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# Ring-opening polymerization of cyclic esters by pincer complexes derived from alkaline earth metals

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**We report the synthesis and characterization of new Ca(II) and Mg(II) complexes of the type [Ph—PPP]MR (M = Ca, R = $N(SiMe_3)_2$ (1); M = Mg, R = $^n$Bu (2)) where Ph—$PPP^-$ is a tridentate monoanionic ligand (Ph—PPP—H = bis(2-diphenylphosphinophenyl) phosphine). Reaction of the opportune metal precursor ($Ca[N(SiMe_3)_2]_2.THF_2$ or $Mg^nBu_2$) with 1 equiv. of the pro-ligand Ph—PPP_H produces the corresponding calcium amido (1) or magnesium butyl (2) complex in high yield. Solution NMR studies show monomeric and kinetically stable structures for both species. The obtained complexes efficiently mediate the ring-opening polymerization of ε-caprolactone showing a turnover frequency of 40 000 $h^{-1}$. In the presence of a hexogen alcohol, up to 2000 equiv. of monomer are converted by using a low loading of catalyst (5 μmol). Kinetic studies show a first-order reaction in monomer concentration. Copyright © 2014 John Wiley & Sons, Ltd.**

**Keywords:** calcium; magnesium; ring-opening polymerization; cyclic esters

## Introduction

Aliphatic polyesters such as polycaprolactone (PCL) and polylactide (PLA) represent an important class of biomaterials. Since the products following their hydrolysis can be metabolized or excreted from the human body via normal metabolic pathways, they have found successful applications in medical and pharmaceutical fields for the preparation of sutures, dental devices, orthopedic devices, drug delivery systems and scaffolds for tissue engineering.[1,2]

For biomedical applications a fine tailoring of the mechanical properties and degradation profiles of these materials is crucial. The election route for producing aliphatic polyesters with designed macromolecular architectures, in terms of chain end groups, molecular weights, molecular weight distribution and microstructure, is the ring-opening polymerization (ROP) of the related cyclic esters promoted by single-site metal catalysts.[3–5]

Various discrete metal complexes have been employed in the ROP of cyclic esters and these include both main group and transition metals.[6–8] Since residual trace amounts of the catalyst may contaminate the polymeric product, the use of catalysts based on biological benign metals such as group IV, Ca, Mg, Zn and Fe is highly desirable for biomedical applications.[9–15]

Recently, special attention has been given to the exploration of catalysts based on zinc[16–21] and magnesium[17,21–26] complexes. Despite their dimensional similarities, in terms of ionic radii (0.74 and 0.72 Å, respectively) they exhibit rather different chemical properties, since magnesium (2+) is considered a hard metal, while zinc (2+) is soft.

Conversely, the organometallic and coordination chemistry of calcium is much less developed than that of magnesium and zinc. Calcium is hard like the $Mg^{2+}$ ion but it is significantly larger (ionic radius = 1.14 Å); therefore its heteroleptic complexes usually show very low stability as they readily decompose by ligand redistribution reactions in Schlenk-type equilibria to generate the corresponding homoleptic species.[27–30] Since the ligand redistribution reactions become more probable with the increase of the ionic radius of the metal, while stable heteroleptic magnesium complexes are easily accessible, the analogous calcium complexes are extremely scarce and known essentially as amido derivatives. To prevent detrimental rearrangements of ligands and to guarantee a certain stability of heteroleptic calcium complexes, an opportune design of the ancillary ligand is decisive.

In the last years, very few examples of heteroleptic calcium complexes as initiators for the ROP of cyclic esters have been reported.[20,31–36] The first were developed by Chisholm *et al.*, which described calcium complexes supported by sterically encumbered tris(pyrazolyl)borates.[37–39] However, ancillary ligands able to stabilize heteroleptic species are still very limited, and the most popular examples are essentially restricted to aminotrop(on)iminates,[40] β-diketiminates[41–43] or Schiff-base ligands.[44,45] In the last few years, some examples of stable cationic calcium complexes have been reported by Carpentier *et al.*[46–48]

Recently we explored the coordination chemistry of phosphido pincer ligands toward different metals, such as zinc, aluminum and group 3 metals.[49–51] In the coordination to hard metal centers, such as aluminum and group 3 metals, complexes in which the metal center is chelated by a $\kappa^3$-PPP pincer ligand have been obtained. Conversely, in the case of the zinc, a soft metal center, the pincer ligand acts as a flexible coordination environment. Density functional theory (DFT) studies about the ring-opening polymerization promoted by zinc complexes highlighted the importance of the coordinative flexibility of the ancillary

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ligand to promote the coordination of the monomer at the metal reactive center.[52]

In this contribution we extend the use of a tridentate phosphine-based pincer ligand to the synthesis of new heteroleptic complexes of calcium and magnesium.

The synthesized complexes have been tested as catalysts for the ROP of ε-caprolactone (ε-CL) and lactides, and compared with the related zinc complex previously reported.

## Results and Discussion

### Synthesis and Characterization

The pro-ligand Ph—PPP_H has been synthesized following a previously published synthetic procedure.[53]

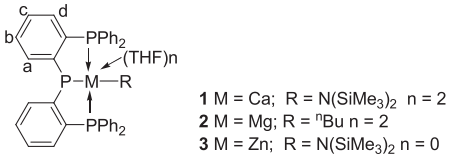
The reaction of $Ca[N(SiMe_3)_2]_2.THF_2$ with 1 equiv. of the pro-ligand Ph—PPP_H in benzene at room temperature gives the complex [Ph—PPP]$CaN(SiMe_3)_2$ (**1**) in quantitative yield (see Scheme 1). After removal of the solvent, by evaporation under reduced pressure, complex **1** has been isolated as a pale-yellow extremely air-sensitive solid. It was fully soluble in ethers and in aromatic solvents such as toluene, and mostly insoluble in hexane.

The parent magnesium complex [Ph—PPP]Mg$^n$Bu (**2**) has been obtained by alkane elimination reaction of the proligand Ph—PPP—H and 1 equiv. of $Mg^nBu_2$ in benzene/THF solution at room temperature.

Both complexes **1** and **2** have been characterized by multinuclear NMR spectroscopy ($^1$H, $^{13}$C, $^{31}$P NMR) and elemental analysis.

NMR and elemental analysis of complexes **1** and **2** are coherent with six-coordinate structures consisting of one phosphido pincer ligand, one labile ligand (amido or alkyl group) and two molecules of THF coordinated at the metal center.

In the $^1$H NMR spectrum of complex **1** ($C_6D_6$, 25°C) the methyl protons of the bis(trimethylsilyl) amido group appear as a single signal at 0.08 ppm. In the aromatic region, a single set of signals is detected, suggesting that the two phenyl groups on each phosphorus are equivalent. Coherently, in the $^{31}$P{$^1$H} NMR spectrum two resonances are observed: a doublet for the two equivalent neutral phosphine donors ($\delta = -4.96$ ppm) and a triplet for the anionic phosphorous donor ($\delta = -10.2$ ppm). Both resonances are shifted downfield from the corresponding ligand precursor ($\delta = -10.9$ ppm for $Ph_2P$— and $\delta = -53.8$ ppm for $Ar_2PH$). All NMR data support the $\kappa_3$ coordination mode of the ancillary ligand to the metal center and suggest a highly symmetric structure of complex **1** in solution coherent with an averaged-$C_{2v}$ symmetry on the NMR timescale. Complex **1** is stable in solution at room temperature for days, as no evidence of detrimental Schlenk-type equilibrium phenomena involving $[Ph—PPP]_2Ca$ and $Ca[N(SiMe_3)_2]_2$ have been detected during monitoring by $^1$H NMR of a solution of **1** in $C_6D_6$ over a period of several days at room temperature.




**Scheme 1.** Structures of the metal complexes **1–3**.

In solution, complex **2** shows the same symmetry discussed for complex **1**. In the $^{31}$P{$^1$H}NMR spectrum a doublet for the two equivalent neutral phosphorus donors ($\delta = -10.7$ ppm) and a triplet for the anionic phosphido donor (at $-41.4$ ppm) are observed. The $^{31}$P NMR chemical shift of the phosphido donor moves toward higher field in comparison to that observed for the larger calcium ion. This difference can be due to the higher ionicity of the metal–phosphorus bond in complex **1**, which leads to enhanced charge on the phosphorus atom and to better charge back-donation from phosphorus into the phenyl $\pi$ system. This effect is also evident in the $^{13}$C NMR spectrum of complex **1**, in which a downfield shift of the *ipso*-carbon atom of approximately 20 ppm compared to the signal of the same carbon of the neutral phosphine proligand is observed. This trend is coherent with that observed for arylphosphanide complexes of the alkaline earth metals.[54]

Although, according to Pearson's HSAB theory,[55] the formation of bonds between hard alkaline earth metal cations and soft phosphorus donor ligands should be disfavored, in this case complexes stable at room temperature are obtained. Probably, the incorporation of phosphorus donor atoms into a chelating structure of a pincer-type ligand mitigates this difficulty, stabilizing the coordination at the metal by the formation of two five-membered metallacycles.

### Ring-Opening Polymerization Studies

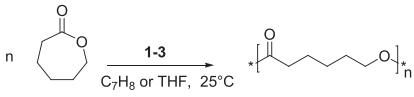
The ability of the heteroleptic complexes **1** and **2** to promote the ROP of ε-CL was examined (Scheme 2). The obtained polymers have been characterized by $^1$H NMR and gel permeation chromatography (GPC). The most representative results are summarized in Table 1. These data have been compared with the results previously reported for the analogous zinc complex **3** (see Scheme 1).

Both complexes **1** and **2** are efficient initiators for the ROP of ε-CL to give high-molecular-weight polymers.

The calcium amide complex **1** shows high efficiency in the ring-opening polymerization of ε-CL under mild reaction conditions and with a very low loading of initiator (5 μmol). A turnover frequency of 40 000 $h^{-1}$ (run 1 of Table 1) is achieved at room temperature.

The molecular weight distribution of the produced polymers is monomodal, although the measured $M_n$ values are twice the calculated $M_n$ values assuming the growth of one polymer chain per calcium initiator. This suggests that, possibly, only a fraction of the metal complex is involved in catalysis, most likely as a result of an inefficient initiation by the poor nucleophilic amide group.

Upon addition of one equivalent of isopropanol, a more efficient control on the molecular weights is achieved as demonstrated by the good agreement between the theoretical and experimental values (cf. runs 1 and 2 of Table 1). Reasonably, the isopropoxide initiating group, formed by alcoholysis of the amido group, mimics more efficiently the putative propagating group of the presumed active species; thus polymeric chains of predictable molecular weights and narrow molecular weight distribution are produced.




**Scheme 2.** Ring-opening polymerization of ε-CL initiated by complexes **1–3**.

**Table 1.** Ring-opening polymerization of ε-CL initiated by complexes 1–3[a]

| Run | Cat. | Solvent | $^{i}$PrOH (equiv.) | [ε-CL]/ [I] | Time (s) | Yield[b] (%) | $M_n^{c}$ $_{GPC}$($\times10^3$) | $M_n^{th\ d}$ ($\times10^3$) | $M_w/M_n^{c}$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | **1** | Toluene | — | 400 | 30 | 82 | 83.7 | 37.4 | 2.47 |
| 2 | **1** | Toluene | 1 | 400 | 30 | 100 | 45.0 | 45.7 | 1.29 |
| 3 | **1** | Toluene | 6 | 400 | 30 | 96 | 12.4 | 7.3 | 1.27 |
| 4 | **1** | Toluene | 10 | 500 | 180 | 100 | 16.2 | 5.7 | 1.31 |
| 5 | **1** | Toluene | 10 | 1000 | 180 | 100 | 27.3 | 11.4 | 1.52 |
| 6 | **1** | Toluene | 10 | 2000 | 240 | 98 | 43.1 | 22.4 | 1.44 |
| 7 | **1** | THF | — | 400 | 30 | 47 | 22.9 | 21.5 | 1.59 |
| 8 | **1** | THF | 1 | 400 | 40 | 76 | 40.6 | 34.6 | 1.27 |
| 11 | **1** | THF | 10 | 2000 | 240 | 47 | 20.4 | 10.7 | 1.15 |
| 12 | **2** | Toluene | — | 400 | 30 | 100 | 120.0 | 25.6 | 1.77 |
| 13 | **2** | Toluene | 1 | 400 | 30 | 100 | 47.8 | 45.6 | 1.13 |

[a]Reaction conditions : [I] =2.5 mM , 2 ml solvent, at 25°C.
[b]Conversion of ε-CL as determined by $^1$H NMR spectral data.
[c]Experimental $M_n$ (gmol$^{-1}$) and $M_w/M_n$ (PDI) values were determined by GPC in THF using polystyrene standards and corrected using a factor of 0.56.
[d]$M_n^{th}$ ( gmol$^{-1}$) = 114.14 × ([ε-CL]/[$^{i}$PrOH ]) × conversion ε-CL.

Upon addition of an excess of $^{i}$PrOH, complex **1** provides an efficient binary catalytic system for the 'immortal' ROP of ε-CL (runs 2–6, Table 1). The conversion of 2000 equiv. of monomer is achieved in few minutes at room temperature by using only 5 μmol of metal catalyst.

The molar masses of the obtained PCLs depend on the monomer/alcohol ratio, indicating that the number of polymer molecules increases proportionally to the equivalents of added alcohol. This suggests that the isopropyl alcohol acts as chain transfer agent and that the rate constant $k_{tr}$ for transfer between growing chains and resting alcohol molecules or the dormant hydroxy-end-capped polymer chains was far greater than that for chain propagation ($k_{pr}$; Scheme 3). In all cases the distribution of molecular weights is monomodal but the molecular weights are significantly higher than those theoretically calculated. Plausibly, in the presence of more than 1 equiv. of alcohol, the calcium complex **1** might lead to the formation of polynuclear species.[56]

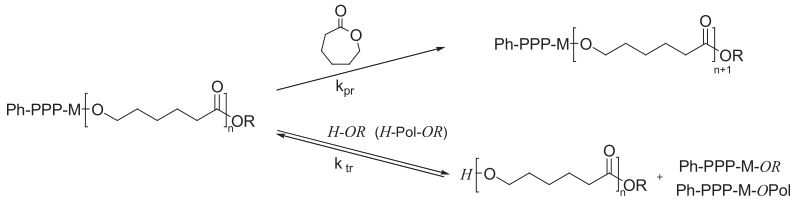
The polymerization of ε-CL shows a high solvent dependence. The use of THF as polymerization solvent decelerates the polymerization because it competes with monomer for metal coordination (cf. runs 1 and 7, Table 1). As already observed in toluene solution, in the presence of 1 equiv. of alcohol, a lightly increased polymerization activity is observed (cf. runs 1 and 7, Table 1) while, in the presence of more than 1 equiv., the agreement between the experimental $M_n$ values and the expected values is lost as a consequence of a plausible formation of polynuclear species.

Compound **1** shows no activity in $CH_2Cl_2$ solution under the same polymerization conditions, which could be due to the well-documented reactivity of calcium complexes toward chlorinated solvents. In general, calcium amide derivatives react with chlorinated hydrocarbon solvents, leading to chloro-metal complexes, presumably via initial deprotonation of the acidic protons of $CH_2Cl_2$ by the strong amide base.[38,44]

$^1$H NMR analysis of a low-molecular-weight PCL sample obtained by carrying out a polymerization experiment in the presence of 200 equiv. of monomer and 20 equiv. of isopropanol discloses the presence of isopropyl ester end groups (—COOCH$(CH_3)_2$; 1.26 and 5.00 ppm), generated via insertion of the monomer unit into the Ca—OCH$(CH_3)_2$ bond, and hydroxyl end groups ($CH_2CH_2OH$; 3.64 ppm), generated by hydrolysis of the growing chain (see Fig. 1).

These data suggest that, in the presence of isopropanol, the OiPr group is the only initiating moiety involved in the polymerization process; therefore, a coordination–insertion mechanism should be operative.

The parent magnesium complex **2** shows a similar activity to the heavier congener calcium (cf. runs 1 and 2 with runs 12 and 13, Table 1). The zinc complex **3** is intrinsically less active than its group II-based equivalents and the conversion of about 400 equiv. of monomer was obtained only after 6 h.[52] This is in line with the trend previously observed for these metals in the ROP of cyclic esters[37,38,46,57,58] and could be correlated with the expected degree of ionic or polar character of the M-X bond (X = initiating group). Moreover, according to DFT calculations, coordination of the monomer to the zinc reactive center is possible only after dechelation of one arm of the pincer ligand, while for the six-coordinated complexes **1** and **2** this might occur by an easy substitution of the coordinated solvent.




**Scheme 3.** ROP of ε-CL promoted by the binary catalytic systems **1–2**/$^{i}$PrOH.

## Polymerization of Lactide

Complexes **1** and **2** have also been assessed as initiators for the ROP of L-, D- and *rac*-lactide (Scheme 4). The obtained polymers have been characterized by NMR and GPC. The most representative results are summarized in Table 2.

In the ROP of lactide, the calcium complex **1** shows good activity. The conversion of 200 equiv.

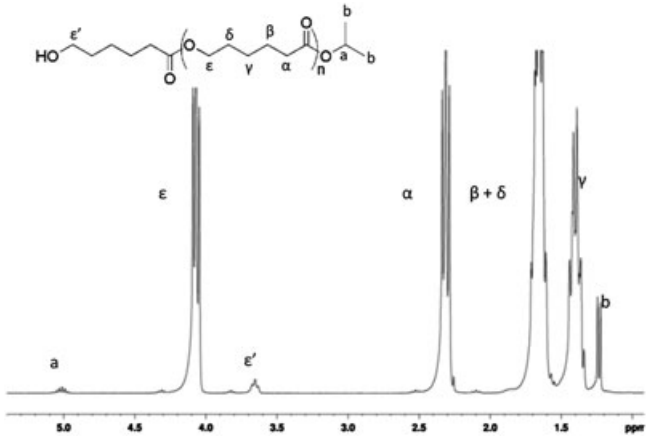



**Figure 1.** $^1$H NMR spectrum (400 MHz, $CDCl_3$, 25°C) of low-molecular-weight PCL. Reaction conditions: [ε-CL]/[**1**]/[$^i$PrOH] = 200:1:20, $T$ = 25°C, $t$ = 30 s.

of the monomer L-LA is achieved within 1 h, under mild polymerization conditions (room temperature in toluene solution; see run 14, Table 2). The same activity is observed in the polymerization of the enantiomer D-lactide (see run 18, Table 2), while a reduced reactivity is achieved in the presence of the racemic mixture (see run 19, Table 2).

Differently from that observed for the polymerization of ε-CL, the experimental $M_n$ values of the PLAs produced by **1** show narrow polydispersity indexes (PDIs ranging from 1.17 to 1.27) and they are also in good agreement with the $M_n$ values theoretically calculated. Reasonably, this might be a consequence of a lower propagation rate in comparison to the initiation rate.

The molecular weights $M_n$ of the resulting polymers increase linearly with the conversion (runs 14–16, Table 2). This further proves the controlled character of the polymerization reaction.

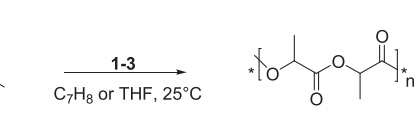
The tacticity of the resulting polymers has been investigated by examination of the methine region of the homonuclear decoupled $^1$H NMR spectra. The polymers obtained from the enantiopure monomers L- and D-LA (runs 14–18, Table 2) are isotactic; thus no epimerization of the stereogenic centers occurs in the course of polymerization. Atactic PLAs are obtained from racemic lactide (runs 19 and 23, Table 2) when either toluene or THF is used as polymerization solvent.

Kinetics studies show that the polymerization of L-LA by **1** follows a first-order dependence on the concentration of lactide, with an apparent propagation rate constant $k_{app} = 8.333 \times 10^{-2}$ min$^{-1}$ at 25 °C (Fig. 2).

Both calcium and magnesium complexes show lower activity in the ROP of lactide than that observed toward ε-CL, in agreement with the behavior commonly observed in the ROP of these monomers.[59,60] In the ROP of lactide, no significant differences, either in terms of activity or molecular weight control, are detected when an equivalent of alcohol is added to the initiator (run 17, Table 2).

Surprisingly, in the ROP of lactide, the reactivity of the zinc complex **3** is comparable to that of the group II metal initiators and is higher than that observed toward ε-CL.[61] The activity is further improved in the presence of 1 equiv. of alcohol. DFT calculations performed for complex **3** suggest that the difference in polymerization rates of the two monomers is attributable to the different coordination steps. In fact, coordination of lactide is energetically more favorable than that of caprolactone.

The parent complexes of the metals of group II are definitely higher Lewis acid than zinc and this should favor the coordination of the monomer but, at the same time, the high stability of the formed adducts should slow down the subsequent insertion step.




**Scheme 4.** Ring-opening polymerization of lactide initiated by complexes **1–3**.

**Table 2.** Ring-opening polymerization of lactides by **1–3**[a]

| Run | Cat. | Monomer | Time (min) | Yield (%) | $M_{n,GPC}$[b] ($\times 10^3$) | $M_{n,th}$[c] ($\times 10^3$) | $M_w/M_n$[b] |
|---|---|---|---|---|---|---|---|
| 14 | **1** | L-LA | 15 | 30 | 7.5- | 8.6 | 1.17 |
| 15 | **1** | L-LA | 30 | 61 | 15.5 | 17.6 | 1.17 |
| 16[d] | **1** | L-LA | 60 | 95 | 23.2 | 27.4 | 1.20 |
| 17 | **1** | L-LA | 60 | 97 | 24.1 | 28.8 | 1.17 |
| 18 | **1** | D-LA | 30 | 50 | 12.6 | 14.4 | 1.16 |
| 19 | **1** | *rac*-LA | 30 | 24 | 7.2 | 6.9 | 1.12 |
| 20 | **2** | L-LA | 30 | 94 | 29.8 | 26.5 | 1.27 |
| 21 | **3** | L-LA | 60 | 70 | 389.2 | 20.2 | 1.23 |
| 22[d] | **3** | L-LA | 20 | 91 | 8.8 | 8.7 | 1.05 |
| 23[e] | **1** | *rac*-LA | 60 | 12 | 3.0 | 3.1 | 1.03 |

[a]All reactions were carried out at 25°C with [**I**] = 2.5 mM ([LA]/[**I**] = 200 in 2 ml toluene.

[b]Experimental $M_n$ (corrected using a factor of 0.58) and PDI values were determined by GPC analysis in THF using polystyrene standards.

[c]Calculated $M_n$ of PLA (in gmol$^{-1}$) =144.14 × ([LA]/[$^i$PrOH] × conversion L-LA.

[d]One equivalent of $^i$PrOH was added.

[e]THF was used as solvent.

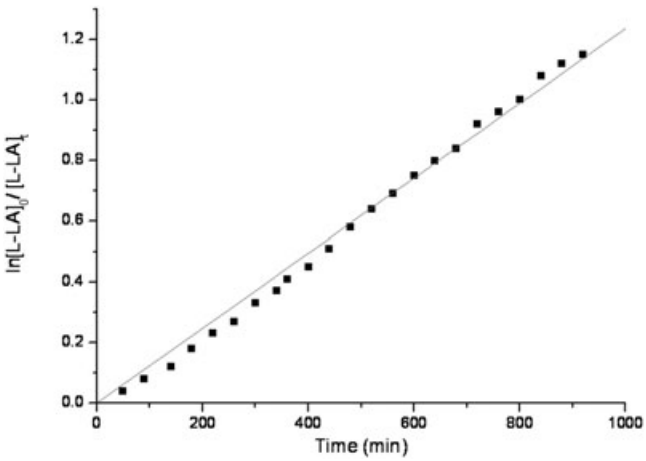



**Figure 2.** Pseudo-first-order kinetic plot for ROP of L-LA promoted by **1**. Pseudo-first-order rate constant $k_{app} = 8.333 \times 10^{-2} \pm 6.5 \times 10^{-4}$ min$^{-1}$ ($R$ = 0.9976). Reaction conditions: [**1**] = 8.3 mM, [L-LA]/[**1**] = 100; $C_7D_8$; $T$ = 25 °C.

## Conclusions

In this paper we report the synthesis and characterization of new calcium and magnesium complexes with a tridentate phosphido pincer ligand. Both complexes are stable in solution and no evidence of detrimental Schlenk-type equilibrium is detected. This demonstrates the ability of an uncommon coordination, such as a phosphorous-based pincer ligand, to efficiently coordinate the hard Lewis acid metals of group II.

Complexes **1** and **2** show excellent catalytic activity in the ROP of ε-CL in comparison to the parent zinc complex. Conversely, in the ROP of lactide the difference of reactivity among all complexes is less significant. Reasonably, because of the high Lewis acidity of the group II metals the insertion step is not favored. In all cases the polymerization reactions are well controlled and produce high molecular weight polymers.

## Experimental

### General Procedures: Materials and Methods

All manipulations of air- and/or water-sensitive compounds were carried out under dry nitrogen atmosphere using a Braun Labmaster glovebox or standard Schlenk line techniques. Glassware and vials used in the polymerization were dried in an oven at 120°C overnight and exposed to vacuum–nitrogen cycle three times. Hexane and THF (Carlo Erba) were purified by distillation from sodium benzophenone ketyl. Toluene (Carlo Erba) was purified by distillation from sodium. Anhydrous dibutyl magnesium (Aldrich) was used as received. All deuterated solvents were dried using molecular sieves. The proligand Ph—PPP—H was prepared according to published procedures.[53] Lactide (Aldrich) was purified by $P_2O_5$ and then by two subsequent crystallizations from hot toluene. After purification, lactide was stored at – 20 °C under the inert atmosphere of the glovebox. ε-Caprolactone (Aldrich) was dried with $CaH_2$ for 24 h at room temperature, then distilled under reduced pressure and kept over activated 3 Å molecular sieves. All other chemicals were commercially available and used as received unless otherwise stated.

The metal precursor $Ca[N(SiMe_3)_2]_2.THF_2$ was prepared as described elsewhere.[57,62]

### Instruments and Measurements

NMR spectra were recorded on Bruker Avance 400 spectrometer ($^1$H, 400.00 MHz; $^{13}$C, 100.62 MHz; $^{31}$P 161.97 MHz) at 25°C, unless otherwise stated. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., and degassed and dried over activated 3 Å molecular sieves prior to use. Chemical shifts ($\delta$) are listed as parts per million and coupling constants ($J$) in hertz. $^1$H NMR spectra are referenced using the residual solvent peak at $\delta$ 7.16 for $C_6D_6$ and $\delta$ 7.27 for $CDCl_3$. $^{13}$C NMR spectra are referenced using the residual solvent peak at $\delta$ 128.39 for $C_6D_6$ and $\delta$ 77.23 for $CDCl_3$. $^{31}$P NMR spectra are referenced externally using 85% $H_3PO_4$ at $\delta = 0.00$.

Molecular weights ($M_n$ and $M_w$) and the molecular mass distribution ($M_w/M_n$) of polymer samples were measured by GPC at 30°C, using THF as solvent, flow rate of eluent 1 ml min$^{-1}$ and narrow polystyrene standards as reference. The measurements were performed on a Waters 1525 binary system equipped with a Waters 2414 RI detector using four Styragel columns (range 1000–1 000 000 Å). Every value was the average of two independent measurements. It was corrected using the factor of 0.58 for polylactide and 0.56 for polycaprolactone according to the literature.[63–65] Elemental analyses were performed in the microanalytical laboratory of the institute.

### Synthesis of [(*o*-$C_6H_4PPh_2)_2PCa(NSiMe_3)_2(THF)_2$] (1)

A benzene solution (3 ml) of Ph—PPP—H ligand (0.170 g, 0.31 mmol) was added slowly to a benzene solution (2 ml) of $[Ca(NSiMe_3)_2(THF)_2]$ (0.152 g, 0.31 mmol) to give a red solution. After being stirred for 60 min, all volatiles were removed under vacuum, and the residue red solid was washed with cold hexane and then dried up at reduced pressure for 3 h (yield 0.266 g, 98%. The crude solid was recrystallized from hexane at −20°C to obtain a microcrystalline powder (yield after crystallization 63.4%).

$^1$H NMR (400 MHz, $C_6D_6$, 298 K): $\delta$ 7.92 (m, 2H, C*H* phenyl (*a*)), 7.51 (t, $^3J_{H-H} = 8$ Hz; 2H, C*H* phenyl,(b)), 7.24 (t, $^3J_{H-H} = 8$ Hz; 8H, C*H*, *ortho* Ph)), 7.10–7.01 (m, 2H, C*H*, phenyl (d)), 6.96–6.88 (m, 12 H, C*H*, *para* and *meta* Ph)), 6.66 (t, $J_{H-H} = 8$ Hz; 2H, phenyl (c)), 3.56 (m, 8H, α $CH_2$ of THF), 1.30 (m, 8H, β $CH_2$ of THF), 0.08 (s, 18H, Si(*CH*)$_3$).

$^{13}$C{$^1$H} NMR (100.62 MHz, $C_6D_6$): $\delta$ 166.5 (td, $J_{C-P} = 43$ Hz, $J_{C-P} = 22$ Hz, $C_{ipso}$—P (phosphido)), 138.1 (dt, $J_{C-P} = 23$ Hz, $J_{C-P} = 4$ Hz, *C*H, Ph), 136.2 (td, $J_{C-P} = 48$ Hz, $J_{C-P} = 20$ Hz, $C_{ipso}$—$PPh_2$) 134.2 (t, $J_{C-P} = 7$ Hz, *C*H; Ph), 131.8 (d, $J_{C-P} = 6$ Hz, *C*H; Ph), 132.5 (t, $J_{C-P} = 6$ Hz, *C*H; Ph), 132.0 (m, $C_{ipso}$—P (phosphine)), 130.2 (s, CH; Ph), 128.4 (d, $J_{C-P}$ =7 Hz, CH, Ph), 127.8 (s, CH; Ph), 70.1 (s, 4C, α-THF), 25.7 (s, 4C, β-THF), 2.3 (s, 6C, NSi(*CH*$_3$)$_3$).

$^{31}$P NMR (161.97 MHz, $C_6D_6$, 298 K): $\delta$ −4.96 (d, 2 P, $^3J_{P-P} = 109$ Hz), −10.2 (t, 1 P, $^3J_{P-P} = 109$ Hz).

Elemental analysis (%) calcd for $C_{50}H_{62}CaNO_2P_3Si_2$: C, 66.86; H, 6.96; N, 1.56; found: C 66.93, H 6.81; N, 1.52.

### Synthesis of [(*o*-$C_6H_4PPh_2)_2PMg^nBu$ $(THF)_2$ (2)

A benzene/THF solution (3 ml/1 ml) of Ph—PPP—H ligand (0.518 g, 0.9 mmol) was added slowly to a solution (0.9 ml of a 1 M solution in heptane) of $Mg^nBu_2$ 0.1 M, to give a deep-orange solution. After stirring for 60 min, all volatiles were removed under vacuum, and the residue red solid was washed with cold hexane, and then dried up at reduced pressure for 3 h (yield 0.820 g, 93%). The crude solid was recrystallized from hexane at −20°C to obtain an orange crystalline powder.

$^1$H NMR (400 MHz, $C_6D_6$, 298 K): $\delta$ 7.80 (m, 2H, C*H* phenyl (*a*)), 7.47 (m; 8H, *CH*, *ortho* Ph), 7.21 (t, $^3J_{H-H} = 4$ Hz; 4H, C*H* *para* Ph), 7.10–6.94 (m, 12H, *CH*, *CH* *para* Ph, C*H* phenyl (*b* and *d*)), 6.71 (t, $J_{H-H} = 7$ Hz; 2H, phenyl (c)), 3.56 (m, 8H, α $CH_2$ THF), 1.30 (m, 8H, β $CH_2$ THF), 1.57 (m, 2H, Mg—$CH_2$ $CH_2$ $CH_2CH_3$), 1.12 (t, 3H, Mg—$CH_2$ $CH_2$ $CH_2CH_3$), 0.19 (m, 3H, Mg—$CH_2$—$CH_2$—$CH_2$ $CH_3$), −0.12 (t, 2H, Mg—$CH_2$).

$^{13}$C{$^1$H} NMR (100.62 MHz, $C_6D_6$, 298 K): $\delta$ 152.3 (td, *C*—P, $J_{C-P} = 33$ Hz, $J_{C-P} = 21$ Hz, $C_{ipso}$—P (phosphido)), 136.2 136.1 136.2 (td, $J_{C-P} = 31$ Hz, $J_{C-P} = 20$ Hz, $C_{ipso}$—$PPh_2$), 134.6, 132.1, 130.4, 129.9, 128.7, 126.0, 67.9 (s, 4C, α-THF), 31.6 (Mg—$CH_2$—$CH_2$—), 31.4 (Mg—$CH_2$—$CH_2$—$CH_2$), 25.4 (s, 4C, β-THF), 14.2 (Mg—$CH_2$—$CH_2$—$CH_2$—$CH_3$), 7.8 (Mg—$CH_2$).

$^{31}$P NMR (161.97 MHz, $C_6D_6$, 298 K): $\delta$ −10.7 (d, 2 P, $^3J_{P-P} = 147$ Hz), −41.4 (t, 1 P, $^3J_{P-P} = 147$ Hz).

Elemental analysis (%) calcd for $C_{50}H_{62}MgNO_2P_3Si_2$: C, 68.05; H, 7.08; N, 1.59; found: C 67.92, H 6.91; N, 1.53.

### Polymerization Experiments

*General procedures for the polymerization of caprolactone and lactides*

In a Braun Labmaster glovebox, a 4 ml vial was charged with a solution of metal initiator (5.0 μmol) in the appropriate solvent (0.5 ml), to which the alcohol was eventually added, and the resulting solution was rapidly added to a solution of the monomer in the same solvent (1.5 ml). The mixture was immediately stirred with a magnetic stir bar at 25°C for the predicted time. After specified time intervals an aliquot of the crude material was sampled by pipette and quenched in wet $CDCl_3$. The sample was subjected to monomer conversion determination, which was monitored by integration of monomer versus polymer in $^1$H NMR spectra. The reaction mixture was quenched with wet *n*-hexane. The precipitates collected from the bulk mixture were dried in air, dissolved with dichloromethane and sequentially precipitated into methanol. The obtained polymer was collected by filtration and further dried in a vacuum oven at 60°C for 16 h.

*Kinetic experiments*

In a typical experiment carried out in a Braun Labmaster glovebox, the initiator solution (4 μmol in 0.5 ml of $C_7D_8$) was injected into a Teflon-valved J. Young NMR tube loaded with the solid monomer (100 equiv.). The sample was thermostated at the required temperature. The polymerization reaction was monitored via $^1$H NMR analysis from the integration of polymer and monomer signals. The characteristic chemical shift for lactide monomer in deuterated toluene is 4.12 ppm (q, CH; lactide); for the corresponding polymer it is 5.12 ppm (q, CH; polylactide).

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