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Single-Site Cobalt and Zinc Catalysts for the Ring-Opening Polymerization of Lactide

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Abstract. Novel zinc(II) and cobalt(II) complexes containing tripodal mono(phenolate) ligands have been synthesized and characterized. The resulting mononuclear complexes act as efficient initiators in the polymerization of *rac*-lactide to provide the corresponding biodegradable poly(lactic acid). Most of these polymerizations proceeded in a controlled fashion, giving polymers with narrow polydispersities and experimental molecular weights in good agreement with calculated values.

Keywords. Homogeneous Catalysis, Poly(lactic acid), Zinc, Cobalt

Introduction

Disposal of olefin-based materials has led to serious environmental pollution. Therefore, biodegradable polymers have gained much attention as a replacement for conventional

synthetic polymers. Considering a decreasing feedstock and increasing economic and social pressures to reduce our dependence on petroleum, development of such biodegradable polymers has become fertile research ground.¹ Among the biodegradable polymers that have been developed during the last two decades,² poly(lactic acid) (PLA) is of particular interest.³ These polymers, derived from renewable resources, have many properties similar or superior to traditional olefin-based polymers with the added benefit of biodegradability. Thus, research concerning PLA synthesis has been intense in both industrial and academic laboratories. Although several methods exist for synthesis of PLA, the most promising is the ring-opening polymerization (ROP) of lactide.^{4,5} Therefore, there has been particular emphasis over the past decade on the synthesis of metal-based or organic catalysts that are active ROP initiators for the synthesis of PLA.^{4a,4b,6}

Recent advances in catalyst design from our group and others have led to the synthesis of well-defined achiral metal-based complexes supported by phenolate ligands.^{7,8,9} Some of these derivatives have shown quite interesting performance for the polymerization of racemic lactide (*rac*-LA). As part of our ongoing effort to develop new catalysts for the ring-opening polymerization of cyclic esters, we report herein the synthesis and reactivity of new tripodal mono(phenolate) zinc and cobalt complexes.

Results

Synthesis of Mono(phenolate) Metal Complexes. The monophenolate pro-ligands **1-3** were prepared by reductive amination, following a one-pot procedure using commercially available and easily accessible starting materials (Figure 1).¹⁰ Such ligand architecture allows for electronic and steric variations on the different donor fragments (Figure 1). All spectroscopic data of **1-3** are given in the Experimental Section.

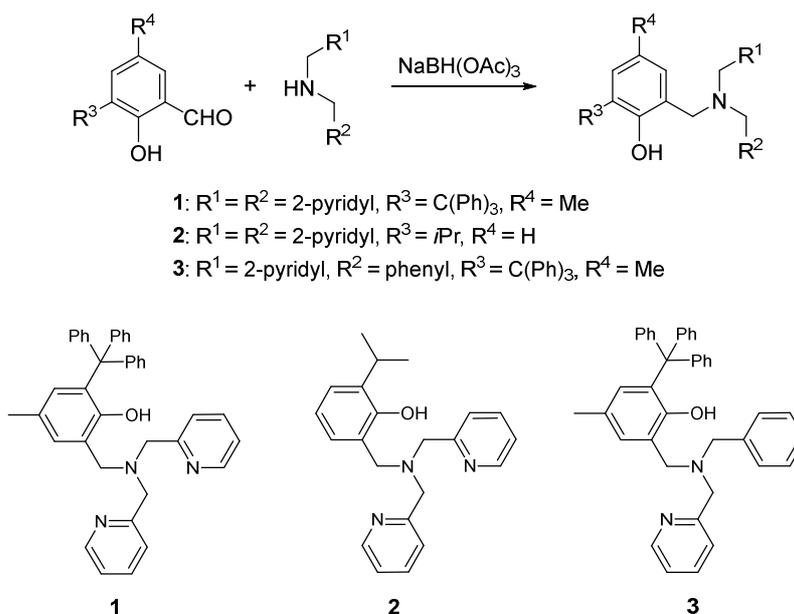
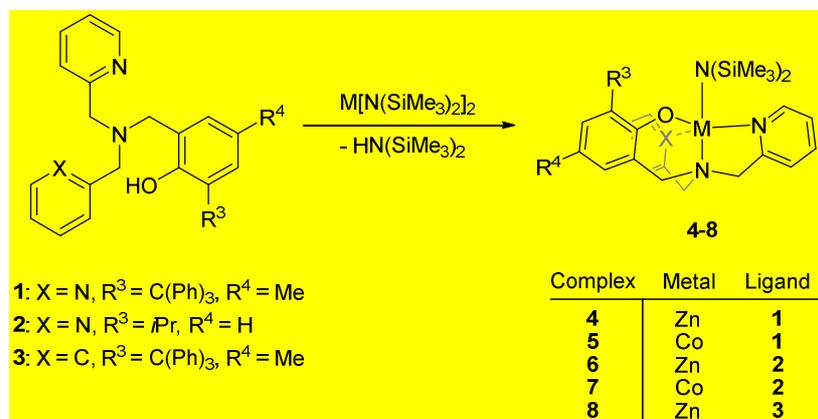


Fig. 1. Synthesis of mono(phenolate) pro-ligands **1-3**

The coordination chemistry of the ligands was studied towards zinc and cobalt bisamide derivatives.^{11,12} Homoleptic metal precursors $M[N(\text{SiMe}_3)_2]_2$ ($M = \text{Co}, \text{Zn}$) were reacted with one equivalent of the mono(phenols) **1-3** to give the corresponding heteroleptic cobalt and zinc complexes $\{(L)M[N(\text{SiMe}_3)_2]\}$ **4-8** in good yields (Scheme 1).^{13,14} The products, which were isolated as solids by evaporation of volatiles and washing of the residues with pentane, are moisture- and air-sensitive, readily soluble in aromatic hydrocarbons (benzene, toluene) and slightly soluble in aliphatic hydrocarbons (pentane, hexane). These complexes were characterized by mass spectrometry, elemental analysis, and NMR spectroscopy for diamagnetic zinc complexes **4**, **6** and **8**. Also, the crystal structure of complex **4** was determined by X-ray diffraction studies (Figure 2). Summary of X-ray data collection and refinement are listed in Table S1. The solid-state structure of **4** revealed the monomeric nature of the complex which adopts a distorted tetrahedral coordination geometry of the zinc atom. Only one pyridyl moiety is coordinated to the Zn center, which illustrates the strongly favored

formation of the four-coordinated Zn species.¹⁵ One bulky bis(trimethylsilyl)amido group occupies the remaining *cis* positions.



Scheme 1. Synthesis of metal complexes 4-8

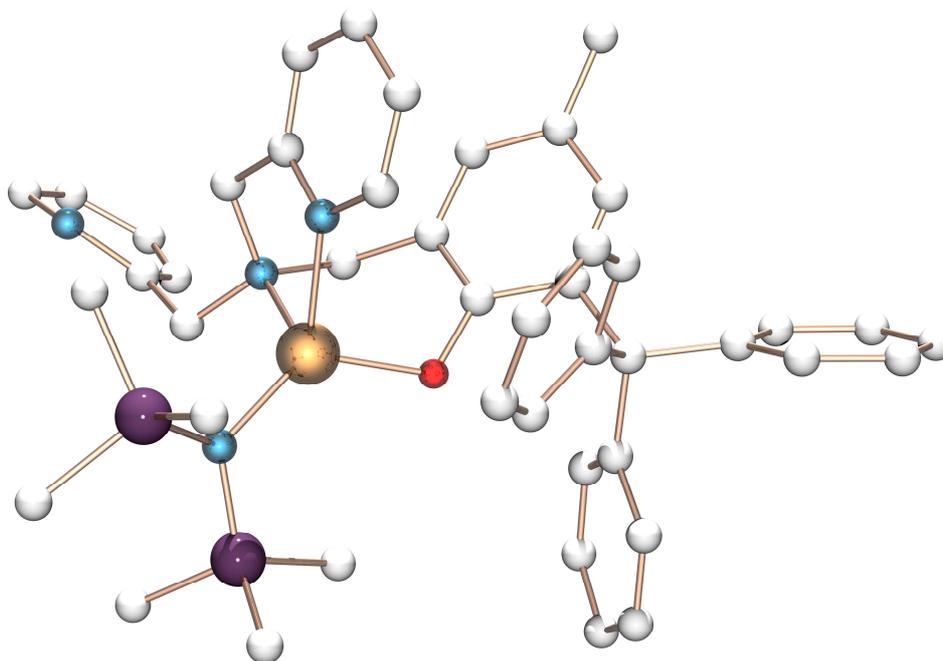
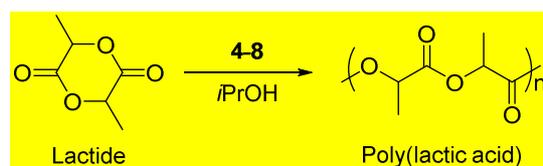


Fig. 2. Crystal structure of complex 4. Hydrogen atoms and solvent molecule are omitted for clarity. Orange zinc, blue N, red O, violet Si.

Reactivity towards *rac*-lactide. Lactide polymerization was investigated with zinc and cobalt complexes **4-8** (Scheme 2). Representative polymerization data are given in Table 1. Homopolymerization of *rac*-lactide with the prepared complexes proceeds rapidly at room temperature for monomer-to-initiator ratios up to 400. The molecular weight distributions are all unimodal, indicative of a single-site behavior.



Scheme 2. Synthesis of PLA

To examine the effects of the metal center on the polymerization behavior, the lactide polymerization ability of complexes **4** and **5** having the same phenolate substituents was first evaluated (Table 1, Entries 1 & 2). Both amido derivatives act as efficient initiators for the ROP of lactide under mild conditions. For instance, polymerization initiated by **4** in toluene at room temperature proceeded with turnover frequencies of *ca.* 66 h⁻¹ (Table 1, Entry 1). The *in-situ* generated alkoxide complexes proved much better initiators than the amido precursors (Table 1, Entries 3-4). Addition of isopropanol to the polymerization reaction resulted in better initiation efficiency and affected the activity of the metal complexes. All the polymers produced with these isopropoxide derivatives have narrow molecular weight distributions and number-average molecular masses (M_n) values close to the theoretical ones, assuming that each isopropoxy group initiates the polymerization. Also, using an alkoxy initiator highly affects the rate of polymerization reaction, with TOFs (up to 492 h⁻¹) approximately an order of magnitude higher than the corresponding amido initiator. Reducing or increasing the reaction temperature resulted in no significant change of the polymerization control (Table 1, Entries 5 & 6).

To study the influence of the ligand substituents on the catalytic activity, the lactide polymerization ability of complexes having various substituents was then examined. Bulky groups were chosen as the phenolate substituent **R**³ in order to favor mononuclear complex formation.⁷ The factors investigated include steric and possible electronic effects derived from the substituents on the aromatic rings, as well as on the (potentially) pendant pyridine arm.^{7,8,16} Complexes **6** and **7**, which bear *ortho*-isopropyl groups at the phenolate rings, gave much higher catalytic activity for the polymerization of *rac*-LA (Table 1, Entries 7 & 8). In particular, the Zn derivative shows turnover frequency values up to 19440 h⁻¹. This increasing activity trend may be logically accounted for by the decreasing bulkiness of the *ortho* substituents, going from CPh₃ to *i*Pr. As already reported by Gibson for a series of metal complexes stabilized by monoanionic phenoxyamine ligands, the denticity of the ligands can vary from tridentate for zinc complexes to tetradentate for cobalt derivatives, depending on the coordination requirement of the metal centers.¹⁷ As a zinc center therefore requires a lower electron count (and a lower coordination number) than a cobalt center, a zinc-based complex will be more accessible (*e.g.*, to lactide) than its cobalt counterpart, thereby allowing to achieve higher catalytic activities. By substituting a tetradentate ligand with a tridentate ligand (Table 1, Entries 3 & 9), we evidenced an increase of the polymerization activity. The trityl-substituted system **8** was very active, with a TOF of 5340 h⁻¹, but less active than its isopropyl analogue.

In terms of stereoselectivity, all zinc-based systems led to isotactic-rich PLAs, while cobalt complexes enabled the production of isotactically enriched or heterotactic-rich PLAs, depending on the nature of the ligand used.

Table 1. Polymerization of *rac*-lactide.^[a]

Entry	Complex	[M]/[I]/[<i>i</i> PrOH]	Time [min]	Yield ^[b] [%]	M_n ^[c] [kDa]	PDI ^[c]	P_m ^[d]	TOF [h ⁻¹]
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1	4	200/1/0	60	33	43.2	1.35	0.65	66
2	5	200/1/0	60	28	13.3	1.69	0.39	56
3	4	200/1/1	20	40	10.0	1.04	0.64	240
4	5	200/1/1	20	82	25.1	1.06	0.39	492
5 ^[e]	4	200/1/1	5	79	20.8	1.07	0.64	1896
6 ^[f]	4	100/1/1	180	90	13.3	1.06	0.65	30
7	6	400/1/1	1	81	47.8	1.33	0.65	19440
8	7	100/1/1	2	81	23.6	1.09	0.74	2430
9	8	200/1/1	2	89	27.0	1.09	0.72	5340

[a] Reactions performed at RT in toluene at [lactide] = 1 M, unless otherwise stated. [b] As determined by the integration of ¹H NMR methine resonances of lactide and PLA. [c] M_n and M_w/M_n of polymer determined by SEC-RI in THF at RT using polystyrene standards and M_n corrected by the Mark-Houwink parameter (0.58). [d] P_m is the probability of forming a new *m*-triad. [e] Reaction performed at 50°C. [f] Reaction performed at 0°C.

The reaction mechanism of the ROP of LA was then investigated by DFT calculations (B3PW91). The structure of the starting complex was constructed starting from the solid-state structure of **4**, in which the amido group coordinated to the Zn metal center was replaced by an isopropoxy initiating group. As shown in Figure 3, the ring-opening of LA proceeds *via* two major transition states. The first of these, **B**, involves nucleophilic attack of the zinc-alkoxide at the coordinated C_{carbonyl} of LA. DFT calculations demonstrated that the most favorable pathway for the first ring-opening of lactide occurs with a complex adopting a distorted trigonal bipyramidal geometry of the Zn atom. We also optimized the geometry of the first insertion product, **G**, arising from the ring-opening of a single lactide unit at the (L)ZnOiPr center (Figure 4). The resulting five-coordinate zinc center of **G** exhibits a highly distorted trigonal bipyramidal geometry. The most favorable conformation was found to be a five-membered Zn-lactate, with a dative bond between the zinc center and the carbonyl oxygen of the ring-opened LA unit.

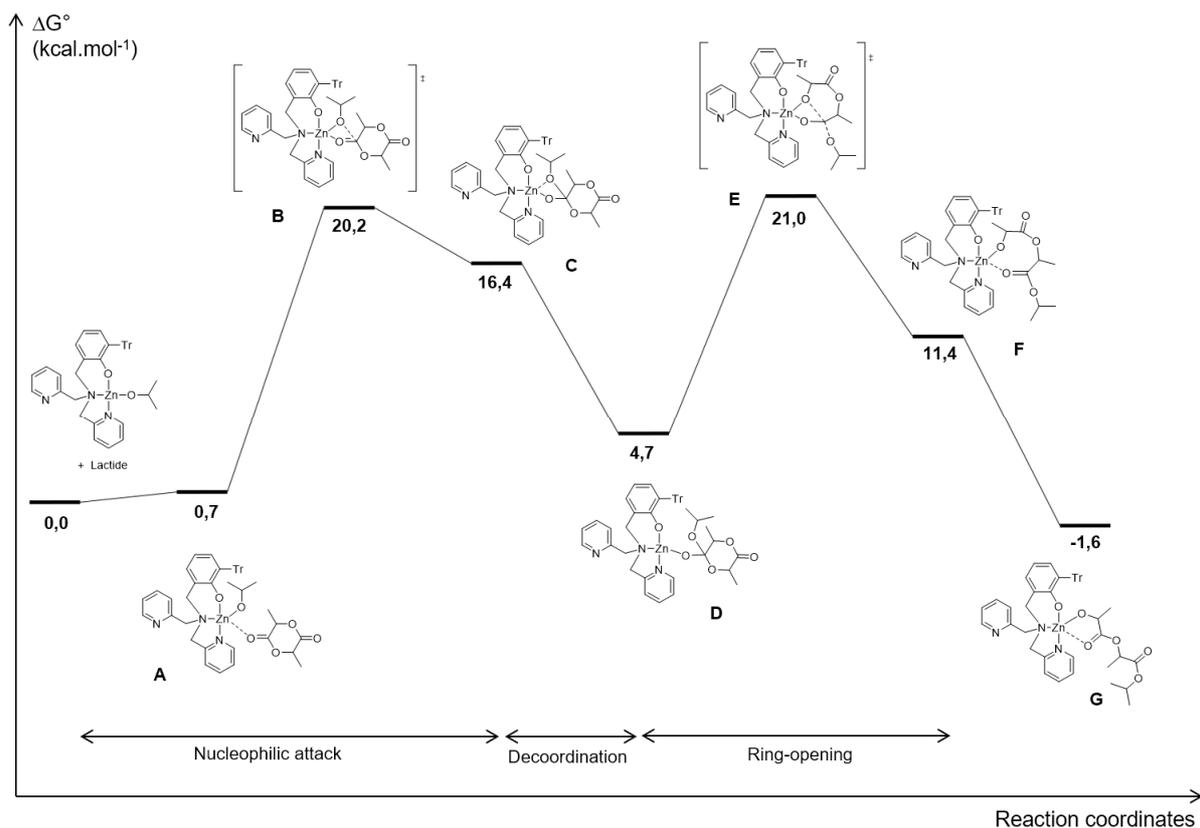


Fig. 3. Computed free enthalpy reaction pathway of the first ROP of LA mediated by a pentacoordinated zinc species A.

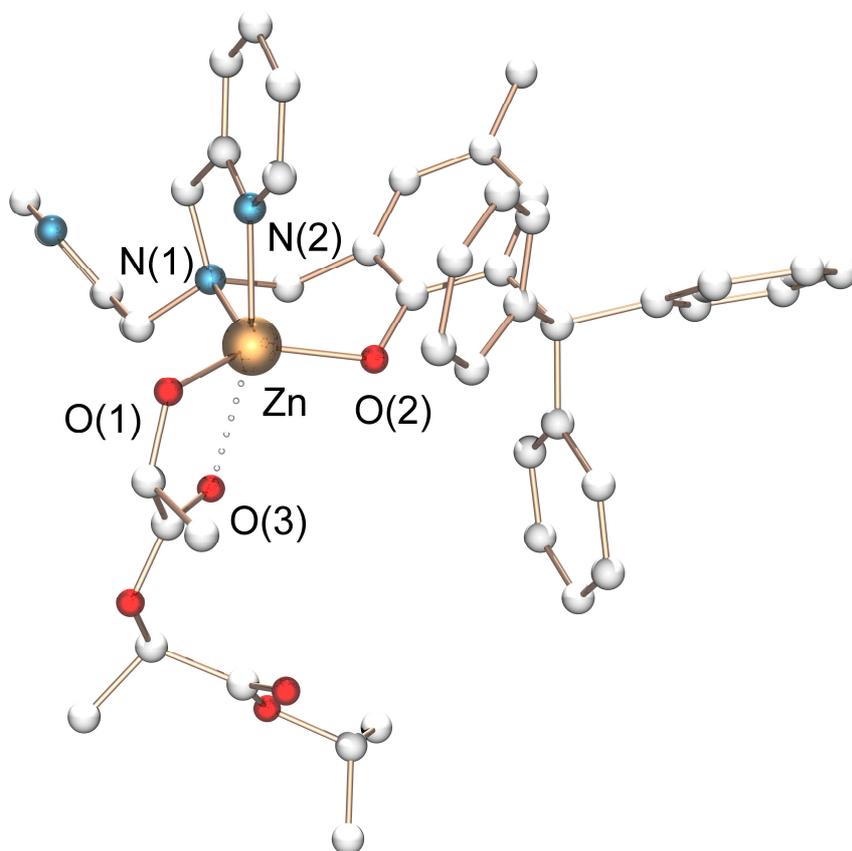


Fig. 4. Optimized structure of zinc alkoxo intermediate complex **G** potentially involved after LA ring-opening. Hydrogen atoms are omitted for clarity. Orange zinc, blue N, red O. Selected bond lengths [Å]: Zn-N(1) 2.223, Zn-N(2) 2.163, Zn-O(1) 1.880, Zn-O(2) 1.936, Zn-O(3) 2.487.

Conclusion.

We have reported a new series of zinc and cobalt complexes supported by readily available tripodal ligands. These organometallic catalysts, and particularly the zinc derivatives, are highly active in mild conditions for the ring-opening polymerization of lactide, affording high molecular weight poly(lactic acid). These results suggest a number of new avenues for biodegradable polymers.

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Appendix A. Supplementary material

The following are the Supplementary data to this article:

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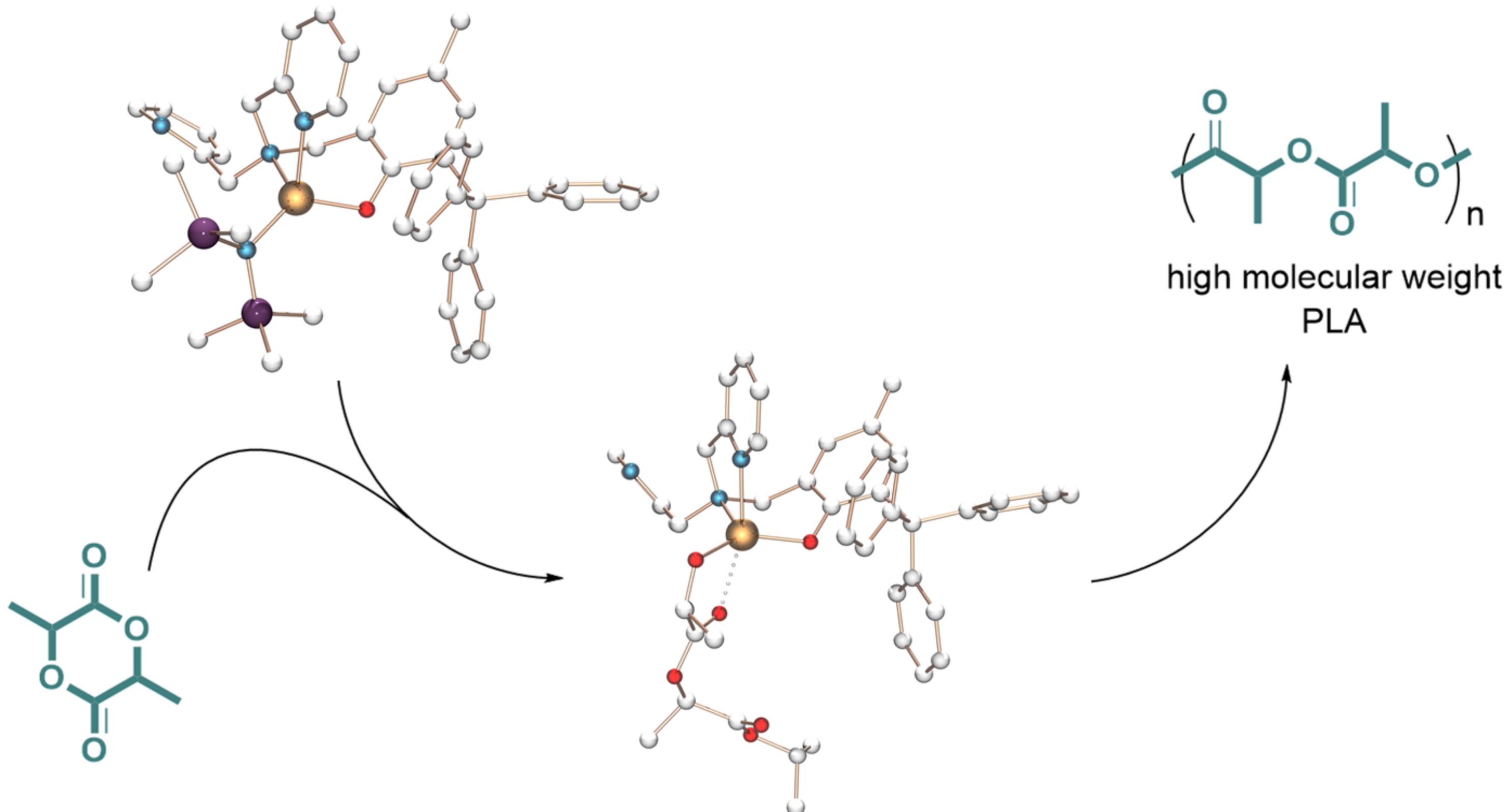
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- new Zn(II) and Co(II) initiators
- high activity at room temperature
- controlled polymerization