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Preparation and Characterization of Aluminum Alkoxides Coordinated on salen-Type Ligands: Highly Stereoselective Ring-Opening Polymerization of *rac*-Lactide

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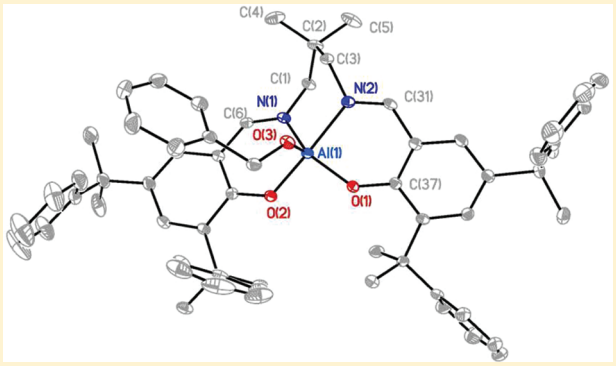
Supporting Information

ABSTRACT: A series of salen-type ligands (L^1H_2–L^6H_2) with sterically bulky cumyl groups have been synthesized. Reaction of these ligands with $AlMe_3$ yields the mononuclear aluminum complexes [LAlMe] (**1**–**3**) or dinuclear species [$L_2Al_2Me_4$] (**4**–**6**), respectively. Further reaction of [LAlMe] (**1**–**3**) with benzyl alcohol produces [LAl(OBn)] (**1a**–**3a**), respectively. Solid-state structural studies reveal that complexes **1a** and **2a** are mononuclear; however, complex **6** is a dinuclear species. Aluminum alkoxides **1a**–**3a** are highly stereoselective in the ROP of *rac*-lactide, producing polylactide (PLA) with 94–97% enantiomeric selectivity (P_m) at high conversion. Their high enantioselectivity leads to PLA with high T_m (205 °C). The polymerization of L-lactide by these complexes also shows good living features with narrow PDI values (M_w/M_n = 1.06–1.25) signaling less or no transesterification, which can be further verified by MALDI-TOF mass spectrometric analysis.



INTRODUCTION

Polylactides (PLAs) have been widely used in many applications, ranging from packing to biomedical devices, due to their unique biodegradable, biocompatible, and permeable properties.[1] They can be prepared by direct polycondensation of lactic acid or by ring-opening polymerization (ROP) of lactides using a suitable homogeneous catalyst.[2] Among the various preparation methods of PLAs, ring-opening polymerization of lactides (LAs) using metal complexes as catalysts/initiators has been proven to be the most effective method. Over the past decades, numerous metal complexes have been used as catalysts/initiators for ROP of lactides and many of them have been proven to have high activity, low toxicity, and low cost and are able to produce high-molecular-weight polymers with low polydispersity.[3] Recently, there has been greater demand for the control of the stereochemistry of insertion of the lactide monomer into the PLA chain, since the mechanical properties of PLAs rely on its microstructure.[4] However, catalysts for the ROP of *rac*-lactide offering good control of the microstructure of PLA are relatively rare as compared to those for ROP of L-LA.

Aluminum complexes constitute the most effective and versatile synthetic strategy for preparing amorphous to semicrystalline PLAs with a wide range of physical, mechanical, and degradation properties.[5] Over the past decade, several aluminum species with N,O-donor ligands have been emerged as ring-opening polymerization catalysts, among which alkoxido and amino–alkoxido derivatives have been found to be particularly efficient.[6] Previously, a series of the aluminum alkoxides supported on bisphenolate have been prepared in our group and these complexes have demonstrated good catalytic activities toward polymerization of ε-caprolactone and L-lactide.[7] Aluminum salen and half-salen complexes are easily prepared,[8] and most of them have shown highly stereocatalytic activity toward the ROP of *rac*-lactide.[9] We report herein the preparation of a series of aluminum salen complexes with cumyl groups on ortho and para positions and their activities toward the ROP of lactides.

RESULTS AND DISCUSSION

Syntheses and Characterization. Though many aluminum salen complexes have shown great stereoselectivity toward ring-opening polymerization of *rac*-lactide, the influence of substituents and linkers on salen affecting the stereoselectivity toward the ROP of *rac*-lactide remains an interesting topic. As a result, a series of salen-type ligands with sterically bulky cumyl groups (−CMe_2Ph) at the ortho and para positions have been synthesized in moderate to high yield (Scheme 1). The reaction of L^1H_2–L^3H_2 with 1 mol equiv of $AlMe_3$ yields [LAlMe] (**1**–**3**), respectively. Further reaction of compounds **1**–**3** with a stoichiometric amount of benzyl alcohol (BnOH) gives the corresponding aluminum alkoxide complexes [LAl(OBn)] (**1a**–**3a**). All six complexes have been fully characterized. For instance, the ^1H NMR spectrum of aluminum alkoxide complex

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Scheme 1. Preparation of salen-Type Ligands and Their Aluminum Complexes

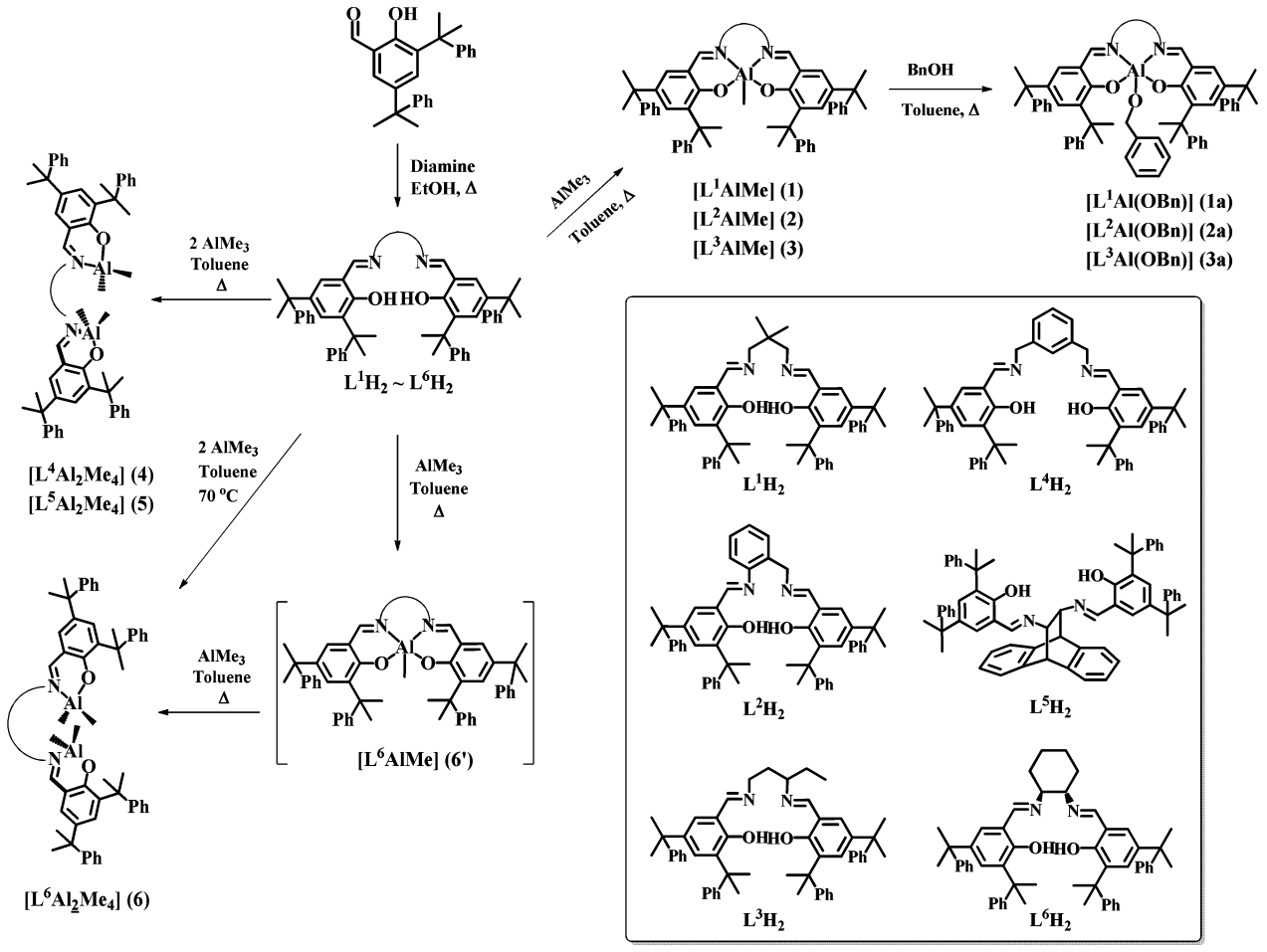

Table 1. Comparison of ^{1}H NMR Data for Ligands L^1H_2–L^3H_2, 1–3, and 1a–3a[a]

	L^1H_2	L^2H_2	L^3H_2	1	2	3[b]	1a	2a	3a
–*HC*=N	8.14 (s)	8.41 (s)	8.24 (s)	8.06 (s)	8.16 (s)		7.90 (s)	8.21 (s)	7.97 (s)
		8.23 (s)	8.22 (s)		8.10 (s)			8.16 (s)	7.96 (s)
C=N*CH*$_2$–	3.26(s)	4.67 (s)	3.44(m)	3.27 (d)	4.79 (d)		3.47 (d)	4.81 (d)	4.06 (t)
				3.12 (d)	4.07 (d)		3.06 (d)	4.19 (d)	3.44 (t)
–O*CH*$_2$Ph							3.97 (br)	3.81–3.59(m)	4.33–4.30(m)
Al–Me				–1.42 (s)	–1.61 (s)				

[a]All peaks of the ligands and aluminum complexes were characterized by ^{1}H NMR. [b]Not isolated and determined.

1a displays a broad signal at δ 3.97 ppm corresponding to CH_2 groups on the benzyl alkoxy group. The imine proton (N=C*H*) appears at 7.90 ppm, which is about 0.2 ppm upfield from that of the free salen ligand, L^1H_2. It is worth noting that peaks for NCH_2C split from a sharp singlet peak in the free ligand **1** to two doublets in complex **1a** due to the formation of an AlNCCCN six-membered ring, resulting in an AB pattern of NCH_2 hydrogens at the backbone. In addition, two CH_3 groups on the amine backbone in L^1-H_2 also split into two singlet peaks at δ 0.87 and 0.73, respectively. The phenomenon is the result of the AlNCCCN six-membered ring causing different chemical environments between the inner and outer ring. This different environment can be verified by X-ray crystal structure studies. Similar results were found for compounds **2a** and **3a**. For instance, the methylene peak of alkoxide is a broad signal from δ 3.81 to 3.59 for complex **2a**, and the signals corresponding to NCH_2N protons appear at δ 4.81 and 4.19 ppm, respectively. A comparison of ^{1}H NMR data for ligands L^1H_2–L^3H_2, **1**–**3**, and **1a**–**3a** are summarized in Table 1.

However, ligands L^4H_2 and L^5H_2 react with 2 molar equiv of $AlMe_3$, yielding the metal complexes [$L^nAl_2Me_4$] (**4** and **5**), as shown in Scheme 1. Unfortunately, further reaction of **4** and **5** with 4 mol equiv of BnOH did not successfully give aluminum alkoxide complexes. The ^{1}H NMR spectrum of the methyl group on the metal center displays two singlet peaks at δ –1.32 and –1.33 ppm for **4** and two doublet peaks at –1.05 and –1.36 ppm for **5**. The reaction of L^6H_2 with trimethylaluminum in toluene at 70 °C gives a mixture of the dinuclear species [$L^6Al_2Me_4$] (**6**) and the momonuclear species [L^6AlMe] (**6′**). After the reaction, complete removal of the solvent under vacuum results in a sticky yellow residue. Compound **6′** was precipitated by adding dry *n*-hexane to the sticky residue and stirring for 30 min. Interestingly, yellow crystals of compound **6** were obtained from the filtrate of the *n*-hexane extract after

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storage overnight at room temperature and it was found that **6** was the major product in the mixture of **6′** and **6**. It is evident that the higher solubility of the compound **6** as compared to that of compound **6′** in *n*-hexane results in single crystals of **6**. Fresh samples of complex **6′**, dissolved in chloroform-*d*, display an intense upfield signal at δ −1.40 corresponding to the Al−CH_3 moiety, similar to the ^{1}H NMR spectral pattern of salen aluminum alkyl complexes.[10] Signals corresponding to N=C*H* protons appear at δ 8.27 and 8.03 ppm, integrated as 1:3 with the signal corresponding to the Al−CH_3 moiety. This confirms a difference in the chemical environment of the N=C*H* protons in comparison to that of **6**. Similar differences in the ^{1}H NMR pattern are recorded for signals corresponding to the NC*H* protons of the cyclohexyl ring, in which case complex **6′** displays two signals, one at δ 3.02 resolving as a multiplet and the other at δ 2.55 resolving as a doublet, suggesting chemically nonequivalent protons and confirming a tetradentate donor arrangement of salen around the central Al. In contrast, protons of the NC*H* moiety of the cyclohexyl unit display chemically equivalent signals at δ 3.45 ppm in the case of complex **6**. Complexes **1a**−**3a**, **4**−**6**, and **6′** have been fully characterized by ^{1}H and ^{13}C NMR and elemental analysis. Fortunately, crystals of aluminum complexes suitable for X-ray structure determinations could be obtained from a hexane/toluene mixed solution.

Crystal Structure Determination. The molecular structures of **1a**, **2a**, and **6** were determined by the X-ray diffraction methods (for crystallographic data see Table S1 in the Supporting Information) and the structures were solved by direct methods using the SHELXTL package.[11] The molecular structures of **1a** and **2a** are depicted in Figures 1 and 2,

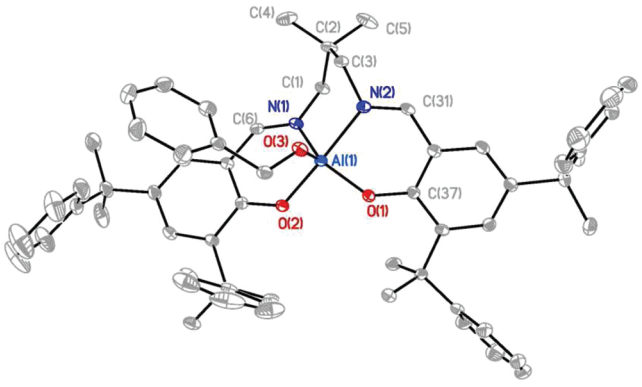

Figure 1. Molecular structure of [L^1Al(OBn)] (**1a**) with thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Al(1)−O(3) = 1.7381(11), Al(1)−O(1) = 1.7788(10), Al(1)−O(2) = 1.8289(10), Al(1)−N(1) = 1.9828(12), Al(1)−N(2) = 2.0227(12); O(3)−Al(1)−O(1) = 122.59(5), O(3)−Al(1)−O(2) = 100.03(5), O(1)−Al(1)−O(2) = 91.50(5), O(3)−Al(1)−N(1) = 115.78(5), O(1)−Al(1)−N(1) = 120.49(5), O(2)−Al(1)−N(1) = 89.02(5), O(3)−Al(1)−N(2) = 86.28(5), O(1)−Al(1)−N(2) = 89.31(5), O(2)−Al(1)−N(2) = 171.91(5), N(1)−Al(1)−N(2) = 83.64(5).

respectively. The structure shows that complexes **1a** and **2a** are both mononuclear with a five-coordinate aluminum center bonding to a benzyl alkoxide and an N,N,O,O-tetradentate salen ligand. The two largest angles in each complex are O(2)−Al(1)−N(2) = 171.91(5)° and O(3)−Al(1)−O(1)° = 122.59(5) in **1a**, while the other angles in **2a** are O(1)−Al−N(2) = 173.99(6)° and O(2)−Al−N(1) = 124.41(6)°. The τ

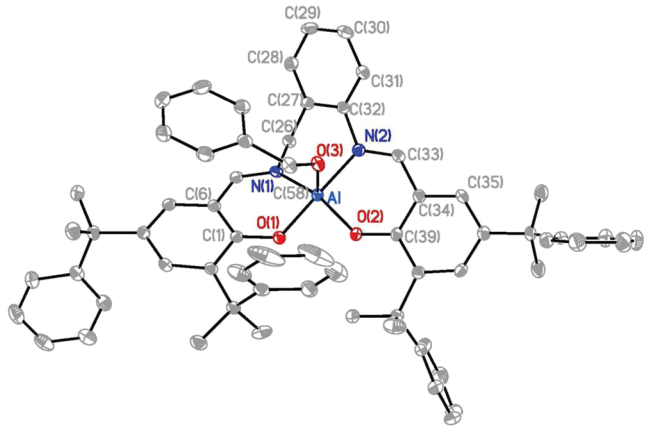

Figure 2. Molecular structure of [L^2Al(OBn)] (**2a**) with thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Al−O(3) = 1.7330(11), Al−O(2) = 1.7863(12), Al−O(1) = 1.8339(12), Al−N(1) = 1.9734(14), Al−N(2) = 2.0606(14); O(3)−Al−O(2) = 124.35(6), O(3)−Al−O(1) = 100.41(6), O(2)−Al−O(1) = 89.98(5), O(3)−Al−N(1) = 110.20(6), O(2)−Al−N(1) = 124.41(6), O(1)−Al−N(1) = 90.17(5), O(3)−Al−N(2) = 85.44(5), O(2)−Al−N(2) = 87.78(5), O(1)−Al−N(2) = 173.99(6), N(1)−Al−N(2) = 86.50(5).

values of **1a** and **2a** are 0.822 and 0.826, respectively, indicating the geometries around the Al center of both complexes are distorted trigonal bipyramidal (tbp) rather than square pyramidal (sqp).

As depicted in Figure 3a, complex **6** shows a dinuclear feature in the solid state in which two Al atoms are four-coordinated, bonding to one N, one O, and two C atoms of the methyl anion groups adopting a tetrahedral geometry around both Al centers. The O(1) and N(1) atoms and (in another set) N(2) and O(2) of the salen are bonded to Al(1) and Al(2) atoms, forming two distorted-boat-shaped rings consisting of N(1)−C(7)−C(6)-C(1)−O(1)−Al(1) and N(2)−C(14)−C(15)-C(20)−O(2)−Al(2) units. In compound **6**, Al atoms are located completely away from the ONNO plane of the salen, which is in stark contrast to the geometry of the Al alkyl or alkoxy complexes consisting of tetradentate ONNO donor salen. This unusual formation of a dinuclear geometry is probably due to the rigid chair conformation of the cyclohexyl ring and trans arrangement of the NN unit and also subsequent steric congestion contributed by the phenyl groups of the ortho and para cumyl groups. It is important to note the N(1)−C(8)−C(13)−N(2) connectivity, in which N(1) and N(2) exist in different planes with a the bond angles N(1)−C(8)−C(13) = 109.08(15)° and C(8)−C(13)−N(2) = 109.04(15)°. In compound **6**, the methyl anions (C(57)−C(60)) bonded to the Al(1) and Al(2) centers are oriented toward the outer side of the six-membered rings consisting of Al(1)−O(1)−C(1)−C(6)−C(7)−N(1) and Al(2)−O(2)−C(20)−C(15)−C(14)−N(2). These methyl anions are placed in two perpendicular planes that are also perpendicular to the plane formed by the slightly distorted six-membered rings. The Al(1) center displays angles C(58)−Al(1)−N(1) = 114.36(9)° and C(57)−Al(1)−N(1) = 105.76(9)° and a similarly perpendicular arrangement of the methyl in the other six-membered rings consisting of Al(2) center with angles C(60)−Al(2)−N(2) = 106.25(9)° and C(59)−Al(2)−N(2) = 112.60(8)°, respectively. Figure 3b displays a chair conformation exhibited by the cyclohexyl unit

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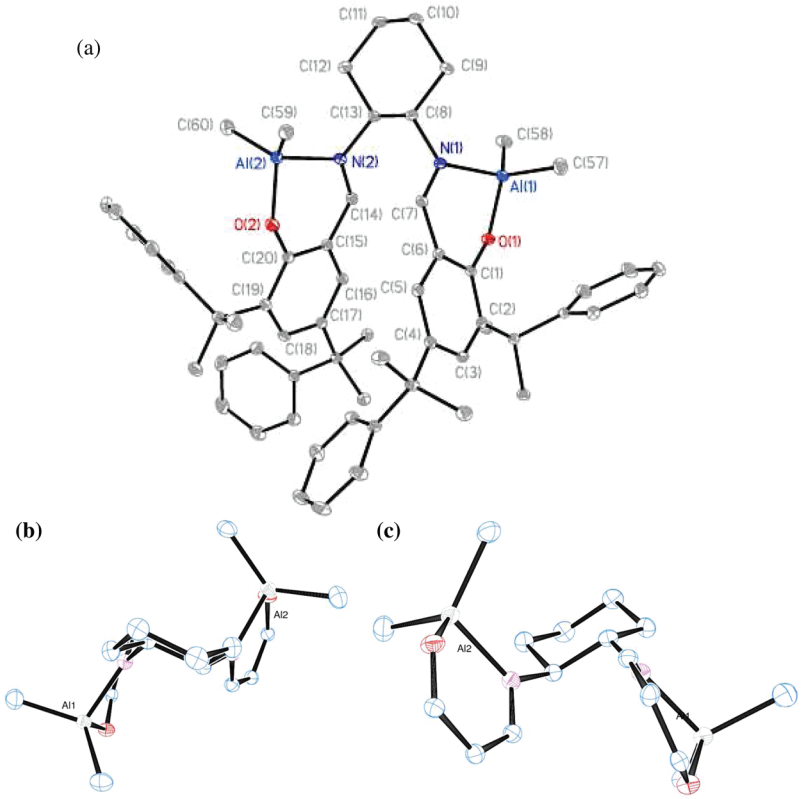
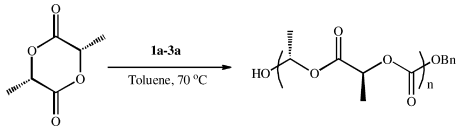


Figure 3. (a) Molecular structure of $[L^6Al_2Me_4]$ (**6**) with thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Al(1)−O(1) = 1.7786(13), Al(1)−C(57) = 1.948(2), Al(1)−C(58) = 1.954(2), Al(1)−N(1) = 1.9738(16), Al(2)−O(2) = 1.7706(14), Al(2)−C(60) = 1.953(2), Al(2)−C(59) = 1.957(2), Al(2)−N(2) = 1.9807(16); O(1)−Al(1)−C(57) = 111.96(8), O(1)−Al(1)−C(58) = 110.25(8), C(57)−Al(1)−C(58) = 118.06(10), O(1)−Al(1)−N(1) = 93.71(6), C(57)−Al(1)−N(1) = 105.78(8), C(58)−Al(1)−N(1) = 114.43(8), O(2)−Al(2)−C(60) = 113.41(8), O(2)−Al(2)−C(59) = 105.95(8), C(60)−Al(2)−C(59) = 121.38(9), O(2)−Al(2)−N(2) = 93.87(6), C(60)−Al(2)−N(2) = 106.29(8), C(59)−Al(2)−N(2) = 112.60(8). (b) Chair conformation of the cyclohexyl unit and Al(1) and Al(2) in different planes. (c) Two six-membered rings with $AlMe_2$ units in different planes.

Table 2. Ring-Opening Polymerization of L-Lactide Initiated by 1a−3a[a]



entry	cat.	time (h)	$[I]_0/[M]_0$	conversn (%)[b]	M_n(GPC)[c]	M_n(calcd)[d]	PDI[e]
1	**1a**	12	1/50	96	11 600 (6 700)	7 000	1.11
2	**1a**	12	1/100	96	24 000 (13 900)	14 000	1.10
3	**1a**	12	1/150	96	37 600 (21 800)	21 000	1.10
4	**1a**	12	1/200	97	46 200 (26 800)	28 000	1.11
5	**2a**	12	1/50	92	11 500 (6 700)	6 700	1.08
6	**2a**	12	1/75	96	18 100 (10 500)	10 400	1.08
7	**2a**	12	1/125	97	25 200 (14 600)	14 000	1.09
8	**2a**	12	1/150	98	36 200 (21 000)	21 000	1.07
9	**3a**	12	1/100	72	18 800 (10 900)	10 500	1.06

[a]Reaction conditions: 70 °C, toluene (10.0 mL), [I] = 5 mM. [b]Obtained from the ^{1}H NMR analysis. [c]Obtained from GPC analysis and calibrated by polystyrene standard. Values in parentheses are the values obtained from GPC times 0.58.[13] [d]Calculated from the molecular weight of M_w(LA) × $[M]_0/[BnOH]_0$ × conversion + M_w(BnOH). [e]Obtained from GPC.

of the complex **6**. The average Al−Me bond length in complex **6** is ∼1.95 Å, which is consistent with the same in reports of similar aluminum methyl complexes.[10,12]

Ring-Opening Polymerization of L-Lactide. Ring-opening polymerization of L-lactide using complexes **1a−3a** (5.0 mM) as an initiator has been systematically studied at 70 °C (Table 2). Each of these complexes displayed good activities for the polymerization of L-lactide with 72−97% conversion within 12 h with good molecular weight control between the molar masses determined by GPC analysis (M_n(GPC)) and those calculated (M_n(calcd)), as well as narrow distributions ranging from 1.06 to 1.10. The linear relationship of **1a** and **2a** between the M_n and $[M]_0/[I]_0$ ratio and the low polydispersity index

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(PDI) of the polymer simply point to the highly controlled and "living" character of the polymerization process (Figure 4).

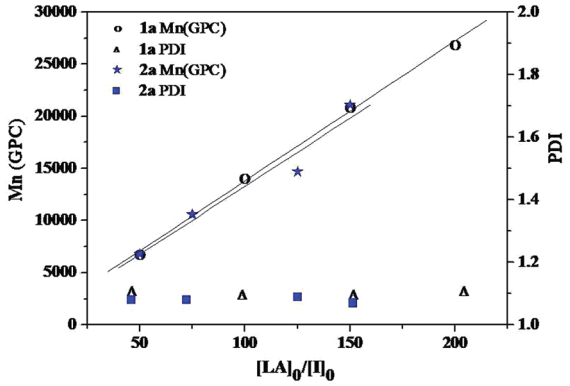

Figure 4. Polymerization of L-LA catalyzed by **1a** and **2a** in toluene at 70 °C. The relationship between M_n versus PDI of polymer and the initial mole ratio $[LA]_0/[I]_0$ is shown.

ROP of L-lactide initiated by complexes **4**–**6** in the presence of BnOH with a [I]/[M]/[BnOH] ratio of 1/200/4 are summarized in Table 3. Experimental results indicate that **6** is an efficient initiator for the polymerization of L-lactide, in which case >90% conversion was noted within 9 h at 70 °C. Further investigations of **6** by varying the monomer to initiator ratio ($[LA]_0/[BnOH]_0$) from 50 to 200 showed that the livingness of the polymerization is maintained even at different ratios (Table 3). However, complexes **4** and **5** have less catalytic activity, probably due to the sterically bulky substituent on the diamine retarding the reaction rate.

MALDI-TOF Mass Spectroscopic Studies. MALDI-TOF (matrix-assisted laser desorption/ionization time-of-flight) mass spectra have been widely used to determine the size of repeating units as well as the initiator group and end group masses.[14] In order to understand the structure and composition of the PLA obtained, a MALDI-TOF spectrum of PLA (entry 1, Table 3) was performed using HABA as a matrix, as shown in Figure 5. In the results, accurate estimates of M_n by MALDI-TOF are limited to nearly monodisperse polymer samples and the mass spectrum shows a cluster of homologous peaks separated by a molecular mass of ~144 Da corresponding to one L-lactide repeating unit, indicating that the intermolecular transesterification did not happen in polymerization. Further, no peaks are found in the mass spectra of the polymer which is

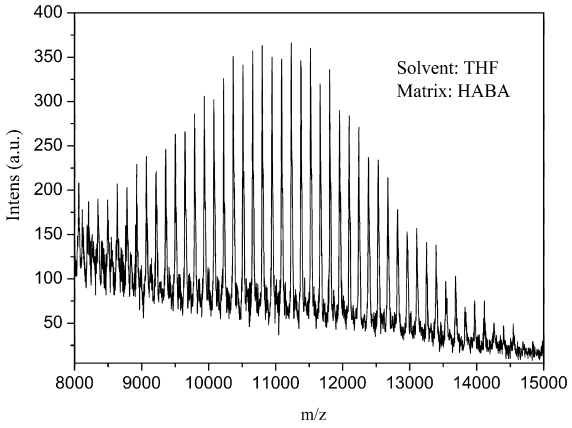

Figure 5. MALDI-TOF-MS spectrum of poly(L-LA) prepared by ROP of L-LA using **1a** as an initiator.

associated with the internal transesterification reaction (72.0 Da).

Stereoselective Polymerization of *rac*-Lactide. It has been known that the physical and degradation properties of PLA are dramatically dependent on the stereochemistry of the polymer chain. Since Spassky et al. illustrated highly stereoselective polymerization of *rac*-lactide initiated by aluminum Schiff base complexes,[15] many salen-based aluminum alkoxides acting as catalysts with high stereocontrol in the ring-opening polymerization of *rac*-lactide have been reported.[6g,h,16] To investigate the influence of the ligand geometry and metal ions on the stereochemistry of the polymerization process, ROP of *rac*-LA was performed using both aluminum alkoxide complexes **1a**–**3a** and aluminum methyl complexes **4**–**6** in the presence of benzyl alcohol (Table 4). Complexes **1a** and **2a** exhibit very high isotactic selectivity: P_m = 0.97 in **1a** and P_m = 0.94 in **2a**, estimated from a homodecoupled ^{1}H NMR, with conversion >90% at 70 °C in toluene. The slight selectivity difference between **1a** and **2a** might be due to the flexibility of the backbone, in which 2,2-dimethyl-1,3-diamine is more flexible than 2-(aminomethyl)aniline. This hypothesis can be verified by the X-ray structure results. The N(1)–N(2) distance is 2.671 Å in **1a** and 2.765 Å in **2a**, indicating that harsh and crowded conditions near the active metal center induce higher selectivity. To produce the greater selectivity, complex **3a** is designed with a ligand bearing a huge steric

Table 3. Ring-Opening Polymerization of L-Lactide Initiated by 4–6[a]

entry	cat.	time (h)	$[I]_0/[M]_0/[BnOH]_0$	conversn (%)[b]	M_n(GPC)[c]	M_n(calcd)[d]	PDI[e]
1	**4**	12	1/200/4	57	6 400 (3 700)	4 200	1.08
2	**5**	12	1/200/4	61	7 600 (4 200)	4 400	1.08
3	**6**	8	1/200/4	99	13 800 (8 000)	7 200	1.25
4	**4**	24	1/200/4	72	7 900 (4 600)	5 300	1.08
5	**5**	55	1/200/4	94	10 700 (6 200)	6 800	1.13
6	**6**	8	1/200/4	99	13 800 (8 000)	7 200	1.25
7	**6**	8	1/100/2	95	12 800 (7 400)	7 000	1.21
8	**6**	9	1/200/2	94	24 100 (14 000)	13 600	1.24
9	**6**	9	1/300/2	91	34 500 (20 100)	19 800	1.29
10	**6**	10	1/400/2	88	46 200 (26 800)	25 500	1.26

[a]Reaction conditions: 70 °C, toluene (10.0 mL), [I] = 5 mM. [b]Obtained from the ^{1}H NMR analysis. [c]Obtained from GPC analysis and calibrated by polystyrene standard. Values in parentheses are the values obtained from GPC times 0.58.[13] [d]Calculated from the molecular weight of $M_{w(LA)}$ x $[M]_0/[BnOH]_0$ x conversion + $M_{w(BnOH)}$. [e]Obtained from GPC.

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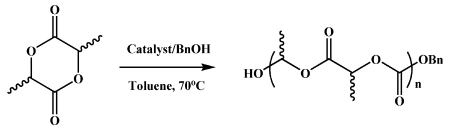
Table 4. Ring-Opening Polymerization of *rac*-Lactide[a]



entry	cat.	time (h)	$[I]_0/[M]_0/[BnOH]_0$	conversn (%)[b]	M_n(GPC)[c]	M_n(calcd)[d]	PDI[e]	P_m	T_m (°C)
1	**1a**	12	1/100/0	94	21 000 (12 200)	13 500	1.07	0.97	203
2	**2a**	12	1/100/0	90	20 000 (11 600)	13 000	1.08	0.94	185
3	**3a**	24	1/100/0	57	10 900 (6 300)	6 400	1.06	0.97	205
4	**4**	39	1/200/4	45	*f*	3 240	*f*	*f*	
5	**5**	55	1/200/4	70	6 300 (3 700)	5 000	1.10	0.33	
6	**6**	18	1/100/2	93	13 400 (7 800)	6 800	1.27	0.60	
7	**6′**	18	1/100/2	73	10 700 (6 200)	5 400	1.28	0.76	150

[a]Reaction conditions: 70 °C, toluene (10.0 mL), [I] = 5 mM. [b]Obtained from the ^{1}H NMR analysis. [c]Obtained from GPC analysis and calibrated by polystyrene standard. Values in parentheses are the values obtained from GPC times 0.58.[13] [d]Calculated from the molecular weight of M_w(LA) × $[M]_0/[BnOH]_0$ × conversion + M_w(BnOH). [e]Obtained from GPC. (The original GPC data have been placed in the Supporting Information in Table S4.) [f]Not determined.

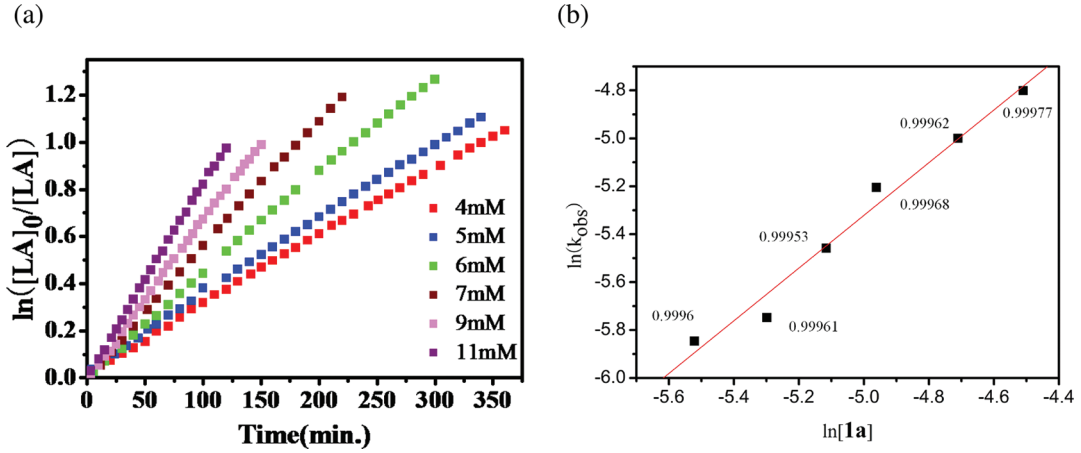


Figure 6. (a) Linear plots of $[LA]_0/[LA]$ versus time, demonstrating the first-order dependence on monomer concentration ($[LA]_0$ = 0.25 M; $[\mathbf{1a}]_0$ = 4, 5, 6, 7, 9, 11 mM in *d*-toluene at 70 °C). (b) Linear plot of ln k_p versus ln [**1a**] for the polymerization of L-lactide with **1a** as an initiator (*d*-toluene, 70 °C, $[LA]_0$ = 0.25 M).

cumyl substituent and flexible amine backbone to induce a suitable geometry for *rac*-lactide polymerization.

Although the conversion did not reach 90% during the 12 h, it shows superior selectivity with P_m = 0.97. Aluminum methyl complexes **4** and **5** for *rac*-LA polymerization in the presence of benzyl alcohol have good molecular weight control but unfortunately do not have selectivity in the reaction. In addition, complex **6** exhibits >90% conversion at 70 °C in toluene with a low isotactic selectivity (P_m = 59−60%); however, an improvement of the isotactic selectivity (P_m = 76%) was noted in the polymerization of *rac*-LA catalyzed by **6′** in the presence of BnOH. The different results of **6** and **6′** in catalytic systems are consistent with the trend of the highly isotactic preference displayed by a large number of aluminum alkoxide and methyl complexes of a wide range of salen ligands. In general, the mononuclear complexes **1a**−**3a** and **6** have higher selectivity than dinuclear aluminum complexes **4**−**6**, probably because the mononuclear complex can provide a special geometry space for the monomer L-LA and D-LA to enter and react with the active mental center.

The stereoselective ring-opening polymerization (ROP) of *rac*-lactide is an important target of research in academia as well as in industry because different micro sequences result in different polymers. For instance, the melting point (T_m) of the commercial homochiral PLLA is 170 °C; however, the melting point of poly(*rac*-LA) with high isotacticity (P_m > 0.9) can increase to 190 °C or even >200 °C (P_m > 0.95), which is a superior material. As shown in Table 4, the melting point of poly(*rac*-LA) obtained from **3a** (entry 3, Table 4) with high P_m > 0.97 is up to 205 °C on the basis of DSC analysis. Thermal experimental results suggest that the obtained PLAs can be categorized as the multiblock stereocopolymer $(PLLA\text{-}PDLA)_n$.[17]

Kinetic Studies of Polymerization of Lactides by 1a. In order to understand the mechanism for polymerization of L-LA by **1a**−**3a**, kinetic studies of **1a** have been systematically investigated with various concentrations of **1a** (4, 5, 6, 7, 9, and 11 mol L^{-1}, respectively) with respect to a constant concentration [LA] (0.25 M) at 70 °C. In each case, the plot of ln $([LA]_0/[LA])$ versus time (min) is linear, indicating that polymerization proceeds with the first-order dependence on monomer concentration (Figure 6a). Hence, the rate of polymerization may be written as $-d[LA]/dt = k_{obs}[LA]^x$, where $k_{obs} = k_p[\mathbf{1a}]^y$, in which k_p is the propagation rate constant. To determine the order in aluminum complex (y), the linear relationship between ln $k_p$versus ln [**1a**] (Figure 6b) reveals that the order in the initiator (slope) is ca. 1.0 (1.099) and the polymerization rate constant, k_p, is 1.192 M^{-2} min^{-1},

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determined by the y intercept of the regression line. Therefore, the overall rate equation is $-d[LA]/dt = k[LA][\mathbf{1a}]$. This rate law is consistent with a mechanism involving coordinative insertion at a single Al site. The alkoxide group as an initiator for ROP was analyzed by ^{1}H spectroscopic studies.[18] Due to its high isotactic selectivity, it is expected that the polymerization rate of *rac*-lactide will be the same as that for L-lactide. Indeed, experimental results show that $k_{obs} = 0.058$ h^{-1} for *rac*-lactide is exactly the same as that for L-lactide of $k_{obs} = 0.054$ h^{-1}, as shown in Figure 7.

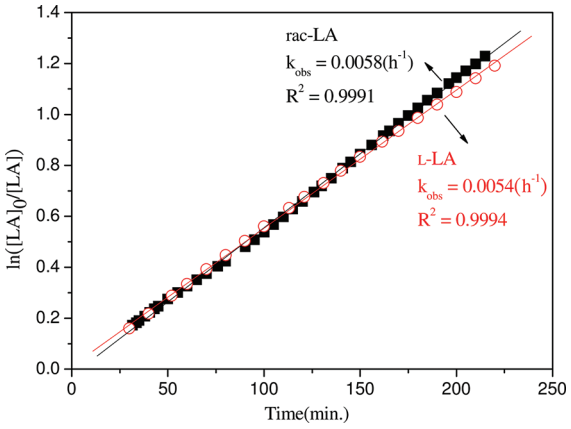

Figure 7. Comparison of kinetic data for polymerizations of *rac*-LA and L-LA by complex **1a**. Conditions: $[LA]_0 = 0.25$ M; $[\mathbf{1a}]_0 = 7$ mM in *d*-toluene at 70 °C.

CONCLUSIONS

A series of aluminum alkyl and aluminum alkoxide complexes have been synthesized and fully characterized. Complexes **1a**−**3a** show efficient activity for ROP of L-lactide. In addition, complexes **1a**−**3a** display high stereoselectivity toward *rac*-lactide with P_m values up to 97%, where the highest melting point could be 205 °C. At the same time, these aluminum complexes can avoid transesterfication effectively and in the MALDI-TOF spectrum show separate homologous peaks (144.0 Da). The kinetic of the polymerization of L-lactide, catalyzed by **1a**, was investigated using in situ ^{1}H NMR spectroscopy and revealed a first-order dependence for both the L-lactide and **1a**.

EXPERIMENTAL SECTION

General Methods and Materials. All manipulations were carried out under a dry nitrogen atmosphere. Solvents were dried by refluxing at least 24 h over sodium/benzophenone (*n*-hexane, toluene, THF), phosphorus pentoxide (CH_2Cl_2), or anhydrous magnesium sulfate (benzyl alcohol). L-Lactide was purchased from the Bio Invigor Corp. and recrystallized from a toluene solution prior to use. Deuterated solvents (Aldrich) were dried over molecular sieves. Other reagents were purchased from Aldrich or Acros and used without further purification. 3,5-Bis(α,α-dimethylbenzyl)-2-hydroxybenzaldehyde[19] and *trans*-11,12-diamino-9,10-dihydro-9,10-ethanoanthracene[20] were prepared according to the literature methods.

Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) or 600 (600 MHz for ^{1}H and 150 MHz for ^{13}C) spectrometer with chemical shifts given in parts per million (ppm) from internal TMS. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. Melting points were determined using a Büchi 535m instrument. GPC measurements were performed on a Jasco PU-2080 PLUS HPLC pump system equipped with a differential Jasco RI-2031 PLUS refractive index detector using THF (HPLC grade) as an eluent (flow rate 1.0 mL/min, at 40 °C). The chromatographic column was JORDI Gel DVB 10$\hat{0}$3 Å, and the calibration curve was made by primary polystyrene standards to calculate M_n(GPC). Differential scanning calorimetry (DSC) was carried out with a Perkin-Elmer STA6000 instrument. The sample was heated from 30 to 300 °C at a rate of 20 °C/min. Matrix-assisted laser desorption ionization-time-of-flight mass spectrometry (MALDI-TOF MS) analyses were carried out with a Bruker Autoflex III TOF/TOF equipped with an MCP detector. The sample was dissolved in THF, and the matrix was 2,5-dihydroxybenzoic acid (HABA). Ions formed by a pulsed UV laser beam with 3 ns bandwidth (nitrogen laser λ was 337 nm) were accelerated through 20 kV, and the detection voltage was set at 1.7 kV.

General Procedures for Ligands L^1-H_2–L^6-H_2. Ligands were prepared by the reaction of 3,5-bis(α,α-dimethylbenzyl)-2-hydroxybenzaldehyde (7.16 g, 20 mmol) with the corresponding diamine (10.5 mmol) in refluxing ethanol (50.0 mL) for 12 h, and the reaction mixture was then cooled to room temperature, giving a yellow precipitate. The yellow powder was collected by filtration and dried under vacuum.

N,N′-3,5-Bis(α,α-dimethylbenzyl)-2-hydroxysalicylidene-2,2-dimethyl-1,3-diamine (L^1-H_2). Yield: 6.2 g (75%). ^{1}H NMR (CD_3Cl, 400 MHz, ppm): δ 13.35 (2H, s, O*H*), 8.14 (2H, s, N=C*H*), 7.32−7.01 (24H, m, Ar*H*), 3.26 (4H, s, $CH_2C(CH_3)_2CH_2$), 1.71 (12H, s, $C(CH_3)$), 1.68 (12H, s, $C(CH_3)$), 0.89 (3H, s, $CH_2C(CH_3)_2CH_2$), 0.88 (3H, s, $CH_2C(CH_3)_2CH_2$). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 166.2 (ArC=N), 157.8 (ArCOH), 150.7 ($ArCC(CH_3)_2$), 150.5 ($ArCC(CH_3)_2$), 139.4 (Ar*C* cumyl), 136.0 (Ar*C* cumyl), 129.1, 127.9, 127.7, 126.7, 125.7, 125.6, 124.9 (Ar*C*), 117.9 (Ar*C*C=N), 68.3 (NCH_2CMe_2), 42.4 ($C(CH_3)_2$), 42.2 ($C(CH_3)_2$), 36.2 ($CH_2CMe_2CH_2$), 30.9 ($C(CH_3)_2$), 29.3 ($C(CH_3)_2$), 24.3 ($CH_2C(CH_3)CH_2$). Anal. Calcd (found) for $C_{55}H_{62}N_2O_2$: N, 3.58 (3.53); C, 84.36 (84.11); H, 7.98 (7.79).

N,N′-3,5-Bis(α,α-dimethylbenzyl)-2-hydroxysalicylidene-2-(aminomethyl)aniline (L^2-H_2). Yield: 6.7 g (80%). ^{1}H NMR (CD_3Cl, 400 MHz, ppm): δ 13.33 (1H, s, O*H*), 13.11 (1H, s, O*H*), 8.41 (1H, s, N=C*H*), 8.23 (1H, s, N=C*H*), 7.38−6.96 (28H, m, Ar*H*), 4.67 (2H, s, C=NCH_2Ar), 1.70 (6H, s, CH_3), 1.68 (6H, s, CH_3), 1.67 (6H, s, CH_3), 1.62 (6H, s, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 166.7 (ArC=N), 164.2 (ArC=N), 157.9 (ArCOH), 157.8 (ArCOH), 151.8, 150.9, 150.7, 150.6, 150.4 ($ArCC(CH_3)_2$), 147.2 (ArCN=C), 140.4, 139.5 ($ArCC(CH_3)_2$), 136.6, 136.1 ($ArCC(CH_3)_2$), 132.0 ($ArCCH_2N$), 130.4, 130.4, 129.2, 128.8, 128.5, 128.2, 128.1, 127.9, 126.8, 125.8, 125.7, 125.7, 125.24, 125.1 (ArC), 118.6 (ArCC=N), 118.5 (ArC), 118.2 (ArCC=N), 58.9 ($ArCH_2N$=C), 42.4, 42.3, 42.1, 42.0 ($C(CH_3)_2$), 30.9, 30.8, 29.3, 29.2 ($C(CH_3)_2$). Anal. Calcd (found) for $C_{57}H_{58}N_2O_2$: N, 3.49 (3.67); C, 85.25 (85.03); H, 7.28 (7.43).

N,N′-3,5-Bis(α,α-dimethylbenzyl)-2-hydroxysalicylidene-1,3-pentanediamine (L^3-H_2). Yield: 6.4 g (78%). ^{1}H NMR (CD_3Cl, 400 MHz, ppm): δ 13.61 (1H, s, O*H*), 13.45 (1H, s, O*H*), 8.24 (1H, s, N=C*H*), 8.22 (1H, s, N=C*H*), 7.33−7.21 (22H, m, Ar*H*), 7.15 (1H, d, J = 2.0 Hz, Ar*H*), 7.09 (1H, d, J = 2.4 Hz, Ar*H*), 3.44 (2H, m, C=NCH_2), 3.06−2.98(1H, m, $CH_2CH_2CH(C_2H_5)$), 1.95 (2H, m, $CH_2CH_2CH(C_2H_5)$), 1.84−1.98 (24H, m, $C(CH_3)_2$), 1.64 (2H, m, $CHCH_2CH_3$), 0.87 (3H, t, $CHCH_2CH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 166.6, 164.6 (ArC=N), 157.8 (ArCOH), 150.7, 150.7, 150.6, 150.6 ($ArCC(CH_3)_2$), 139.4, 139.3 (Ar*C* cumyl), 136.1, 135.9 (Ar*C* cumyl), 129.1, 128.8, 127.9, 127.8, 127.7, 127.6, 127.6, 126.7, 125.6, 124.9 (Ar, ArCHN), 117.9, 117.7 (ArCC=N), 69.1 ($NCH(C_2H_5)$), 56.1 ($NCH_2CH_2CH(C_2H_5)$), 42.4, 42.2, 42.09 ($C(CH_3)_2$), 36.7 ($NCH_2CH_2CH(C_2H_5)$), 30.9, 30.9 ($C(CH_3)_2$), 29.5, 29.4, 29.4 ($C(CH_3)_2$), 29.2, 29.1 ($NCH_2CH_2CH(CH_2CH_3)$), 10.7 ($NCH(CH_2CH_3)$). Anal. Calcd (found) for $C_{55}H_{62}N_2O_2$: N, 3.58 (3.58); C, 84.36 (84.53); H, 7.98 (7.95) .

N,N′-3,5-Bis(α,α-dimethylbenzyl)-2-hydroxysalicylidene-3-(aminomethyl)benzylamine (L^4-H_2). Yield: 5.6 g (65%). ^{1}H NMR (CD_3Cl, 400 MHz, ppm): δ 13.33 (2H, s, O*H*), 8.29 (2H, s, N=C*H*),

7.35−7.03 (27H, m, Ar*H*), 4.60 (4H, s, NCH_2Ar), 1.71 (12H, s, C(CH_3)$_2$), 1.65 (12H, s, C(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 166.1 (ArC=N), 157.6 (ArCOH), 150.7, 150.5 (ArCC-(CH_3)$_2$), 139.5 (Ar*C* cumyl), 138.3 (ArCCH_2N=C), 136.1 (Ar*C* cumyl), 129.0, 128.9, 128.7, 128.0, 127.9, 127.7, 127.6, 126.9, 126.7, 125.7, 125.6, 125.5, 125.0 (*Ar*, ArCHN), 118.0 (ArCC=N), 62.8 (NCH_2Ar), 42.3 (C(CH_3)$_2$), 42.1 (C(CH_3)$_2$), 30.9 ((CH_3)$_2$), 29.3 (C(CH_3)$_2$). Anal. Calcd (found) for $C_{58}H_{60}N_2O_2$: N, 3.43 (3.47); C, 85.25 (84.84); H, 7.40 (7.37).

N,N′-3,5-Bis(α,α-dimethylbenzyl)-2-hydroxysalicylidene-trans-11,12-diamino-9,10-dihydro-9,10-ethanoanthracene (L^5-H$_2$). Yield: 7.2 g (75%). ^{1}H NMR (CD_3Cl, 600 MHz, ppm): δ 12.30 (2H, s, O*H*), 8.15 (2H, s, N=C*H*), 7.31−7.06 (30H, m, Ar*H*), 6.94 (2H, m, Ar*H*), 4.10 (2H, s, ArHC=NCHC*H*Ar), 3.45 (2H, s, ArHC=NC*H*), 1.68−1.67 (18H, m, C(CH_3)$_2$), 1.60 (6H, m, C(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ 165.4 (Ar*C*=N), 157.4 (Ar*C*−OH), 150.9 (ArCC(CH_3)$_2$), 150.3 (ArCC(CH_3)$_2$), 140.6 (Ar*C* cumyl), 139.6 (quaternary carbon atom of backbone), 139.5 (quaternary carbon atom of backbone), 136.1 (Ar*C*- cumyl), 129.3,128.0, 127.9, 127.6, 126.6, 126.5, 126.2, 125.8, 125.6, 125.6, 124.9, 123.8 (Ar*C*), 117.7 (ArCC=N), 76.3 (ArCHCHN=C), 51.9 (Ar*C*HCHN=C), 42.3, 42.1 (C(CH_3)$_2$), 30.8, 29.8, 28.7 (C(CH_3)$_2$). Anal. Calcd (found) for $C_{66}H_{64}N_2O_2$: N, 3.05 (3.08); C, 86.42 (86.34); H, 7.03 (6.91).

N,N′-3,5-Bis(α,α-dimethylbenzyl)-2-hydroxysalicylidene-(±)-trans-1,2-cyclohexanediamine (L^6-H$_2$). Yield: 5.3 g (63%). ^{1}H NMR (CD_3Cl, 400 MHz, ppm): δ 13.23 (2H, s, O*H*), 8.07 (2H, s, *H*C=N), 7.09−7.27 (20H, m, Ar*H*), 6.91 (4H, s, Ar*H*), 3.12 (2H, d, C*H*), 1.73 (4H, m, C*H*), 1.65 (18H, s, C(CH_3)$_2$), 1.53 (6H, s, C(CH_3)$_2$), 1.51 (m, 2H, C*H*), 1.26 (m, 2H, C*H*). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 165.5 (ArC=N), 157.9 (ArCOH), 150.9 (ArCC(CH_3)$_2$), 139.6 (Ar*C* cumyl), 135.6, 129.5, 128.2, 127.9, 126.9, 125.8, 125.8, 125.2 (Ar*C*), 118.2(ArCC=N), 72.4 (Cy*C*), 42.6 (C(CH_3)$_2$Ph), 31.2 (Cy*C*), 30.5 (Cy*C*), 28.9 (Cy*C*), 24.5 (Cy*C*). Anal. Calcd (found) for $C_{52}H_{62}N_2O_2$: C, 84.59 (84.66); H, 7.86 (8.09); N, 3.52 (3.18).

(L^1-AlMe) (1). A solution of $AlMe_3$ (1.05 mL, 2.1 mmol) in hexane was added slowly to a solution with vigorously stirred ice-cold toluene (30.0 mL) containing L^1-H_2 (1.56 g, 2.0 mmol), and the mixture was then refluxed for 12 h. The solution was cooled to 25 °C, and the supernatant was removed by filtration. The resulting solid was dried under vacuum, yielding a light yellow powder. Yield: 1.32 g (80%). ^{1}H NMR (CD_3Cl, 400 MHz, ppm): δ 8.06 (2H, s, N=C*H*Ar), 7.40−7.19 (20H, m, Ar*H*), 7.09 (2H, d, J = 2.8 Hz, Ar*H*), 7.01 (2H, d, J = 2.8 Hz, Ar*H*), 3.27 (2H, d, J = 11.6 Hz, NCH_2C(CH_3)$_2$), 3.12 (2H, d, J = 12.0 Hz, NCH_2C(CH_3)$_2$), 2.00 (6H, s, C(CH_3)$_2$), 1.85 (6H, s, C(CH_3)$_2$), 1.70 (12H, s, C(CH_3)$_2$), 1.16 (3H, s, $CH_2C(CH_3)_2CH_2$), 1.04 (3H, s, $CH_2C(CH_3)_2CH_2$), −1.42 (3H, s, AlCH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 169.2 (ArC=N), 163.0 (Ar*C*−OH), 150.8, 150.6 (ArCC(CH_3)$_2$), 140.5 (Ar*C* cumyl), 136.7 (Ar*C* cumyl), 134.1, 128.8, 127.9, 127.5, 126.7, 126.6, 125.4, 124.9 (Ar*C*), 118.4 (Ar*C*C=N), 67.4 (NCH_2CMe$_2$), 43.2, 42.0 (C(CH_3)$_2$), 36.2 ($CH_2CMe_2CH_2$), 31.6 (C(CH_3)$_2$), 29.4 (C(CH_3)$_2$), 28.0 (C(CH_3)$_2$), 25.9, 25.5 (CH_2C-(CH_3)CH_2), −8.8 (Al−CH_3). Anal. Calcd (found) for $C_{56}H_{63}AlN_2O_2$: N, 7.71 (7.77); C, 81.72 (79.39); H, 7.71 (7.77).

(L^2-AlMe) (2). The synthetic method of complex **2** is the same as for complex **1**. Yield: 1.43 g (85%). ^{1}H NMR (CD_3Cl, 600 MHz, ppm): δ 8.16 (1H, s, N=C*H*Ar), 8.10 (1H, s, N=C*H*Ar), 7.38−7.35 (1H, m, Ar*H*), 7.29−7.17 (20H, m, Ar*H*), 7.11−7.05 (4H, m, Ar*H*), 7.00 (2H, br, Ar*H*), 6.91 (1H, br, Ar*H*), 4.79 (1H, d, J = 12.6.Hz, ArCH_2N), 4.07 (1H, d, J = 13.2 Hz, ArCH_2N), 2.04 (6H, s, C(CH_3)$_2$), 2.04 (6H, s, C(CH_3)$_2$), 1.95 (4H, s, C(CH_3)$_2$), 1.74 (8H, s, C(CH_3)$_2$), 1.69 (6H, s, C(CH_3)$_2$), −1.61 (3H, s, AlCH_3). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ 172.3, 166.2 (ArC=N), 164.6, 162.1 (ArCOH), 150.8, 150.6, 150.5, 150.3 (ArCC(CH_3)$_2$), 148.5 (Ar*C*N), 141.0, 140.0 (Ar*C* cumyl), 137.9, 136.3 (Ar*C* cumyl), 134.8, 134.7 (Ar*C*), 130.6 (ArCCH$_2$N), 129.9, 129.7, 129.4, 129.0, 128.2, 127.9, 127.6, 127.4, 127.1, 126.8, 126.7, 126.6, 126.3, 125.5, 125.3 124.8, 121.0 (Ar*C*), 119.3, 117.8 (Ar*C*C=N), 63.4 (ArCH$_2$N=C), 43.4, 42.8, 42.1, 42.0 (C(CH_3)$_2$), 31.4, 30.6, 30.6, 30.5, 29.3, 27.5, 27.3 (C(CH_3)$_2$), −7.8 (Al−CH_3). Anal. Calcd (found) for $C_{58}H_{59}AlN_2O_2$: N, 3.32 (3.42); C, 82.63 (81.93); H, 7.05 (7.58).

(L^1-AlOBn) (1a). A solution of $AlMe_3$ (1.05 mL, 2.1 mmol) in hexane was added slowly to a solution with vigorously stirred ice-cold toluene (30.0 mL) containing L^1-H_2 (1.56 g, 2.0 mmol). The mixture was then refluxed overnight and cooled to room temperature. BnOH (0.21 mL, 2 mmol) was then added, and the mixture was refluxed for 12 h, during which time the solution color changed from yellow to pale green. The solution was cooled to 25 °C and the supernatant removed by filtration. The resulting solid was dried under vacuum, yielding a pale green powder. Yield: 1.55 g (85%). ^{1}H NMR (CD_3Cl, 600 MHz, ppm): δ 7.90 (2H, s, N=C*H*Ar), 7.26−6.83 (29H, m, Ar*H*), 3.97 (2H, br, OCH_2Ph), 3.47 (2H, d, J = 11.4 Hz, NCH_2C(CH_3)$_2$), 3.06 (2H, d, J = 12.0 Hz, NCH_2C(CH_3)$_2$), 1.94 (6H, s, C(CH_3)$_2$), 1.71 (6H, s, C(CH_3)$_2$), 1.56 (12H, d, J = 3.6 Hz, C(CH_3)$_2$), 0.87 (3H, s, $CH_2C(CH_3)_2CH_2$), 0.73 (3H, s, CH_2C-(CH_3)$_2$CH$_2$). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 169.6 (ArC=N), 163.1 (ArCOH), 150.6 (ArCC(CH_3)$_2$), 150.5 (ArCC(CH_3)$_2$), 145.7 (Al−OCH$_2$CAr), 139.9 (Ar*C* cumyl), 137.3 (Ar*C* cumyl), 134.5, 129.0, 127.9, 127.7, 127.4, 126.8, 126.7, 125.6, 125.4, 125.1 (Ar*C*), 118.5 (Ar*C*C=N), 68.4 (NCH$_2$CMe$_2$), 65.2 (OCH$_2$Ph), 43.3, 42.2 (C(CH_3)$_2$), 35.7 ($CH_2CMe_2CH_2$), 30.6 (C(CH_3)$_2$), 30.5 (C(CH_3)$_2$), 29.8 (C(CH_3)$_2$), 28.0 (C(CH_3)$_2$), 25.4 ($CH_2C(CH_3)CH_2$), 25.2 ($CH_2C(CH_3)CH_2$). Anal. Calcd (found) for $C_{62}H_{67}AlN_2O_3$: N, 3.03 (3.09); C, 81.37 (80.73); H, 7.38 (6.99).

(L^2-AlOBn) (2a). The synthetic procedures for complex **2a** were the same as those for complex **1a**. Yield: 1.53 g (82%). ^{1}H NMR (CD_3Cl, 400 MHz, ppm): δ 8.21 (1H, s, N=C*H*Ar), 8.16 (1H, s, N=C*H*Ar), 7.52−6.77 (31H, m, Ar*H*), 6.37 (2H, m, Ar*H*), 4.81 (1H, d, J = 13.2 Hz, C=NCH_2Ar), 4.19 (1H, d, J = 12.8 Hz, C=NCH_2Ar), 3.81−3.59 (2H, m, OCH_2Ph), 2.03 (3H, s, C(CH_3)$_2$), 1.94 (6H, s, C(CH_3)$_2$), 1.67 (3H, s, C(CH_3)$_2$), 1.58 (6H, s, C(CH_3)$_2$), 1.53 (6H, s, C(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ 172.3, 168.1 (ArC=N), 164.5, 162.5 (ArCOH), 150.5, 150.3, 150.2 (ArCC(CH_3)$_2$), 149.1 (Ar*C*N), 145.7 (Al−OCH$_2$CAr), 140.5, 139.4 (Ar*C* cumyl), 138.4, 136.9 (Ar*C* cumyl), 135.4, 135.3 (Ar*C*), 130.4 (ArCCH$_2$N), 130.0, 129.7, 129.0, 128.2, 127.9, 127.8, 127.6, 127.0, 126.9, 126.8, 126.7, 126.7, 126.6, 126.0, 125.5, 125.4, 125.3, 125.1, 124.8, 121.6 (Ar*C*), 119.1, 117.9 (Ar*C*C=N), 64.5 (OCH$_2$Ph), 63.5 (ArCH$_2$N=C), 43.6, 43.0, 42.0 (C(CH_3)$_2$), 31.6, 30.6, 30.5, 30.1, 28.8, 28.1, 27.6 (C(CH_3)$_2$). Anal. Calcd (found) for $C_{64}H_{63}AlN_2O_3$: N, 3.00 (3.06); C, 82.20 (83.49); H, 6.79 (7.12).

(L^3-AlOBn) (3a). The synthetic procedure was similar to that for complex **1a**. Yield: 1.73 g (75%). ^{1}H NMR (CD_3Cl, 400 MHz, ppm): δ 7.97 (1H, s, N=C*H*Ar), 7.96 (1H, s, N=C*H*Ar), 7.26−6.81 (29H, m, Ar*H*), 4.33−4.30 (2H, m, OCH_2Ph), 4.06 (1H, t, C=NCH_2), 3.44 (1H, t, C=NCH_2), 3.26−2.98 (1H, m, $CH_2CH_2CH(C_2H_5)$), 1.85−1.44 (26H, m, $CH_2CH_2CH(C_2H_5)$, C(CH_3)$_2$, (2H, m, CHCH_2CH$_3$)), 0.62 (3H, t, CHCH$_2$CH_3). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ 168.9, 167.6 (Ar*C*=N), 163.5, 163.1 (ArCOH), 151.1, 150.9, 150.6, 150.5 (Ar*C*C(CH_3)$_2$), 146.2 (Al−OCH$_2$CAr), 139.9, 139.8 (Ar*C* cumyl), 137.2, 137.0 (Ar*C* cumyl), 134.8, 133.5, 129.0, 128.9, 128.5, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 126.8, 126.6, 126.5, 126.5, 126.2, 125.4, 125.3, 125.1, 124.8 (Ar*C*), 118.4, 118.3 (Ar*C*C=N), 72.3 (NCH(C_2H_5)), 64.9 (OCH$_2$Ph), 55.9 (NCH$_2$CH$_2$CH-(C_2H_5)), 43.4, 43.0 (*C*(CH3)2), 42.0, 41.9(C(CH_3)$_2$), 33.4 (NCH$_2$CH$_2$CH(C_2H_5)), 30.9, 30.9 (C(CH_3)$_2$), 29.5, 29.5, 29.4 (C(CH_3)$_2$), 29.2, 29.1 (NCH$_2$CH$_2$CH(CH_2CH_3)), 10.83 (NCH-(CH_2CH_3)). Anal. Calcd (found) for $C_{62}H_{67}AlN_2O_3$:N, 3.06 (2.89); C, 81.37 (81.54); H, 7.38 (7.68).

(L^4-Al$_2$Me$_4$) (4). A solution of $AlMe_3$ in toluene (2.05 mL, 4.10 mmol) was added slowly to a yellow solution of L^4-H_2 (1.63 g, 2 mmol) in toluene (20.0 mL) at room temperature under N_2, and the mixture was then refluxed for 12 h. The volatile materials were removed under vacuum, and the resulting sticky yellow residue was dried completely under vacuum. Yield: 1.73 g (93%). ^{1}H NMR (CD_3Cl, 400 MHz, ppm): δ 8.01 (2H, s, N=C*H*), 7.43−6.95 (27H, m, Ar*H*), 4.55 (4H, s, NCH_2Ar), 1.69 (12H, s, C(CH_3)$_2$), 1.57 (12H, s, C(CH_3)$_2$), −1.32, −1.33 (12H, s, Al(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 171.3 (ArC=N), 161.0 (ArCOH), 150.6, 150.4

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(ArC-$C(CH_3)_2$), 140.6 138.3 ($ArCCH_2N{=}C$), 135.6 (ArC cumyl), 133.5, 130.1, 129.7, 129.4, 128.1, 127.5, 126.7, 125.7, 125.5, 124.7, 118.0 (ArC), 117.9 ($ArCC{=}N$), 60.1 (NCH_2Ar), 42.7, 42.3, 42.2, 42.0 ($C(CH_3)_2$), 30.8, 28.8 ($C(CH_3)_2$), −10.5 (Al-CH_3). Anal. Calcd (found) for $C_{62}H_{70}Al_2N_2O_2$: N, 3.01 (2.98); C, 80.14 (80.15); H, 7.59 (7.29).

(L^5-Al_2Me_4) (5). Methods for complex **5** were the same as those for **4**. Yield: 1.65 g (90%). ^{1}H NMR (CD_3Cl, 600 MHz, ppm): δ 7.44−7.06 (28H, m, Ar*H*), 6.27 (2H, s, N=C*H*), 6.21 (2H, s, Ar*H*) 4.35 (2H, s, ArHC=NC*H*), 3.85 (2H, s, ArHC=NCHC*H*Ar), 1.66 (6H, s, $C(CH_3)_2$), 1.65 (6H, s, $C(CH_3)_2$), 1.59 (12H, s, $C(CH_3)_2$), −1.05 (6H, d, J = 1.2 Hz, $Al(CH_3)_2$), −1.36 (6H, d, J = 1.2 Hz, $Al(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 168.4 (ArC=N), 161.1 (ArCOH), 151.6 ($ArCC(CH_3)_2$), 150.2 ($ArCC(CH_3)_2$), 140.4 (ArC cumyl), 138.1 (quaternary carbon atom of backbone), 137.0 (quaternary carbon atom of backbone), 133.9, 130.5, 128.0, 127.7, 127.5, 127.4, 126.7, 125.7, 125.5, 124.7, 124.6 (ArC), 117.7 (ArCC=N), 65.4 (ArCHCHN=C), 51.1 (ArCHCHN=C), 42.2, 42.0 ($C(CH_3)_2$), 30.8, 30.5, 29.1, 28.5 ($C(CH_3)_2$), −10.1, −11.0 (Al−CH_3). Anal. Calcd (found) for $C_{70}H_{74}Al_2N_2O_2$: C, 81.68 (80.21); H, 7.25 (7.95); N, 2.72 (2.95).

Preparation of [$L^6Al_2(Me)_4$] (6) and [L^6AlMe] (6′). A solution of trimethylaluminum in toluene (2.25 mL, 4.50 mmol) was added to a yellow solution of the ligand L^6-H_2 (1.19 g, 1.50 mmol) in toluene (20.0 mL) at room temperature under N_2, and the mixture was stirred for 4 h. Then the mixture was stirred at 70 °C for 12 h. The solvent and excess of $AlMe_3$ were removed under vacuum, and the resulting sticky yellow residue was completely dried. To this was added dry *n*-hexane (20.0 mL), and the mixture was stirred for 30 min. The resulting light yellow precipitate of [L^6AlMe] was collected by vacuum filtration. The solid was further washed with dry *n*-hexane (10.0 mL × 2) and dried under vacuum. Yield: 0.37 g (30%). The filtrate of the *n*-hexane extract was stored for 2 days at room temperature, which resulted in yellow single crystals and crystalline solids of [$L^6Al_2Me_4$] which crashed out of the solution. Solids were collected by vacuum filtration and dried under vacuum. Yield: 0.41 g (46%).

[$L^6Al_2Me_4$] (6). ^{1}H NMR (CD_3Cl, 400 MHz, ppm): δ 7.77 (2H, s, *H*C=N), 7.06−7.28 (20H, m, Ar*H*), 6.80 (4H, s, Ar*H*), 3.45 (2H, dd, J = 6.2 Hz, C*H*), 2.13 (2H, m, C*H*), 1.89 (2H, m, C*H*), 1.78 (12H, s, $C(CH_3)_2$), 1.62 (6H, m, CH_3), 1.42 (6H, s, CH_3), 1.30 (4H, m, C*H*), −0.77 (6H, s, Al−CH_3), −1.40 (6H, s, Al−CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 173.4, 161.5, 150.7, 150.6, 140.5, 138.5, 134.7, 129.6, 128.3, 127.8, 127.0, 125.9, 125.7, 125.1, 117.6 (*H*C=N, ArC), 71.7 (CyC), 42.4 ($C(CH_3)_2Ph$), 42.1 ($C(CH_3)_2Ph$), 32.2 ($C(CH_3)_2Ph$), 31.8 ($C(CH_3)_2Ph$), 30.9 ($C(CH_3)_2Ph$), 27.1 (CyC), 24.6 (CyC), 22.9 (CyC), 14.3 (*Cy*C), −7.4 (Al−CH_3), −8.3 (Al−CH_3). Anal. Calcd (found) for $C_{60}H_{72}Al_2N_2O_2$: C, 79.44 (79.48); H, 8.00 (8.35); N, 3.09 (3.65).

[L^6AlMe] (6′). ^{1}H NMR (CD_3Cl, 400 MHz, ppm): δ 8.27 (1H, s, *H*C=N), 8.03 (1H, s, *H*C=N), 7.11−7.35 (20H, m, Ar*H*), 6.95 (1H, s, Ar*H*), 6.83 (2H, s, Ar*H*), 3.56 (1H, m, C*H*), 3.02 (1H, m, C*H*), 2.55 (1H, m, C*H*), 2.35 (1H, m, C*H*), 2.11 (2H, m, C*H*), 2.08 (3H, s, CH_3), 2.04 (3H, s, CH_3), 1.98 (3H, s, CH_3), 1.80 (3H, s, CH_3), 1.69 (6H, s, CH_3), 1.59 (6H, s, CH_3), 1.45 (2H, m, C*H*), 1.35 (2H, m, C*H*), −1.40 (s, 3H, Al−CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 168.6, 161.4, 155.9, 151.1, 150.9, 140.7, 137.3, 136.6, 134.8, 129.8, 128.1, 127.9, 126.9, 125.7, 125.1, 118.9, 118.4 (HC=N, ArC), 66.2 (s, NCH), 62.4 (NCH), 44.1 ($C(CH_3)_2Ph$), 43.4 ($C(CH_3)_2Ph$), 42.3 ($C(CH_3)_2Ph$), 42.2 ($C(CH_3)_2Ph$), 31.8 (CyC), 28.6 (CyC), 27.3 (CyC), 24.0 (CyC), 14.3 (Al−CH_3). Anal. Calcd (found) for $C_{57}H_{63}AlN_2O_2$: N, 3.35 (3.18); C, 81.98 (81.66); H, 7.60 (7.10).

Conversion of 6′ to 6. To a toluene solution (10.0 mL) of **6′** (0.360 mmol) was added a trimethylaluminum solution (0.718 mmol) at room temperature under N_2, and the mixture was stirred for 2 h. Then the mixture was stirred for 12 h at 70 °C. The solvent was evaporated to dryness to obtain a yellow residue. To this was added dry *n*-hexane (20.0 mL), and the mixture was stored for 12 h at room temperature. The precipitated yellow solid was filtered under vacuum and dried (0.140 g, 43%). ^{1}H and ^{13}C NMR characterization data of the isolated compound were compared with those of **6**, which gave a complete match.

Typical Polymerization Procedures of L-Lactide for 1a−3a. A mixture of **1a** (0.05 mmol) and L-lactide (0.720 g, 5.0 mmol) in toluene (10.0 mL) was stirred at 70 °C for 12 h. The reaction was quenched by the addition of water (0.5 mL), and *n*-hexane (100.0 mL) was added to give a white solid.

Typical Polymerization Procedures of L-Lactide for 4−6. L-Lactide (0.720 g, 5.0 mmol) was added to a mixture of the aluminum methyl complex **4** (0.05 mmol) and BnOH (0.20 mmol) in toluene (10.0 mL), and the resulting solution was stirred at 70 °C for 12 h. The reaction was quenched by the addition of water (0.5 mL), and *n*-hexane (100.0 mL) was added to give a white solid.

Typical Polymerization Procedures of *rac*-Lactide for 1a−3a. A mixture of **1a** (0.05 mmol) and *rac*-lactide (0.72 g, 5.0 mmol) in toluene (10 mL) was stirred at 70 °C for 12 h, and the reaction was then quenched by the addition of water (1.0 mL). On addition of *n*-hexane (90.0 mL), the polymer precipitated as a white crystalline solid. The solid was then filtered, washed with cold *n*-hexane (10.0 mL) twice, and dried under vacuum.

Typical Polymerization Procedures of *rac*-Lactide for 4−6 and 6′. A mixture of complex **4** (0.05 mmol), BnOH (0.20 mmol), and *rac*-lactide (0.72 g, 5.0 mmol) in toluene (10.0 mL) was stirred at 70 °C for 18 h. The reaction was then quenched by the addition of water (0.5 mL) and *n*-hexane (100.0 mL), and the polymer was precipitated to give a white crystalline solid.

X-ray Crystallographic Studies. Suitable crystals of **1a**, **2a**, and **6** were covered with perfluoropolyether vacuum oil (Aldrich, Fombliny) held on a glass fiber and mounted on CryoLoop (Hampton Research) and cooled rapidly under a stream of cold nitrogen gas using an Oxford Diffraction Ltd. Gemint R and S. The space group determination was based on a check of the Laue symmetry and systematic absences and was confirmed using the structure solution. The structure was solved by direct methods using the SHELXTL package. All non-H atoms were located from successive Fourier maps, and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms. Crystallographic data for complexes **1a**, **2a**, and **6** are given in in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files, text, figures, and tables giving details of the crystal structure determination of compounds **1a**, **2a**, and **6** and additional experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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