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Preparation, Characterization, and Catalytic Studies of Magnesium Complexes Supported by NNO-Tridentate Schiff-Base Ligands

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A series of magnesium benzyl alkoxides, $[LMg(\mu\text{-}OBn)]_2$ (**1**−**8**), supported by NNO-tridentate Schiff-base ligands are prepared by the reactions of $Mg(OBn)_2$ with one molar equivalent of related Schiff-base ligands (L^1H−L^8H) in toluene. The molecular structures of compounds **2**, **3**, **7**, and **8** are characterized by X-ray structure determination. All of these compounds are crystallized as penta-coordinated dimers, and the central magnesium atoms are bridged by the oxygen atoms of benzyl alkoxides. The catalytic activities of complexes **1**−**8** toward the ring-opening polymerization of L-lactide are investigated. Experimental results indicate that the reactivity of $[LMg(\mu\text{-}OBn)]_2$ (**1**−**8**) is dramatically affected by the electronic effect of the substituents on the Schiff-base ligands, and **4** has the highest activity among them.

Introduction

Phenolate ligands containing nitrogen donors, such as phenoxyamine[1] and phenoxyimine[2] ligands, have been widely used in the stabilization of metal complexes across main group and transition metals. For example, several nickel complexes bearing salicylaldimine used in olefin polymerization have been reported.[3] Particularly, salicylaldiminato nickel complexes with a single active site have shown great activity toward the polymerization of ethylene with a very low number of branches in the absence of cocatalysts at low temperatures and pressures.[3a] In addition, the zinc bis-salicylaldimine complexes were used as catalysts for the copolymerization of CO_2 and cyclohexene oxide, producing poly(cyclohexane carbonate) with greater than 99% carbonate linkages.[4]

Metal complexes containing phenoxyamine or phenoxyimine ligands have been interested and examined as catalysts and initiators in the ring-opening polymerization (ROP).[5−8] For instance, zinc complexes supported by phenoxyamine bearing an additional amine arm were used in lactide polymerization and have shown the fastest rate among zinc complexes ever reported at that time, yielding polylactides with molecular weights as large as 130 kg/mol and relatively narrow molecular weight distributions (PDI = 1.34).[5a] The dinuclear complexes of zinc, magnesium, and cobalt derived from a phenoxyamine bearing two ethylenediamine arms were synthesized and studied regarding their cyclic ester

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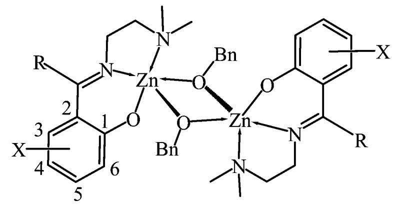
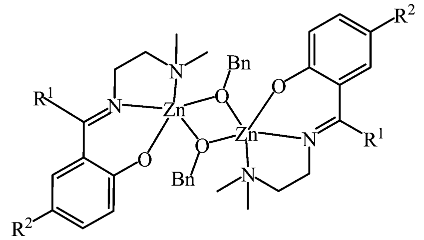
Chart 1



Ia: R = H; X = 4-H
Ib: R = H; X = 3,4-benzo
Ic: R = H; X = 4-Cl
Id: R = H; X = 4-Br
Ie: R = H; X = 4,6-di-^{t}Bu

Chart 2



IIa: R^1=CH$_3$, R^2=H
IIb: R^1=CH$_3$, R^2=Cl
IIc: R^1=CH$_3$, R^2=Br
IId: R^1=CH$_3$, R^2=OMe
IIIa: R^1=Ph, R^2=H
IIIb: R^1=Ph, R^2=Cl

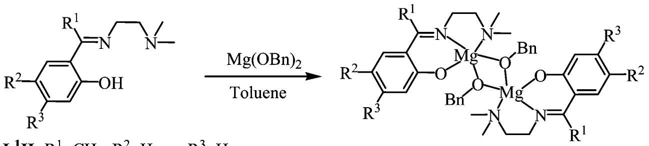
polymerization reactivity.[6b] Most recently, a monoether salen-like ligand and its related magnesium and zinc complexes were prepared and characterized. Experimental results show that these complexes efficiently initiate the ring-opening polymerization of L-lactide and rac-lactide in a controlled fashion.[7b] These properties exhibited by metal alkoxides with phenoxyamine or phenoxyimine ligands in ROP reactions encouraged us to prepare novel phenoxyiminato complexes.

Recently, a series of NNO-tridentate Schiff-base zinc alkoxides in which R = H was synthesized (Chart 1).[8a] Experimental results indicate that these complexes are excellent initiators toward the controlled polymerization of L−LA, and their activities are dramatically affected by the substituent on the phenyl ring of the NNO-tridentate Schiff-base ligands. Unfortunately, no magnesium complexes of this type have been isolated. Most recently, the effect of the substituents on the imine carbon was investigated by changing the substituents on the imine carbon from H to Me or Ph (Chart 2).[8b] However, these complexes revealed no difference in the electronic effect of the substituents because of their high activities. As a result, we describe herein the preparation and catalytic studies of magnesium alkoxides coordinated on a NNO-tridentate Schiff-base. The electronic effect of the substituent on the tridentate ligand will also be discussed.

Results and Discussion

Synthesis and Spectroscopic Studies. The magnesium benzyl alkoxy complex, [$L^1Mg(\mu$-OBn)]$_2$ (**1**), was prepared by the reaction of Mg(OBn)$_2$ with one molar equivalent of 2-[1-(2-dimethylaminoethylimino)ethyl]phenol (L^1H) in toluene at room temperature, as shown in Scheme 1. Similarly, complexes [LMg(μ-OBn)]$_2$ (**2**−**8**) were prepared in an analogous manner to that of **1**. The NNO-tridentate Schiff-base ligand (L−H) is able to provide strong coordination between the amino group and the Mg atom and therefore stabilizes the magnesium alkoxide, [LMg(μ-OBn)]$_2$ (**1**−**8**), without further ligand exchange, which has been observed in many other magnesium complexes. Complexes **1**−**8** were evaluated on the basis of ^{1}H and ^{13}C NMR, as well as elemental analysis. The ^{1}H spectrum of compound **1** shows the resonance peaks for N(CH_3)$_2$ and CH_3C=N methyls overlapped as one broad band at 2.18 ppm as compared to 2.36 ppm in the free ligand. Two sets of triplet resonances for the methylenes (C=NCH_2 and C=NCH$_2$$CH_2$) of the ligand shift upfield to 3.06 ppm ($\Delta\delta$ = 0.63 ppm) and 2.36 ppm ($\Delta\delta$ = 0.39 ppm), respectively, as compared to 3.69 and 2.75 ppm for the free ligand, indicating that the nitrogen atoms of the ligand took part in the coordination to the magnesium ions. In addition, the methylene hydrogens of the bridging benzyl alkoxides were observed to be magnetically nonequivalent with the ^{1}H chemical shifts at 4.70 and 4.58 ppm, and the $^2J_{HH}$ value of 12.0 Hz. All of these data are in agreement with the results of the following structural analyses. The molecular structures and coordination modes of **2**, **3**, **7**, and **8** were further verified by the X-ray single-crystal diffraction studies.

Scheme 1. Preparation of NNO-Tridentate Schiff-Base Magnesium Alkoxides



L^1H: R^1=CH$_3$, R^2=H, R^3=H
L^2H: R^1=CH$_3$, R^2=Cl, R^3=H
L^3H: R^1=CH$_3$, R^2=Br, R^3=H
L^4H: R^1=CH$_3$, R^2=OMe, R^3=H
L^5H: R^1=CH$_3$, R^2=H, R^3=OMe
L^6H: R^1=Ph, R^2=H, R^3=H
L^7H: R^1=Ph, R^2=Cl, R^3=H
L^8H: R^1=Ph, R^2=H, R^3=OMe

1: R^1=CH$_3$, R^2=H, R^3=H
2: R^1=CH$_3$, R^2=Cl, R^3=H
3: R^1=CH$_3$, R^2=Br, R^3=H
4: R^1=CH$_3$, R^2=OMe, R^3=H
5: R^1=CH$_3$, R^2=H, R^3=OMe
6: R^1=Ph, R^2=H, R^3=H
7: R^1=Ph, R^2=Cl, R^3=H
8: R^1=Ph, R^2=H, R^3=OMe

Molecular Structure Studies. Suitable crystals for the X-ray structure determination of **2**, **3**, **7**, and **8** were obtained from a layered dichloromethane−hexane solution. The molecular structure of **2** is depicted in Figure 1, and the selected bond distances and angles for **2**, **3**, **7**, and **8** are compared in Table 1. Complex **2** was a dimeric form with a Mg/O(2)/Mg(A)/O(2A) planar core bridged by the oxygen

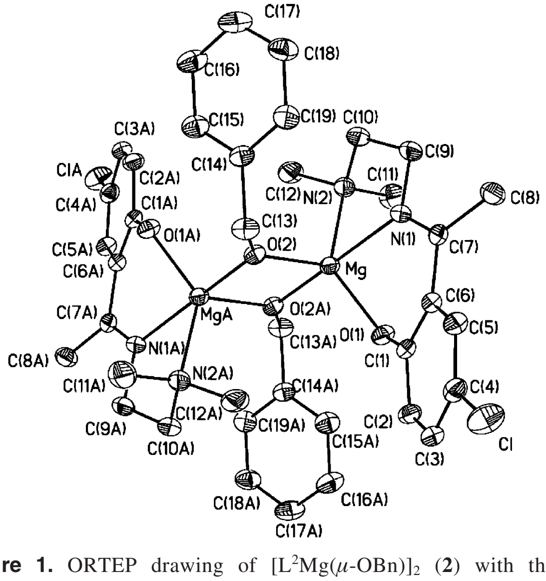


Figure 1. ORTEP drawing of [$L^2Mg(\mu$-OBn)]$_2$ (**2**) with thermal ellipsoids drawn at the 20% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Comparison of the Selected Bond Distances (Å) and Bond Angles of **2**, **3**, **7**, and **8**

	2	**3**	**7**	**8**
Mg−O(1)	1.943(2)	1.943(2)	1.9271(17)	1.9377(14)
Mg−O(2)	1.949(2)	1.946(3)	1.9489(17)	1.9581(14)
Mg−O(2A)	1.989(2)	1.981(3)	2.0116(16)	2.0112(13)
Mg−N(1)	2.188(3)	2.177(4)	2.195(2)	2.1760(16)
Mg−N(2)	2.223(2)	2.213(3)	2.230(2)	2.2362(19)
Mg···MgA	2.957(2)	2.946(3)	2.9702(14)	2.9586(11)
O(1)−Mg−O(2)	117.47(9)	118.35(12)	118.24(8)	115.28(6)
O(1)−Mg−O(2A)	98.59(8)	98.27(13)	96.37(7)	96.38(6)
O(2)−Mg−O(2A)	82.69(8)	82.80(13)	82.84(7)	83.63(5)
O(1)−Mg−N(1)	82.89(9)	82.79(14)	83.75(7)	84.55(6)
O(2)−Mg−N(1)	102.35(9)	101.85(14)	110.20(7)	107.99(6)
O(2A)−Mg−N(1)	173.45(10)	174.11(13)	165.22(8)	166.76(6)
O(1)−Mg−N(2)	130.99(10)	131.06(15)	135.81(8)	137.13(7)
O(2)−Mg−N(2)	110.55(9)	109.53(13)	105.53(8)	107.00(7)
O(2A)−Mg−N(2)	96.45(9)	97.03(13)	94.63(8)	94.94(6)
N(1)−Mg−N(2)	77.92(9)	78.07(13)	75.53(8)	75.84(6)

atoms of benzyl alkoxide groups in the solid state, and the planar core features two similar Mg−O distances of 1.949(2) and 1.989(2) Å. The geometry around the magnesium atoms was penta-coordinated, adopting a distorted trigonal-bipyramid with the imine nitrogen, N(1), and one of bridging oxygen atom, O(2A), sitting on the axial positions and the O(1), O(2), and N(2) atoms on the equatorial positions. The Mg atom was ca. 0.1156 Å above the O(1)/O(2)/N(2) mean plane with a compressed axial O(2A)−Mg−N(1) bond angle of 173.45(10)° and equatorial O(1)−Mg−O(2), O(1)−Mg−N(2), and O(2)−Mg−N(2) bond angles of 117.47(9), 130.99(10), and 110.55(9)°, respectively. The bond distances of Mg−O(1), Mg−N(1), and Mg−N(2) were 1.943(2), 2.188(3), and 2.223(2) Å, respectively. These bond distances are similar to those found in monoether salen-like Mg(II) complexes.[7b] The molecular structure of complex **3** is shown in Figure S1 (Supporting Information).

The X-ray single-crystal structure of **7** also reveals a dimeric character with a Mg_2O_2 coplanar core, and the penta-coordinated magnesium center was bridged by the oxygen atom of the benzyl alkoxide group, as illustrated in Figure 2. However, the geometry of Mg was intermediate between square-pyramidal and trigonal-bipyramidal ($\tau = 0.49$). Therefore, the coordination geometry was heavily distorted from that of a regular trigonal bipyramid. The axial O(2A)−Mg−N(1) bond angle was compressed from 180 to 165.22(8)°, and the corresponding equatorial bond angles ranged from 105.53(8) to 135.81(8)°. The N(1), N(2), and O(1) atoms of the ligand were chelated to the Mg center, forming a six-membered ring and a five-membered ring. In the five-membered ring, the O(1)−Mg−N(1) bite angle was 83.75(7)°, and the bond distances of Mg−O(1) and Mg−N(1) were 1.9271(17) and 2.195(2) Å, respectively. In the six-membered ring, the N(1)−Mg−N(2) bite angle was 75.53(8)°, and the Mg−N(2) bond distance was 2.230(2) Å. The molecular structure of complex **8** is shown in Figure S2 (Supporting Information).

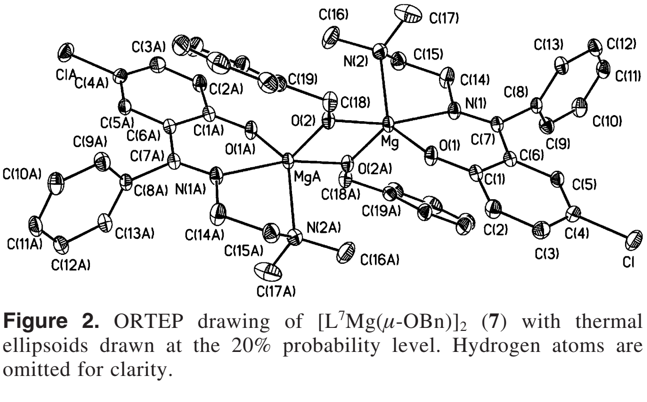


Figure 2. ORTEP drawing of $[L^7Mg(\mu\text{-OBn})]_2$ (**7**) with thermal ellipsoids drawn at the 20% probability level. Hydrogen atoms are omitted for clarity.

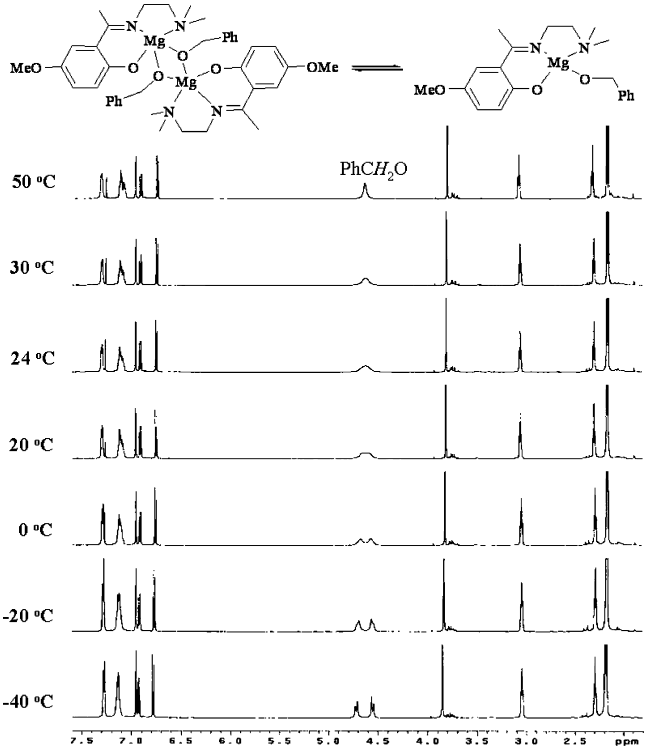
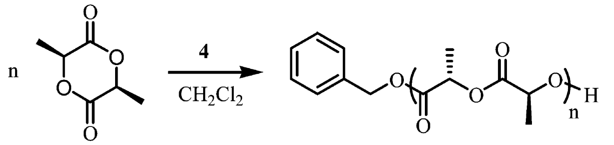


Figure 3. ^1H spectrum of $[L^4Mg(\mu\text{-OBn})]_2$ (**4**) in $CDCl_3$ with variable temperature.

^1H NMR Variable-Temperature Studies. The ^1H spectrum of compound **4** (Figure 3) in $CDCl_3$ at 20 °C shows one set of resonance peaks. When the temperature decreases from +20 to −40 °C, the corresponding broad signal for $PhCH_2O$ at 4.6 ppm split into two broad peaks and finally appeared as a doublet of doublets at −40 °C. The result reveals that these two $PhCH_2O$ protons are in nonequilibrium at low temperatures. While the temperature increases slowly from −40 to +50 °C, the corresponding doublet of doublets for $PhCH_2O$ becomes broadened and appears as a sharp singlet at high temperatures, indicating a rapid equilibrium between the dimeric and monomeric species. The coalescence temperature is observed at ca. 24 °C. Furthermore, variable-temperature ^1H studies of compound **7** were also performed, which showed a similar result as that observed for **4** (see Figure S3, Supporting Information).

Ring-Opening Polymerization of L-Lactide. As shown in Table 2, polymerization of L-lactide using **4** (5.0 mM) as an initiator in CH_2Cl_2 at 0 °C was studied. Experimental results indicated that **4** was an efficient initiator for the polymerization of L-lactide. The polymerization can reach completion within 3.5 h at 0 °C when the monomer-to-initiator ratio ($[M]_0/[I]_0$) ranged from 50 to 200. The high polymerization control and the "living" character were demonstrated by the linear relationship between Mn and

Table 2. Polymerization of L-Lactide Initiated by **4** (5.0 mM) in CH_2Cl_2 (10.0 mL) at 0 °C for 3.5 h



entry	$[LA]_0$/[**4**]	conv (%)^a	Mn (calcd)^b	Mn (NMR)^a	Mn (obsd)^c	PDI
1	50	98	3600	3100	5300 (3100)	1.10
2	100	92	6700	6700	12100 (7000)	1.06
3	150	83	9100	9200	18200 (10600)	1.06
4	200	83	12100	12100	23600 (13700)	1.07

^{a} Obtained from ^{1}H analysis. ^{b} Calculated from the MW(LA) × $[LA]_0$/2[**4**] × conversion yield + MW(BnOH). ^{c} Obtained from GPC analysis and calibrated by polystyrene standard. Values in parentheses are the values obtained from GPC times 0.58.[9,10]

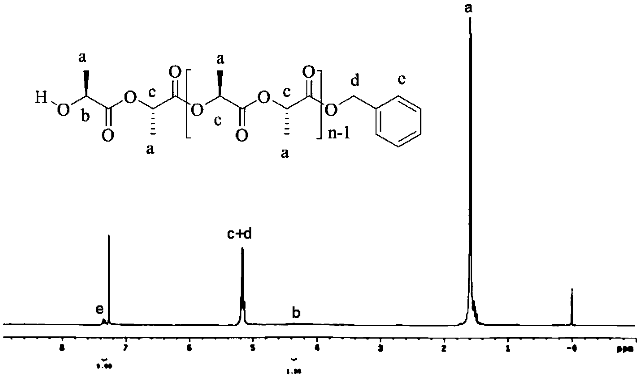


Figure 4. ^{1}H spectrum of PLLA-50 (50 indicates $[LA]_0$/[**4**] = 50).

$[M]_0/[I]_0$ as well as the low polydispersity index (PDI) for the polymers, ranging from 1.06 to 1.10.

To understand the initiating process, ^{1}H studies on the PLLA initiated by **4** were carried out as shown in Figure 4. The ^{1}H spectrum of PLLA prepared using a $[LA]_0$/[**4**] ratio of 50:1 indicated that the polymer chain was capped with a benzyl ester on one end and a hydroxyl group on the other end, with the integration ratio close to 5:1 between H_e and H_b. The observed result implied that the initiation occurred through the insertion of a benzyl alkoxy group from compound **4** to L-LA followed by the breaking of the C−O bond of L-LA, yielding a new magnesium alkoxide as an intermediate, which further reacted with excess L-LA to yield polyesters.

Table 3. Polymerization of L-Lactide (250 mM) Using **1**−**8** (5.0 mM) as an Initiator in CH_2Cl_2 (10 mL) at 0 °C for 3.5 h

entry	initiator	conv (%)^a	Mn (calcd)^b	Mn (obs)^c	PDI^c
1	**1**	65	2450	3750 (2200)	1.12
2	**2**	26	1040	1880 (1090)	1.08
3	**3**	24	970	1840 (1070)	1.09
4	**4**	98	3600	5300 (3100)	1.10
5	**5**	58	2120	3086 (1790)	1.05
6	**6**	38	1470	2520 (1460)	1.09
7	**7**	20	830	*d*	*d*
8	**8**	31	1220	2040 (1180)	1.07

^{a} Obtained from ^{1}H analysis. ^{b} Calculated from the MW(LA) × $[LA]_0$/2[Initiator] × conversion yield + MW(BnOH). ^{c} Obtained from GPC analysis and calibrated by polystyrene standard. Values in parentheses are the values obtained from GPC times 0.58.[9,10] ^{d} Not available.

Recently, conflicting effects of electron-donating and -withdrawing substituents affecting the activity of metal complexes on cyclic ester polymerization rates were discussed. For instance, Tolman and co-workers had reported amine bisphenolate aluminum catalysts in which the electronic influence of the ligand substitutents on the rate polymerization of ε-caprolactone was observed. The polymerization was found to occur at different rates when the para substitutents to the phenoxide donor oxygen were varied. Decreasing the electron density around the metal was found to decrease the propagation rate for ring-opening polymerization.[11a] In addition, the electron-withdrawing substitutents on the salen ligands have a damaging effect upon polymerization activities of titanium−salen complexes, whereas the use of electron-donating alkoxy-functionalized ligands increased the polymerization activity to the highest order for a titanium initiator.[11b] However, an increase in catalytic activity was observed for the introduction of the electron-withdrawing substituents at the para positions of the aryl groups of the ligand in the case of β-diketiminate aluminum complexes.[12a] It was also observed that, with increasing electrophilicity of the metal center, the rate of polymerization increased[12b] in tetradentate aminophnoxide aluminum complexes. The kinetics of the ROP of L-lactide were studied using organotin(IV) alkoxides by varying the substitutents on the ligands from electron-withdrawing to -donating groups.[12c] Experimental results indicated that ligands with electron-withdrawing groups somewhat lower the activation energy.

To realize the electronic effect of the substituents on the Schiff-base ligand affecting the activity of magnesium complexes, the activities of complexes **1**−**8** toward ROP of L-lactide were also examined (Table 3). Experimental results showed that all of these complexes initiate the polymerization of L-lactide, and the resulting molecular weight of PLLA was well controlled with narrow polydispersity. On the basis of the experimental data, we concluded that the reactivity varies with different functional groups on the ligand, and reactivity in the order of **4** > **1** > **2** ∼ **3** revealed that, by replacing the *para*-hydrogen on the phenoxy group (**1**) with an electron-donating group such as the methoxy group (**4**), the reactivity increased dramatically (entries 1 and 4). On the other hand, the reactivity decreased substantially with the substitution of an electron-withdrawing group such as Br or Cl (entries 2 and 3). A reasonable explanation for this is that the NNO ligand with an electron-withdrawing group causes the magnesium atom to be more acidic, resulting in a stronger Mg−OR bond, and therefore the insertion reaction from the Mg−OR to L-LA was retarded. It is interesting to note that this remarkable variation in reaction activity was

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also observed by changing R^1 from the methyl to the phenyl group (entries 1 and 6, 2 and 7, and 5 and 8). The reason for the difference was probably due to the resonance ability of the phenyl group decreasing the electron density of the NNO ligand.

The results regarding the electronic effect of Schiff-base magnesium complexes are similar to those of our previous report that investigated the activities of zinc complexes coordinated by NNO-tridentate Schiff-base ligands, in which R = H. In this case, the reactivities toward the controlled polymerization of L-lactide increased with the electron-donor ability of the substituents on the phenyl ring of the NNO-tridentate Schiff-base ligands (Chart 1).[8a] However, replacing the substituents on the imine with H to Me to Ph (chart *2*) reveled no remarkable difference due to their high activities. The conversion can reach from 87 to 100% within 4 min at 0 °C for compounds IIa−d and IIIa,b. It is interesting to note that the Schiff-base zinc complexes are significantly more active than the magnesium complexes in the ring-opening polymerization of L-lactide, and the result is rather rare. A similar result has been found in the NNO−aminophenolato system reported by Tolman and co-workers, in which zinc complexes are significantly more active in the ring-opening polymerization of L-lactide than their analogous magnesium derivatives.[6b] Furthermore, though the crystallographic data of **2**, **3**, **7**, and **8** show that these complexes were dimeric in the solid state, the monomeric intermediate seemed to be the active species during polymerization on the basis of the variable-temperature ^{1}H studies and the polymerization results.

Conclusions

A series of NNO-tridentate Schiff-base magnesium alkoxides is synthesized. The magnesium complexes are crystallized as penta-coordinated dimers bridging through the oxygen atoms of the bezyl alkoxides. All of these magnesium alkoxides have shown good activities toward the controlled polymerization of L-LA, and the reactivity increases upon adding the electron-donating group to the Schiff-base ligands and decreases upon putting the electron-withdrawing group on the Schiff-base ligands.

Experimental Section

General Procedures. All manipulations were carried out under a dry nitrogen atmosphere. Solvents were dried by refluxing for at least 24 h over sodium/benzophenone (hexane, toluene, and THF), phosphorus pentoxide (CH_2Cl_2), calcium hydride (benzaldehyde), or anhydrous magnesium sulfate (benzyl alcohol). L-Lactide was purchased from the Bio Invigor Corporation and recrystallized from a toluene solution prior to use. Deuterated solvents (Aldrich) were dried over molecular sieves. Others regents were purchased from Aldrich or Acros and used without further purification. Ligands (L^1H-L^4H, L^6H, and L^7H) were prepared by the condensation reaction following literature procedures.[8b] ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity Inova-600 (600 MHz for ^{1}H and 150 MHz for ^{13}C) or a Varian Mercury-400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) spectrometer, with chemical shifts given in parts per million (ppm) from the internal TMS. Microanalyses were performed using an Elementar vario EL III CHN-OS Rapid instrument. The IR spectra in the region of 4000−400 cm^{-1} were recorded as KBr plates on a Bruker EQUINOX55 spectrometer. The GPC measurements were performed on a Hitachi L-7100 system equipped with a differential Bischoff 8120 using THF (HPLC grade) as an eluent. The molecular weight and polydispersity of PLA were calculated using polystyrene as a standard reference.

Synthesis of 2-{1-[2-(Dimethylamino)ethylimino]ethyl}-5-methoxyphenol (L^5H). Ligand L^5H was synthesized by the reaction of 2-dimethylaminoethylamine (1.06 g, 12.0 mmol) and 2-hydroxy-4-methoxyacetophenone (1.66 g, 10.0 mmol) in refluxing ethanol (20.0 mL) for 24 h. Volatile materials were removed under a vacuum, and the resulting material was dissolved in hot hexane (30.0 mL). The hexane solution was then cooled at −20 °C to give a yellow powder. Yield: 2.01 g (85.0%). ^{1}H ($CDCl_3$, 400 MHz): δ 7.34 (1H, d, J = 9.2 Hz, ArH), 6.32 (1H, d, J = 2.8 Hz, ArH), 6.22 (1H, dd, J = 9.2, 2.8 Hz, ArH), 3.84 (3H, s, OCH_3), 3.63 (2H, t, J = 13.6 Hz, C=NCH_2), 2.68 (2H, t, J = 13.6 Hz, C=NCH_2CH_2), 2.34 (3H, s, CH_3C=N), 2.33 (6H, s, N$(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.51 (C=N), 171.02, 164.12, 129.33, 111.60, 105.08, 102.39 (*Ar*), 58.90 (OCH_3), 54.96 (C=NCH_2), 45.55 (C=NCH_2CH_2), 45.41 (N$(CH_3)_2$), 14.02 (CH_3C=N). (EI, *m*/*e*): 236 (M^+, 4.78%). Elem anal. calcd for $C_{13}H_{20}N_2O_2$: C, 66.07; H, 8.53; N, 11.85%. Found: C, 66.45; H, 7.92; N, 11.81%. IR (KBr, cm^{-1}): 1613 ($\nu_{C=N}$).

Synthesis of 2-{[2-(Dimethylamino)ethylimino](phenyl)methyl}-5-methoxyphenol (L^8H). Ligand L^8H was prepared by a method similar to that of L^5H using 2-dimethylaminoethylamine (1.06 g, 12.0 mmol) and 2-hydroxy-4-methoxybenzophenone (2.28 g, 10.0 mmol). Yield: 2.39 g (80.0%). ^{1}H ($CDCl_3$, 400 MHz): δ 7.52−7.48 (3H, m, ArH), 7.25−7.22 (2H, m, ArH), 6.63 (1H, d, J = 8.8 Hz, ArH), 6.39 (1H, d, J = 2.4 Hz, ArH), 6.10 (1H, dd, J = 8.8, 2.4 Hz, ArH), 3.78 (3H, s, OCH_3), 3.36 (2H, t, J = 13.6 Hz, C=NCH_2), 2.57 (2H, t, J = 13.6 Hz, C=NCH_2CH_2), 2.20 (6H, s, N$(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.51 (C=N), 170.71, 164.21 133.04, 132.75, 129.18, 128.63, 127.41 112.41 105.50, 101.97 (Ar), 59.50 (OCH_3), 55.13 (C=NCH_2), 47.37 (C=NCH_2CH_2), 45.53 (N$(CH_3)_2$). (EI, *m*/*e*): 298 (M^+, 3.44%). Elem. anal. calcd for $C_{18}H_{22}N_2O_2$: C, 72.46; H, 7.43; N, 9.39%. Found: C, 72.76; H, 7.17; N, 9.28%. IR (KBr, cm^{-1}): 1605 ($\nu_{C=N}$).

Synthesis of $[L^1Mg(\mu\text{-OBn})]_2$ (1). $Mg(^nBu)_2$ (2.05 mL, 1.0 M in hexane, 2.05 mmol) was added to a solution of benzyl alcohol (0.42 mL, 4.0 mmol) in 10.0 mL of toluene, and the mixture was stirred at room temperature for 5.0 h and then dried in a vacuum. A solution of L^1H (0.41 g, 2.0 mmol) in toluene (15.0 mL) was added and stirred for 3 h, during which the formation of a yellow precipitate was observed. The resulting precipitate was collected by filtration and dried under a vacuum to give yellow powder (**1**). Yield: 0.41 g (61.0%). ^{1}H ($CDCl_3$, 400 MHz): δ 7.45 (1H, dd, J = 8.0, 1.6 Hz, ArH), 7.30 (2H, d, J = 6.0 Hz, ArH), 7.20 (1H, td, J = 8.0, 1.6 Hz, ArH), 7.12−7.07 (3H, m, ArH), 6.79 (1H, dd, J = 6.0, 1.2 Hz, ArH), 6.53 (1H, td, J = 8.0, 1.2 Hz, ArH), 4.70 (1H, d, J = 12.0 Hz, OCH_2Ph), 4.58 (1H, d, J = 12.0 Hz, OCH_2Ph), 3.06 (2H, t, J = 6.0 Hz, C=NCH_2), 2.36 (2H, t, J = 6.0 Hz, C=NCH_2CH_2), 2.18 (9H, s, N$(CH_3)_2$, CH_3C=N). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.88 (C=N), 168.88, 168.78, 131.95, 129.80, 127.73, 127.55, 125.89, 124.75, 123.82, 112.12 (*Ar*), 66.58 (OCH_2Ph), 57.55 (C=NCH_2), 46.67 (C=NCH_2CH_2), 44.88 (N$(CH_3)_2$), 18.55 (CH_3C=N). Elem anal. calcd for $C_{38}H_{48}N_4O_4Mg_2$: C, 67.77; H, 7.18; N, 8.32%. Found: C, 68.00; H, 6.97; N, 8.40%. IR (KBr, cm^{-1}): 1599 ($\nu_{C=N}$).

Synthesis of $[L^2Mg(\mu\text{-OBn})]_2$ (2). An analogous method to that of **1** was utilized but where L^2H (0.48 g, 2.0 mmol) was used as a reagent. Yield: 0.47 g (63.0%). ^{1}H ($CDCl_3$, 400 MHz): δ 7.37 (1H, d, $J = 2.8$ Hz, ArH), 7.26 (2H, br, ArH), 7.13 (4H, br, ArH), 6.72 (1H, d, $J = 8.8$ Hz), 4.61 (2H, br,OCH_2Ph), 3.07 (2H, t, $J = 6.0$ Hz, C=NCH_2), 2.33 (2H, t, $J = 6.0$ Hz, C=NCH$_2$CH_2), 2.17 (6H, s, N(CH_3)$_2$), 2.14 (3H, s, CH_3C=N). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 173.31 (C=N), 167.60, 132.19, 129.29, 128.19, 127.74, 126.56, 125.52, 125.33, 116.48 (*Ar*), 66.82 (O*C*H$_2$Ph), 57.78 (C=N*C*H$_2$), 47.13 (C=NCH$_2$*C*H$_2$), 45.16 (N(*C*H$_3$)$_2$), 18.89 (*C*H$_3$C=N). Elem anal. calcd for $C_{38}H_{46}Cl_2N_4O_4Mg_2$: C, 61.48; H, 6.25; N, 7.55%. Found: C, 60.68; H, 6.89; N, 8.24%. IR (KBr, cm^{-1}): 1607 ($\nu_{C=N}$).

Synthesis of [L^{3}Mg(μ-OBn)]$_2$ (3). An analogous method to that of **1** was utilized but where L^{3}H (0.57 g, 2.0 mmol) was used as a reagent. Yield: 0.69 g (83.0%). ^{1}H (CDCl$_3$, 400 MHz): δ 7.49 (1H, d, $J = 2.4$ Hz, ArH), 7.24 (3H, br, ArH), 7.12 (3H br, ArH), 7.67 (1H, d, $J = 9.2$ Hz, ArH), 4.61 (2H, br, OCH_2Ph), 3.07 (2H, t, $J = 5.6$ Hz, C=NCH_2), 2.33 (2H, t, $J = 5.6$ Hz, C=NCH$_2$CH_2), 2.17 (6H, s, N(CH_3)$_2$, 2.14(3H, s, CH_3C=N). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 172.94 (C=N), 167.65, 134.61, 131.98, 127.81, 127.48, 126.11, 126.08, 125.57 103.06 (*Ar*), 66.66 (O*C*H$_2$Ph), 57.46 (C=N*C*H$_2$), 46.81 (C=NCH$_2$*C*H$_2$), 44.83 (N(*C*H$_3$)$_2$), 18.60 (*C*H$_3$C=N). Elem anal. calcd for $C_{38}H_{46}Br_2N_4O_4Mg_2$: C, 54.91; H, 5.58; N, 6.74%. Found: C, 55.39; H, 5.00; N, 6.46%. IR (KBr, cm^{-1}): 1609 ($\nu_{C=N}$).

Synthesis of [L^{4}Mg(μ-OBn)]$_2$ (4). An analogous method to that of **1** was utilized but where L^{4}H (0.47 g, 2.0 mmol) was used as a reagent. Yield: 0.42 g (54.0%). ^{1}H (CDCl$_3$, 400 MHz): δ 7.31−7.29 (2H, br, ArH), 7.13 (3H, br, ArH), 6.95 (2H, d, $J = 3.2$ Hz, ArH), 6.92−6.89 (1H, m, ArH), 6.74 (1H, d, $J = 9.2$ Hz, ArH), 4.63 (2H, br,OCH_2Ph), 3.81 (3H, s, OCH_3), 3.06 (2H, d, $J = 5.6$ Hz, C=NCH_2), 2.32 (2H, t, $J = 5.6$ Hz, C=NCH$_2$CH_2), 2.17 (6H, s, N(CH_3)$_2$), 2.16 (3H, s, CH_3C=N). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 173.36 (C=N), 163.71, 147.25, 127.66, 127.55, 125.83, 124.16, 123.52, 120.17, 113.71 (*Ar*), 66.57 (O*C*H$_2$Ph), 57.59 (O*C*H$_3$), 56.53 (C=N*C*H$_2$), 46.71 (C=NCH$_2$*C*H$_2$), 44.89 (N(*C*H$_3$)$_2$), 18.58 (*C*H$_3$C=N). Elem anal. calcd for $C_{40}H_{52}N_4O_6Mg_2$: C, 65.50; H, 7.15; N, 7.64%. Found: C, 65.36; H, 7.26; N, 7.30%. IR (KBr, cm^{-1}): 1591 ($\nu_{C=N}$).

Synthesis of [L^{5}Mg(μ-OBn)]$_2$ (5). An analogous method to that of **1** was utilized but where L^{5}H (0.47 g, 2.0 mmol) was used as a reagent, and after the reaction was completed, hexane (15.0 mL) was added. The resulting precipitate was collected with a filter and dried in a vacuum to give white powder (**5**). Yield: 0.53 g (69.0%). ^{1}H (CDCl$_3$, 400 MHz): δ 7.36 (1H, d, $J = 9.2$ Hz, ArH), 7.29 (1H, d, $J = 6.8$ Hz, ArH), 7.12−7.07 (3H, m, ArH), 6.28 (1H, d, $J =$ 2.4 Hz, ArH), 6.17 (1H, dd, $J = 8.8$, 2.4 Hz, ArH), 4.69 (1H, s, OCH_2Ph), 4.66 (1H, s, OCH_2Ph), 3.82 (3H, s, OCH_3), 3.06 (2H, d, $J = 6.0$ Hz, C=NCH_2), 2.34 (2H, t, $J = 6.0$ Hz, C=NCH$_2$CH_2), 2.19 (6H, s, N(CH_3)$_2$), 2.13 (3H, s, CH_3C=N). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 173.02 (C=N), 170.91, 163.04, 146.83, 131.05, 127.65, 127.49, 125.73, 118.81, 105.40, 101.37 (*Ar*), 66.62 (O*C*H$_2$Ph), 57.67 (O*C*H$_3$), 54.86 (C=N*C*H$_2$), 46.42 (C=NCH$_2$*C*H$_2$), 44.85 (N(*C*H$_3$)$_2$), 18.25 (*C*H$_3$C=N). Elem anal. calcd for $C_{40}H_{52}N_4O_6Mg_2$: C, 65.50; H, 7.15; N, 7.64%. Found: C, 64.91; H, 6.93; N, 7.46%. IR (KBr, cm^{-1}): 1603 ($\nu_{C=N}$).

Synthesis of [L^{6}Mg(μ-OBn)]$_2$ (6). An analogous method to that of **1** was utilized but where L^{6}H (0.54 g, 2.0 mmol) was used as a reagent. Yield: 0.58 g (73.0%). ^{1}H (CDCl$_3$, 400 MHz): δ 7.44 (2H, br, ArH), 7.39−7.35 (3H, m, ArH), 7.23−7.18 (1H, m, ArH), 7.15−7.09 (3H, m, ArH), 6.87−6.85 (3H, br, ArH), 6.32 (1H, d, $J = 8.0$ Hz, ArH), 6.63 (1H, t, $J = 7.2$ Hz, ArH), 4.93 (2H, br,OCH_2Ph), 2.91 (2H, t, $J = 6.0$ Hz, C=NCH_2), 2.30 (3H, br, C=NCH$_2$CH_2), 2.30 (6H, br, N(CH_3)$_2$). ^{13}C NMR (CDCl$_3$, 400 MHz): 176.49 (C=N), 170.26, 138.15, 133.98, 132.68, 128.42, 128.20, 128.12, 127.95, 127.14, 126.80, 126.02, 123.56, 123.36, 111.80 (*Ar*), 66.23 (O*C*H$_2$Ph), 58.91 (C=N*C*H$_2$), 48.65 (C=NCH$_2$*C*H$_2$), 45.23 (N(*C*H$_3$)$_2$). Elem anal. calcd for $C_{48}H_{52}N_4O_4Mg_2$: C, 72.28; H, 6.57; N, 7.02%. Found: C, 72.07; H, 6.26; N, 6.98%. IR (KBr, cm^{-1}): 1600 ($\nu_{C=N}$).

Table 4. Crystallographic Data for **2** and **7**

	2	**7**
empirical formula	$C_{38}H_{46}Cl_2Mg_2N_4O_4$	$C_{48}H_{50}Cl_2Mg_2N_4O_4$
fw	742.31	866.44
color	yellow	yellow
cryst syst	monoclinic	triclinic
space group	$C2/c$	$P\bar{1}$
a (Å)	21.998(7)	10.5248(18)
b (Å)	10.641(3)	11.0943(18)
c (Å)	17.614(5)	11.1946(19)
α (deg)	90	115.998(3)
β (deg)	108.855(6)	92.117(3)
γ (deg)	90	106.013(3)
Z	4	1
V (Å^3)	3902(2)	1110.3(3)
D_{calcd} (Mg/m^3)	1.264	1.296
F(000)	1568	456
θ range (deg)	2.15−26.02	2.05−26.00
abs coeff (mm^{-1})	0.242	0.223
no. of reflns collected	10497	6169
no. of indep reflns	3815	4308
[a]R1	0.0491	0.0477
[b]wR2	0.1044	0.1284
[c]GOF	1.005	1.001

[a] R1 = $|(|F_o| - |F_c|)/|F_o||$. [b] wR2 = $\{[w(F_o^2 - F_c^2)^2]/[w](F_o^2)^2\}^{1/2}$, $w =$ 0.046 for **2**, $w = 0.085$ for **7**. [c] GoF = $[w(F_o^2 - F_c^2)^2]/(N_{rflns} - N_{params})]^{1/2}$.

Synthesis of [L^{7}Mg(μ-OBn)]$_2$ (7). An analogous method to that of **1** was utilized but where L^{7}H (0.61 g, 2.0 mmol) was used as a reagent. Yield: 0.48 g (55.0%). ^{1}H (CDCl$_3$, 400 MHz): δ 7.41−7.37 (5H, m, ArH), 7.16−7.12 (4H, m, ArH), 6.83−6.78 (3H, m, ArH), 6.57 (1H, d, $J = 2.8$ Hz, ArH), 4.90 (2H, br,OCH_2Ph), 2.91 (2H, t, $J = 6.0$ Hz, C=NCH_2), 2.30 (8H, br, C=NCH$_2$CH_2, N(CH_3)$_2$). ^{13}C NMR (CDCl$_3$, 400 MHz): 175.67 (C=N), 168.75, 146.52, 137.25, 132.68, 132.55, 128.72, 128.61, 127.96, 127.07, 126.67, 126.00, 124.68, 124.11, 115.87 (*Ar*), 66.51 (O*C*H$_2$Ph), 58.86 (C=N*C*H$_2$), 48.80 (C=NCH$_2$*C*H$_2$), 45.23 (N(*C*H$_3$)$_2$). Elem anal. calcd for $C_{48}H_{50}Cl_2N_4O_4Mg_2$: C, 66.54; H, 5.82; N, 6.47%. Found: C, 65.86; H, 5.95; N, 6.44%. IR (KBr, cm^{-1}): 1599 ($\nu_{C=N}$).

Synthesis of [L^{8}Mg(μ-OBn)]$_2$ (8). An analogous method to that of **1** was utilized but where L^{8}H (0.60 g, 2.0 mmol) was used as a reagent. Yield: 0.67 g (78.0%). ^{1}H (CDCl$_3$, 400 MHz): δ ^{1}H (CDCl$_3$, 400 MHz): δ 7.44 (2H, d, $J = 8.0$ Hz, ArH), 7.38−7.34 (3H, m, ArH), 7.15−7.08 (3H, m, ArH), 6.83−6.81 (2H, m, ArH), 6.53 (1H, d, $J = 8.0$ Hz, ArH), 6.33 (1H, d, $J = 2.8$ Hz, ArH), 5.97 (1H, dd, $J = 8.8$, 2.8 Hz, ArH), 4.96 (2H, br, OCH_2Ph), 3.81 (3H, s OCH_3), 2.88 (2H, t, $J = 6.0$ Hz, C=NCH_2), 2.30 (8H, br, C=NCH$_2$CH_2, N(CH_3)$_2$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 175.72 (C=N), 172.29, 163.77, 146.97, 138.40, 135.23, 128.40, 127.98, 127.86, 127.14, 126.77, 125.67, 117.98, 104.91, 101.38 (*Ar*), 66.54 (O*C*H$_2$Ph), 59.04 (O*C*H$_3$), 54.91 (C=N*C*H$_2$), 48.37 (C=NCH$_2$*C*H$_2$), 45.23 (N(*C*H$_3$)$_2$). Elem anal. calcd for $C_{50}H_{56}N_4O_6Mg_2$: C, 70.02; H, 6.58; N, 6.53%. Found: C, 70.63; H, 6.72; N, 6.90%. IR (KBr, cm^{-1}): 1609 ($\nu_{C=N}$).

Typical Polymerization Procedures. A typical polymerization procedure was exemplified by the synthesis of entry 4 (Table 2) using compound **4** as an initiator at 0 °C. The conversion yield (83.0%) of PLLA was analyzed by ^{1}H spectroscopic studies. Compound **4** (0.037 g, 0.05 mmol) was added to a rapidly stirred solution of L-lactide (1.44 g, 10.0 mmol) in CH_2Cl_2 (10.0 mL). The reaction mixture was stirred at 0 °C for 3.5 h and then quenched by the addition of a methanol solution (2.0 mL); *n*-hexane (100.0 mL) was added to the above mixture to give a white solid. The white solid was dissolved in CH_2Cl_2 (10.0 mL), and then *n*-hexane (100.0 mL) was added to give a white crystalline solid. Yield: 0.92 g (64.0%).

X-Ray Crystallographic Studies. Suitable crystals of complexes **2**, **3**, **7** and **8** were sealed in thin-walled glass capillaries under a nitrogen atmosphere and were mounted on a Bruker AXS SMART 1000 diffractometer. Intensity data were collected in 1350 frames with increasing *w* (width of 0.3^o per frame). The absorption correction was based on the symmetry-equivalent reflections using the SADABS program.[13] 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.[14] 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. The crystallographic data of complexes **2** and **7** are summarized in Table 4.

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Supporting Information Available: The ORTEP drawings of compounds **3** and **8** and variable-temperature ^{1}H spectrum of compound **7**, further details of the crystal structure determination of compounds **2**, **3**, **7**, and **8** are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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