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Synthesis and Characterization of Magnesium Alkoxides Incorporated into Bulky Aluminium Tetraphenolate Helices and Application in the Ring-Opening Polymerization of Lactides

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Two aluminium and magnesium heterobimetallic complexes of [(LAl)MgOBn]₂ (**2**) and [(LAl)Mg(OC₂H₄OCH₃)]₂ (**3**), in which $L = N^1, N^1, N^2, N^2$ -tetrakis(2-hydroxy-3,5-dimeth-ylbenzyl)-1,2-ethanediamine, have been synthesized and characterized by NMR spectroscopy, X-ray crystallography, and elemental analysis. The magnesium alkoxide of complex **2** supported by the bulky aluminium tetraphenolates, as a

Introduction

The design and synthesis of heterobimetallic complexes have attracted considerable attention because sometimes they show multiple functionalities and prominent catalytic activity, selectivity over monometallic complexes, and can potentially even achieve chemical transformations that are unprecedented with monometallic catalysts.^[1] For example, heterobimetallic complexes (e.g., Fe, Mo, and Co) at the active site of the enzyme of nitrogenase play a key role in the fixation of atmospheric nitrogen gas.^[2] Hosokawa et al. have proposed and isolated Pd-Cu heterobimetallic species participating in the famous Wacker reaction with PdCl₂ and CuCl₂ as catalysts; the catalytic cycle would come to a halt in the absence of PdCl₂ or CuCl₂.^[3] Heterobimetallic lanthanide-alkali-metal complexes based on binol are versatile catalysts in a wide range of asymmetric reactions that have never been possible with monometallic lanthanide catalysts.^[4] Finally, the heterobimetallic complex of "iBu₃Al-(tmp)Li'' [tmp(H) = 2,2,6,6-tetramethylpiperidine] exhibitshigh chemo- and regioselectivity in proton abstraction reactions of functionalized aromatic substrates because of al-

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rare helical heterobimetallic initiator, can effectively initiate the ring-opening polymerization (ROP) of L-lactide (L-LA) leading to polymers with good molecular weight control and narrow molecular weight distributions. Kinetic studies have shown the overall rate expression is -d[lactide]/dt = k[lactide][complex] for the ROP of L-LA. Furthermore, complex 2 shows modest isotactic selectivity in the ROP of *rac*-lactide.

kali-metal–aluminium synergic effects.^[5] A series of pioneering works reported by Mulvey and co-workers also showed some special synergetic effects in the heterobimetallic complexes in some organic chemical reactions.^[6]

Recently we have focused our research on the development of multi-metallic catalysts for the ring-opening polymerization (ROP) of lactide to obtain biorenewable, biodegradable, and biocompatible polylactide (PLA).^[7] Up to now, many metal complexes have been successfully used to initiate/catalyze the ROP of lactide, giving polymers with the desired molecular weights and narrow molecular weight distributions. Among them, many initiators/catalysts, like diketiminate-zinc,^[8] Salan-Al,^[9] titanium alkoxides,^[10] and Salen-Ln,^[11] show high heterotactic selectivities in the ROP of lactide,^[12] whereas up to now only Salen, Salan, or Salenlike aluminium complexes have shown excellent isotactic selectivities ($P_{\rm m} > 0.9$) in the ROP of *rac*-lactide.^[13] Salen– Al and Salen-like Al systems suffer from low activation and usually a high temperature (>70 °C) is necessary for the polymerization reaction. Although magnesium,^[14] calcium,^[15] and other complexes^[16] show high activity in the ROP of lactide, only modest isotactic selectivities can be achieved. The highly active yttrium phospha-salen initiators very recently reported by Auffrant and Williams and their co-workers showed high isoselectivities ($P_{\rm m} = 0.84$) for the ring-opening polymerization of rac-lactide.[17] Nevertheless, finding other excellent, highly active systems with high isotactic selectivities is still a challenge. Thus, two aluminium and magnesium heterobimetallic bulky complexes were synthesized in this research in which the highly Lewis acidic aluminium metal acts as an auxiliary to fix the bulky and

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chiral environment around the active center. Meanwhile, magnesium metal with alkoxide could act as a highly active initiator. To chelate both metal ions of Al^{III} and Mg^{II} and inhibit side-reactions of the ring-opening polymerization of lactide, the peculiar quadruply charged, sterically hindered ligand of tetraphenolate was chosen. Although the selectivity is not as high as we expected, it presents another possible approach to the design of a new type of heterobimetallic complex for highly active and selective ring-opening polymerization of racemic lactide.

Results and Discussion

Synthesis and Characterization of Complexes 2 and 3

Complex 1 was synthesized by heating a mixture of AlMe₃ and LH₄ for 20 hours at reflux according to a literature method but by replacing Al(O*i*Pr)₃ with AlMe₃.^[18] The above reaction mixture reacts directly with 1 equivalent of $Mg(OBn)_2$ at 25 °C for 12 hours to afford complex 2 in 30% yield after recrystallization (Scheme 1). Complex 2 has been well characterized by NMR spectroscopy and elemental analysis. It is interesting that complex 4 cannot be obtained by the reversed addition sequence of aluminium and magnesium, which also gave complex 2 as the main product, as verified by NMR spectroscopy and X-ray diffraction. This self-assembly behavior may indicate that complex 2 is more stable. To expand this reaction, complex 3 was obtained by the reaction of LH₄, tris(methoxyethoxy)aluminium, and $Mg(nBu)_2$ in 25% yield after recrystallization. The results of the elemental analysis agreed well with the structure, whereas the ¹H NMR spectrum is complicated because of the possible existence of diastereoisomers, which will be discussed below. Both complexes have low solubility in hexane and modest solubility in toluene and thf, and complex **2** is more soluble than complex **3** in CH₂Cl₂. When the methyl groups were replaced by *tert*-butyl groups in this kind of ligand, the ¹H NMR spectra tended to be a mess, even after purification, which indicates that the related complexes cannot be obtained in an acceptable yield, that is, the greater steric hindrance of the ligand possibly inhibits the formation of this type of complex.

Single crystals of complex 2 suitable for structural characterization were obtained from slow cooling of a toluene solution; complex 2 crystallizes as dimers in the centrosymmetric monoclinic space group C2/c. An ORTEP drawing of complex 2 is shown in Figure 1. All is six-coordinated by the four oxygen atoms and two nitrogen atoms of the tetraphenol ligand and its geometry is a distorted octahedron. Mg1 is five-coordinated by three oxygen atoms of one ligand and two oxygen atoms from the benzyloxy groups and adopts a distorted trigonal-bipyramidal geometry, and the two monomers are bridged through the oxygen atoms of two benzyloxy groups. This complex is a racemic compound with two enantiomers in the unit cell with (Λ,Λ) -[(LAl)MgOBn]₂ having the handedness of the two red helices shown in Figure 1. Figure 2 illustrates the chirality at one aluminium center: Two triangular faces of O2-O3-O4 at the front (shown in blue) and N1-O1-N2 at the back (shown in pink) can be chosen, and the three-bladed propellers of O2-N1, O3-O1, and O4-N2 by looking at the molecule along the Mg-Al direction with anticlockwise character indicate that the chirality of the aluminium center can be designated as Λ . Because the dimer can be generated



Scheme 1. Synthesis of complexes 2 and 3.





Figure 1. Molecular structure of (Λ,Λ) -[(LAl)MgOBn]₂ (2) with ellipsoids drawn at the 30% level. Selected bond lengths [Å]: Al(1)–O(1) 1.823(7), Al(1)–O(2) 1.857(6), Al(1)–O(3) 1.841(3), Al(1)–O(4) 2.003(0), Al(1)–N(1) 2.060(6), Al(1)–N(2) 2.048(0). Mg(1)–O(2) 2.201(5), Mg(1)–O(3) 2.100(4), Mg(1)–O(4) 2.012(1), Mg(1)–O(5) 1.993(2), Mg(1)–O(5)ⁱ 1.9578(12). Symmetry code: i: 2 - x, y, 1.5 - z.

from the asymmetric unit through a C_2 rotation, the configurations of both aluminium centers in one dimer are Λ . Therefore the chirality of the dimer shown in Figure 1 can be labeled as (Λ,Λ) , and the other enantiomer of (Δ,Δ) -[(LAI)MgOBn]₂ can also be found in the unit cell, for which the chirality around Al³⁺ is demonstrated in Figure 3. Note that the clear single set of resonances in the ¹H NMR spectrum of complex **2** in CDCl₃ indicates the nonexistence of the *meso* complex in the final product after recrystallization. As far as we know, this kind of structure with two magnesium alkoxides as the active centers located in a chiral helical environment is the first to have been reported.

Single crystals suitable for the structural characterization of complex **3** were also acquired by slow cooling of a toluene solution. Its molecular structure is depicted in Figure 4 with selected bond lengths given in the caption. In contrast to complex **2**, Mg1 is five-coordinated by two oxygen atoms of the tetraphenol ligand and three oxygen atoms of the 2methoxyethoxy groups. The replacement of one phenolic oxygen atom by the methoxy group of 2-methoxyethoxy indicates the potential coordination position of lactide in the ring-opening polymerization with complex **2** as the initiator. However, complex **3** is a *meso* compound composed of two



Figure 2. Chirality at the Al³⁺ center in (Λ,Λ) -[(LAl)MgOBn]₂, top view along the Mg–Al direction.



Figure 3. Chirality at the Al³⁺ center in (Δ,Δ) -[(LAl)MgOBn]₂, top view along the Mg–Al direction.



Complex 2				Complex 3				
S _{ij}			S _{ij}	S_{ij}		S_{ij}		
Al(1)–O(1)	0.578	Mg(1)–O(2)	0.253	Al(1)–O(1)	0.603	Mg(1)–O(3)	0.384	
Al(1)-O(2)	0.527	Mg(1) - O(3)	0.333	Al(1) - O(2)	0.623	Mg(1) - O(4)	0.400	
Al(1) - O(3)	0.550	Mg(1)-O(4)	0.422	Al(1) - O(3)	0.534	Mg(1)-O(5)	0.439	
Al(1)-O(4)	0.355	Mg(1) - O(5)	0.444	Al(1) - O(4)	0.411	Mg(1) - O(6)	0.280	
Al(1) - N(1)	0.512	$Mg(1) - O(5)^{i}$	0.489	Al(1) - N(1)	0.389	$Mg(1) - O(5)^{i}$	0.540	
Al(1) - N(2)	0.529			Al(1) - N(2)	0.480	0() ()		
$z_{\rm j} = 3.051$		$z_{\rm j} = 1.941$		$z_{\rm j} = 3.040$		$z_{\rm j} = 2.043$		

Table 1. Bond valence sums for complexes 2 and 3.

different aluminium chiral centers (Δ , Λ) related by an inversion center. Although the structural analysis demonstrates complex **3** to be a *meso* compound, the existence of chiral (Δ , Δ) and (Λ , Λ) diastereoisomers in the purified solid cannot be ruled out due to the complicated ¹H NMR spectrum of the final recrystallized product in CDCl₃ solution (see Figure S3 in the Supporting Information). That is, it is difficult to separate the air-sensitive diastereoisomers because of their possible similar solubility.



Figure 4. Molecular structure of **3** drawn with ellipsoids at the 30% probability level. Selected bond lengths [Å]: Al(1)–O(1) 1.807(4), Al(1)–O(2) 1.795(7), Al(1)–O(3) 1.852(6), Al(1)–O(4) 1.949(4), Al(1)–N(1) 2.162(6), Al(1)–N(2) 2.084(6). Mg(1)–O(3) 2.047(3), Mg(1)–O(4) 2.032(1), Mg(1)–O(5) 1.998(2), Mg(1)–O(5)ⁱ 1.922(4). Symmetry code: i: -x, 1 - y, -z.

In fact, the sites of Al³⁺ and Mg²⁺ in one molecular complex are difficult to identify for they have the same number of electrons, fortunately bond valence principle gives us an opportunity to distinguish them based on bond lengths obtained from good single-crystal structures. The bond valence sums offer a relatively simple method for determining the oxidation state and assessing the correctness of reported structures. The oxidation state, z_j , can be calculated from the sum of the individual bond valences, s_{ij} , as shown in Equation (1). s_{ij} can be calculated from the observed bond lengths, R_{ij} , by using Equation (2) provided the constants band R_o are known. The constant b is 0.37. This value was determined by Brown and Altermatt^[19] and is generally accepted.^[20]

$$z_i = \Sigma s_{ii} \tag{1}$$

 $s_{ii} = \exp[(R_{o} - R_{ii})/b]$ (2)

The bond valence sums of Al and Mg based on the positions of Al^{3+} and Mg^{2+} in the structures 2 and 3 are close

to the theoretical values of the oxidation states presented in Table 1, which indicates that the structures of complexes **2** and **3** are accurate and credible. After the alternation of Al^{3+} and Mg^{2+} , bond valence sums will seriously deviate from the theoretical values of the oxidation states. ICP-OES (inductively coupled plasma optical emission spectrometry) experiments have also been conducted and the results confirmed the presence of both Al^{3+} and Mg^{2+} in the correct ratio of 1:1 for Al^{3+}/Mg^{2+} . The polymerization reactions reported below can also certify the correct presumption because the two complexes are highly active, like the magnesium alkoxides reported in the literature and unlike the usual poorly active aluminium alkoxide.

ROP of L-Lactide and Kinetic Studies

The ROP of L-lactide initiated by complex 2 was carried out in dichloromethane at 25 °C. As shown in Table 2, complex 2 was found to be an efficient initiator, giving almost complete conversions in about 2 hours for the polymerization of L-lactide with [lactide]₀/[initiator]₀ ratios from 100 to 400. In comparison with aluminium alkoxides, the high activity of complex 2 implies the active center is the alkoxy group coordinated to magnesium. The initiator system showed controllable polymerization performance as evidenced by the linear correlations between the number average molar mass (M_n) and monomer/initiator ratio, and the close agreement between experimental and calculated



Figure 5. Relationship between M_n (\blacksquare) and PDI (\blacktriangle) of the polymer formed by using complex 2 and the initial molar ratios [LA]₀/[I]₀ (entries 1–6 in Table 2).



Table 2. Polymerization of L-LA using complexes 2 and 3.^[a]



Entry	[M] _o /[I] _o	Complex	Time	Conv.[%]	$M_{\rm n}({\rm calcd})^{[{\rm f}]}$	$M_{\rm n}({\rm exp.})^{[{\rm g}]}$	PDI	$P_m^{[h]}$
1	100:1	2	2 h	96	7000	5400	1.13	
2	150:1	2	2 h	98	10700	8300	1.12	
3	200:1	2	2 h	95	13800	12400	1.09	
4	250:1	2	2 h	96	17400	13300	1.06	
5	350:1	2	2 h	98	24800	23000	1.09	
6	400: 1	2	2 h	97	28000	23700	1.13	
7 ^[b]	215:1	2	5 min	41	6400	5200	1.12	
8 ^[b]	215:1	2	15 min	78	12200	10400	1.12	
9 ^[b]	215:1	2	20 min	87	13600	11500	1.08	
10 ^[b]	215:1	2	30 min	93	14500	12500	1.09	
11 ^[c]	100:1	2	2 h	82	6000	5700	1.05	0.55
12 ^[d]	100:1	2	10 h	70	5100	4900	1.08	0.58
13	100:1	3	6 h	36	2700	4700	1.21	
14 ^[e]	100:1	3	3 h	93	6800	7300	1.68	

[a] Conditions: $[I]_0 = 5 \text{ mM}$ at 25 °C in dichloromethane. [b] $[I]_0 = 7 \text{ mM}$, $[LA]_0 = 1.5 \text{ M}$ at 25 °C in CDCl₃. [c] Racemic lactide, $[I]_0 = 4 \text{ mM}$ at room temperature in CH₂Cl₂. [d] Racemic lactide, $[I]_0 = 4 \text{ mM}$ at 0 °C in CH₂Cl₂. [e] $[I]_0 = 5 \text{ mM}$ at 80 °C in toluene. [f] Calculated from the molecular weight of L-LA × [L-LA]_0/2[1] × conversion + molecular weight of BnOH. [g] GPC data in thf vs. polystyrene standards using a correction factor of 0.58.^[22] [h] Obtained from the homonuclear-decoupled ¹H NMR spectrum.

values of M_n (Figure 5). Analysis by ¹H NMR of PLA-100:1 (entry 1) produced at an initial [LA]₀/[initiator]₀ ratio of 100:1 shows a characteristic quadruple methine peak (Figure 6) at $\delta = 5.16$ ppm, which indicates no serious epimerization of the chiral centers in the polymers, confirmed by the homonuclear-decoupled ¹H NMR spectra of the methine region. Peaks at δ = 7.32 (C₆H₅CH₂) and 4.38 ppm (HOCHMe) with an integral ratio of 5:1 between H_e and H_c indicate the polymer chain is capped by one benzyl ester and one hydroxy group, which suggests that polymerization occurs by the insertion of L-lactide into the metal–benz-yloxy bond. Complex **3** was also used as an initiator for the



Figure 6. ¹H NMR spectrum of PLA-100 initiated by complex 2 (entry 1 in Table 2).



ROP of lactide with a [lactide]₀/[initiator]₀ ratio of 100:1 (entries 13 and 14). Only 36% of lactide was converted into polylactide in CH₂Cl₂ in 6 hours giving a polymer with high molecular weight. The lower activity of complex **3** can possibly be ascribed to the difficult coordination of lactide to magnesium at the position occupied by the methoxy group, which leads to the slow initiation of lactide ROP at room temperature. The higher molecular weight and broad PDI can be attributed to the slower initiation of lactide ROP relative to propagation and the possible existence of different active diastereoisomers in complex **3**. Although 93% conversion of lactide can be achieved in toluene in 3 hours at 80 °C (entry 14), the molecular weight distribution of 1.68 is very broad.

Kinetic studies of L-lactide polymerization with complex 2 as initiator were conducted to establish the reaction order in monomer and metal concentration. The conversions of L-lactide with time at various concentrations of complex 2 $([LA]_0 = 1.5 \text{ M}, [I]_0 = 7, 5, 3, \text{ and } 2.5 \text{ mM})$ in CDCl₃ were monitored by ¹H NMR spectroscopy at 25 °C. Note that the initiator system in CDCl3 also showed good control of polymerization, as evidenced by the linear increase in $M_{\rm p}$ with conversion and narrow PDIs (1.08-1.12; Figure 7). In each case, plots of $\ln[(LA)_0/(LA)_t]$ versus time are linear, which indicates polymerization proceeds with a first-order dependence on monomer concentration (Figure 8, $[LA]_0 =$ 1.5 mol L⁻¹, $[I]_0 = 7 \text{ mM}$, $[LA]_0/[I]_0 = 215$, $k_{obs} = 1000 \text{ mm}$ 9.92×10^{-2} min⁻¹). Thus, the rate of polymerization can be written as $-d[LA]/dt = k_{obs}[LA]$ in which $k_{obs} = k[I]^x$ and k is the rate constant. The linear relationship between k_{obs} and $[I]_0$ (Figure 9) reveals the reaction is first order in the initiator. Therefore the overall rate equation is -d[LA]/dt = $k[LA][I] (k = 12.65 L mol^{-1} min^{-1})$. The rate law of -d[LA]/dt = k[LA][I] is the same as that found in other initiator systems,^[12b,14b,14d,21] but different to similar dimeric magnesium alkoxide systems reported by us.[14d]



Figure 7. Plot of molecular weight (M_n) vs. conversion of monomer with complex **2** as initiator for the polymerization of L-lactide. Reagents and conditions: $[LA]_0 = 1.5 \text{ mol } L^{-1}$, $[I]_0 = 0.007 \text{ mol } L^{-1}$, CDCl₃, 25 °C.



Figure 8. First-order kinetic plots for polymerizations using initiators **2**. Reagents and conditions: $[LA]_0 = 1.5 \text{ mol } L^{-1}$; $(\mathbf{V}) [I]_0 = 0.007 \text{ mol } L^{-1}$, $[LA]_0/[I]_0 = 215$, $k_{obs} = 9.92 \times 10^{-2} \text{ min}^{-1}$; $(\mathbf{O}) [I]_0 = 0.005 \text{ mol } L^{-1}$, $[LA]_0/[I]_0 = 300$, $k_{obs} = 5.98 \times 10^{-2} \text{ min}^{-1}$; $(\mathbf{I}) [I]_0 = 0.003 \text{ mol } L^{-1}$, $[LA]_0/[I]_0 = 500$, $k_{obs} = 1.91 \times 10^{-2} \text{ min}^{-1}$; $(\mathbf{F}) [I]_0 = 0.0025 \text{ mol } L^{-1}$, $[LA]_0/[I]_0 = 600$, $k_{obs} = 0.77 \times 10^{-2} \text{ min}^{-1}$; 25 °C. CDCl₃.



Figure 9. Linear plot of k_{obs} vs. [I]₀ for the polymerization of L-LA with complex **2**. Reagents and conditions: [LA]₀ = 1.5 mol L⁻¹, CDCl₃, 25 °C, $k = 12.65 \text{ L mol}^{-1} \text{ min}^{-1}$.

Ring-Opening Polymerization of *rac***-Lactide**

The polymerization of *rac*-lactide initiated by complex **2** was also conducted in CH₂Cl₂, toluene, and thf at room temperature. Complex **2** induces almost no tacticity in the ROP of lactide in toluene and thf, whereas modest selectivities were obtained with CH₂Cl₂ as solvent. The homonuclear-decoupled ¹H NMR spectrum in the methine region of PLA derived from entry 11 shows isotactic predominance with $P_{\rm m} = 0.55$,^[23] a slighter better selectivity of $P_{\rm m} = 0.58$ can be obtained by changing the reaction temperature to 0 °C (see Figure S4 in the Supporting Information). The lower selectivity than expected can be attributed to the possible dissociation of the dimer to monomer because lactide must pass through a chiral channel to the active magne-

sium center in the dimer of complex 2 whereas the monomer only gives an open chiral surrounding around the active magnesium center for less steric handrance. Although the selectivity is not as high as we expected, these kinds of heterobimetallic complexes can provide insights into alternative methods for finding highly active and highly isotactic selective initiator systems.

Conclusions

Two new kinds of aluminium and magnesium heterobimetallic alkoxides 2 and 3 have been synthesized and characterized. The molecular structures of complexes 2 and 3were confirmed by single-crystal X-ray diffraction techniques. Experimental results indicate that the racemic helical complex 2 is an efficient initiator of the controlled ringopening polymerization of L-lactide leading to polymers with good molecular weight control and narrow molecular weight distributions. It also shows modest isotactic selectivity for the ROP of *rac*-lactides.

Experimental Section

Materials and Methods: All the syntheses were performed under dry nitrogen using standard Schlenk techniques. Reagents were purified by standard methods: toluene, n-hexane, and thf were distilled under argon from sodium/benzophenone ketyl prior to use, CH₂Cl₂ was distilled from P₂O₅, BnOH and CH₃OCH₂CH₂OH were distilled from CaH, L-LA and rac-LA were purchased from Daigang BIO Engineer Limited Co. of China and recrystallized from toluene, $Mg(nBu)_2$ and $Al(CH_3)_3$ were purchased from Acros Company. ¹H and ¹³C NMR were recorded with Varian Mercury Plus 300 and 600 MHz spectrometers. ¹H NMR chemical shifts are reported in ppm versus residual protons in $CDCl_3$: $\delta = 7.26$ ppm. ¹³C NMR chemical shifts are reported in ppm versus residual ¹³C in CDCl: δ = 77.2 ppm. GPC analyses were performed with a Waters instrument (M510 pump, U6K injector) equipped with Waters 2414 and Milton Roy differential refractive index detectors and Waters Styrage[®] HR 4E THF 7.8×300 mm column in series. The GPC columns were eluted with tetrahydrofuran at 45 °C at 1.0 mL/min and calibrated with monodisperse polystyrene as a standard reference.

Synthesis of Ligand LH₄: The ligand LH₄ was prepared according to the literature.^[24] 2,4-Dimethylphenol (6 equiv., 60 mmol), 95% paraformaldehyde (4 equiv.), and ethylenediamine (1 equiv.) were heated in a 100 mL pressure flask at 80 °C with stirring for 3 days. The reaction was allowed to cool and methanol (ca. 50 mL) was added to the reaction mixture. This mixture was stirred overnight, the precipitate was isolated by vacuum filtration, and the product was isolated as a white solid, yield 4.47 g (75%).

Synthesis of Complex 2

Method 1: AlMe₃ solution (1.1 mL, 1.1 mmol, 1.0 M solution in hexane) was added dropwise to a stirred solution of LH₄ (0.596 g, 1.0 mmol) in toluene (15.0 mL) at 0 °C. The slurry was warmed slowly to room temperature and stirred for 20 h at 110 °C, and the solution became clear. This solution was then cooled to room temperature and added dropwise to a mixture of MgnBu₂ (1.0 M in hexane, 1.1 mL, 1.1 mmol) and BnOH (1 M in toluene, 2.2 mL, 2.2 mmol) in toluene (8 mL) at 0 °C. The reaction mixture was then

stirred for 12 h at room temperature. The volatiles were removed in vacuo and then the residue was recrystallized to give complex 1 as colorless crystals, yield 0.23 g (30%). ¹H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.30 (m, 4 H, ArH), 6.98 (s, 2 H, ArH), 6.71 (s, 2 H, ArH), 6.62 (s, 8 H, ArH), 6.49 (s, 3 H, ArH), 6.38 (s, 3 H, ArH), 6.25 (s, 4 H, ArH), 4.64 (br., 2 H, NCH₂Ph), 4.39 (d, ${}^{2}J_{1H-}$ _{1H} = 12.0 Hz, 2 H, OCH₂Ph), 4.34(br., 2 H, NCH₂), 3.94 (d, 4 H, NCH₂), 3.67 (br., 2 H, CH₂), 3.29 (d, ${}^{2}J_{1H-1H}$ = 12.0 Hz, 2 H, OCH₂Ph), 3.11 (m, 4 H, CH₂), 2.71 (d, ${}^{2}J_{1H-1H}$ = 11.5 Hz, 2 H, CH₂), 2.63 (br., 2 H, CH₂), 2.51 (dd, J_{1H-1H} = 11.5 Hz, 2 H, CH₂), 2.30 (s, 6 H, CH₃), 2.25 (s, 6 H, CH₃), 2.11 (s, 12 H, CH₃), 2.03 (m, 4 H, CH₂), 2.00(s, 12 H, CH₃), 1.76 (s, 6 H, CH₃), 1.56 (s, 6 H, CH₃) ppm. ¹³C NMR (600 MHz, CDCl₃, 298 K): δ = 156.95, 154.77, 154.48, 152.45, 131.98, 131.71, 130.96, 130.01, 127.61, 127.30, 126.96, 126.79, 126.62, 126.09, 125.71, 125.13, 124.23, 123.73, 122.56, 121.32, 120.42, 65.92, 65.32, 64.83, 63.10, 62.65, 57.16, 56.14, 21.41, 20.58, 20.38, 17.81, 16.33, 15.71, 14.48 ppm. C₉₀H₁₀₂Al₂Mg₂N₄O₁₀·0.5CH₂Cl₂ (1544.83): calcd. C 70.36, H 6.72, N 3.63; found C 69.82, H 6.85, N 3.21.

Method 2: MgnBu₂ (1.0 \times in hexane, 1.1 mL, 1.1 mmol) was added dropwise to a stirred solution of LH₄ (0.596 g, 1.0 mmol) in toluene (15.0 mL) at 0 °C. The slurry was warmed slowly to room temperature and stirred for 12 h, and the solution became clear. A mixture of AlMe₃ solution (1.0 \times solution in hexane, 1.1 mL, 1.1 mmol) and BnOH (1 \times in toluene, 3.3 mL, 3.3 mmol) in toluene (8 mL) was added dropwise to this solution at 0 °C. The reaction mixture was stirred for 20 h at 110 °C. The volatiles were removed in vacuo and then the residue was recrystallized to give complex **2** as colorless crystals.

Synthesis of Complex 3: A mixture of AlMe₃ (1.0 M solution in hexane, 1.1 mL, 1.1 mmol) and CH₃OCH₂CH₂OH (1 M in toluene, 3.3 mL, 3.3 mmol) in toluene (8 mL) was added to a rapidly stirred solution of LH₄ (0.596 g, 1.0 mmol) in toluene (15.0 mL) at 0 °C. The solution was warmed slowly to room temperature and stirred for 20 h at 110 °C. This solution was then cooled to room temperature and added dropwise to a solution of Mg*n*Bu₂ (1.0 M in hexane, 1.1 mL, 1.1 mmol). The reaction was continued for 12 h at room temperature, the volatiles were removed in vacuo, and the residue recrystallized to give complex 3 as a white powder, yield 0.18 g (25.0%). The ¹H NMR spectrum is complicated possibly indicating it is a mixture of diastereoisomers (see Figure S3 in the Supporting Information). $C_{82}H_{102}Al_2Mg_2N_4O_{12}$ (1438.30): calcd. C 68.48, H 7.15, N 3.90; found C 68.20, H 7.18, N 3.56.

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES): Complex 1 (10 mg) was decomposed with 65% HNO₃ (v/v, 2 mL) and make aqueous solution of HNO₃ (100 mL, 5%). The amounts of aluminium and magnesium were then determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, IRIS Advantage, TJA, USA).

Polymerization of L-Lactide: A typical polymerization procedure is exemplified by the synthesis of PLA ($[LA]_0/[I]_0 = 100:1$; Table 2, entry 1) at room temperature. Complex 1 (0.030 g, 0.02 mmol) was added to a rapidly stirred solution of L-lactide (0.288 g) in dichloromethane (4 mL). The reaction mixture was stirred for 2 h at room temperature and then quenched with distilled water (0.5 mL). The solution was concentrated in vacuo and the polymer was redissolved in dichloromethane and then precipitated with excess hexane to give a white crystalline solid. The polymer was then dried in vacuo to a constant weight. Then the molecular weight and polydispersity index (PDI) were determined by GPC.

Kinetics of L-Lactide Polymerization with Complex 2: A $CDCl_3$ solution of monomer was added to a solution of the complex. The



mixture was then stirred at 25 °C under N₂. After appropriate intervals of time, a certain amount of the reaction solution was removed and quenched with distilled water (1 drop). The aliquots were then dried to a constant weight in vacuo and analyzed by ¹H NMR spectroscopy. When the initial concentration of the initiator ([I]₀) was 0.007 mol L⁻¹, the aliquots were concentrated in vacuo and the polymer was redissolved in dichloromethane and precipitated with excess hexane to give a white crystalline solid. The polymer was then dried in vacuo to constant weight. The M_n and PDI of the polymer were obtained by GPC analysis.

Crystallographic Studies: Single-crystal X-ray data collections were performed with a Bruker SMART APEX CCD diffractometer by using graphite-monochromated Mo- K_{α} ($\Lambda = 0.71073$ Å) radiation. Semiempirical absorption corrections were applied using the SAD-ABS program.^[25] The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXS-97 and SHELXL-97 programs.^[26] Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. The crystal data and results of the refinement are summarized in Table 3.

Table 3. Details of the X-ray structure determinations of complexes $\mathbf{2}$ and $\mathbf{3}$.

2	3			
C ₁₁₇ H ₁₁₈ Al ₂ Mg ₂ N ₄ O ₁₀ C ₄₈ H ₅₁ AlMgN ₂ O ₆				
1842.73	803.20			
296(2)	293(2)			
monoclinic	monoclinic			
C2/c	$P2_1/c$			
19.618(5)	15.560(10)			
22.593(6)	15.096(9)			
23.691(6)	24.099(11)			
90.00	90.00			
94.828(3)	126.68(3)			
90.00	90.00			
10463(4)	4540(4)			
4	4			
1.170	1.175			
0.100	0.107			
3912	1704			
2.50-25.15	2.19-23.47			
-23 < h < 24	-17 < h < 17			
-27 < k < 27	-9 < k < 16			
-28 < l < 28	-24 < l < 25			
9945/48/616	6285/565/547			
1.033	1.021			
0.0615	0.0746			
0.1604	0.1117			
0.719, -0.458	0.329, -0.191			
	2 $C_{117}H_{118}Al_2Mg_2N_4O_{10}$ 1842.73 296(2) monoclinic C2/c 19.618(5) 22.593(6) 23.691(6) 90.00 94.828(3) 90.00 10463(4) 4 1.170 0.100 3912 2.50–25.15 -23 < h < 24 -27 < k < 27 -28 < l < 28 9945/48/616 1.033 0.0615 0.1604 0.719, -0.458			

CCDC-918271 (for **2**) and -918272 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): CIF for **2** and **3**, NMR spectrum of complex **2**, and homonuclear-decoupled ¹H NMR spectrum.

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