# Dalton Transactions

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# Different Mechanisms at Different Temperatures for the Ring-Opening Polymerization of Lactide Catalyzed by Binuclear Magnesium and Zinc Alkoxides

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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Two binuclear magnesium and zinc alkoxides supported by a bis-salalen type dinucleating heptadentate Schiff base ligand were synthesized and fully characterized. The two complexes are efficient initiators for the ring-opening polymerization (ROP) of L-lactide, affording polymers with narrow polydispersities and desirable molecular weights. Interestingly, the mechanisms for the ROP of lactide are different at different temperatures. At a high temperature of 130 °C, a coordination-insertion mechanism is reasonable for the bulk melt polymerization of lactide. At a low temperature, the alkoxide cannot initiate the ROP reaction; however, upon addition of external benzyl alcohol into the system, the ROP of lactide can smoothly proceed via an "activated monomer" mechanism. In addition, these complexes display slight stereo-selectivity for the ring-opening polymerization of rac-lactide, affording partially isotactic polylactide in toluene with a $P_m$ value of 0.59.

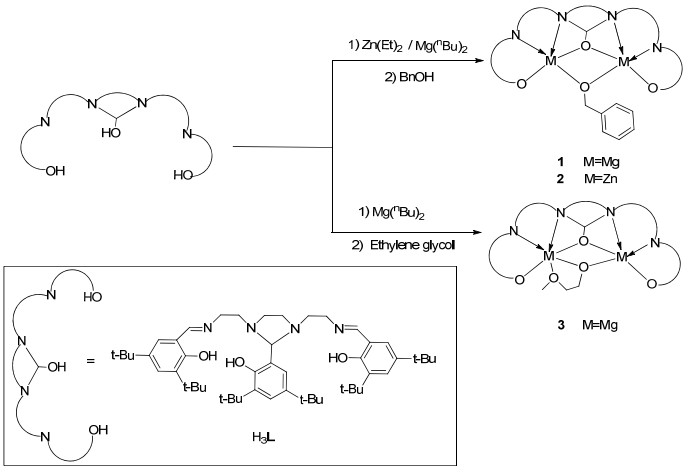
## Introduction

In the past several decades, aliphatic polyesters have drawn wide attention due to their biocompatibility, biodegradability, and permeability.[1] Among them, polylactide (PLA) is an important one which can be applied in wide fields such as packaging, fiber technology, and some important biomedical and pharmaceutical applications.[2] A promising method to prepare PLA is the ring-opening polymerization (ROP) of lactide for the prominent features of a controllable molecular weight and low polydispersity (PDI).[3] By far, a number of metal based catalysts, which consist of an appropriate organic ligand and a central electropositive metal atom such as alkali metals,[4] Mg,[5] Zn,[6] Al,[7] In,[8] Sn,[9] rare earth metals[10] and other metals,[11] were reported to initiate/catalyze the polymerization of lactide. Among them, zinc and magnesium initiators have been studied widely due to their high activities coupled with a superior molecular weight control.[5k, 6b, d] Zinc and magnesium complexes also can stereo-selectively initiate the ROP of rac-lactide,[5b, j, 5l-n, 6a, i, k] and even can show some iso-selectivity in the ROP of rac-lactide reaction in very recently published papers,[6i-k] for example chiral zinc complexes with a high iso-selectivity of $P_m$ = 0.91 and 0.84 were reported by the groups of Du and Ma respectively.[6j, k] In addition zinc and magnesium are nontoxic elements to the human body, zinc and magnesium complexes may be potential excellent initiators for the ROP of lactide considering the future industry application. Therefore, it is worth to explore some new zinc and magnesium initiators further for more insights into the ROP system catalyzed by zinc and magnesium complexes.

With an aim in mind to develop a highly efficient magnesium/zinc system, we reported here two new binuclear magnesium and zinc Shiff base alkoxides supported by a dinucleating heptadentate bis-salalen type ligand for the polymerization of *rac*-lactide. But against our intuition, these complexes are two very rare examples of inactive magnesium/zinc alkoxides at room temperature and even at 80 °C. And it is of interest, that these complexes can be activated for the ROP of lactide upon addition of benzyl alcohol (BnOH) at 80 °C or improving the temperature to 130 °C directly. In this system, two different mechanisms were proposed and verified for the ROP of lactide catalyzed by these magnesium/zinc complexes at different temperatures.

## Results and Discussion

### Synthesis and Characterization of Complexes 1-3




**Scheme 1**. Preparation of complexes **1-3**.

The ligand of 2-(3,5-di-tert-butyl-2-hydroxyphenyl)-1,3-bis[4-(3,5-di-tert-butyl-2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine ($H_3$**L**) was derived from the condensation of 3 equivalent of 3,5-ditertbutyl-salicylaldehyde with triethylenetetramine following a literature procedure.[12] The binuclear yellow complexes **1** and **2** were obtained by treatment of $H_3$**L** with 2.2 equivalent $^nBu_2Mg$ (for **1**) or $ZnEt_2$ (for **2**) and 1.1 equivalent BnOH in toluene solution in 65% and 64% yields, respectively (Scheme 1). Single crystals suitable for X-ray structural determinations of complexes **1** and **2** were obtained from slow cooling of a warm toluene solution. An ORTEP drawing of complex **1** (Figure 1), which crystallizes in the orthorhombic space group Pccn, shows that Mg1 is coordinated by N1, N2, O3, O1, and the oxygen atom O4 of benzyloxy, Mg2 similarly is coordinated by N3, N4, O3, O2, and O4. The pentacoordinated $N_3O_2$ environment around Mg1 forms a distorted square pyramidal geometry ($\tau = 0.41$), and the surrounding of Mg2 is a slightly distorted square pyramidal ($\tau = 0.07$). $\tau$ is a geometric parameter of a five-coordinated metal ion that distinguishes square pyramid (SP) from trigonal bipyramid (TBP) ( $\tau = 0$ for SP and $\tau = 1$ for TBP).[13] The Mg1-O4 bond distance of 1.9655(2) Å are comparable to the magnesium alkoxides bonds in other dimeric magnesium alkoxide complexes.[5d, e, k] Usually dimeric magnesium alkoxide complexes may dissociate in solution which indicates the alkoxide bridge may be broken;[5c, e, h] while in complex **1**, the bridge bonds between benzyloxy group and two magnesium ions may be more firm because an intramolecular bridge of O3, the oxygen of ligand, immobilizes the two magnesium atoms. The solid structure of complex **2** is similar to complex **1 (**Figure 2); the surroundings of Zn1 and Zn2 are distorted square pyramidal with $\tau$ values of 0.49 and 0.05 respectively. In order to mimic an intermediate in the ROP of lactide, complex **3** as a model complex was prepared by the similar procedure of complex **1** when replacing benzyl alcohol with 2-methoxyethanol.[14] In complex **3**, the oxygen atom (O5) of methoxy group can coordinate to magnesium center, which suggests one incoming lactide monomer can coordinate to one of the two magnesium centers in the ROP progress (Figure 3).

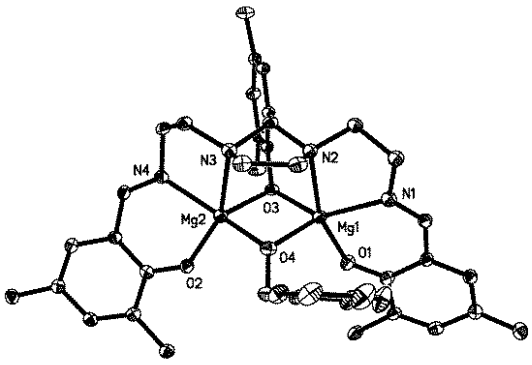



**Figure 1**. Molecular structure of **1** with ellipsoids given at the 30 % probability level (methyl carbon atoms of the tert-butyl groups and all of the hydrogen atoms are omitted for clarity). Selected bond lengths (Å): Mg2–O3 2.015 (2), Mg2–O2 1.938 (2), Mg2–O4 1.964 (2), Mg2–N4 2.121 (3), Mg2–N3 2.380 (3), Mg1–O3 2.011 (2), Mg1–O1 1.943 (2), Mg1–O4 1.962 (2), Mg1–N2 2.317 (3), Mg1–N1 2.135 (3).

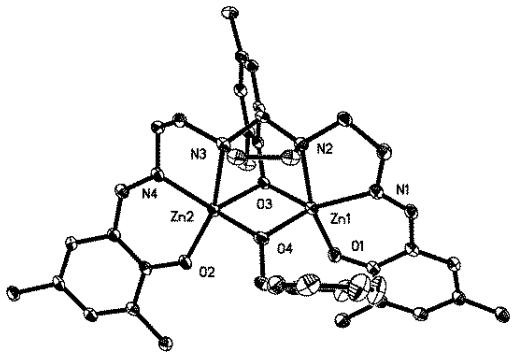



**Figure 2**. Molecular structure of **2** with ellipsoids given at the 30 % probability level (methyl carbon atoms of the tert-butyl groups and all of the hydrogen atoms are omitted for clarity). Selected bond lengths (Å): Zn1–N1 2.042 (3), Zn1–N2 2.305 (3), Zn1–O1 1.981(2), Zn1–O3 2.047 (2), Zn1–O4 1.981 (2), Zn2–N 32.452 (3), Zn2–N4 2.030 (3), Zn2–O2 1.971 (2), Zn2–O3 2.054 (2), Zn2–O4 1.970 (2).

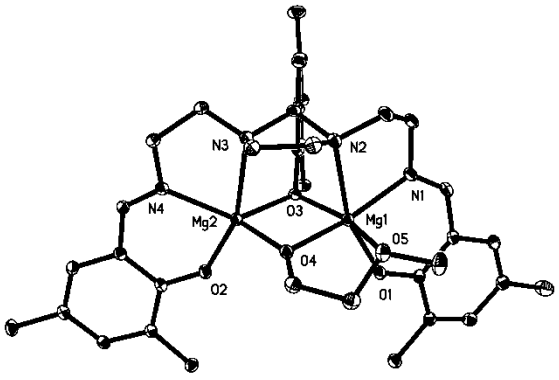



**Figure 3**. Molecular structure of **3** with ellipsoids given at the 30 % probability level (methyl carbon atoms of the tert-butyl groups and all of the hydrogen atoms are omitted for clarity). Selected bond lengths (Å): Mg1—O3 2.058 (2), Mg1—O5 2.222 (2), Mg1—N2 2.365 (2), Mg1—N1 2.136 (2), Mg2—O3 2.006 (2), Mg2—N3 2.426 (2), Mg2—N4 2.143 (2), Mg1—O4 2.007 (2), Mg2—O4 1.944 (2), Mg1—O1 1.967 (2), Mg2—O2 1.946 (2).

**Ring-Opening Polymerization (ROP) of Lactide**

The ROP of L-lactide (L-LA) catalyzed by metal complexes **1** and **2** was systematically examined in both the absence and the presence of benzyl alcohol (BnOH) as a co-initiator. Representative results under different conditions are depicted in Table 1. It was found that both complexes **1** and **2** cannot initiate the ROP of L-lactide in toluene even at 80 °C (Table1, entry 1 and entry 9), which was not expected to our initial design. After a careful analysis of the crystal structures of complexes **1** and **2**, we think the bridging benzyloxy may be deactivated due to the strong binding effect of two magnesium/zinc ions, because of which the strong binding alkoxide cannot transfer to attack the carbonyl of lactide in the ROP progress. Interestingly, upon addition of benzyl alcohol to the system, complex **1** becomes active for the ROP of L-lactide. About 90% conversion can be achieved within 12 h, when a 100:1:1 ratio of $[LA]_0/[Cat.]_0/[BnOH]_0$ was used (Table1, entry 4). The same reaction consumed 40 h in $CH_2Cl_2$ to reach a 93% yield at room temperature (Table1, entry 2), and only 31% lactide can be converted to polymer in THF at 40 °C (Table1, entry 3). Compared to complex **1**, the activity of complex **2** is observably lower because only 15% L-lactide can be converted to polymer in toluene at 80 °C (Table1, entry 10). The polymerization of L-lactide initiated by complex **1** is "living" which can be proved by the fact that the molecular weights of the polymers increased linearly with the ratio of $[LA]_0/[Cat.]_0/[BnOH]_0$ ranging from 20:1:1 to 400:1:6 (Table 1, entries 4-8, Figure S1). It is to note that the calculated molecular weights are based on the ratio of $[LA]_0/\{[BnOH]_0+[Cat.]_0\}$.

Increasing the temperature to 130 °C, both complexes **1** and **2** become active to initiate the ROP reaction without co-initiator of external BnOH in *o*-xylene solution (Table 2, entries 1, 9) or under melt condition (Table 2, entries 2-6, 4-10). The following experiments were performed in melt condition because complexes **1** and **2** can exhibit higher activities than in solution due to the super high monomer concentration in melt polymerization condition. It was interesting to find that zinc complex is more active than magnesium complex at high temperature, which is opposed to the low temperature experiments. We think it possibly results from the different mechanisms at different temperature which will be discussed in the following mechanism part. The polymerizations initiated by **1** and **2** at melt conditions are also controllable both in the absence and the presence of external BnOH because the relationship between molecular weights and $[LA]_0/\{[BnOH]_0+[Cat.]_0\}$ ratios are linear and PDI values are relatively low ranging from 1.12 to 1.48 (Table 2, entries 2-8, 10-15, Figures S2 and S3). Furthermore, epimerization of the chiral centres in PLA does not occur as observed by the homonuclear decoupled $^1$H NMR studies in the methine region.[15] Complex **1** can catalyze the ROP of 5000 equivalent L-lactide in the presence of 50 equivalent BnOH with controlled molecular weight and relatively narrow PDI (Table 2, entry 8). It is to note that the external BnOH just acts as a chain-transfer reagent here and the ROP reaction can also proceed without it; while at a low temperature the external BnOH, as a real initiator, is a prerequisite for ROP of lactide. The ROP of *rac*-lactide catalyzed by complex **1** gave polymers with limited tacticities including heterotacticity, isotacticity, and almost atacticity, on account of the different reaction solvents (Table 3, entry 1-4). According to the homonuclear decoupled $^1$H NMR spectrum at the methine region,[15] a virtually atactic polymer ($P_m$ = 0.51, Table 3, entry 2) was obtained at 25 °C in $CH_2Cl_2$ whereas partially isotactic ($P_m$ = 0.59, Table 3, entry 1, Figure S17) and heterotactic ($P_m$= 0.46, Table 3, entry 3, Figure S17) polylactides were achieved in toluene at 80 °C and in THF at 60 °C respectively. At melt condition (130 $^o$C), the weak iso-slectivity of $P_m$ = 0.54 can be achieved for complex **1** (Table 3, entry 4).

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**Table 1**. Ring-opening polymerization of L-LA with 1-2 in toluene at 80 °C.[a]

| Entry | Cat. | $[Cat.]_0/[L\text{-}LA]_0/[BnOH]_0$ | $t$ (h) | Conv.(%)[b] | $M_{n,obsd}$[c](g/mol) | $M_{n,calcd}$[d](g/mol) | PDI |
|---|---|---|---|---|---|---|---|
| 1 | **1** | 1/100/0 | 12 | 0 | [g] | [g] | [g] |
| 2[e] | **1** | 1/100/1 | 40 | 93 | 6600 | 6800 | 1.11 |
| 3[f] | **1** | 1/100/1 | 12 | 31 | 1900 | 2200 | 1.08 |
| 4 | **1** | 1/100/1 | 12 | 96 | 6900 | 7000 | 1.28 |
| 5 | **1** | 1/20/1 | 12 | 98 | 1600 | 1500 | 1.13 |
| 6 | **1** | 1/50/1 | 12 | 95 | 3500 | 3500 | 1.13 |
| 7 | **1** | 1/80/1 | 12 | 95 | 5300 | 5600 | 1.18 |
| 8 | **1** | 1/400/6 | 12 | 94 | 8100 | 7800 | 1.18 |
| 9 | **2** | 1/100/0 | 12 | 0 | [g] | [g] | [g] |
| 10 | **2** | 1/100/1 | 12 | 15 | [g] | [g] | [g] |

[a]Conditions: All manipulations were carried out under a dry nitrogen atmosphere, 0.01 mmol of catalyst, 5 mL toluene. [b]Determined by $^1$H NMR spectroscopy. [c]Experimental Mn and PDI determined by GPC in THF against polystyrene standards and corrected using the factor 0.58.[16] [d]Calculated from the molecular weight of L-LA × $[LA]_0/\{[BnOH]_0 + [Cat.]_0\}$ × conversion yield + $M_{BnOH}$. [e]In $CH_2Cl_2$ at 25 °C. [f]In THF at 60 °C. [g]Not determined.

**Table 2**. Ring-opening polymerization of L-LA with **1-2** in melt condition at 130 °C.[a]

| Entry | Cat. | $[Cat.]_0/[L\text{-}LA]_0/[BnOH]_0$ | *t* | Conv.(%)[b] | $M_{n,obsd}$[c] (g/mol) | $M_{n,calcd}$[d] (g/mol) | PDI |
|---|---|---|---|---|---|---|---|
| 1[e] | **1** | 1/100/0 | 1h | 19 | 2600 | 2800 | 1.19 |
| 2 | **1** | 1/20/0 | 1h | 96 | 2600 | 2900 | 1.18 |
| 3 | **1** | 1/50/0 | 1h | 93 | 6800 | 6800 | 1.16 |
| 4 | **1** | 1/100/0 | 1h | 96 | 13000 | 14000 | 1.37 |
| 5 | **1** | 1/150/0 | 1h | 90 | 19400 | 19600 | 1.20 |
| 6 | **1** | 1/200/0 | 1h | 87 | 21350 | 25200 | 1.32 |
| 7 | **1** | 1/400/5 | 2.5 h | 88 | 8600 | 8600 | 1.48 |
| 8 | **1** | 1/5000/50 | 14 h | 80 | 12000 | 11400 | 1.38 |
| 9[e] | **2** | 1/100/0 | 1 h | 66 | 8800 | 9600 | 1.16 |
| 10 | **2** | 1/50/0 | 30 min | 93 | 6600 | 6800 | 1.18 |
| 11 | **2** | 1/100/0 | 30 min | 90 | 14500 | 13100 | 1.28 |
| 12 | **2** | 1/150/0 | 30 min | 94 | 19900 | 20400 | 1.17 |
| 13 | **2** | 1/200/0 | 30 min | 86 | 24500 | 24900 | 1.15 |
| 14 | **2** | 1/400/0 | 1 h | 80 | 40100 | 46200 | 1.12 |
| 15 | **2** | 1/400/10 | 30 min | 92 | 4800 | 4900 | 1.15 |

[a] Conditions: All manipulations were carried out under a dry nitrogen atmosphere, 0.01 mmol of catalyst, 130°C. [b]Determined by $^1$H NMR spectroscopy. [c] Experimental $M_n$ and PDI determined by GPC in THF against polystyrene standards and corrected using the factor 0.58.[16] [d]Calculated from the molecular weight of L-LA × $[LA]_0/\{[BnOH]_0 + [Cat.]_0\}$ × conversion yield + $M_{BnOH}$. [e] In 5 mL *o*-xylene.

**Table 3**. *Rac*-Lactide Polymerization Catalyzed by **1**.[a]

| Entry | Cat. | $[Cat.]_0/[rac\text{-}LA]_0/[BnOH]_0$ | *t* | Conv.(%)[b] | $M_{n,obsd}$[c](g/mol) | $M_{n,calcd}$[d](g/mol) | PDI | $P_m$[e] |
|---|---|---|---|---|---|---|---|---|
| 1[f] | **1** | 1/100/1 | 12 h | 97 | 6900 | 7100 | 1.09 | 0.59 |
| 2[g] | **1** | 1/100/1 | 40 h | 93 | 6600 | 6800 | 1.11 | 0.51 |
| 3[h] | **1** | 1/100/1 | 26 h | 61 | 4400 | 4400 | 1.12 | 0.46 |
| 4[i] | **1** | 1/100/1 | 20 min | 97 | 7000 | 7100 | 1.39 | 0.54 |

[a] Conditions: All manipulations were carried out under a dry nitrogen atmosphere, 0.01 mmol of catalyst, 5 mL solvent (except entry 4). [b]Determined by $^1$H NMR spectroscopy. [c] Experimental Mn and PDI determined by GPC in THF against polystyrene standards and corrected using the factor 0.58.[16] [d] Calculated from the molecular weight of rac-LA × $[LA]_0/\{[BnOH]_0 + [Cat.]_0\}$ × conversion yield + $M_{BnOH}$. [e]Determined by analysis of all of the tetrad signals in the methine region of the homonuclear-decoupled $^1$H NMR spectrum.[15] [f]In toluene at 80 °C. [g]In $CH_2Cl_2$ at 25 °C. [h]In THF at 60 °C. [i] Bulk melt polymerization at 130 °C.

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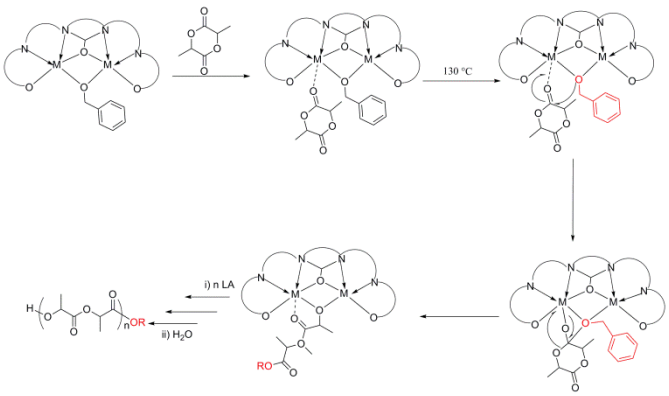
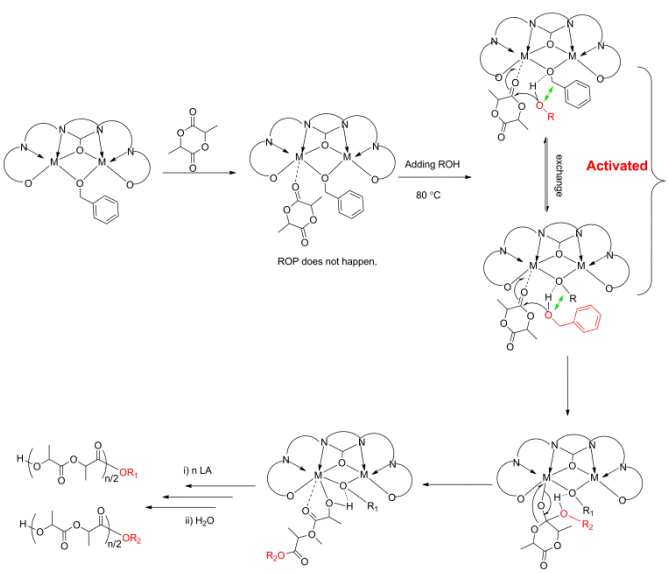



**Scheme 2**. A coordination-insertion mechanism proposed for the ring-opening polymerization of lactide catalyzed by complexes **1** and **2** at 130 °C. Note LA can coordinate to magnesium atom from a front site close to t-butyl group or a back site close to imine group, here only the mechanism from a front site was drawn for clarity.




**Scheme 3**. An activated monomer mechanism proposed for the ring-opening polymerization of lactide catalyzed by complexes **1** and **2** at a low temperature. Note the coordination of LA or the hydrogen-bonding interaction of BnOH to the bridge alkoxide can happen from a front site close to t-butyl group or a back site close to imine group, here only the mechanism from a front site was drawn for clarity.

### The ROP Mechanisms at Different Temperatures

In order to get more insight into the different performances of complexes **1** and **2** at different temperatures, the mechanisms at different temperatures were studied. Firstly, complex **1** is stable at 130 °C because after keeping complex **1** at 130 °C for one hour the $^1$HNMR spectrum does not change compared with the spectrum at room temperature (Figure S4). When mixing one equivalent L-lactide with complex **1** in $CDCl_3$, the imine hydrogens (N=CH) peak of complex **1** at 8.11 ppm split to two peaks at 7.82 ppm and 8.09 ppm (Figure S5), which indicates one monomer can coordinate to one magnesium center and one asymmetric intermediate complex formed. In complex **3**, a model complex of the intermediate species, the oxygen atom of methoxy group can coordinate to magnesium center, which also confirmed one of the two nuclear centers can be occupied by one incoming lactide monomer (Figure 3). As the above ROP experiments shown, the benzyloxy is deactivated by the binuclear construction; thus, complexes **1** and **2** cannot initiate the ROP of LA at a low temperature. Heating the reaction to 130 °C, the benzyloxy becomes active to initiate the ROP of lactide. The $^1$H NMR spectrum of final PLLA prepared using a $[LA]_0/[\mathbf{1}]$ ratio of 20 revealed the polymer chains were end-capped by one benzyl ester and a hydroxyl, suggesting that the initiation occurred through the insertion of the benzyloxy group from **1** into L-lactide (Table 2, entry 2, Figure S6). The ESI-MASS mass spectra of the final polymers confirmed it further by a series of peaks at 0.5 (72m + 108 + 19 + 18) with a charge of +2, which can be assigned to $m(C_3H_4O_2) + BnOH + H_3O^+ + NH_4^+$ (Figure S7). It is to be noted that there are another two series of peaks at 0.5 × (144m + 108 + 18 + 1) and 0.33 × (144m + 108 + 3 × 18) with a charge of +2 and + 3, which can be assigned to $m(C_3H_4O_2) + BnOH + NH_4^+ + H^+$ and $m(C_3H_4O_2) + BnOH + 3 \times NH_4^+$ (Figures S8), respectively. Thus the ROP mechanism at 130 °C is a normal coordination-insertion mechanism as most of metal alkoxide complexes (Scheme 2). Because the bridging interaction of alkoxide between two metal ions is strong, the nucleophilic attack of alkoxide to lactide is difficult and becomes a rate-limiting step in the ROP reaction. Comparatively the experimental results show the ROP reaction is slower for binuclear magnesium complex **1** than binuclear zinc complex **2**, because the transfer of alkoxide is more difficult in binuclear magnesium complex due to a stronger bridging effect than in zinc binuclear complex which can be deduced from the hard-soft acid-base (HSAB) principle. In another aspect, the mimic complex **3** suggests one carbonyl group at the alkoxy end of polymer chain can coordinate to magnesium atom for complex **1**. The chelating carbonyl group will compete with the approaching LA or alcohol molecule, while this chelate effect is weak or less likely for complex **2** with a soft zinc atom center. Thus, for this particular dinuclear system, the chelate effect also can suggest **1** may be a slower initiator than **2** at higher temperatures.

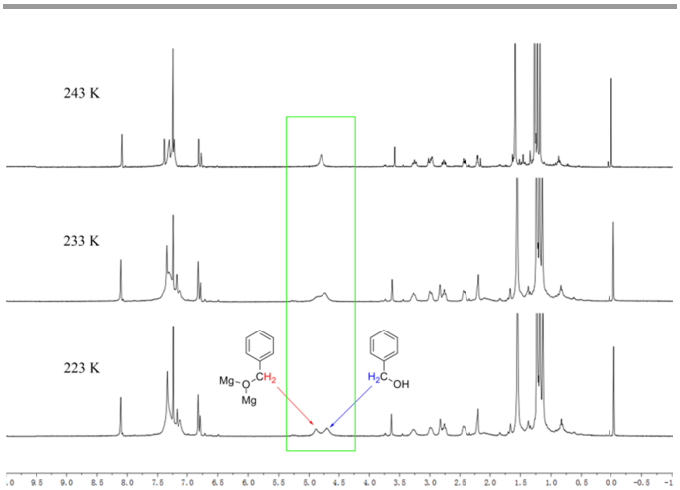



**Figure 4.** $^1$H NMR spectra taken at different temperatures of **1** ($T_c$= 233K, $\Delta G^{\neq}$ = 11.1 kcal mol$^{-1}$, $^1$H NMR (400 MHz)).

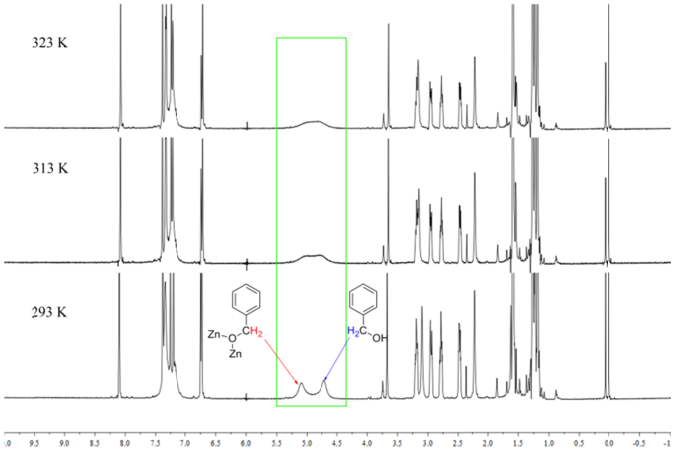



**Figure 5.** $^1$H NMR spectra taken at different temperatures of **2** ($T_c$ = 313K, $\Delta G^{\neq}$ = 14.44 kcal mol$^{-1}$, $^1$H NMR (600 MHz)).

At room temperature, complex **1** can change to be active upon addition of one equivalent benzyl alcohol into the system as a co-initiator (Table 1, entry 2). We think the mechanism at room temperature should be different to the coordination-insertion mechanism at 130 °C. In order to get more information about this mechanism at a low temperature, some NMR experiments were done. After mixing one equivalent benzyl alcohol with complex **1** in $CDCl_3$, the methylene signals of BnOH and benzyloxy in complex **1** combine to one peak at 4.81 ppm (Figure 4), which means benzyloxy in complex **1** can exchange with the free benzyl alcohol. Decreasing the temperature to -40 °C, this peak split to two peaks at 4.75 ppm and 4.95 ppm which can be assigned to free BnOH and benzyloxy in complex **1**. When mixing one equivalent benzyl alcohol with complex **2**, similar behavior can be found (Figure 5). Line shape analysis of the $^1$H NMR spectra of complexes **1** and **2** in $CDCl_3$ measured at variable temperatures revealed a coalesce temperature ($T_c$) and exchange reaction barriers $\Delta G^{\neq}$ of 11.1 kcal/mol (233K, $^1$H NMR (400 MHz)) and 14.44 kcal/mol (313 K, $^1$H NMR (600 MHz)) for **1** and **2** respectively (Figures 4 and 5). Thus the exchange of external benzyl alcohol with benzyloxy group in complex **1** or **2** may play a very key role for the ROP of lactide at a low temperature. In order to confirm the exchange of external benzyl alcohol with benzyloxy group again, 9-anthracenemethanol was added into the system to replace the free BnOH. It is found that both the 9-anthracenemethanol group and benzyloxy group can be found in the end of the final group (Figure S9) and the observed molecular weights of final polymers agreed with $[LA]_0/\{[BnOH]_0+[Cat.]_0\}$ (Tables 1-3). Therefore, we speculate the ROP mechanism at a low temperature changes to be an "activated monomer" mechanism: lactide is activated via the coordination to metal center, then the external benzyl alcohol, which can be activated via transferring a proton to the bridging benzyloxy group in complex **1** or **2**, attacks lactide to initiate the ROP reaction (Scheme 3). Such a mechanism has been previously proposed for a series of indium and gallium complexes reported by Carpentier, Williams, and co-workers.[17] At a low temperature, the magnesium complex **1** is more active than zinc complex **2**, and this trend is different to the one at a high temperature. Because the alcohol can be easily activated at a low temperature evidenced by the quick exchange reaction between alcohol and alkoxy group, the rate-limiting step of the ROP reaction changes to be the activation of monomer which agrees with the activated monomer mechanism.[17] Based on the HSAB principle, the lactide monomer can be activated more easily on magnesium ion than on zinc ion, so the magnesium complex **1** is more active at a low temperature in the presence of external alcohol. Anyway, the different activity trend of zinc complex and magnesium complex at different temperatures can reasonably be explained by the change of the ROP mechanism.

## Conclusion

In summary, two novel binuclear complexes **1** and **2** supported by a bis-salalen ligand have been synthesized and these complexes can catalyze the ROP of lactide under a controllable mode. It is interesting to found that the mechanisms of the ROP of lactide are different at different temperatures: a coordination-insertion mechanism is suitable at a melt condition (130 °C); while, at a low temperature the ROP proceeds via an activated monomer mechanism. The stereoselectivity of ROP of *rac*-LA also has been demonstrated to afford a slightly isotactic preference ($P_m$ = 0.59) in toluene and heterotactic preference ($P_m$ = 0.54) in THF.

## Experimental Section

### General Considerations

All manipulations were carried out under a dry nitrogen atmosphere. Solvents, lactide and benzyl alcohol were purified before using and stored in solvent reservoirs which contained 4Å molecular sieves and were purged with nitrogen. $^n$Bu$_2$Mg (1.0 M in hexane) and Zn(Et)$_2$ (1.0 M in hexane) were purchased from Aldrich and used as received. Commercial

chemicals were purchased and used without further purification. $^1$H NMR and $^{13}$C NMR spectra were recorded using spectrometers of the Varian Mercury Plus family with chemical shifts given in parts per million from the peak of internal TMS. Microanalyses were performed by using a Heraeus CHN-O-RAPID instrument. The GPC measurements were performed on a Hitachi L-700 system equipped with a differential Bischoff 8120 RI detector by using THF (HPLC grade) as an eluent running at 1 mL/min. Molecular weights and molecular weight distributions were calculated using polystyrene as standard.

**Synthesis of [L(Mg)$_2$BnO] (1)**

A solution of 2-(3,5-di-tert-butyl-2-hydroxyphenyl)-1,3-bis[4-(3,5-di-tert-butyl-2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine ($H_3$**L**) (0.79 g, 1.0 mmol) and $^n$Bu$_2$Mg (2.2 mL, 2.2 mmol, 1.0 M in hexane) was stirred in toluene (20 mL) at 0 °C under nitrogen atmosphere for 3 h, 1.1 mL BnOH (1.0 M in toluene, 1.1 mmol) was then slowly added to the solution. After stirring 4 h at room temperature, the light yellow solution was filtered through Celite. The filtrate was left overnight at room temperature, yellowish crystals were obtained. Yield：0.62 g (65%). $^1$H NMR (300 MHz, $CDCl_3$, 298 K, ppm): $\delta$ 8.10 (s, 2H, N=C*H*), 7.39 (d, 2H, *J* = 2.7 Hz, Ar*H*), 7.26-7.30 (m, 2H, OCH$_2$Ar*H*), 7.25 (d, 1H, *J* = 2.7 Hz, Ar*H*), 7.14-7.20 (m, 3H, OCH$_2$Ar*H*), 6.82 (d, 2H, *J* = 2.7 Hz, Ar*H*), 6.78 (d, 1H, *J* = 2.7 Hz, Ar*H*), 4.94 (s, 2H, OC*H*$_2$ArH), 3.60 (s, 1H, NC*H*N), 3.15-3.25 (m, 2H, NC*H*$_2$), 2.90-3.05 (m, 4H, NC*H*$_2$), 2.68-2.80 (m, 2H, NC*H*$_2$), 2.35-2.45 (m, 2H, NC*H*$_2$), 2.12-2.22 (m, 2H, NC*H*$_2$), 1.61 (s, 18H, C(C*H*$_3$)$_3$), 1.28 (s, 18H, C(C*H*$_3$)$_3$), 1.23 (s, 9H, C(C*H*$_3$)$_3$), 1.19 (s, 9H, C(C*H*$_3$)$_3$). $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K, ppm): $\delta$ 171.39, 168.81, 158.95, 141.41, 141.32, 139.31, 133.23, 129.00, 128.68, 128.39, 128.20, 128.12, 127.63, 126.98, 125.82, 125.73, 125.27, 122.06, 118.59, 93.99, 66.13, 55.73, 54.92, 51.03, 35.60, 35.13, 33.96, 33.71, 31.70, 31.53, 30.32, 30.13. Anal. Calcd for $C_{58}H_{82}Mg_2N_4O_4$: C 73.49, H 8.72, N 5.91. Found: C 73.40, H 8.67, N 5.88.

**Synthesis of [L(Zn)$_2$BnO] (2)**

A solution of $H_3$**L** (0.79 g, 1.0 mmol) and $ZnEt_2$ (2.2 mL, 2.2 mmol, 1.0 M in hexane) was stirred in toluene (20 mL) at 0 °C under nitrogen atmosphere for 3 h, 1.1 mL BnOH (1.0 M in toluene, 1.1 mmol) was then slowly added to the solution. After stirring 4 h at room temperature, the yellow solution was filtered through Celite. The filtrate was left overnight at room temperature, yellowish crystals were obtained. Yield：0.66 g (64%). $^1$H NMR (400 MHz, $CDCl_3$, 298 K, ppm): $\delta$ 8.10 (s, 2H, N=C*H*), 7.38 (d, 2H, *J* = 2.4 Hz, Ar*H*), 7.28-7.33 (m, 2H, OCH$_2$Ar*H*), 7.20 (d, 1H, *J* = 2.4 Hz, Ar*H*), 7.11-7.17 (m, 3H, OCH$_2$Ar*H*), 6.74 (d, 2H, *J* = 2.4 Hz, Ar*H*), 6.73 (d, 1H, *J* = 2.4 Hz, Ar*H*), 5.11 (s, 2H, OC*H*$_2$ArH), 3.66 (s, 1H, NC*H*N), 3.14-3.18 (m, 4H, NC*H*$_2$), 2.90-2.94 (m, 2H, NC*H*$_2$), 2.74-2.79 (m, 2H, NC*H*$_2$), 2.44-2.48 (m, 2H, NC*H*$_2$), 2.19-2.23 (m, 2H, NC*H*$_2$), 1.60 (s, 18H, C(C*H*$_3$)$_3$), 1.27 (s, 18H, C(C*H*$_3$)$_3$), 1.24 (s, 9H, C(C*H*$_3$)$_3$), 1.19 (s, 9H, C(C*H*$_3$)$_3$). $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K, ppm): $\delta$ 171.13, 170.81, 161.27, 141.41, 141.92, 141.72, 139.29, 137.77, 133.39, 128.97, 128.73, 128.36, 128.16, 127.25, 126.03, 125.24, 125.16, 122.16, 116.32, 93.42, 65.94, 55.67, 53.80, 50.98, 35.64, 35.20, 33.93, 33.64, 31.68, 31.40, 30.37, 29.95. Anal. Calcd for $C_{58}H_{82}Zn_2N_4O_4$: C 67.63, H 8.02, N 5.44. Found: C 67.52, H 7.91, N 5.33.

**Synthesis of [L(Mg)$_2$OCH$_2$CH$_2$OCH$_3$] (3)**

A solution of $H_3$**L** (0.79 g, 1.0 mmol) and $^n$Bu$_2$Mg (2.2 mL, 2.2 mmol, 1.0 M in hexane) was stirred in toluene (20 mL) at 0 °C under nitrogen atmosphere for 3 h, 1.1 mL 2-methoxyethanol (1.0 M in toluene, 1.1 mmol) was then slowly added to the solution. After stirring 4 h at room temperature, the yellow solution was filtered through Celite. The filtrate was left overnight at room temperature, yellowish crystals were obtained. Yield：0.58 g (63%). $^1$H NMR (300 MHz, $CDCl_3$, 298 K, ppm) $\delta$ 7.99 (s, 2H, N=C*H*), 7.31 (d, 2H, *J* = 2.4 Hz, Ar*H*), 7.18 (d, 1H, *J* = 2.4 Hz, Ar*H*), 6.82 (d, 1H, *J* = 2.4 Hz, Ar*H*), 6.74 (d, 2H, *J* = 2.4 Hz, Ar*H*), 4.01 (m, 2H, OC*H*$_2$CH$_2$O), 3.71 (s, 1H, NC*H*N), 3.66-3.68 (m, 2H, OCH$_2$C*H*$_2$OCH$_3$), 3.64-3.66 (m, 2H, NC*H*$_2$), 3.12-3.25 (m, 2H, NC*H*$_2$), 3.08 (s, 3H, CH$_2$OC*H*$_3$), 2.96-3.07 (m, 2H, NC*H*$_2$), 2.76-2.86 (m, 2H, NC*H*$_2$), 2.65-2.74 (m, 2H, NC*H*$_2$), 2.55-2.64 (m, 2H, NC*H*$_2$), 1.53 (s, 18H, C(C*H*$_3$)$_3$), 1.24 (s, 9H, C(C*H*$_3$)$_3$), 1.23 (s, 18H, C(C*H*$_3$)$_3$), 1.09 (s, 9H, C(C*H*$_3$)$_3$), $^{13}$C NMR (75 MHz, $CDCl_3$, 298 K, ppm) $\delta$ 170.57, 168.93, 160.13, 149.82, 141.44, 140.93, 138.39, 132.12, 128.11, 127.97, 125.32, 122.87, 118.58, 95.17, 74.54, 61.33, 58.68, 55.94, 55.38, 53.66, 51.45, 35.51, 35.03, 33.92, 33.64, 31.80, 31.55, 30.22, 29.94. Anal. Calcd for $C_{54}H_{82}Mg_2N_4O_5$: 70.82, H 9.02, N 6.12. Found: C 70.62, H 8.99, N 6.32.

**Polymerization of L-LA catalyzed by complexes 1-2**

A typical polymerization procedure is exemplified by the synthesis of PLLA-50 (the number 50 indicates the designed $[LA]_0/\{[Cat.]_0 + [BnOH]_0\}$ ratio) at 80 °C (Table 1, Entry 4). The polymerization conversion was analyzed by $^1$H NMR spectroscopy. In a glove-box, an initiator solution from a stock solution in toluene was injected sequentially to a 100 mL schlenk tube loaded with L-lactide (0.144 g, 1 mmol), complex **1** (0.0095 g, 0.01 mmol) and 5 mL toluene. After the solution was stirred at 80 °C for 12 h, an aliquot was withdrawn and quenched quickly with wet hexane, the reaction mixture was quenched at the same time with addition of one drop 0.33 M $CH_3COOH$ aqueous. The solvent was then removed under vacuum; a white crystalline solid was obtained by recrystallization with the mixed solvents of hexane/$CH_2Cl_2$ and dried under vacuum.

**X-ray crystallographic studies**

The data were collected using a SuperNova (Dual) X-ray diffractometer equipped with a graphite-monochromated Cu/Mo Kα radiation source (λ = 1.54184/0.71073 Å). The structures were solved by direct methods using the Siemens SHELXTL PLUS program.[18] Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. All hydrogen atoms were placed by geometrical

considerations and were added to the structure-factor calculations. The crystallographic data are summarized in Table S1 and selected bond lengths and bond angles are collected in Table S2.

## Acknowledgements

Financial support from the National Natural Science Foundation of China (No. 21271092 and 21171078), the Science Foundation of Gansu Province of China (1308RJ2A121), the project for the National Basic Science Personnel Training Fund (J1103307), and the ScGrid of the Supercomputing Center of the Chinese Academy of Sciences are gratefully acknowledged.

## Notes and references

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† NMR spectra of the three complexes, the polymerization studies, CIF file that provides the crystallographic data for complex **1, 2** and **3** with CCDC reference numbers of 1045608, 1027498 and 1045550. This material is available free of charge via the Internet at http://pubs.rsc.org.

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