Di-Zinc Aryl Complexes: CO₂ Insertions and Applications in Polymerisation Catalysis

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Abstract: Two new di-zinc aryl complexes, [LZn₂Ph₃] and [LZn₂(C₆F₅)₂], coordinated by a diphenol tetraamine macrocyclic ligand are prepared and fully characterized, including by single crystal X-ray diffraction experiments. The complexes’ reactivities with monomers including carbon dioxide, cyclohexene oxide, phthalic anhydride, iso-propanol and phenol are investigated using both experimental studies and density functional theory calculations. In particular, [LZn₂Ph₃] readily inserts carbon dioxide to form a carboxylate, at 1 bar pressure, whereas [LZn₂(C₆F₅)₂] does not react. Under these conditions [LZn₂Ph₃] shows moderate activity in the ring-opening copolymerisation of cyclohexene oxide / carbon dioxide (TOF = 20 h⁻¹); cyclohexene oxide / phthalic anhydride (TOF = 33 h⁻¹) and the ring opening polymerisations of rac-lactide (TOF = 99 h⁻¹) and ε-caprolactone (TOF = 5280 h⁻¹).

Introduction

Since their original discovery by Frankland in 1848,[1] organometallic zinc compounds have become a well-established component of the synthetic chemists’ toolbox. They have been successfully applied as stoichiometric reagents in Negishi cross-coupling reactions,[2] metal halogen exchange,[3] the alkylation of trifluoromethyl ketones[4] and the epoxidation of enones.[5] Zinc is an attractive choice of metal for catalysis,[6] due to its low toxicity, cost and lack of colour and redox chemistry. Homogeneous zinc catalysts show promise in reactions including the ring opening polymerisation (ROP) of cyclic esters,[7] the formation of cyclic carbonates,[8] aldol reactions[9] and hydroamination reactions.[10] They have been particularly effective as catalysts for CO₂/epoxide ring-opening copolymerisation ( ROCOP), which provides a useful method of adding value to captured CO₂.[11] Some of the most active and selective are zinc complexes coordinated by β-diamo- or phenoxy-amine ligand scaffolds.[12] With some of these different catalyst systems, short chain telechelic polycarbonates have been observed,[13] which are potentially useful for chain extension reactions to form block copolymers,[14] polyurethanes,[15] or nanomaterials.[16] The presence of such α,ω-dihydroxyl end capped polymers is generally attributed to the presence of diols, formed through the reaction of epoxides with trace water, which act as chain transfer agents during polymerisation. Darenbourg recently gleaned further insight into the nature of this reaction, and established that this hydrolysis is catalysed by the polymerisation catalyst, [(salen)Co(O₂CCF₃)], in both CO₂/cyclohexene oxide (CHO) and CO₂/propylene oxide (PO) ROCOP systems. Careful spectroscopic studies demonstrated that these [(salen)Co(O₂CCF₃)] catalysed hydrolysis reactions occur prior to any initiation of CO₂/epoxide ROCOP, as the catalyst is initially occupied in the conversion of epoxides to diols.[17] Fundamental reactivities of polymerisation catalysts towards oxygenated small-molecules in ROCOP systems, including alcohols, carbon dioxide and other monomers, are of particular relevance to further understand the reactions occurring with chain transfer agents, and for the preparation of new catalysts for CO₂/epoxide ROCOP, and so we studied the reactivity of zinc catalyst systems with a range of small molecules. Controlling the nature of the bond between the metal and the initiating group or growing polymer chain end is of key interest in polycarbonate synthesis,[18] and has led to the development of “switchable” zinc catalysts, which can catalyse both the ROP of lactones and the ROCOP of epoxides with CO₂ or anhydrides, thus enabling the controlled synthesis of block copolymers from a mixture of monomers.[19]

Considering the general reactivity of zinc alkyl complexes, there are a number of reports of reactions with alcohols or carboxylic acids.[19] The insertion of CO₂ into Zn-alkoxide bonds has also been studied in depth.[11b] Some examples relevant to catalysis include the reversible insertion of CO₂ into di-zinc alkoxide complexes based on a macrocyclic bis(anilido)tetramine ligand, to form di-zinc carbonate and mixed carbonate/alkoxide products.[20] Considering BDI-Zn complexes, which are well-studied catalysts for CO₂/epoxide ROCOP, zinc-alkoxides rapidly insert CO₂, whilst the epoxide coordination and ring-opening is an equilibrium process.[11b, 19b] Despite these insightful studies, the reaction of Zn-alkyl complexes with carbon dioxide remains much less explored,[21] and the initial reactivity of such complexes in the presence of CO₂, epoxide and diols is still not well understood. Kinetic studies have shown that CO₂ insertion occurs rapidly for a series of zinc hydride complexes, to form the corresponding zinc formate complexes, where the reaction kinetics were limited by the rate of CO₂ dissolution in toluene solvent ($k_{obs} = 0.033$ M min⁻¹).[22]
Recently, some of us reported a diphenol tetraamine based macrocyclic ligand which was used to prepare a series of dinuclear catalysts,[12b, 24] including di-zinc carboxylate compounds. These complexes showed activities for both the ROCOP of CO₂/epoxide and of epoxide/anthrydride, and were notable in being able to selectively polymerize at just 1 bar pressure of CO₂. Here, we apply the same ligand and investigate the potential to prepare di-zinc bis(aryl) precatalysts. To gain insight into the reactions that may occur between such precatalysts and the key monomers or chain transfer agents present during polymerisation (Scheme 1), the reactivity of the complexes towards stoichiometric epoxide (CHO), phthalic anhydride (PA), CO₂, and alcohols was explored. The effect of electron-withdrawing substituents on the aryl co-ligand was also compared, through experimental and computational comparisons, between di-zinc bis(phenyl) and di-zinc bis(pentafluorophenyl) complexes.

Results and Discussion

Complex Synthesis (LZnPh₂ and LZn(CF₃)₃s)

The macrocyclic pro-ligand LH₂ (Scheme 2) was prepared according to literature methods[12b] and cleanly deprotonated using two equivalents of either ZnPh₂ or Zn(CF₃)₂, in THF at -40 °C. The di-zinc complexes [LZnPh₂] (1, 81 % yield) and [LZn(CF₃)₂] (2, 52 % yield) were afforded, respectively (Scheme 2). For both 1 and 2, colourless block crystals suitable for X-ray diffraction studies were obtained by gradual cooling of a hot benzene solution to 25 °C.

Structural elucidation via X-ray diffraction revealed that the two complexes are very similar, and sit across a centre of symmetry at the middle of the Zn₂O₂ rings (Fig. 1). In contrast to other related di-Zn complexes based on LH₂, where the ligand adopts a bowl shape, here the ligand adopts an “S” shape.[24b] The pentacoordinate Zn atoms, which are bound within the ligand, each share two phenol-O oxygen atoms. For both 1 and 2, there is a significant difference between the two different Ar-O-Zn bond lengths, of 0.13 Å in 1, and 0.09 Å in 2. Completing the pentacoordinate geometry, each Zn also bonds to two amine nitrogen atoms and one aryl-C atom. The aryl-C-Zn bond lengths lie within the expected range,[26] although the bond is 0.03 Å shorter in 1 than in 2. One curious feature is the presence of H-F interactions in 2, observed between the amine NH and the fluoryl substituents (F(21)-H(8): 2.56(1) Å). Nevertheless, the nature of the co-ligand does not appear to affect the phenol C-O bond length, which is almost identical within 1 [O(1)-C(1), 1.341(2) Å] and 2 [1.338(2) Å].

![Scheme 1](image1.png)

![Scheme 2](image2.png)

Figure 1. Molecular structures of a) [LZnPh₂) and b) [LZn(CF₃)₃]. Hydrogen atoms and benzene molecules are omitted for clarity.

The ¹H NMR spectrum of 1 is rather complex at room temperature in C₆D₆, d₆-THF and CDCl₃. However, at high temperature (403 K in d₆-TCE) an averaged spectrum is obtained consistent with a symmetric structure (Fig. S1-S2). Contrary to 1, the ¹H NMR spectrum of 2 shows well-defined signals at room temperature in CDCl₃ (Fig. S3-S5). For both 1 and 2, the formation of a zinc-zinc complex was evidenced by four distinct benzylic and methylene resonances. COSY experiments showed that these benzylic and methylene resonances both couple to the NH resonance at 2.43 ppm in 1, and 2.54 ppm in 2. The ¹³F NMR spectrum of 2 reveals three
sharp resonances for the ortho-, meta- and para- resonances, which suggests that the solid state H-F interactions are not maintained at 25 °C in solution.

The 1H NMR spectrum of 1 is rather complex at room temperature in CD2Cl2, d8-THF and CDCl3. However, at high temperature (403 K) in d8-TCE an averaged spectrum is obtained consistent with a symmetric structure (Fig. S1-S2). Contrary to 1, the 1H NMR spectrum of 2 shows well-defined signals at room temperature in CDCl3 (Fig. S3-S5). For both 1 and 2, the formation of a zinc-zinc complex was evidenced by four distinct benzylic and methylene resonances. COSY experiments showed that these benzylic and methylene resonances both couple to the NH resonance at 2.43 ppm in 1, and 2.54 ppm in 2. The 13C NMR spectrum of 2 reveals three sharp resonances for the ortho-, meta- and para- resonances, which suggests that the solid state H-F interactions are not maintained at 25 °C in solution.

Reactivity Studies

It was of interest to investigate the reactivity of 1 and 2 towards CO2, to probe their potential use as polymerisation catalysts.[12b, 24] It was observed that 1 reacted with CO2 at 1 bar of CO2 pressure, in CD2Cl2 at 25 °C to afford the corresponding dibenzoate complex [Zn2(OOC-Ph)2]3 (Scheme 2), with complete conversion occurring after two hours, as observed by 1H NMR analysis (Scheme 2, Fig. S6). The rate of CO2 insertion was significantly enhanced by heating the solution to 80 °C, affording complete conversion of 1 to 3, within 5 minutes.

To unambiguously confirm the formation of the dibenzoate complex from CO2 insertion into 1, 3 was independently synthesized via direct metallation of LH2 by zinc carboxylate Zn(OOC-Ph)2, at 25 °C in THF (Scheme 2). The 1H NMR spectrum was identical to that obtained from CO2 insertion into 1. Colourless block crystals suitable for X-ray diffraction were obtained at 25 °C from a benzene/THF solvent system, enabling structural elucidation of 3 (Fig. 2). The ligand adopts a distorted “S” shape holding two pentacoordinate Zn centres, each with a pendant κ1,O benzoate ligand, two bridging phenol-O atoms and two secondary amine N atoms. The benzoate C-O bonds differ significantly in length, as the bonds to O(52) and O(42) are 0.05 Å shorter, suggesting that these contain the most double bond character and that O(40) and O(50) are the anionic donors. At 3.1009(5) Å, the Zn···Zn separation is 0.16 Å shorter than 1. This is likely to result from the shortened aryl-O-Zn bonds, which are 0.03 and 0.13 Å shorter than in 1. Additional, hydrogen bonding interactions between the benzoate-O and the amine-NH [O(42)-H(18); 2.15(2) Å] provide further stabilization for 3.

Complex 3 reproducibly gave rather complex NMR spectra, at high and low temperatures, in a range of different solvents including CDCl3, CD2Cl2 and d8-THF. However, in d8-methanol, a much better resolved 1H NMR spectrum was obtained (Fig. S7-S8). The spectrum confirmed the formation of the di-zinc complex, there are diastereotopic benzylic (4.23 and 3.34 ppm) and methylene (2.91 - 2.83 ppm) resonances, and the NH resonance is observed at 3.15 ppm. It possesses C2 symmetry in methanol solution. The benzoate ligands are clearly present as evidenced by the deshielded ortho-phenyl resonance at 7.87 ppm. In the 13C NMR spectrum, quaternary carbon resonances were too weak to be observed (including by HMBC experiments) and so a 13C carbon labelled sample of 3 was prepared, by the reaction of 1 with two equivalents of 13C labelled benzoic acid. The carbonyl resonance of 3 is clearly observed at 174.6 ppm, shifted from free benzoic acid (170.1 ppm).

**Figure 2.** Molecular structure of 3. Hydrogen atoms and a benzene solvent molecule are omitted for clarity.

In contrast, the fluoryl analogue, complex 2, did not react with CO2 under identical reaction conditions. It is proposed that this decrease in nucleophilicity of the aryl group, due to the electron withdrawing fluoryl substituents, disfavours CO2 insertion. This is supported by the observation of a longer, weaker Zn-C bond in 2 (2.049(1) Å) compared to 1 (2.016(1) Å) in the solid state crystal structure. A theoretical study was carried out in order to gain a better understanding of the CO2 insertion into the Zn-aryl bonds. DFT was used to calculate the potential energy surface for the stepwise CO2 insertion into the Zn-aryl bond for complexes 1 and 2 (Fig. 3), to provide insight into the activation energy barriers and the relative stability of the intermediates and products. The calculations were carried out using DFT protocol wb97xd/6-31G(d)/def2-spcf (ccpcm = dichloromethane) at 353 K, which has previously shown a good agreement with experiments for related reaction studies of similar dinuclear zinc complexes (refer to ESI for further details).[24] This study focussed on the previously unreported barrier of CO2 insertion into the Zn-aryl bond and the calculations reveal the energy barrier to be 9.0 kcal mol-1 higher for 2' (overall barrier ΔG = +28.7 kcal mol-1) than for 1 (overall barrier ΔG = +19.7 kcal mol-1). The carbonate products derived from complex 1 are more stable than the corresponding fluoryl analogues obtained from 1' (ΔΔG up to 20.4 kcal/mol between 1'CO2 and 2'CO2), giving further support.
Figure 3: Potential energy surface for the first single CO$_2$ insertion into the zinc aryl bond of 1 (black) and 2 (blue); DFT protocol: wb97x-d/6-31G(d)/cpcm=DCM/Temp=353 K. The ancillary ligand structure is omitted for clarity. Interactive version of the figure available at doi.org/10.14469/hpc/2222.

to the experimental observation that CO$_2$ inserts more readily into the Zn-Ph bond than the Zn-C$_6$F$_5$ analogue.

The calculated mechanism shows CO$_2$ insertion occurring at only one metal centre, without participation of the second metal or second aryl co-ligand (Fig. 3). NBO analysis was carried out for III-TS$^{CO_2}$ which shows a significant interaction between the Zn-C bond and incoming C(CO$_2$) atom (see ESI, Fig. S9). This contrasts with what was previously observed in the case of a bridging acetate co-ligand, where CO$_2$ insertion into a Zn-alkoxide bond occurs via a bimetallic mechanism, along with 'shuttling' of the electron density of the acetate co-ligand to balance the charge.

Considering the most stable conformation VI$^{CO_2}$, the second CO$_2$ insertion into I was found to occur via a bimetallic mechanism, with nucleophilic attack of the aryl to the CO$_2$, and forming a complex with the carboxylate coordinated to one metal centre; concomitantly, the bridging co-ligand balances the charges. The energy barrier for this second insertion was found to be 18.6 kcal.mol$^{-1}$ (between VI$^{CO_2}$ and VII$^{CO_2}$), which lies close to that determined for the first CO$_2$ insertion (19.7 kcal.mol$^{-1}$). Overall, the formation of the bis-carboxylate complex, IX$^{CO_2}$, is highly thermodynamically favoured, with $\Delta G = -49.5$ kcal.mol$^{-1}$.

Unfortunately, it was not possible to gain experimental evidence for the formation of any intermediates V$^{CO_2}$ -- VII$^{CO_2}$ to confirm this step-wise model of CO$_2$ insertion (i.e. monitoring of the reaction by NMR spectroscopy detected only product 3). However, it seems reasonable to conclude that the insertion of CO$_2$ into the Zn-Ph bond is accessible under the reaction conditions, while the CO$_2$ insertion with the fluoryl analogue has a significantly higher energy barrier and is thermodynamically less favoured overall.

A catalyst system, prepared from the in situ reaction of 1 with 1,2-cyclohexenediol, has previously been applied towards the controlled synthesis of block co-polymers, through selective catalysis combining the ROP of ε-CL with the ROCOP of epoxides and anhydrides. However, this catalyst system was prepared and used in situ without detailed characterization. Thus, it was of interest to investigate the reactivity of 1 and 2 with alcohols (Scheme 1). In these studies, iso-propanol was used as a model for the chain transfer agent 1,2-cyclohexenediol. It was selected as a secondary alcohol of similar steric bulk but which simplified spectroscopic characterization and computational studies compared to 1,2-cyclohexenediol (vide infra). Although a THF solution of 1...
proved stable in the presence of iso-propanol (2 equivalents) at 25 °C, heating the reaction mixture to 60 °C for 18 hours led to complete consumption of 1 (Scheme 2). 1H NMR analysis, in d8-THF, revealed the formation of a new species, [LZn(2)(OPh)2](4), along with the formation of benzene (singlet at 7.30 ppm) (Fig. S10-S12). As the copolymerisations are typically performed at temperatures above 60 °C, this finding suggests that zinc-alkoxide species can form readily under polymerisation conditions. In contrast to the broad, convoluted 1H spectrum of 1 in d8-THF at 298K, 4 has a sharp, well-resolved 1H spectrum. Complex 4 was most clearly characterized by the iso-propoxide methyne (4.11 ppm) and methyl signals (0.96 ppm) which were shifted compared to free alcohol. Integration of the relevant resonances confirms the 2:1 iso-propanol:ligand ratio, showing that complete conversion of both the Zn-Ph bonds to Zn-OPr groups has occurred. Catalyst 2 also reacted with iso-propanol, under reflux conditions in d8-THF, however a mixture of species was observed, which included 4 and Cp2ZnH, along with unreacted 2 and 1PrOH. The reagents 2 and 1PrOH were still observed after 3 days at reflux, most likely because the presence of the electron withdrawing fluoryl substituents decreases the Brønsted basicity of the phenyl group. Despite several attempts, X-ray quality crystals of 4 could not be obtained. Instead, the analogous reaction of 1 with phenol (2 equivalents) was performed, which led to the formation of the corresponding di-zinc bis(phenolate) complex [LZn(2)(OH)2](5) (Fig. 4). Its 1H NMR and HSQC experiments reveal the presence of diastereotopic benzylic and methylene protons (Fig. S13-S14). Only one NH environment is observed, suggesting that the hydrogen bonding present in the solid state structure of 5 is not maintained in THF solution at 328 K.

Crystals of 5 suitable for X-ray diffraction were crystallized from a mixed THF/DCM solvent system. The molecular structure is centrosymmetric and very similar to 1, where the ligand adopts an “S” shaped conformation and both Zn centres are pentacoordinated by the macrocyclic ligand scaffold (two phenol O and two amine N) and a terminal phenol group. There is a significant difference in bond lengths between the bridging and terminal phenols, where the terminal C-O-Zn bond is significantly shorter (by 0.09 Å) than the bridging phenolate bonds from the macrocycle.

The reactivity of complex 1 with iso-propanol was studied computationally, using DCM solvent and 353.15 K to mimic polymerisation conditions. The lowest energy pathway was found to have the incoming iso-propanol molecule approaching the concave face of the “bowl” shaped complex (Figure 5). The energy barrier for the first protonolysis of 1 with iso-propanol is +19.9 kcal mol⁻¹, which is almost identical to the calculated energy barrier for CO₂ insertion (+19.7 kcal mol⁻¹). The product of the first protonolysis (V⁺OR) is thermodynamically favourable (-17.7 kcal mol⁻¹). The intermediate can then react with a second equivalent of iso-propanol, with an energy barrier of +25.4 kcal mol⁻¹, to yield complex 4 (VIII⁺OR) which is calculated to have a relative energy of -37.3 kcal mol⁻¹, compared to complex 1 (I). This product can also be formed if the protonolysis intermediate (V⁺OR) were to undergo a ligand conformational rearrangement, to give a more stable intermediate V⁺OR (by 2.2 kcal mol⁻¹). Subsequently, the reaction pathway with iso-propanol approaching from the concave face (Vb⁺OR) has a lower energy barrier of +20.5 kcal mol⁻¹. The calculations show that the energy barriers for the protonolysis pathways are easily accessible, under polymerisation conditions, and that the products formed are highly stable relative to complex 1. A key finding is that protonolysis, by reaction with chain transfer agents present during polymerisation, is likely to be a highly favourable reaction and that zinc alkoxide complexes might be considered as the active sites for such catalytic systems.

**Polymerisation Studies**

Following the successful reaction of 1 with CO₂, its catalytic activity within CHO/CO₂ copolymerisation was tested. The polymerisations were run at 0.1 mol % catalyst loading (vs the epoxide, CHO), using 1 bar of CO₂ pressure (Table 1, entry 1), as analogous di-Zn catalysts have previously shown acceptable activity under these conditions. The phenyl catalyst 1 is active (TOF = 20 h⁻¹) and exhibits good CO₂ uptake, giving > 99 % carbonate linkages. The polymerisation is well-controlled, with a monomodal distribution and a narrow dispersity (1.06). 1 displays similar activity to the previously reported acetate analogue, [LZn(2)(OAc)2] (TOF = 18 h⁻¹, entry 4), and significantly outperforms the bromide complex [LZn(2)Br2], which is completely inactive under identical reaction conditions. Notably, the MALDI-TOF analysis shows that the purified product is a telechelic polymer terminated by hydroxyl groups (Fig. S15), a feature which has been observed with some different catalysts for this copolymerisation. The formation of dihydroxyl end-capped polymers is consistent with reactions of [LZn(2)Ph2] with alcohol (1,2-cyclohexanediol) to form the active site. The reactivity studies have also demonstrated the capability of 1 to react with CO₂ within 5 minutes at 80 °C, suggesting that the product di-zinc bis(benzoate) complex could initiate copolymerisation. However, benzoate end groups were
Figure 5: Potential energy surface for the first and second protonolysis of the zinc-aryl bond of 1, with iso-propanol; DFT protocol: ωb97xd/6-31G(d)/cpcm=DCM/Temp=353.15 K (data available at doi.org/10.14469/hpc/2144). The ancillary ligand structure is omitted for clarity.

not observed in the NMR spectroscopy or MALDI-ToF analysis. Thus it seems likely that the reaction of the zinc aryl complex with diols, occurs even more rapidly than with CO₂ and is responsible for the true initiation under these conditions. In line with this observation, catalyst 2 is also active for CHO/CO₂ ROCOP, in spite of its complete lack of reactivity towards either CHO or CO₂ in model reactions. Rather, 2 is proposed to react with alcohols to generate active alkoxide initiators (Scheme 1).

Using catalyst 2, once again a telechelic polymer is formed, as confirmed by SEC and MALDI-ToF analysis (Fig. S16). For both 1 and 2, the theoretical M_n values are approximately 12 times greater than the experimental values, which provides further support for the presence of a chain transfer agent. The zinc benzoate analogue, 3, was also active for CO₂/epoxide copolymerisation (entry 3) and the MALDI-ToF analysis of the resultant polymer confirmed the presence of both α-benzoate, ω-hydroxy and α, ω-hydroxy end-capped polymers (Fig. S17). The presence of α-benzoate end-groups was confirmed by 1H NMR spectroscopy (Fig. S18).

It has previously been shown that analogues of 1 and 2 with acetate and halide co-ligands were effective catalysts for the ROCOP or epoxide (CHO)/anhydride (phthalic anhydride PA), and that when a mixture of monomers is present, anhydride insertion occurs more rapidly than CO₂ insertion. In order to gain further understanding of the polymerisations, complex 1 was tested as a catalyst for the ROCOP of PA/CHO, using a 1 mol% catalyst loading at 100 °C, and neat epoxide as the solvent. After 3 hours, 100% conversion was achieved (Table 1, entry 5), with 98% of alternating enchainment (% ester linkages). The polymerisation is well-controlled, giving a monomodal MW distribution and a narrow dispersity (D = 1.10). Here, 1 displays a slightly superior activity (TOF = 33 h⁻¹) compared to its acetate (TOF = 24 h⁻¹) and halide (TOF = 17 h⁻¹) analogues, under analogous conditions. Theoretical
Table 1. Results for ROP of CHO/CO₂, PA/CHO and cyclic esters using catalysts 1, 2, 3 and LZn2(OAc)₂.

<table>
<thead>
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<th>Entry</th>
<th>Monomer /s</th>
<th>Cat./PA/CHO Monomer</th>
<th>T (°C)</th>
<th>Time</th>
<th>TOF (h⁻¹)</th>
<th>Mw (g/mol)</th>
<th>[D]</th>
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[a] Determined by 'H NMR. [b] Polymer molecular weights were determined using SEC, calibrated by polystyrene standards, and correction factors were applied as reported previously (1.85 for PA/CHO,[10] 0.58 for PLA[20] or 0.56 for PCL[21]). [c] CO₂ = 1 bar. [d] Reaction conditions: 1:100:900 molar ratio of catalyst:PA:CHO; [e] Assuming 2 chains grow per catalyst; [f] Reaction conditions: 1:200:900 molar ratio of catalyst:PA:CHO; [g] Reaction conditions: 1:100:800 molar ratio of catalyst:PA:CHO; [h] Reaction conditions: [M]₀ = 1 M.

Calculations suggest that the phenyl co-ligand could ring open PA, as the energy barrier is +29.9 kcal mol⁻¹, and the reaction gives a net energy gain of 30.5 kcal mol⁻¹ (Fig. S19). However, the polyester analysis by MALDI-ToF again shows only a series of a,ω-dihydoxy-terminal polymers.[25a, 28] In this case, the reactivity barrier for insertion of PA into the zinc-phenyl bond is significantly greater than the competing protonolysis pathway, by 10.0 kcal mol⁻¹. This suggests that the reaction of complex 1 with alcohols is thermodynamically more favourable than the reaction with PA. It is supported by the absence of phenyl-capped polymers experimentally. Although 2 displays good activity for CHO/PA RCOP (TOF = 24 h⁻¹, entry 6), it is less active than 1 and the polymerisation is poorly controlled, with a broad dispersity (Đ = 2.27) and low polyester selectivity (23 % polyester vs polyether). It is therefore observed that the C₇F₅ co-ligand has a detrimental effect, although the exact nature of this influence is not completely clear.

Previously a catalyst system formed in situ by reaction between 1 and 1,2-cyclohexanediol was investigated for the ROP of ε-CL.[30a] This showed that the catalyst was highly effective but polymers with different topologies were formed: indeed, there was evidence for chains both end-capped by diol and chain extended from the diol. This is because the diol contains two sterically hindered secondary alkoxide groups, which are relatively slower to initiate polymerisations. Given this previous study, it was of interest to study the activation of catalyst 1 with a monofunctional alcohol, so as to ensure that there is only a single type of chain structure. In the presence of iso-propanol, 1 was therefore applied to the ROP of rac-lactide and ε-caprolactone (Table 1, entries 9-13). Under all conditions tested, 1 demonstrated good catalytic activity under immortal polymerisation conditions (TOF = 5280 h⁻¹, entry 9). The dispersities are broad, especially for polycaprolactone (PCL). This is attributed to the Zn-Ph reaction with alcohol occurring relatively more slowly at ambient temperature. A series of resonances assigned to a-iso-propoxide, ω-hydroxy end-capped polycaprolactone is observed in the MALDI-ToF spectrum (Fig. S20, Table 1, entry 9).

The results show that di-zinc arylic 1 can readily react with alcohols, either deliberately added or present as a result of the reaction of water and epoxide, to generate Zn-alkoxide active sites that can readily initiate polymerisations. In contrast, the di-zinc acetate complex, LZn₂OAc₂, does not react with alcohols and lactones and so is not a suitable catalyst for ROP (entry 11 and 13). It is known that the Zn-carboxylate can react with epoxides to generate Zn-alkoxide species in situ, which initiate the ROP of lactones, as applied by our group to prepare “switchable” catalysts.[18e]

Alternatively, the Zn-alkoxide can readily insert CO₂, whereas its acetate precursor cannot. Although 1 can insert CO₂ into the Zn-C bond to form a carboxylate, the observation of a,ω-dihydoxy end capped polymers suggests that reaction of 1 with alcohols occurs more rapidly (Scheme 1). While the acetate catalysts can also undergo chain transfer reactions with added alcohols or water,[15a, 23a] these reactions presumably occur after epoxide opening generates the Zn-alkoxide species.
Conclusions

In summary, two di-aryl zinc complexes have been synthesized from the same macrocyclic ligand and characterized using X-ray crystallographic and NMR spectroscopic studies. It clearly inserts CO$_2$ under mild conditions, whilst 2 is inactive, highlighting differences caused by the electron withdrawing fluoroyl substituents. The complexes also react readily with alcohols, to generate the di-zinc bis(alkoxide) complexes, which were fully characterized. Both 1 and 2 efficiently initiate the alternating copolymerisations of cylohexene oxide/carbon dioxide and cyclohexene oxide/phthalic anhydride, demonstrating similar activities to the well-established acetate analogue. The reactivity and theoretical studies suggest that the competing reactions of 1 with CO$_2$ or diols are both viable initiation mechanisms for CO$_2$/epoxide ROCOP. However, the polymerisation studies suggest that the protonolysis of 1 and 2, with added or generated alcohols, occurs more rapidly than CO$_2$ insertion, and is the predominant initiation mechanism. The in situ generated alkoxide complex is also an effective catalyst for the ROP of cyclic esters, including both rac-lactide and ε-caprolactone, whereas the acetate analogue is completely inactive.

Overall, these studies have led to an improved understanding of the reactivity of di-zinc bis(aryl) catalysts, and show how these versatile catalysts can be applied to a range of ROP and ROCOP processes. We expect that the role alcohols can play in the initial stages of initiator formation, will facilitate the development of improved future catalyst systems, which will be the focus of our future studies.

Experimental Section

All metal complexes were synthesized under anhydrous conditions, using MBraun gloveboxes and standard Schlenk techniques. Solvents and reagents were obtained from Sigma Aldrich or Stem and were used as received unless stated otherwise. THF was dried by refluxing over sodium and benzophenone and stored under nitrogen. iso-propanol was dried over calcium hydride and distilled prior to use. Cyclohexene oxide (CHO) was dried over CaH$_2$ and fractionally distilled under nitrogen. Phthalic anhydride was purified by dissolving in benzene, filtering off impurities, recrystallizing from chloroform and then subliming. All dry solvents and reagents were stored under nitrogen and degassed by several freeze-pump-thaw cycles. Research grade carbon dioxide was used for all copolymerisation studies. Macrocyclic ligand LH$_2$ was synthesized following literature procedures.$^{[12b]}$ NMR spectra spectra were recorded using a Bruker AV 400 MHz spectrometer. Correlations between proton and carbon atoms were obtained by using COSY and HSQC NMR spectroscopic methods. Elemental analysis was determined by Stephen Boyer at London Metropolitan University. SEC was performed using two Mixed Bed PSS SDV linear S columns 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 ($M_w$) was determined by comparison against polystyrene standards, with a correction factor of 1.85 for PA/CHO.$^{[19]}$ 0.58 for PLA,$^{[20]}$ and 0.56 for PCL.$^{[20]}$ The polymer samples were dissolved in SEC grade THF and filtered prior to analysis.

Crystal Structure Determination: Single crystal data were measured at low temperature using an Agilent Xcalibur PX 3E diffractometer, and the structures were refined using the SHELXTL and SHELX-2013 program systems. Selected parameters are given in the Supporting Information and full details are given in the deposited cif files. CCDC reference numbers 1498754 – 1498757 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Complex synthesis

LZn$_2$(Ph)$_4$ – (1): A THF solution (5 mL) of H$_2$L (318 mg, 0.57 mmol) was cooled to -40 °C. To this, a pre-cooled (-40 °C) THF solution (2 mL) of diphenyl zinc (253 mg, 1.04 mmol) was added. The resultant cloudy solution was stirred overnight at 25 °C, filtered then washed with cold THF. The bis-zinc phenyl complex I was isolated as a white powder (381 mg, 0.46 mmol, 81 % yield), X-ray quality crystals were obtained by gradual cooling of a hot benzene solution of 1 to 25 °C. H NMR (CDCl$_3$, 400 MHz, 403 K) $\delta$ 7.40 (s, 5H, Ph), 7.00 (s, 4H, Ar), 4.81 (br. m, 4H, CH$_2$H$_2$)$_2$, 3.37 (br. d, 4H, $\delta_{CH2}$ = 13.3 Hz, CH$_2$H$_2$)$_2$, 2.96 (br. d, 4H, $\delta_{CH2}$ = 10.1 Hz, CH$_2$H$_2$)$_2$, 2.89 (br. m, 4H, CH$_2$H$_2$)$_2$, 2.47 (br. m, 4H, NH)$_2$ (1.84, Bu$_3$), 1.31 (s, 6H, CH$_3$), 1.07 (s, 6H, CH$_3$)$_2$. 13C NMR (CDCl$_3$, 100 MHz, 293 K) $\delta$ 138.5 (Cquat, Aryl), 128.1 (Ph), 128.0 (Cquat, Aryl), 128.8 (CH, Aryl), 128.3 (Cquat, Aryl), 63.5 (CH), 56.7 (CH)$_3$, 33.4 and 33.3 (Cquat, Bu and Cquat, CMes), 31.3 (Bu), 27.9 (CH$_3$), 21.5 (CH$_3$). Anal. Calc. for LZn$_2$(Ph)$_4$: C, 65.98; H, 7.77; N, 6.68.

LZn$_2$(C$_6$F$_5$)$_4$ – (2): To a pre-cooled THF solution (-40 °C, 5 mL) of H$_2$L (200 mg, 0.36 mmol) was added a pre-cooled (-40 °C) THF solution (2 mL) of Zn(C$_6$F$_5$)$_2$ (289 mg, 0.72 mmol). After addition, a white suspension started to form. The reaction mixture was allowed to react overnight at 25 °C, and then filtered. The solid product was subsequently washed with cold THF and dried under vacuum to isolate the pure di-zinc complex 2 as a white powder (180 mg, 0.19 mmol, 52 % yield). H NMR (CDCl$_3$, 400 MHz, 298 K) $\delta$ 6.75 (s, 4H, Ar), 4.31 (dd, 4H, $\delta_{CH2}$ = 13.3 Hz, CH$_2$H$_2$)$_2$, 3.33 (d, 4H, $\delta_{CH2}$ = 13.3 Hz, CH$_2$H$_2$)$_2$, 3.04 (dd, 4H, $\delta_{CH2}$ = 12.0 Hz, $\delta_{CH2}$ = 13.9 Hz, Cquat, Aryl), 2.69 (d, 4H, $\delta_{CH2}$ = 12.0 Hz, CH$_2$H$_2$)$_2$, 2.54 (dd, 4H, $\delta_{CH2}$ = 12.0, $\delta_{CH2}$ = 14.0 Hz, NH)$_2$, 1.24 (s, 6H, CH$_3$), 1.21 (s, 18H, Bu)$, 1.04$ (s, 6H, CH$_3$), 13C NMR (CDCl$_3$, 100 MHz, 298 K) $\delta$ 160.8 (Cquat, Aryl), 136.7 (Cquat, Aryl), 126.3 (CH, Aryl), 126.3 (Cquat, Aryl), 62.7 (CH)$_3$, 58.1 (CH$_3$)$_3$, 34.1 and 33.7 (Cquat, Bu and Cquat, CMes), 31.7 (CH$_3$)$_3$, 28.6 (CH$_3$)$_3$, 20.5 (CH$_3$)$_3$. 19F NMR (CDCl$_3$, 377 MHz, 298 K) $\delta$ -115.1 (br. s, 2F), -157.6 (t, 4F, J = 20 Hz), -160.8 (m, 4F). Anal. Calc. for LZn$_2$(C$_6$F$_5$)$_4$: C, 54.40; H, 5.36; N, 5.52; Found: C, 54.25; H, 5.45; N, 5.39.

LZn$_3$(OCCF$_3$)$_2$ – (3): To a pre-cooled THF solution (-40 °C, 5 mL) of H$_2$L (200 mg, 0.36 mmol) was added a pre-cooled (-40 °C) THF solution (2 mL) of Zn(OCCF$_3$)$_2$ (223 mg, 0.72 mmol.). A homogeneous solution was produced upon addition, which was stirred overnight at room temperature. After 18 hours, a white suspension formed, which was isolated via filtration and washed with hexane. The filtrate was cooled down in the freezer (-30 °C) to give a second crop of the white precipitate. Both solids were collected and dried under vacuum to afford 3 as white solid (234 mg, 72 % yield overall). H NMR (d$_2$-methanol, 400 MHz, 298 K) $\delta$ 7.88 (br. m, 4H, o-Ph), 7.36 (tt, 2H, $\delta_{Ph}$ = 7.6 Hz, $\delta_{Ph}$ = 1.5 Hz, p-Ph), 7.28 (tt, 4H, $\delta_{Ph}$ = 7.6 Hz, m-Ph), 6.98 (s, 4H, Ar), 4.23 (dd, 4H, $\delta_{CH2}$ = 12.0 Hz, CH$_2$H$_2$)$_2$, 3.34 (d, 4H, CH$_2$H$_2$)$_2$, 3.15 (dd, 4H, $\delta_{CH2}$ = 12.0 Hz, NH)$_2$, 2.91-2.83 (m, 8H, Cquat and Cquat'), 1.45 (s, 3H, CH$_3$), 1.45 (s, 3H, CH$_3$)$_3$, 1.19 (s, 18H, Bu), 1.04 (s, 3H, CH$_3$). 19F NMR (d$_2$-methanol, 100 MHz, 298 K) $\delta$ -174.64 (C=O), 131.9 (p-Ph), 130.6 (p-Ph), 129.3 (CH, Aryl), 128.9 (Cquat).
Keywords: Ring-opening copolymerisation • ring opening polymerisation • CO2 insertion • reactivity studies • organozinc catalysts


Versatile catalysis: Reactivity studies of zinc-aryl complexes towards carbon dioxide, alcohols, epoxides and anhydrides are investigated using a combination of experimental methods and density functional theory calculations. The catalyst systems are active for both ring opening copolymerisation of epoxide with CO₂ or anhydrides, and the ring-opening polymerisation of lactones.