Macrocyclic Dizinc(II) Alkyl and Alkoxide Complexes: Reversible CO₂ Uptake and Polymerization Catalysis Testing

Charles Romain, Michael S. Bennington, Andrew J. P. White, Charlotte K. Williams, and Sally Brooker

Supporting Information

ABSTRACT: The synthesis of three new dizinc(II) complexes bearing a macrocyclic [2 + 2] Schiff base ligand is reported. The bis(anilido)tetraimine macrocycle reacts with diethylzinc to form a bis(ethyl)dizinc(II) complex, \([\text{LEt}_2\text{Zn}_2\text{Et}_2]\) (1). The reaction of complex 1 with isopropyl alcohol is reported, forming a bis(isopropyl alkoxide)dizinc complex, \([\text{LEt}_2\text{Zn}((\text{PrO})_2)]\) (2). Furthermore, complex 1, with 2 equiv of alcohol, is applied as an initiator for racemic lactide ring-opening polymerization. It shows moderately high activity, resulting in a pseudo-first-order rate constant of \(9.8 \times 10^{-3}\) min⁻¹, with [LA] = 1 M and [initiator] = 5 mM at 25 °C and in a tetrahydrofuran solvent. Polymerization occurs with good control, as evidenced by the linear fit to a plot of molecular weight versus conversion, the narrow dispersities, and the limited transesterification. The same initiating system is inactive for the ring-opening copolymerization of carbon dioxide (CO₂) and cyclohexene oxide at 80 °C and 1 bar of CO₂ pressure. However, stoichiometric reactions between complex 2 and CO₂, at 1 bar pressure, result in the reversible formation of new dizinc carbonate species, \([\text{LEt}_2\text{Zn}((\text{PrO})_2)]\) (3a) and \([\text{LEt}_2\text{Zn}((\text{PrO}CO_2))_2]\) (3b), and the reaction was studied using density functional theory calculations. All of the new complexes, 1–3b, are fully characterized, including NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction.

INTRODUCTION

The synthesis of dinuclear zinc(II) complexes is relevant for an understanding of the coordination chemistry and for applications as models for the active sites for various metalloenzymes or in catalysis. In polymerization catalysis, dizinc complexes have proven to be highly effective for both ring-opening polymerization (ROP) of lactones and ring-opening copolymerization (ROCOP) of carbon dioxide (CO₂) and epoxides. Both processes are societally relevant because they enable renewable resources to be used in the synthesis of useful, commodity materials. In the case of lactide polymerization, the monomer derives from lactic acid, which is harvested from various plants, including sugar cane, maize, and rice. The product, polylactide (PLA), is attracting significant commercial attention as a renewable alternative to petrochemicals, such as polyolefins, for applications in packaging, fibers as well as for specialist medical applications. A recent review highlights some current challenges and opportunities in PLA catalysis. ROCP of CO₂ and epoxides is also a sustainable process because it allows the partial replacement of epoxides, which have a high embedded energy, with CO₂, resulting in a lowering of the environmental footprint for the product polyls. It has recently been shown that CO₂ captured from a power station can be applied in the process. The polyls are proposed to be suitable for use in the preparation of polyurethanes, which are ubiquitous in foam, adhesive, and elastomer applications. Both polymerizations require the application of an initiator, which mediates the rate, selectivity, and properties of the resulting materials.

Currently, some of the most promising initiators for these polymerizations are homogeneous dinuclear zinc complexes, due, in part, to high rates of reaction, good selectivities, and favorable properties of the metal ion, including a lack of color, redox chemistry, relatively high abundance, and lower toxicity. Considering the CO₂/cyclohexene oxide ROCOP, the first reports describing zinc complexes date back to the inception of the field and the use of diethylzinc, with protic reagents, to prepare in situ the so-called “initiating system”. Such systems are ill-defined mixtures of zinc alkyl, hydroxide, and cluster complexes; they showed low rates. In the intervening decades, many better and well-defined homogeneous complexes have been reported. For example, Darenbourg and co-workers pioneered the application of zinc phenolate catalysts, which showed moderate rates but could be fully characterized. Coates and co-workers made a major advance when

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they reported single-site zinc $\beta$-(diiminate) complexes, A (Chart 1), the best of which has a turnover frequency (TOF) of 730 h$^{-1}$ (7 bar, 50 °C). In a detailed study of the initiator kinetics, it was proposed that the most active catalysts are loosely associated dimeric complexes and that a dinuclear mechanism may be operative. In 2005, Lee and co-workers reported bis(anilido)aniline dizinc complexes, B (Chart 1), which showed a TOF of 290 h$^{-1}$ (12 bar, 80 °C). In 2009, some of us reported a dizinc macrocyclic complex, C (Chart 1), which showed a moderate TOF of 25 h$^{-1}$ (1 bar, 80 °C) but was able to operate at just 1 bar of CO$_2$ pressure.

Subsequently, we have investigated various other metal complexes of this macrocycle and shown that high TOF values of $\sim$5000 h$^{-1}$ can be obtained using dimagnesium catalysts. A number of researchers tethered together zinc $\beta$-diiminate complexes in order to overcome the entropy limitations of dimeric catalysts. The geometry and structure of the tethering group were shown to be very important, with a number of well-characterized complexes being reported by various groups as unreactive, while Rieger and co-workers proposed that using flexible tether groups was important. Indeed, earlier this year, Rieger and co-workers optimized the design strategy for such tethered $\beta$-diiminate catalysts, D (Chart 1), and were able to record a “record-breaking” TOF of 155000 h$^{-1}$ (30 bar, 100 °C). Thus, there is considerable interest and potential for the development of new ligand scaffolds that direct dizinc coordination and that may yield further insight into the features required for successful catalysis.

## RESULTS AND DISCUSSION

Here, a 22-membered Schiff base macrocycle, H$_2$LEt$^\text{Et}$ (Figure 1), featuring tetraimine and diphenylamine moieties, was selected for investigation because some of us had reported success in forming dinuclear complexes with transition metals, research done with the expectation that such macrocycles could be a good scaffold for new generations of dinuclear catalysts. The ligand was synthesized via the [2 + 2] condensation of diphenylamine-2,2’-dicarboxaldehyde with diaminoethane, according to the methods previously reported. Previously, this type of macrocycle was shown to form dinuclear complexes, and related smaller macrocycles to form mononuclear complexes, whereby the diphenylamine NH moieties...
are deprotonated, with metal ions including zinc(II), copper(II), nickel(II), iron(II), and cobalt(II).50,51,53–56

However, most of these previous complexes either have been cationic species or were prepared in aqueous media: both features are unsuitable for polymerization catalysis. Hence, our approach here was to deliberately target neutral d zinc complexes of the form \([\text{LEt}^2 \text{Zn}_2 \text{X}_2]\), where \(X\) is a suitable initiating group for polymerization, such as an alkyl, alkoxide, or carbonate group. Zinc(II) was selected because of its strong precedence in various ROP and ROCOP catalyses and for ease of complex characterization.

In order to prepare anhydrous dizinc(II) complexes, \(\text{ZnEt}_2\) was selected as a suitable reagent because it both enables clean in situ deprotonation of the aniline groups (releasing ethane gas) and delivers the desired ethylzinc(II) moiety to the resulting anionic \(\text{N}_3\)-donor coordination “pocket”. The addition of 2 equiv of \(\text{ZnEt}_2\) to a suspension of the macrocycle, in tetrahydrofuran (THF), led to clean formation of a dizinc bis(alkyl) complex, \([\text{LEt}^2 \text{Zn}_2 \text{Et}_2]\) (1), in high yield (87%) (Figure 1). The \(^1\text{H NMR spectrum (25 °C, C}_6\text{D}_6)\) of 1 is consistent with the formation of two rigid (N,N,N)-zinc chelates. Some notable features of the \(^1\text{H NMR spectrum include (a) the complete absence of signals assigned to the NH proton (δ_{NH} = 11.90 ppm; Figure S4) consistent with the formation of anilido donors, (b) a significant shift of the resonance assigned to the imine protons to lower chemical shifts, consistent with all four imines being coordinated to the two zinc(II) centers (from 8.28 ppm for H_2L to 7.36 ppm for 1), and (c) a highly symmetric solution structure, indicative of a \(C_2\) symmetric complex. In fact, the \(^1\text{H NMR spectrum shows one imine resonance, four aromatic resonances, two multiplets for the diasterotopic methylene protons on the linker group and equivalent ethyl groups (Figures S1–S3). In contrast, the \(^1\text{H NMR spectrum in THF-d}_4 (25 °C) indicates that there are two isomeric complexes, present as major (~85%) and minor (~15%) species; both show highly symmetric structures. This is tentatively attributed to the coordination of THF at the zinc centers, leading to different ligand conformations (Figure S5). Variable-temperature (VT) \(^1\text{H NMR analyses over the range −80 and +70 °C showed a significant broadening of all of the ligand signals at around −60 °C, suggesting that there may be an equilibrium between the two isomers (Figure S6). Next, it is important to establish the thermal stability of 1 because polymerization will be conducted at 80 °C. Thus, a solution of 1 (C_6D_6) was maintained, under an inert atmosphere, at 80 °C for 16 h. No significant changes to the \(^1\text{H NMR spectrum were observed. This is rather different from the results reported by Dagorne and co-workers for \([(\text{BIAN})\text{ZnEt}]\) complexes, where the addition of ethyl groups to the ligand imine moieties was observed.57 In this case, the macrocyclic complex showed good stability and thus has the potential to be applied as a polymerization catalyst.

**X-ray Crystallography.** Dark-orange crystals of complex 1-C_6H_6 were obtained by hexane diffusion into a benzene solution, and the structure was determined (Figure 2).

The two zinc(II) centers are coordinated in the two tridentate \(N_3\)-donor “pockets” of the macrocycle, with each bound to a deprotonated secondary amine nitrogen atom (\(\text{N}_{\text{anilido}}\)) and the two flanking imine nitrogen atoms (\(\text{N}_{\text{imine}}\)). Each zinc center is also coordinated to the ethyl ligand, giving overall a \(CN_3\)-donor environment. In contrast to the solution structures, the macrocycle binds the zinc(II) centers slightly asymmetrically, with one longer [2.119(2) and 2.103(2) Å] and one shorter [2.022(2) and 2.041(2) Å] Zn−N_{anilido} bond. As anticipated, the zinc(II) centers exhibit somewhat distorted tetrahedral coordination environments, with \(\tau_g = 0.78\) and 0.80.58 This contrasts with the copper(II) centers in the previously reported \([\text{LEt}^2\text{Pr}/\text{Cu}^2\text{(OAc)}_2]_2\) derivatives (22-, 24-, and 26-membered, respectively), which have \(\tau_g = 0.31−0.41\), consistent with distorted square-planar geometries.50 In the solid-state structure of 1, the macrocycle retains a flat overall conformation, and the two zinc(II) centers sit above their respective \(N_3\)-donor planes, on the same side of the macrocycle, by 1.009 Å (Zn1) and 1.022 Å (Zn2). Because of the flat macrocycle conformation, the Zn−Zn distance is 5.0270(4) Å, whereas the Cu−Cu distance was 3.6072(8) Å in the more folded \([\text{LEt}^2\text{Pr}/\text{Cu}^2\text{(OAc)}_2]_2\) complex, showing the high flexibility and adaptability to different metal centers of this macrocyclic ligand. Recently, Rieger and co-workers have reported a series of flexibly tethered bis(β-diminate) dinceral zinc complexes, some of which show unprecedented high activities in CO_2/epoxide copolymerization catalysis (Chart 1).39,41,42 In the solid-state structure reported for one of those catalysts, there is a large intermetallic separation, 7.7 Å; however, calculations have shown that the flexibility of the ligand allows separations of 5−5.5 Å to be achieved for some of the key proposed polymerization intermediates.51 In our previous work, using phenolate or thiophenolate macrocycle ancillary ligands, the solid-state structures show Zn−Zn separations of 3.03−3.07 Å,39,40

**Polymerization Catalysis.** Complex 1 was tested for activity in CHO/CO_2 copolymerization reactions, using 2 equiv

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**Figure 1.** Synthesis of dinuclear zinc complex 1. Reagents and conditions: (a) 2 Et_2Zn, THF, −40 to +25 °C, 16 h.

**Figure 2.** Molecular structure of 1 (for clarity, hydrogen atoms and benzene of solvation are not shown).
of alcohol as the initiating group. The polymerizations were run at 1 bar of CO2 pressure and 80 °C and in neat CHO (catalyst loading of 0.1 mol %). However, under these conditions, only the starting epoxide was observed (Table S1).

Dinuclear zinc(II) complexes have also previously been reported for ROP of cyclic esters;43–48,61 therefore, 1 was also tested for ROP of rac-LA (Figure 3 and Table 1). Complex 1 showed good activity using 2 equiv of isopropyl alcohol, at a 1 equiv/catalyst concentration (Figure 4), with the experimental monomer conversion (Figure 4), with the experimental

Figure 3. ROP of rac-LA initiated by 1. Reagents and conditions: (a) catalyst 1 (1 equiv), isopropyl alcohol (2 equiv), rac-LA (200 equiv), THF, 25 °C, and 80 min.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes 1, 2, 3a-I, and 3a-II

|          | 1  | 3a-I | 3a-II |
|----------|----|------|-------|
| Zn1−N1  | 2.023(17) | 2.180(2) | 2.166(3) |
| Zn1−N9  | 2.005(18) | 2.013(2) | 1.986(2) |
| Zn1−N17 | 2.116(16) | 2.187(2) | 2.200(3) |
| Zn2−N20 | 2.040(17) | 2.191(2) | 2.179(2) |
| Zn2−N28 | 1.999(18) | 2.011(2) | 1.997(2) |
| Zn3−N36 | 2.103(18) | 2.209(2) | 2.154(2) |
| Zn1−C39 | 1.991(2)  |  |  |
| Zn2−C41 | 1.988(4)  |  |  |

Because of symmetry, the numbering scheme for 3a-II is inconsistent with the other complexes, so the closest equivalent alternatives have been used. Bond lengths unreliable because of disorder; see the Supporting Information for more details.

showed good activity using 2 equiv of isopropyl alcohol, at a 1 M concentration of rac-LA in THF, 5 mM concentration of catalyst (1:200 loading catalyst/lactide), and 25 °C. The complex was an efficient catalyst, converting >78% of rac-LA to polymer within ~1 h at room temperature. The atactic PLA had a molecular weight (MW) in close agreement with the value predicted on the basis of the catalyst concentration, assuming that both zinc sites initiate chain growth, and the MW distribution was narrow (D < 1.10).

The matrix-assisted laser desorption ionization time-of-flight (MALDI-ToF) spectrum of the resulting PLA confirmed the absence of significant transesterification side reactions, as shown by a single series of peaks separated by 144 amu, corresponding to rac-LA units (Figure S7). The spectrum also confirmed the isopropoxide chain end group, in accordance with a coordination–insertion mechanism. The polymerization was monitored by taking regular aliquots; there was a linear correlation between the PLA molecular weight (Mn) and monomer conversion (Figure 4), with the experimental molecular weight closely matching the theoretical value. The plot of ln([LA]0/[LA]) versus reaction time, monitored from 20 to 80% monomer conversion, shows a linear fit, in accordance with a first-order dependence of the rate on the monomer concentration (Figure 4). The gradient represents the pseudo-first-order rate coefficient, kobs = 9.8 × 10−3 min⁻¹, the value of which is within the range observed for other good/fast catalysts, under the same conditions.30,11,22 The catalyst does show a clear induction period, from 0 to 20% conversion, during which there would be a nonlinear fit to the data. It is proposed that, during this period, formation of the alkoxide species occurs at a rate concurrent with polymerization, indeed such effects have been observed by others in rac-LA ROP.62,63

Zinc Alkoxide Complex. In order to get a better understanding of the behavior of complex 1 in both polymerization studies, formation of the true propagating species was targeted. In rac-LA ROP, the propagating species is proposed to be a zinc alkoxide derivative, formed in situ by reaction with alcohol, while for the CO2/CHO ROCOP, the intermediates would be zinc alkoxide and carbonate species. Initially, the reaction of 1 with isopropyl alcohol (PrOH) to form the alkoxide initiating group was studied (Figure 5). Whereas 1 slowly reacts with PrOH (2.2–10 equiv vs 1) in THF or C6D6 at 25 °C, upon heating of the mixture to 60 °C, there is essentially quantitative formation of the corresponding alkoxide derivative, [L3Zn(PrO)2] (2), as determined by 1H NMR spectroscopy (Figure S8).

Interestingly, 1H NMR spectroscopic monitoring of the reaction showed that, at room temperature, there were new signals around 12.0 ppm, attributed to the formation of NH moieties and consistent with the alcohol protonating the ancillary ligand rather than reacting with the zinc-bound alkyl groups. This is in line with the remaining characteristic high field signals attributed to the zinc-coordinated ethyl groups, at 0.41 ppm; only minor traces of ethane (0.85 ppm) can be observed. After heating of the reaction to 60 °C for 2 h, there was quantitative conversion to a single product, along with the formation of significant quantities of ethane. The 1H, 13C, and 1H−13C HSQC/HMBC spectra (Figure S10) are consistent with the product being the dizinc bis(isopropoxide) complex 2 (Figure 5). The 1H NMR spectrum shows the expected ligand signals, with significant broadening of the methylene signals in the tether group, as well as signals characteristic of the zinc-coordinated isopropoxide group (3.8, 0.60 and 0.61 ppm). The 13C NMR spectrum confirms the assignment of the alkoxide signals (63.4 and 28.1 ppm). Complex 2 has a high symmetry in solution, with just one peak being observed for the imine protons plus four aromatic signals. In addition, signals characteristic of the NH moieties are absent. On the basis of the in situ NMR monitoring, it is proposed that the zinc alkoxide derivative 2 forms by a two-stage process in which the initial reaction with alcohol protonates the anilido group, and in the second step, intramolecular deprotonation of the NH moiety by the zinc-bound ethyl group occurs. Complex 2 can be successfully synthesized in THF and isolated on a preparative scale in 30% yield. The molecular structure of 2 (Figures 5 and 6) has been confirmed by X-ray diffraction (XRD) studies on crystals obtained by hexane diffusion in a THF solution.

All bonding and geometrical parameters for complex 2 (Table 1) are as expected and are in line with those of the structure of complex 1. Each of the two zinc(II) centers is contained in a tridentate N3 binding pocket, binding through...
the deprotonated amine and two imine nitrogen atoms. The zinc(II) centers are also coordinated to two μ²-bridging oxygen atoms from the two isopropoxide ligands, leading to distorted five-coordination N₃O₂-donor environments (τ₅ = 0.47 and 0.48). Interestingly, complex 2 features a more planar central structure than complex 1, with the zinc(II) centers lying close to their respective N₃ planes (0.020−0.075 Å out-of-plane compared to 1.009−1.022 Å) and the two N₃ planes inclined by only ca. 10.6−15.2° compared to 28.5° in 1.

**Zinc Carbonate Complex.** ROCOP of CHO/CO₂ was not found to be successful using catalyst 1 with 2 equiv of alcohol. It is expected that complex 1 reacts with isopropyl alcohol, under the conditions of catalysis (80 °C), to yield the alkoxide derivative 2, from which propagation can occur. Thus, it was of interest to establish the reactivity of complex 2 toward
a CO₂-free atmosphere, by diffusion of hexane into a THF solution of the complex, under a N₂ atmosphere. It may be that, in the absence of a CO₂ atmosphere, there is a tendency for decarbonylation to form 3a. In line with this proposal, degassing a solution containing 3b, with subsequent removal of the volatile products, leads to formation of the bis(alkoxide) complex 2, along with minor traces of decomposition products. These results suggest that there is an equilibrium between the alkoxide and carbonate species that can be perturbed by both temperature and CO₂. Indeed, related reversible CO₂ insertion was also observed by Coates and co-workers using zinc β-diiminate alkoxide complexes, although in that case, a higher pressure of CO₂ was required to access the carbonate.²⁸ Here, it is notable that the macrocycle complex is able to rapidly, and reversibly, insert CO₂ at 1 bar of pressure. In addition, the reaction of the zinc ethyl complex 1 with excess isopropyl alcohol (10 equiv) and 1 bar of CO₂ pressure leads to the same carbonate products as those obtained by reaction of the isolated alkoxide derivative 2 with CO₂. This suggests that formation of the carbonate species is likely to occur during the attempted catalysis using 1 and the failure to function as a catalyst relates to the reaction between the carbonate and epoxide rather than a failure to insert CO₂. Another interesting observation is the isolation of crystals of the zinc carbonate–alkoxide complex. In the previous study of CO₂ in a zinc alkoxide derivative, Coates and co-workers isolated a carbonate–alkoxide complex also [rather than the bis(carbonate) species].²⁸ They proposed that this species was a resting state in catalysis, and this was subsequently supported by a detailed theoretical study carried out by Rieger and co-workers, using the tethered β-diiminate complexes, which showed a high stability for such mixed carbonate–alkoxide intermediates.¹¹

The structure of 3a was found to contain two crystallographically independent complexes, 3a-I and 3a-II. While complex 3a-I sits in a general position, complex 3a-II is situated across a C₂ axis (which bisects the Zn₃–Zn₃A, N61–N61A, and N77–N77A vectors). Unfortunately, both the isopropoxide and carbonate bridging ligands are disordered about this axis, rendering the Zn–O bond lengths unreliable. Otherwise, all bonding and geometrical parameters for complexes 3a-I and 3a-II are as expected and are in line with those of the structure of complex 2, featuring a relatively planar central structure and twisted phenyl rings (57.52°–64.62°).

Overall, the most obvious difference across all four complexes is a marked change in the conformation of the N₆ macrocycle on going from terminal coligands in 1 (Figure 2) to bridging coligands in 2 (Figure 6) and 3a-I/3a-II (Figure 8). The length and width of the macrocycle as measured by the N9–N28, N1–N7, and N20–N36 separations are given in Table 1 and show how the introduction of bridging ligands shortens and widens the macrocycle in 2 and 3a-I/3a-II compared to the conformation with terminal coligands seen in 1 [N9–N28 (head units) = 8.339(3) Å in 1 compared to 6.960(3)–7.330(5) Å in 2 and 3a-I/3a-II; imines N1–N17 and N20–N36 = 3.386(2) and 3.352(2) Å in 1 compared to 4.319(4)–4.386(3) Å in 2 and 3a-I/3a-II]. The acetate coligands in the previously reported [L²⁺(Pr/Bu)Cu₂²⁺(OAc)₂] derivatives are terminal not bridging, so similar to complex 1, the head unit N···N separations are long, ranging from 5.211 to 8.201 Å, while the linker is increased, and correspondingly the Cu···Cu separations range from 3.607 to 5.265 to 5.838 Å: the pairs of imine N···N separations for these three complexes fall in a tighter range, 3.810–3.827 Å.³⁰ Associated with the change from terminal to bridging coligands is a shortening of the Zn···Zn separation from 5.0270(4) Å in 1 to 2.9448(8) Å in 2, 3.2062(5) Å in 3a-I, and 3.3373(8) Å in 3a-II. In each of 1, 2, and 3a-I/3a-II, the Zn–N bonds to the amino nitrogen atoms N9 and N28 are shorter than those to the imino nitrogen atoms N1, N17, N20, and N36, as was seen in the previously reported [L²⁺(Pr/Bu)Cu₂²⁺(OAc)₂] complexes.³⁰

Figure 8. Structure of one (3a-I) of the two independent complexes present in the crystal of 3a.
and across 2 and 3a-I, the Zn–O bonds to the alkoxide ligands are shorter than those to the carbonate ligand (with 3a-II excluded because of the disorder discussed above).

In order to get a better understanding of the insertion of CO₂ into the zinc alkoxide bonds, a theoretical study using DFT calculations was carried out. The free energy profile, including the key transition states, was calculated for the reaction between 2 and 2 equiv of CO₂ (Figures 9 and 10). The calculations were carried out using the protocol \( \omega \text{b97XD/6-31G(d)/scrf(cpcm = benzene)} \); 298 K.

Figure 9. Potential energy surface for the first CO₂ insertion reaction between 2 (labeled I here) and one CO₂ molecule, forming 3a (labeled VIIb here). The ancillary ligand structure is omitted for clarity. DFT protocol: \( \omega \text{b97XD/6-31G(d)/scrf(cpcm = benzene)} \); 298 K.

Figure 10. Potential energy surface for the second insertion reaction between 2 and one CO₂ molecule, i.e., insertion of one CO₂ into 3a to form 3b (labeled Xc here). The ancillary ligand structure is omitted for clarity. DFT protocol: \( \omega \text{b97xd/6-31G(d)/scrf(cpcm = benzene)} \); 298 K.
was calculated from the atomic coordinates available from the solid-state structure of 2. The CO₂ approach to one of the faces of the complex concomitantly leads to decoordination of one of the bridging alkoxide groups to form intermediate IV via III-TS at ΔG = ±20.2 kcal mol⁻¹ (see Figure S14). The calculations suggest that there are noncovalent interactions between CO₂ and the zinc imine moiety, which orients the CO₂ orthogonal to the alkoxide group (see Figure S15).

It is notable that decoordination of the μ-alkoxide group to form IV is thermodynamically unfavorable, reinforcing the relative stability of I (compound 2). However, the favorable orientation of CO₂ in intermediate IV facilitates access to the transition state V-TS (ΔΔG = +4.5 kcal mol⁻¹; overall barrier ΔG = +22.9 kcal mol⁻¹), where the alkoxide group attacks the carbon atom of CO₂. Concurrently, the CO₂ molecule rotates so as to allow carbonate coordination at the metal center, i.e., formation of the intermediate VIa. The formation of VIa, from IV via V-TS, has been confirmed by intrinsic reaction coordinate (IRC) calculations (Figure S16). Subsequent decoordination and reorienation of the carbonate group leads to various thermodynamically favored structures including structure VIIb (ΔG = −6.4 kcal mol⁻¹), which has the same structure as the isolated crystals of complex 3a.

The next step is to investigate the second CO₂ insertion, into the remaining alkoxide bond in VIIb, the structure of which was calculated from the atomic coordinates of 3a (determined by X-ray crystallography). Again the insertion of CO₂ occurs by decoordination of the μ-alkoxide group, accompanied by rotation of the carbonate group, leading to intermediate VII (ΔG = +8.5 kcal mol⁻¹), which has a coordinative vacancy at the zinc center. The next step involves the direct coordination of CO₂ to the zinc center, leading to intermediate VIII, where the CO₂ molecule is oriented orthogonal to the alkoxide group (Figure S18). The attack by the alkoxide group on the coordinated CO₂ leads to formation of the bis(carbonate) intermediate, Xa, via a relatively low-energy transition state (ΔG³ = 19.0 kcal mol⁻¹) and ΔΔG = 25.4 kcal mol⁻¹ from VIIb). The formation of Xa, from VIII via IX-TS, was confirmed by IRC calculations (Figure S17). Subsequent decoordination and rotation of the carbonate groups lead to various isomers, including structure VIIIIB (ΔG = −6.8 kcal mol⁻¹), featuring one bridging k²-carbonate group and one μ-carbonate group.

In both steps, the relatively low-energy barriers for CO₂ insertions (<25 kcal mol⁻¹) are in accordance with the experimental results, where insertion of CO₂ occurs at room temperature and 1 bar of pressure. It is proposed that the dinuclearity of the complex is important in stabilizing CO₂ insertion by allowing its favorable orientation relative to the alkoxide group and, at the same time, by stabilizing the carbonate species formed by enabling it to bridge between the two metal centers. It is also notable that various zinc carbonate isomers (VIa,b and Xa–c) are observed by DFT, each featuring different coordination modes of the carbonate groups and all with somewhat similar relative energies, which may go some way to explaining the mixture of carbonate species observed by ¹H NMR spectroscopy.

### CONCLUSIONS

In conclusion, the high yielding synthesis and reactivity of the dizinc(II) bis(alkyl) complex 1, coordinated by a Schiff base macrocyclic ancillary ligand, are reported. The dizinc bis(alkyl) complex reacts with isopropyl alcohol, at slightly elevated temperatures, to form the dizinc bis(isopropoxide) complex 2, which has been fully characterized, including by X-ray crystallography. The alkoxide derivative (2) is a good model for the propagating species during lactide ROP, and indeed, the alkyl complex, in the presence of isopropyl alcohol, is a moderately efficient and well-controlled catalyst for rac-LA polymerization. The same catalytic system, however, is not able to copolymerize cyclohexene oxide/CO₂ despite showing rapid and reversible insertion of CO₂ into the zinc alkoxide moieties. The stoichiometric reaction between the dizinc bis(alkoxide) derivative and 1 bar of CO₂ leads to the evolution of dizinc carbonate moieties (3a and 3b) as established by NMR spectroscopy and a carbonate alkoxide derivative characterized by X-ray crystallography. The insertion of CO₂ into the dizinc bis(alkoxide) species is also studied using DFT, which reveals that there are low barriers to insertion and that the reaction could proceed in a stepwise manner, forming a relatively stable dizinc carbonate–alkoxide intermediate.

Overall, this study confirms that using this new type of dinucleating macrocycle may indeed be a useful strategy to prepare zinc alkoxide derivatives that are suitable as lactone ROP catalysts and that undergo rapid insertion of CO₂ at 1 bar of pressure. Further work is necessary to optimize the coordination environment so as to enable efficient CO₂/epoxide copolymerization, and this will be the focus of future activities.

### EXPERIMENTAL SECTION

#### Materials and Methods

All reactions were conducted under an atmosphere of dry N₂, using standard Schlenk-line techniques, and in a nitrogen-filled glovebox. Solvents and reagents were obtained from commercial sources (Sigma-Aldrich). The metal-free Schiff base macrocycle H₂L was prepared as described previously. Tetrahydrofuran (THF), toluene, and hexane were distilled from sodium/benzophenone, under dry N₂. Cyclohexane oxide was dried over 3 Å molecular sieves. rac-lactide (rac-LA) was crystallized from anhydrous toluene and sublimed under vacuum twice prior to use.

NMR spectra were recorded on a Bruker AV400 instrument. The residual proteo solvent peaks were used as internal references in the ¹H and ¹³C NMR spectra (ppm). Homonuclear-decoupled ¹H(¹H) NMR spectra were performed on a Bruker Av500 spectrometer, equipped with a z-gradient bbo/S mm tunable probe and a BMSM GAB 10 A gradient amplifier providing a maximum gradient output of 5.35 G cm⁻¹. ¹H NMR spectra for all lactide polymerizations were performed on a Bruker Av400 or Av500 instrument. PLA number- and molecular sieves. rac-lactide (rac-LA) was crystallized from anhydrous toluene and sublimed under vacuum twice prior to use.

NMR spectra were recorded on a Bruker AV400 instrument. The residual proteo solvent peaks were used as internal references in the ¹H and ¹³C NMR spectra (ppm). Homonuclear-decoupled ¹H(¹H) NMR spectra were performed on a Bruker Av500 spectrometer, equipped with a z-gradient bbo/S mm tunable probe and a BMSM GAB 10 A gradient amplifier providing a maximum gradient output of 5.35 G cm⁻¹. ¹H NMR spectra for all lactide polymerizations were performed on a Bruker Av400 or Av500 instrument. PLA number- and multiple stationary points (Mₙ/Mₚ; D) were determined using size-exclusion chromatography. Two mixed-bed PSS–SDV linear S columns were used in series, with THF as the eluent, at a flow rate of 1 mL min⁻¹, on a Shimadzu LC-20AD instrument operating at 40 °C. The instrument was calibrated using narrow MW polystyrene standards, and a correction factor of 0.58 was applied to the raw MW data, as reported by Penczek and co-workers. MALDI-ToF spectrometry measurements were performed on Waters/Micromass MALDI micro MX spectrometer, using positive ionization in reflectron mode. The samples were prepared by dissolving the polymers, the dithralon matrix, and potassium trifluororacete, as the cationizing agent, in a 1:1:1 ratio, in THF (all solutions being at 10 mg mL⁻¹).

#### Computational Details

All calculations were performed using the Gaussian09 suite of codes (revision C.01). Calculations were carried out at the DFT level of theory, using hybrid functional oB97X-D. All atoms, including zinc, have been described with a 6-31G(d) basis set. Geometry optimizations were carried out without any symmetry restrictions. Conductor-like polarizable continuum model (CPCM) was used with benzene as the solvent to model solvation. The nature of the extremum was verified with analytical frequency calculations: the stationary points (minima) do not feature imaginary modes, and all transition states reveal precisely one imaginary mode corresponding to...
the intended reaction. For III-**TS and VII-**TS, IRC calculations were performed, which also confirmed the identity of the transition state. **Complex Syntheses.** **LZnEt2 (1).** A ZnEt2 (99.1 mg, 0.80 mmol) solution in THF (4 mL, −40 °C) was added to a precooled solution of H2L (200 mg, 0.40 mmol) in THF (5 mL, −40 °C). The mixture slowly turned red and became homogeneous after 30 min. The solution was allowed to react at 25 °C for 10 h. Then, the volatile components were evaporated, the residue was washed (pentane), and compound 1 was isolated as a red solid (241 mg, 87%). Suitable crystals of 1·C6D6 for X-ray analysis were obtained by hexane diffusion into a benzene solution of 1. Elem. anal. Calcd: C, 63.03; H, 5.59; N, 12.26. Found: C, 63.09; H, 5.60; N, 12.23. **1H NMR (400 MHz, C6D6): δ 7.36 (4 H, N=CH), 7.26 (4 H, 4, aryl-H), 6.96 (ddd, 4 H, 8 H, 4, aryl-H), 6.71 (ddd, 4 H, 4, aryl-H), 6.50 (ddd, 4 H, 8 H, 4, aryl-H), 3.86 (ddd, 4 H, 8 H, 4, aryl-H), 1.50 (s, 36 H, CH3(CH2)2NAr), 0.48 (s, 36 H, CH3(CH2)2NAr).**

**Isolated Sample.** In a sealed vial, isopropyl alcohol (167 mL, 17.4 mmol) was added to a THF solution (10 mL) of ZnEt2 (150 mg, 0.22 mmol) to yield a suspension of H2L (200 mg, 0.40 mmol), in THF (4 mL, −40 °C). The mixture slowly turned red and became homogeneous after 30 min. The solution was allowed to react at 25 °C for 20 h and then heated at 60 °C for 16 h, which leads to the formation of 2. Suitable crystals for X-ray analysis were obtained by hexane diffusion into a THF solution of 2. **1H NMR (400 MHz, THF-d8): δ 7.32 (4 H, N=CH), 7.22 (4 H, 8 H, 4, aryl-H), 6.93 (ddd, 4 H, 8 H, 4, aryl-H), 6.58 (ddd, 4 H, 8 H, 4, aryl-H), 4.13 (4 H, CH2), 3.85 (CH2), 2.70 (2 H, CH2), 0.61 (s, 2 H, CH2).**

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