

Geometry change in a series of zirconium compounds during lactide ring opening polymerization

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Supporting Information Placeholder

ABSTRACT: A new series of zirconium compounds, (salfen)Zr(OⁱBu)₂ (salfen = N,N'-bis(2,4-di-*tert*-butylphenoxy)-1,1'-ferrocene-diimine), (salfen)Zr(OⁱPr)₂, and (salfen)Zr(OⁿPr)₂, was synthesized and characterized, featuring a cis-β coordination geometry for the major isomer found in solution. An isomerization between the trans and cis-β coordination geometry was observed at ca. 100 °C in solution. This isomerization was also observed in the presence of L-lactide (LA) before its ring opening polymerization could occur. The isolation of a (salfen)Zr(OⁿPr)₂ lactide intermediate supports the change to the trans coordination geometry necessary before polymerization.

INTRODUCTION

Biodegradable polymers, especially polyesters, are promising solutions to the pollution generated by conventional plastics.¹⁻¹¹ While polyesters can be obtained using enzymatic methods, the ring-opening polymerization of cyclic esters catalyzed by metal complexes¹¹⁻¹³ or small organic molecules¹³⁻¹⁴ is a well-known, controlled process, which allows the synthesis of polymers with specific properties. Zirconium alkoxide complexes have been used as catalysts for the ring opening polymerization of lactide for several decades.^{13, 15-16} Zirconium tetra-*n*-propoxide, for example, could reach 94% lactide conversion at 90 °C after 24 hours. Recently, in order to achieve controlled polymerization, the synthesis of novel zirconium compounds has been pursued. For example, ONNO-type tetradentate ligands, derived from Schiff bases (Chart 1), were successful in supporting zirconium catalysts for the ring opening polymerization of lactones.¹⁵ Compounds featuring both a saturated backbone (Chart 1), reported by Kol et al.,¹⁹ and unsaturated C=N backbone (Chart 1), reported by Chakraborty et al.,²⁰ showed a good activity toward the ring opening polymerization of cyclic esters. Zirconium precatalysts bearing other tetradentate ligands, such as the OSSO and OSNO-type, were designed and synthesized later.²¹⁻²³

The structure of the above six-coordinated metal complexes was studied systematically, and it was shown that they can adopt three possible geometries at the metal center: cis-α, cis-β, and trans (Figure 1); among these, the cis-β geometry is non-symmetrical,²⁴ while the other two are symmetrical. For all the group 4 metal precatalysts, it was reported that different geometries have distinct activities during the lactone ring-opening polymerization: trans and cis-α compounds are usually active, while cis-β compounds show only a low activity.²²⁻²⁹

In 2015, B. Long and co-workers reported a titanium(IV) salfen (salfen = 1,1'-di(2,4-di-*tert*-butyl-6-salicylimine)ferrocene) complex displaying a cis-β geometry (Chart 2).³⁰ By comparison, the geometry of a titanium complex supported by a different ferrocene modified Schiff base, previously reported by N. Long and coworkers, was trans.³¹ In B. Long's paper, the ring opening polymerization of L-LA with the reduced state catalyst was significantly slower than that with the oxidized state catalyst, which represented an opposite trend in catalytic activity as compared with most catalysts employed in redox switchable ring opening polymerization.³²⁻⁴² However, if the catalyst was oxidized in the presence of L-LA and then reduced back, the reduced species showed a dramatically increased polymerization rate. Once it was oxidized back *in situ*, the newly formed compound had no activity toward the ring opening polymerization of LA anymore. Although further investigations are needed to explain this phenomenon, based on the *in situ* ¹H NMR spectra and the cyclic voltammetry (CV) experiments, the authors proposed that the geometry of the catalyst was changed from its original cis-β conformation to either a cis-α or trans conformation by using the redox reagents in the presence of LA. In the absence of LA, the geometry of the catalyst remained cis-β after oxidation. Thus, the authors proposed that when the oxidation and reduction reactions were carried out in the presence/absence of monomers, the polymerization activity was completely different.

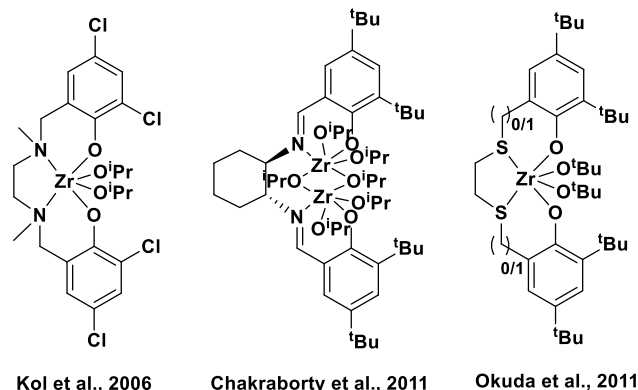


Chart 1 Zirconium complexes used as precatalysts for lactone ring opening polymerization.

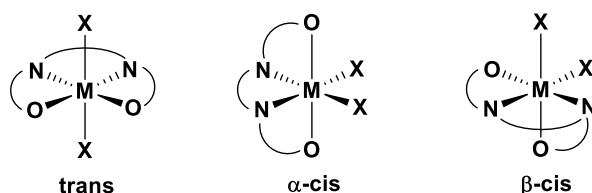


Figure 1 Different coordination geometries of group 4 metal complexes supported by tetradentate ligands.

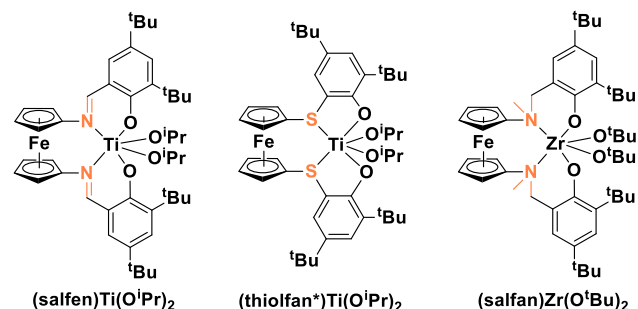


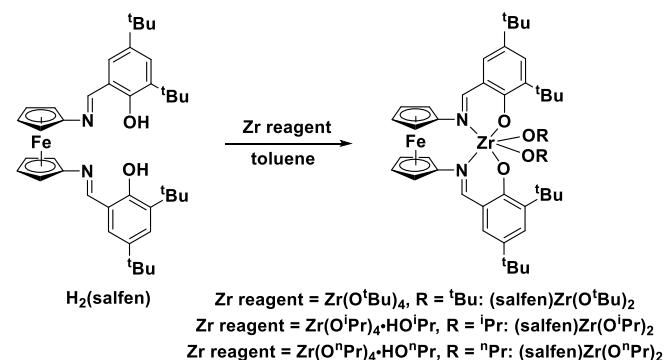
Chart 2 Previously reported ferrocene-derived Schiff base group 4 metal complexes.

Our group has been interested in the redox switchable polymerization of lactide and its copolymerization with other monomers.^{35–39, 41–50} We were able to show that changing the oxidation state of iron in a ferrocene-based ligand modified the reactivity of a metal complex toward a certain monomer. Various ferrocene ligands were designed in the past few years and their corresponding metal compounds showed orthogonal activity toward cyclic ester polymerization. For example, (thiolfan*)Ti(OiPr)₂ (Chart 2, thiolfan* = 1,1'-di(2,4-di-*tert*-butyl-6-thiophenoxide)ferrocene) can polymerize L-lactide (LA) in the reduced state and ε-caprolactone in the oxidized state; (salfan)Zr(OtBu)₂ (Chart 2, salfan = 1,1'-bis(di-2,4-*tert*-butyl-6-N-methylmethylenephenoxy)ferrocene) can polymerize LA in the reduced state and cyclohexene oxide (CHO) in the oxidized state.³⁹ We became interested in studying a ferrocene-derived Schiff base zirconium complex in order to simplify the ligand design and to compare its activity with that reported by Long et al. for the corresponding titanium complex. Herein, we discuss our results that indicate that a geometry change is ob-

served for the corresponding zirconium complexes at a temperature above ambient conditions. Furthermore, such a geometry change is necessary for these precatalysts to become active in lactide ring opening polymerization.

RESULTS AND DISCUSSION

Synthesis and characterization of the zirconium complexes. Three compounds, (salfen)Zr(OtBu)₂, (salfen)Zr(OiPr)₂, and (salfen)Zr(OⁿPr)₂, were synthesized from the reaction of H₂(salfen) with Zr(OtBu)₄, Zr(OiPr)₄·HOiPr and Zr(OⁿPr)₄·HOⁿPr (Scheme 1).



Scheme 1 Synthesis of zirconium complexes.

The ¹H NMR spectrum (Figure 2) of (salfen)Zr(OtBu)₂ indicated a non-symmetrical geometry at zirconium, and was different from the ¹H NMR spectrum of the symmetrical compound (salfan)Zr(OtBu)₂ (salfan = 1,1'-bis(di-2,4-*tert*-butyl-6-N-methylmethylenephenoxy)ferrocene), previously reported by our group.³⁹ This asymmetry made each proton on the aryl, imine, ferrocene, and alkoxide moieties to be magnetically non-equivalent. The solid state molecular structure (Figure 3) indicated a cis-β coordination geometry, which explained the asymmetrical peaks observed in the ¹H NMR spectrum.^{24, 30}

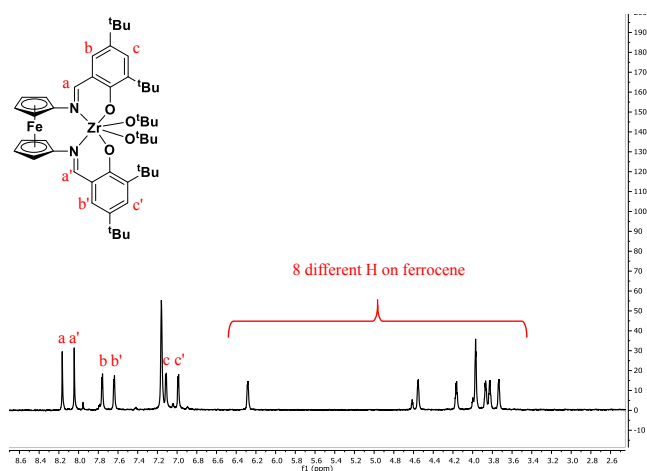


Figure 2 ¹H NMR spectrum (500 MHz, 25 °C, C₆D₆) of (salfen)Zr(OtBu)₂.

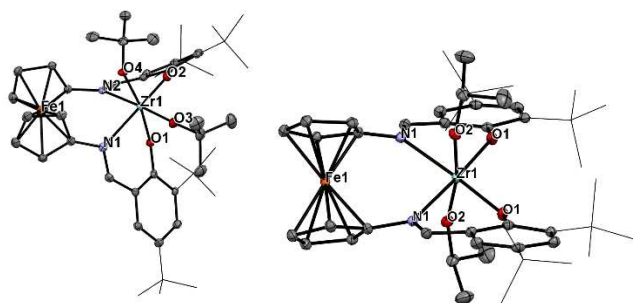


Figure 3 Thermal ellipsoid (50% probability) representation of (salfen)Zr(O^{*t*}Bu)₂ (left, cis-β) and (salfen)Zr(O^{*i*}Pr)₂ (right, trans). Hydrogen atoms were removed and aryl *t*-butyl groups are drawn as sticks for clarity.

Similar ¹H NMR spectra were obtained for (salfen)Zr(O^{*i*}Pr)₂ and (salfen)Zr(O^{*n*}Pr)₂. For both cases, however, there was always a set of small peaks that corresponded to another isomer (Figure 4), which could not be separated by purification through filtration or crystallization. The single crystals obtained from these solutions corresponded to these minor isomers, which showed a trans geometry in the solid state structure (Figure 3). Therefore, we hypothesized that the two isomers are in equilibrium with each other, with the cis-β geometry as the major isomer in solution at room temperature. This hypothesis was probed by variable temperature ¹H NMR spectroscopy (Figure 5) performed on (salfen)Zr(O^{*n*}Pr)₂. At 100 °C, the peaks coalesce, indicating the existence of a fast equilibrium on the NMR timescale between the two isomers. The ¹H NMR spectrum reverted to that of the original sample after cooling to room temperature. The trans and cis-β geometry isomer percent content for all three zirconium complexes is listed in Table 1.

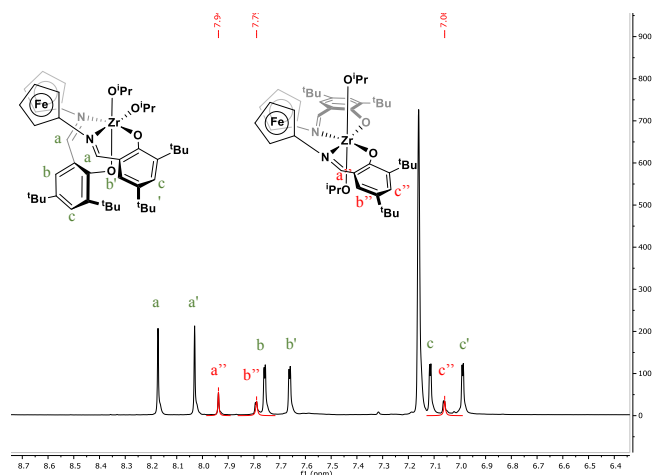


Figure 4 ¹H NMR spectrum (500 MHz, 25 °C, C₆D₆) of (salfen)Zr(O^{*i*}Pr)₂.

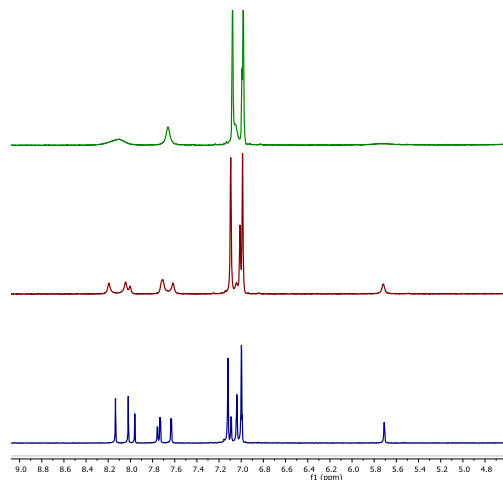


Figure 5 ¹H NMR spectra (500 MHz, *d*₈-toluene) of (salfen)Zr(O^{*n*}Pr)₂ at 25 °C (bottom), 70 °C (middle), and 100 °C (top).

Table 1 cis-β and trans geometry isomer contribution for each zirconium alkoxide in C₆D₆ solution at room temperature.

Compound	cis-β	trans
(salfen)Zr(O ^{<i>t</i>} Bu) ₂	95%	5%
(salfen)Zr(O ^{<i>i</i>} Pr) ₂	84%	16%
(salfen)Zr(O ^{<i>n</i>} Pr) ₂	71%	29%

DFT calculations were performed to compare the ground state energies of the zirconium complexes in both isomeric forms (Table S3, entries 1-8). For a model compound, in which the ^{*t*}Bu groups on the phenoxides and the alkoxides (R = ^{*t*}Bu, ^{*i*}Pr, and ^{*n*}Pr) were replaced with H and methoxides, respectively, the trans isomer was found to be 1.7 kcal/mol higher in energy than the cis-β isomer, in agreement with experimental observations. Calculations on the full molecules also agree with the experimental observations (salfen)Zr(O^{*t*}Bu)₂ and (salfen)Zr(O^{*i*}Pr)₂, for which the cis-β isomer is more stable than the trans isomer by 1.1 and 0.4 kcal/mol, respectively. In the case of (salfen)Zr(O^{*n*}Pr)₂, the trans appeared slightly more favorable by 0.4 kcal/mol than the cis-β isomer. Although the calculations on the full molecules do not reproduce the expected isomer ratio for (salfen)Zr(O^{*n*}Pr)₂, the trend of an increasing amount of trans isomer present at room temperature from (salfen)Zr(O^{*t*}Bu)₂ to (salfen)Zr(O^{*i*}Pr)₂ and to (salfen)Zr(O^{*n*}Pr)₂ is reproduced well.

Polymerization of LA with the three zirconium complexes. The three compounds were then used as pre-catalysts for LA homopolymerization reactions (Table 2). Compound (salfen)Zr(O^{*t*}Bu)₂ did not work (Table 2, entry 1), but both (salfen)Zr(O^{*i*}Pr)₂ (entry 2) and (salfen)Zr(O^{*n*}Pr)₂ (entry 3) showed good activity for LA polymerization, with (salfen)Zr(O^{*i*}Pr)₂ giving a slightly better yield: at 100 °C in benzene solution, (salfen)Zr(O^{*i*}Pr)₂ reacted with 100 equiv. LA in 24 hours to give a 70% conversion, and (salfen)Zr(O^{*n*}Pr)₂ reacted with 100 equiv. LA in 24 hours to give a 60% conversion.

Table 2. Polymerization of LA or ϵ -caprolactone (CL) with the three zirconium alkoxides.^a

Entry	precatalyst	Temp. (°C)	Time (h)	Conv. ^b (%)
1	(salfen)Zr(O ⁱ Bu) ₂	100	24	<3
2	(salfen)Zr(O ⁱ Pr) ₂	100	24	70
3	(salfen)Zr(O ⁿ Pr) ₂	100	24	60
4	(salfen)Zr(O ⁱ Pr) ₂	70	24	<3
5	(salfen)Zr(O ⁱ Pr) ₂	100/70	2/22	21
6	(salfen)Zr(O ⁱ Pr) ₂	100	24	<3
7	(salfen)Zr(O ⁿ Pr) ₂	100	24	<3

^a All experiments were conducted in 0.8 mL of C₆D₆, with 0.004 mmol zirconium compound and 0.4 mmol LA, except for entries 6 and 7, when CL was used (1:100 equivalents), and hexamethylbenzene as an internal standard; ^b the conversion was calculated from the integration of ¹H NMR peaks against those of hexamethylbenzene. Dispersity and molar mass information can be found in Table S1.

¹H NMR monitoring experiments showed that (salfen)Zr(OⁱPr)₂ and (salfen)Zr(OⁿPr)₂ experienced a geometry change during polymerization after 2 hours at 100 °C (Figures S17-18). On the other hand, such a change was not observed for (salfen)Zr(OⁱBu)₂ at 100 °C after 24 hours (Figure S19). After the geometry change, (salfen)Zr(OⁱPr)₂ and (salfen)Zr(OⁿPr)₂ started catalyzing the polymerization of LA. Such activity was not observed for (salfen)Zr(OⁱBu)₂, an observation consistent with similar reports indicating no activity for cis- β geometry compounds.^{24, 51-52} The same reaction (Table 2, entry 4) was tested at 70 °C, but less than 5% conversion was observed after 24 hours. A control experiment (Table 2, entry 5) was designed as follows: firstly, the sample was heated at 100 °C for 2 hours, then at 70 °C for 22 hours. This experiment showed 7% conversion after the first two hours of heating at 100 °C and then 21% overall conversion, demonstrating that the geometry change from cis- β to trans is necessary for the polymerization to occur.

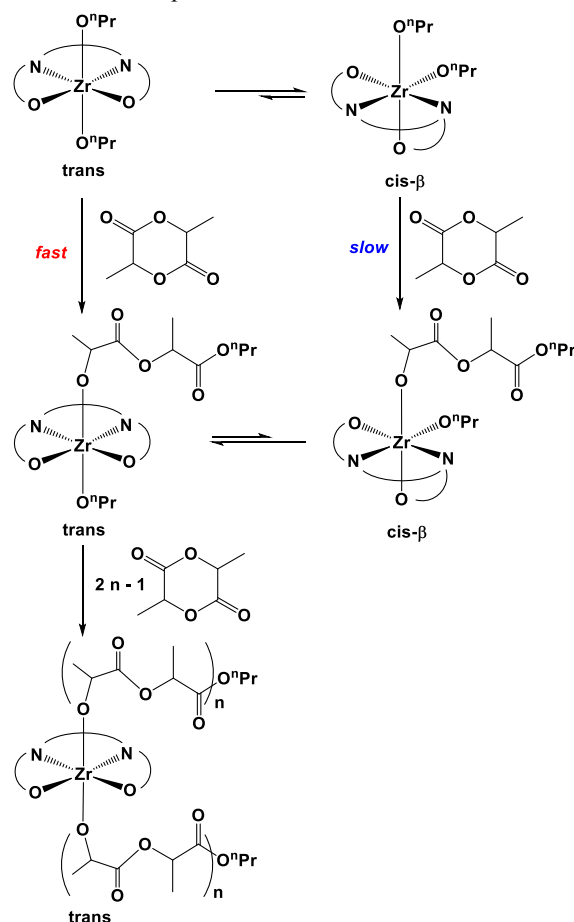
(salfen)Zr(OⁱPr)₂ and (salfen)Zr(OⁿPr)₂ were also tested for CL homopolymerization (Table 2, entry 6 and 7) but neither of them showed activity. No polymerization or geometry change of the zirconium compound was observed after heating either zirconium complex at 100 °C for 24 hours in the presence of CL. Though it was proved that the zirconium compounds could isomerize to the trans geometry at 100 °C by themselves, CL did not allow the geometry change to occur.

Although (salfen)Zr(OⁱPr)₂ did not react with ϵ -caprolactone, we reasoned that once the geometry change can be induced, the results would be different. Therefore, an experiment was designed to have (salfen)Zr(OⁱPr)₂ and 100 equivalents of LA reacting for 24 hours at 100 °C first, giving a conversion of 74%, after which, 100 equivalents of CL was added and reacted for another 24 hours at 100 °C, giving a CL conversion of 12% and LA conversion of 90%. This result shows that during the second 24 hours, CL did get polymerized. DOSY NMR spectroscopy was used to show that the product is a copolymer (Figure S16).

In order to understand further the relationship between polymerization and geometry change, we decided to isolate the product of a 1:1 molar equivalent reaction between a zirconium alkoxide and LA (Eq 1). Compound (salfen)Zr(OⁿPr)₂ was chosen since it has the highest trans geometry isomer ratio at 298 K. The (salfen)Zr(OⁿPr)₂-LA addition compound was successfully synthesized and isolated as a precipitate from *n*-hexane. The corresponding NOESY (Figure S20) spectrum indicated that the structure is consistent with a ring opened lactide product.

Variable temperature ¹H NMR spectroscopic studies with (salfen)Zr(OⁿPr)₂-LA complex (Figures S11, S22, and S23) indicate that, at room temperature, a mixture of the two isomers, cis- β and trans is present. At -30 °C, the trans isomer predominates, indicating that it is the thermodynamically favored isomer, unlike the case of the zirconium bis-alkoxide complexes. As the temperature was increased, the trans to cis- β interconversion became faster, indicated by the broadening of the NMR peaks.

In order to determine whether the length of the polymer chain has an influence on the cis- β to trans isomerization, we performed another set of variable temperature NMR experiments while the LA polymerization was ongoing (100 equivalents LA added but conversion stopped only at 40%). In this case, there was no difference between the spectra taken at temperatures ranging from 25 °C to 100 °C (Figure S25). The spectra are consistent with the presence of the trans isomer.



Scheme 2 Proposed reactions between (salfen)Zr(OⁿPr)₂ and LA.

A comparison of ^1H NMR spectra corresponding to (salfen)Zr(OⁿPr)₂, (salfen)Zr(OⁿPr)₂-LA and (salfen)Zr-polymer (Figures S26-27) showed that peaks for cis-β (salfen)Zr(OⁿPr)₂ were present alongside the mixture of trans and cis-β isomers of (salfen)Zr(OⁿPr)₂-LA. This finding indicates that it is possible that the cis-β isomer reacts with LA to form cis-β (salfen)Zr(OⁿPr)₂-LA or that cis-β (salfen)Zr(OⁿPr)₂-LA originates only from the trans to cis-β isomerization and the amount of cis-β (salfen)Zr(OⁿPr)₂ present at the end of the reaction is unreacted starting material. These possibilities are shown in Scheme 2.

Computational studies also support the fact that the trans isomer of (salfen)Zr(OⁿPr)₂-LA is more stable than the cis-β form. The products of the ring opening polymerization of one L-lactide by cis-β and trans zirconium modeled complexes (aryl ¹Bu groups replaced by hydrogen atoms) were calculated with the full OⁿBu, OⁿPr, and OⁿPr ligands (Table S3, entries 18-23). In all cases, trans (salfen)Zr(OⁿPr)₂-LA is more favorable than the cis-β isomer by xx, yy, and zz kcal/mol, respectively.

CONCLUSION

We synthesized and characterized a series of zirconium alkoxide complexes bearing a ferrocene unit in the ligand backbone. All three compounds adopted a cis-β coordination geometry as the major isomer in solution in room temperature. The solid state molecular structures showed, however, that although (salfen)Zr(OⁱBu)₂ crystallized as the cis-β isomer, the trans isomer of (salfen)Zr(OⁱPr)₂ and (salfen)Zr(OⁿPr)₂ was characterized by single crystal X-ray diffraction. An equilibrium between the cis-β and trans isomers is established in solution as supported by variable temperature ^1H NMR spectroscopy. Compounds (salfen)Zr(OⁱPr)₂ and (salfen)Zr(OⁿPr)₂ catalyzed the ring opening polymerization of LA after a geometry change to the trans isomer occurred. The product isolated from a 1:1 LA to (salfen)Zr(OⁿPr)₂ addition, along with computational studies, also supported the conclusion that a geometry change to the trans isomer is necessary for the reaction with LA to occur.

EXPERIMENTAL SECTION

General considerations. All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques or an MBraun inert-gas glovebox. Solvents were purified using a two-column solid-state purification system by the method of Grubbs⁵³ and transferred to the glovebox without exposure to air. NMR solvents were obtained from Cambridge Isotope Laboratories, degassed, and stored over activated molecular sieves prior to use. ^1H NMR spectra were recorded on Bruker 300 and Bruker 500 spectrometers at room temperature in C₆D₆ or CDCl₃. Chemical shifts are reported with respect to internal solvent: 7.16 ppm (C₆D₆) and 7.26 ppm (CDCl₃) for ^1H NMR spectra. Cyclohexene oxide and 1,2-difluorobenzene were distilled over CaH₂ and brought into the glovebox without exposure to air. L-Lactide and hexamethylbenzene were recrystallized from toluene at least twice before use. 2,4-Di-*tert*-butylphenol, *n*-BuLi, cobaltocene, Zr(OⁱBu)₄, Zr(OⁱPr)₄·HOⁿPr and Zr(OⁿPr)₄·HOⁿPr were purchased from VWR and used as received. AcFcBAR^{F54} and H₂(salfen)³⁹ were synthesized following previously published procedures. Molar masses of the polymers were determined with a GPC-MALS instrument at UCLA. GPC-MALS uses a Shimadzu Prominence-i LC 2030C 3D instrument equipped with an autosampler, two MZ Analysentechnik MZ-Gel SDplus LS 5 μm, 300 × 8 mm linear columns, and Wyatt DAWN HELEOS-II and Wyatt Optilab T-REX apparatus. The column temperature was set at 40 °C. A flow rate of 0.70 mL/min was used, and sam-

ples were dissolved in chloroform or THF. dn/dc values were calculated for PLA and PCHO by making five solutions of increasing concentration (0.1–1.0 mg/mL), directly injecting them into the RI detector sequentially, and using the batch dn/dc measurement methods in the Astra software. The dn/dc values for PLA and PCHO were calculated to be 0.024 and 0.086 mL/g, respectively, over three trials.

DFT calculations. Calculations were performed at the density functional theory level in Turbomole.^{55–56} Geometry optimizations and frequency calculations were carried out with the TPSS functional,^{57–60} the def2-SVP basis set was used on all non-metal atoms^{61–62} and the def2-TZVPP basis set was used for Fe and Zr.⁶² Single point energies were calculated with the TPSSH functional^{58–60, 63} and the def2-TZVPP basis set was used on all atoms. DFT-D3 was applied on all calculations to account for dispersion corrections.⁶⁴ For solvation effects, COSMO^{65–66} was applied with the dielectric constant corresponding to benzene (ε = 2.27). All structures were confirmed by their vibrational frequencies; intermediate structures were characterized by zero imaginary frequencies. The Gibbs free energy was calculated as the sum of the *in vacuo* electronic energy, solvation free energy, zero-point energy, and the entropic and thermal corrections obtained from the frequency calculations at 298.15 K and 1 atm.

Synthesis of (salfen)Zr(OⁱBu)₂. H₂(salfen) (194.6 mg, 0.3 mmol) and Zr(OⁱBu)₄ (115.0 mg, 0.3 mmol) were each dissolved in 5 mL toluene. Both solutions were cooled to -78 °C for 10 min and then combined. The mixture was stirred at -78 °C for 30 min and warmed to room temperature for 2 h. The volatiles were removed under a reduced pressure and the resulting solids were dissolved into hexanes and filtered through Celite. The hexanes solution was concentrated under vacuum and put into a -30 °C freezer to give (salfen)Zr(OⁱBu)₂ as an amorphous precipitate after four days; yield: 134 mg (51%). ^1H NMR (300 MHz, C₆D₆, 298 K, δ, ppm): 8.17 (s, 1H, N=CH), 8.04 (s, 1H, N=CH), 7.76 (d, 1H, *m*-OC₆H₂), 7.64 (d, 1H, *m*-OC₆H₂), 7.11 (d, 1H, *m*-OC₆H₂), 6.99 (d, 1H, *m*-OC₆H₂), 6.27 (s, 1H, C₅H₄), 4.6–3.7 (m, 7H, C₅H₄), 1.78 (s, 9H, OC(CH₃)₃), 1.59 (s, 9H, OC(CH₃)₃), 1.41 (s, 9H, C(CH₃)₃), 1.35 (s, 9H, C(CH₃)₃), 1.33 (s, 9H, C(CH₃)₃), 1.16 (s, 9H, C(CH₃)₃). ^{13}C NMR (500 MHz, C₆D₆, 298 K, δ, ppm): 174.3 (N=C), 165.3 (N=C), 162.4 (*m*-OC₆H₂), 161.7 (*m*-OC₆H₂), 139.7 (*m*-OC₆H₂), 138.6 (*m*-OC₆H₂), 138.4 (*m*-OC₆H₂), 137.5 (*m*-OC₆H₂), 130.3 (*m*-OC₆H₂), 129.6 (*m*-OC₆H₂), 129.5 (*m*-OC₆H₂), 127.3 (*m*-OC₆H₂), 123.7 (*m*-OC₆H₂), 123.2 (*m*-OC₆H₂), 111.6 (*m*-OC₆H₂), 107.6 (C₅H₄), 76.2 (C₅H₄), 75.4 (C₅H₄), 70.3 (C₅H₄), 69.2 (C₅H₄), 68.1 (C₅H₄), 67.9 (C₅H₄), 66.4 (C₅H₄), 66.3 (C₅H₄), 65.2 (OC(CH₃)₃), 62.6 (OC(CH₃)₃), 35.5 (C(CH₃)₃), 34.9 (C(CH₃)₃), 34.1 (C(CH₃)₃), 33.8 (C(CH₃)₃), 33.1 (C(CH₃)₃), 31.9 (C(CH₃)₃), 31.3 (C(CH₃)₃), 30.4 (C(CH₃)₃), 29.9 (C(CH₃)₃). Anal. Calcd. for (salfen)Zr(OⁱBu)₂·(C₆H₁₄)_{0.5} (C₅₁H₇₅N₂O₄FeZr): C, 66.06; H, 8.15; N, 3.02; Found: C, 65.63; H, 8.52; N, 2.91.

Synthesis of (salfen)Zr(OⁱPr)₂. H₂(salfen) (163.0 mg, 0.25 mmol) was dissolved in toluene (5 mL) and Zr(OⁱPr)₄·HOⁿPr (193.9 mg, 0.5 mmol) was dissolved in toluene (10 mL), respectively. Both solutions were cooled to -78 °C for 10 min and combined. The mixture was stirred at -78 °C for 30 min and move to room temperature for 2 h. The volatiles were removed under a reduced pressure for 5 h. The solids were dissolved again in toluene, stir for 2 h and the volatiles were removed under a reduced pressure again for 5 h, and repeat this “dissolve-stir-pump” procedure for one more time. The solids were dissolved into hexanes and filtered through Celite. The hexanes solution was concentrated under reduced pressure and put into freezer to give (salfen)Zr(OⁱPr)₂ as a crystalline precipitate after four days. Yield: 102 mg (47%). ^1H NMR (300 MHz, C₆D₆, 298 K, δ, ppm): 8.17 (s, 1H, N=CH), 8.03 (s, 1H, N=CH), 7.76 (d, 1H, *m*-OC₆H₂), 7.66 (d, 1H, *m*-OC₆H₂), 7.11 (d, 1H, *m*-OC₆H₂), 6.99 (d, 1H, *m*-OC₆H₂), 5.83 (s, 1H, C₅H₄), 4.60 (m, 1H, OCH(CH₃)₂), 4.30 (m, 1H, OCH(CH₃)₂), 4.4–3.8 (m, 7H, C₅H₄), 1.78 (s, 6H, OCH(CH₃)₂), 1.47 (s, 6H, OCH(CH₃)₂), 1.34 (s, 18H, C(CH₃)₃), 1.32 (s, 18H, C(CH₃)₃). ^{13}C NMR (500 MHz, C₆D₆, 298 K, δ, ppm): 173.3 (N=C), 164.8 (N=C), 162.5 (*m*-OC₆H₂), 161.7 (*m*-OC₆H₂), 139.6 (*m*-OC₆H₂), 138.7 (*m*-OC₆H₂), 138.6 (*m*-OC₆H₂), 137.6 (*m*-OC₆H₂), 130.0 (*m*-OC₆H₂), 129.6 (*m*-OC₆H₂), 129.3 (*m*-OC₆H₂), 123.5 (*m*-OC₆H₂), 123.1 (*m*-OC₆H₂), 111.4, 107.7 (C₅H₄), 71.7 (C₅H₄), 70.6 (C₅H₄), 70.0 (C₅H₄), 69.7 (C₅H₄), 68.5 (C₅H₄), 67.9 (C₅H₄), 67.3 (C₅H₄), 66.5, (C₅H₄), 64.7, 62.3 (OCH(CH₃)₂), 35.5

(C(CH₃)₃), 35.1 (C(CH₃)₃), 34.6 (C(CH₃)₃), 33.8 (C(CH₃)₃), 31.3 (C(CH₃)₃), 30.1 (C(CH₃)₃), 29.9 (C(CH₃)₃), 27.3 (C(CH₃)₃), 26.4 (OCH(CH₃)₂), 26.3 (OCH(CH₃)₂). Anal. Calcd. for C₄₆H₆₄N₂O₄FeZr: C, 64.54; H, 7.53; N, 3.27. Found: C, 64.42; H, 7.36; N, 3.17.

Synthesis of (salphen)Zr(OⁿPr)₂. H₂(salphen) (163.0 mg, 0.25 mmol) was dissolved in toluene (5 mL) and Zr(OⁿPr)₄•HOⁿPr (193.9 mg, 0.5 mmol) was dissolved in toluene (10 mL), respectively. Both solutions were cooled to -78 °C for 10 min and combined. The mixture was stirred at -78 °C for 30 min and move to room temperature for 2 h. The volatiles were removed under a reduced pressure for 5 h. The solids were dissolved again in toluene, stirred for 2 h and the volatiles were removed under a reduced pressure again for 5 h; this “dissolve-stir-pump” procedure was repeated for one more time. Finally, the solids were dissolved into hexanes and filtered through Celite. The hexane solution was concentrated under reduced pressure and put into freezer to give (salphen)Zr(OⁿPr)₂ as a crystalline precipitate after four days. Yield: 113 mg (53%). ¹H NMR (500 MHz, C₆D₆, 298 K, δ, ppm): 8.17 (s, 1H, N=CH), 8.03 (s, 1H, N=CH), 7.76 (d, 1H, *m*-OC₆H₂), 7.65 (d, 1H, *m*-OC₆H₂), 7.10 (d, 1H, *m*-OC₆H₂), 6.98 (d, 1H, *m*-OC₆H₂), 5.76 (s, 1H, C₅H₄), 4.38 (m, 2H, OCH₂CH₂CH₃), 4.28 (m, 2H, OCH₂CH₂CH₃), 4.5-3.8 (m, 7H, C₅H₄), 1.88 (m, 4H, OCH₂CH₂CH₃), 1.78 (m, 6H, OCH₂CH₂CH₃), 1.47 (s, 18H, C(CH₃)₃), 1.33 (s, 18H, C(CH₃)₃). ¹³C NMR (500 MHz, C₆D₆, 298 K, δ, ppm): 174.2 (N=C), 169.7 (N=C), 163.4 (*m*-OC₆H₂), 162.5 (*m*-OC₆H₂), 140.6 (*m*-OC₆H₂), 138.7 (*m*-OC₆H₂), 138.6 (*m*-OC₆H₂), 137.6 (*m*-OC₆H₂), 129.9 (*m*-OC₆H₂), 129.6 (*m*-OC₆H₂), 129.4 (*m*-OC₆H₂), 124.1 (*m*-OC₆H₂), 123.9 (*m*-OC₆H₂), 112.0 (C₅H₄), 108.7 (C₅H₄), 73.3 (C₅H₄), 72.8 (C₅H₄), 72.1 (C₅H₄), 71.0 (C₅H₄), 68.5 (C₅H₄), 67.9 (C₅H₄), 67.3 (C₅H₄), 65.8 (C₅H₄), 65.6 (OCH₂CH₂CH₃), 63.3 (OCH₂CH₂CH₃), 36.8 (OCH₂CH₂CH₃), 36.4 (OCH₂CH₂CH₃), 34.6 (OCH₂CH₂CH₃), 33.8 (OCH₂CH₂CH₃), 31.3 (C(CH₃)₃), 30.1 (C(CH₃)₃), 29.9 (C(CH₃)₃), 28.9 (C(CH₃)₃), 28.5 (C(CH₃)₃), 28.1 (C(CH₃)₃). Anal. Calcd. for C₄₆H₆₄N₂O₄FeZr: C, 64.54; H, 7.54; N, 3.27. Found: C, 63.97; H, 7.48; N, 3.18.

Synthesis of (salphen)Zr(OⁿPr)₂-LA. (salphen)Zr(OⁿPr)₂ (207.6 mg, 0.24 mmol) and LA (35.7 mg, 0.24 mmol) were added to benzene (4.5 mL). The mixture was sealed in a Schlenk tube, brought out of the glovebox, heated and stirred at 100 °C overnight. The Schlenk tube was brought into the glovebox the next day. The volatiles were removed under a reduced pressure and the solids were dissolved in hexanes and filtered through Celite. The hexanes solution was concentrated under reduced pressure and put into a freezer to give the compound as a needle-shape crystalline precipitate after 7 days. Yield: 85 mg (35%). ¹H NMR (300 MHz, C₆D₆, 298 K, δ, ppm): 8.11 (s, 2H, N=CH), 7.71 (s, 2H, *m*-OC₆H₂), 7.02 (s, 2H, *m*-OC₆H₂), 5.33 (br, 2H, C₅H₄), 4.66 (br, 2H, C₅H₄), 4.16 (br, 2H, C₅H₄), 4.07 (br, 2H, C₅H₄), 4.88 (s, 2H, OCH(CH₃)COO), 3.81 (br, 2H, OCH₂CH₂CH₃), 3.79 (br, 2H, OCH₂CH₂CH₃), 1.84 (br, 3H, OCH(CH₃)COO), 1.59 (br, 3H, OCH(CH₃)COO), 1.41 (br, 2H, OCH₂CH₂CH₃), 1.23 (br, 2H, OCH₂CH₂CH₃), 1.30 (br, 36H, C(CH₃)₃), 0.89 (br, 6H, OCH₂CH₂CH₃). ¹³C NMR (500 MHz, C₆D₆, 298 K, δ, ppm): 176.1 (COO), 171.3 (N=C), 162.8 (*m*-OC₆H₂), 139.8 (*m*-OC₆H₂), 139.5 (*m*-OC₆H₂), 130.9 (*m*-OC₆H₂), 128.0 (*m*-OC₆H₂), 124.2 (*m*-OC₆H₂), 108.4 (C₅H₄), 75.0 (OCHCOO), 69.8 (C₅H₄), 69.3 (C₅H₄), 68.9 (C₅H₄), 68.7 (C₅H₄), 67.7 (C₅H₄), 66.5 (C₅H₄), 65.9 (C₅H₄), 64.8 (C₅H₄), 34.7 (C(CH₃)₃), 32.2 (C(CH₃)₃), 31.0 (OCH₂CH₂CH₃), 22.9 (OCH₂CH₂CH₃). Anal. Calcd. for (salphen)Zr(OⁿPr)₂-LA•(C₆H₁₄)_{0.5} (C₅₅H₇₉N₂O₈FeZr): C, 63.32; H, 7.63; N, 2.69. Found: C, 63.27; H, 7.46; N, 2.65.

Polymerization of LA by (salphen)Zr(OⁿPr)₂. To a C₆D₆ (0.7 mL) solution of (salphen)Zr(OⁿPr)₂ (3.4 mg, 4.0 μmol) in a J. Young NMR

tube were added a solution of hexamethylbenzene (8.1 mg, 5.0 μmol) in C₆D₆ (0.1 mL) and LA powder (57.6 mg, 0.4 mmol). The reaction mixture was heated to 100 °C for 24 hours and monitored by ¹H NMR spectroscopy. At the end, the reaction mixture was dissolved in CH₂Cl₂ and poured into cold methanol; a white solid precipitated briefly and was filtered.

Copolymerization of LA and CL by (salphen)Zr(OⁿPr)₂. To a C₆D₆ (0.7 mL) solution of (salphen)Zr(OⁿPr)₂ (3.4 mg, 4.0 μmol) in a J. Young NMR tube were added a solution of hexamethylbenzene (8.1 mg, 5.0 μmol) in C₆D₆ (0.1 mL) and LA powder (57.6 mg, 0.4 mmol). The reaction mixture was heated to 100 °C for 24 hours and monitored by ¹H NMR spectroscopy. CL (45.6 mg, 4.0 μmol) was added after, and heated for another 24 hours, monitoring by ¹H NMR spectroscopy. At the end, the reaction mixture was dissolved in CH₂Cl₂ and poured into cold methanol; a white solid precipitated briefly and was filtered.

ASSOCIATED CONTENT

Supporting Information. NMR spectra, GPC traces, X-ray, and DFT calculation data. This material is available free of charge via the Internet at <http://pubs.acs.org>. Cifs were deposited with CCDC, numbers 1864411-1864413.

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Notes

The authors declare no competing financial interest.

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REFERENCES

1. *The New Plastics Economy – Rethinking the future of plastics*; World Economic Forum, Ellen MacArthur Foundation, McKinsey & Company, 2016; p <http://www.ellenmacarthurfoundation.org/publications>.
2. Haward, M., Plastic pollution of the world's seas and oceans as a contemporary challenge in ocean governance. *Nat. Commun.* **2018**, *9* (1), 667.
3. Zhu, J.-B.; Watson, E. M.; Tang, J.; Chen, E. Y.-X., A synthetic polymer system with repeatable chemical recyclability. *Science* **2018**, *360* (6387), 398-403.
4. Hong, M.; Chen, E. Y. X., Chemically recyclable polymers: a circular economy approach to sustainability. *Green Chem.* **2017**, *19* (16), 3692-3706.
5. Hong, M.; Chen, E. Y. X., Towards Truly Sustainable Polymers: A Metal-Free Recyclable Polyester from Biorenewable Non-Strained γ -Butyrolactone. *Angew. Chem. Int. Ed.* **2016**, *55* (13), 4188-4193.
6. Watts, A.; Kurokawa, N.; Hillmyer, M. A., Strong, Resilient, and Sustainable Aliphatic Polyester Thermoplastic Elastomers. *Biomacromolecules* **2017**, *18* (6), 1845-1854.
7. Schneiderman, D. K.; Hillmyer, M. A., Aliphatic Polyester Block Polymer Design. *Macromolecules* **2016**, *49* (7), 2419-2428.
8. Zhu, Y.; Romain, C.; Williams, C. K., Sustainable polymers from renewable resources. *Nature* **2016**, *540* (7633), 354-362.
9. Williams, C. K.; Hillmyer, M. A., Polymers from Renewable Resources: A Perspective for a Special Issue of Polymer Reviews. *Polym. Rev.* **2008**, *48* (1), 1-10.
10. Ragauskas, A. J.; Williams, C. K.; Davison, B. H.; Britovsek, G.; Cairney, J.; Eckert, C. A.; Frederick, W. J.; Hallett, J. P.; Leak, D. J.; Liotta, C. L.; Mielenz, J. R.; Murphy, R.; Templer, R.; Tschaplinski, T., The Path Forward for Biofuels and Biomaterials. *Science* **2006**, *311* (5760), 484-489.
11. Tian, H.; Tang, Z.; Zhuang, X.; Chen, X.; Jing, X., Biodegradable synthetic polymers: Preparation, functionalization and biomedical application. *Prog. Polym. Sci.* **2012**, *37* (2), 237-280.
12. Kaihara, S.; Matsumura, S.; Mikos, A. G.; Fisher, J. P., Synthesis of poly(L-lactide) and polyglycolide by ring-opening polymerization. *Nat. Protoc.* **2007**, *2*, 2767.
13. O'Keefe, B. J.; Hillmyer, M. A.; Tolman, W. B., Polymerization of lactide and related cyclic esters by discrete metal complexes. *J. Chem. Soc., Dalton Trans.* **2001**, (15), 2215-2224.
14. Zhang, X.; Jones, G. O.; Hedrick, J. L.; Waymouth, R. M., Fast and selective ring-opening polymerizations by alkoxides and thioureas. *Nat. Chem.* **2016**, *8*, 1047.
15. Sauer, A.; Kapelski, A.; Fliedel, C.; Dagorne, S.; Kol, M.; Okuda, J., Structurally well-defined group 4 metal complexes as initiators for the ring-opening polymerization of lactide monomers. *Dalton Trans.* **2013**, *42* (25), 9007-9023.
16. Guillaume, S. M.; Kirillov, E.; Sarazin, Y.; Carpentier, J.-F., Beyond Stereoselectivity, Switchable Catalysis: Some of the Last Frontier Challenges in Ring-Opening Polymerization of Cyclic Esters. *Chem. Eur. J.* **2015**, *21* (22), 7988-8003.
17. Kricheldorf, H. R.; Berl, M.; Scharnagl, N., Poly(lactones). 9. Polymerization mechanism of metal alkoxide initiated polymerizations of lactide and various lactones. *Macromolecules* **1988**, *21* (2), 286-293.
18. Miola-Delaite, C.; Hamaide, T.; Spitz, R., Anionic coordinated polymerization of ϵ -caprolactone with aluminium, zirconium and some rare earths alkoxides as initiators in the presence of alcohols. *Macromol. Chem. Phys.* **1999**, *200* (7), 1771-1778.
19. Gendler, S.; Segal, S.; Goldberg, I.; Goldschmidt, Z.; Kol, M., Titanium and Zirconium Complexes of Dianionic and Trianionic Amine-Phenolate-Type Ligands in Catalysis of Lactide Polymerization. *Inorg. Chem.* **2006**, *45* (12), 4783-4790.
20. Saha, T. K.; Ramkumar, V.; Chakraborty, D., Salen Complexes of Zirconium and Hafnium: Synthesis, Structural Characterization, Controlled Hydrolysis, and Solvent-Free Ring-Opening Polymerization of Cyclic Esters and Lactides. *Inorg. Chem.* **2011**, *50* (7), 2720-2722.
21. Stopper, A.; Okuda, J.; Kol, M., Ring-Opening Polymerization of Lactide with Zr Complexes of {ONSO} Ligands: From Heterotactically Inclined to Isotactically Inclined Poly(lactic acid). *Macromolecules* **2012**, *45* (2), 698-704.
22. Buffet, J.-C.; Okuda, J., Group 4 metal initiators for the controlled stereoselective polymerization of lactide monomers. *Chem. Commun.* **2011**, *47* (16), 4796-4798.
23. Buffet, J.-C.; Martin, A. N.; Kol, M.; Okuda, J., Controlled stereoselective polymerization of lactide monomers by group 4 metal initiators that contain an (OSSO)-type tetradentate bis(phenolate) ligand. *Polym. Chem.* **2011**, *2* (10), 2378-2384.
24. Gregson, C. K. A.; Blackmore, I. J.; Gibson, V. C.; Long, N. J.; Marshall, E. L.; White, A. J. P., Titanium-salen complexes as initiators for the ring opening polymerisation of rac-lactide. *Dalton Trans.* **2006**, (25), 3134-3140.
25. Chmura, A. J.; Davidson, M. G.; Jones, M. D.; Lunn, M. D.; Mahon, M. F.; Johnson, A. F.; Khunkamchoo, P.; Roberts, S. L.; Wong, S. S. F., Group 4 Complexes with Aminebisphenolate Ligands and Their Application for the Ring Opening Polymerization of Cyclic Esters. *Macromolecules* **2006**, *39* (21), 7250-7257.
26. Kim, S. H.; Lee, J.; Kim, D. J.; Moon, J. H.; Yoon, S.; Oh, H. J.; Do, Y.; Ko, Y. S.; Yim, J.-H.; Kim, Y., Titanium complexes containing new dianionic tetradentate [ONNO]-type ligands with benzyl substituents on bridging nitrogen atoms: Syntheses, X-ray structures, and catalytic activities in ring opening polymerization of lactide. *J. Organomet. Chem.* **2009**, *694* (21), 3409-3417.
27. Jones, M. D.; Davidson, M. G.; Kociok-Kohn, G., New titanium and zirconium initiators for the production of polylactide. *Polyhedron* **2010**, *29* (2), 697-700.
28. Cameron, P. A.; Jhurry, D.; Gibson, V. C.; White, A. J. P.; Williams, D. J.; Williams, S., Controlled polymerization of lactides at ambient temperature using [5-Cl-salen]AlOMe. *Macromol. Rapid Commun.* **1999**, *20* (12), 616-618.
29. Yeori, A.; Gendler, S.; Groysman, S.; Goldberg, I.; Kol, M., Salalen: a hybrid Salan/Salen tetradentate [ONNO]-type ligand and its coordination behavior with group IV metals. *Inorg. Chem. Commun.* **2004**, *7* (2), 280-282.
30. Brown, L. A.; Rhinehart, J. L.; Long, B. K., Effects of Ferrocenyl Proximity and Monomer Presence during Oxidation for the Redox-Switchable Polymerization of L-Lactide. *ACS Catal.* **2015**, *5* (10), 6057-6060.
31. Gregson, C. K. A.; Gibson, V. C.; Long, N. J.; Marshall, E. L.; Oxford, P. J.; White, A. J. P., Redox Control within Single-Site Polymerization Catalysts. *J. Am. Chem. Soc.* **2006**, *128* (23), 7410-7411.
32. Hermans, C.; Rong, W.; Spaniol, T. P.; Okuda, J., Lanthanum complexes containing a bis(phenolate) ligand with a ferrocene-1,1'-diylidithio backbone: synthesis, characterization, and ring-opening polymerization of rac-lactide. *Dalton Trans.* **2016**, *45* (19), 8127-8133.
33. Sauer, A.; Buffet, J.-C.; Spaniol, T. P.; Nagae, H.; Mashima, K.; Okuda, J., Switching the Lactide Polymerization Activity of a Cerium Complex by Redox Reactions. *ChemCatChem* **2013**, *5* (5), 1088-1091.

34. Biernesser, A. B.; Li, B.; Byers, J. A., Redox-Controlled Polymerization of Lactide Catalyzed by Bis(imino)pyridine Iron Bis(alkoxide) Complexes. *J. Am. Chem. Soc.* **2013**, *135* (44), 16553-16560.
35. Wei, J.; Riffel, M. N.; Diaconescu, P. L., Redox Control of Aluminum Ring-Opening Polymerization: A Combined Experimental and DFT Investigation. *Macromolecules* **2017**, *50* (5), 1847-1861.
36. Quan, S. M.; Wei, J.; Diaconescu, P. L., Mechanistic Studies of Redox-Switchable Copolymerization of Lactide and Cyclohexene Oxide by a Zirconium Complex. *Organometallics* **2017**, *36* (22), 4451-4457.
37. Lowe, M. Y.; Shu, S.; Quan, S. M.; Diaconescu, P. L., Investigation of redox switchable titanium and zirconium catalysts for the ring opening polymerization of cyclic esters and epoxides. *Inorg. Chem. Front.* **2017**, *4*, 1798-1805.
38. Quan, S. M.; Wang, X.; Zhang, R.; Diaconescu, P. L., Redox Switchable Copolymerization of Cyclic Esters and Epoxides by a Zirconium Complex. *Macromolecules* **2016**, *49* (18), 6768-6778.
39. Wang, X.; Thevenon, A.; Brosmer, J. L.; Yu, I.; Khan, S. I.; Mehrkhodavandi, P.; Diaconescu, P. L., Redox Control of Group 4 Metal Ring-Opening Polymerization Activity toward ϵ -Lactide and ϵ -Caprolactone. *J. Am. Chem. Soc.* **2014**, *136* (32), 11264-11267.
40. Broderick, E. M.; Thuy-Boun, P. S.; Guo, N.; Vogel, C. S.; Sutter, J.; Miller, J. T.; Meyer, K.; Diaconescu, P. L., Synthesis and Characterization of Cerium and Yttrium Alkoxide Complexes Supported by Ferrocene-Based Chelating Ligands. *Inorg. Chem.* **2011**, *50* (7), 2870-2877.
41. Broderick, E. M.; Guo, N.; Wu, T.; Vogel, C. S.; Xu, C.; Sutter, J.; Miller, J. T.; Meyer, K.; Cantat, T.; Diaconescu, P. L., Redox control of a polymerization catalyst by changing the oxidation state of the metal center. *Chem. Commun.* **2011**, *47*, 9897-9899.
42. Broderick, E. M.; Guo, N.; Vogel, C. S.; Xu, C.; Sutter, J.; Miller, J. T.; Meyer, K.; Mehrkhodavandi, P.; Diaconescu, P. L., Redox Control of a Ring-Opening Polymerization Catalyst. *J. Am. Chem. Soc.* **2011**, *133* (24), 9278-9281.
43. Abubekarov, M.; Wei, J.; Swartz, K. R.; Xie, Z.; Pei, Q.; Diaconescu, P. L., Preparation of multiblock copolymers via step-wise addition of ϵ -lactide and trimethylene carbonate. *Chem. Sci.* **2018**, *9* (8), 2168-2178.
44. Abubekarov, M.; Khan, S. I.; Diaconescu, P. L., Ferrocene-bis(phosphinimine) Nickel(II) and Palladium(II) Alkyl Complexes: Influence of the Fe-M (M = Ni and Pd) Interaction on Redox Activity and Olefin Coordination. *Organometallics* **2017**, *36* (22), 4394-4402.
45. Shepard, S. M.; Diaconescu, P. L., Redox-Switchable Hydroelementation of a Cobalt Complex Supported by a Ferrocene-Based Ligand. *Organometallics* **2016**, *35* (15), 2446-2453.
46. Huang, W.; Diaconescu, P. L., Reactivity and Properties of Metal Complexes Enabled by Flexible and Redox-Active Ligands with a Ferrocene Backbone. *Inorg. Chem.* **2016**, *55* (20), 10013-10023.
47. Abubekarov, M.; Shepard, S. M.; Diaconescu, P. L., Switchable Polymerization of Norbornene Derivatives by a Ferrocene-Palladium(II) Heteroscorpionate Complex. *Eur. J. Inorg. Chem.* **2016**, *2016* (15-16), 2634-2640.
48. Wang, X.; Brosmer, J. L.; Thevenon, A.; Diaconescu, P. L., Highly Active Yttrium Catalysts for the Ring-Opening Polymerization of ϵ -Caprolactone and δ -Valerolactone. *Organometallics* **2015**, *34* (19), 4700-4706.
49. Quan, S. M.; Diaconescu, P. L., High activity of an indium alkoxide complex toward ring opening polymerization of cyclic esters. *Chem. Commun.* **2015**, *51*, 9643 - 9646.
50. Broderick, E. M.; Diaconescu, P. L., Cerium(IV) Catalysts for the Ring-Opening Polymerization of Lactide. *Inorg. Chem.* **2009**, *48*, 4701-4706.
51. Clarkson, G. J.; Gibson, V. C.; Goh, P. K. Y.; Hammond, M. L.; Knight, P. D.; Scott, P.; Smit, T. M.; White, A. J. P.; Williams, D. J., Group 4 catalysts for ethene polymerization containing tetradentate salicylaldiminato ligands. *Dalton Trans.* **2006**, (46), 5484-5491.
52. Chen, H.; White, P. S.; Gagné, M. R., Synthesis and Reactivity of Titanium(IV)-Salen Complexes Containing Oxygen and Chloride Ligands. *Organometallics* **1998**, *17* (24), 5358-5366.
53. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J., Safe and Convenient Procedure for Solvent Purification. *Organometallics* **1996**, *15* (5), 1518-1520.
54. Dhar, D.; Yee, G. M.; Spaeth, A. D.; Boyce, D. W.; Zhang, H.; Dereli, B.; Cramer, C. J.; Tolman, W. B., Perturbing the Copper(III)-Hydroxide Unit through Ligand Structural Variation. *J. Am. Chem. Soc.* **2016**, *138* (1), 356-368.
55. Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C., Electronic structure calculations on workstation computers: The program system turbomole. *Chem. Phys. Lett.* **1989**, *162* (3), 165-169.
56. Treutler, O.; Ahlrichs, R., Efficient molecular numerical integration schemes. *J. Chem. Phys.* **1995**, *102* (1), 346-354.
57. Dirac, P. A. M., Quantum mechanics of many-electron systems. *Proc. Royal Soc. Lond.* **1929**, *123* (792), 714-733.
58. Slater, J. C., A Simplification of the Hartree-Fock Method. *Phys. Rev.* **1951**, *81* (3), 385-390.
59. Perdew, J. P.; Wang, Y., Accurate and simple analytic representation of the electron-gas correlation energy. *Phys. Rev. B* **1992**, *45* (23), 13244-13249.
60. Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E., Climbing the Density Functional Ladder: Nonempirical Meta-Generalized Gradient Approximation Designed for Molecules and Solids. *Phys. Rev. Lett.* **2003**, *91* (14), 146401.
61. Weigend, F.; Häser, M.; Patzelt, H.; Ahlrichs, R., RI-MP2: optimized auxiliary basis sets and demonstration of efficiency. *Chem. Phys. Lett.* **1998**, *294* (1), 143-152.
62. Weigend, F.; Ahlrichs, R., Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7* (18), 3297-3305.
63. Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P., Comparative assessment of a new nonempirical density functional: Molecules and hydrogen-bonded complexes. *J. Chem. Phys.* **2003**, *119* (23), 12129-12137.
64. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H., A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132* (15), 154104.
65. Klamt, A.; Schuurmann, G., COSMO: a new approach to dielectric screening in solvents with explicit expressions for the screening energy and its gradient. *J. Chem. Soc., Perkin Trans. 2* **1993**, (5), 799-805.
66. Schäfer, A.; Klamt, A.; Sattel, D.; Lohrenz, J. C. W.; Eckert, F., COSMO Implementation in TURBOMOLE: Extension of an efficient quantum chemical code towards liquid systems. *Phys. Chem. Chem. Phys.* **2000**, *2* (10), 2187-2193.

