Syntheses of Mononuclear and Dinuclear Aluminum Complexes Stabilized by Phenolato Ligands and Their Applications in the Polymerization of ε-Caprolactone: A Comparative Study

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S *Supporting Information*

ABSTRACT: A series of mono- and dinuclear aluminum alkyl complexes stabilized by phenolato ligands have been prepared through alkane elimination reactions. Treatment of piperazidine-bridged bis(phenol)s $C_4H_8N_2[1,4-(2-OH-3,5-Me_2-C_6H_2CH_2)_2]$ $(H_2[ONNO]^1)$, $C_4H_8N_2[1,4-(2-OH-3-^tBu-5-Me-C_6H_2CH_2)_2]$ $(H_2[ONNO]^2)$, and $C_4H_8N_2[1,4-(2-OH-3,5-^tBu_2-C_6H_2CH_2)_2]$ $(H_2[ONNO]^3)$ with 2.5−3 equiv of AlR_3 (R = Me, Et) afforded dinuclear aluminum complexes $(AlMe_2)_2[ONNO]^1$ (1), $(AlMe_2)_2[ONNO]^2$ (2), $(AlMe_2)_2[ONNO]^3$ (3), $(AlEt_2)_2[ONNO]^1$ (4), $(AlEt_2)_2[ONNO]^2$ (5), and $(AlEt_2)_2[ONNO]^3$ (6), respectively. In order to compare the catalytic activities of these bimetallic complexes with their mononuclear counterparts, mono(phenolato) aluminum complexes $AlMe_2[ON]^1$ (7), $AlMe_2[ON]^2$ (8), $AlMe_2[ON]^3$ (9), $AlEt_2[ON]^2$ (10), and $AlEt_2[ON]^3$ (11) were synthesized from reactions of 1 equiv of $AlMe_3$ or 2 equiv of $AlEt_3$ with phenols that bear piperidine moieties, i.e., $[2-(CH_2NC_5H_{10})-4,6-Me_2-C_6H_2OH$ $(H[NO]^1)$, $2-(CH_2NC_5H_{10})-4-Me-6-^tBu-C_6H_2OH$ $(H[NO]^2)$, and $2-(CH_2NC_5H_{10})-4,6-^tBu_2-C_6H_2OH$ $(H[NO]^3)]$, respectively. In comparison, reactions of $H[NO]^n$ (n = 2, 3) with 0.5 equiv of $AlEt_3$ led to the isolation of mononuclear monoalkyl complexes $AlEt[NO]^2_2$ (12) and $AlEt[NO]^3_2$ (13), respectively. All complexes have been characterized by elemental analysis and NMR spectroscopy, and the solid state structures of 5 complexes have been determined by X-ray diffraction analysis. The activities of both binuclear and mononuclear aluminum complexes in initiating the ring-opening polymerization (ROP) of ε-caprolactone have also been investigated and compared. In general, these phenolato-Al complexes showed high activities in initiating the ROP in the absence of alcohols. More importantly, dinuclear complexes have been found to be 2−8 times more active than their mononuclear counterparts, which provides evidence for the cooperation between two metal centers in the former.
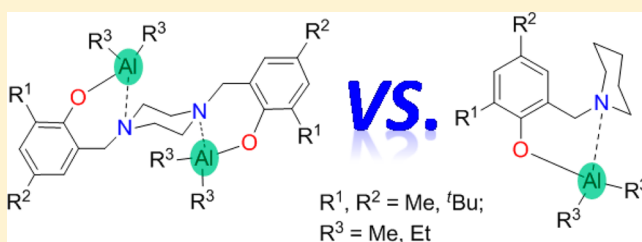
INTRODUCTION

Bimetallic complexes supported by binucleating ligands have been a focus of current research as they not only possess diverse structures but also find wide applications in catalysis. Superior to mononuclear systems, bimetallic architectures facilitate the cooperation between two metal centers under certain circumstances, which have been proven critical in improving their activities in mediating organic transformations[1] and polymerizations.[2] To control and tune this synergistic process, it is important to explore different binucleating ligands to modify the steric and electronic features of resulting complexes.[3] To date, a large number of binucleating ligands, such as bridged bis(amidinato),[4] bis(diketiminato),[5] and bis(indenyl)[6] ligands, have been employed to stabilize bimetallic complexes. Some of them indeed have demonstrated promising catalytic activity and/or selectivity in homogeneous catalysis in comparison with their monometallic counterparts,

as exemplified by pioneering work by Marks et al. on bimetallic catalysts for ethylene polymerization[7] and other reactions.[6,8]

Bridged bis(phenolato) ligands are useful and potentially binucleating ancillary ligands with attractive features.[9] For instance, they are easily available and tunable, which allows systematic study on the relationship between ligands and catalytic activities of pertinent metal complexes. Moreover, they are capable of stabilizing a wide range of metal centers, and forming complexes of versatile structures. Both mono-[10] and dinuclear[11] aluminum complexes supported by such ligands have been studied. Although there are reports on the cooperation between two aluminum centers stabilized by a single-frame bis(phenolato) ligand, detailed studies and direct comparisons are still limited.[11a,c,g,h,j] We have recently

communicated that piperazidine-bridged bis(phenolato) ligands were used to stabilize dinuclear aluminum alkyl complexes, which were found to be highly active for the ring-opening polymerization (ROP) of ε-caprolactone (ε-CL).[12] Encouraged by these findings, we moved on to explore whether cooperative behaviors exist in such systems, and to search for initiators of higher activity for ε-CL polymerization. Therefore, a series of dinuclear aluminum alkyl complexes carrying bis(phenolato) ligands of different steric and electronic properties, and related mononuclear aluminum complexes as their "half units", were prepared, which made direct comparison possible. Activities of all these complexes in initiating the polymerization of ε-CL were thus studied and compared, which revealed profound cooperation of two aluminum centers in dinuclear systems.

■ RESULTS AND DISCUSSION

Bimetallic Aluminum Complexes 1−6. As communicated earlier, the alkane elimination reaction of 3 equiv of AlR$_3$ (R = Me, Et) with the piperazidine-bridged bis(phenolato) ligand precursor H$_2$[ONNO][1] (R$_1$ = R$_2$ = Me) in THF gave rise to bimetallic aluminum alkyl complexes **1** and **4** in good yields of 85% and 69%, respectively (Scheme 1).[12]

Scheme 1. Synthesis of Bimetallic Aluminum Complexes 1−6
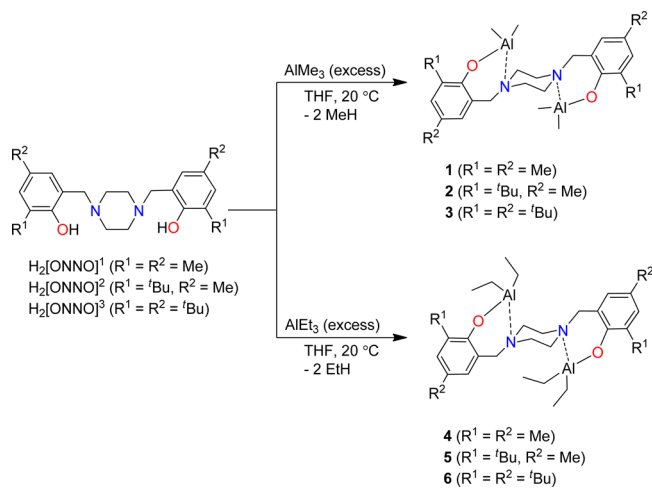
This straightforward strategy was then extended to ligands of different steric bulk. Treatment of ligand precursors H$_2$[ONNO][2] (R$_1$ = ^{t}Bu, R$_2$ = Me) and H$_2$[ONNO][3] (R$_1$ = R$_2$ = ^{t}Bu) with AlMe$_3$ in a 1:2.5 molar ratio afforded bimetallic aluminum methyl complexes (AlMe$_2$)$_2$[ONNO][2] (**2**) and (AlMe$_2$)$_2$[ONNO][3] (**3**) in good yields of 83% and 85%, respectively (Scheme 1). In analogy, these ligand precursors reacted with AlEt$_3$ yielding aluminum ethyl complexes (AlEt$_2$)$_2$[ONNO][2] (**5**) and (AlEt$_2$)$_2$[ONNO][3] (**6**) in 78% and 82% yields, respectively (Scheme 1).

All complexes have been characterized by elemental analyses and NMR spectroscopy. In their ^{1}H NMR spectra, only one set of signals for the two phenolate moieties are observed, suggesting symmetric structures of these complexes in solution. The disappearance of the O−H signals of the ligand precursors corroborates the successful deprotonation. Moreover, the appearance of resonances for the methyl and ethyl groups in the high-field region (1.59 to −0.71 ppm) supports the incorporation of alkyl groups in the complexes. Benzylic

protons are found to be resonating as singlets in the range 3.95−3.14 ppm, and signals assignable to the piperazidine protons appear in the region 3.15−1.89 ppm.

Complexes **1−6** are all sensitive to air and moisture. Their crystals decomposed within a few minutes when exposed to air, but neither the crystals nor the solution showed any sign of decomposition after several months when stored under argon. They show similar solubilities and are all soluble in THF, moderately soluble in toluene, and slightly soluble in aliphatic solvents such as hexane and pentane.

The solid state structures of bimetallic aluminum complexes **1−4** and **6** were unambiguously confirmed by X-ray diffraction analysis on single crystals. The structures of **2** and **3** are depicted in Figures 1 and 2, respectively, and those of **1**, **4**,[12]
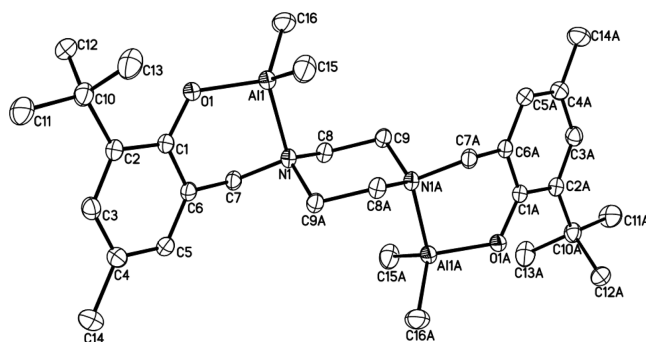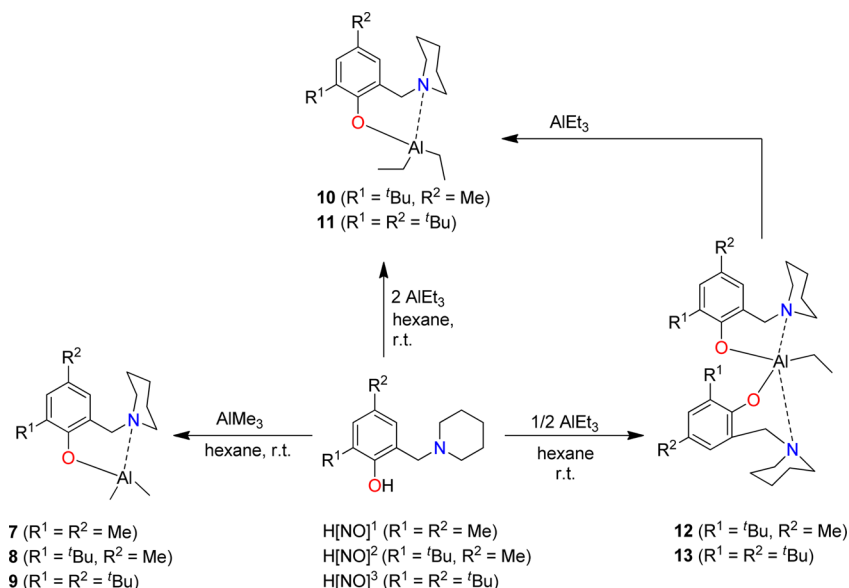
Figure 1. ORTEP diagram of complex **2**·THF. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and THF molecules are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Al1−O1 1.7583(14), Al1−C16 1.953(3), Al1−C15 1.957(2), Al1−N1 2.0722(16), O1−C1 1.354(2); O1−Al1−C16 111.63(9), O1−Al1−C15 110.44(10), C16−Al1−C15 115.93(13), O1−Al1−N1 98.07(6), C16−Al1−N1 108.66(9), C15−Al1−N1 110.64(9).

and **6**[11a] have been reported in previous publications. All complexes possess symmetric bimetallic structures. The piperazidine ring adopts a chair conformation, which is
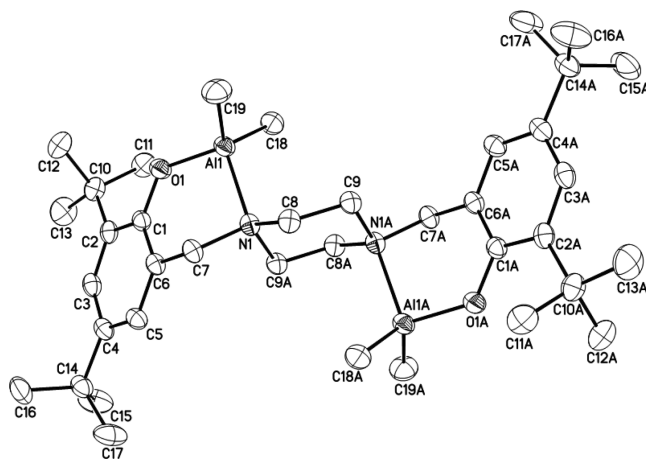
Figure 2. ORTEP diagram of complex **3**. Thermal ellipsoids are drawn at the 20% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Al1−O1 1.7504(13), Al1−C18 1.952(2), Al1−C19 1.957(2), Al1−N1 2.0692(16), O1−C1 1.349(2); O1−Al1−C18 110.42(9), O1−Al1−C19 113.34(9), C18−Al1−C19 116.19(11), O1−Al1−N1 96.65(6), C18−Al1−N1 111.85(8), C19−Al1−N1 106.62(9).

Scheme 2. Synthesis of Monometallic Aluminum Complexes 7−13

7 (R^1 = R^2 = Me)
8 (R^1 = ^{t}Bu, R^2 = Me)
9 (R^1 = R^2 = ^{t}Bu)

10 (R^1 = ^{t}Bu, R^2 = Me)
11 (R^1 = R^2 = ^{t}Bu)

H[NO]^1 (R^1 = R^2 = Me)
H[NO]^2 (R^1 = ^{t}Bu, R^2 = Me)
H[NO]^3 (R^1 = R^2 = ^{t}Bu)

12 (R^1 = ^{t}Bu, R^2 = Me)
13 (R^1 = R^2 = ^{t}Bu)

consistent with a previously reported bimetallic yttrium complex of ligand [ONNO]^3.[13] Each of the aluminum centers is coordinated by two carbon atoms from two alkyl groups, as well as one oxygen atom and one nitrogen atom from the piperazidine-bridged bis(phenolato) ligand to form a distorted tetrahedral geometry. The Al−O, Al−N, and average Al−C bond lengths fall in a similar range of reported data.[10a,b,l,11a] The Al−C bonds in aluminum methyl complexes **1−3** [1.954(7), 1.955(3), and 1.958(7) Å] are shorter than those in ethyl complexes **4** [1.961(3) and 1.964(3) Å][12] and **6** [1.9687(18) and 1.9632(18) Å].[11a] For the aluminum methyl complexes **1−3**, the Al−O bonds get shorter as the substituents of the ligands get more electron donating [**1**, 1.7687(13) Å; **2**, 1.7583(14) Å; **3**, 1.7504(13) Å].

Monometallic Aluminum Complexes 7−13. In order to compare the catalytic activities of bimetallic complexes **1−6** with their "half units", we attempted to synthesize mononuclear aluminum complexes bearing chelating phenolato ligands.

The ligand precursors H[NO]^1, H[NO]^2, and H[NO]^3 were treated with AlMe$_3$ in a 1:1 molar ratio in hexane, and mono(phenolato) aluminum complexes AlMe$_2$[ON]^1 (**7**), AlMe$_2$[ON]^2 (**8**), and AlMe$_2$[ON]^3 (**9**) were isolated in moderate to good yields of 53−78%, respectively (Scheme 2).

In the ^{1}H NMR spectra of aluminum methyl complexes **7−9**, the benzylic protons resonate as singlets in the range 3.40−3.25 ppm, respectively. The signals corresponding to the methyl groups bound to the aluminum centers were found in the upfield region of −0.26 to −0.39 ppm. In their ^{13}C NMR spectra, resonances at around −9.0 ppm are assigned to the methyl groups.

However, treatment of the ligand precursor H[NO]^1 with 1 equiv of AlEt$_3$ led to ill-defined species. Reaction between H[NO]^2 and AlEt$_3$ in a 1:1 molar ratio in hexane gave rise to a mixture of expected aluminum diethyl complex **10** as well as bis(phenolato) aluminum monoethyl complex **12** in a 2:1 ratio (Scheme 2), as evidenced by its ^{1}H NMR spectrum (Figure 3, middle). The two doublets (marked with #) centered at 4.09 and 3.56 ppm are assigned to the diastereotopic benzylic protons of **12**, while the singlet (marked with *) at 3.30 ppm corresponds to the same group of **10**. It is speculated that the

aluminum diethyl complex **10** formed first, and one of its basic ethyl groups removed the proton of excess ligand precursor H[NO]^2. The resulting phenolato ligand thus bound to the complex fragment to form complex **12**. Further study on different reaction conditions revealed that **12** was preferred when H[NO]^2 reacted with 0.5 equiv of AlEt$_3$, while **10** formed exclusively in the yield of 65% when the ratio was adjusted to 1:2. This finding clearly demonstrates the basicity difference between methyl and ethyl groups, as the methyl groups of complex **8** could not further deprotonate H[NO]^2. A similar observation has been reported by Fulton et al.[11a]

In the ^{1}H NMR spectrum of complex **12** (Figure 3, top), besides the two doublets corresponding to the benzylic group (*vide supra*), the protons of the methylene group coordinated to the aluminum center are also diastereotopic, and give rise to two quartets at 0.47 and 0.34 ppm, respectively. The methyl group resonates as a pseudotriplet at 1.31 ppm. Moreover, their integration is in the ratio of 1:2 to that of the phenolato ligand, supporting that complex **12** bears two phenolato ligands and one ethyl group.

In the ^{1}H NMR spectrum of complex **10** (Figure 3, bottom), two signals are observed at 1.46 and 0.23 ppm, respectively, corresponding to the coordinating ethyl groups. Their integration is also consistent with the composition of **10**.

Reactions of H[NO]^3 with different amounts of AlEt$_3$ gave the same results. When the ligand precursor was treated with 2 equiv of AlEt$_3$, mono(phenolato) aluminum complex AlEt$_2$[ON]^3 (**11**) was isolated in 59% yield (Scheme 2). On the other hand, reaction with 0.5 equiv of AlEt$_3$ afforded bis(phenolato) aluminum monoethyl complex AlEt[ON]$^3_2$ (**13**) in 65% yield. In addition, further reaction of **13** with 1 equiv of AlEt$_3$ also led to the isolation of AlEt$_2$[ON]^3 (**11**). In the ^{1}H NMR spectra of complexes **11** and **13**, signals of the benzyl and ethyl groups show patterns similar to those of complexes **10** and **12**, respectively, and do not require further comments.

Similar to complexes **1−6**, complexes **7−13** are also air and moisture sensitive, and both their crystals and solutions are stable when stored under argon. They show good solubility in solvents such as THF, toluene, and hexane.
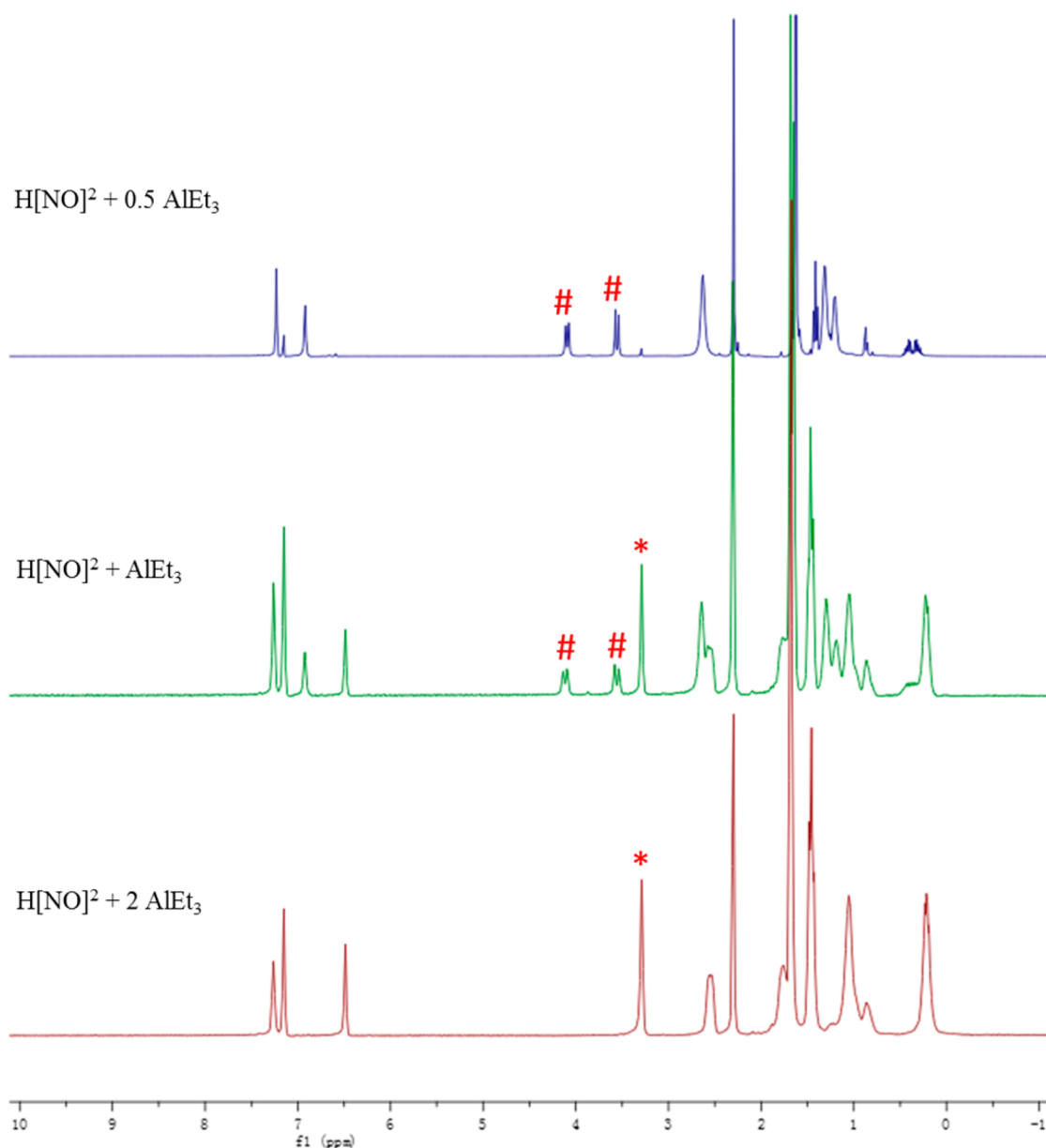
Figure 3. ^{1}H NMR spectra of products from reactions of H[NO]^2 with different amounts of AlEt$_3$. Signals marked with # are due to the benzylic protons of complex **12**, while those marked with * correspond to the benzylic protons of complex **10**.

The molecular structures of complexes **7**, **10**, and **13** were finally confirmed by X-ray diffraction analysis on single crystals. The aluminum center in complex **7** is coordinated by one chelating phenolato ligand and two methyl groups in a distorted tetrahedral manner (Figure 4). The Al−C bond distances amount to 1.957(3) and 1.956(3) Å, respectively, which are comparable with those in complex **1** [1.957(2) and 1.960(2) Å]. The length of the Al−O bond [1.7628(17) Å] is also identical to that in complex **1** [1.7687(13) Å] within 3σ, while the Al−N bond becomes shorter [**1**, 2.0868(15) Å; **7**, 2.0564(16) Å] as a result of replacing piperazidine with piperidine. Similar to complex **7**, there are one chelating phenolato ligand and two ethyl groups which form a distorted tetrahedral geometry in complex **10** (Figure 5).

Complex **13** also adopts a distorted tetrahedral geometry, in which one phenolato ligand coordinates to the Al center in a chelating manner, while the other phenolato ligand coordinates through the oxygen atom (Figure 6). One ethyl ligand takes up the fourth coordination site. The length of Al1−O1 amounts to 1.740(3) Å, which is slightly longer than Al1−O2 (1.724(3) Å).

Polymerization Studies. Although dinuclear aluminum alkyl complexes stabilized by bis(phenolato) ligands have been reported and studied in the polymerization of ε-CL,[11a−d,f,j,k] direct comparison of dinuclear complexes with their mononuclear counterparts remains rare.[11a,c,j] The activities of dinuclear aluminum complexes **1**−**6**, as well as monometallic complexes **7**−**11** in the polymerization of ε-CL, are thus investigated and compared to elucidate the influence of the binuclear architectures. All complexes were first tested at 70 °C in toluene with the monomer to Al ratio 200:1, and the results obtained after 4 h reaction showed that in general these bimetallic complexes are active under relatively mild conditions, with moderate to good yields of 34−92% obtained (Table 1). On the basis of the standard raised by Redshaw et al., they show moderate activities.[14] It is noteworthy that in all circumstances no additional alcohol was required in order to get decent
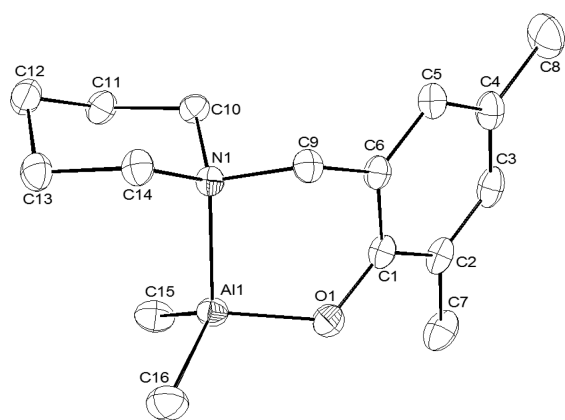
Figure 4. ORTEP diagram of complex **7**. Thermal ellipsoids are drawn at the 20% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Al1−O1 1.7628(17), Al1−C16 1.957(3), Al1−C15 1.956(3), Al1−N1 2.0564(17), O1−C1 1.347(3); O1−Al1−C16 110.91(11), O1−Al1−C15 109.91(12), C15−Al1−C16 116.32(13), O1−Al1−N1 98.17(8), C15−Al1−N1 112.84(10), C16−Al1−N1 107.19(10).
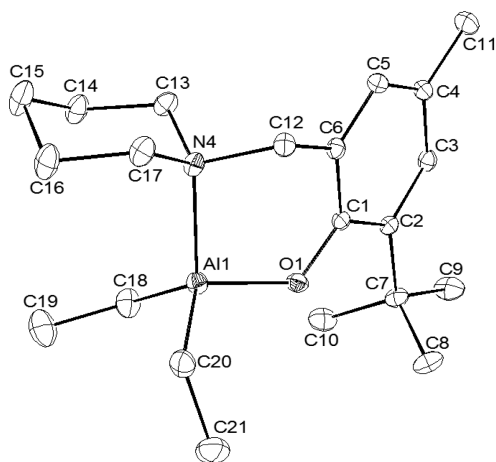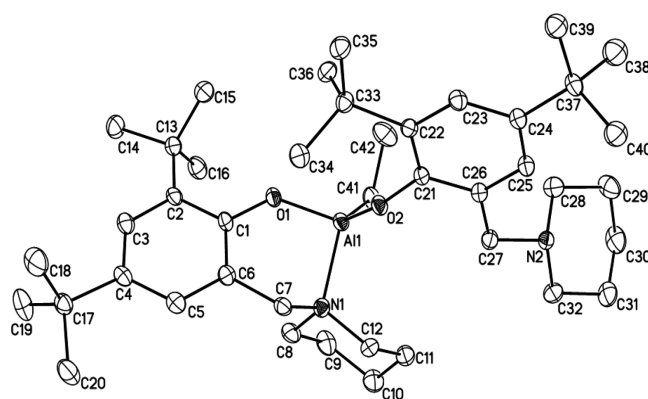

Figure 5. ORTEP diagram of complex **10**. Thermal ellipsoids are drawn at the 20% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Al1−O1 1.7613(14), Al1−C20 1.970(2), Al1−C18 1.969(2), Al1−N4 2.0433(17), O1−C1 1.346(2); O1−Al1−C20 109.89(8), O1−Al1−C18 109.80(8), C20−Al1−C18 114.31(10), O1−Al1−N4 97.50(7), C20−Al1−N4 108.50(13), C18−Al1−N4 115.18(9).

Figure 6. ORTEP diagram of complex **13**. Thermal ellipsoids are drawn at the 20% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Al1−O2 1.724(3), Al1−O1 1.740(3), Al1−C41 1.944(5), Al1−N1 2.013(4), O1−C1 1.356(5), O2−C21 1.359(5); O2−Al1−O1 113.40(15), O2−Al1−C41 116.57(19), O1−Al1−C41 108.79(19), O2−Al1−N1 100.37(16), O1−Al1−N1 94.54(15), C41−Al1−N1 121.2(2).

Table 1. Polymerization of ε-CL Initiated by Complexes 1−11[a]

entry	initiator	CL:Al	T (°C)	time (h)	yield[b] (%)	M_n[c] (×10⁴)	PDI[c]
1	1	400:2	70	4	44	3.93	1.47
2	2	400:2	70	4	64	10.55	1.81
3	3	400:2	70	4	59	14.18	2.04
4	4	400:2	70	4	34	7.98	1.98
5	5	400:2	70	4	92	16.52	1.89
6	6	400:2	70	4	72	17.28	2.03
7	7	200:1	70	4	20	8.58	1.67
8	7	200:1	70	10	77	9.69	1.84
9	7	200:1	70	12	93	11.46	1.99
10	8	200:1	70	10	37	8.44	1.69
11	8	200:1	70	24	87	14.41	1.93
12	9	200:1	70	10	53	9.11	1.98
13	9	200:1	70	24	97	12.43	1.87
14	10	200:1	70	10	27	6.11	1.93
15	10	200:1	70	24	75	13.17	1.94
16	11	200:1	70	10	32	8.97	1.96
17	11	200:1	70	24	73	13.90	1.76

[a]Polymerization conditions: toluene as solvent, $[ε\text{-CL}]_0$ = 1 mol/L; N_2 atmosphere. [b]Yield: weight of polymer obtained/weight of monomer used. [c]Measured by GPC in THF calibrated with standard polystyrene samples and corrected by a factor of 0.56.

conversions.[15] However, polymers of relatively broad distribution (PDI = 1.47−2.04) were obtained, which implies that the polymerization process is not well under control.

Comparison of activities of different complexes revealed substantial differences (Table 1). In general, dinuclear aluminum ethyl complexes showed higher activities than their methyl counterparts (Table 1, entries 5 vs 2, 6 vs 3). Moreover, complexes **2** and **5** bearing ligands of moderate steric bulk are more active than their respective analogues, i.e., complexes **1** and **3** or **4** and **6** (Table 1, entries 1−3 and 4−6).

Mononuclear complexes showed poorer activities and gave rise to lower yields of 20−50% after 4−10 h reaction under otherwise the same conditions (Table 1, entries 7, 10, 12, 14, and 16). Prolonging the reaction time to 12−24 h led to improved yields of 73−97% (Table 1, entries 9, 11, 13, 15, 17). These findings clearly imply that mononuclear complexes are

far less efficient than the dinuclear analogues (Table 1, entries 1 vs 7, 2 vs 10, 3 vs 12, 5 vs 14, 6 vs 16).

The addition of alcohol usually leads to dramatically accelerated polymerization process yielding polymers of narrower PDIs.[12] Indeed, at a lower temperature of 60 °C, good yields of 91−98% were obtained in the presence of EtOH with the monomer to Al ratio amounting to 1000:1 (Table 2). The bimetallic complex **5** still outperformed the mononuclear analogue **10**. Moreover, polymers of smaller PDIs were obtained, implying a better control exerted by the initiators. It is thus deduced that the number of initiating groups on average in the bimetallic complex **5** is 2 times those in the monometallic complex **10**. This finding rules out the possibility that the activity difference arises from different numbers of

Table 2. Polymerization of ε-CL Initiated by Complexes 5 and 10[a]

entry	initiator	CL:Al:EtOH	T (°C)	time (h)	yield[b] (%)	M_c^c (×10⁴)	M_n^d (×10⁴)	PDI[d]	no. of initiating groups
1	**5**	2000:2:2	60	6	98	11.17	13.69	1.28	1.63
2	**5**	2000:2:4	60	6	96	5.47	7.3	1.18	3.02
3	**10**	1000:1:1	60	6	93	10.6	17.21	1.37	0.62
4	**10**	1000:1:2	60	6	91	5.19	7.7	1.27	1.35

[a]Polymerization conditions: toluene as solvent, $[ε\text{-CL}]_0 = 1$ mol/L; N_2 atmosphere. [b]Yield: weight of polymer obtained/weight of monomer used. [c]$M_c = 114.14 \times ([ε\text{-CL}]_0:[\text{initiator}]_0) \times ([\text{initiator}]_0:[\text{EtOH}]_0) \times$ yield %. [d]Measured by GPC in THF calibrated with standard polystyrene samples and corrected by a factor of 0.56.
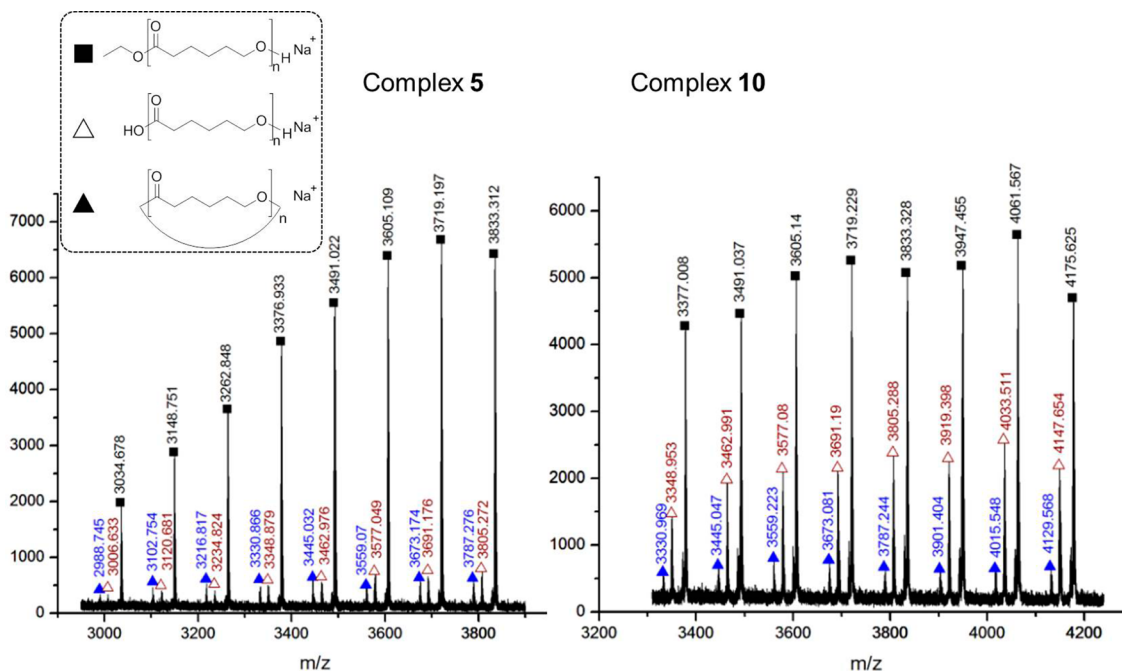
Figure 7. MALDI-TOF mass spectra of oligomers initiated by complex **5** (left) and **10** (right) in the presence of EtOH.

initiating groups per Al center, which provides further evidence for the cooperation in the dinuclear system.

End group analysis by MALDI-TOF-MS on oligomers prepared in the presence of mixtures of EtOH and **5** or **10** was performed. The results show the presence of OEt capped oligomers as the major component in both cases (Figure 7). A small amount of cyclic and OH capped oligomers was also detected.

To gain more insights into the polymerization process, a kinetic study was carried out with dinuclear complex **5** and its mononuclear counterpart **10**, respectively. Polymerization at temperatures of 50−90 °C was conducted, and the yields were determined at stated intervals (Supporting Information Table S1 and S2). In all cases, the plots of $\ln[ε\text{-CL}]_0/[ε\text{-CL}]_t$ as a function of time at different temperatures exhibit a good linear relationship (Figures 8 and 9), and imply a first-order disappearance of the monomer concentration. The rate law of $-\text{d}[ε\text{-CL}]/\text{dt} = k_{app}[ε\text{-CL}]_t$ is suggested, whereas k_{app} denotes the apparent polymerization rate constant.

Under identical conditions, the ROP of ε-CL initiated by either dinuclear **5** or mononuclear **10** proceeded at different rates, as demonstrated by corresponding k_{app} values (Figures 8 and 9). At 50−70 °C, the polymerization mediated by **5** was around 4−8 times faster than that by **10**. Further increasing the reaction temperature led to a dramatic improvement in the polymerization rates in both cases. And at 90 °C the polymerization initiated by **5** is still 2 times faster than that
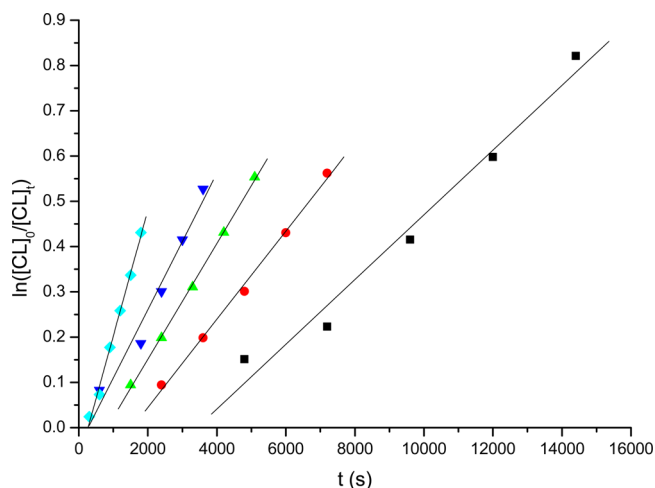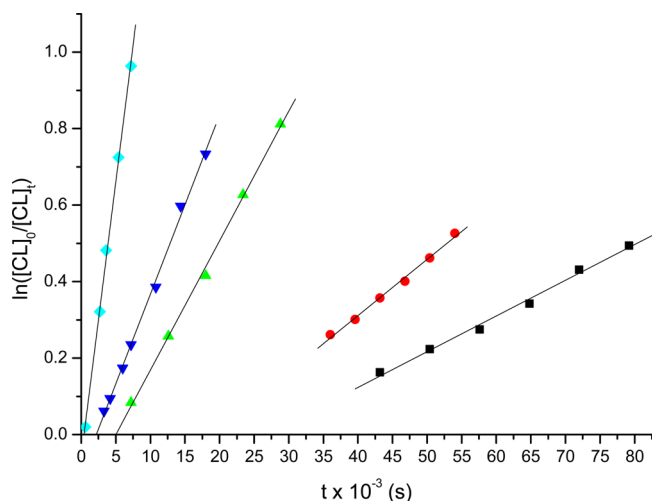

Figure 8. Semilogarithmic plots of the polymerization of ε-CL initiated by complex **5** at different temperatures. Polymerization conditions: toluene as solvent, $[ε\text{-CL}]_0 = 1$ mol/L; CL:Al = 400:2; N_2 atmosphere. Black ■: 50 °C, $k_{app} = (7.15 \pm 0.64) \times 10^{-5}$ s⁻¹, $R^2 = 0.988$. Red ●: 60 °C, $k_{app} = (9.73 \pm 0.35) \times 10^{-5}$ s⁻¹, $R^2 = 0.998$. Green ▲:70 °C, $k_{app} = (1.28 \pm 0.02) \times 10^{-4}$ s⁻¹, $R^2 = 0.999$. Dark blue ▼: 80 °C, $k_{app} = (1.51 \pm 0.16) \times 10^{-4}$ s⁻¹, $R^2 = 0.983$. Light blue ◆: 90 °C, $k_{app} = (2.77 \pm 0.10) \times 10^{-4}$ s⁻¹, $R^2 = 0.997$.

Figure 9. Semilogarithmic plots of the polymerization of ε-CL initiated by complex **10** at different temperatures. Polymerization conditions: toluene as solvent, $[\varepsilon\text{-CL}]_0 = 1$ mol/L; CL:Al = 200:1; N$_2$ atmosphere. Black ■: 50 °C, $k_{app} = (9.33 \pm 0.38) \times 10^{-6}$ s^{-1}, $R^2 = 0.997$. Red ●: 60 °C, $k_{app} = (1.47 \pm 0.06) \times 10^{-5}$ s^{-1}, $R^2 = 0.997$. Green ▲: 70 °C, $k_{app} = (3.38 \pm 0.09) \times 10^{-5}$ s^{-1}, $R^2 = 0.999$. Dark blue ▼: 80 °C, $k_{app} = (4.68 \pm 0.11) \times 10^{-5}$ s^{-1}, $R^2 = 0.999$. Light blue ◆: 90 °C, $k_{app} = (1.44 \pm 0.03) \times 10^{-4}$ s^{-1}, $R^2 = 0.999$.

by **10**. Apparently, the dinuclear structure led to dramatic enhancement of catalytic activities (*vide supra*). Since in both mono- and dinuclear systems the aluminum centers are in the same steric environment, it is reasonable to deduce that the cooperation of the two metal centers in dinuclear complexes account for their better performance.

Polymerizations with different monomer to initiator ratios were also studied, and k_{app} values were found to increase linearly with initiator concentrations (Figure 10), which reveals that the orders of initiators **5** and **10** are both first-order as well. The rate law is thus deduced as $-\mathrm{d}[\varepsilon\text{-CL}]/\mathrm{d}t = k_p[\text{initiator}]_t[\varepsilon\text{-CL}]_t$, where $k_{app} = k_p[\text{initiator}]_t$, and k_p is the propagation rate constant.
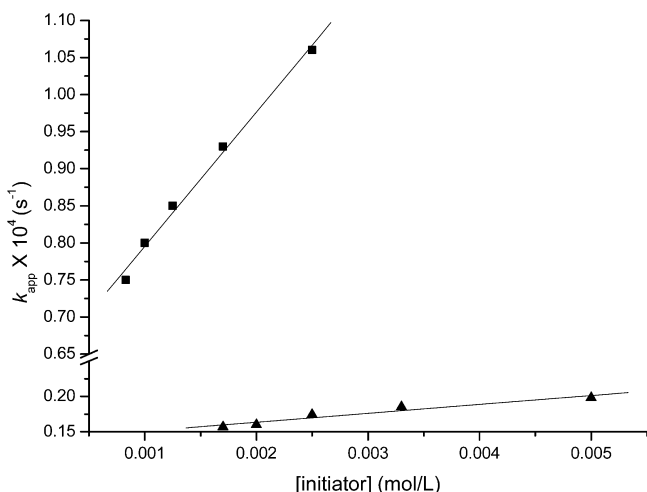
Figure 10. Plots of k_{app} vs initiator concentrations. Polymerization conditions: toluene as solvent, $[\varepsilon\text{-CL}]_0 = 1$ mol/L; 70 °C; N$_2$ atmosphere. Black ■: complex **5**, $R^2 = 0.993$. Black ▲: complex **10**, $R^2 = 0.968$.

Since k_{app} values at different temperatures were available (*vide supra*), k_p values were obtained according to the equation $k_{app} = k_p[\text{initiator}]_0$. On the basis of the Eyring equation, the curve of $\ln(k_p/T)$ versus $1/T$ was plotted (Figure 11). From the
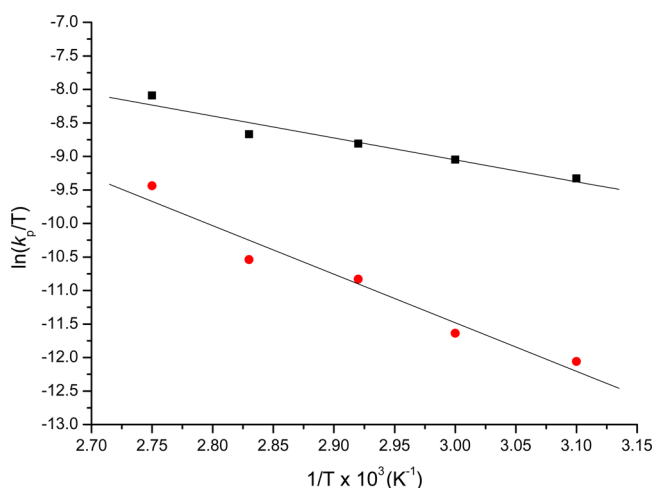
**Figure 11.** Plots of $\ln(k_p/T)$ vs $1/T$. Black ■: complex **5**, $R^2 = 0.968$. Red ●: complex **10**, $R^2 = 0.977$.

slopes and intercepts of the curves, the enthalpy and entropy of activation were determined as follows: $\Delta H^{\ddagger} = 6(1)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -46(3)$ cal mol^{-1} K^{-1} for dinuclear **5**, while $\Delta H^{\ddagger} = 14(2)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -27(5)$ cal mol^{-1} K^{-1} for mononuclear **10**. The Gibbs energy of activation $\Delta G_{298}^{\ddagger}$ is thus calculated to be 20 kcal mol^{-1} (for **5**) and 22 kcal mol^{-1} (for **10**), respectively. The lower free energy barrier of the ROP initiated by dinuclear complex **5** as compared to that by dinuclear **10** explains the observation of different polymerization rates (*vide supra*).

On the basis of all findings described above, a plausible mechanism has been proposed to elaborate on the cooperation between the two Al centers in dinuclear complexes supported by piperazidine-bridged bis(phenolato) ligands (Scheme 3). A

Scheme 3. Plausible Mechanism for the Polymerization of ε-CL Initiated by Bimetallic Al Complexes
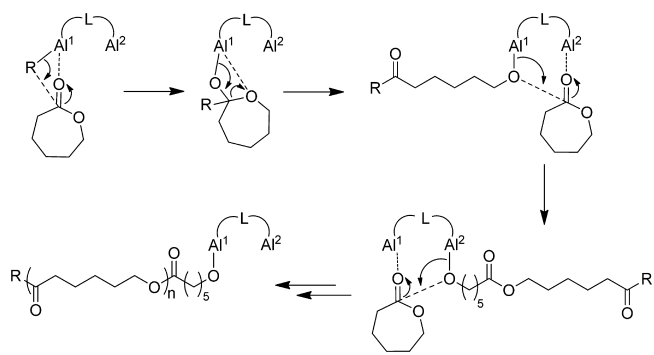
coordination−insertion mechanism has been proposed, in which an acyl−oxygen bond cleavage occurs, and one monomer inserts into one Al−alkyl bond. A second monomer coordinates to a proximal Al center, which is activated for insertion into the newly formed Al−O bond. The polymer chain thus shuttles between two Al centers, leading to a highly efficient polymerization process.[16]

■ CONCLUSION

We have reported the syntheses of a series of mono- and dinuclear aluminum alkyl complexes bearing phenolato ligands of different steric and electronic properties. Bimetallic complexes $(AlR_2)_2[ONNO]$ (**1–3**, R = Me; **4–6**, R = Et) were prepared by the alkane elimination reactions of piperazidine-bridged bis(phenol) with 2.5–3 equiv of AlR_3. Monometallic dialkyl complexes $AlR_2[ON]$ (**7–9**, R = Me; **10–11**, R = Et) as well as monoalkyl complexes $AlR[ON]_2$ **12–13** that bear a piperidine moiety were also synthesized. The activities of both mono- and dinuclear complexes for initiating the polymerization of ε-caprolactone were investigated and compared. In general these aluminum alkyl complexes are active initiators in the absence of alcohols, and polymers of moderate to good yields were obtained under mild conditions. Kinetic studies revealed that the activity of dinunclear complexes is around 2–8 times of that of mononuclear counterparts, which may stem from the synergistic effects provided by the dinuclear architecture. Research in our lab is ongoing to further understand this system.

■ EXPERIMENTAL SECTION

General Considerations. Complexes described here are all air and moisture sensitive; hence, all manipulations were performed under an argon atmosphere using standard Schlenk techniques and a glovebox. $AlMe_3$ and $AlEt_3$ are commercially available. THF, toluene, and hexane were distilled from sodium benzophenoneketyl before use. $PhCH_2OH$ was dried and distilled over sodium turnings and stored over activated 3 Å molecular sieves. ε-Caprolactone (ε-CL) was purchased from Arcos, dried over CaH_2 for 48 h, and distilled under reduced pressure. Deuterated solvents (C_6D_6 and d_8-THF) were purchased from CIL. $H_2[ONNO]^1$ ($C_4H_8N_2[1,4-(2-O-3,5-Me_2-C_6H_2CH_2)_2]$), $H_2[ONNO]^2$ ($C_4H_8N_2[1,4-(2-O-3-{}^tBu-5-Me-C_6H_2CH_2)_2]$), $H_2[ONNO]^3$ ($C_4H_8N_2[1,4-(2-O-3,5-{}^tBu_2-C_6H_2CH_2)_2]$), $H[NO]^1$ ($[2-(CH_2NC_5H_{10})-4,6-Me_2-C_6H_3OH)$, $H[NO]^2$ ($2-(CH_2NC_5H_{10})-4-Me-6-{}^tBu-C_6H_3OH)$, $H[NO]^3$ ($2-(CH_2NC_5H_{10})-4,6-{}^tBu_2-C_6H_3OH)$, $(AlMe_2)_2[ONNO]^1$ (**1**), and $(AlEt_2)_2[ONNO]^1$ (**4**) were prepared according to published methods.[12,17] Carbon, hydrogen, and nitrogen analyses were performed by direct combustion with a Carlo-Erba EA-1110 instrument. NMR (^{1}H, ^{13}C) spectra were recorded on a Unity Varian spectrometer at 25 °C. Molecular weight and molecular weight distribution (PDI) were determined against a polystyrene standard by gel permeation chromatography (GPC) on a PL 50 apparatus, and THF was used as eluent at the flow rate of 1.0 mL/min at 40 °C.

$(AlMe_2)_2[ONNO]^2$ (2). $AlMe_3$ (7.5 mL, 1 M solution in heptane) was added slowly to a solution of $H_2[ONNO]^2$ (1.32 g, 3.00 mmol) in 20 mL of THF at 0 °C. The reaction mixture was warmed slowly to room temperature, and was stirred overnight during which period a white precipitate formed. All the volatiles were removed under vacuum, and the residue was redissolved in hot THF (25 mL) and was allowed to cool to room temperature affording colorless crystalline solid after several days (1.37 g, 83%). Anal. Calcd for $C_{32}H_{52}Al_2N_2O_2$: C, 69.79; H, 9.52; N, 5.09. Found: C, 69.88; H, 9.46; N, 5.33%. ^{1}H NMR (THF-d_8, 300 MHz): δ 7.02 (s, 2H, Ar–H), 6.75 (s, 2H, Ar–H), 3.95 (s, 4H, Ar–CH$_2$), 3.15–2.95 (m, 8H, pip-CH), 2.19 (s, 6H, CH$_3$), 1.36 (s, 18H, ^{t}Bu), −0.71 (s, 12H, Al-CH$_3$). ^{13}C NMR (THF-d_8, 75 MHz): δ 157.4, 139.0, 129.3, 129.2, 126.2, 121.0 (Ar–C), 63.1 (ArCH$_2$), 47.2 (pip-C), 35.5, 30.2, 21.1 (^{t}Bu and CH$_3$), −9.4 (Al-CH$_3$).

$(AlMe_2)_2[ONNO]^3$ (3). $AlMe_3$ (7.5 mL, 1 M solution in heptane) was added slowly to a solution of $H_2[ONNO]^3$ (1.57 g, 3.00 mmol) in 20 mL of THF at 0 °C. The reaction mixture was warmed slowly to room temperature, and was stirred overnight. THF was evaporated to about 1 mL under vacuum, and 15 mL of hexane was added. The precipitate was removed by centrifugation. Colorless crystals were obtained at 5 °C after several days (1.62 g, 85%). Anal. Calcd for $C_{38}H_{64}Al_2N_2O_2$: C, 71.89; H, 10.16; N, 4.41. Found: C, 71.76; H, 10.25; N, 4.53%. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.60–7.56 (m, 2H, Ar–H), 6.72–6.71 (m,

2H, Ar–H), 3.14–3.08 (m, 4H, Ar–CH$_2$), 2.49 (br-s, 2H, pip-CH), 2.25 (d, J = 9.7 Hz, 2H, pip-CH), 1.93 (d, J = 9.7 Hz, 4H, pip-CH), 1.69 (s, 18H, ^{t}Bu), 1.46 (s, 18H, ^{t}Bu), −0.52 (s, 12H, Al-CH$_3$). ^{13}C NMR (C_6D_6, 75 MHz): δ 156.4, 139.6, 138.3, 125.3, 124.7, 119.4 (Ar–C), 63.0 (ArCH$_2$), 50.6, 46.0 (pip-C), 35.4, 34.3, 32.0, 30.1 (^{t}Bu), −8.1 (Al-CH$_3$).

$(AlEt_2)_2[ONNO]^2$ (5). $AlEt_3$ (3.75 mL, 2 M solution in toluene) was added slowly to a solution of $H_2[ONNO]^2$ (1.32 g, 3.00 mmol) in 20 mL of THF at 0 °C. The reaction mixture was warmed slowly to room temperature, and was stirred overnight. The solvent was removed under reduced pressure, and the residue was dissolved in a mixture of hot toluene/hexane (1:3 v/v). White solids were obtained at 5 °C after several days (1.42 g, 78%). Anal. Calcd for $C_{36}H_{60}Al_2N_2O_2$: C, 71.25; H, 9.97; N, 4.62. Found: C, 71.31; H, 9.82; N, 4.65%. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.25 (s, 2H, Ar–H), 6.46 (s, 2H, Ar–H), 3.21 (s, 4H, Ar–CH$_2$), 2.35 (m, 4H, pip-CH), 2.22 (s, 6H, CH$_3$), 1.95 (m, 4H, pip-CH), 1.66 (s, 18H, ^{t}Bu), 1.43 (t, J = 8.2 Hz, 12H, AlCH$_2$–CH$_3$), 0.16–0.40 (q, J = 8.2 Hz, 8H, Al-CH$_2$). ^{13}C NMR (C_6D_6, 75 MHz): δ 156.5, 138.7, 129.2, 128.2, 125.8, 119.2 (Ar–C), 62.5 (ArCH$_2$), 49.4, 45.8 (pip-C), 36.0, 29.8, 20.7 (^{t}Bu and CH$_3$), 9.5 (AlCH$_2$–CH$_3$), 0.8 (Al-CH$_2$).

$(AlEt_2)_2[ONNO]^3$ (6). $AlEt_3$ (3.75 mL, 2 M solution in toluene) was added slowly to a solution of $H_2[ONNO]^3$ (1.57 g, 3.00 mmol) in 20 mL of THF at 0 °C. The reaction mixture was warmed slowly to room temperature, and was stirred overnight. THF was evaporated completely under vacuum, and the residue was washed with hexane (3 × 5 mL). The resulting powder was dissolved in hot hexane (25 mL), and colorless crystals were obtained from a concentrated hexane solution (about 15 mL) at 5 °C after several days (1.70 g, 82%). Anal. Calcd for $C_{42}H_{72}Al_2N_2O_2$: C, 73.00; H, 10.50; N, 4.05. Found: C, 72.33; H, 10.52; N, 4.23%. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.57 (d, J = 2.4 Hz, 2H, Ar–H), 6.74 (d, J = 2.4 Hz, 2H, Ar–H), 3.21 (s, 4H, Ar–CH$_2$), 2.35 (m, 4H, pip-CH), 1.89 (m, 4H, pip-CH),1.68 (s, 18H, ^{t}Bu), 1.38 (s, 18H, ^{t}Bu), 1.46 (t, 12H, AlCH$_2$–CH$_3$), 0.2 (m, 8H, Al-CH$_2$). ^{13}C NMR (C_6D_6, 75 MHz): δ 156.6, 139.5, 138.3, 125.4, 124.6, 118.9 (Ar–C), 62.3 (ArCH$_2$), 49.3, 45.9 (pip-C), 35.5, 34.2, 32.0, 30.0 (^{t}Bu), 9.6 (AlCH$_2$CH$_3$), 0.8 (Al-CH$_2$).

$AlMe_2[ON]^1$ (7). $AlMe_3$ (4.45 mL, 1 M solution in heptane) was added slowly to a solution of $H[NO]^1$ (0.98 g, 4.45 mmol) in 20 mL of hexane at 0 °C. The reaction mixture was warmed slowly to room temperature, and was stirred overnight. The precipitate was removed by centrifugation, and the clear solution was concentrated. Colorless crystals were obtained at room temperature after several days (0.96 g, 78%). Anal. Calcd for $C_{16}H_{26}AlNO$: C, 69.79; H, 9.52; N, 5.09. Found: C, 69.83; H, 9.59; N, 5.10%. ^{1}H NMR (C_6D_6, 400 MHz): 6.98 (s, 1H, Ar–H), 6.47 (s, 1H, Ar–H), 3.31 (s, 2H, Ar–CH$_2$), 2.58 (m, 2H, N(CH$_2$)$_5$), 2.45 (s, 3H, CH$_3$), 2.26 (s, 3H, CH$_3$), 1.81 (m, 2H, N(CH$_2$)$_5$), 1.16–0.79 (m, 6H, N(CH$_2$)$_5$), −0.39 (m, 6H, AlCH$_3$). ^{13}C NMR (C_6D_6, 75 MHz): δ 156.5, 132.5, 127.9, 127.5, 125.3, 119.3 (Ar–C), 58.9 (ArCH$_2$), 52.9 (N–C), 23.0, 21.0, 20.7, 16.8 (^{t}Bu, CH$_3$ and CH$_3$), −9.0 (Al-CH$_3$).

$AlMe_2[ON]^2$ (8). $AlMe_3$ (2.97 mL, 1 M solution in heptane) was added slowly to a solution of $H[NO]^2$ (0.78 g, 2.97 mmol) in 20 mL of THF at 0 °C. The reaction mixture was warmed slowly to room temperature, and was stirred overnight. The solvent was removed under reduced pressure, and the residual oil was dissolved in hot THF (about 10 mL). The precipitate was removed by centrifugation. Colorless crystals were obtained at room temperature after several days (0.74 g, 78%). Anal. Calcd for $C_{19}H_{32}AlNO$: C, 71.89; H, 10.16; N, 4.41. Found: C, 71.91; H, 10.22; N, 4.45%. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.29 (s, 1H, Ar–H), 6.51 (s, 1H, Ar–H), 3.25 (s, 2H, Ar–CH$_2$), 2.56 (m, 2H, N(CH$_2$)$_5$), 2.31 (s, 3H, CH$_3$), 1.69 (m, 2H, N(CH$_2$)$_5$, overlap with ^{t}Bu signal), 1.69 (s, 9H, ^{t}Bu), 1.21–0.78 (m, 6H, N(CH$_2$)$_5$), −0.37 (m, 6H, Al-CH$_3$). ^{13}C NMR (C_6D_6, 75 MHz): δ 157.1, 138.5, 128.7, 128.5, 125.0, 120.9 (Ar–C), 59.6 (ArCH$_2$), 53.3 (N–C), 35.1, 30.0, 23.0, 21.3 (^{t}Bu, CH$_3$ and CH$_2$), −9.0 (Al-CH$_3$).

$AlMe_2[ON]^3$ (9). $AlMe_3$ (4.68 mL, 1 M solution in heptane) was added slowly to a solution of $H[NO]^3$ (1.42 g, 4.68 mmol) in 20 mL of hexane at 0 °C. The reaction mixture was warmed slowly to room temperature, and was stirred overnight. The solvent was removed

under reduced pressure, and the residual oil was dissolved in 15 mL of pentane. The precipitate was removed by centrifugation. Colorless crystals were obtained at 5 °C after several days (0.89 g, 53%). Anal. Calcd for $C_{22}H_{38}AlNO$: C, 73.50; H, 10.65; N, 3.90. Found: C, 73.53; H, 10.74; N, 3.99%. ^1H NMR (C_6D_6, 300 MHz): δ 7.70 (s, 1H, Ar—H), 6.92 (s, 1H, Ar—H), 3.40 (s, 2H, Ar—CH$_2$), 2.71 (m, 2H, N(CH$_2$)$_5$), 1.83 (m, 9H, ^tBu), 1.77 (br-s, 2H, N(CH$_2$)$_5$), 1.54 (m, 9H, ^tBu), 1.26 (m, 2H, N(CH$_2$)$_5$), 1.12 (m, 2H, N(CH$_2$)$_5$), 0.91 (m, 2H, N(CH$_2$)$_5$), −0.26 (m, 6H, AlCH$_3$). ^{13}C NMR (C_6D_6, 75 MHz): δ 157.0, 138.7, 138.0, 124.7, 124.6, 120.4 (Ar—C), 60.3 (ArCH$_2$), 53.3 (N—C), 35.4, 34.3, 32.2, 30.1, 22.9, 21.3 (^tBu and CH$_2$), −9.0 (Al-CH$_3$).

AlEt$_2$[ON]^2 (10). AlEt$_3$ (4.47 mL, 2 M solution in toluene) was added slowly to a solution of H[NO]^2 (1.17 g, 4.47 mmol) in 20 mL of hexane at 0 °C. The reaction mixture was warmed slowly to room temperature, and was stirred overnight. The solvent was removed under reduced pressure, and the residue was washed with hexane (3 × 5 mL). The powder obtained was dissolved in hot hexane (18 mL), and colorless crystals were obtained from a concentrated hexane solution (about 15 mL) at room temperature after several days (1.00 g, 65%). Anal. Calcd for $C_{21}H_{36}AlNO$: C, 73.00; H, 10.50; N, 4.05. Found: C, 73.08; H, 10.57; N, 4.12%. ^1H NMR (C_6D_6, 300 MHz): δ 7.26 (s, 1H, Ar—H), 6.49 (s, 1H, Ar—H), 3.29 (s, 2H, Ar—CH$_2$), 2.55 (br-s, 2H, N(CH$_2$)$_5$), 2.30 (s, 3H, CH$_3$), 1.77 (br-s, 2H, N(CH$_2$)$_5$), 1.68 (s, 9H, ^tBu), 1.48 (t, J = 8.2 Hz, 6H, AlCH$_2$CH_3), 1.05−0.84 (q, J = 8.2 Hz, 6H, N(CH$_2$)$_5$), 0.23 (m, 4H, Al-CH$_2$). ^{13}C NMR (C_6D_6, 100 MHz): δ 149.9, 145.0, 140.9, 128.9, 125.5, 125.0 (Ar—C), 61.6 (ArCH$_2$), 55.2 (N—C), 36.3, 34.2, 32.9, 31.4, 22.5, 22.3 (^tBu and CH$_2$), −3.9 (AlCH$_2$—CH$_3$), −8.1 (Al-CH$_2$).

AlEt$_2$[ON]^3 (11). AlEt$_3$ (3.00 mL, 2 M solution in toluene) was added slowly to a solution of H[NO]^3 (0.91 g, 3.00 mmol) in 20 mL of hexane at 0 °C. The reaction mixture was warmed slowly to room temperature, and was stirred overnight. The solvent was removed under reduced pressure, and the residue was washed with hexane (3 × 5 mL). The powder obtained was dissolved in hot hexane (10 mL), and colorless crystals were obtained from a concentrated hexane solution (about 7 mL) at 5 °C after several days (0.69 g, 59%). Anal. Calcd for $C_{24}H_{42}AlNO$: C, 74.37; H, 10.92; N, 3.61. Found: C, 74.45; H, 10.97; N, 3.65%. ^1H NMR (C_6D_6, 400 MHz): δ 7.55 (d, J = 2.4 Hz, 1H, Ar—H), 6.80 (d, J = 2.4 Hz, 1H, Ar—H), 3.33 (s, 2H, Ar—CH$_2$), 2.61−2.58 (m, 2H, N(CH$_2$)$_5$), 1.79−1.74 (m, 2H, N(CH$_2$)$_5$), 1.69 (s, 9H, ^tBu), 1.46 (t, J = 9.0 Hz, 6H, AlCH$_2$—CH$_3$), 1.42 (s, 9H, ^tBu), 1.15−1.03 (m, 6H, N(CH$_2$)$_5$), 0.25−0.14 (q, J = 9.0 Hz, 4H, Al-CH$_2$). ^{13}C NMR (C_6D_6, 75 MHz): δ 157.1, 138.6, 138.0, 124.7, 124.5, 120.0 (Ar—C), 60.1 (ArCH$_2$), 53.0 (N—C), 35.5, 34.3, 32.2, 30.0, 23.0, 21.1 (^tBu and CH$_2$), 9.8 (AlCH$_2$CH$_3$), 0.6 (AlCH$_2$).

AlEt[ON]$^2_2$ (12). AlEt$_3$ (0.75 mL, 2 M solution in toluene) was added slowly to a solution of H[NO]^2 (0.79 g, 3.01 mmol) in 20 mL of hexane at 0 °C. The reaction mixture was warmed slowly to room temperature, and was stirred overnight. All the volatiles were removed under vacuum, and 15 mL of hexane was added. The precipitate was removed by centrifugation. Colorless crystals were obtained at room temperature after several days (0.50 g, 57%). Anal. Calcd for $C_{36}H_{57}AlN_2O_2$: C, 74.96; H, 9.96; N, 4.86. Found: C, 75.00; H, 10.02; N, 4.93%. ^1H NMR (C_6D_6, 400 MHz): 7.23 (s, 2H, Ar—H), 6.92 (s, 2H, Ar—H), 4.11 (d, J = 13.6 Hz, 2H, ArCHH), 3.57 (d, J = 13.6 Hz, 2H, ArCHH), 2.63 (m, 8H, N(CH$_2$)$_5$), 2.30 (s, 6H, CH$_3$), 1.63 (s, 18H, C(CH$_3$)$_3$), 1.43 (t, J = 9.0 Hz, 3H, AlCH$_2$CH_3), 1.32 (m, 6H, N(CH$_2$)$_5$), 1.21 (m, 6H, N(CH$_2$)$_5$), 0.49−0.26 (q, J = 9.0 Hz, 2H, AlCH$_2$). ^{13}C NMR (C_6D_6, 75 MHz): δ 155.5, 138.4, 128.8, 127.8, 126.0, 124.2 (Ar—C), 56.9 (ArCH$_2$), 52.7 (N—C), 35.1, 30.7, 24.1, 22.5, 21.1, 14.3 (^tBu and CH$_2$), 10.0 (AlCH$_2$CH$_3$), −0.2 (AlCH$_2$).

AlEt[ON]$^3_2$ (13). AlEt$_3$ (0.75 mL, 2 M solution in toluene) was added slowly to a solution of H[NO]^3 (0.91 g, 3.00 mmol) in 20 mL of hexane at 0 °C. The reaction mixture was warmed slowly to room temperature, and was stirred overnight. All the volatiles were removed under vacuum, and 15 mL of hexane was added. The precipitate was removed by centrifugation. Colorless crystals were obtained at room temperature after several days (0.64 g, 65%). Anal. Calcd for $C_{42}H_{69}AlN_2O_2$: C, 76.32; H, 10.52; N, 4.24. Found: C, 76.38; H,

10.53; N, 4.27%. ^1H NMR (C_6D_6, 300 MHz): δ 7.51 (s, 2H, Ar—H), 7.09 (s, 2H, Ar—H), 4.16 (d, J = 13.6 Hz, 2H, Ar—CH$_2$), 3.57 (d, J = 13.6 Hz, 2H, Ar—CH$_2$), 2.61 (m, 8H, N(CH$_2$)$_5$), 1.62 (s, 18H, ^tBu), 1.39 (t, J = 9.0 Hz, 3H, AlCH$_2$CH_3), 1.35 (s, 18H, ^tBu), 1.25−1.11 (m, 12H, N(CH$_2$)$_5$), 0.40−0.25 (q, J = 9.0 Hz, 2H, Al-CH$_2$). ^{13}C NMR (C_6D_6, 75 MHz): δ 155.6, 139.4, 137.7, 125.0, 123.7, 123.7 (Ar—C), 56.9 (ArCH$_2$), 52.4 (N—C), 35.5, 34.4, 32.1, 30.7, 24.1, 22.2 (^tBu and CH$_2$), 10.3 (AlCH$_2$CH_3), −0.5 (Al-CH$_2$).

Typical Procedure for Polymerization. A 50 mL Schlenk flask was charged with the desired amount of initiator and EtOH (when necessary) in toluene. The solution was stirred for 2 min in glovebox at 70 °C (60 °C in the presence of EtOH), and the desired amount of toluene along with ε-CL were then added to the solution. The solution was stirred for the prescribed time, during which period an increased viscosity was observed. The reaction mixture was quenched by the addition of 1 M HCl—ethanol solution, and poured into methanol to precipitate the polymer, which was dried under vacuum and weighed.

Oligomer Preparation. The oligomerization of ε-CL was carried out with complex **5** or **10** as the initiator in 10 mL of toluene at 70 °C in the ratio of $[\varepsilon\text{-CL}]_0/[\text{initiator}]_0 = 5$ ($[\varepsilon\text{-CL}]_0 = 0.0936$ mol/L). The reaction mixture was stirred for 10 min (for **5**) or 30 min (for **10**), and then quenched by adding n-hexane. The oligomers precipitated were collected and dried under vacuum.

X-ray Diffraction Studies. Suitable single crystals of complexes **2**, **3**, **7**, **10**, and **13** were sealed in a thin-walled glass capillary for determining the single-crystal structure. Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode using Mo Kα radiation (λ = 0.710 70 Å). The diffracted intensities were corrected for Lorentz polarization effects and empirical absorption corrections. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All of the non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. The structures were solved and refined using SHELEXL-97 programs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Data for polymerization of ε-CL initiated by complex **5** or **10** at different temperatures, semilogarithmic plots of the polymerization of ε-CL initiated by complex **5** or **10** with varying monomer to initiator ratios, and crystallographic data for **2**·THF, **3**, **7**, **10**, and **13** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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