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

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

Charles Romain,[b]† Jennifer A. Garden,[c]† Gemma Trott,[a] Antoine Buchard,[d] Andrew J. P. White[b] and Charlotte K. Williams[a]*

Abstract: Two new di-zinc aryl complexes, [LZn₂Ph₂] 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, [LZn₂Ph₂] readily inserts carbon dioxide to form a carboxylate, at 1 bar pressure, whereas [LZn₂(C₆F₅)₂] does not react. Under these conditions [LZn₂Ph₂] 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-diiminate 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. Darensbourg 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.[14a] 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,[17] 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.[18]

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)tetraimine 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, 19c] 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]

[a] Department of Chemistry, Chemistry Research Laboratory
University of Oxford, 12 Mansfield Road, Oxford, OX2 3TA, UK
E-mail: charlotte.williams@chem.ox.ac.uk
[b] Department of Chemistry
Imperial College London, London, SW7 2AZ, UK
[c] EastCHEM School of Chemistry
University of Edinburgh, Edinburgh, EH9 3FJ, UK
[d] Department of Chemistry
University of Bath, Bath, BA2 7AY, UK
† These authors contributed equally to this work.

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Recently, some of us reported a diphenol tetraamine based macrocyclic ligand which was used to prepare a series of dinuclear catalysts,[13d, 23] including di-zinc carboxylate compounds.[12b, 24] These complexes showed activities for both the ROCOP of CO_2/epoxide and of epoxide/anhydride, and were notable in being able to selectively polymerize at just 1 bar pressure of CO_2.[25] 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), CO_2, 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.
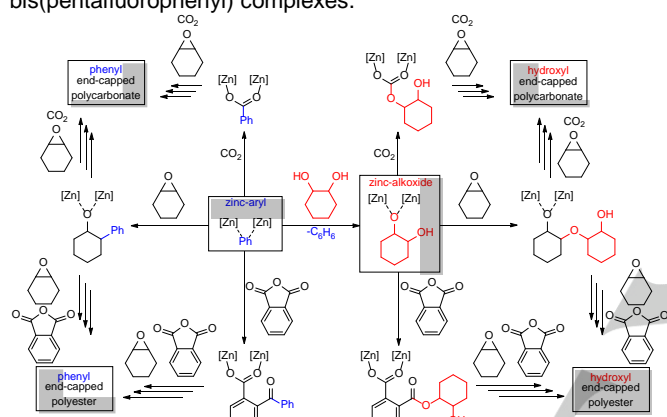
Scheme 1 Reactivity overview of the plausible reactions of di-zinc aryl complexes with monomers CO_2, CHO and PA, in the presence of chain transfer agent 1,2-cyclohexenediol.

Results and Discussion

Complex Synthesis (LZn₂Ph₂ and LZn₂(C₆F₅)₂)

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(C₆F₅)₂, in THF at -40 °C. The di-zinc complexes [LZn₂Ph₂] (**1**, 81 % yield) and [LZn₂(C₆F₅)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 Zn_2O_2 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 ArO-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].
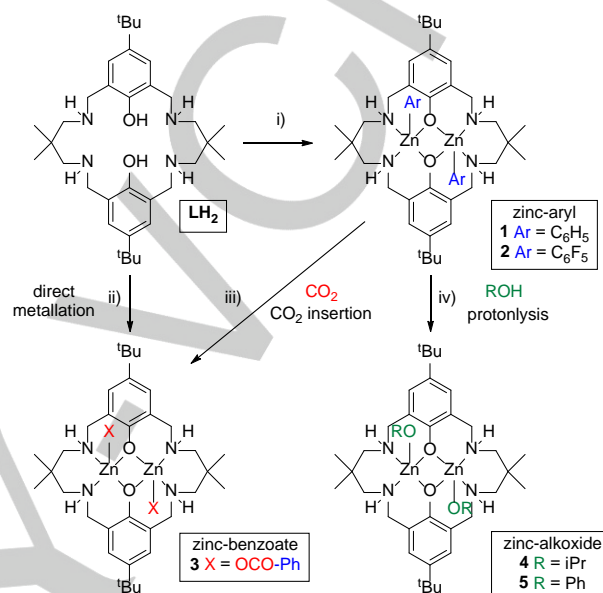
Scheme 2. Reactivity overview showing the synthesis of zinc complexes **1**-**5**. Reaction conditions: i) -40 °C to 25 °C, THF solvent, 18 h; **1**, ZnPh₂ (2 equiv.), 81 % crystalline yield; **2**, Zn(C₆F₅)₂ (2 equiv.), 52 % crystalline yield; ii) Zn(OCO-Ph)₂ (2 equiv.), -40 °C to 25 °C, THF, 18 h, 72 % yield; iii) Starting from **1**, CO_2 (1 bar), 2 h at 25 °C or 5 minutes at 80 °C; iv) Starting from **1** (1 equiv.); **4**, iso-propanol (2 equiv.), 60 °C, THF, 18 h; **5**, phenol (2 equiv.), 25 °C, THF, 18 h, 32 % crystalline yield.
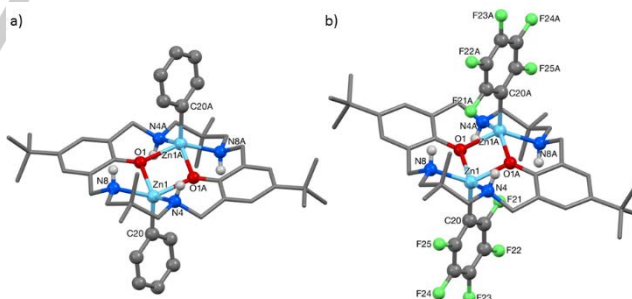
Figure 1. Molecular structures of a) [LZn₂Ph₂] and b) [LZn₂(C₆F₅)₂]. Hydrogen atoms and benzene molecules are omitted for clarity.

The ^1H NMR spectrum of **1** is rather complex at room temperature in C₆D₆, d₈-THF and CDCl₃. However, at high temperature (403 K in d₂-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 N*H* resonance at 2.43 ppm in **1**, and 2.54 ppm in **2**. The ^{19}F NMR spectrum of **2** reveals three

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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 CO_2, to probe their potential use as polymerisation catalysts.[12b, 24] It was observed that **1** reacted with CO_2 at 1 bar of CO_2 pressure, in C_6D_6 at 25 °C, to afford the corresponding dibenzoate complex [$LZn_2(OCO-Ph)_2$, **3**] with complete conversion occurring after two hours, as observed by ^{1}H NMR analysis (Scheme 2, Fig. S6). The rate of CO_2 insertion was significantly enhanced by heating the solution to 80 ºC, affording complete conversion of **1** to **3**, within 5 minutes.

To unambiguously confirm the formation of the dibenzoate complex from CO_2 insertion into **1**, **3** was independently synthesized *via* direct metallation of **LH₂** by zinc carboxylate $Zn(OCO-Ph)_2$, at 25 °C in THF (Scheme 2). The ^{1}H NMR spectrum was identical to that obtained from CO_2 insertion into **1**. Colourless block crystals suitable for X-ray diffraction were obtained at 25 ºC 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 κ^1-*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 $CDCl_3$, C_6D_6 and d_8-THF. However, in d_4-methanol, a much better resolved ^{1}H 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 N*H* resonance is observed at 3.15 ppm. It possesses C_2 symmetry in methanol solution. The benzoate ligands are clearly present as evidenced by the deshielded *ortho*-phenyl resonance at 7.87 ppm. In the ^{13}C NMR spectrum, quaternary carbon resonances were too weak to be observed (including by HMBC experiments) and so a ^{13}C carbonyl labelled sample of **3** was prepared, by the reaction of **1** with two equivalents of ^{13}C labelled benzoic acid. The carbonyl resonance of **3** is clearly observed at 174.6 ppm, shifted from free benzoic acid (170.1 ppm).
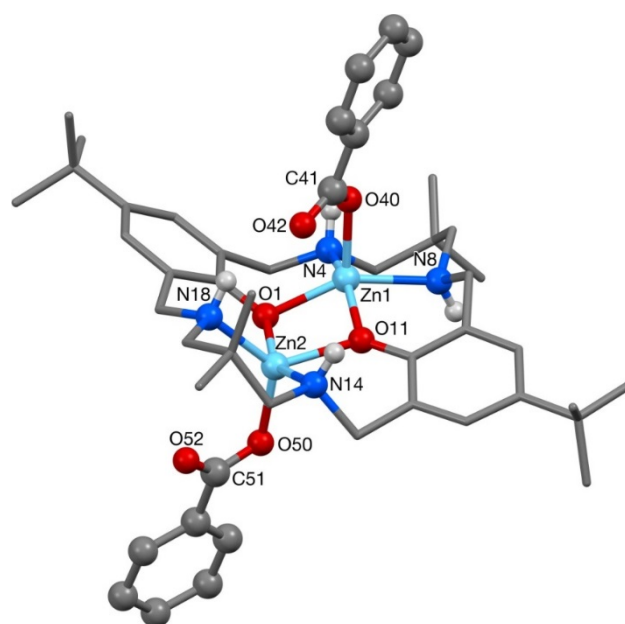

Figure 2. Molecular structure of **3**. Hydrogen atoms and a benzene solvent molecule are omitted for clarity.

In contrast, the fluoryl analogue, complex **2**, did not react with CO_2 under identical reaction conditions. It is proposed that the decrease in nucleophilicity of the aryl group, due to the electron withdrawing fluoryl substituents, disfavours CO_2 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.[27] A theoretical study was carried out in order to gain a better understanding of the CO_2 insertion into the Zn-aryl bonds. DFT was used to calculate the potential energy surface for the stepwise CO_2 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 ωb97xd/6-31G(d)/srcf(cpcm = 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).[24b] This study focussed on the previously unreported barrier of CO_2 insertion into the Zn-aryl bond and the calculations reveal the energy barrier to be 9.0 kcal mol^{-1} higher for I' (overall barrier ΔG = +28.7 kcal mol^{-1}) than for I (overall barrier ΔG = +19.7 kcal mol^{-1}). The carbonate products derived from complex I are more stable than the corresponding fluoryl analogues obtained from I' (ΔΔG up to 20.4 kcal/mol between **VI^{CO2}** and **VI$^{CO2'}$**), giving further support to the experimental observation that CO_2 inserts more readily into the Zn-Ph bond than the Zn-C_6F_5 analogue.
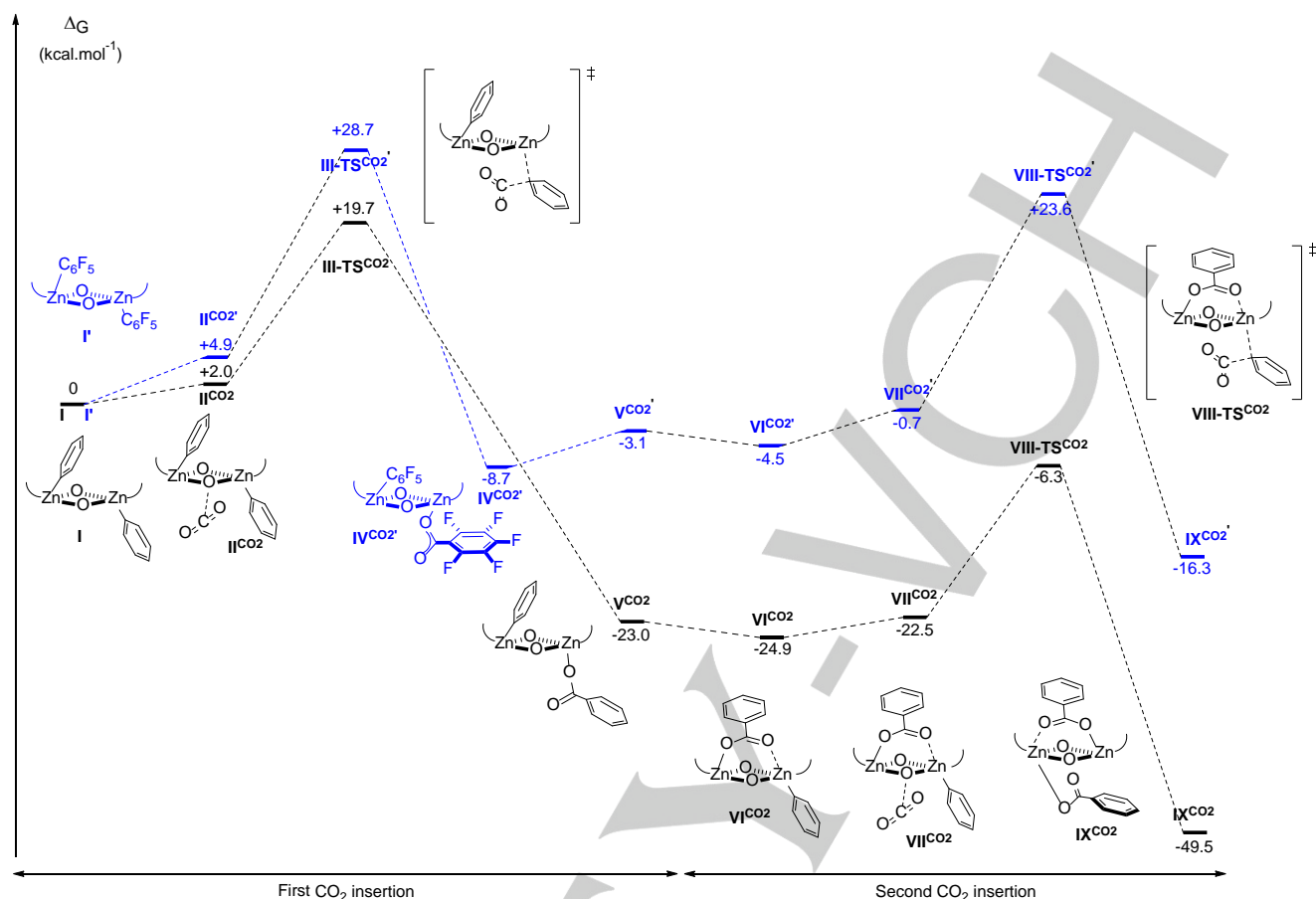
Figure 3: Potential energy surface for the first single CO_2 insertion into the zinc aryl bond of **1** (black) and **2** (blue); DFT protocol: wb97xd/6-31G(d)/cpcm=DCM/Temp=353 K. The ancillary ligand structure is omitted for clarity. Interactive version of the figure available at doi.org/10.14469/hpc/2222.

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^{CO2}** which shows a significant interaction between the Zn-C bond and incoming $C_{(CO2)}$ 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.[24b] To allow a comparison between these two systems, the potential energy surface for the second CO_2 insertion was investigated (Fig. 3). Considering the most stable conformation **VI^{CO2}**, 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^{CO2}** and **VIII^{CO2}**), 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^{CO2}**, is highly thermodynamically favoured, with ΔG = -49.5 kcal.mol^{-1}.

Unfortunately, it was not possible to gain experimental evidence for the formation of any intermediates **V^{CO2}** – **VII^{CO2}** 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.[19e] 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). ^{1}H NMR analysis, in d_8-THF, revealed the formation of a new species, $[LZn_2(O^iPr)_2]$ (**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.[12d] In contrast to the broad, convoluted ^{1}H spectrum of **1** in d_8-THF at 298K, **4** has a sharp, well-resolved ^{1}H 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-O^{i}Pr groups has occurred. Catalyst **2** also reacted with *iso*-propanol, under reflux conditions in d_8-THF, however a mixture of species was observed, which included **4** and C_6F_5H, along with unreacted **2** and ^{i}PrOH. The reagents **2** and ^{i}PrOH 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 $[LZn_2(OPh)_2]$ (**5**, Fig. 4). Its ^{1}H 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 CO_2 insertion (+19.7 kcal.mol^{-1}). The product of the first protonolysis (V_a^{HOR}) 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** ($VIII^{2HOR}$) 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_a^{HOR}) were to undergo a ligand conformational rearrangement, to give a more stable

intermediate V_b^{HOR} (by 2.2 kcal.mol^{-1}). Subsequently, the reaction pathway with *iso*-propanol approaching from the concave face (VIb^{2HOR}) 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
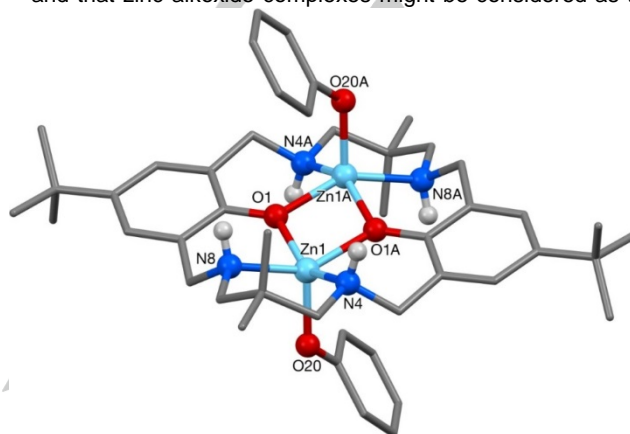
active sites for such catalytic systems.

Figure 4: Molecular structure of **5**. Hydrogen atoms and one DCM molecule are omitted for clarity.

Polymerisation Studies

Following the successful reaction of **1** with CO_2, its catalytic activity within CHO/CO_2 copolymerisation was tested. The polymerisations were run at 0.1 mol % catalyst loading (vs the epoxide, CHO), using 1 bar of CO_2 pressure (Table 1, entry 1), as analogous di-Zn catalysts have previously shown acceptable activity under these conditions.[11j] The phenyl catalyst **1** is active (TOF = 20 h^{-1}) and exhibits good CO_2 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),[12b] and significantly outperforms the bromide complex $[LZn_2Br_2]$, which is completely inactive under identical reaction conditions.[25b] 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.[13] The formation of dihydroxyl end-capped polymers is consistent with reactions of $[LZn_2Ph_2]$ with alcohol (1,2-cyclohexenediol) to form the active site.[14a] The reactivity studies have also demonstrated the capability of **1** to react with CO_2, within 5 minutes at 80 °C, suggesting that the product di-zinc bis(benzoate) complex could initiate copolymerisation. However, benzoate end groups were
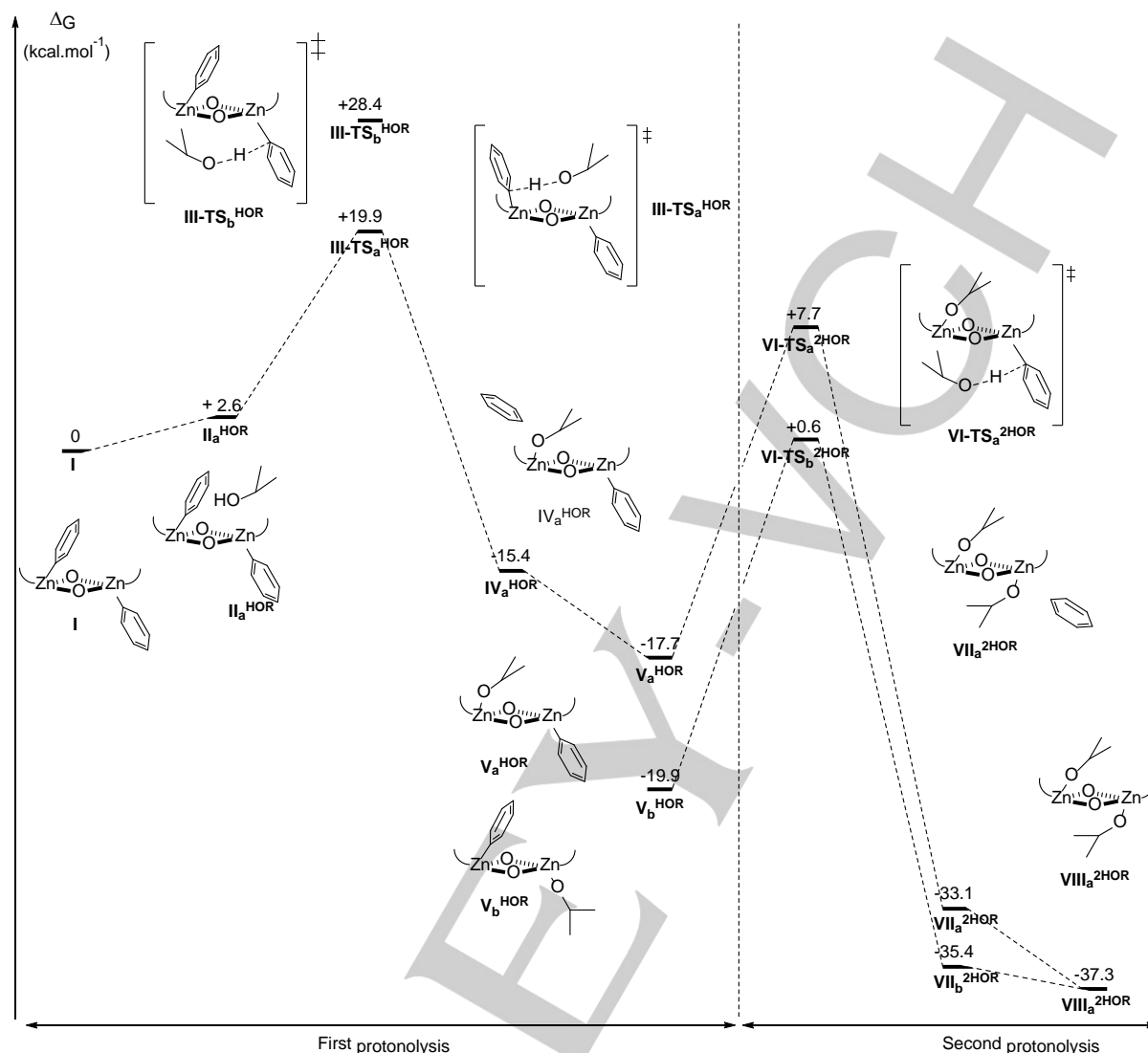
Figure 5: Potential energy surface for the first and second protonolysis of the zinc-aryl bond of **1**, with *iso*-propanol; DFT protocol: ωb97xd/6-31G(d)/cpcm=DCM/Temp=353.15 K (data available at doi.org/10.14469/hpc/2144). The ancillary ligand structure is omitted for clarity.

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 CO_2 and is responsible for the true initiation under these conditions. In line with this observation, catalyst **2** is also active for CHO/CO_2 ROCOP, in spite of its complete lack of reactivity towards either CHO or CO_2 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).[14a] 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 CO_2/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 ^{1}H 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),[25] and that when a mixture of monomers is present, anhydride insertion occurs more rapidly than CO_2 insertion.[18a] 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 (Đ = 1.10). Here, **1** displays a slightly superior activity (TOF = 33 h^{-1}) compared to its acetate (TOF = 24 h^{-1})[25a] and halide (TOF = 17 h^{-1})[25b] 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**.

Entry	Monomer /s	Cat./^{i}PA/ Monomer	T (°C)	Time	TOF[a] (h^{-1})	M$_{n(exp)}$[b] g/mol	[Đ][b]	M$_{n(theo)}$ g/mol
1	CHO/CO₂[c]	**1**/-/1000	80	20 h	20	4780	1.06	55440
2	CHO/CO₂[c]	**2**/-/1000	80	20 h	20	4280	1.08	56860
3	CHO/CO₂[c]	**3**/-/1000	80	20 h	24	6100	1.18	66810
4[12b]	CHO/CO₂[c]	**LZn₂(OAc)₂**/-/1000	80	24 h	18	6200	1.19	62550
5	PA/CHO[d]	**1**/-/100	100	3 h	33	8620	1.10	12300[e]
6	PA/CHO[d]	**2**/-/100	100	3 h	24	19600	2.27	8870[e]
7	PA/CHO[f]	**1**/-/200	100	3 h	21	5610	1.12	7880[e]
8[25a]	PA/CHO[g]	**LZn₂(OAc)₂**/-/100	100	1 h	24	2570	1.20	2960[e]
9	ε –CL (tol)[h]	**1**/4/500	80	5 min	5280	3900	1.72	13150
10	ε –CL (CH₂Cl₂)[h]	**1**/4/500	25	150 min	188	4130	1.61	13410
11	ε –CL (CH₂Cl₂)[h]	**LZn₂(OAc)₂**/4/500	25	150 min	0	-	-	-
12	*rac*-LA (tol)[h]	**1**/4/200	80	2 h	99	7110	1.29	7130
13	*rac*-LA (tol)[h]	**LZn₂(OAc)₂**/4/200	80	24 h	0	-	-	-

[a] Determined by ^{1}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,[19e] 0.58 for PLA[29] or 0.56 for PCL[30]); [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: 1:200:800 molar ratio of catalyst:PA:CHO; [g] Reaction conditions: 1:100:800 molar ratio of catalyst:PA:CHO; [h] Reaction conditions: [M]₀ = 1M.

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 α,ω-dihydroxyl-terminated 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 ROCOP (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 C₆F₅ 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 that 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 α-*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 aryl **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.[18c]

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 α,ω-dihydroxyl 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,[15e, 23a] these reactions presumably occur after epoxide opening generates the Zn-alkoxide species.

Conclusions

In summary, two di-arylzinc complexes have been synthesized from the same macrocyclic ligand and characterized using X-ray crystallographic and NMR spectroscopic studies. **1** cleanly inserts CO_2 under mild conditions, whilst **2** is inactive, highlighting differences caused by the electron withdrawing fluoryl 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 cyclohexene 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 Strem 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 **LH₂** 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_n) was determined by comparison against polystyrene standards, with a correction factor of 1.85 for PA/CHO,[19e] 0.58 for PLA,[29] and 0.56 for PCL.[30] 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

LZn₂(Ph)₂ – (1): A THF solution (5 mL) of **H₂L** (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 **1** 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. ¹H NMR (CD_2Cl_4, 400 MHz, 403 K) δ_H 7.40 (s, 5H, Ph), 7.00 (s, 4H, Aryl), 4.81 (br. m, 4H, C$H_aH_{a'}$), 3.37 (br. d, 4H, $^2J_{HaHa'}$ = 13.3 Hz, CH$_aH_{a'}$), 2.96 (br. d, 4H, $^2J_{HaHa'}$ = 10.1 Hz, C$H_bH_{b'}$), 2.89 (br. m, 4H, CH$_bH_{b'}$), 2.47 (br. m, 4H, NH), 1.36 (s, 18H, ^{t}Bu), 1.31 (s, 6H, CH₃), 1.07 (s, 6H, CH₃). ¹³C NMR (CD_2Cl_4, 100 MHz, 403 K) δ_C 138.5 (C_{quat}, Aryl), 128.1 (Ph), 128.0 (C_{quat}, Aryl), 126.8 (CH, Aryl), 123.9 (C_{quat}, Aryl), 63.5 (CH_2), 56.7 (CH_2), 33.4 and 33.3 (C_{quat}, ^{t}Bu and C_{quat}, CMe_2), 31.3 (^{t}Bu), 27.9 (CH₃), 21.5 (CH₃). Anal. Calc. for LZn₂(Ph)₂: C, 66.10; H, 7.72; N, 6.70. Found: C, 65.98; H, 7.77; N, 6.68.

LZn₂(C₆F₅)₂ – (2): To a pre-cooled THF solution (-40 °C, 5 mL) of **H₂L** (200 mg, 0.36 mmol) was added a pre-cooled (-40 °C) THF solution (2 mL) of $Zn(C_6F_5)_2$ (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). ¹H NMR ($CDCl_3$, 400 MHz, 298 K) δ_H 6.75 (s, 4H, Aryl), 4.31 (dd, 4H, $^2J_{HaHa'}$ = 13.3 Hz, $^3J_{HaNH}$ = 12.0 Hz, C$H_aH_{a'}$), 3.33 (d, 4H, $^2J_{HaHa'}$ = 13.3 Hz, CH$_aH_{a'}$), 3.04 (dd, 4H, $^2J_{HbNH}$ = 12.0 Hz, C$H_bH_{b'}$), 2.69 (d, 4H, $^2J_{HbHb'}$ = 12.0 Hz, CH$_bH_{b'}$), 2.54 (dd, 4H, $^3J_{HbNH}$ = 12.0, $^3J_{HbNH}$ = 14.0 Hz, NH), 1.24 (s, 6H, CH₃), 1.21 (s, 18H, ^{t}Bu), 1.04 (s, 6H, CH₃). ¹³C{H} NMR ($CDCl_3$, 100 MHz, 298 K) δ_C 160.6 (C_{quat}, Aryl), 136.7 (C_{quat}, Aryl), 126.3 (CH, Aryl), 123.3 (C_{quat}, Aryl), 62.7 (CH_2), 58.1 (CH_2), 34.1 and 33.7 (C_{quat}, ^{t}Bu and C_{quat}, CMe_2), 31.7 (CH₃, ^{t}Bu), 28.6 (CH₃), 20.5 (CH₃). ¹⁹F NMR ($CDCl_3$, 377 MHz, 298 K) δ_F -115.1 (br. s, 2F), -157.6 (t, 4F, J = 20 Hz), -160.8 (m, 4F). Anal. Calc. for LZn₂(C₆F₅)₂: C, 54.40; H, 5.36; N, 5.52; Found: C, 54.25; H, 5.45; N, 5.39.

LZn₂(OCO-Ph)₂ – (3): To a precooled THF solution (-40 °C, 5 mL) of **H₂L** (200 mg, 0.36 mmol.) was added a precooled (-40 °C) THF suspension (2 mL) of $Zn(OCO-Ph)_2$ (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 isolate 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). ¹H NMR (d₄-methanol, 400 MHz, 298 K) δ_H 7.88 (br. m., 4H, *o*-Ph), 7.36 (tt, 2H, $^3J_{HpHm}$ = 7.6 Hz, $^4J_{HpHo}$ = 1.5 Hz, *p*-Ph), 7.28 (t, 4H, $^3J_{HmHp}$ = 7.6 Hz, *m*-Ph), 6.98 (s, 4H, Aryl), 4.23 (dd, 4H, $^3J_{HaNH}$ = 12.0 Hz, C$H_aH_{a'}$), 3.34 (d, 4H, CH$_aH_{a'}$), 3.15 (dd, 4H, $^3J_{NHHa}$ = 12.0 Hz, NH), 2.91-2.83 (m, 8H, C$H_bH_{b'}$ and CH_bH_b), 1.45 (s, 3H, CH₃), 1.21 (s, 6H, CH₃), 1.19 (s, 18 H, ^{t}Bu), 1.04 (s, 3H, CH₃). ¹³C{H} NMR (d₄-methanol, 100 MHz, 298 K) δ_C 174.64 (C=O), 131.9 (*p*-Ph), 130.6 (*o*-Ph), 129.3 (CH, Aryl), 128.9 (C_{quat}),

128.8 (m-Ph), 124.7 (C_{quat}), 64.5 (CH_2), 57.1 (CH_2), 35.0 (C_{quat}), 34.5 (C_{quat}), 32.1 (CH_3, ^tBu), 32.1 (CH_3), 28.9 (CH_3), 21.4 (CH_3). Not all signals for C_{quat} were detected. Anal. Calc. for $LZn_2(OCO\text{-}Ph)_2$: C, 62.41; H, 6.98; N, 6.06; Found: C, 62.59; H, 7.02; N, 5.98.

$LZn_2(O^iPr)_2$ – (4): *NMR scale experiment*: In a Youngs tap NMR tube, ^iPrOH (3.7 µL, 48 µmol) was added to a suspension of $LZn_2(Ph)_2$ (20 mg, 24 µmol) in pre-cooled d_8-THF (-40 °C, 0.6 mL). The mixture was allowed to react at room temperature for 15 minutes then was heated at 60 °C for 18 hours to afford a homogeneous solution featuring $L^1Zn_2(O^iPr)_2$ as the major product (along with formation of benzene), as determined by NMR spectroscopy. ^1H NMR (d_8-THF, 400 MHz, 298 K) δ_H 7.30 (s, 12H, benzene), 6.81 (s, 4H, Aryl), 5.23 (dd, 4H, $^2J_{HaHa'}$ = 12.5 Hz, $^3J_{HaNH}$ = 11.0 Hz, CH_aHa'), 4.10 (sept, 2H, $^3J_{HH}$ = 6.0 Hz, CH O^iPr), 3.17 (d, 4H, $^2J_{HaHa'}$ = 12.5 Hz, CH$_a$$H_{a'}$), 2.89 (dd, 4H, $^2J_{HbHb'}$ = 13.3Hz, $^3J_{HbNH}$ = 13.3 Hz, CH_bHb'), 2.60 - 2.57 (m, 8H, CH_2 and NH), 1.28 – 1.22 (m, 40 H, ^tBu and CH_3), 0.96 (d, 12H, $^3J_{HH}$ = 6 Hz, CH_3 O^iPr). $^{13}C\{H\}$ NMR (d_8-THF, 100 MHz, 298 K) δ_C 161.7 (C_{quat}, Aryl), 136.1 (C_{quat}, Aryl), 129.2 (benzene), 126.9 (CH, Aryl), 125.5 (C_{quat}, Aryl), 66.5 (CH, O^iPr), 63.7 (CH_2), 58.1 (CH_2), 34.5 (C_{quat}, ^tBu), 34.2 (C_{quat}, ^tBu), 32.3 (CH_3, ^tBu), 31.0 (CH_3, O^iPr), 28.8 (CH_3), 21.0 (CH_3).

$LZn_2(PhO)_2$ – (5): Complex **1** was prepared on a 0.24 mmol scale, following the procedure described above. Phenol (45 mg, 0.48 mmol) was added in situ and the reaction mixture was allowed to stir for 18 hours. The resultant white solid was isolated via filtration and was dried under vacuum, to give **5** as a white powder (66 mg, 32 % yield). ^1H NMR (d_8-THF, 500 MHz, 328 K) δ_H 6.78 (s, 4H, Aryl), 6.70 (dd, 4H, $^3J_{HmHo}$ = 8.5 Hz, $^3J_{HmHp}$ = 7.8 Hz, m-Ph), 6.55 (d, 4H, $^3J_{HoHm}$ = 8.5 Hz, $^4J_{HoHp}$ = 1.0 Hz, o-Ph), 6.09 (t, 2H, $^3J_{HpHm}$ = 7.3 Hz, $^4J_{HpHo}$ = 1.0 Hz, p-Ph), 4.99 (dd, 4H, $^2J_{HaHa'}$ = 12.9 Hz, $^3J_{HaNH}$ = 11.1 Hz, CH_aHa'), 3.24 (d, 4H, $^2J_{HaHa'}$ = 12.9 Hz, CH$_a$$H_{a'}$), 3.07 (dd, 4H, $^3J_{NHHb}$ = 13.6 Hz, $^3J_{NHHa}$ = 11.1 Hz, $^3J_{NHHb'}$ = 3.6 Hz, NH), 2.98 (dd, 4H, $^2J_{HbHb'}$ = 10.6 Hz, $^3J_{HbNH}$ = 13.6 Hz, CH_bHb'), 2.71 (dd, 4H, $^2J_{HbHb'}$ = 10.6 Hz, $^3J_{Hb'NH}$ = 3.6 Hz, CH_bHb'), 1.27 (br. m, 12H, ^tBu and CH_3), 1.23 (s, 3H, CH_3), 1.18 (s, 9 H, ^tBu), 1.16 (s, 3H, CH_3), 0.98 (s, 3H, CH_3). Residual DCM at 5.46 ppm. $^{13}C\{H\}$ NMR (d_8-THF, 126 MHz, 328 K) δ_C 129.2 (m-Ph), 127.0 (CH Aryl), 119.7 (o-Ph), 112.7 (p-Ph), 63.9 (CH_2), 57.8 (CH_2), 32.1 (CH_3), 32.0 (CH_3), 32.0 (CH_3, ^tBu), 28.0 (CH_3), 21.1 (CH_3). Signals for C_{quat} were not detected. Anal. Calc. for $LZn_2(PhO)_2$: C, 63.67; H, 7.43; N, 6.46; Found: C, 63.54; H, 7.53; N, 6.55.

Supporting Information

Complete computational details, NMR data for complexes **1**-**5** and selected polymers, crystal data and refinement for compounds **1**-**3** and **5**. Complementary data available free of charge from the Imperial College High Performance Computing Service Data Repository at doi.org/10.14469/hpc/2144.

Acknowledgements

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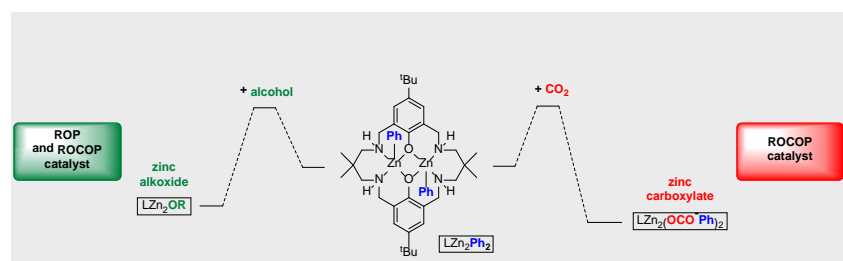
Charles Romain,[b] Jennifer A. Garden,[c] Gemma Trott,[a] Antoine Buchard,[d] Andrew J. P. White[b] and Charlotte K. Williams[a]*

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

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 CO_2 or anhydrides, and the ring-opening polymerisation of lactones.