Dinuclear Zinc Salen Catalysts for the Ring Opening Copolymerization of Epoxides and Carbon Dioxide or Anhydrides

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Supporting Information

ABSTRACT: A series of four dizinc complexes coordinated by salen or salan ligands, derived from ortho-vanillin and bearing (±)-trans-1,2-diaminocyclohexane (L1) or 2,2-dimethyl-1,3-propanediamine (L2) backbones, is reported. The complexes are characterized using a combination of X-ray crystallography, multinuclear NMR, DOSY, and MALDI-TOF spectroscopies, and elemental analysis. The stability of the dinuclear complexes depends on the ligand structure, with the most stable complexes having imine substituents. The complexes are tested as catalysts for the ring-opening copolymerization (ROCOP) of CO2/epoxide (CHO) and phthalic anhydride (PA)/CHO. All complexes are active, and the structure/activity relationships reveal that the complex having both L2 and imine substituents displays the highest activity. In the ROCOP of CO2/CHO its activity is equivalent to other metal salen catalysts (TOF = 44 h⁻¹) at a catalyst loading of 0.1 mol %, 30 bar of CO2, and 80 °C, while for the ROCOP of PA/CHO, its activity is slightly higher than other metal salen catalysts (TOF = 198 h⁻¹) at a catalyst loading of 1 mol % and 100 °C. Poly(ester-block-carbonate) polymers are also afforded using the most active catalyst by the one-pot terpolymerization of PA/CHO/CO2.

INTRODUCTION

Salen ligands, initially derived from the condensation of salicylaldehyde and ethylenediamine, are of fundamental importance in coordination chemistry and catalysis. They have been extensively studied since the pioneering work of Jacobsen1 and Katsu.2 using a chiral [Mn(salen)] complex for asymmetric organic reactions, where it is proposed that they show better performances due to cooperative interactions between the two metal centers.3,4 Exactly this type of metal cooperation has also been proposed to be an important criterion in the preparation of highly active catalysts for the ring-opening copolymerization (ROCOP) of CO2 and epoxides.5

One of the first well-characterized dinuclear catalysts for CO2/epoxide ROCOP was a zinc β-diaminate (BDI) complex that was shown to adopt dimeric structures in the most active catalysts.6 Since this pivotal finding, many highly active dinuclear catalysts have been developed including those based on macrocyclic,7 BDI,8 Trost type “pro-phenolate”,9 porphyrin,10 and anilido-aldimine11 ligand scaffolds, typically coordinated to zinc, although other transition metal systems have also been investigated.12 Mechanistic studies and density functional theory calculations have highlighted that the catalyst activity seems to be highly dependent on the flexibility of the ligand and the distance between the two metal centers.13,14 To date, one of the most active catalyst systems for the synthesis of poly(cyclohexene carbonate) (PCHC), reported earlier this year by Rieger and co-workers;15,16 is based on a flexible dizinc complex, coordinated by two β-diaminate moieties that are linked through the phenyl rings (TOF = 155 000 h⁻¹ at a catalyst loading of 0.0125 mol %, 100 °C, and 30 bar of CO2).

Mononuclear salen ligands coordinated to either Co(III) or Cr(III) centers and combined with a Lewis base/ionic cocatalyst have also been widely employed as catalysts for CO2/epoxide ROCOP.17,18 In this case, the separation between the metal and the cocatalyst is of key of importance for the high activity.19 Nozaki and co-workers pioneered a new generation of “cocatalyst tethered” salen complexes, which show a significant improvement in the catalyst activity.20 The combination of tethering together the salen catalyst and...
catalyst was subsequently successfully applied by various researchers, including Lu and Lee, to prepare some of the most active catalysts reported for ROCOP (TOF > 20 000 h⁻¹). A further benefit is that some of these tethered catalysts can be reclaimed from the polymer and recycled without significant loss in performance.

Another successful strategy, also initially developed by Nozaki and co-workers, has been to join together two distinct metal salen catalysts and to combine them with cocatalysts. Such dinuclear catalysts are coordinated by two salen ancillary ligands that have been covalently linked to one another; the catalysts show higher activity than mononuclear counterparts, particularly at low catalyst loadings. Given the precedence for salen ligands and the promise of dinuclear catalysts, it is perhaps surprising that there is, so far, only a single report of ROCOP catalysts where a single salen ancillary ligand coordinates two metals. The catalyst comprises a multidendate bis(benzotriazole iminophenol) ligand coordinated to two Zn(II), Ni(II), or Co(II) metal centers. The best activities were achieved with the di-Ni(II) catalyst, which for the ROCOP of CHO/CO₂ shows a TOF of 53 h⁻¹, at 120 °C and 20 bar of CO₂. These encouraging results using dinuclear salen catalysts inspired the current development of new dinuclear salen ligands and the investigation of their coordination chemistry and catalytic applications for CO₂/CHO and phthalic anhydride (PA)/CHO ROCOP. When developing new polymerization catalysts, it is attractive to target low-cost ligands, ideally derived from renewables, which can be obtained from a range of plants. In addition, ortho-vanillin is an attractive starting material, as it is inexpensive and commercially available; furthermore, the targeted ligands were obtained on a large scale in only 1 d, through a simple, one-pot synthetic method (Scheme 1).

**RESULTS AND DISCUSSION**

Using ortho-vanillin as a starting point, four new ligands were synthesized, isolated, and characterized. As mentioned, ortho-vanillin is an attractive starting material, as it is inexpensive and commercially available; furthermore, the targeted ligands were obtained on a large scale in only 1 d, through a simple, one-pot synthetic method (Scheme 1).

First, the amination of ortho-vanillin, using the relevant diamine [[(±)-trans-1,2-diaminocyclohexane (L₁) or 2,2-dimethyl-1,3-propanediamine (L₂)]], gave the desired imine product (L₃₊H, L₃₋H, Scheme 1). The ligands differ according to the diamine “linker” group and were selected on the basis that such C₂ and C₃ linkers are common components of successful ROCOP catalysts. Subsequent in situ reduction of the imine moieties on the salen ligands was performed, using NaBH₄ to obtain the corresponding amines and salan ligands (L₄₊H, L₄₋H, Scheme 1). All four ligands were obtained in near quantitative yields and did not require purification (Figure S1–8).

**Metal Complexations.** L₁₊H, L₁₋H, and L₂₊H were reacted with 2 equiv of [Zn(OAc)₂·(H₂O)] to afford the corresponding bis(zinc acetate) complexes (Scheme 2) in good yields (62–68%).

Crystals suitable for X-ray diffraction studies were obtained for L₁₋Zn₂(OAc)₂ by slow diffusion of pentane into a concentrated dichloromethane solution. The molecular structure of L₁₋Zn₂(OAc)₂ shows that both the zinc centers are pentacoordinated by the ligand framework (Figure 1 and Figure S9, Table 1); one within the “enclosed” phenolic pocket, and the other in the “open” cavity. A κ²-coordinated acetate ligand provides stabilization for the dinuclear complex by bridging between the two Zn centers. The zinc center enclosed in the small pocket is coordinated via two nitrogen centers, two phenolic oxygen centers, and one acetate oxygen in a distorted square pyramidal geometry (C₁ = 0.16). In contrast, the zinc occupying the open pocket has a distorted trigonal bipyramidal structure.
The 1H NMR spectra of imine complexes L1aZn2(OAc)2 and L2aZn2(OAc)2 confirm the two metal atoms are coordinated, with all the resonances experiencing grouped shifts in comparison to the free ligands (Figure S11–14). A particularly significant shift was observed for the imine signal in CDCl3 from 13.84 ppm in L1aH to 8.23 ppm for L1aZn2(OAc)2 (Figure S11) and from 14.14 ppm in L2aH to 8.08 ppm for L2aZn2(OAc)2 (Figure S13). The broadness of the methylene resonances and the loss of the phenolic proton resonance also confirm the deprotonation of the ligand and the coordination of a zinc center. The appearance of two new singlet resonances at 2.00 and 1.97 ppm are assigned as the zinc-coordinated 1H resonances at 2.11 ppm is assigned to both the zinc-coordinated solvent was convoluted (Figures S20 and S21), no signals corresponding to the free ligand were observed; instead, three new sets of resonances were present. MALDI-TOF analysis of the mixture revealed the presence of L2bZn2(OAc)2 (M+1-OAc = 563 g/mol) along with two higher molecular weight species, assigned as L2bZn3(OAc)4 ([M+1-OAc = 745 g/mol] and L2bZn4(OAc)4 (M+1-OAc = 999 g/mol)) (Figure S22). DOSY analysis of the product mixture in C6D6 showed a range of diffusion coefficients [−9.1 × 10⁻⁹ m²/s to −9.3 × 10⁻¹⁰ m²/s)] (Figure S23). A comparison of the diffusion coefficients obtained from a calibration plot of known standards gave a predicted molecular weight range of 496 g/mol to 977 g/mol, which is in agreement with the presence of products L2bZn2(OAc)2 (621 g/mol), L2bZn3(OAc)4 (802 g/mol), and (L2b)2Zn3(OAc)2 (1061 g/mol) in the solution state.

An alternative synthetic route was investigated using a stepwise procedure via the synthesis of a monometallic intermediate, L1aZn (Scheme 4), followed by its reaction with Zn(OAc)2, and was expected to afford the dinuclear complex L2bZn2(OAc)2 (Scheme 5). Accordingly, when L2bH was deprotonated, using either Zn(OAc)2 or Et2Zn in dry MeOH or THF, respectively, the formation of a white precipitate was observed. The solid-state structure of L2bZn was determined as both the THF and methanol solvates (Figures S24–26). Although the two solvates are very distinct crystallographically (with the structure of the THF solvate containing one independent C₂-symmetric complex, whereas that of the methanol solvate contains two independent C₇-symmetric complexes), the conformations of all three
Scheme 4. Reaction of L2bH with 1 equiv of Et2Zn and the Formation of the Dimeric Structure (L2b)2Zn2

(i) 1 equiv of Et2Zn in THF, 22 °C, 16 h or 1 equiv of Zn(OAc)2 in MeOH, 22 °C, 16 h.

Scheme 5. Reaction of (L2b)2Zn2 with Et2Zn and Zn(OAc)2

(i) 1 equiv of Et2Zn in THF, 22 °C, 16 h (ii) 1 equiv of L2bH in C6D6 (iii) 1 equiv of Zn(OAc)2 in THF, 22 °C, 16 h.

complexes are very similar. For simplicity, only the THF solvate will be discussed here, with full crystallographic details being provided in the Supporting Information. The molecular structure of L2bZn reveals that it is dimeric and possesses C2 symmetry, with a central {Zn2O2} ring, where one phenolic oxygen from each ligand bridges between the two zinc metal centers (Figure 2 and Table 2). The symmetry-related zinc centers adopt a trigonal bipyramidal geometry (τ = 0.70) and are bound to three phenolic oxygens in a fac fashion. The complexation of the zinc leads to the formation of six-membered rings, providing stabilization for the dimeric complex. The methoxy groups do not coordinate to zinc, and so the open pocket remains available for the coordination of another metal center. Multinuclear (1H, 13C) NMR spectroscopy along with two-dimensional (2D) NMR and DOSY experiments suggest that the dimeric structure is retained in solution (Figures S27–S29).

To investigate whether the dimer (L2b)2Zn2 can be cleaved by the coordination of a second metal, the reaction of (L2b)2Zn3 with 1 equiv of Et2Zn was performed (Scheme 5). This reaction was selected because reactions involving Et2Zn are generally fast and because the formation of dinuclear complexes can be monitored by following the distinctive 1H NMR signals of the Zn-ethyl groups. The 1H NMR spectrum of the product, in C6D6, showed no trace of the unreacted dimer, and all resonances experienced an upfield shift, consistent with the incorporation of a second zinc center within the ligand scaffold (Figures S30 and S31). Two different sets of characteristic Zn-ethyl resonances are observed, with two triplets at 2.05 and 1.79 ppm and the corresponding quartets at 0.94 and 0.61 ppm. These Zn-ethyl chemical shifts are significantly different than those of diethylzinc [1.11 ppm (t) and 0.12 ppm (q) in C6D6], confirming the coordination of the second zinc center within the ligand scaffold.

3H DOSY NMR spectroscopy shows that all the resonances possess the same diffusion coefficient (Figure S32). The estimation of the molecular weight based on the diffusion coefficient, using a calibration plot, gave a calculated molecular weight of 503 g/mol, which is consistent with the formation of a monomeric L2bZn2Et2 product (561 g/mol). Nevertheless, block colorless crystals, obtained from a saturated THF solution of L2bZn2Et2 at 22 °C, corresponded to the starting dimer (L2b)2Zn2.

To emphasize the lability of the metal centers within this ligand scaffold, 1 equiv of free ligand was added to a solution of L2bZn2Et2 in C6D6 (Scheme 5). The instantaneous formation of a precipitate was observed, with concomitant release of ethane. The white precipitate was isolated, dissolved in d8-THF, and the resultant spectrum correspond to the dimer (L2b)2Zn2. Finally, when the dimer (L2b)2Zn2 was reacted with 1 equiv of Zn(OAc)2 at room temperature, the same product mixture was obtained as when the parent ligand was reacted with 2 equiv of Zn(OAc)2 (Scheme 5).

Further investigations were performed to quantify the ratio of the reaction products L2bZn2(OAc)2, L2bZn2(OAc)4, and (L2b)2Zn3(OAc)4. Complexes L2bZn3(OAc)4 and (L2b)2Zn3(OAc)4 were independently synthesized by the reaction of L2bH with 3 equiv or 1.5 equiv of Zn(OAc)2 in THF, respectively (Scheme 6). Colorless block crystals of L2bZn3(OAc)4 suitable for X-ray diffraction were obtained by slow diffusion of pentane into a saturated dichloromethane solution of L2bZn3(OAc)4 (Figure 3, Table 3, and Figure S33).

The molecular structure reveals that Zn1 and Zn2 each possess an octahedral coordination sphere, while Zn3 is tetrahedral. Zn1 occupies the enclosed phenolic pocket and is coordinated by both phenolic oxygen centers and both amine nitrogens, with two bridging acetate ligands completing its coordination sphere. Zn2 occupies the open phenolic pocket and is

Table 2. Selected Bond Lengths (Å) and Angles (deg) for (L2b)2Zn2

| Bond/Angle | Length (Å) | Angle (deg) |
|------------|-----------|-------------|
| Zn(1)--O(1) | 1.925(2) | O(1)--Zn(1)--N(13) 131.60(9) |
| Zn(1)--O(21') | 2.00(4) | O(1')--Zn(1)--O(21') 116.99(8) |
| Zn(1)--O(21) | 2.088(2) | O(21')--Zn(1)--N(13) 110.84(8) |
| Zn(1)--N(9) | 2.160(2) | O(21')--Zn(1)--N(9) 173.79(7) |
| Zn(1)--N(13) | 2.109(2) | O(21')--Zn(1)--N(13) 90.70(8) |
| C(20)--O(21) | 1.336(3) | O(21')--Zn(1)--O(21) 79.11(7) |
| Zn(1)--Zn(1) | 3.1557(5) | O(1)--Zn(1)--O(21) 91.19(7) |
coordinated by both methoxy groups, although the bond distance is quite long [Zn2−O24, 2.330(4) Å and Zn2−O20, 2.576(4) Å], with two bridging acetate ligands providing further stabilization. Zn3 is only coordinated to one phenolic oxygen and is coordinated to the other zinc centers via two κ₂-bridging acetate ligands, with coordination by an additional, terminal acetate ligand. The ligand adopts a bowl shape and has a very similar structure to the related trizinc complex coordinated by a bis(phenolate) tetra(amine) macrocycle.11f The ¹H NMR spectrum of L₂bZn₃(OAc)₄ is consistent with the formation of a trizinc complex (Figure S34). Although the acetate resonance overlaps with the NH and methylene ligand resonances, the integration gives good agreement with the presence of four acetate coligands coordinated to the metal centers. In addition, the DOSY spectrum shows that all the resonances possess the same diffusion coefficient, suggesting that the trizinc structure is retained in C₆D₆ solution (Figure S36). The estimation of the complex molecular weight, based on the diffusion coefficient, gave a calculated molecular weight of 725 g/mol, which is in close agreement with the calculated value (802 g/mol). The product is also stable, under reflux conditions in THF solution, over a period of 16 h (Figure S37).

The reaction of 1.5 equiv of Zn(OAc)₂ with L₂bH gave a convoluted ¹H NMR spectrum in C₆D₆ (Figure S38). No signals from the unreacted ligand, dimer (L₂b)₂Zn₂, or the trimetallic species L₂bZn₃(OAc)₄ were observed, suggesting that a new product is formed. DOSY spectroscopy reveals that the new resonances all possess the same diffusion coefficient (Figure S39), corresponding to a molecular weight of 978 g/mol, which is in close agreement with the value for (L₂b)₂Zn₃(OAc)₂ (1063 g/mol). Although crystals of (L₂b)₂Zn₃(OAc)₂ suitable for X-ray diffraction experiments could not be obtained, it was possible to grow crystals for the closely related trizinc bis(chloride) complex, (L₂b)₂Zn₃Cl₂ (Figure S40), providing further support for the formation of a trizinc complex coordinated by the ancillary ligands.32

Scheme 6. Reaction of L₂bH with (i) 1.5 equiv and (ii) 3 equiv of Zn(OAc)₂

(i) 1.5 equiv of Zn(OAc)₂ in THF, 22 °C, 16 h; (ii) 3 equiv of Zn(OAc)₂ in THF, 22 °C, 16 h.

Table 3. Selected Bond Lengths (Å) of L₂bZn₃(OAc)₄

| Entry  | Catalyst | TON | TOF (h⁻¹) | % Carbone | % selectivity | Mₙ (g/mol⁻¹) | D (°) | Time (h) |
|--------|----------|-----|-----------|-----------|--------------|--------------|-------|----------|
| 1      | L₁₁Zn₂(OAc)₂ | 15  | 0.2       | 71        | >49          | 840          | 1.09  | 4 d      |
| 2      | L₁₁Zn₂(OAc)₂ | 14  | 0.1       | 77        | >77          | 400          | 1.10  | 4 d      |
| 3      | L₁₁Zn₂(OAc)₂ | 45  | 2         | >99       | >99          | 1500         | 1.3   | 1 d      |
| 4      | L₁₁Zn₂(OAc)₂ mix | 9  | 2         | >99       | >99          | 80           | -     | 4.5 h    |
| 5      | L₁₁Zn₂(OAc)₂ mix | 30 | 0.3      | >88       | >88          | 1000         | 1.17  | 4 d      |
| 6      | L₁₁Zn₂(OAc)₂ | 19  | 3         | >99       | >99          | 82           | -     | 6 h      |
| 7      | L₁₁Zn₂(OAc)₂ | 24  | 1         | >99       | >99          | 93           | -     | 24 h     |
| 8      | (L₁₁Zn₂(OAc)₂ | 23  | 1         | >99       | >99          | 77           | 400   | 1.17     |
| 9      | trizinc macrocycle catalyst | 99 | 17       | >99       | >99          | 1300         | 1.23  | 6 h      |
| 10     | trizinc macrocycle catalyst | 96 | 4        | >99       | >99          | 97           | 3400  | 1.21     |

*Copolymerization conditions: catalyst/CHO = 1 mol %, 80 °C, 1 bar of CO₂. †TON = number of moles of epoxide consumed per mole of catalyst. ‡TOF = TON/h. §Determined by comparison of the integrals of signals arising from the methylene protons in the ¹H NMR spectra due to copolymer carbonate linkages (δ = 4.65 ppm), copolymer ether linkages (δ = 3.45 ppm), and the signals due to the cyclic carbonate byproduct (δ = 4.00 ppm). ††Determined by SEC in THF calibrated using polystyrene standards. ††Catalyst/CHO = 0.5 mol %. ††Catalyst/CHO = 0.1 mol %.
Comparison of $^1$H NMR spectra of $\text{L}_2\text{aZn}_2(\text{OAc})_2$ and $(\text{L}_2\text{b})_2\text{Zn}_2(\text{OAc})_2$ with the spectra of products obtained from the reaction of $\text{L}_2\text{h}$ with 2 equiv of $\text{Zn(}\text{OAc})_2\cdot\text{H}_2\text{O}$ suggests that $\text{L}_2\text{aZn}_2(\text{OAc})_4$ and $(\text{L}_2\text{b})_2\text{Zn}_2(\text{OAc})_4$ are the two major products (Figure S41). DOSY spectroscopy of the mixture provides further support for this observation, as two major species are observed with diffusion coefficients that correspond exactly to the values obtained for the independently prepared complexes $\text{L}_2\text{aZn}_2(\text{OAc})_4$ and $(\text{L}_2\text{b})_2\text{Zn}_2(\text{OAc})_4$ (Figures S23, S36, and S39).

A third product is also present, albeit in very low concentration, which is likely to be the dinuclear complex $\text{L}_2\text{bZn}_2(\text{OAc})_2$. These findings suggest that using this ligand, the formation of the dinuclear complex is not favorable and that metal rearrangement occurs to form $\text{L}_2\text{bZn}_2(\text{OAc})_4$ and $(\text{L}_2\text{b})_2\text{Zn}_2(\text{OAc})_2$. This was further supported as $\text{L}_2\text{bZn}_2(\text{OAc})_2$ was isolated as a white precipitate from the reaction of $\text{L}_2\text{h}$ and 2 equiv of $\text{Zn(}\text{OAc})_2\cdot\text{H}_2\text{O}$ in dry THF at $-78^\circ\text{C}$. As the dinuclear complex could not be isolated, the $\text{L}_2\text{bZn}_2(\text{OAc})_2$ mixture, $\text{L}_2\text{bZn}_2(\text{OAc})_4$, and $(\text{L}_2\text{b})_2\text{Zn}_2(\text{OAc})_2$ were each tested within polymerization studies.

**Polymerization Catalysis.** The series of dizinc complexes were tested as catalysts for the ROCOP of CO$_2$ and CHO, at 1 bar of pressure of CO$_2$ and 80 °C (Table 4). As other dizinc catalysts are active under these conditions, the reaction provides a useful benchmark for comparison.$^{11e,13a,18}$ All catalysts displayed a low activity; therefore, high catalyst loadings were required to convert CHO and CO$_2$ to PCHC. In particular, complexes containing the $\text{L}_1$ ligand backbone $\text{[L}_1\text{Zn}_2(\text{OAc})_2]$ and $\text{L}_1\text{bZn}_2(\text{OAc})_2$ showed negligible TOF values ($\leq0.1$ h$^{-1}$; Entries 1 and 2) at a catalyst loading of 1 mol % versus CHO. These low activities are attributed to the poor solubility of the catalyst in CHO. With the $\text{L}_2$ backbone, the $\text{L}_2\text{bZn}_2(\text{OAc})_2$ mixture displayed improved solubility in hot CHO and showed slightly higher TOF values of 2 h$^{-1}$ (Entry 4). However, after the first 4.5 h of reaction, a white precipitate formed, and the TOF decreased to 0.3 h$^{-1}$.

Similarly, $\text{L}_2\text{aZn}_2(\text{OAc})_4$ was active during the first 6 h of polymerization (TOF = 5 h$^{-1}$; Entry 6) with similar activity to that of the trizinc macrocycle catalyst reported previously (TOF = 56 h$^{-1}$; Entry 10).$^{11j}$ However, the polymers have only low carbonate linkage content and with much better polymer selectivities ($M_\text{w} = 18800 \text{ g/mol}$, $D = 1.6$). These results show that the more flexible $\text{L}_2$ backbone gave catalysts with higher activity than those with the $\text{L}_1$ backbone.

The series of catalysts was also tested for the ROCOP of PA and CHO. In 2014, Lu et al. reported that $\text{L}_1\text{aZn}_2(\text{OAc})_2\cdot\text{H}_2\text{O}$ could polymerize maleic anhydride and CHO when a cocatalyst such as $\text{N}_2\text{N'}$-dimethylanilinopropyridine was present.$^{20}$ In all cases, the catalysts could fully polymerize PA, in 16 h, without the need for a cocatalyst (Table 6). While the imine complexes afforded the corresponding polyesters (PE) with high selectivity and no ether linkages, the amine complexes provided the polymers with a greater proportion of ether linkages. A possible explanation for this trend is that the more electron-donating amine decreases the Lewis acidity of the metal center, thereby decreasing the likelihood of successive ring opening two CHO molecules. Comparing the catalyst activities, $\text{L}_1\text{aZn}_2(\text{OAc})_2$ (Entry 1) gave activities (TOF = 70 h$^{-1}$) similar to some of the best catalysts based on chromium, cobalt, or aluminum salen/salophen complexes,$^{18a}$ all of which require the use of a cocatalyst. However, $\text{L}_2\text{bZn}_2(\text{OAc})_2$ (Entry 3) was significantly more active (TOF = 198 h$^{-1}$) than the majority of other known catalysts for this reaction, under similar conditions.$^{13b}$

![Inorganic Chemistry](https://example.com/image)

**Table 5. Copolymerization** of CO$_2$ and CHO at 30 bar of CO$_2$

| entry | catalyst | TON$^b$ | TOF$^d$ ($h^{-1}$) | % carbonate$^c$ | % selectivity$^d$ |
|-------|----------|---------|-------------------|-----------------|-----------------|
| 1     | $\text{L}_1\text{aZn}_2(\text{OAc})_2$ | 34      | 2                 | >99             | 98              |
| 2     | $\text{L}_2\text{bZn}_2(\text{OAc})_2$ | 16      | 1                 | >99             | 89              |
| 3     | $\text{L}_2\text{aZn}_2(\text{OAc})_4$ | 706     | 44                | >99             | 94              |
| 4     | $\text{L}_2\text{bZn}_2(\text{OAc})_2$ | 29      | 2                 | >99             | 94              |
| 5     | $\text{L}_2\text{bZn}_2(\text{OAc})_4$ | 147     | 9                 | 75              | 87              |
| 6     | $(\text{L}_2\text{b})_2\text{Zn}_2(\text{OAc})_2$ | 28      | 2                 | >99             | 89              |

$^a$Copolymerization conditions: catalyst/CHO = 0.1 mol %, 80 °C, 30 bar of CO$_2$, 16 h. $^b$TON = number of mole of epoxide consumed per mole of catalyst. $^d$TOF = TON/h. $^c$Determined by comparison of the integrals of signals arising from the methylene protons in the $^1$H NMR spectra due to copolymer carbonate linkages ($\delta = 4.65$ ppm), copolymer ether linkages of moles of epoxide ($\delta = 4.54$ ppm), and the signals due to the cyclic carbonate byproduct ($\delta = 4.00$ ppm).$^{11e}$

Previously, it has been reported that some dizinc complexes show activities that are dependent on the CO$_2$ pressure; indeed, such effects were usually observed for complexes coordinated by flexible ligands.$^{17}$ Therefore, the catalysts were also tested at 30 bar of CO$_2$ pressure. In all cases, an improvement in the catalytic activity was observed, as all the complexes produced PCHC at much lower catalyst loading (0.1 mol % catalyst vs CHO). On the one hand, the activity of $\text{L}_1\text{aZn}_2(\text{OAc})_2$, $\text{L}_2\text{bZn}_2(\text{OAc})_2$, the $\text{L}_1\text{aZn}_2(\text{OAc})_2$ mixture, and $(\text{L}_2\text{b})_2\text{Zn}_2(\text{OAc})_2$ were still very low (Table 5, Entries 1, 2, 4, and 6, respectively). On the other hand, $\text{L}_1\text{aZn}_2(\text{OAc})_2$ (Entry 3) and $\text{L}_2\text{bZn}_2(\text{OAc})_4$ (Entry 5) showed a significant enhancement in their catalytic activities (TOF = 44 and 9 h$^{-1}$, respectively) and polymer selectivities. The best catalyst, $\text{L}_1\text{aZn}_2(\text{OAc})_2$, has comparable activity to other metal salen catalysts$^{16e,20a}$ and to the dinickel salen complex that was previously reported by Ko and co-workers (TOF = 56 h$^{-1}$).$^{26}$

At 80 °C, $\text{L}_2\text{bZn}_2(\text{OAc})_2$ formed PCHC with a very high carbonate linkage content, with much better polymer selectivities ($M_\text{w} = 18800 \text{ g/mol}$, $D = 1.6$). These results show that the more flexible $\text{L}_2$ backbone gave catalysts with higher activity than those with the $\text{L}_1$ backbone.

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A series of dinuclear zinc salen complexes that are active catalysts for carbon dioxide/cyclohexene oxide and phthalic anhydride/cyclohexene oxide ROCOP were investigated. These studies highlight the influence of the ligand structures on the catalytic activity and the stability of the dinuclear complexes. Ligands containing imine moieties resulted in complexes that were more stable than the amine analogues. Consequently, a mixture of products, deriving from metal coordination, was obtained with the more flexible amine ligand, highlighting its complex solution coordination chemistry. The catalytic studies indicate that complexes with the more flexible 2,2-dimethyl propylene backbones are more active than those with the trans-1,2-cyclohexylene backbones. Further, the complexes with imine substituents showed much lower diastereomeric ratios. For both catalysts, the samples were prepared as follows: 10 mg/mL THF solutions of the complex, matrix, and additive were separately precipitated. Then, 20 μL of the complex and 20 μL of the matrix solution were mixed, along with 10 μL of the additive solution, if required. This mixture (2 μL) was then spotted on the MALDI plate and allowed to dry.

**X-ray Diffraction.** Data were collected using an Agilent Xcalibur 3E diffractometer, and the structures were refined using the SHELXTL and SHELX-2013 program systems. The crystallographic data table of all the compounds can be found in the Supporting Information (Table S4).

**Elemental Analysis.** Elemental analysis was determined by Stephen Boyer at London Metropolitan University.

**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, on a Shimadzu LC-20AD instrument at 40 °C. Polymer molecular weight (Mn) was determined by comparison against polystyrene standards. The polymer samples were dissolved in SEC-grade THF and packed into the column system at a flow rate of 1 mL/min using a Shimadzu LC-20AD instrument at 40 °C.

**Typical Procedure for the Amination of o-Vanillin (L1H and L2H).** The appropriate diamine (trans-1,2-diaminocyclohexane (1.87 g, 0.016 mol) or 2,2-dimethyl-1,3-propanediamine (1.67 g, 0.016 mol)) in MeOH (5 mL) was added dropwise to a pale yellow solution.
of o-vanillin (5 g, 0.033 mol) in MeOH (50 mL). Upon addition of the diamine, a deep yellow solution was obtained. The mixture was stirred for 4 h at 22 °C, and the solvent was subsequently removed under vacuum to give a yellow powder. (Yields: L1bH: 6.1 g, 100% and L2bH: 5.9 g, 100%). 1H and 13C NMR spectra are in accordance with reported literature values.33,34

**Elemental analysis** for C26H30N2O8Zn2 (629 g/mol): Calculated: C, 49.62; H, 4.81; N, 7.52%. Found: C, 49.21; H, 4.69; N, 7.38%.

**L1bH:** Elemental analysis for C26H30N2O8Zn2 (382.86 g/mol): Calculated: C, 69.09; H, 6.85; N, 7.32%. Found: C, 69.21; H, 6.93; N, 7.38%.

**L2bH:** Elemental analysis for C26H30N2O8Zn2 (370.49 g/mol): Calculated: C, 62.6%, 506 mg). Elemental analysis for C25H30N2O8Zn2 (617 g/mol): Calculated: C, 49.31; H, 5.41; N, 4.42%. Found: C, 49.18; H, 5.34; N, 4.39%.

**Synthesis of L2bZn(OAc)2.** A solution of Zn(OAc)2·2(H2O) (440 mg, 2 mmol) in MeOH (15 mL) was added to a solution of L2bH (370 mg, 1 mmol) in MeOH (3 mL), and the reaction mixture was stirred at 22 °C for 16 h. After removal of all volatiles in vacuo, L2bZn(OAc)2 was isolated as a yellow powder. The pure product was obtained after washing with pentane followed by crystallization from THF/pentane at −40 °C (yield: 68%, 420 mg).

1H NMR (400 MHz, CDCl3, 298 K) δ 8.08 (s, 2H, N=CH), 6.84 (d, J = 7.9 Hz, 2H, m-Ph), 6.74 (dd, J = 8.0 Hz, 1.7 Hz, 2H, m-Ph), 6.60 (t, J = 7.8 Hz, 2H, p-Ph), 3.87 (s, 6H, O=CH3), 3.72 (s, 4H, N=CH2-C), 1.97 (s, 6H, OAc), 1.05 (s, 6H, C(CH3)3). 13C NMR (101 MHz, CDCl3, 298 K) δ 171.1 (CH=CH), 150.4 (i-Ph), 126.4 (m-Ph, 118.1 (o-Ph), 115.1 (p-Ph), 113.8 (m-Ph), 74.7 (CH3=CH), 55.9 (O=CH3), 35.3 (CH2=C(CH3)=), 24.8 (C(CH3)3), 23.0 (N=CH2-C). Elemental analysis for C26H30N2O8Zn2 (671 g/mol): Calculated: C, 48.64; H, 4.90; N, 4.54%. Found: C, 48.64; H, 5.03; N, 4.45%.

**Synthesis of L1aZn(OAc)2.** Under a nitrogen atmosphere, L1bH (1 g, 2.64 mmol) was dissolved in dry THF (35 mL). Subsequently, ZnEt2 (326 mg, 2.64 mmol) was dissolved in dry THF (5 mL) and added dropwise into the ligand solution. The reaction mixture was then stirred for 22 °C for 16 h. L1bZn(OAc)2 was isolated via canular transfer of the solvent as a white powder (yield: 62%, 726 mg).

1H NMR (400 MHz, 2H2O) (2 equiv) in MeOH (15 mL) was added in one portion into a solution of L2bH (500 mg) in MeOH (3 mL). The reaction mixture was stirred at 22 °C for 16 h, prior to removal of all volatiles in vacuo. A THF solution of Zn(OAc)2 (88 mg, 0.53 mmol) in MeOH (50 mL) was added to a solution of L1bH (100 mg) in MeOH (5 mL). The reaction mixture was stirred at 22 °C for 16 h. The dizinc complex L1aZn(OAc)2 and L2bZn(OAc)2 were isolated as a white powder via filtration (yields: L1aZn(OAc)2: 65%, 398 mg and L2bZn(OAc)2: 62%, 506 mg).

**Synthesis of (L2b)2Zn2.** A solution of Zn(OAc)2·2(H2O) (2 equiv) in MeOH (5 mL) was added in one portion into a solution of L1bH or L2bH (500 mg) in MeOH (5 mL). The reaction mixture was stirred at 22 °C for 16 h. The dizinc complexes L1bZn(OAc)2 and L2bZn(OAc)2 were isolated as a white powder via filtration (yields: L1bZn(OAc)2: 65%, 398 mg and L2bZn(OAc)2: 62%, 506 mg).
to give L2bZn3(OAc)4 as a white powder. The pure product was obtained by washing with pentane.

1H NMR (400 MHz, CDCl3, 298 K) δ 6.66 (dd, J = 7.1, 2.1 Hz, 2H, m-Ph), 6.65 (m, 4H, m-Ph + p-Ph), 4.29 (t, J = 11.7 Hz, 2H, Ph-CH2NH), 3.52 (s, 6H, OAc), 2.77 (J, δ = 11.2 Hz, 2H, Ph-CH2NH), 2.60 (t, J = 13.8, 11.3 Hz, 2H, NH-CH2CH3), 2.05 (t, J = 8.1 Hz, 3H, Zn-CH2C(=O)3), 1.79 (t, J = 8.1 Hz, 3H, Zn-CH2C(=O)3), 1.69 (J, δ = 11.50 Hz, 2H, NH-CH2CH3), 1.48 (q, J = 8.1 Hz, 2H, Zn-CH2C(=O)3), 0.94 (q, J = 8.1 Hz, 2H, Zn-CH2C(=O)3), 0.86 (t, J = 13.3 Hz, 2H, NH), 0.61 (s, 3H, OCH3), 0.83 (s, 3H, CH3), 0.33 (s, 3H, CH3), 0.03 (s, 3H, C(=O)), −0.37 (s, 3H, CH3). 13C NMR (101 MHz, CDCl3, 298 K) δ 150.3 (p-Ph), 149.3 (o-Ph), 149.4 (p-Ph), 123.1 (m-Ph), 113.9 (m-Ph), 111.1 (p-Ph), 61.7 (NH−CH−C), 55.9 (O−CH3), 54.8 (Ph−CH−NH), 33.6 (C(=O)), 27.8 (C(=O)), 20.5 (C(=O)), 15.0 (Zn−CH2), −1.7 (Zn−CH2), −3.8 (Zn−CH2). Elemental Analysis for C50H44N4O12Zn2 (561 g/mol): Calculated: C, 53.49; H, 4.62; N, 4.99%. Found: C, 53.55; H, 7.19; N, 4.84%.

PA/C02/CHO Polymerization Reactions at 1 bar of CO2 Pressure. The zinc catalyst (1 equiv) was suspended in CHO (1 mL, 100 equiv) under nitrogen atmosphere in a Schlenk tube charged with a stirrer bar. The Paar reactor was purged five times with CO2. The reaction mixture was degassed three times and then heated to 80 °C under 1 bar of CO2 pressure. The crude polymer was obtained by evaporation of the remaining CHO under reduced pressure. Polymers were purified by precipitation from a THF solution in MeOH to yield a white powder.

PA/CHO Polymerization Reactions at 30 bar of CO2 Pressure. The zinc catalyst (1 equiv) was suspended in CHO (6 mL, 1000 equiv) under nitrogen atmosphere in a Schlenk tube charged with a stirrer bar. The Paar reactor was purged five times with CO2. The reaction mixture was transferred into the reactor at 1 atm of CO2 pressure. The crude polymer was obtained by evaporation of the remaining CHO under reduced pressure. Polymers were dissolved in THF then purified by precipitation from MeOH to yield a white powder.

PA/CHO Polymerization Reactions. The zinc catalyst (1 equiv) was suspended in CHO (1 mL, 800 equiv) under nitrogen atmosphere in screw cap vial charged with a stirrer bar. PA (100 equiv) was added, and the vial was closed, sealed, and heated to 100 °C. The crude polymer was obtained by evaporation of the remaining CHO under reduced pressure. Polymers were dissolved in THF then purified by precipitation from MeOH to yield a white powder.

Terpolymerization of PA/CO2/CHO. L2bZn3(OAc)4 (36.6 mg, 0.059 mmol, 1 equiv) and PA (877 mg, 5.93 mmol, 100 equiv) were suspended in CHO (6 mL, 59.3 mmol, 1000 equiv) under nitrogen atmosphere in Schlenk tube charged with a stirrer bar. The Parr reactor was purged five times with CO2. The reaction mixture was then transferred into the reactor at 1 atm of CO2 pressure. The pressure was then adjusted to 30 bar at 100 °C. Aliquots were taken after 2 and 18 h by a depressurization—repressurization procedure at 100 °C. The crude polymer was obtained by evaporation of the remaining CHO under reduced pressure. Polymers were purified by precipitation from a THF solution in MeOH to yield a white powder.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b02233.

The complete experimental procedures and characterization data for all new compounds and copolymers. (PDF) Single-crystal X-ray structure information in CIF format. (CIF)

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**Notes**

The authors declare no competing financial interest.

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