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Dinuclear aluminum complexes supported by amino- or imino-phenolate ligands: synthesis, structures, and ring-opening polymerization catalysis of *rac*-lactide†

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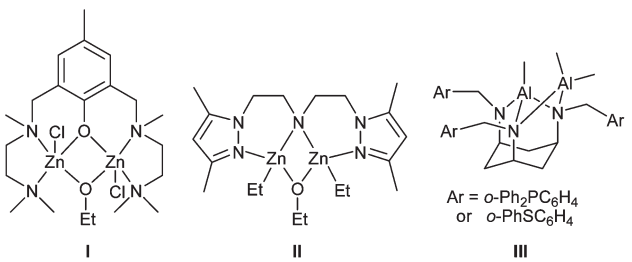
Two series of ligand precursors [2-OH-3-(CH_2NR_2)-5-MeC_6H_2]$_2CH_2$ (**1**: NR_2 = NMe_2; **2**: NR_2 = $N(CH_2)_4$; **3**: NR_2 = $N(CH_2)_5$; **4**: NR_2 = N(Me)Ph) and [2-OH-3-(CH=NR)-5-MeC_6H_2]$_2CH_2$ (**10**: R = 2,6-$Pr^i_2C_6H_3$; **11**: R = *p*-MeC_6H_4; **12**: R = *p*-ClC_6H_4; **13**: R = *p*-$MeOC_6H_4$; **14**: R = Bu^t) were prepared. These compounds reacted with $AlMe_3$ to afford corresponding dinuclear aluminum complexes [$AlMe_2${2-O-3-(CH_2NR_2)-5-MeC_6H_2}]$_2CH_2$ (**6**: NR_2 = NMe_2; **7**: NR_2 = $N(CH_2)_4$; **8**: NR_2 = $N(CH_2)_5$; **9**: NR_2 = N(Me)Ph) and [$AlMe_2${2-O-3-(CH=NR)-5-MeC_6H_2}]$_2CH_2$ (**15**: R = 2,6-$Pr^i_2C_6H_3$; **16**: R = *p*-MeC_6H_4; **17**: R = *p*-ClC_6H_4; **18**: R = *p*-$MeOC_6H_4$; **19**: R = Bu^t). All the compounds were characterized by ^1H and ^{13}C NMR spectroscopy and elemental analyses. Complexes **6** and **16** were additionally characterized by single crystal X-ray diffraction techniques. Catalysis of the aluminum complexes towards the ring-opening polymerization of *rac*-lactide was evaluated in the presence of benzyl alcohol. All the polymerization reactions proceed in a controlled manner.

Introduction

Polylactides (PLA) have attracted great interest over the past decades due to their biodegradable and biocompatible properties.[1] The ring-opening polymerization (ROP) of lactides using metal complexes as the catalysts or initiators is the most effective method for the synthesis of PLA. So far, a great many complexes of metals such as magnesium,[2] aluminum,[3] zinc,[4,5] and tin[6] have been reported to be effective for the ROP of lactides. Among these catalysts or initiators, bimetallic complexes are relatively scarce although several examples have been reported. For example, Tolman *et al.* reported a dizinc-monoalkoxide complex supported by a dinucleating ligand (**I**, Chart 1) to be a highly active catalyst for the controlled polymerization of lactides.[7a] Carpentier *et al.* showed that a dinuclear complex of zinc bearing an amino-bis(pyrazolyl) ligand (**II**, Chart 1) initiates polymerization of *rac*-lactide at 20 °C to yield atactic polymers with controlled molecular masses and relatively narrow polydispersities.[7b] Thibault and Fontaine proved that bimetallic aluminum complexes supported by functionalized trisamido ligands (**III**, Chart 1) are active in the polymerization of ε-caprolactone and *rac*-lactide.[7c] In some systems bimetallic complexes exhibit higher catalytic activity than corresponding mononuclear ones for the ROP of cyclic esters and this is ascribed to cooperative effects.[8] For example, Redshaw *et al.* confirmed that two remote dialkylaluminum centers supported by a macrocyclic Schiff base ligand exhibit beneficial cooperative effects in catalyzing the ROP of ε-caprolactone.[8a] In order to learn more about the catalysis of bimetallic systems, we initiated a study on the ROP of cyclic esters using bimetallic complexes as the catalysts. Herein we report synthesis and characterization of bimetallic aluminum complexes supported by *N*,*O*-chelate ligands and catalysis of the complexes in the ROP of *rac*-lactide.



I II III

Chart 1 Examples of bimetallic catalysts for the ring-opening polymerization of cyclic esters.

Results and discussion

Synthesis and characterization of compounds

Synthesis of compounds **1–4** and their aluminum complexes **6–9** is shown in Scheme 1. Compounds **1–3** were prepared by

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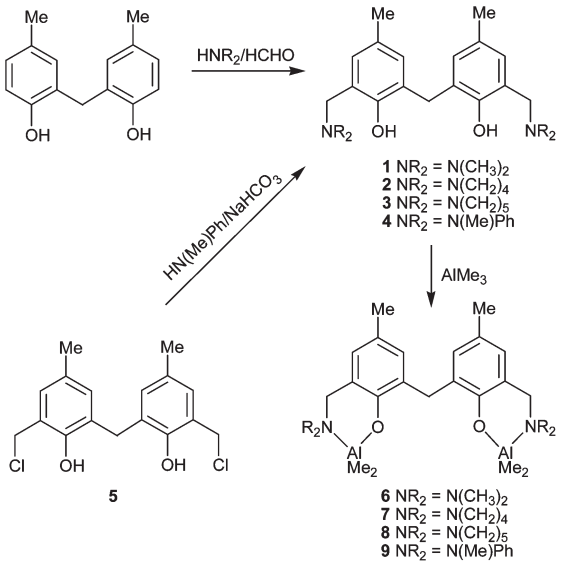


Scheme 1 Synthesis of compounds **1–4** and **6–9**.

the Mannich reaction from 2-[(2-hydroxy-5-methylphenyl)-methyl]-4-methylphenol, HCHO and corresponding secondary amines. However, a similar procedure was unsuccessful for the synthesis of compound **4**. Alternatively, compound **4** was synthesized from PhNH(Me) and corresponding benzyl chloride derivative, **5**. Treatment of compounds **1–4** with excess $AlMe_3$ in toluene afforded dinuclear aluminum complexes **6–9**. It should be indicated that the reactions between **1–4** and $AlMe_3$ require an elevated temperature, otherwise the reactions can not go to completion.

Compounds **1–4** were characterized by ^1H and ^{13}C NMR spectroscopy and elemental analyses. The analytical results match the calculated values very well. The NMR spectra are consistent with the respective structure of the compounds. Complexes **6–9** gave also satisfactory elemental analytical results. The ^1H NMR spectrum of each complex exhibits single Al–Me signal, showing all the four methyl groups to be chemically equivalent and the two aluminum atoms have the same coordination environments in each molecule. In addition, the ^1H NMR spectra of complexes **6–9** do not display the signals of the OH group. This implies that the OH groups in **1–4** have been transformed to $OAlMe_2$ through the reactions. The coordination mode of the aluminum atom in complex **6** has been confirmed by single crystal X-ray diffraction. The ORTEP drawing is presented in Fig. 1, along with selected bond lengths and angles. In the molecule, each aluminum atom is four coordinate and has a distorted tetrahedral coordination geometry. The Al–O distance of an average of 1.759 Å is very close to that in the mononuclear aluminum complex Me_2Al-[O-2-Bu^t-6-{Me_2NCH_2}C_6H_3] (1.758(1) Å).[9] The Al–N distances of 2.027(4) Å and 1.996(4) Å, respectively, are slightly shorter than that in Me_2Al[O-2-Bu^t-6-{Me_2NCH_2}C_6H_3] [2.036(1) Å].[9] The Al–C distances ranging from 1.935(5) Å to 1.952(4) Å are comparable to corresponding ones in Me_2Al[O-2-Bu^t-6-{Me_2NCH_2}C_6H_3].[9] In complex **6**, the C(21)–Al(1)–C(22) angle of 117.9(2)° is wider than that of C(23)–Al(2)–C(24) [112.9(3)°], and the former is close to that in Me_2Al[O-2-Bu^t-6-{Me_2NCH_2}-C_6H_3] [118.13(7)°].[9] The angles of C–Al–O and C–Al–N in complex **6** are comparable to corresponding ones in Me_2Al-[O-2-Bu^t-6-{Me_2NCH_2}C_6H_3].[9]

Synthesis of compounds **10–19** is shown in Scheme 2. The bis(imine-phenols) **10–14** were prepared through condensation of 2,2′-methylene bis(4-methyl-6-formylphenol) with two equiv. of primary amines in refluxing ethanol. Compounds **10** and **14** were purified by removing ethanol and then washing with hexane. Compounds **11–13** formed precipitates in ethanol and were purified by recrystallizing from toluene. Treatment of **10–14** with excess $AlMe_3$ in toluene afforded dinuclear aluminum complexes **15–19**. Each of **10–19** gave a satisfactory elemental analytical result. The ^1H and ^{13}C NMR spectra are consistent with their respective structure. The NMR spectra of

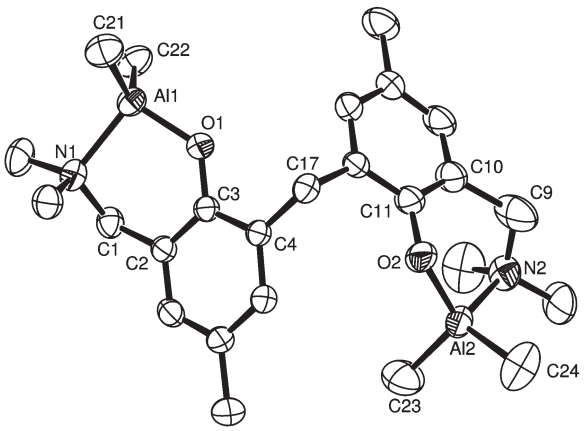
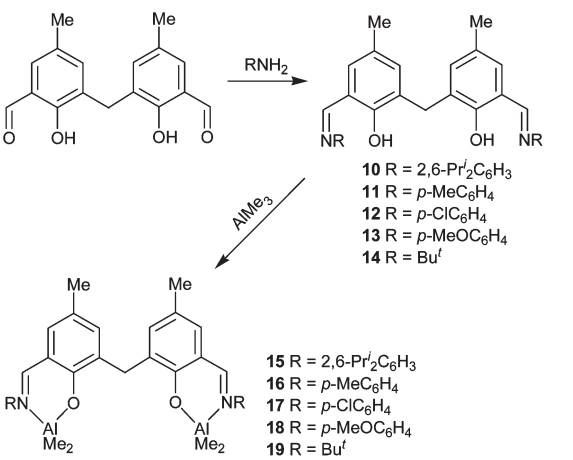


Fig. 1 The ORTEP diagram of complex **6** (30% probability thermal ellipsoids). Selected bond lengths (Å) and angles (°): Al(1)–O(1) 1.760(3), Al(1)–N(1) 2.027(4), Al(1)–C(21) 1.948(5), Al(1)–C(22) 1.952(4), Al(2)–O(2) 1.758(3), Al(2)–N(2) 1.996(4), Al(2)–C(23) 1.949(5), Al(2)–C(24) 1.935(5), O(1)–Al(1)–C(21) 113.55(18), O(1)–Al(1)–C(22) 110.95(18), C(21)–Al(1)–C(22) 117.9(2), O(1)–Al(1)–N(1) 96.45(14), C(21)–Al(1)–N(1) 108.64(19), C(22)–Al(1)–N(1) 106.85(19), O(2)–Al(2)–C(23) 114.0(2), O(2)–Al(2)–C(24) 112.8(2), C(24)–Al(2)–C(23) 112.9(3), O(2)–Al(2)–N(2) 96.88(17), C(23)–Al(2)–N(2) 109.6(2), C(24)–Al(2)–N(2) 109.5(2).



Scheme 2 Synthesis of compounds **10–19**.

complexes **15–19** also exhibit a single Al–Me signal for each complex, implying that two aluminum atoms in a molecule have the same coordination environments and the methyl groups are chemically equivalent.

Complex **16** was further characterized by single crystal X-ray diffraction. The ORTEP drawing is shown in Fig. 2, along with selected bond lengths and angles. The skeletal structure of **16** is similar to that of **6**. Thus, each of the central aluminum atoms is four coordinate and displays distorted tetrahedral geometry. However, some differences of bond lengths and bond angles between the two complexes are noted. For example, the Al–O distance (av. 1.767 Å) in complex **16** is slightly longer than that in complex **6** (av. 1.759 Å). The Al–N distance of an average of 1.9665 Å in complex **16** is shorter than that in complex **6** (av. 2.0115 Å). This results from different hybrids of the nitrogen atoms in two complexes. The Al–O and Al–N distances in complex **16** are comparable to corresponding ones in $Me_2Al[O\text{-}2\text{-}Bu^t\text{-}6\text{-}\{(2,4,6\text{-}Me_3C_6H_2)\text{-}N{=}CH\}C_6H_3]$ (1.7748(19) and 1.965(2) Å, respectively).[10] In addition, the nitrogen atoms in complex **16** show approximately planar geometry, sum of the angles around the nitrogen atoms being 359.96° (for N1) and 359.63° (for N2), respectively. The C2–N1 and C10–N2 distances are 1.292(4) Å and 1.297(4) Å, respectively, which are indicative of C–N double bonds.

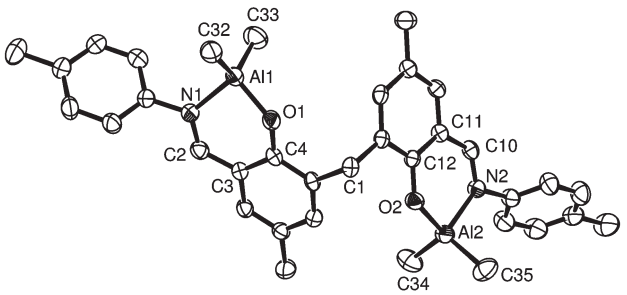


Fig. 2 The ORTEP diagram of complex **16** (30% probability thermal ellipsoids. The toluene molecule is omitted.). Selected bond lengths (Å) and angles (°): Al(1)–O(1) 1.772(3), Al(1)–C(32) 1.942(4), Al(1)–C(33) 1.965(4), Al(1)–N(1) 1.970(3), Al(2)–O(2) 1.762(3), Al(2)–C(34) 1.949(4), Al(2)–C(35) 1.954(4), Al(2)–N(2) 1.963(3), O(1)–Al(1)–C(32) 112.55(16) O(1)–Al(1)–C(33) 111.28(18), C(32)–Al(1)–C(33) 119.36(17), O(1)–Al(1)–N(1) 94.45(14), C(32)–Al(1)–N(1) 108.57(17), C(33)–Al(1)–N(1) 107.53(17), O(2)–Al(2)–C(34) 110.61(18), O(2)–Al(2)–C(35) 112.69(16), C(34)–Al(2)–C(35) 118.14(19), O(2)–Al(2)–N(2) 94.59(13), C(34)–Al(2)–N(2) 111.68(16), C(35)–Al(2)–N(2) 106.55(17).

Ring-opening polymerization of *rac*-lactide

The ROP of *rac*-lactide using **6–9** and **15–19** as catalysts was studied and the results are listed in Table 1. The experimental results show that all the dinuclear aluminum complexes are active in the ROP of *rac*-lactide in the presence or absence of BnOH. However, in the absence of BnOH, the catalytic activities are lower and lead to higher PDI in comparison with the catalytic systems using BnOH (entries 1 and 8). It was also noted that in the absence of BnOH the catalytic polymerization with complex **15** leads to a higher molecular weight of PLA than the calculated value. It seems only one active site is in action in the catalyst molecule (entry 8). In the presence of two equiv. of BnOH, complex **6** drives 93% conversion of *rac*-LA in 21 h at 70 °C when the monomer-to-catalyst ratio ($[LA]_0$–$[\mathbf{6}]_0$) is 100 : 1. The molecular weight of the PLA measured by GPC is close to the theoretical value calculated from the monomer : BnOH molar ratio and shows low polydispersity, which imply the polymerization is well controlled (entry 2). In the case of the 400 : 1 : 2 ratio of lactide : **6** : BnOH, the polymerization reaction still proceeds smoothly and is also well controlled (entry 3). When the ratio of lactide : **6** : BnOH was changed to 400 : 1 : 4, the molecular weight of the polymer was still proportional to the monomer : BnOH molar ratio and the molecular weight distribution of the polymer was narrow. These are the characteristics of immortal polymerization.[11] Complexes **7** and **8** exhibit similar catalytic activity to complex **6** in the presence of BnOH (entries 5 and 6). However, the molecular weight

Table 1 The ROP of *rac*-LA catalyzed by complexes **6–9** and **15–19**[a]

Entry	Cat.	$[Cat]_0 : [BnOH]_0 : [LA]_0$	Time (h)	Conv.[b] (%)	M_c[c] (10^{-3})	M_n[d] (10^{-3})	PDI[d]
1	**6**	1 : 0 : 100	24	44	3.3	3.3	1.86
2	**6**	1 : 2 : 100	21	93	6.8	6.4	1.20
3	**6**	1 : 2 : 400	45	47	13.8	13.4	1.20
4	**6**	1 : 4 : 400	45	61	8.9	6.4	1.16
5	**7**	1 : 2 : 100	25	94	6.9	9.9	1.27
6	**8**	1 : 2 : 100	25	90	6.6	6.5	1.21
7	**9**	1 : 2 : 100	33	50	3.7	2.9	1.14
8	**15**	1 : 0 : 100	24	74	5.4	10.5	1.33
9	**15**	1 : 2 : 100	16	93	6.8	7.0	1.16
10	**15**	1 : 2 : 400	60	54	15.7	11.3	1.11
11	**15**	1 : 4 : 400	60	75	10.9	10.4	1.09
12	**16**	1 : 2 : 100	24	79	5.8	4.7	1.11
13	**17**	1 : 2 : 100	24	91	6.7	5.5	1.08
14	**18**	1 : 2 : 100	24	95	7.0	7.1	1.20
15	**19**	1 : 2 : 100	24	91	6.7	5.6	1.11

[a] All polymerizations were carried out in toluene at 70 °C, $[LA]_0$ = 0.5 M. [b] Measured by ^1H NMR spectra. [c] $M_c = 144.13 \times ([LA]_0/[BnOH]_0) \times$ conv.% + 108.13. In the absence of BnOH (entries 2 and 9), $M_c = 144.13 \times ([LA]_0/[Cat.]_0)/2 \times$ conv.%. [d] Determined by GPC using polystyrene as the standard, multiplied by 0.58.[12]

of the polymer catalyzed by **7**/BnOH is higher than the calculated value. Complex **9** shows lower catalytic activity than **6–8**, but the molecular weights of the polymers determined by GPC are close to a theoretical value calculated according to the monomer : BnOH molar ratio (entry 7). The lower activity of complex **9** compared to complexes **6–8** may be because of the presence of phenyl groups on the nitrogen atoms in **9**, which leads to weaker electron donor ability of the nitrogen atoms. Among complexes **15–19** complex **15**/BnOH system displays highest activity and complex **16**/BnOH shows the lowest activity when the ratio of lactide : catalyst : BnOH is 100 : 1 : 2. Under the same conditions, complexes **17**, **18** and **19** exhibit similar catalytic activity. The high activity of complex **15** is probably related to the steric hindrance of the aryl groups on the nitrogen atoms. In each case the determined molecular weight by GPC matches the calculated value very well and the molecular weight distribution is narrow (entries 9 and 12–15). When the ratio of lactide : **15** : BnOH is 400 : 1 : 2, the polymerization reaction proceeds slower and the determined molecular weight of the polymer is lower than the calculated value. However, when the ratio of lactide : **15** : BnOH is 400 : 1 : 4, the reaction proceeds faster and the molecular weight of the polymer matches the calculated value very well (entries 10 and 11). Under comparable conditions, complexes **7** and **8** show similar catalytic activity to complexes **17–19**.

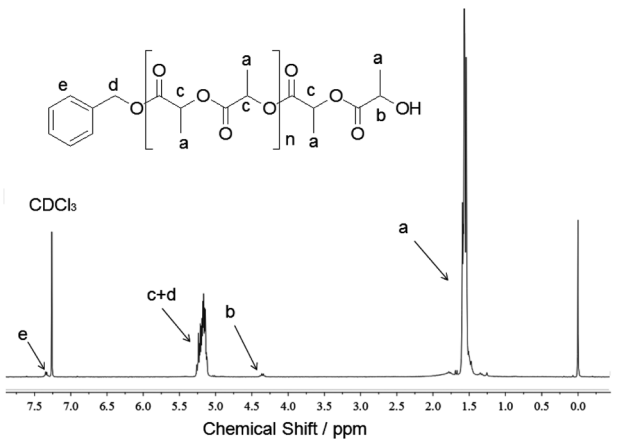
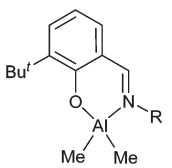


Fig. 3 The ^{1}H NMR spectrum of PLA initiated by **6**-BnOH (entry 2, Table 1).



A1 R = 2,6-Pr$^i_2$C$_6$H$_3$
A2 R = Ph
A3 R = Bu^t

Chart 2

The ^{1}H NMR spectrum of the resulting polymer (Fig. 3) shows no ligand signals or terminal methyl signals. This means that the polymerization is not initiated by the Al–O bonds of the ligand or Al–Me bonds. Alternatively, the polymer chain is capped with one benzyl ester and one hydroxyl end. The molecular weights determined by GPC are close to the calculated values based on the monomer : BnOH molar ratio in most cases as mentioned above. These results are consistent with an insertion mechanism of a benzyl alkoxy group into the lactide.

Homonuclear decoupled ^{1}H NMR spectra in the methine range of PLA (see Fig. S1 in ESI†) showed that slightly prevailing isotactic PLAs were obtained using complexes **6** and **15** as the catalysts.[13]

The catalytic activities of the dinuclear aluminum complexes **15**, **16** and **19** were compared with those of corresponding mononuclear aluminum complexes **A1–A3** (Chart 2) reported previously[10] and the results are presented in Table 2. **A1** has the same N-substituent as complex **15**. In the presence of Bu^{n}OH **A1** drives polymerization of *rac*-LA in 23% yield in 24 h at 80 °C when the ratio of lactide : **A1** : Bu^{n}OH is 100 : 1 : 1. Complex **15** shows higher activity. It leads to 75% yield of PLA in 24 h at 80 °C when the ratio of lactide : **15** : Bu^{n}OH is 200 : 1 : 2. Complex **A2** has a similar N-substituent (Ph) as **16** (*p*-MeC$_6$H$_4$) and complex **A3** has the same N-substituent as **19**. Under the same conditions, **16** and **19** also display higher activity than **A2** and **A3**, respectively. The higher activity of the dinuclear complexes is probably due to a cooperative effect. In the catalytic process, one aluminum atom serves as the Lewis acid, and an alkoxy group bound to the second aluminum center attacks the carbonyl group of the incoming lactide. But other factors such as the effect of substituents on 2-position of aromatic rings cannot be ruled out.

Kinetic studies of *rac*-lactide polymerization catalyzed by the dinuclear aluminum complexes in the presence of BnOH

Table 2 The ROP of *rac*-LA catalyzed by complexes **15**, **16**, **19** and mononuclear aluminum complexes **A1–A3**[a]

Entry	Cat.	$[Cat.]_0 : [BuOH]_0 : [LA]_0$	Yield[b] (%)	TOF (h^{-1})	M_n[c] ($\times 10^{-3}$)	PDI[c]
1	**A1**	1 : 1 : 100	23	0.96	13.5	1.10
2	**15**	1 : 2 : 200	75	3.13	16.7	1.06
3	**A2**	1 : 1 : 100	19	0.79	10.8	1.11
4	**16**	1 : 2 : 200	39	1.63	9.0	1.11
5	**A3**	1 : 1 : 100	4	0.17	—	—
6	**19**	1 : 2 : 200	68	2.83	12.1	1.08

[a] All polymerizations were run in toluene at 80 °C for 24 h in the presence of Bu^{n}OH, $[LA]_0$ = 1.0 mol cm^{-3}. [b] Isolated yield. [c] Determined by GPC in THF using polystyrene as the standard.

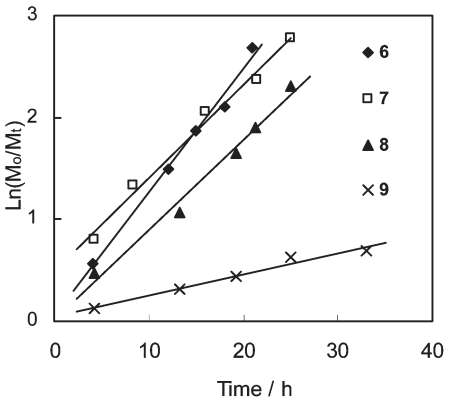


Fig. 4 Plots of ln([M]$_0$/[M]) *versus* time for the polymerization of *rac*-LA catalyzed by **6–9**. [M]$_0$–[Al]–[BnOH]$_0$ = 100 : 1 : 2, [M]$_0$ = 0.5 M; solvent: toluene; polymerization temperature: 70 °C.

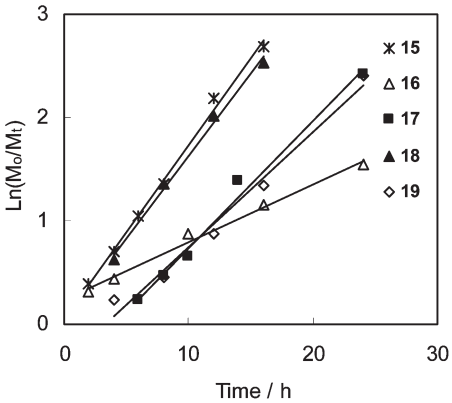


Fig. 5 Plots of ln([M]$_0$/[M]) *versus* time for the polymerization of *rac*-LA catalyzed by **15–19**. [M]$_0$–[Al]–[BnOH]$_0$ = 100 : 1 : 2, [M]$_0$ = 0.5 M; solvent: toluene; polymerization temperature: 70 °C.

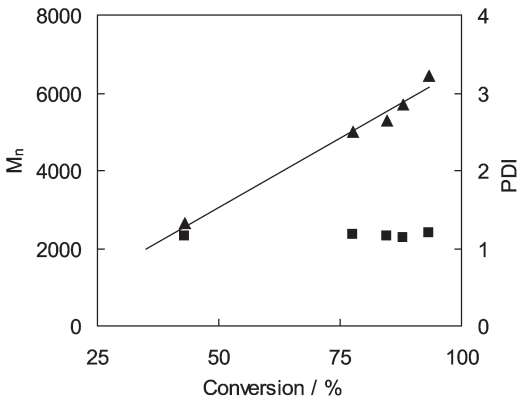


Fig. 6 Plots of PLA M_n (▲GPC) and polydispersity (■, M_w/M_n) as a function of *rac*-LA conversion using complex **6** at 70 °C. [M]$_0$: [Al]$_0$: [BnOH]$_0$ = 100 : 1 : 2, [M]$_0$ = 0.5 M; solvent: toluene.

were also carried out. Plots of ln([LA]$_0$/[LA]$_t$) *versus* time using each catalyst exhibit a good linear relationship (Fig. 4 and 5). This indicates that the polymerization proceeds with first-order dependence on monomer concentration in each case.

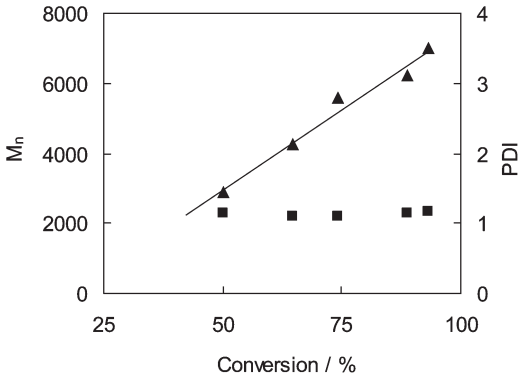


Fig. 7 Plots of PLA M_n (▲GPC) and polydispersity (■, M_w/M_n) as a function of *rac*-LA conversion using complex **15** at 70 °C. [M]$_0$: [Al]$_0$: [BnOH]$_0$ = 100 : 1 : 2, [M]$_0$ = 0.5 M; solvent: toluene.

This also implies that the polymerizations are controllable. A further indicator of controlled polymerization is the linear relationship between number-average molecular weight and conversion throughout the reaction process in the polymerization using complexes **6** and **15**, respectively, as catalysts, along with low polydispersity (Fig. 6 and 7). These facts also show that the polymerizations have the "living" character.

Conclusions

We have synthesized and characterized two classes of dinuclear aluminum complexes supported by *N*,*O*-chelate ligands. In the presence of BnOH, the complexes are efficient catalysts for the ROP of *rac*-lactide and the reactions lead to polymers with good molecular weight control and narrow molecular weight distribution. The catalytic activity of the complexes is affected by the substituents on the coordinated N atoms. Two aluminum centers in the dinuclear aluminum complexes may have a cooperative effect in the catalytic process.

Experimental

General

All air or moisture sensitive manipulations were performed under dry N_2 using standard Schlenk techniques. Solvents were distilled under nitrogen over sodium (toluene) or sodium/benzophenone (*n*-hexane and diethyl ether). 2-[(2-Hydroxy-5-methylphenyl)-methyl]-4-methylphenol,[14] 2-(chloromethyl)-6-[[3-(chloromethyl)-2-hydroxy-5-methylphenyl]-methyl]-4-methylphenol[15] and 2,2′-methylene bis(4-methyl-6-formylphenol)[16] were prepared according to reported methods. $AlMe_3$ (2 M in toluene) was purchased from Acros Organics and used as received. $CDCl_3$ and C_6D_6 were purchased from Cambridge Isotope Laboratories and stored over activated molecular sieves ($CDCl_3$) or Na/K alloy (C_6D_6). Other chemicals and solvents were purchased from commercial venders. NMR spectra were recorded on a Bruker av300 spectrometer at ambient temperature. The chemical shifts of ^{1}H and ^{13}C NMR spectra were

referenced to TMS or internal solvent resonances. Elemental analyses were performed by the Analytical Center of the University of Science and Technology of China. Gel permeation chromatography (GPC) measurements were performed on a Waters 150C instrument equipped with UltraStyragel columns (10^3, 10^4, and 10^5 Å) and a 410 refractive index detector, using monodispersed polystyrene as the calibration standard. THF (HPLC grade) was used as an eluent at a flow rate of 1 cm^3 min^{-1}.

Synthesis of [2-OH-3-(CH_2NMe_2)-5-MeC_6H_2]$_2CH_2$ (1)

A mixture of 2-[(2-hydroxy-5-methylphenyl)methyl]-4-methylphenol (3.00 g, 13.14 mmol), dimethylamine (33% w/w aqueous solution, 4.80 g), formaldehyde (37%–40% w/w aqueous solution, 5.20 g), and ethanol (50 cm^3) was refluxed for 12 h and then cooled to room temperature. Hydrobromic acid (48% w/w aqueous solution, 6.0 cm^3) was added to the solution. The resulting mixture was stirred for 30 min. The solvent was removed from the mixture under vacuum. The residue was washed using THF and then neutralized with saturated $NaHCO_3$ solution (100 cm^3). The resulting mixture was extracted with CH_2Cl_2 (3 × 30 cm^3). The organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum to give a white powder of **1** (2.50 g, 56%), mp 106–108 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.20 (s, 6H, Ar*Me*), 2.33 (s, 12H, N*Me*), 3.61 (s, 4H, NCH_2), 3.95 (s, 2H, ArCH_2Ar), 6.66 (s, 2H, Ar-*H*), 6.82 (s, 2H, Ar-*H*), 10.33 (b, 2H, O*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.71, 28.99, 44.53, 62.91, 121.20, 126.93, 127.53, 127.58, 130.05, 153.55. Anal. calcd for $C_{21}H_{30}N_2O_2$·0.06CH_2Cl_2: C, 72.78; H, 8.73; N, 8.06%. Found: C, 72.78; H, 8.63; N, 7.82%.

Synthesis of [2-OH-3-{$CH_2N(CH_2)_4$}-5-MeC_6H_2]$_2CH_2$ (2)

Compound **2** was synthesized according to the same procedure as for that of **1**, but pyrrolidine (1.89 g, 26.57 mmol) was used instead of dimethylamine. After similar work-up, compound **2** was obtained as a white powder (3.60 g, 69%), mp 124–126 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.85 (m, 8H, CH_2), 2.18 (s, 6H, Ar*Me*), 2.67 (m, 8H, CH_2), 3.81 (s, 4H, NCH_2Ar), 3.91 (s, 2H, ArCH_2Ar), 6.69 (s, 2H, Ar-*H*), 6.81 (s, 2H, Ar-*H*), 9.80 (b, 2H, O*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.71, 23.74, 29.40, 53.44, 58.52, 121.42, 126.90, 127.50, 127.64, 130.11, 153.35. Anal. calcd for $C_{25}H_{34}N_2O_2$: C, 76.10; H, 8.69; N, 7.10%. Found: C, 76.32; H, 8.67; N, 6.83%.

Synthesis of [2-OH-3-{$CH_2N(CH_2)_5$}-5-MeC_6H_2]$_2CH_2$ (3)

Compound **3** was synthesized using the same procedure as for that of **1**, but piperidine (2.34 g, 27.48 mmol) was used instead of dimethylamine. After similar work-up, compound **3** was obtained as a white powder (3.70 g, 67%), mp 116–118 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.51 (m, 4H, CH_2), 1.64 (m, 8H, CH_2), 2.18 (s, 6H, Ar*Me*), 2.52 (m, 8H, CH_2), 3.64 (s, 4H, NCH_2Ar), 3.95 (s, 2H, ArCH_2Ar), 6.65 (s, 2H, Ar-*H*), 6.79 (s, 2H, Ar-*H*), 11.06 (b, 2H, O*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.69, 24.18, 25.89, 29.01, 53.93, 62.34, 120.89, 127.02, 127.46, 128.41, 129.81, 153.62. Anal. calcd for $C_{27}H_{38}N_2O_2$: C, 76.74; H, 9.06; N, 6.63%. Found: C, 76.50; H, 8.83; N, 6.52%.

Synthesis of [2-OH-3-{CH_2N(Me)Ph}-5-MeC_6H_2]$_2CH_2$ (4)

A mixture of 2-(chloromethyl)-6-[[3-(chloromethyl)-2-hydroxy-5-methyl-phenyl]methyl]-4-methylphenol (1.50 g, 4.61 mmol), *N*-methylaniline (1.20 g, 11.20 mmol), $NaHCO_3$ (1.50 g, 17.86 mmol), and THF (50 cm^3) was refluxed for 12 h and then cooled to room temperature. The solvent was removed under vacuum. CH_2Cl_2 (100 cm^3) and H_2O (100 cm^3) were added to the residue. The resulting mixture was stirred for 30 min. The organic layer was separated and dried over $MgSO_4$, filtered, and concentrated under vacuum to give a crude product. The crude product was washed with *n*-hexane three times to give a white powder of **4** (1.30 g, 67%), mp 120–122 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.23 (s, 6H, N*Me*), 2.89 (s, 6H, Ar*Me*), 3.90 (s, 2H, ArCH_2Ar), 4.39 (s, 4H, NCH_2Ar), 6.75 (s, 2H, Ar-*H*), 6.93 (m, 2H, Ar-*H*), 7.00 (m, 4H, Ar-*H*), 7.04 (s, 2H, Ar-*H*), 7.30 (d, J = 9 Hz, 4H, Ar-*H*), 9.57 (b, 2H, O*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.78, 30.36, 39.98, 57.16, 116.86, 120.51, 123.11, 127.06, 127.39, 127.46, 129.34, 130.11, 150.55, 150.97. Anal. calcd for $C_{31}H_{34}N_2O_2$·0.06CH_2Cl_2: C, 79.10; H, 7.29; N, 5.94%. Found: C, 79.03; H, 7.45; N, 5.81%.

Synthesis of [2-($OAlMe_2$)-3-(CH_2NMe_2)-5-MeC_6H_2]$_2CH_2$ (6)

$AlMe_3$ (1.00 cm^3, 2.0 M solution in toluene, 2.00 mmol) was added to a stirred solution of **1** (0.30 g, 0.88 mmol) in toluene (20 cm^3) at about −80 °C. The mixture was warmed to room temperature, stirred for 12 h at room temperature and for another 12 h at 80 °C. The resulting mixture was cooled to room temperature. The solvent was removed under vacuum. The residue was dissolved in diethyl ether (20 cm^3) and then filtered. The filtrate was concentrated *in vacuo* to give colorless crystals of **6** (0.23 g, 57%), mp 181–183 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ −0.46 (s, 12H, Al*Me*), 1.55 (s, 12H, N*Me*), 2.32 (s, 6H, Ar*Me*), 3.04 (s, 4H, NCH_2Ar), 4.56 (s, 2H, ArCH_2Ar), 6.38 (s, 2H, Ar-*H*), 7.53(s, 2H, Ar-*H*). ^{13}C NMR (C_6D_6, 75 MHz): δ −10.79, 20.88, 30.37, 44.48, 62.89, 120.09, 125.40, 127.60, 128.07, 132.74, 133.01. Anal. calcd for $C_{25}H_{40}Al_2N_2O_2$: C, 66.06; H, 8.87; N, 6.16%. Found: C, 66.24; H, 8.65; N, 6.02%.

Synthesis of [2-($OAlMe_2$)-3-{$CH_2N(CH_2)_4$}-5-MeC_6H_2]$_2CH_2$ (7)

$AlMe_3$ (0.92 cm^3, 2.0 M solution in toluene, 1.84 mmol) was added to a stirred solution of **2** (0.30 g, 0.76 mmol) in toluene (20 cm^3) at about −80 °C. The mixture was warmed to room temperature, stirred for 12 h at room temperature and for another 12 h at 80 °C. The resulting mixture was cooled to room temperature. The solvent was removed from the mixture under vacuum. The residue was dissolved in diethyl ether (20 cm^3) and filtered. The filtrate was concentrated and cooled to about −80 °C to afford colorless crystals (0.22 g, 57%), mp 201–203 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ −0.41 (s, 12H, Al*Me*), 1.12 (m, 8H, NCH_2CH_2), 2.02–2.35 (m, 8H, NCH_2CH_2), 2.35 (s, 6H, Ar*Me*), 3.21 (s, 4H, NCH_2Ar), 4.60 (s, 2H, ArCH_2Ar), 6.42 (s, 2H, Ar-*H*), 7.57 (s, 2H, Ar-*H*). ^{13}C NMR (C_6D_6, 75 MHz): δ −10.35, 15.59, 22.40, 30.40, 53.81, 59.56, 120.72, 125.17,

129.34, 132.42, 133.09, 156.38 ppm. Anal. calcd for $C_{29}H_{44}Al_2N_2O_2$: C, 68.75; H, 8.75; N, 5.53%. Found: C, 68.61; H, 8.48; N, 5.52%.

Synthesis of [2-(OAlMe$_2$)-3-{CH$_2$N(CH$_2$)$_5$}-5-MeC$_6$H$_2$]$_2$CH$_2$ (8)

The same procedure as for that of **6** was used, but **3** was used instead of **2**. Thus, reaction of **3** (0.30 g, 0.71 mmol) with $AlMe_3$ (0.85 cm^3, 1.70 mmol) afforded, after similar workup, colorless crystals of **7** (0.24 g, 63%), mp 160–162 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ −0.36 (s, 12H, Al*Me*), 0.89 (m, 4H, CH_2), 1.03–1.05 (m, 8H, CH_2), 2.10–2.35 (m, 8H, CH_2), 2.36 (s, 6H, Ar*Me*), 3.32 (s, 4H, NCH_2Ar), 4.57 (s, 2H, ArCH_2Ar), 6.46 (s, 2H, Ar-*H*), 7.60(s, 2H, Ar-*H*). ^{13}C NMR (C_6D_6, 75 MHz): δ −8.93, 15.60, 20.73, 22.99, 30.27, 52.61, 58.75, 119.35, 125.35, 129.33, 132.22, 133.22, 156.36. Anal. calcd for $C_{31}H_{48}Al_2N_2O_2{\cdot}0.5Et_2O$: C, 69.32; H, 9.34; N, 4.90%. Found: C, 69.51; H, 9.08; N, 4.82%.

Synthesis of [2-(OAlMe$_2$)-3-{CH$_2$N(Me)Ph}-5-MeC$_6$H$_2$]$_2$CH$_2$ (9)

The same procedure as for that of **5** was used, but **4** was used instead of **1**. Thus, treatment of **4** (0.30 g, 0.64 mmol) with $AlMe_3$ (0.80 cm^3, 2.0 M solution in toluene, 1.60 mmol) afforded, after similar workup, colorless crystals of **8** (0.27 g, 73%), mp 250–252 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ −0.29 (s, 12H, Al*Me*), 2.19 (s, 6H, Ar*Me*), 2.42 (s, 6H, N*Me*), 4.30–4.60 (b, 6H, NCH_2Ar + ArCH_2Ar), 6.74 (s, 2H, *Ar*), 6.83–6.91 (m, 6H, *Ar*), 7.09–7.14 (m, 4H, Ar-*H*), 7.22 (s, 2H, Ar-*H*). ^{13}C NMR (C_6D_6, 75 MHz): δ −9.01, 20.81, 20.83, 33.39, 55.87, 117.14, 122.03, 125.25, 128.13, 129.53, 129.57, 129.61, 129.63, 129.65, 129.70, 131.71, 148.98 ppm. Anal. calcd for $C_{35}H_{44}Al_2N_2O_2$: C, 72.64; H, 7.66; N, 4.84%. Found: C, 72.36; H, 7.63; N, 4.60%.

Synthesis of [2-OH-3-{CH=N(2,6-Pr$^i_2$C$_6$H$_3$)}-5-MeC$_6$H$_2$]$_2$CH$_2$ (10)

A mixture of 2,2′-methylene bis(4-methyl-6-formylphenol) (1.50 g, 5.28 mmol), 2,6-diisopropylaniline (1.87 g, 10.55 mmol) and ethanol (50 cm^3) was refluxed for 12 h and then cooled to room temperature. The solvent was removed from the mixture under vacuum. The residue was washed using *n*-hexane three times to give a yellow powder of **10** (1.70 g, 53%), mp 160–162 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.18 (d, J = 9 Hz, 24H, CH*Me*$_2$), 2.29 (s, 6H, Ar*Me*), 3.00 (m, 4H, C*H*Me$_2$), 4.17 (s, 2H, ArCH_2Ar), 7.04 (s, 2H, Ar-*H*), 7.15–7.18 (m, 8H, Ar-*H*), 8.27 (s, 2H, N=C*H*), 13.15 (b, 2H, O*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.60, 23.73, 28.24, 28.61, 118.05, 123.37, 125.43, 127.92, 128.41, 130.57, 135.31, 138.96, 146.63, 157.32, 166.94. Anal. calcd for $C_{41}H_{50}N_2O_2$: C, 81.69; H, 8.36; N, 4.65%. Found: C, 81.41; H, 8.19; N, 4.75%.

Synthesis of [2-OH-3-{CH=N(*p*-MeC$_6$H$_4$)}-5-MeC$_6$H$_2$]$_2$CH$_2$ (11)

A mixture of 2,2′-methylene bis(4-methyl-6-formylphenol) (1.50 g, 5.28 mmol), *p*-toluidine (1.14 g, 10.64 mmol) and ethanol (50 cm^3) was refluxed for 12 h. The mixture was filtered to afford a yellow powder of **11** (1.9 g, 78%), mp 212–214 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.28 (s, 6H, Ar*Me*), 2.38 (s, 6H, Ar*Me*), 4.12 (s, 2H, Ar*CH*$_2$Ar), 7.06 (s, 2H, Ar-*H*), 7.17 (s, 2H, Ar-*H*),7.46 (m, 8H, Ar-*H*), 8.59 (s, 2H, N=*CH*), 13.55 (b, 2H, O*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.65, 21.19, 28.26, 118.63, 121.11, 127.76, 128.40, 130.09, 130.45, 135.03, 136.74, 146.17, 157.14, 162.01. Anal. calcd for $C_{31}H_{30}N_2O_2$: C, 80.49; H, 6.54; N, 6.06. Found: C, 80.31; H, 6.53; N, 5.98%.

Synthesis of [2-OH-3-{CH=N(*p*-ClC$_6$H$_4$)}-5-MeC$_6$H$_2$]$_2$CH$_2$ (12)

The same procedure as for that of **10** was used, but 4-chloroaniline (1.35 g, 10.58 mmol) was employed instead of 2,6-diisopropylaniline. The crude product was further purified by recrystallization from toluene to give a yellow powder of **12** (2.0 g, 75%), mp 222–224 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.28 (s, 6H, Ar*Me*), 4.09 (s, 2H, ArCH_2Ar), 7.14 (s, 2H, Ar-*H*), 7.06 (s, 2H, Ar-*H*), 7.24 (d, J = 9 Hz, 4H, Ar-*H*), 7.38 (d, J = 9 Hz, 4H, Ar-*H*), 8.55 (s, 2H, N=C*H*), 13.20 (b, 2H, O*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.63, 28.70, 118.42, 122.56, 128.23, 128.43, 129.63, 130.74, 132.37, 135.59, 147.30, 157.17, 163.25. Anal. calcd for $C_{29}H_{24}Cl_2N_2O_2$: C, 69.19; H, 4.81; N, 5.56%. Found: C, 69.26; H, 4.88; N, 5.55%.

Synthesis of [2-OH-3-{CH=N(*p*-MeOC$_6$H$_4$)}-5-MeC$_6$H$_2$]$_2$CH$_2$ (13)

The same procedure as for that of **10** was used, but 4-methoxyaniline (1.30 g, 10.56 mmol) was used instead of 2,6-diisopropylaniline. The crude product was further purified by recrystallization from toluene to give a yellow powder of **12** (1.9 g, 73%), mp 185–187 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.26 (s, 6H, Ar*Me*), 3.82 (s, 6H, O*Me*), 4.10 (s, 2H, ArCH_2Ar), 6.93 (d, J = 9 Hz, 4H, Ar-*H*), 7.03 (s, 2H, Ar-*H*), 7.10 (s, 2H, Ar-*H*), 7.25 (d, J = 9 Hz, 4H, Ar-*H*), 8.55 (s, 2H, N=C*H*), 13.52 (b, 2H, O*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.64, 28.60, 55.64, 114.70, 118.72, 122.36, 127.73, 128.39, 130.30, 134.80, 141.72, 157.03, 158.77, 160.78. Anal. calcd for $C_{31}H_{30}N_2O_4$: C, 75.28; H, 6.11; N, 5.66%. Found: C, 75.45; H, 6.41; N, 5.66%.

Synthesis of [2-OH-3-(CH=NCMe$_3$)-5-MeC$_6$H$_2$]$_2$CH$_2$ (14)

The same procedure as for that of **10** was used, but *tert*-butylamine (0.78 g, 10.66 mmol) was employed instead of 2,6-diisopropylaniline. After similar workup, compound **14** was obtained as a yellow powder (1.8 g, 86%), mp 118–120 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.33 (s, 18H, C*Me*$_3$), 2.23 (s, 6H, Ar*Me*), 4.04 (s, 2H, ArCH_2Ar), 6.94 (s, 2H, Ar-*H*), 6.95 (s, 2H, Ar-*H*), 8.42 (s, 2H, N=C*H*), 14.35 (b, 2H, O*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.61, 28.22, 29.78, 56.90, 118.09, 126.77, 128.50, 129.53, 133.87, 157.94, 159.88. Anal. calcd for $C_{25}H_{34}N_2O_2$: C, 76.10; H, 8.69; N, 7.10%. Found: C, 76.24; H, 8.48; N, 6.98%.

Synthesis of [2-(OAlMe$_2$)-3-{CH=N(2,6-Pr$^i_2$C$_6$H$_3$)}-5-MeC$_6$H$_2$]$_2$CH$_2$ (15)

The same procedure as for that of **6** was used, but compound **10** was employed instead of **1**. Thus, reaction of **10** (0.50 g, 0.83 mmol) with $AlMe_3$ (1.30 cm^3, 2.60 mmol) in toluene generated, after similar workup, yellow crystals of **15** (0.32 g, 54%), mp 260–262 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ −0.23 (s, 12H, Al*Me*), 0.86 (d, J = 6 Hz, 12H, CH*Me*$_2$), 1.27 (d, J = 6 Hz, 12H, CH*Me*$_2$), 2.21 (s, 6H, *Me*Ar), 3.15 (m, 4H, C*H*Me$_2$), 4.37 (s, 2H,

ArCH_2Ar), 6.50 (s, 2H, Ar-*H*), 7.08–7.14 (m, 6H, Ar-*H*), 7.76 (s, 2H, N=C*H*), 7.81 (s, 2H, *Ar*). ^{13}C NMR (C_6D_6, 75 MHz): δ −8.61, 20.34, 22.67, 25.97, 28.45, 30.77, 119.13, 124.46, 126.74, 128.43, 132.79, 133.22, 141.66, 142.61, 142.87, 162.24, 173.74. Anal. calcd for $C_{45}H_{60}Al_2N_2O_2$: C, 75.60; H, 8.46; N, 3.92%. Found: C, 75.48; H, 8.56; N, 3.89%.

Synthesis of [2-(OAlMe$_2$)-3-{CH=N(*p*-MeC$_6$H$_4$)}-5-MeC$_6$H$_2$]$_2$CH$_2$ (16)

AlMe$_3$ (1.00 cm^3, 2.0 M solution in toluene, 2.00 mmol) was added to a stirred solution of **11** (0.30 g, 0.65 mmol) in toluene (20 cm^3) at about −80 °C. The mixture was warmed to room temperature and stirred for 12 h. The solvent was removed under vacuum. The residue was washed with *n*-hexane (30 cm^3) and then dissolved in toluene (5 cm^3). *n*-Hexane (30 cm^3) was added to the solution to give light yellow crystals of **16** (0.18 g, 48%), mp 180–182 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ −0.10 (s, 12H, Al*Me*), 2.00 (s, 6H, Ar*Me*), 2.21 (s, 6H, Ar*Me*), 4.33 (s, 2H, ArCH_2Ar), 6.30 (s, 2H, Ar-*H*), 6.81 (d, *J* = 6 Hz, 4H, Ar-*H*), 6.92 (d, *J* = 6 Hz, 4H, Ar-*H*, 7.42 (s, 2H, Ar-*H*), 7.77(s, 2H, N=C*H*). ^{13}C NMR (C_6D_6, 75 MHz): δ −8.33, 20.35, 20.82, 30.76, 118.89, 122.29, 126.29, 130.42, 133.24, 136.60, 137.60, 141.23, 144.93, 161.88, 169.61. Anal. calcd for $C_{35}H_{40}Al_2N_2O_2$: C, 73.15; H, 7.02; N, 4.87%. Found: C, 73.39; H, 7.13; N, 4.62%.

Synthesis of [2-(OAlMe$_2$)-3-{CH=N(*p*-ClC$_6$H$_4$)}-5-MeC$_6$H$_2$]$_2$CH$_2$ (17)

Complex **17** was synthesized using the same procedure as for that of **6**, but compound **12** was employed instead of **1**. Thus, treatment of **12** (0.30 g, 0.60 mmol) with AlMe$_3$ (0.90 cm^3, 1.80 mmol) produced, after similar workup, yellow crystals of **17** (0.20 g, 54%), mp 187–189 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ −0.22 (s, 12H, Al*Me*), 2.21 (s, 6H, Ar*Me*), 4.25 (s, 2H, ArCH_2Ar), 6.33 (s, 2H, Ar-*H*), 6.65 (d, *J* = 9 Hz, 4H, Ar-*H*), 6.93 (d, *J* = 9 Hz, 4H, Ar-*H*), 7.23 (s, 2H, Ar-*H*), 7.70 (s, 2H, N=C*H*). ^{13}C NMR (C_6D_6, 75 MHz): δ −8.47, 20.34, 30.87, 118.72, 123.74, 126.51, 129.97, 132.98, 133.35, 133.65, 141.70, 145.57, 162.14, 170.66. Anal. calcd for $C_{33}H_{24}Al_2N_2O_2$: C, 64.39; H, 5.57; N, 4.55%. Found: C, 64.61; H, 5.58; N, 4.44%.

Synthesis of [2-(OAlMe$_2$)-3-[CH=N(*p*-MeOC$_6$H$_4$)]-5-MeC$_6$H$_2$]$_2$CH$_2$ (18)

Complex **18** was synthesized employing the same procedure as for that of **6**, but compound **13** was used instead of **1**. Thus, treatment of **13** (0.50 g, 1.01 mmol) with AlMe$_3$ (1.50 cm^3, 3.00 mmol) afforded, after similar workup, yellow crystals of **18** (0.30 g, 49%), mp 220–222 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ −0.21 (s, 12H, Al*Me*), 2.21 (s, 6H, Ar*Me*), 3.23 (s, 6H, O*Me*), 4.37 (s, 2H, ArCH_2Ar), 6.36 (s, 2H, Ar-*H*), 6.59 (d, *J* = 6 Hz, 4H, Ar-*H*), 6.90 (d, *J* = 6 Hz, 4H, Ar-*H*), 7.40 (s, 2H, Ar-*H*), 7.77(s, 2H, N=C*H*). ^{13}C NMR (C_6D_6, 75 MHz): δ −8.62, 20.39, 31.35, 55.68, 115.54, 119.68, 123.51, 124.50, 127.43, 127.74, 127.84, 133.14, 140.33, 141.04, 168.87. Anal. calcd for $C_{35}H_{40}Al_2N_2O_4$: C, 69.29; H, 6.65; N, 4.62%. Found: C, 69.40; H, 6.85; N, 4.43%.

Synthesis of [2-(OAlMe$_2$)-3-(CH=NCMe$_3$)-5-MeC$_6$H$_2$]$_2$CH$_2$ (19)

AlMe$_3$ (0.90 cm^3, 2.0 M solution in toluene, 1.80 mmol) was added to a stirred solution of **14** (0.30 g, 0.76 mmol) in toluene (20 cm^3) at about −80 °C. The mixture was warmed to room temperature and stirred for 12 h. The solvent was removed from the mixture under vacuum. The residue was dissolved in diethyl ether (20 cm^3) and filtered. The filtrate was concentrated and cooled to about −80 °C to afford colorless crystals of **19** (0.19 g, 49%), mp 185–187 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ −0.19 (s, 12H, Al*Me*), 1.00 (s, 18H, CMe_3), 2.22 (s, 6H, Ar*Me*), 4.27 (s, 2H, ArCH_2Ar), 6.36 (s, 2H, Ar-*H*), 7.59 (s, 2H, N=C*H*), 7.70 (s, 2H, Ar-*H*). ^{13}C NMR (C_6D_6, 75 MHz): δ −5.93, 20.40, 29.79, 30.58, 59.26, 118.43, 125.74, 132.77, 132.85, 140.27, 160.83, 168.42. Anal. calcd for $C_{29}H_{44}Al_2N_2O_2$: C, 68.75; H, 8.75; N, 5.53%. Found: C, 68.54; H, 9.05; N, 5.77%.

X-ray crystallography

Single crystals of complexes **6** and **16** were respectively mounted in Lindemann capillaries under nitrogen. Diffraction data were collected at 298(2) K on a Bruker Smart CCD area-detector with graphite-monochromated Mo K$_\alpha$ radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS-97[17] and refined against F^2 by full-matrix least-squares using SHELXL-97.[18] Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in Table 3.

Polymerization of *rac*-LA

A typical polymerization procedure is exemplified by the synthesis of PLA using complex **6** as a catalyst in the presence of

Table 3 Details of the X-ray structure determinations of complexes **6** and **16**

	6	**16**·0.5C$_6$H$_5$Me
Empirical formula	$C_{25}H_{40}Al_2N_2O_2$	$C_{38.5}H_{44}Al_2N_2O_2$
Fw	454.55	620.72
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	16.1331(15)	9.1161(8)
b (Å)	9.5710(8)	13.6920(11)
c (Å)	22.699(2)	15.7135(13)
α (°)	90	104.683(2)
β (°)	128.290(2)	91.7960(10)
γ (°)	90.00	103.913(2)
V (Å^3)	2751.0(4)	1832.7(3)
Z	4	2
D_{calcd} (g cm^{-3})	1.098	1.125
F (000)	984	662
μ (mm^{-1})	0.127	0.113
θ range for data collecn (°)	2.29 to 25.02	2.34 to25.02
No. of reflns collected	13 616	9701
No. of indep reflns (R_{int})	4850(0.0678)	6382(0.0471)
No. of data/restraints/params	4850/0/290	6382/0/441
Goodness of fit on F^2	1.029	1.012
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0673, wR_2 = 0.1509	R_1 = 0.0597, wR_2 = 0.0911
R indices (all data)	R_1 = 0.1572, wR_2 = 0.1751	R_1 = 0.1700, wR_2 = 0.1049
Largest diff peak and hole [e Å^{-3}]	0.607 and −0.392	0.179 and −0.140

two equiv. of benzyl alcohol. To a Schlenk tube was charged with *rac*-LA (0.495 g, 3.43 mmol), BnOH (0.69 cm^3, 0.1 M solution in toluene, 0.069 mmol) and toluene (4.2 cm^3). The mixture was heated to 70 °C. To the stirred mixture a solution of complex **6** in toluene (2.0 cm^3, 0.01715 M, 0.0343 mmol) was added *via* a syringe. After the solution was stirred at 70 °C for 21 h, the polymerization reaction was terminated by addition of several drops of glacial acetic acid. After stirring for 0.5 h at room temperature, the resulting solution was dropped into *n*-hexane to give a white precipitate. The precipitate was collected by filtration, and dried under vacuum to give a white solid.

For the GPC analysis, the sample was dissolved in dichloromethane, passed through a short neutral aluminum oxide column, precipitated in methanol and dried under vacuum.

For the kinetic studies, samples were taken from the reaction mixture using a syringe at a desired time interval.

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