free polymers and new active species. The formed shorter chain polymers would also react with the polymerization intermediates with longer polymer chains to produce longer chain free poly-

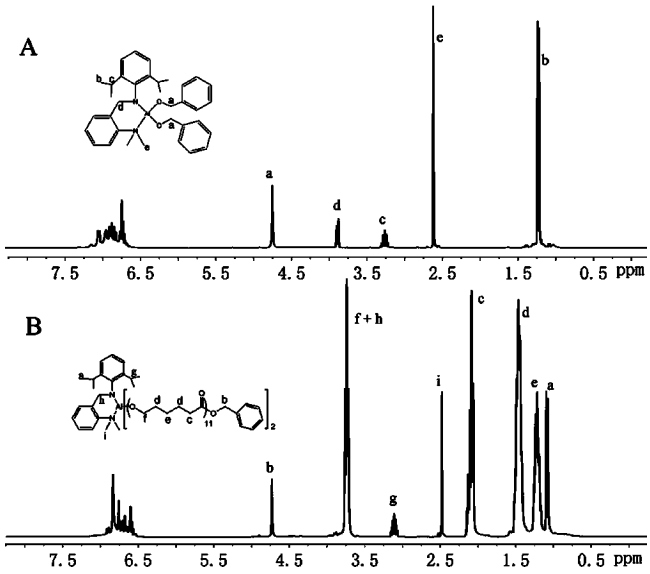
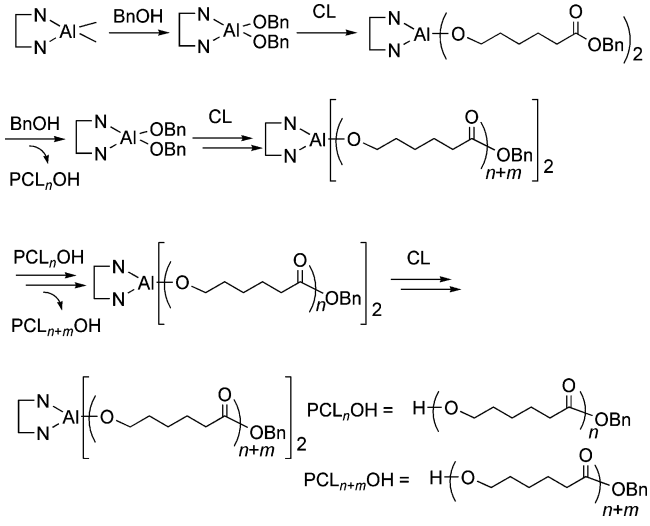



Figure 4. $^1$H NMR spectra of (A) complex **4** in $CDCl_3$, and (B) the reaction mixture of complex **4** and CL in $CDCl_3$ at room temperature.

mers and new polymerization intermediates. Finally, the polymerization reaction stops when the monomer is totally consumed.




Scheme 2. The proposed mechanism for the ROP of CL.

## Conclusions

In conclusion, several Al complexes supported by bidentate *N*,*N*-dimethylaniline–arylamido ligands and *N*,*N*-diethylaniline–arylamido ligands have been synthesized in good yields by the reaction of free ligands **2a**–**h** with $AlMe_3$ (1.0 equiv.). All complexes were fully characterized by $^1$H and $^{13}$C NMR spectroscopy along with elemental analyses. The structures of **3c** and **3e** were determined by X-ray crystallography, and the structural analysis revealed that the Al center of these complexes adopts a distorted tetrahedral geometry with the metal center chelated by the amine and amido nitrogen atoms of their bidentate ligands. Complexes **3a**–**h** are all efficient catalysts for the ROP of CL in the presence of benzyl alcohol and catalyze the polymerization of CL in a living fashion. The catalytic activity of complexes **3a**–**e** increases with an increase in the steric bulk of the aryl groups at the amido N atom in the *N*,*N*-dimethylaniline–arylamido ligands, whereas the catalytic activity of complexes **3f**–**h** increases first and then decreases with an increase in the steric bulk of the aryl groups in the *N*,*N*-diethylaniline–arylamido ligands. In addition, the catalytic activity of these catalyst systems increases with an increase in polymerization temperature from 20 to 70 °C and also changes with the BnOH/Al molar ratio with the highest catalytic activity being observed at the BnOH/Al molar ratio of 2:1. Benzyloxyaluminum complex **4** was synthesized and tested as the active catalyst for the ROP of CL, which supports the proposed mechanism for the polymerization.

## Experimental Section

**General:** All reactions were performed using standard Schlenk techniques in an atmosphere of high-purity nitrogen or glove-box techniques. Toluene, hexane, and $Et_2O$ were dried by heating at reflux over sodium and benzophenone and then distilled under nitrogen prior to use. $C_6D_6$ and $CDCl_3$ were dried with $CaH_2$ for 48 h and vacuum-transferred into an air-free flask. *n*BuLi and $AlMe_3$ were purchased from Aldrich and used as received. Compounds **1d**, **1e**, and **2e** were prepared according to a literature procedure.[11] $^1$H and $^{13}$C NMR spectra were measured using a Varian Mercury-300 NMR spectrometer. Elemental analyses were performed with a Perkin–Elmer 2400 analyzer. GPC measurements were performed with a Waters-410 system using $CH_2Cl_2$ as the eluent (flow rate: 1 mL min$^{-1}$, at 25 °C). Molecular weights and molecular weight distributions were calculated using polystyrene as standard.

***ortho*-$C_6H_4$($NMe_2$)CHO (A):** After removal of the solvent of *n*BuLi (79 mL, 79 mmol), *N*,*N*-dimethylaniline (10 mL) was added at 0 °C with stirring, gently heating to 80 °C for 24 h, during which a yellow solid was formed. DMF (6.0 mL) in $Et_2O$ (40 mL) was added to the mixture at 0 °C. After stirring for 12 h, the reaction was quenched with $H_2O$ (30 mL), and the organic phase was separated, washed with brine, and dried with magnesium sulfate. The solvent was removed in vacuo to give the crude product as a yellow oil. Pure product was obtained by column chromatography (10% ethyl acetate in hexanes) as a yellow oil (9.2 g, 78%). $C_9H_{11}NO$ (149.19): calcd. C 72.46, H 7.43, N 9.39; found C 72.38, H 7.38, N 9.26. $^1$H NMR (300 MHz, $CDCl_3$, 293 K): $\delta$ = 10.22 (s, 1 H, C*H*O), 7.75 (d, 1 H, Ph-*H*), 7.46 (d, 1 H, Ph-*H*), 7.06 (d, 1 H, Ph-*H*), 7.01 (t, 1 H, Ph-*H*), 2.92 (s, 6 H, NC$H_3$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K): $\delta$ = 191.05, 155.66, 134.49, 130.81, 126.89, 120.49, 117.51, 45.42 ppm.

***ortho*-$C_6H_4$($NEt_2$)CHO (B):** Under an atmosphere of nitrogen, *n*BuLi (35 mL, 35 mmol) was added dropwise to a stirred $Et_2O$ solution (50 mL) of *N*,*N*-diethylaniline (5 mL) in the presence of TMEDA (5 mL). The mixture was gently heated to reflux for 24 h. DMF (3.1 mL) in $Et_2O$ (20 mL) was added to the mixture at 0 °C. After stirring for 12 h, the reaction was quenched with $H_2O$ (30 mL), and the organic phase was separated, washed with brine, and dried with magnesium sulfate. The solvent was removed in vacuo to give the crude product as a yellow oil. Pure product was

obtained by column chromatography (dichloromethane/hexane, 2:1) as a yellow oil (1.7 g, 30%). $C_{11}H_{15}NO$ (177.24): calcd. C 74.54, H 8.53, N 7.90; found C 74.49, H 8.50, N 7.94. $^1$H NMR (300 MHz, $CDCl_3$, 293 K): $\delta$ = 10.36 (s, 1 H, C*H*O), 7.82 (d, 1 H, Ph-*H*), 7.49 (t, 1 H, Ph-*H*), 7.17 (d, 1 H, Ph-*H*), 7.07 (d, 1 H, Ph-*H*), 3.18 (q, 4 H, NC$H_2$CH$_3$), 1.06 (t, 6 H, NCH$_2$C$H_3$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K): $\delta$ = 191.72, 154.34, 134.02, 128.60, 122.54, 122.15, 121.47, 48.72, 12.09 ppm.

***ortho*-C$_6$H$_4$(NMe$_2$)CH=NC$_6$H$_3$*i*Pr$_2$-2,6 (1a):** A solution of *ortho*-$C_6H_4(NMe_2)CHO$ (2.24 g, 15.0 mmol) and 2,6-diisopropylaniline (2.83 mL, 15.0 mmol) in MeOH (20 mL) was stirred at room temperature for 12 h. The mixture was then cooled to 0 °C for a couple of hours to precipitate the product. The precipitate was collected on a filter and washed with cool MeOH (5 mL) to give the product as a yellow crystalline material (3.7 g, 80%). $C_{21}H_{28}N_2$ (308.46): calcd. C 81.77, H 9.15, N 9.08; found C 81.74, H 9.14, N 9.12. $^1$H NMR (300 MHz, $CDCl_3$, 293 K): $\delta$ = 8.58 (s, 1 H, C*H*=N), 8.24 (d, 1 H, Ph-*H*), 7.47 (t, 1 H, Ph-*H*), 7.03–7.16 (m, 5 H, Ph-*H*), 3.04 [m, 2 H, C*H*(CH$_3$)$_2$], 2.81 (s, 6 H, NC$H_3$), 1.20 [d, 12 H, CH(C$H_3$)$_2$] ppm. $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K): $\delta$ = 160.26, 154.46, 149.26, 137.21, 131.25, 128.74, 127.62, 123.36, 122.42, 122.25, 118.24, 45.27, 27.30, 22.08 ppm.

***ortho*-C$_6$H$_4$(NMe$_2$)CH=NC$_6$H$_3$Et$_2$-2,6 (1b):** A mixture of *ortho*-$C_6H_4(NMe_2)CHO$ (3.13 g, 21.0 mmol) and 2,6-diethylaniline (3.46 mL, 21.0 mmol) in MeOH (20 mL) was stirred for 12 h. The solvent was removed in vacuo to give the crude product as a yellow oil. Pure product was obtained by column chromatography (5% ethyl acetate in hexanes) as a yellow solid (4.95 g, 84%). $C_{19}H_{24}N_2$ (280.41): calcd. C 81.38, H 8.63, N 9.99; found C 81.35, H 8.60, N 10.05. $^1$H NMR (300 MHz, $CDCl_3$, 293 K): $\delta$ = 8.59 (s, 1 H, C*H*=N), 8.16 (d, 1 H, Ph-*H*), 7.44 (t, 1 H, Ph-*H*), 7.04–7.15 (m, 5 H, Ph-*H*), 2.78 (s, 6 H, NCH$_3$), 2.52 (q, 4 H, C$H_2$CH$_3$), 1.16 (t, 6 H, CH$_2$C$H_3$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K): $\delta$ = 171.89, 156.03, 142.46, 136.86, 136.79, 136.14, 129.06, 125.80, 116.01, 115.01, 114.73, 56.84, 18.67, 8.24 ppm.

***ortho*-C$_6$H$_4$(NMe$_2$)CH=NC$_6$H$_3$Me$_2$-2,6 (1c):** This compound was prepared in the same way as described above for **1a** with *ortho*-$C_6H_4(NMe_2)CHO$ (2.98 g, 20.0 mmol) and 2,6-dimethylaniline (2.44 mL, 20.0 mmol) as starting materials. The product (3.94 g, 78%) was obtained as a yellow powder. $C_{17}H_{20}N_2$ (252.35): calcd. C 80.91, H 7.99, N 11.10; found C 80.88, H 8.07, N 11.05. $^1$H NMR (300 MHz, $CDCl_3$, 293 K): $\delta$ = 8.56 (s, 1 H, C*H*=N), 8.17 (d, 1 H, Ph-*H*), 7.44 (t, 1 H, Ph-*H*), 7.14–6.95 (m, 5 H, Ph-*H*), 2.79 (s, 6 H, NC$H_3$), 2.16 (s, 6 H, C$H_3$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K): $\delta$ = 161.36, 154.59, 151.79, 131.62, 128.82, 127.96, 127.81, 126.91, 123.25, 122.34, 118.23, 45.50, 18.28 ppm.

***ortho*-C$_6$H$_4$(NEt$_2$)CH=NC$_6$H$_3$*i*Pr$_2$-2,6 (1f):** This compound was prepared in the same way as described above for **1a** with **B** (0.890 g, 5.0 mmol) and 2,6-diisopropylaniline (0.94 mL, 5.0 mmol) as starting materials. The product (1.13 g, 67%) was obtained as a yellow powder. $C_{23}H_{32}N_2$ (336.51): calcd. C 82.09, H 9.58, N 8.32; found C 82.13, H 9.54, N 8.33. $^1$H NMR (300 MHz, $CDCl_3$, 293 K): $\delta$ = 8.69 (s, 1 H, C*H*=N), 8.24 (d, 1 H, Ph-*H*), 7.47 (t, 1 H, Ph-*H*), 7.03–7.16 (m, 5 H, Ph-*H*), 3.05 [m, 2 H, C*H*(CH$_3$)$_2$], 3.05 (m, 4 H, NC$H_2$CH$_3$), 1.19 [d, 12 H, CH(C$H_3$)$_2$], 0.96 (t, 6 H, NCH$_2$C$H_3$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K): $\delta$ = 161.19, 152.45, 150.12, 137.88, 132.84, 132.80, 132.76, 131.57, 127.80, 124.02, 123.06, 48.88, 27.98, 23.70, 12.39 ppm.

***ortho*-C$_6$H$_4$(NEt$_2$)CH=NC$_6$H$_3$Me$_2$-2,6 (1g):** This compound was prepared in the same way as described above for **1a** with **B** (1.06 g, 6.0 mmol) and 2,6-dimethylaniline (0.73 mL, 6.0 mmol) as starting materials. The product (1.33 g, 79%) was obtained as a yellow powder. $C_{19}H_{24}N_2$ (280.41): calcd. C 81.38, H 8.63, N 9.99; found C 81.41, H 8.67, N 9.92. $^1$H NMR (300 MHz, $CDCl_3$, 293 K): $\delta$ = 8.67 (s, 1 H, C*H*=N), 8.20 (d, 1 H, Ph-*H*), 7.45 (t, 1 H, Ph-*H*), 7.20–6.95 (m, 5 H, Ph-*H*), 3.08 (q, 4 H, NC$H_2$CH$_3$), 2.16 (s, 6 H, C$H_3$), 0.99 (t, 6 H, NCH$_2$C$H_3$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K): $\delta$ = 161.87, 152.31, 152.10, 132.35, 131.48, 128.00, 127.76, 127.18, 123.57, 123.39, 122.46, 48.64, 18.43, 12.33 ppm.

***ortho*-C$_6$H$_4$(NMe$_2$)CH$_2$NHC$_6$H$_3$*i*Pr$_2$-2,6 (2a):** A solution of $LiAlH_4$ (0.681 g, 18.0 mmol) in $Et_2O$ (10 mL) was added to a solution of **1a** (3.70 g, 12.0 mmol) in $Et_2O$ (30 mL) at 0 °C. The mixture was warmed to room temperature and stirred for 5 h. The reaction was quenched with cooled $H_2O$ (20 mL), and the organic phase was separated, washed with brine, and dried with magnesium sulfate. The solvent was removed in vacuo to give the crude product as a yellow oil. Pure product was obtained by distillation under reduced pressure as a yellow solid (2.83 g, 76%). $C_{21}H_{30}N_2$ (310.48): calcd. C 81.24, H 9.74, N 9.02; found C 81.27, H 9.73, N 9.00. $^1$H NMR (300 MHz, $CDCl_3$, 293 K): $\delta$ = 7.42 (d, 1 H, Ph-*H*), 7.28 (t, 1 H, Ph-*H*), 7.21 (d, 1 H, Ph-*H*), 7.05–6.11 (m, 4 H, Ph-*H*), 4.07 (s, 2 H, C$H_2$N), 3.89 (br., 1 H, N*H*), 3.40 [m, 2 H, C*H*(CH$_3$)$_2$], 2.72 (s, 6 H, NC$H_3$), 1.25 [d, 12 H, C*H*(CH$_3$)$_2$] ppm. $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K): $\delta$ = 152.83, 143.58, 142.67, 135.16, 129.69, 128.16, 124.01, 123.62, 123.49, 120.01, 53.05, 45.30, 27.49, 24.34 ppm.

***ortho*-C$_6$H$_4$(NMe$_2$)CH$_2$NHC$_6$H$_3$Et$_2$-2,6 (2b):** This compound was prepared in the same way as described above for **2a** with **1b** (3.53 g, 12.6 mmol) and $LiAlH_4$ (0.720 g, 18.9 mmol) as starting materials. The product (2.92 g, 82%) was obtained as a yellow solid. $C_{19}H_{26}N_2$ (282.42): calcd. C 80.80, H 9.28, N 9.92; found C 80.83, H 9.26, N 9.91. $^1$H NMR (300 MHz, $CDCl_3$, 293 K): $\delta$ = 7.47 (d, 1 H, Ph-*H*), 7.30 (t, 1 H, Ph-*H*), 7.22 (d, 1 H, Ph-*H*), 7.08–6.98 (m, 4 H, Ph-*H*), 4.15 (s, 2 H, C$H_2$N), 3.87 (br., 1 H, N*H*), 2.74 (s, 6 H, NC$H_3$), 2.54 (q, 4 H, C$H_2$CH$_3$), 1.27 (t, 6 H, CH$_2$C$H_3$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K): $\delta$ = 152.75, 145.34, 136.76, 129.61, 128.04, 126.59, 125.93, 123.82, 122.69, 119.80, 51.25, 45.22, 24.21, 15.05 ppm.

***ortho*-C$_6$H$_4$(NMe$_2$)CH$_2$NHC$_6$H$_3$Me$_2$-2,6 (2c):** This compound was prepared in the same way as described above for **2a** with **1c** (2.95 g, 11.7 mmol) and $LiAlH_4$ (0.670 g, 17.6 mmol) as starting materials. The product (2.02 g, 68%) was obtained as a yellow oil. $C_{17}H_{22}N_2$ (254.37): calcd. C 80.27, H 8.72, N 11.01; found C 80.30, H 8.70, N 11.00. $^1$H NMR (300 MHz, $CDCl_3$, 293 K): $\delta$ = 7.39 (d, 1 H, Ph-*H*), 7.26 (t, 1 H, Ph-*H*), 7.17 (d, 1 H, Ph-*H*), 7.05 (t, 1 H, Ph-*H*), 6.99 (d, 2 H, Ph-*H*), 6.82 (t, 1 H, Ph-*H*), 4.17 (s, 2 H, C$H_2$N), 3.87 (br., 1 H, N*H*), 2.72 (s, 6 H, NC$H_3$), 2.30 (s, 6 H, C$H_3$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K): $\delta$ = 152.70, 146.41, 134.95, 129.78, 128.71, 128.71, 128.04, 123.65, 121.83, 119.65, 49.38, 45.18, 18.35 ppm.

***ortho*-C$_6$H$_4$(NMe$_2$)CH$_2$NHC$_6$H$_4$Me-4 (2d):** This compound was prepared in the same way as described above for **2a** with **1d** (2.57 g, 10.8 mmol) and $LiAlH_4$ (0.610 g, 16.2 mmol) as starting materials. The product (2.05 g, 79%) was obtained as a yellow oil. $C_{16}H_{20}N_2$ (240.34): calcd. C 79.96, H 8.39, N 11.66; found C 79.90, H 8.38, N 11.72. $^1$H NMR (300 MHz, $CDCl_3$, 293 K): $\delta$ = 7.37 (d, 1 H, Ph-*H*), 7.26–6.97 (m, 5 H, Ph-*H*), 6.62 (d, 2 H, Ph-*H*), 4.40 (s, 2 H, C$H_2$N), 3.92 (br., 1 H, N*H*), 2.76 (s, 6 H, NC$H_3$), 2.24 (s, 3 H, C$H_3$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K): $\delta$ = 152.36, 146.24, 133.34, 129.63, 129.23, 127.82, 126.44, 123.28, 119.15, 113.06, 44.94, 44.84, 20.37 ppm.

***ortho*-C$_6$H$_4$(NEt$_2$)CH$_2$NHC$_6$H$_3$*i*Pr$_2$-2,6 (2f):** This compound was prepared in the same way as described above for **2a** with **1f** (1.01 g, 3.0 mmol) and $LiAlH_4$ (0.17 g, 4.5 mmol) as starting materials. The

product (0.84 g, 83%) was obtained as a yellow oil. $C_{23}H_{34}N_2$ (338.53): calcd. C 81.60, H 10.12, N 8.28; found C 81.53, H 10.15, N 8.32. $^1$H NMR (300 MHz, $CDCl_3$, 293 K): $\delta$ = 7.46 (d, 1 H, Ph-*H*), 7.28 (t, 1 H, Ph-*H*), 7.21–7.12 (m, 5 H, Ph-*H*), 4.10 (s, 2 H, C$H_2$N), 3.53 (br., 1 H, N*H*), 3.42 [m, 2 H, CH(C$H_3$)$_2$], 3.06 (q, 4 H, NC$H_2$CH$_3$), 1.24 [d, 12 H, CH(C$H_3$)$_2$], 1.03 (t, 6 H, NCH$_2$C$H_3$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K): $\delta$ = 142.93, 137.39, 129.53, 128.31, 124.16, 123.75, 123.55, 123.07, 122.75, 118.50, 52.46, 48.30, 27.52, 24.37, 12.20 ppm.

***ortho*-C$_6$H$_4$(NEt$_2$)CH$_2$NHC$_6$H$_3$Me$_2$-2,6 (2g):** This compound was prepared in the same way as described above for **2a** with **1g** (1.12 g, 4.0 mmol) and $LiAlH_4$ (0.23 g, 6.0 mmol) as starting materials. The product (1.02 g, 91%) was obtained as a yellow oil. $C_{19}H_{26}N_2$ (282.42): calcd. C 80.80, H 9.28, N 9.92; found C 80.83, H 9.23, N 9.94. $^1$H NMR (300 MHz, $CDCl_3$, 293 K): $\delta$ = 7.45 (d, 1 H, Ph-*H*), 7.26 (t, 1 H, Ph-*H*), 7.19 (m, 2 H, Ph-*H*), 7.01 (d, 2 H, Ph-*H*), 6.84 (t, 1 H, Ph-*H*), 4.18 (s, 2 H, CH$_2$N), 3.68 (br., 1 H, N*H*), 3.08 (q, 4 H, NC$H_2$CH$_3$), 2.38 (s, 6 H, C$H_3$), 1.06 (t, 6 H, NCH$_2$C$H_3$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K): $\delta$ = 146.70, 137.80, 129.96, 129.60, 128.85, 127.61, 124.30, 123.10, 121.95, 118.03, 65.64, 48.76, 18.56, 12.52 ppm.

***ortho*-C$_6$H$_4$(NEt$_2$)CH$_2$NHC$_6$H$_5$ (2h):** This compound was prepared in the same way as described above for **2a** with **1h** (1.39 g, 5.5 mmol) and $LiAlH_4$ (0.31 g, 8.3 mmol) as starting materials. The product (1.22 g, 87%) was obtained as a yellow oil. $C_{17}H_{22}N_2$ (254.37): calcd. C 80.27, H 8.72, N 11.01; found C 80.21, H 8.75, N 11.04. $^1$H NMR (300 MHz, $CDCl_3$, 293 K): $\delta$ = 7.37 (d, 1 H, Ph-*H*), 7.25–7.17 (m, 4 H, Ph-*H*), 7.06 (t, 1 H, Ph-*H*), 6.66 (m, 3 H, Ph-*H*), 4.40 (s, 2 H, C$H_2$N), 3.65 (br., 1 H, N*H*), 3.02 (q, 4 H, NCH$_2$CH$_3$), 1.05 (t, 6 H, NCH$_2$CH$_3$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K): $\delta$ = 148.58, 136.04, 129.12, 127.36, 123.93, 122.62, 118.28, 117.08, 113.61, 112.8, 48.01, 44.69, 12.62 ppm.

***ortho*-C$_6$H$_4$(NMe$_2$)(CH$_2$NC$_6$H$_3$*i*Pr$_2$-2,6)AlMe$_2$ (3a):** $AlMe_3$ (1.0 M in toluene, 2.0 mL, 2.0 mmol) was added to a solution of **2a** (0.62 g, 2.0 mmol) in toluene (20 mL) at –10 °C with stirring. The reaction mixture was gently heated to 80 °C for 24 h. After removal of the solvent, the product was recrystallized from hexane to give the desired complex as a colorless crystalline solid (0.62 g, 84%). $C_{23}H_{35}AlN_2$ (366.52): calcd. C 75.37, H 9.63, N 7.64; found C 75.40, H 9.61, N 7.65. $^1$H NMR (300 MHz, $CDCl_3$, 293 K): $\delta$ = 7.32 (m, 3 H, Ph-*H*), 7.02 (m, 1 H, Ph-*H*), 6.94–6.93 (m, 2 H, Ph-*H*), 6.71 (m, 1 H, Ph-*H*), 4.45 (s, 2 H, C$H_2$N), 3.95 [m, 2 H, C*H*(CH$_3$)$_2$], 2.41 (s, 6 H, NC$H_3$), 1.41 [q, 12 H, CH(C$H_3$)$_2$], –0.63 (s, 6 H, AlC$H_3$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K): $\delta$ = 149.12, 147.93, 145.99, 136.09, 130.60, 127.60, 127.16, 124.87, 124.11, 118.74, 60.74, 44.91, 27.52, 26.23, 25.15, –9.97 ppm.

***ortho*-C$_6$H$_4$(NMe$_2$)(CH$_2$NC$_6$H$_3$Et$_2$-2,6)AlMe$_2$ (3b):** This compound was prepared in the same way as described above for **3a** with **2b** (0.62 g, 2.2 mmol) and $AlMe_3$ (2.2 mL, 2.2 mmol) as starting materials. The product (0.65 g, 87%) was obtained as a colorless crystalline solid. $C_{21}H_{31}AlN_2$ (338.47): calcd. C 74.52, H 9.23, N 8.28; found C 74.39, H 9.32, N 8.34. $^1$H NMR (300 MHz, $CDCl_3$, 293 K): $\delta$ = 7.32–7.28 (m, 3 H, Ph-*H*), 6.99–6.94 (m, 3 H, Ph-*H*), 6.71 (m, 1 H, Ph-*H*), 4.38 (s, 2 H, C$H_2$N), 3.0 (q, 4 H, C$H_2$CH$_3$), 2.40 (s, 6 H, NC$H_3$), 1.38 (t, 6 H, CH$_2$C$H_3$), –0.63 (s, 6 H, AlC$H_3$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K): $\delta$ = 149.64, 146.00, 144.21, 136.13, 130.69, 127.52, 127.10, 126.68, 124.27, 118.73, 59.37, 45.02, 24.50, 16.38, –9.90 ppm.

***ortho*-C$_6$H$_4$(NMe$_2$)(CH$_2$NC$_6$H$_3$Me$_2$-2,6)AlMe$_2$ (3c):** This compound was prepared in the same way as described above for **3a** with **2c** (0.46 g, 1.8 mmol) and $AlMe_3$ (1.8 mL, 1.8 mmol) as starting materials. The product (0.50 g, 89%) was obtained as a colorless crystalline solid. $C_{19}H_{27}AlN_2$ (310.41): calcd. C 73.52, H 8.77, N 9.02; found C 73.50, H 8.75, N 9.00. $^1$H NMR (300 MHz, $C_6D_6$, 293 K): $\delta$ = 7.25 (d, 2 H, Ph-*H*), 7.13 (t, 1 H, Ph-*H*), 6.93 (m, 3 H, Ph-*H*), 6.69 (m, 1 H, Ph-*H*), 4.32 (s, 2 H, C$H_2$N), 2.52 (s, 6 H, NC$H_3$), 2.36 (s, 6 H, C$H_3$), –0.65 (s, 6 H, AlC$H_3$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $C_6D_6$, 293 K): $\delta$ = 150.81, 1415.98, 138.29, 136.26, 130.74, 129.03, 127.40, 127.05, 123.84, 118.62, 57.19, 44.94, 19.57, –9.78 ppm.

***ortho*-C$_6$H$_4$(NMe$_2$)(CH$_2$NC$_6$H$_4$Me-4)AlMe$_2$ (3d):** This compound was prepared in the same way as described above for **3a** with **2d** (0.72 g, 3.0 mmol) and $AlMe_3$ (3.0 mL, 3.0 mmol) as starting materials. The product (0.82 g, 92%) was obtained as a colorless crystalline solid. $C_{18}H_{25}AlN_2$ (296.39): calcd. C 72.94, H 8.50, N 9.45; found C 72.96, H 8.45, N 9.48. $^1$H NMR (300 MHz, $CDCl_3$, 293 K): $\delta$ = 7.37–7.28 (m, 6 H, Ph-*H*), 7.00 (d, 1 H, Ph-*H*), 6.69 (d, 1 H, Ph-*H*), 4.49 (s, 2 H, C$H_2$N), 2.92 (s, 6 H, NC$H_3$), 2.25 (s, 3 H,C$H_3$), –0.85 (s, 6 H, AlC$H_3$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K): $\delta$ = 151.93, 145.32, 134.62, 131.78, 129.62, 128.45, 127.64, 123.77, 118.61, 114.38, 53.87, 44.91, 20.52, –10.20 ppm.

***ortho*-C$_6$H$_4$(NMe$_2$)(CH$_2$NC$_6$H$_5$)AlMe$_2$ (3e):** This compound was prepared in the same way as described above for **3a** with **2e** (0.56 g, 2.5 mmol) and $AlMe_3$ (2.5 mL, 2.5 mmol) as starting materials. The product (0.66 g, 93%) was obtained as a colorless crystalline solid. $C_{17}H_{23}AlN_2$ (282.36): calcd. C 72.31, H 8.21, N 9.92; found C 72.35, H 8.25, N 9.83. $^1$H NMR (300 MHz, $CDCl_3$, 293 K): $\delta$ = 7.37–7.30 (m, 4 H, Ph-*H*), 7.20 (t, 2 H, Ph-*H*), 6.77 (d, 2 H, Ph-*H*), 6.62 (t, 1 H, Ph-*H*), 4.50 (s, 2 H, C$H_2$N), 2.93 (s, 6 H, NC$H_3$), –0.84 (s, 6 H, AlC$H_3$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K): $\delta$ = 154.03, 154.01, 134.13, 131.53, 128.79, 128.27, 127.41, 118.37, 114.66, 114.26, 53.39, 44.64, –10.51 ppm.

***ortho*-C$_6$H$_4$(NEt$_2$) (CH$_2$NC$_6$H$_3$*i*Pr$_2$-2,6)AlMe$_2$ (3f):** This compound was prepared in the same way as described above for **3a** with **2f** (0.34 g, 1.0 mmol) and $AlMe_3$ (1.0 mL, 1.0 mmol) as starting materials. The product (0.36 g, 92%) was obtained as a colorless crystalline solid. $C_{25}H_{39}AlN_2$ (394.57): calcd. C 76.10, H 9.96, N 7.10; found C 76.15, H 9.93, N 7.18. $^1$H NMR (300 MHz, $CDCl_3$, 293 K): $\delta$ = 7.51 (d, 1 H, Ph-*H*), 7.36 (m, 3 H, Ph-*H*), 7.24–7.11 (m, 3 H, Ph-*H*), 4.35 (s, 2 H, C$H_2$N), 3.69 [m, 2 H, C*H*(CH$_3$)$_2$], 3.50 (m, 4 H, NC$H_2$CH$_3$), 1.25 [d, 12 H, CH(C$H_3$)$_2$], 1.19 (t, 6 H, NCH$_2$C$H_3$), –1.04 (s, 6 H, AlCH$_3$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K): $\delta$ = 149.52, 142.84, 135.82, 130.81, 129.45, 127.56, 126.67, 124.31, 123.15, 121.69, 60.81, 44.40, 27.14, 25.92, 24.38, 9.20, –8.52 ppm.

***ortho*-C$_6$H$_4$(NEt$_2$) (CH$_2$NC$_6$H$_3$Me$_2$-2,6)AlMe$_2$ (3g):** This compound was prepared in the same way as described above for **3a** with **2g** (0.42 g, 1.5 mmol) and $AlMe_3$ (1.5 mL, 1.5 mmol) as starting materials. The product (0.44 g, 87%) was obtained as a colorless crystalline solid. $C_{21}H_{31}AlN_2$ (338.47): calcd. C 74.52, H 9.23, N 8.28; found C 74.48, H 9.27, N 8.23. $^1$H NMR (300 MHz, $CDCl_3$, 293 K): $\delta$ = 7.32 (d, 1 H, Ph-*H*), 7.29 (t, 1 H, Ph-*H*), 7.24 (m, 2 H, Ph-*H*), 7.05 (d, 2 H, Ph-*H*), 6.91 (t, 1 H, Ph-*H*), 4.34 (s, 2 H, C$H_2$N), 3.55 (m, 4 H, NC$H_2$CH$_3$), 2.31 (s, 6 H, C$H_3$), 1.20 (t, 6 H, NCH$_2$C$H_3$), –1.03 (s, 6 H, AlC$H_3$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K): $\delta$ = 150.84, 143.42, 138.32, 136.09, 130.89, 128.20, 126.94, 126.59, 123.02, 121.66, 57.30, 44.40, 19.18, 9.06, –8.25 ppm.

***ortho*-C$_6$H$_4$(NEt$_2$) (CH$_2$NC$_6$H$_5$)AlMe$_2$ (3h):** This compound was prepared in the same way as described above for **3a** with **2h** (0.51 g, 2.0 mmol) and $AlMe_3$ (2.0 mL, 2.0 mmol) as starting materials. The product (0.52 g, 84%) was obtained as a colorless crystalline solid. $C_{19}H_{27}AlN_2$ (310.41): calcd. C 73.52, H 8.77, N 9.02; found C 73.56, H 8.73, N 9.07. $^1$H NMR (300 MHz, $CDCl_3$, 293 K): $\delta$ =

7.37–7.23 (m, 4 H, Ph-*H*), 7.17 (t, 2 H, Ph-*H*), 6.75–6.63 (m, 3 H, Ph-*H*), 4.43 (s, 2 H, C$H_2$N), 3.42 (m, 4 H, NC$H_2$CH$_3$), 1.15 (t, 6 H, NCH$_2$C$H_3$) –0.79 (s, 6 H, AlC$H_3$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 293 K): $\delta$ = 146.88, 135.25, 131.90, 129.27, 128.92, 127.61, 127.15, 114.76, 114.67, 90.49, 53.96, 47.48, 10.23, –8.24 ppm.

***ortho*-C$_6$H$_4$(NMe$_2$)(CH$_2$NC$_6$H$_3$*i*Pr$_2$-2,6)Al-(OCH$_2$C$_6$H$_5$)$_2$ (4):** To a solution of **3a** (0.37 g, 1.0 mmol) in toluene (20 mL) was added BnOH (1.0 M in toluene, 2.0 mL, 2.0 mmol) at –10 °C. The reaction mixture was allowed to gently warm to room temperature and stirred for 1 h. After removal of the solvent, the crude product was recrystallized from *n*-hexane to give the pure product as a colorless crystalline solid (0.50 g, 90%). $C_{35}H_{43}AlN_2O_2$ (550.71): calcd. C 76.33, H 7.87, N 5.09; found C 76.28, H 7.83, N 5.16. $^1$H NMR (300 MHz, $CDCl_3$, 293 K): $\delta$ = 7.46–7.08 (m, 17 H, Ph-*H*), 5.01 (s, 4 H, OC$H_2$), 4.08 (s, 2 H, C$H_2$N), 3.42 [m, 2 H, C*H*(CH$_3$)$_2$], 2.74 (s, 6 H, NC$H_3$), 1.28 [d, 12 H, CH(C$H_3$)$_2$] ppm. $^{13}$C{$^1$H} NMR (75 MHz, $C_6D_6$, 293 K): $\delta$ = 152.87, 143.63, 142.69, 130.05, 129.69, 128.73, 128.68, 128.21, 128.15, 124.01, 123.60, 123.49, 120.02, 90.35, 67.15, 53.01, 45.31, 27.50, 24.34 ppm.

**General Procedure for the Polymerization of CL:** To a rapidly stirred solution of CL in toluene (the amounts of CL and toluene were calculated based on the conditions given in Table 2) was added a solution of a catalyst (0.19 mmol) and appropriate amount of BnOH in toluene (5 mL) under a nitrogen atmosphere at the desired temperature. After the reaction mixture was stirred for a prescribed period or until the reaction mixture became very viscous and could not be stirred, the reaction was quenched by the addition of an excess amount of aqueous acetic acid (1.0 N). The polymer was then precipitated by adding MeOH (100 mL) into the mixture, collected on a frit, washed with MeOH (3 × 10 mL), and dried in vacuo up to a constant weight.

**Crystal Structure Determination:** Single crystals of **3c** and **3e** suitable for X-ray structural analysis were obtained from *n*-hexane at –20 °C. Diffraction data of **3c** were collected at 293 K with a Rigaku R-AXIS RAPID IP diffractometer equipped with graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å). Diffraction data of **3e** was collected at 293 K with a Bruker SMART-CCD diffractometer equipped with graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å). Details of the crystal data, data collections, and structure refinements are summarized in Table 3. The structures were solved by direct methods and refined by full-matrix least-squares on *F*2. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in idealized position. All calculations were performed using the SHELXTL[17] crystallographic software packages. CCDC-703530 (for **3c**) and -703531 (for **3e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Supporting Information** (see footnote on the first page of this article): Molecular structure of **3e**.

Table 3. Crystal data and structural refinements details for **3c** and **3e**.

| | **3c** | **3e** |
|---|---|---|
| Formula | $C_{19}H_{27}AlN_2$ | $C_{17}H_{23}AlN_2$ |
| *Fw* | 310.41 | 282.35 |
| Crystal system | orthorhombic | monoclinic |
| Space group | $P2_12_12_1$ | $P2_1/c$ |
| *a* [Å] | 7.9459(16) | 17.3507(13) |
| *b* [Å] | 15.360(3) | 12.5371(9) |
| *c* [Å] | 15.453(3) | 16.7569(12) |
| $\alpha$ [°] | 90 | 90 |
| $\beta$ [°] | 90 | 117.9610(10) |
| $\gamma$ [°] | 90 | 90 |
| *V* [Å$^3$] | 1886.0(7) | 3219.6(4) |
| *Z* | 4 | 8 |
| $D_{calcd.}$ [gcm$^{-3}$] | 1.093 | 1.165 |
| *F*(000) | 672 | 1216 |
| $\Theta$ range for data collection | 3.17 to 27.48° | 1.33 to 26.03° |
| Limiting indices | $-10 \le h \le 9$ | $-21 \le h \le 21$ |
| | $-19 \le k \le 19$ | $-15 \le k \le 6$ |
| | $-19 \le l \le 19$ | $-20 \le l \le 20$ |
| No. of data/restraints/parameters | 4224/0/205 | 6344/0/369 |
| Goodness-of-fit on $F^2$ | 0.911 | 1.023 |
| Final *R* indices $I > 2\sigma(I)$ | $R_1$[a] = 0.0594 | $R_1$[a] = 0.0549 |
| | $wR_2$[b] = 0.0816 | $wR_2$[b] = 0.1214 |
| *R* indices (all data) | $R_1$[a] = 0.1714 | $R_1$[a] = 0.0811 |
| | $wR_2$[b] = 0.1067 | $wR_2$[b] = 0.1345 |
| $R_{int}$ | 0.1456 | 0.0414 |

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$.

## Acknowledgments

This work was supported by the National Natural Science Foundation of China (Nos. 20772044 and 20674024).

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Received: February 16, 2009
Published Online: July 15, 2009

  