Inorganica Chimica Acta 368 (2011) 179–186

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Bimetallic amidinate aluminum methyl complexes: Synthesis, crystal structure and activity for ε-caprolactone polymerization

Yinlin Lei [a], Fei Chen [a], Yunjie Luo [a,*], Ping Xu [a,b], Yaorong Wang [b], Yong Zhang [b]

[a] Organometallic Chemistry Laboratory, Ningbo Institute of Technology, Zhejiang University, Ningbo 315100, China
[b] College of Chemistry, Chemical Engineering and Material Science, Suzhou University, Suzhou 215123, China

ARTICLE INFO

Article history:
Received 6 August 2010
Received in revised form 16 December 2010
Accepted 3 January 2011
Available online 8 January 2011

Keywords:
Aluminum
Bridged amidinate ligands
Synthesis
Characterization
Ring-opening polymerization

ABSTRACT

Four novel bridged-amidines $\mathbf{H_2L}$ (1,4-R^1[C(NR^2)(NHR^2)]$_2$ (R^1 = C$_6$H$_4$, R^2 = 2,6-^{i}Pr$_2$C$_6$H$_3$ ($\mathbf{H_2L^1}$), R^1 = C$_6$H$_4$, R^2 = 2,6-Me$_2$C$_6$H$_3$ ($\mathbf{H_2L^2}$), R^1 = C$_6$H$_{10}$, R^2 = 2,6-^{i}Pr$_2$C$_6$H$_3$ ($\mathbf{H_2L^3}$), R^1 = C$_6$H$_{10}$, R^2 = 2,6-Me$_2$C$_6$H$_3$ ($\mathbf{H_2L^4}$)) were prepared in 65–78% isolated yields by the condensation reaction of dicarboxylic acid with four equimolar amounts of amines in the presence of PPSE (polyphosphoric acid trimethylsilyl ester) at 180 °C. Alkane elimination reaction of AlMe$_3$ with 0.5 equivalent of the bridged-amidines ($\mathbf{H_2L}$) in THF at room temperature afforded the corresponding bimetallic aluminum methyl complexes Me$_2$Al**L**AlMe$_2$ ($\mathbf{L^1}$ (**1**), $\mathbf{L^2}$ (**2**), $\mathbf{L^3}$ (**3**), $\mathbf{L^4}$ (**4**)) in 83–93% isolated yields. In order to understand whether the bimetallic complexes could show cooperative effect in the polymerization, their related mononuclear analogues **L**AlMe$_2$ ($\mathbf{L^5}$ (**5**), $\mathbf{L^6}$ (**6**), $\mathbf{L^7}$ (**7**), $\mathbf{L^8}$ (**8**)) had also been synthesized in 85–91% isolated yields by treatment of AlMe$_3$ with 1 equivalent of amidines **HL** ([PhC(N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$]H ($\mathbf{HL^5}$), [PhC(N-2,6-Me$_2$C$_6$H$_3$)$_2$]H ($\mathbf{HL^6}$), [CyC(N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$]H ($\mathbf{HL^7}$), [CyC(N-2,6-Me$_2$C$_6$H$_3$)$_2$]H ($\mathbf{HL^8}$)) in THF at room temperature. All these complexes were characterized by elemental analysis, FT-IR, and NMR spectroscopy. The crystal structures of $\mathbf{H_2L^3}$, **1**, **3**, **5** and **7** were determined by X-ray diffraction. In all these amidinate aluminum methyl complexes, Al is four-coordinated by two nitrogen atoms from the dihapto-amidinate ligand and two methyl groups to adopt a distorted tetrahedral geometry. These complexes showed activity towards the ring-opening polymerization of ε-caprolactone at room temperature to give unimodal molecular weight distribution polyesters.

1. Introduction

In search for ancillary ligands to replace cyclopentadienides to create non-metallocene species, amidinate anions [R^{1}C(NR^2)(NR^3)]$^-$ are one kind of the ideal candidates, for their steric and electronic properties can be easily modified by tuning the substituents R^1, R^2 and R^3. Indeed, amidinate anions have found many applications in coordination chemistry, and also as ancillary ligands to form metal complexes as catalysts/initiators in organic transformation and polymerization [1]. Very recently, a promising progress in amidinate design is the development of bi-functional ligands with two amidinate moieties bridged by a linker unit [2–7]. The linked bis-amidinates can mainly be classified into three types (Chart 1). It is programmed that such dianionic ligands could support bimetallic complexes, which are expected to possess unique or more efficient homogeneous catalytic processes than mononuclear species, benefiting from the cooperative effects between proximate functional groups or adjacent active metal centers [8,9]. Over the past two decades, interest in amidinate ligated alkylaluminum complexes has understandably flourished, resulting from the fact that such species could serve as reagents in organic synthesis, as catalyst precursors for polymerization, and as precursors for thin film deposition [10–24]. To date, however, only a few examples of dinuclear aluminum complexes with bridged amidinate ligands have been reported [9,25–27], in which the reactivity of such species has not been explored to our knowledge. Herein, we would like to report the preparation and characterization of several new bridged-amidines, as well as their dinuclear aluminum methyl complexes. Some related mononuclear aluminum methyl complexes have also been synthesized and characterized in order to compare their ε-caprolactone polymerization behavior with related dinuclear species.

2. Results and discussion

2.1. Synthesis and characterization of the bridged amidines H_2L^{1-4}

Differently from a classical routine for the synthesis of *N*,*N*′-disubstituted amidines [6], a much more straightforward strategy was employed to prepare the bridged amidines, as we have reported previously to obtain symmetric amidines [28]. The

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* Corresponding author at: Organometallic Chemistry Laboratory, Ningbo Institute of Technology, Zhejiang University, Ningbo 315100, China. Tel.: +86 574 88130085; fax: +86 574 88130130.

E-mail address: lyj@nit.zju.edu.cn (Y. Luo).

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doi:10.1016/j.ica.2011.01.003

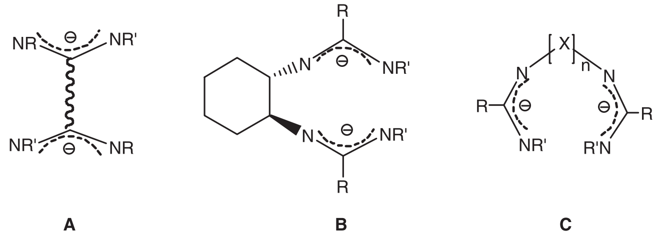


Chart 1.

reactions of dicarboxylic acids with four equimolar amounts of amines in the presence of PPSE (polyphosphoric acid trimethylsilyl ester) at 180 °C gave a series of bridged amidines **H_2L^{1-4}** (1,4-$R^1[C(NR^2)(NHR^2)]_2$ ($R^1 = C_6H_4$, $R^2 = 2,6\text{-}^i\text{Pr}_2C_6H_3$ (**H_2L^1**), $R^1 = C_6H_4$, $R^2 = 2,6\text{-Me}_2C_6H_3$ (**H_2L^2**), $R^1 = C_6H_{10}$, $R^2 = 2,6\text{-}^i\text{Pr}_2C_6H_3$ (**H_2L^3**), $R^1 = C_6H_{10}$, $R^2 = 2,6\text{-Me}_2C_6H_3$ (**H_2L^4**)) in good isolated yields as off-white/pale-green powders, after extractive work-up and solvent evaporation (Scheme 1). Recrystallization from hot toluene or THF provided the pure bridged amidines as white/pale-green solids or microcrystals. These compounds were characterized by NMR, HRMS, FT-IR, and elemental analysis. ^1H NMR spectra of **H_2L^{1-4}** indicated that the N–H proton resonances appear as a broad singlet between 5.2 and 5.7 ppm. Room temperature ^1H NMR spectra of isopropyl groups on the aromatic rings (**H_2L^1** and **H_2L^3**) showed one septet for isopropyl methine proton and two doublets (1:1 ratio) due to restricted rotation about N–Ar bonds, whereas those of methyl groups on the aromatic rings (**H_2L^2** and **H_2L^4**) exhibited only one singlet.

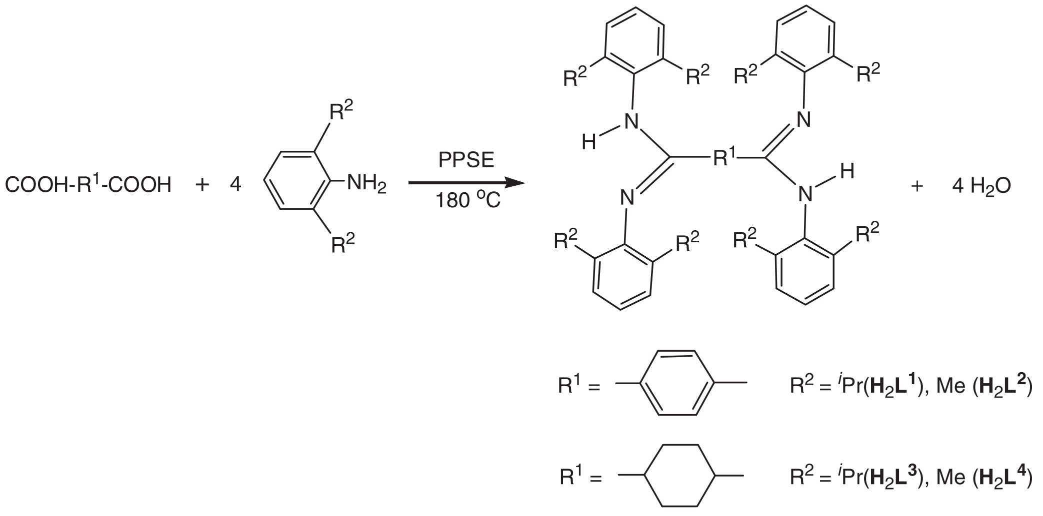
Evaporation of toluene solution at room temperature afforded **H_2L^3** as colorless crystals. The solid structure of **H_2L^3** was confirmed by single crystal structural determination, and its crystal data are summarized in Table 1. As illustrated in Fig. 1, there is an inversion center in the molecule, and the cyclohexylene linkage adopts a chair conformation to reduce steric hindrance of the two amidine moieties. Moreover, each amidine exist in the *E-syn* configuration, which is energetically more favored than its *Z* counterpart.

2.2. Synthesis and characterization of amidinate aluminum methyl complexes

Treatment of $AlMe_3$ with 0.5 equivalent of the bridged-amidines **H_2L** in THF at room temperature afforded the corresponding bimetallic aluminum methyl complexes Me_2Al**L**$AlMe_2$ (**L^1** (**1**), **L^2** (**2**), **L^3** (**3**), **L^4** (**4**)) in 83–93% isolated yields (Scheme 2). The reactions proceeded via protonolysis of Al–C_{methyl} bonds, with elimination of methane as shown in Scheme 2. Employing the same synthetic strategy, mononuclear amidinate aluminum methyl complexes **5**–**8** could be prepared in 85–91% isolated yields (Scheme 3).

Complexes **1**–**8** are all air- and moisture-sensitive, soluble in THF, toluene, diethyl ether, and slightly soluble in aliphatic solvents such as hexane and pentane. They were characterized by elemental analysis, FT-IR, and NMR spectroscopy. Room-temperature ^1H NMR spectra of **1**–**8** in C_6D_6 showed only one singlet for the methyl resonances of Al–*Me*, which are identical to the equivalent resonances in the related mononuclear analogues [11,13,17,18,21].

Single crystals of **1**, **3**, **5**, and 7 suitable for X-ray diffraction were grown from THF at −30 °C. Their molecular structures with selected bond distances and bond angles are shown in Figs. 2–5, crystallographic data are summarized in Table 1. All these amidinate aluminum methyl complexes are solvent-free, and Al is four-coordinated by two nitrogen atoms from the dihapto-amidinate ligand and two methyl groups to adopt a distorted tetrahedral geometry [11]. Thus, only the structure of **1** is discussed here. The methyl groups bonded to Al atom are oriented above and below the NCNAl plane to minimize interaction with the amidinate moiety. The Al–CH_3 and Al–N distances are in the range from 1.933(4) to 1.946(5) Å, and from 1.934(3) to 1.952(3) Å, respectively. These values are comparable to those in the related dinuclear amidinate aluminum complexes 1,4-$C_6H_4[C\{N^i\text{Pr}\}_2AlMe_2]_2$ [25], 4,6-benzofuran$[C\{N^i\text{Pr}\}_2AlMe_2]_2$ [9], and 4,6-(9,9-simethylxanthene)$[C\{N^i\text{Pr}\}_2AlMe_2]_2$ [9]. The bite angles of N–Al–N are 68.33(11) and 68.43(11)°, which are consistent with those in 1,4-$C_6H_4[C\{N^i\text{Pr}\}_2AlMe_2]_2$ [25], 4,6-benzofuran$[C\{N^i\text{Pr}\}_2AlMe_2]_2$ [9], and 4,6-(9,9-dimethylxanthene)$[C\{N^i\text{Pr}\}_2AlMe_2]_2$ [9]. The $\{RC(NR')_2\}Al$ core forms a nearly planar metallacycle (N–Al–N–C torsion angles <1.72°). The almostly equal values of the C–N bond distances in the amidinate moieties, and of the Al–N distances establish that the bonding in the N–C–N unit is delocalized. The Al–Al bond distances in **1** and **3** are 10.49 and 10.58 Å, respectively, which are much longer than those in 4,6-benzofuran$[C\{N^i\text{Pr}\}_2AlMe_2]_2$ (6.51 Å) [9], and 4,6-(9,9-dimethylxanthene)$[C\{N^i\text{Pr}\}_2AlMe_2]_2$ (5.93 Å) [9].



Scheme 1.

Table 1
Crystal date and refinement parameters for $\mathbf{H_2L^3}$, **1**, **3**, **5** and **7**.

	$H_2L^3{\cdot}2(C_4H_8O)$	$1{\cdot}0.25(C_6H_5CH_3)$	**3**	**5**	**7**
Formula	$C_{56}H_{82}N_4{\cdot}2(C_4H_8O)$	$C_{60}H_{84}Al_2N_4{\cdot}0.25(C_6H_5CH_3)$	$C_{60}H_{90}Al_2N_4$	$C_{33}H_{45}N_2Al$	$C_{33}H_{51}N_2Al$
Formula weight	953.45	938.31	921.32	496.69	502.74
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	Trigonal	Triclinic	Monoclinic	Trigonal	Trigonal
Space group	R-3:H	$P\bar{1}$	$P2_1/n$	$P3_121$	$P3_121$
a (Å)	30.603(4)	12.5187(14)	10.364(2)	14.969(4)	15.052(3)
b (Å)	30.603(4)	22.013(3)	21.357(5)	14.969(4)	15.052(3)
c (Å)	17.212(3)	22.081(3)	13.584(3)	12.230(4)	12.516(2
α (°)	90.00	89.470(5)	90	90.00	90.00
β (°)	90.00	85.191(5)	96.879(6)	90.00	90.00
γ (°)	120.00	87.212(6)	90	120.00	120.00
V (Å^3)	13 960(3)	6056.1(12)	2985.0(12)	2373.3(12)	2455.9(8)
Z	9	4	2	3	3
D_{calc} (g cm^{-3})	1.021	1.029	1.025	1.043	1.020
μ (mm^{-1})	0.061	0.086	0.086	0.085	0.083
$F(0\,0\,0)$	4716	2042	1008	810	828
Crystal size (mm)	0.60 × 0.50 × 0.50	0.80 × 0.55 × 0.30	0.80 × 0.40 × 0.20	0.60 × 0.60 × 0.50	0.80 × 0.70 × 0.50
θ_{max} (°)	25.34	25.35	25.35	25.36	25.33
Reflections collected	46 040	59 044	24 815	23 174	23 907
Independent reflections	5666	22 005	5165	2891	2996
No. of variables	300	1246	285	159	159
Goodness-of-fit (GOF) on F^2	1.222	1.176	1.195	1.144	1.134
R [$I > 2\sigma(I)$]	0.1464	0.0989	0.1283	0.0666	0.0988
wR	0.3337	0.1833	0.2395	0.1663	0.2802

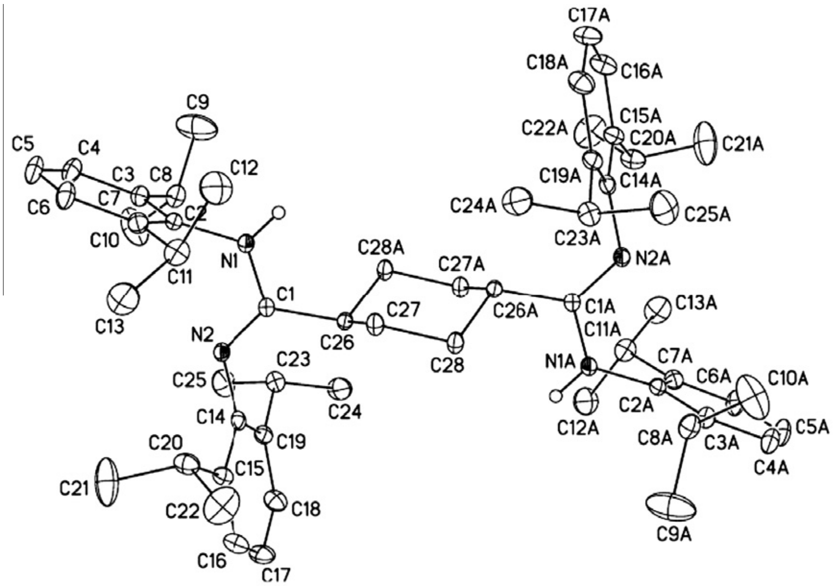
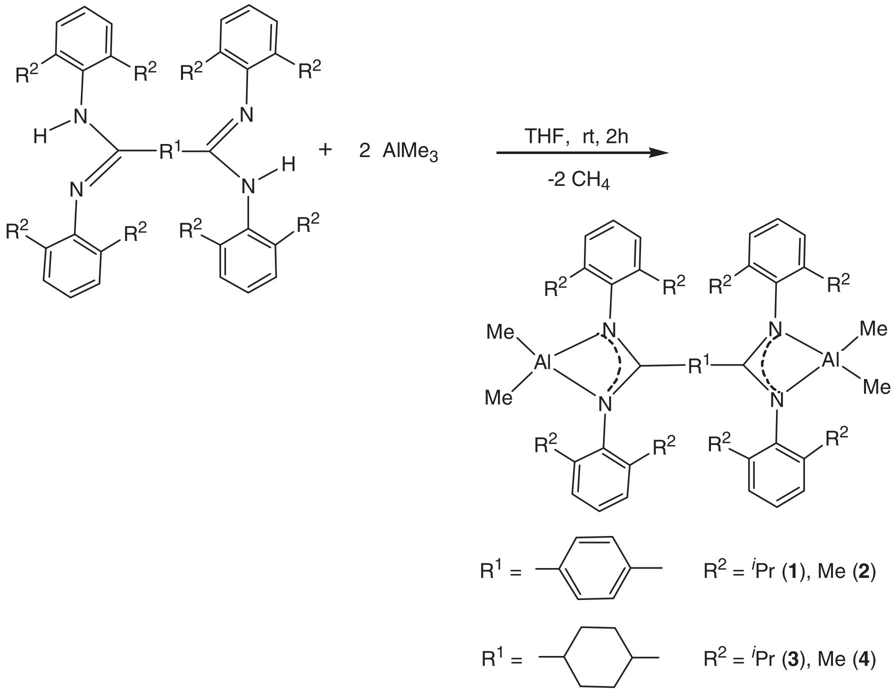


Fig. 1. Molecular structure of $\mathbf{H_2L^3}$ showing 10% thermal ellipsoids. Hydrogen atoms, except N–H, are omitted for clarity. Selected bond lengths (Å) and angles (°): N1–C1 = 1.346(5), C1–N2 = 1.299(5), N1–H = 0.8600, C1–C26 = 1.522(5), N1–C1–N2 = 120.0(3).

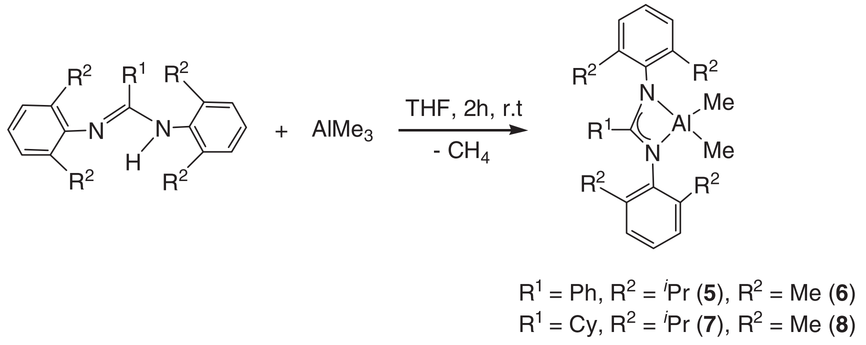
2.3. ε-Caprolactone polymerization initiated by the amidinate aluminum methyl complexes

To investigate the reactivity of the bimetallic amidinate aluminum methyl complexes, these complexes were employed as initiators for the ring-opening polymerization of ε-caprolactone. The selected mononuclear amidinate aluminum methyl complexes were also involved in this experiment to reveal whether these bimetallic species could exhibit "a" cooperative effect in the polymerization. The preliminary results are summarized in Table 2.

All these neutral amidinate aluminum methyl complexes showed activity towards ε-caprolactone polymerization in toluene at room temperature. Unfortunately, the bimetallic aluminum methyl complexes showed very similar polymerization activity compared to the related mononuclear analogues. Although each bimetallic complex possesses two metal centers, GPC curves of the resulting polymers were all unimodal with relatively narrow molecular weight distributions ($M_w/M_n \leqslant 1.65$), which were slightly broader than those from mononuclear complexes ($M_w/M_n \leqslant 1.40$). The corrected molecular weights of M_n were much greater than the calculated molecular weights, suggesting rather low initiation efficiency with these initiators. Taking the activity and M_n into consideration, each metal center in the bimetallic complexes seems to be independent in the polymerization and possesses quite similar initiation capability. These bimetallic aluminum methyl complexes were not able to show cooperative effect, partially due to the "remote" distances (>10 Å) of two aluminum atoms or the lack of an available coordination site. However, the polymerization activity was somewhat dependent on the amidinate ligands. For example, employing the 1,4-phenylene



Scheme 2.



Scheme 3.

group as a bridge, the initiation capability of the resulting complexes increased with decreasing the steric hindrance of the amidinates (runs 1 and 2). In addition, the 1,4-phenylene-bridged amidinate complexes also showed slightly higher activity than the 1,4-cycloheyene-bridged species.

3. Conclusions

In summary, a novel series of mononuclear and dinuclear amidinate aluminum methyl complexes were prepared in good isolated yields by alkane elimination reaction between aluminum tris(methyl) complex and the corresponding parent amidines. These complexes were active for the ring-opening polymerization of ε-caprolactone to give high molecular weight ($M_n > 10^3$) and unimodal molecular weight distribution polyesters. No cooperative effect was observed in this polymerization system.

4. Experimental

4.1. Materials and procedures

All manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques and an argon-filled glovebox operating at less than 1 ppm oxygen and 1 ppm moisture. Solvents (toluene, hexane, and THF) were distilled from sodium/benzophenone ketyl, degassed by the freeze–pump–thaw method, and dried over fresh Na chips in the glovebox. Dichloromethane and ε-caprolactone (Acros) were dried by stirring with CaH_2, and distilled before use. P_2O_5 was purchased from Sinopharm Chemical Reagent Co. Ltd. Hexamethyldisiloxane, 2,6-diisopropylaniline, 2,6-dimethylaniline, terephthalic acid, 1,4-cyclohexanedicarboxylic acid, and $AlMe_3$ (1 M pentane solution) were purchased from Acros, and used as received. Deuterated solvents ($CDCl_3$, C_6D_6, and THF-d_8) were obtained from CIL. Polyphosphoric acid trimethylsilyl ester (PPSE), ([PhC(N-2,6-$^iPr_2C_6H_3$)$_2$]H (**HL^5**), [PhC(N-2,6-$Me_2C_6H_3$)$_2$]H (**HL^6**), [CyC(N-2,6-$^iPr_2C_6H_3$)$_2$]H (**HL^7**), and [CyC(N-2,6-$Me_2C_6H_3$)$_2$]H (**HL^8**)) were prepared according to the literature [29,30].

Samples of aluminum complexes for NMR spectroscopic measurements were prepared in the glovebox using J. Young valve NMR tubes. NMR (^{1}H, ^{13}C) spectra were recorded on a Bruker AVANCE III spectrometer at 25 °C, and referenced internally to residual solvent resonances unless otherwise stated. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion on a Carlo-Erba EA-1110 instrument, quoted data are the average of at least two independent determinations. FT-IR spectra

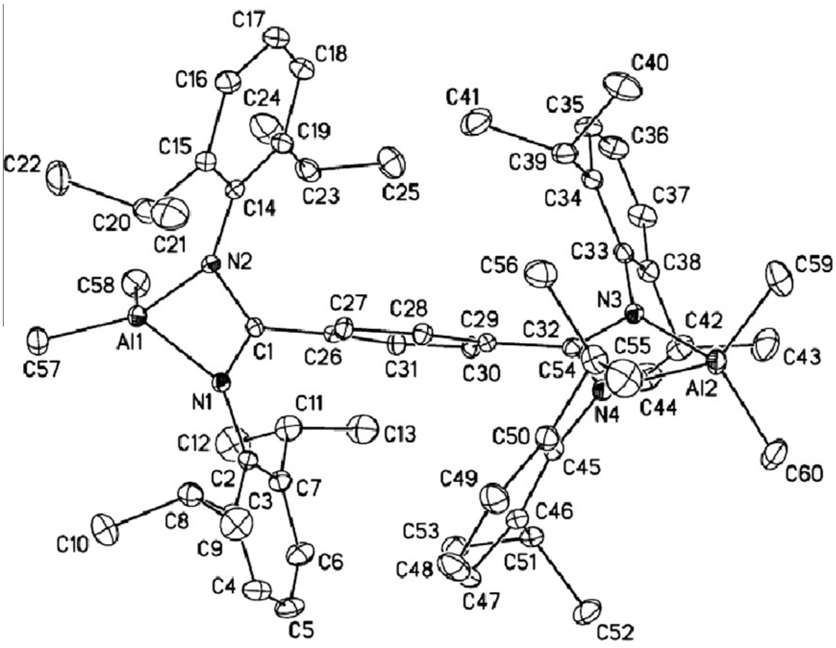


Fig. 2. Molecular structure of $Me_2AlL^1AlMe_2$ (**1**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 10% probability level. Selected bond lengths (Å) and angles (°): N1–C1 = 1.334(4), C1–N2 = 1.329(4), Al1–N1 = 1.940(3), Al1–N2 = 1.944(3), Al1–C57 = 1.933(4), Al1–C58 = 1.938(5), N1–Al1–N2 = 68.33(11), C57–Al1–C58 = 116.5(2), N1–C1–N2 = 110.0(3), N3–C32 = 1.342(4), N4–C32 = 1.339(4), Al2–N3 = 1.934(3), Al2–N4 = 1.952(3), Al2–C59 = 1.946(5), Al2–C60 = 1.940(4), N4–Al1–N3 = 68.43(11), C60–Al1–C59 = 119.7(2), N4–C32–N3 = 109.2(3).

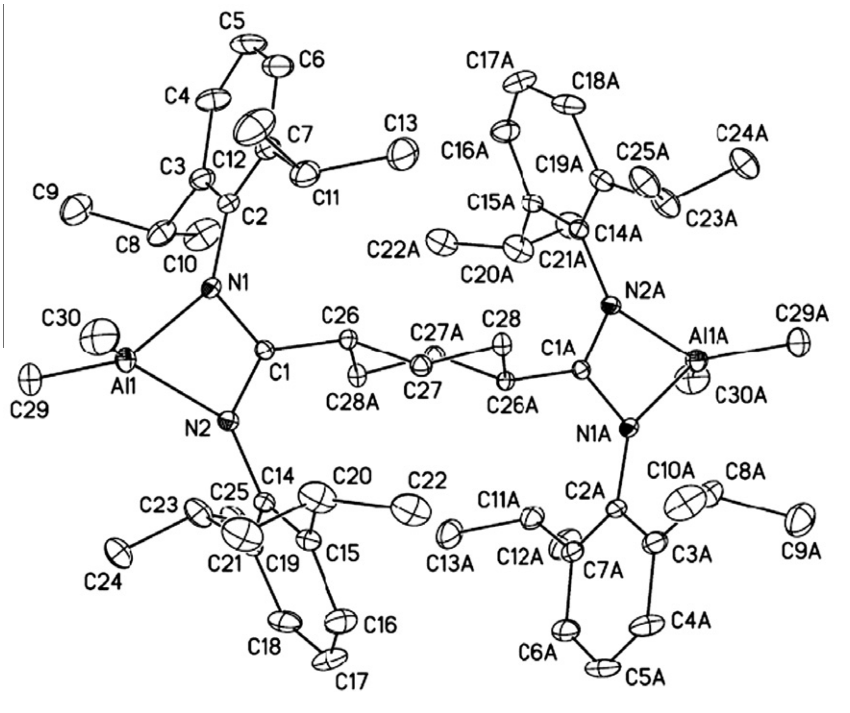


Fig. 3. Molecular structure of $Me_2AlL^3AlMe_2$ (**3**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 10% probability level. Selected bond lengths (Å) and angles (°): N1–C1 = 1.326(5), C1–N2 = 1.343(5), Al1–N1 = 1.927(4), Al1–N2 = 1.944(4), Al1–C29 = 1.943(6), Al1–C30 = 1.942(6), N1–Al1–N2 = 68.53(14), C30–Al1–C29 = 116.9(3), N1–C1–N2 = 109.5(3).

were recorded on a Bruker TENSOR 27 spectrometer. TOF HRMS data were obtained from a Micromass OR-TOF spectrometer. Melting points were not calibrated. Molecular weight and molecular weight distribution of the polymers were measured by PL GPC 50 at 40 °C using THF as eluent against polystyrene standards, flow rate: 1 mL/min, sample concentration: 1 mg/mL.

4.2. Synthesis of p-phenylene-bis(N,N′-bis(2,6-diisopropylphenyl)formamidine) 1,4-$C_6H_4[C(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(NH\text{-}2,6\text{-}{}^iPr_2C_6H_3)]_2$ (H_2L^1)

In a Schlenk flask, P_2O_5 (9.0 g, 63.4 mmol), hexamethyldisiloxane (20 mL, 93.7 mmol), and dry dichloromethane (20 mL) were re-

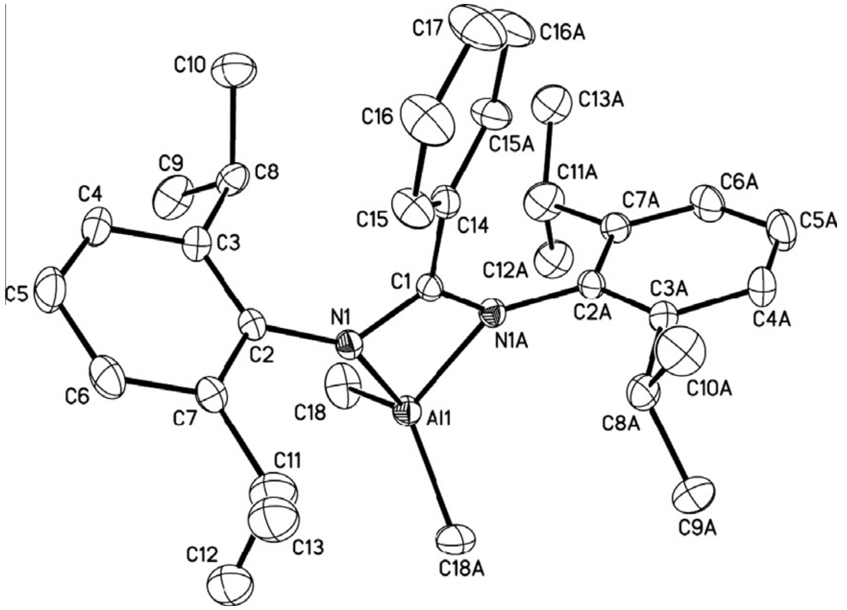


Fig. 4. Molecular structure of L^2AlMe_2 (**5**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 10% probability level. Selected bond lengths (Å) and angles (°): N1–C1 = 1.336(3), Al1–N1 = 1.938(3), Al1–C18 = 1.949(4), N1–Al1–N1A = 68.75(14), C18–Al1–C18A = 116.9(3), N1–C1–N1A = 110.0(3).

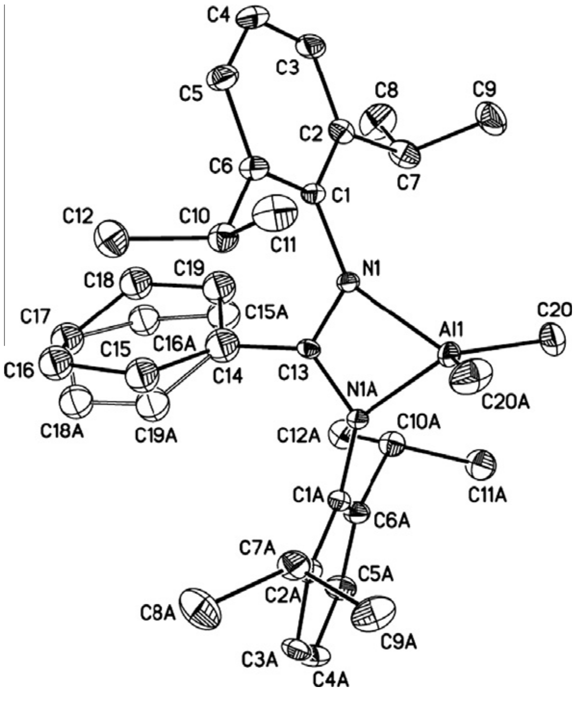
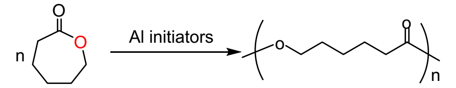


Fig. 5. Molecular structure of L^4AlMe_2 (**7**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 10% probability level. Selected bond lengths (Å) and angles (°): N1–C13 = 1.307(5), Al1–N1 = 1.917(4), Al1–C20 = 1.947(8), N1–Al1–N1A = 68.15(19), C20–Al1–C20A = 117.1(6), N1–C13–N1A = 110.5(5).

Table 2
Polymerization of ε-caprolactone (CL) initiated by amidinate aluminum complexes.[a]



Run	Initiator	Yield[b] (%)	$M_{n,calcd}$[c] ($\times 10^{-4}$)	$M_{n,obsd}$[d] $\times 10^{-4}$	M_w/M_n[d]
1	**1**	78.4	0.56	1.84	1.65
2	**2**	83.4	0.60	1.59	1.47
3	**3**	74.5	0.53	1.09	1.56
4	**4**	79.6	0.57	1.18	1.51
5	**5**	73.9	1.05	2.97	1.21
6	**6**	81.8	1.17	2.46	1.36
7	**7**	76.8	1.09	2.65	1.32
8	**8**	85.3	1.22	2.81	1.40

[a] Polymerization conditions: $[CL]_0/[Al]_0 = 250$, [CL] = 1 M, in toluene, $t = 4$ h, 25 °C.

[b] Yield: weight of polymer obtained/weight of monomer used.

[c] M_n of PCL calculated from $M_{n,calcd} = 114 \times ([CL]/n[Al]) \times$ yield. Monoclear complexes, $n = 2$; bimetallic complexes, $n = 4$.

[d] Determined by GPC at 40 °C in THF relative to polystyrene standards; corrected by the Mark–Houwink equation $M_{n,obsd} = 0.58M_n$ (GPC) [28].

fluxed for 30 min. Then the volatiles were removed under vacuum to afford a viscous syrup PPSE. Terephthalic acid (0.62 g, 3.75 mmol) and 2,6-diisopropylaniline (3.0 mL, 15.08 mmol) were added to this viscous syrup, and the mixture was reacted at 180 °C for 8 h. The resulting mixture was poured into 1 M NaOH solution (150 mL) to produce an oily product, which was allowed to solidify overnight. The solid was washed with water and recrystallized from toluene to give the title compound as pale green powder. Yield: 2.16 g (75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85 (d, $J = 6.4$ Hz, 12H, $CH(CH_3)_2$), 0.94 (d, $J = 6.4$ Hz, 12H, $CH(CH_3)_2$), 1.16 (d, $J = 6.4$ Hz, 12H, $CH(CH_3)_2$), 1.32 (d, $J = 6.4$ Hz, 12H, $CH(CH_3)_2$), 3.10–3.15 (m, 8H, $CH(CH_3)_2$), 5.65 (s, 2H, N–H), 6.95–7.23 (m, 16H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.4, 22.5, 24.2, 25.4 ($CH(CH_3)_2$), 24.4 ($CH(CH_3)_2$), 25.4 ($CH(CH_3)_2$), 28.3 ($CH(CH_3)_2$), 28.3, 28.6 ($CH(CH_3)_2$), 122.5, 123.2, 127.7, 127.9, 133.7, 136.0, 139.2, 143.5, 145.3 (Ar–C), 153.4 (NCN). FT-IR (KBr, cm^{-1}): 3432 (s), 2962 (s), 2868 (m), 1618 (s), 1585 (m), 1465 (m), 1434 (m), 1384 (m), 1358 (m), 1255 (w), 1188 (w), 760 (m). *Anal.* Calc. for $C_{56}H_{74}N_4$: C, 83.74; H, 9.29; N, 6.98. Found: C, 83.42; H, 9.84; N, 6.74%. HRMS $[C_{56}H_{74}N_4]^+$: calcd 802.5913, found 802.5938. mp 222 °C.

4.3. Synthesis of p-phenylene-bis(N,N′-bis(2,6-dimethylphenyl) formamidine) 1,4-$C_6H_4[C(N\text{-}2,6\text{-}Me_2C_6H_3)(NH\text{-}2,6\text{-}Me_2C_6H_3)]_2$ (H_2L^2)

H_2L^2 was prepared by a procedure similar to that of H_2L^1. Using terephthalic acid (0.62 g, 3.75 mmol) and 2,6-dimethylaniline (1.85 mL, 15.0 mmol), the title compound was produced as pale green powder after recrystallization from toluene. Yield: 1.70 g (78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.07 (s, 12H, CH_3), 2.31 (s, 12H, CH_3), 5.68 (s, 2H, N–H), 6.87, 6.90, 7.10, 7.28 (m, 16H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.9, 19.0 (CH_3), 123.1, 126.7, 127.6, 128.0, 128.2, 128.6, 134.8, 136.3, 136.8, 145.7 (Ar–C), 153.4 (NCN). FT-IR (KBr, cm^{-1}): 3375 (s), 2917 (m), 1630 (s), 1587 (m), 1462 (m), 1348 (m), 1205 (m), 766 (m). *Anal.* Calc. for $C_{40}H_{42}N_4$: C, 83.01; H, 7.37; N, 9.68. Found: C, 83.18; H, 7.65; N, 9.16%. HRMS $[C_{40}H_{42}N_4]^+$: calcd 578.3409, found 578.3419. mp 278 °C.

4.4. Synthesis of p-cyclohexylene-bis(N,N′-bis(2,6-diisopropylphenyl) formamidine) $1,4\text{-}C_6H_{10}[C(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(NH\text{-}2,6\text{-}{}^iPr_2C_6H_3)]_2$ (H_2L^3)

H_2L^3 was prepared by a procedure similar to that of H_2L^1. Using 1,4-cyclohexanedicarboxylic acid (0.62 g, 3.75 mmol) and 2,6-diisopropylaniline (3.0 mL, 15.0 mmol), the title compound was produced as white powder after recrystallization from toluene. Yield: 2.16 g (71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.97 (d, *J* = 6.8 Hz, 12H, $CH(CH_3)_2$), 1.12 (d, 12H, $CH(CH_3)_2$), 1.25 (d, *J* = 6.8, 12H, Hz, $CH(CH_3)_2$), 1.26 (d, *J* = 6.8 Hz, 12H, $CH(CH_3)_2$), 1.68 (m, 4H, CH_2), 1.86 (d, *J* = 7.2 Hz, 4H, CH_2), 2.15 (brs, 2H, CH), 3.04–3.08 (m, 4H, $CH(CH_3)_2$), 3.14–3.20 (m, 4H, $CH(CH_3)_2$), 5.20 (s, 2H, N–H), 6.98 (t, *J* = 7.6 Hz, 2H, Ar–H), 7.10 (d, *J* = 8.0 Hz, 8H, Ar–H), 7.25 (t, *J* = 7.6 Hz, 2H, Ar–*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.8, 23.0, 24.1, 25.5 ($CH(CH_3)_2$), 28.0, 28.1 ($CH(CH_3)_2$), 30.3 (Cy–CH_2), 38.1 (Cy–CH), 122.9, 123.0, 123.8, 128.3, 132.6, 139.2, 143.7, 147.0 (Ar–C), 159.3 (NCN). FT-IR (KBr, cm^{-1}): 3365 (m), 2961 (s), 2927 (m), 2867 (m), 1632 (s), 1586 (m), 1459 (m), 1432 (m), 1385 (m), 1346 (w), 763 (m). *Anal.* Calc. for $C_{56}H_{80}N_4$: C, 83.11; H, 9.96; N, 6.92. Found: C, 83.57; H, 9.69; N, 6.74%. HRMS $[C_{56}H_{80}N_4]^+$: calcd 808.6383, found 808.6425. mp 272 °C.

4.5. Synthesis of p-cyclohexylene-bis(N,N′-bis(2,6-dimethylphenyl) formamidine) $1,4\text{-}C_6H_{10}[C(N\text{-}2,6\text{-}Me_2C_6H_3)(NH\text{-}2,6\text{-}Me_2C_6H_3)]_2$ (H_2L^4)

H_2L^4 was prepared by a procedure similar to that of H_2L^1. Using 1,4-cyclohexanedicarboxylic acid (0.62 g, 3.75 mmol) and 2,6-dimethylaniline (1.85 mL, 15.0 mmol), the title compound was produced as white powder after recrystallization from THF. Yield: 1.4 g (65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.69 (m, *J* = 9.5, 4H, CH_2), 1.89 (m, *J* = 7.0 Hz, 4H, CH_2), 2.07 (brs, 2H, CH), 2.18(d, *J* = 4.8 Hz, 24H, CH_3), 5.28 (s, 2H, N–H), 6.85 (t, *J* = 7.4 Hz, 2H, Ar–H), 7.03 (m, 10H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.8, 18.8 (CH_3), 30.7 (Cy–CH_2), 38.6 (Cy–CH), 122.5, 127.4, 128.2, 128.6, 128.9, 135.9, 136.4, 145.7 (Ar–C), 159.7 (NCN). FT-IR (KBr, cm^{-1}): 3442 (s), 2924 (m), 1641 (s), 1589 (m), 1473 (m), 1389 (w), 1222 (w), 1094 (w), 765 (m). *Anal.* Calcd. for $C_{40}H_{48}N_4$: C, 82.15; H, 8.27; N, 9.58. Found: C, 81.92; H, 8.36; N, 9.72%. HRMS $[C_{40}H_{48}N_4]^+$: calcd 584.3879, found 584.3853. mp 340 °C.

*4.6. Synthesis of $Me_2AlL^1AlMe_2$ (**1**)*

$AlMe_3$ (2 mL, 1.0 M, 2 mmol) was added drop by drop to a THF solution (30 mL) of H_2L^1 (0.803 g, 1.0 mmol) at room temperature to give a clear green solution. After the resulting reaction mixture was stirred for 2 h at room temperature, the solvents were removed under reduced pressure to give pale green powder, which was extracted by Et_2O. Concentrating and then cooling the extraction at −35 °C overnight afforded the titled complex as colorless needle crystals (0.83 g, 0.91 mmol, 91% based on Al). ^{1}H NMR (400 MHz, C_6D_6): δ −0.12 (s, 12H, Al–Me_2), 0.74, 1.16 (d, 48H, $CH(CH_3)_2$), 3.39 (m, 8H, $CH(CH_3)_2$), 6.86, 6.97 (m, 16H, Ar–*H*). ^{13}C NMR (100 HMz, C_6D_6): δ −9.9 (Al–CH_3) 22.9, 26.2 ($CH(CH_3)_2$), 28.6 ($CH(CH_3)_2$), 123.8, 126.2, 128.7, 131.3, 137.5, 144.1 (Ar–*C*), 172.8 (NCN). FT-IR (KBr, cm^{-1}): 2962 (s), 2868 (s), 1618 (s), 1585 (m), 1465 (s), 1359 (s), 1325 (m), 800 (m), 762 (s). *Anal.* Calc. for $C_{60}H_{84}Al_2N_4$: C, 78.73; H, 9.25; N, 6.12. Found: C, 78.39; H, 9.01; N, 5.87%.

*4.7. Synthesis of $Me_2AlL^2AlMe_2$ (**2**)*

2 was prepared by a procedure similar to that of **1**. Using $AlMe_3$ (2 mL, 1.0 M, 2 mmol) and H_2L^2 (0.578 g, 1.0 mmol), **2** was produced as colorless needle crystals (0.57 g, 0.83 mmol, 83% based on Al). ^{1}H NMR (400 MHz, C_6D_6): δ −0.24 (s, 12H, CH_3), 1.98 (s, 24H, CH_3), 6.64 (s, 4H, Ar–*H*), 6.73, 6.75, 6.78, 6.79 (m, 12H, Ar–*H*). ^{13}C NMR (100 HMz, C_6D_6): δ −9.0 (Al–CH_3), 19.1 (Ar–CH_3), 125.2, 128.1, 128.6, 132.7, 133.3, 144.0 (Ar–*C*), 171.0 (NCN). FT-IR (KBr, cm^{-1}): 2922 (s), 1624 (s), 1589 (s), 1471 (s), 1390 (s), 1304 (s), 1256 (m), 1199 (m), 1094 (m), 857 (m), 711 (s). *Anal.* Calc. for $C_{44}H_{52}Al_2N_4$: C, 76.49; H, 7.59; N, 8.11. Found: C, 76.35; H, 7.37; N, 7.78%.

*4.8. Synthesis of $Me_2AlL^3AlMe_2$ (**3**)*

3 was prepared by a procedure similar to that of **1**. Using $AlMe_3$ (2 mL, 1.0 M, 2 mmol) and H_2L^3 (0. 809 g, 1.0 mmol), **3** was isolated as pale yellow powder, which was extracted by Et_2O. Concentrating and then cooling the extraction at −35 °C overnight gave the titled complex as colorless needle crystals (0.83 g, 0.93 mmol, 93% based on Al). ^{1}H NMR (400 MHz, C_6D_6): δ −0.49 (s, 12H, Al–CH_3), 0.57 (m, 4H, Cy–CH_2), 0.98, 1.01 (d, 48H, $CH(CH_3)_2$), 1.09 (m, 4H, Cy–CH_2), 1.91 (m, 2H, Cy–*CH*), 3.19 (m, 8H, $CH(CH_3)_2$), 6.93, 6.98 (m, 12H, Ar–*H*). ^{13}C NMR (100 HMz, C_6D_6): δ −9.8 (CH_3), 22.3, 26.3 ($CH(CH_3)_2$), 28.3 ($CH(CH_3)_2$), 25.1, 27.8 (Cy–CH_2), 40.8 (Cy–CH), 123.4, 126.2, 137.5, 144.6 (Ar–*C*), 178.4 (NCN). FT-IR (KBr, cm^{-1}): 2962 (s), 1633 (s), 1586 (m), 1467 (s), 1384 (s), 1321 (s), 1187 (m), 1054 (m), 753 (s). *Anal.* Calc. for $C_{60}H_{90}Al_2N_4$: C, 78.22; H, 9.85; N, 6.08. Found: C, 77.95; H, 9.61; N, 5.79%.

*4.9. Synthesis of $Me_2AlL^4AlMe_2$ (**4**)*

4 was prepared by a procedure similar to that of **1**. Using $AlMe_3$ (2 mL, 1.0 M, 2 mmol) and H_2L^4 (0.584 g, 1.0 mmol), **4** was produced as pale yellow powder, which was extracted by THF. Concentrating and then cooling the extraction at −35 °C overnight gave the titled complex as colorless needle crystals (0.64 g, 0.92 mmol, 92% based on Al). ^{1}H NMR (400 MHz, C_6D_6): δ −0.35 (s, 12H, CH_3), 0.76 (m, 4H, Cy–CH_2), 1.53 (m, 4H, Cy–CH_2), 1.79 (m, 2H, Cy–*CH*), 2.11 (s, 24H, Ar–CH_3), 6.81–6.89 (m, 12H, Ar–*H*). ^{13}C NMR (100 HMz, C_6D_6): δ −8.3 (Al–CH_3), 19.1 (Ar–CH_3), 27.9 (Cy–CH_2), 40.5 (Cy–*C*H), 125.3, 127.8, 133.9, 141.2 (Ar–*C*), 177.5 (NCN). FT-IR (KBr, cm^{-1}): 2930 (s), 1639 (s), 1589(m), 1471 (s), 1388 (m), 1211 (m), 769 (s). $C_{42}H_{58}Al_2N_4$: C, 74.97; H, 8.69; N, 8.33. Found: C, 74.68; H, 8.51; N, 7.97%.

*4.10. Synthesis of L^5AlMe_2 (**5**)*

$AlMe_3$ (2 mL, 1.0 M, 2 mmol) was added drop by drop to a THF solution (30 mL) of HL^5 (0.881 g, 2.0 mmol) at room temperature to give a clear green solution. After the resulting reaction mixture was stirred for 2 h at room temperature, the solvents were removed under reduced pressure to give pale green powder, which was washed by hexane. Recrystallization from toluene/hexane solution afforded the titled complex as pale green block crystals (0.9 g, 91% based on Al). ^{1}H NMR (400 MHz, C_6D_6): δ −0.06 (s, 6H, Al–Me_2), 0.93, 1.26 (d, 24H, $CH(CH_3)_2$), 3.62 (m, 4H, $CH(CH_3)_2$), 6.59, 6.61, 6.62 (m, 3H, Ar–*H*), 6.70, 7.02, 7.06, 7.07, 7.11, 7.13 (m, 8H, Ar–*H*). ^{13}C NMR (100 HMz, C_6D_6): δ −9.8 (CH_3) 22.9, 25.8 ($CH(CH_3)_2$), 28.7 ($CH(CH_3)_2$), 124.1, 126.2, 128.2, 130.5, 139.5, 143.8 (Ar–*C*), 172.8 (NCN). FT-IR (KBr, cm^{-1}): 2962 (s), 2867 (s), 1623 (s), 1587 (m), 1465 (s), 1357 (m), 1189 (m), 1031 (m), 771 (s). *Anal.* Calc. for $C_{33}H_{45}AlN_2$: C, 79.80; H, 9.13; N, 5.64. Found: C, 79.32; H, 8.93; N, 5.59%.

4.11. Synthesis of L^6AlMe_2 (**6**)

$AlMe_3$ (2 mL, 1.0 M, 2 mmol) was added drop by drop to a THF solution (30 mL) of HL^6 (0.803 g, 1.0 mmol) at room temperature to give a clear green solution. After the resulting reaction mixture was stirred for 2 h at room temperature, the solvents were removed under reduced pressure to give pale green powder, which was extracted by Et_2O. Concentrating and then cooling the extraction at −35 °C overnight afforded the titled complex as colorless needle crystals (0.78 g, 0.85 mmol, 85% based on Al). ^{1}H NMR (400 MHz, C_6D_6): δ −0.14 (s, 6H, Al–*Me*$_2$), 2.25 (s, 12H, Ar–C*H*$_3$), 6.58 (m, 3H, Ar–*H*), 6.84 (m, 6H, Ar–*H*), 7.02 (m, 2H, Ar–*H*). ^{13}C NMR (100 HMz, C_6D_6): δ −8.7 (Al–*C*H$_3$) 19.3 (Ar–*C*H$_3$) 125.1, 128.7, 130.8, 133.6, 141.8 (Ar–*C*), 172.2 (N*C*N). FT-IR (KBr, cm^{-1}): 2922 (s), 2843 (m), 1623 (s), 1576 (m), 1471 (s), 1378 (m), 1194 (m), 1093 (m), 775 (s), 698 (s). *Anal.* Calc. for $C_{25}H_{29}AlN_2$: C, 78.09; H, 7.60; N, 7.29. Found: C, 78.53; H, 7.72; N, 7.61%.

4.12. Synthesis of L^7AlMe_2 (**7**)

7 was prepared by a procedure similar to that of **5**. Using $AlMe_3$ (1 mL, 1.0 M, 1 mmol) and HL^7 (0.334 g, 1.0 mmol), **7** was produced as pale yellow powder (0.34 g, 88%). ^{1}H NMR (400 MHz, C_6D_6): δ −0.35 (s, 6H, Al–C*H*$_3$), 0.56 (m, 4H, Cy–C*H*$_2$), 1.06 (m, 2H, Cy–C*H*$_2$), 1.21 (m, 2H, Cy–C*H*$_2$), 1.23, 1.30 (d, 24H, CH(C*H*$_3$)$_2$), 1.73 (m, 2H, Cy–C*H*$_2$), 2.34 (m, 1H, Cy–C*H*), 3.59 (m, 4H, C*H*(CH$_3$)$_2$), 7.14 (m, 6H, Ar–*H*). ^{13}C NMR (100 HMz, C_6D_6): δ −8.9 (*C*H$_3$), 23.0, 26.8 (CH(*C*H$_3$)$_2$), 28.7 (*C*H(CH$_3$)$_2$), 25.4, 25.6, 29.1 (Cy–*C*H$_2$), 41.7 (Cy–*C*H), 123.8, 126.5, 138.0, 145.2 (Ar–*C*), 179.7 (N*C*N). FT-IR (KBr, cm^{-1}): 2928 (s), 2866 (s), 1633 (s), 1586 (m), 1463 (s), 1385 (m), 1189 (m), 761 (s). *Anal.* Calc. for $C_{33}H_{51}AlN_2$: C, 78.84; H, 10.22; N, 5.57. Found: C, 78.65; H, 9.86; N, 5.94%.

4.13. Synthesis of L^8AlMe_2 (**8**)

8 was prepared by a procedure similar to that of **5**. Using $AlMe_3$ (1 mL, 1.0 M, 1 mmol) and HL^8 (0.23 g, 1.0 mmol), **8** was produced as pale yellow powder (0.34 g, 89%). ^{1}H NMR (400 MHz, C_6D_6): δ −0.25 (s, 6H, Al–C*H*$_3$), 0.52 (m, 4H, Cy–C*H*$_2$), 1.06 (m, 2H, Cy–C*H*$_2$), 1.20 (m, 2H, Cy–C*H*$_2$), 1.72 (m, 2H, Cy–C*H*$_2$), 2.18 (m, 1H, Cy–C*H*), 2.32 (s, 12H, Ar–C*H*$_3$), 6.96 (m, 6H, Ar–*H*). ^{13}C NMR (100 HMz, C_6D_6): δ −7.9 (*C*H$_3$), 19.4 (Ar–*C*H$_3$), 25.5, 26.3, 28.5 (Cy–*C*H$_2$), 41.7 (Cy–*C*H), 125.4, 128.3, 134.5, 141.8 (Ar–*C*), 178.8 (N*C*N). FT-IR (KBr, cm^{-1}): 2927 (s), 2853 (s), 1636 (s), 1589 (s), 1473 (s), 1385 (m), 1228 (m), 767 (s). *Anal.* Calc. for $C_{25}H_{35}AlN_2$: C, 76.89; H, 9.03; N, 7.17. Found: C, 76.43; H, 9.76; N, 7.34%.

4.14. A typical procedure for ε-caprolactone polymerization (run 1, Table 2)

In a 20 mL Schleck flask, **1** (20 mg, 22 μmol), ε-caprolactone (627 mg, 5.5 mmol), and toluene (5.0 mL) were stirred at 25 °C for a pre-determined time. The polymerization was terminated by quenching with excess ethanol containing 5% *aq*. HCl. The polymer was collected, and dried under vacuum at 60 °C to a constant weight (492 mg, 78.4%).

4.15. X-ray crystallographic study

Suitable single crystals of complexes 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 ($\lambda = 0.71070$ 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 the non-hydrogen atoms were refined anisotropically. The structures were solved and refined using SHELXL-97 program. CCDC 776820–776824 contains the supplementary crystallographic data for $\mathbf{H_2L^3}$, **1**, **3**, **5** and **7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

This work was partly financial supported by the State Key Laboratory of Rare Earth Resource Utilization (RERU2011020), Zhejiang Provincial Natural Science Foundation (Y4090617), Science and Technology Department of Zhejiang Province (2010R10020), and Ningbo Municipal Science Foundation (2009D10015).

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