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# Group 1, 2 and Zn(II) Heterodinuclear Catalysts for Epoxide/CO<sub>2</sub> Ring Opening Copolymerization

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## **Abstract**

A series of heterodinuclear complexes are reported where both Zn(II) and a metal from Group 1 or 2 are chelated by a macrocyclic diphenolate-tetra-amine ligand. The complexes are characterized in the solid state, where relevant by single crystal X-ray crystallography and elemental analysis, and in solution, using NMR spectroscopy and mass spectrometry. The complex

synthesis is achieved by reaction of the ligand with diethyl zinc, to form the mono-zinc complex, *in situ*, followed by subsequent coordination of the second metal; this method enables heterodinuclear conversions >90 % as determined by NMR spectroscopy. Alternatively, the same heterodinuclear complexes are accessed by reaction between the two homodinuclear complexes, at elevated temperatures for extended periods. These findings suggest that most of the heterodinuclear complexes are the thermodynamic products; the only exception is the Na(I)/Zn(II) complex which is unstable with respect to the homodinuclear counterparts. The catalytic activities and selectivity of the stable heterodinuclear complexes are compared, against each other and the relevant homodinuclear analogues, for the ring opening copolymerization (ROCOP) of CO<sub>2</sub> and CHO. Nearly all the heterodinuclear complexes are less active than the di-zinc analogues, but the Mg(II)/Zn(II) catalyst is more active. The co-ligand influences the product selectivity, with iodide ligands resulting in cyclic carbonate formation and carboxylate ligands in a high selectivity for polycarbonate.

## **Introduction**

Heterodinuclear cooperativity is a potential means to enhance catalytic activity beyond conventional ligand design.<sup>1-2</sup> Synergic interactions between two different metals has been proposed as responsible for enhanced activity in homogeneous catalysis ranging from metallation,<sup>3</sup> CH bond activation,<sup>4-6</sup> and CF bond activation,<sup>7-9</sup> lactone ring opening polymerization (ROP),<sup>10-12</sup> olefin polymerization<sup>13-17</sup> and, relevant to this work, the ring opening copolymerization (ROCOP) of CO<sub>2</sub> and epoxides.<sup>18-22</sup>

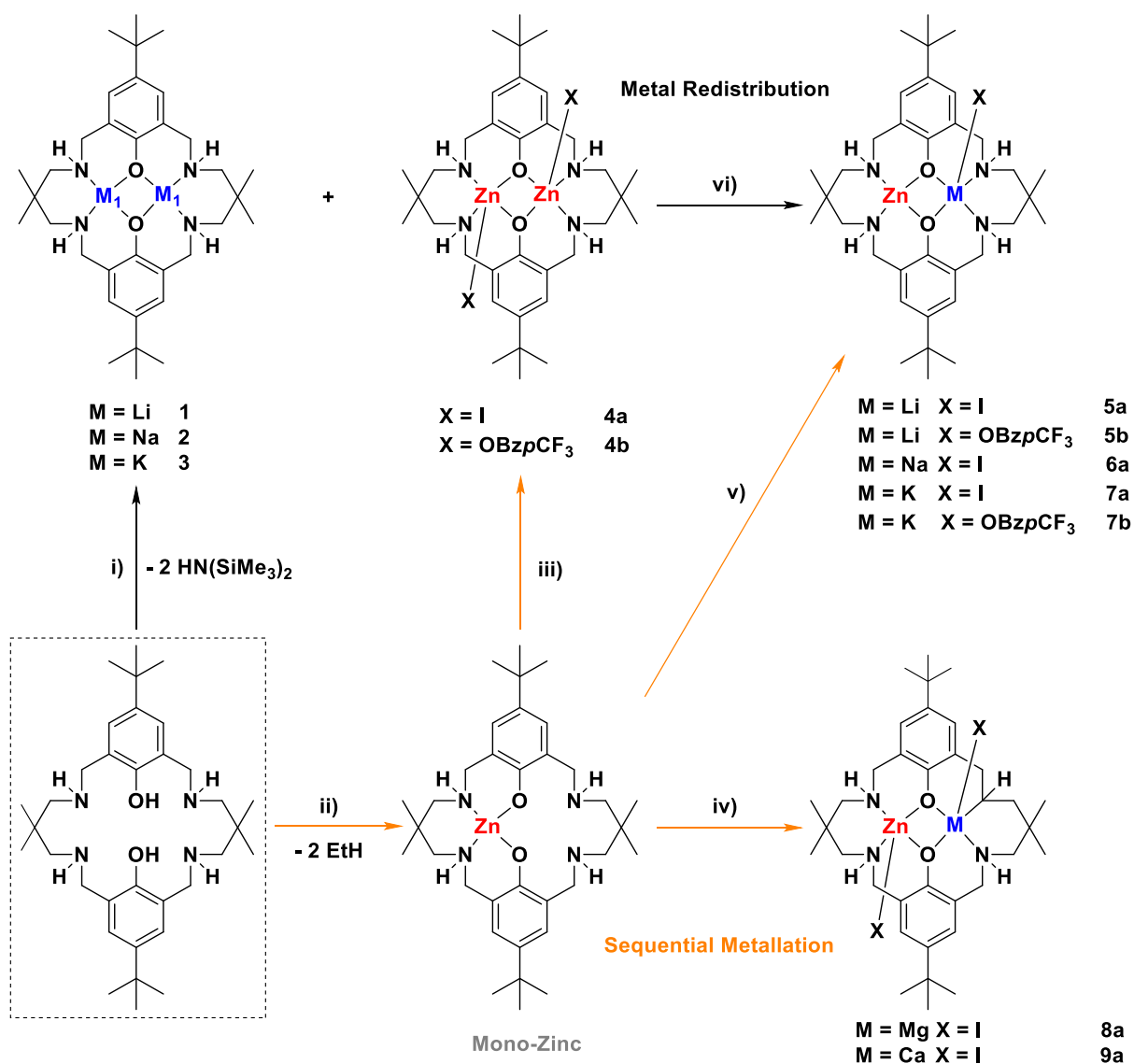
Here, new heterodinuclear complexes are applied as catalysts for the ring opening copolymerization (ROCOP) of epoxides with CO<sub>2</sub>. The product aliphatic polycarbonates contain

from 30-50% carbon dioxide in the polymer backbone; the reaction is an efficient method to add value to waste CO<sub>2</sub> to produce a commercially viable material.<sup>23-26</sup> The structures of the resulting polycarbonates influence their applications, with low molar mass, hydroxyl-telechelic polycarbonates used to prepare polyurethanes which show equivalent or better properties than equivalent materials prepared from polyether or polyester polyols.<sup>25, 27-30</sup> Additionally, the CO<sub>2</sub>-containing polyurethanes result in significant reductions in greenhouse gas emissions and fossil depletion compared to conventional products.<sup>31-33</sup> Higher molar mass CO<sub>2</sub>-derived polycarbonates may be applied as packaging plastics, engineering polymers, coatings, elastomers and adhesives.<sup>34-36</sup> The viability of CO<sub>2</sub>/epoxide ROCOP depends on the selection of the metal catalyst which in turn controls rates, polymer molar mass and polymer composition (selectivity).<sup>37-40</sup> Amongst the highest performing catalysts are dinuclear, dimeric or bicomponent metal complexes.<sup>35, 41-47</sup> For highly active dinuclear catalyst, it is commonly proposed that one metal activates the epoxide while the other provides the attacking nucleophile.<sup>40</sup> Following this hypothesis, we have reported a series of (homo)dinuclear Zn(II), Mg(II), Co(II/III) and Fe(III) catalysts, coordinated by a macrocyclic ancillary ligand, which show promising activities at 1 bar carbon dioxide pressure (i.e. at low pressure).<sup>48-51</sup> Detailed kinetic, mechanistic and theoretical studies suggested the catalysts operate by a 'chain shuttling' mechanism and that the rate-limiting step is metal-carbonate attack on coordinated epoxide.<sup>52-53</sup> Building from the mechanistic hypothesis, a Zn(II)/Mg(II) heterodinuclear catalyst showed a 5-fold higher rate than either di-zinc or di-magnesium counterparts, or combinations of them.<sup>19</sup> This promising result highlights the potential to increasing performance using heterodinuclear complexes but so far there are very few examples of such complexes.

Here, a range of new complexes combining metals from Groups 1 or 2 with zinc are targeted. The selection of the metals is driven by the strong track record for zinc in this field of polymerization catalysts. In contrast, although there are a few reports of testing of alkaline earth metals, specifically Ca(II), none were found to be active.<sup>54-56</sup> Nonetheless, metals from Groups 1 and 2 are interesting candidates for further investigation because they are highly Lewis acidic, which should enhance epoxide coordination, and may be expected to form labile metal-carbonate bonds, which could accelerate the likely rate limiting step. One potential pitfall may be their propensity to form labile, ionic complexes which may result in metal redistribution side-reactions.

## **Results and Discussion**

Two strategies are employed to synthesize well-defined heterodinuclear complexes: (1) a one-pot reaction between the two homodinuclear complexes (metal redistribution reaction) or (2) sequential reaction of the ligand with first one metal, to produce a mono-metalated intermediate which is subsequently reacted with the second metal (sequential metalation) (Scheme 1). One-pot syntheses are synthetically attractive but the under-pinning principle is that the heterodinuclear complex should be the thermodynamic product, however, until now such stability is unknown. On the other hand, sequential metalation reactions are synthetically challenging but careful control of the reaction conditions, such as solvents, rate of reagent addition and temperature, may allow control over the formation of thermodynamic or kinetic reaction products. Here, both synthetic methods are applied to evaluate the complex stabilities and to assess the best synthetic routes to heterodinuclear complexes (Scheme 1).



Scheme 1: Synthesis of complexes **1-9**. i)  $\text{M}(\text{N}(\text{Si}(\text{CH}_3)_2))$ , THF, 25 °C, 16 h, > 75 %. ii)  $\text{ZnEt}_2$ , THF, 25 °C, 1 h. iii)  $\text{MX}_2$  (where M = Zn and X = I, OBz $\rho$ CF $_3$ ), THF, 25 °C, 16 h. > 70 %. iv)  $\text{MX}_2$  (where M = Mg, Ca and X = I, OBz $\rho$ CF $_3$ ), THF, 100 °C, 24 h. > 70 %. v)  $\text{MX}$  (where M = Li, Na, K and X = I, OBz $\rho$ CF $_3$ ), THF, 100 °C, 16 h, > 75 %. vi) THF, 100 °C, 24 h.

Firstly, homodinuclear Group 1 complexes, **1-3**, were synthesised by reaction between the macrocyclic ligand and the corresponding metal (I) amide precursor, in THF at 25 °C. The products were isolated as white powders in high yields (> 75 %) and were characterised, in solution, using NMR spectroscopy (Fig. S1-S13). Single crystals of complexes **1** and **2** were also characterized

using X-ray crystallography (Fig. S14-S15). In the solid state both **1** and **2** are dimeric, with **1** displaying a distorted cubane ( $\text{Li}_4\text{O}_4$ ) structure where each lithium centre adopts a tetrahedral geometry. For **1**, Li(1) and Li(2) atoms favour bonding to phenoxide-oxygen centres over amine-nitrogens centres, where the converse is true for lithium centres (3) and (4). On the other hand, the sodium atoms in **2** adopt a pentacoordinate, square based pyramidal geometry ( $\tau = 0.02$ ) forming a cubane structure ( $\text{Na}_4\text{O}_4$ ) where bonding to each donor atom is fulfilled (Fig. S14-S15). In solution, DOSY NMR analysis suggests that **1** and **3** exist in a monomer-dimer equilibrium, whereas **2** is dimeric in THF at 25 °C (Fig. S16-S18).

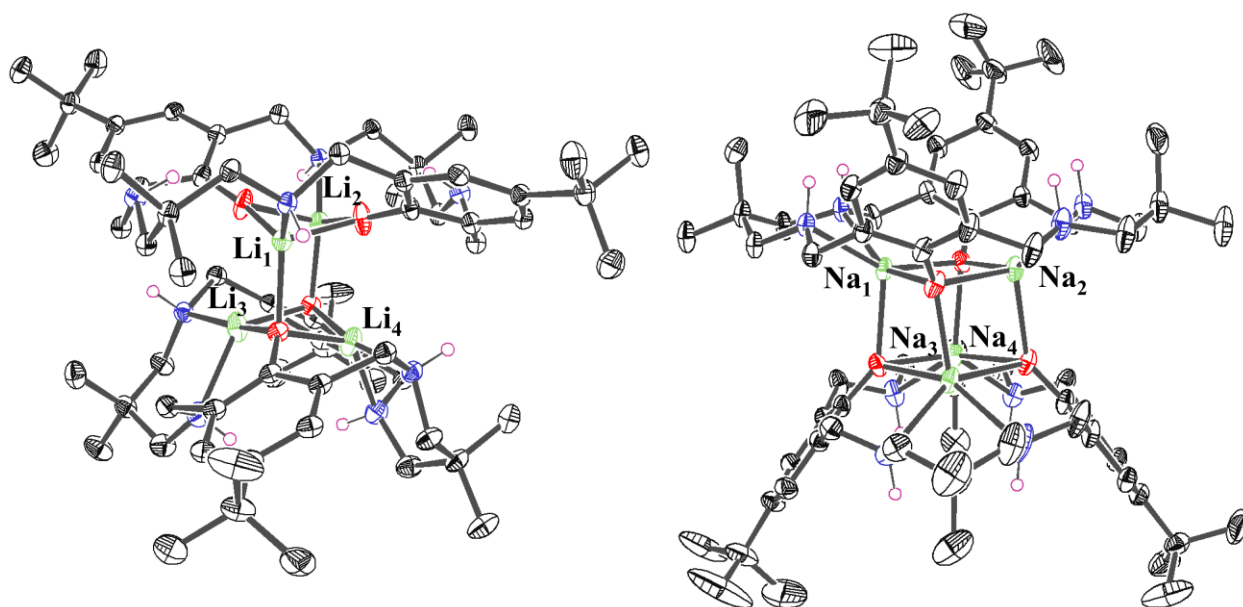


Figure 1: ORTEP representations of the molecular structures of complexes **1** (LHS) and **2** (RHS) obtained by single crystal X-ray diffraction. Disorder and H-atoms (excluding NH) have been omitted for clarity, with thermal ellipsoids represented at 40 % probability (For complete structures see Fig. S14 and S15).

Complexes **4a** and **4b**, the di-zinc complexes, were synthesised by reaction between the macrocyclic ligand and one equivalent of diethyl zinc, immediately followed by the addition of an equivalent of zinc iodide or zinc benzoate. The products were isolated as white powders in >76 %

yield and characterised by NMR spectroscopy (Fig. S19-S27), mass spectrometry (Fig. S28-S29) and X-ray crystallography (Fig. S30-S31). For both complexes, the  $^1\text{H}$  NMR spectra, determined in  $d_8$ -THF, are complex and show many coupled, broadened resonances. In contrast, the  $^1\text{H}$  NMR spectra determined in TCE at 403 K, are straightforward to assign and show characteristic resonances for homodinuclear complex formation including four signals for the diastereotopic methylene and benzylic protons and a single resonance for the phenyl ring protons.

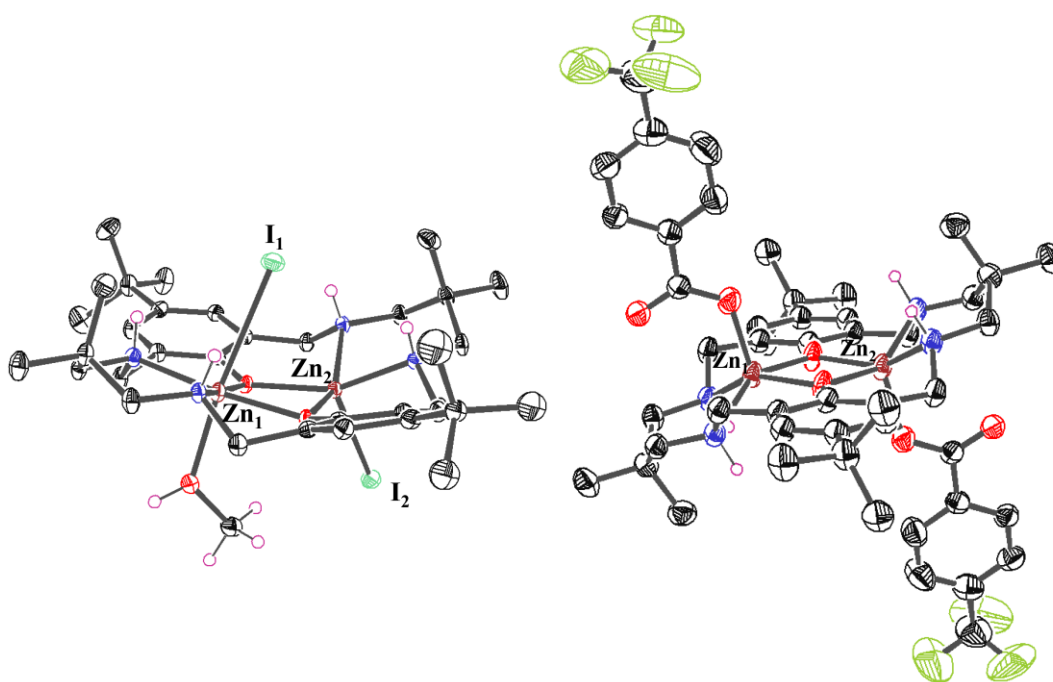


Figure 2: ORTEP representation of the molecular structures of complexes **4a** (LHS) and **4b** (RHS), obtained by single crystal X-ray diffraction. Disorder and H-atoms (excluding N-H) have been omitted for clarity with thermal ellipsoids represented at 40 % probability (for complete structural data see Fig. S30 and S31).

The metal redistribution synthesis was investigated as a route to prepare Group 1/Zn heterodinuclear complexes **5a**, **6a** and **7a** (Scheme 1). The reaction involved heating, at 100 °C, an equimolar mixture of the respective homodinuclear Group 1 complex, **1-3**, with the di-zinc complex **4a**, in  $d_8$ -THF, in an NMR tube. The reaction was monitored periodically using  $^1\text{H}$  NMR



spectroscopy. In the cases of reactions using di-lithium or di-potassium precursors, after 16 hours the homodinuclear complex resonances disappeared and a new set of resonances evolved which are assigned to heterocomplexes **5a** and **7a** (Fig. S32-S33). The detailed spectroscopic characterization of **5a** and **7a** is provided in the supporting information (SI), but it is worth noting that COSY NMR spectroscopy is particularly useful to confirm heterodinuclear complex formation. For example, the COSY spectrum of **5a** shows two coupled phenyl resonances, in comparison to the homodinuclear precursors which each show only one resonance (Fig. S34). Unfortunately, due to the broad proton resonances observed for **7a**, a COSY NMR provided limited information. The reaction between the di-sodium and di-zinc complexes (**2** and **4a**) showed no change to the  $^1\text{H}$  NMR spectrum even after prolonged heating, at 100 °C for 48 h (Fig. S35).

Next, the sequential metalation synthesis was investigated, using the previously reported mono-zincation strategy which involved reaction of the ligand with diethyl zinc to generate a mono-zinc intermediate.<sup>19</sup> This intermediate was not isolated but was reacted in situ with the appropriate metal (I) iodide precursor, in THF at 100 °C for 16 hours. In each case, the  $^1\text{H}$  and 2D NMR spectra are identical to those obtained by the metal redistribution synthesis (Fig. S36-S37). Due to the fluxionality of the complexes, NMR characterisation is complex and is described in supporting information (Fig. S38-S39). Once again, the synthesis of complex **6a** was not feasible and resulted instead in the formation of mixtures of homodinuclear complexes **2** and **4a**. Complex **6a** could be isolated by careful temperature control (-78 °C) and slow addition of a sodium iodide solution (0.1 M in THF) to a dilute solution of ‘mono-zinc’ (11 mM in THF). Under these conditions,  $^1\text{H}$  NMR spectroscopy indicated a 90% conversion to heterodinuclear complex (Fig. S40-S42). Nonetheless, the complex was unstable upon heating and after leaving it at 25 °C for 16 h the heterodinuclear content reduced to ~25 % (Fig. S43). These findings suggest that **6a** is accessed at

low temperatures and hence will be unsuitable for polymerisation catalysis since reactions are conducted at temperatures  $> 80$  °C.

Complexes **5b** and **7b** were also synthesised in the same manner as complexes **5a** and **7a**; characterised by multinuclear NMR spectroscopy (Fig. S44-S51) and mass spectrometry (Fig. S52-S55). Single crystals of **5b** were isolated via recrystallization from DMSO and structural elucidation showed the complex was monomeric in the solid state (Fig. S56). The ligand adopts an unusual ‘crown-shape’ conformation, with NH bonds alternating their direction around the macrocycle. The metal centres in the structure cannot be assigned as zinc or lithium due to their positional disorder, however, heterodinuclear character is strongly indicated as only one coligand is present whereas the di-lithium complex is dimeric with no coligands (Fig. 1) and the di-zinc complex has two coligands (Fig. 2). Both metals adopt pentacoordinate, square based pyramidal geometries ( $M_1 \tau = 0.18$ ,  $M_2 \tau = 0.22$ ) and are coordinated to two amine-nitrogens, two phenolic oxygens and an oxygen from the  $\kappa_2$  chelating benzoate ligand. The intermetallic separation is 2.86(1) Å.

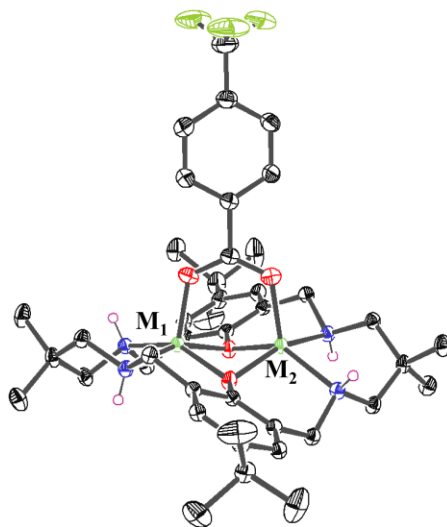


Figure 3: ORTEP representation of the molecular structure of complex **5b**, obtained by single crystal X-ray diffraction. Disorder and H-atoms (excluding N-H) have been omitted for clarity with thermal ellipsoids represented at 40 % probability (for further information see SI and Fig. S56).

The analogous Group 2/Zn complexes **8a** and **9a** were successfully synthesized via the sequential metalation procedure. In these cases, the monozinc intermediate was reacted *in situ* with the respective bis(iodide) metal(II) precursor, in THF at 100 °C. The complexes were isolated after 16 hours as white solids, in > 70 % yield. Complexes **8a** and **9a** were characterized by multinuclear NMR spectroscopy (Fig. S57-66), mass spectrometry (Fig. S67 –S68) and X-ray crystallography (Fig. S69-S70) and bulk purity was confirmed by elemental analysis. The <sup>1</sup>H NMR spectra each show ten resonances, between 2.0 and 5.2 ppm, assigned to the diastereotopic benzylic and methylene protons. The resonances were assigned to the zinc side of the macrocycle by noting common chemical shifts for **8a** and **9a**. Overall for **9a**, all resonances are significantly broader compared to those for **8a**, perhaps due to a weaker complexation of calcium compared to magnesium due to its increased ionic radius (*vide infra*). Each of the complexes shows a DOSY NMR spectrum with a single diffusion coefficient consistent with the formation of a discrete

dinuclear complex. The MALDI-ToF spectra show peaks for the complex cation  $[LZnM(I)]^+$  (i.e. at 765 and 782 amu for **8a** and **9a**, respectively).

Single crystals of **8a** and **9a** were each isolated *via* vapour diffusion of pentane into a saturated solution of complex in THF at  $-40\text{ }^\circ\text{C}$ , under nitrogen. Both structures confirm the formation of discrete heterodinuclear complexes in the solid state (Fig. 4). The ancillary ligand adopts slightly different coordination types, for **8a** a ‘bowl’ shape in which all NH substituents are located on the same side of the complex, whereas for **9a** an ‘S-shaped’ conformation with only two N-H substituents on the same face. In both structures, the zinc atoms are pentacoordinate and adopt a slightly distorted square based pyramidal coordination geometry (**8a**:  $\tau = 0.09$ , **9a**:  $\tau = 0.06$ ). The zinc atoms are each coordinated by two amino-nitrogen centres, two phenolic-oxygen centres and an iodide. For complex **8a**, the magnesium centre is hexacoordinate and adopts an octahedral geometry; it is coordinated by two amine-nitrogens, two phenolic-oxygens, an iodide and by THF (crystallization solvent). The coordination of THF is interesting since it provides a realistic model for epoxide coordination which is clearly relevant to the catalysis. Since the THF molecule is coordinated to the magnesium centre, it may indicate that in the catalytic reaction it is magnesium which activates the epoxide and zinc which provides the carbonate group (see discussion section). For complex **9a**, the calcium centre is heptacoordinate and adopts a capped-trigonal prismatic geometry; it is coordinated by two amine-nitrogens, two phenolic-oxygens, an iodide and two THF molecules. The calcium atom also protrudes significantly,  $1.30(0)\text{ \AA}$ , from the ligand coordination plane (formed by N(3)N(4)O(1)O(2)), particularly when compared to the analogous magnesium centre in complex **8a**,  $0.15(3)\text{ \AA}$ . This lack of planarity in calcium coordination likely arises due to its larger ionic radius and expanded coordination number. The metal-zinc distances are  $3.06(2)$

and 3.35(3) Å for complexes **8a** and **9a** respectively and sit within the range proposed as optimal for dinuclear ROCOP catalysis.<sup>49, 57-58</sup>

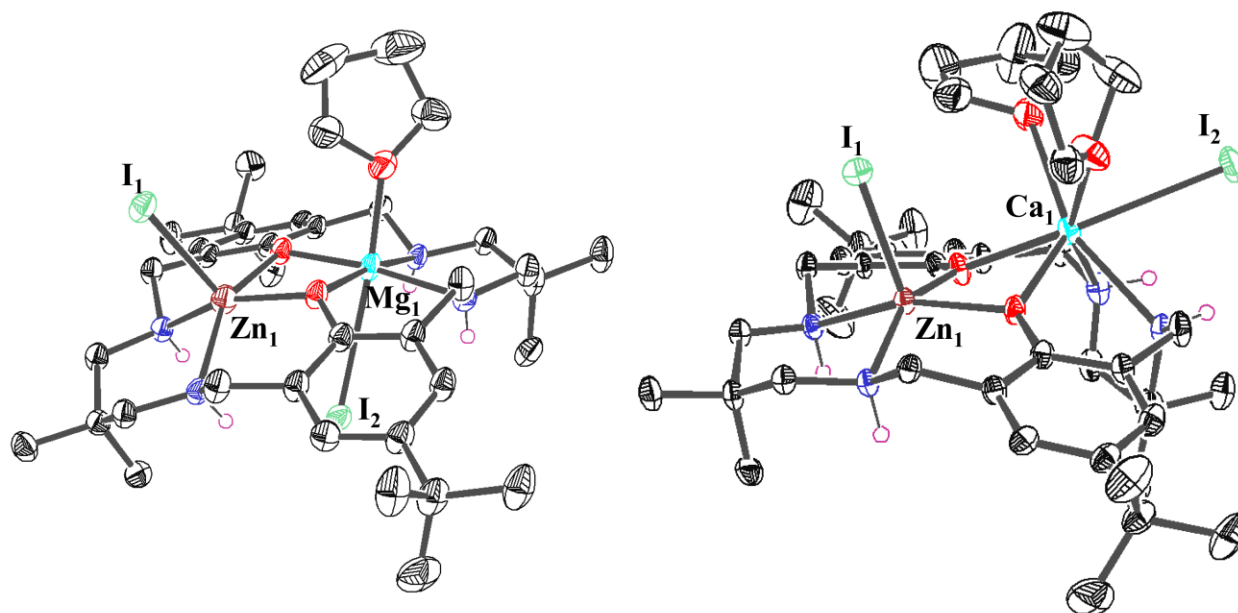


Figure 4: ORTEP representation of crystallographic structures of complexes **8a** (LHS) and **9a** (RHS), obtained by single crystal X-ray diffraction. Disorder and H-atoms (excluding N-H) have been omitted for clarity with thermal ellipsoids represented at 40 % probability (for further information see SI and Fig. S69 and S70).

### Ring Opening Copolymerization of CO<sub>2</sub> and Cyclohexene Oxide (CHO)

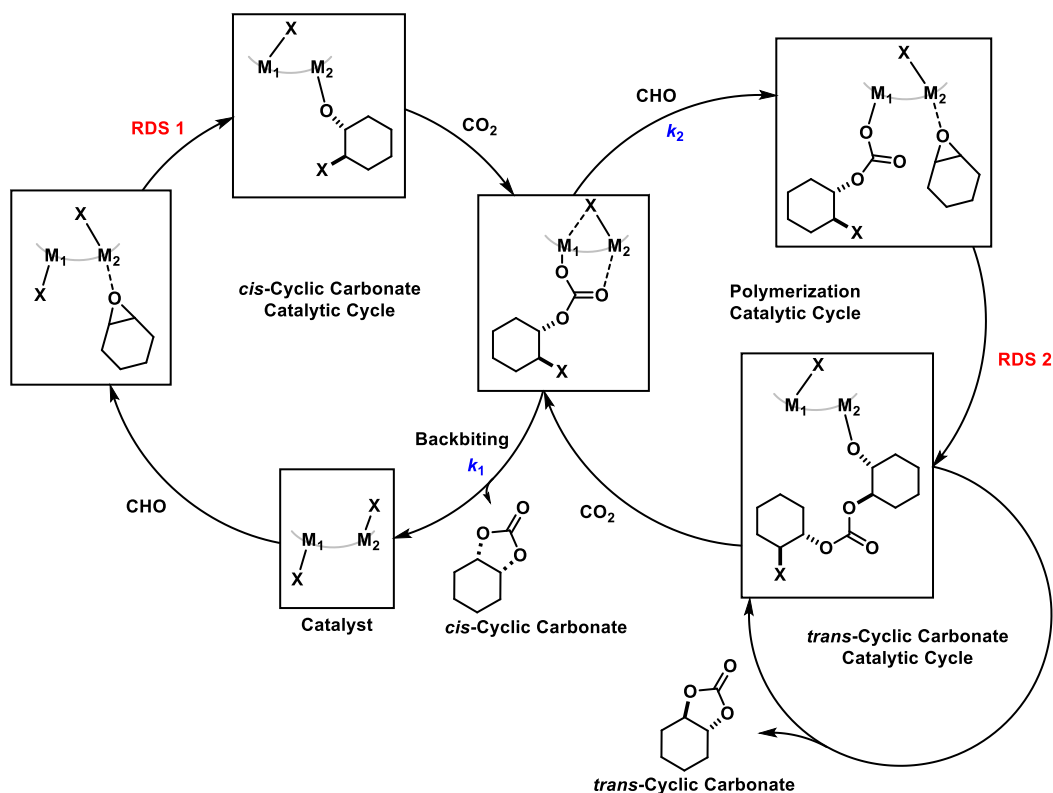
Di-zinc complexes, **4**, and the new heterodinuclear complexes, **5-9**, were each tested in the ROCOP of CO<sub>2</sub> with CHO (Table 1). The polymerizations were carried out at 80 °C, using a 0.1 mol % catalyst loading and at 1 bar CO<sub>2</sub> pressure. Complexes **1-3**, were totally inactive, probably due to their lacking an initiating group. Nonetheless, this result is useful as it rules out the likelihood of any initiation from the ligand.

Table 1: ROCOP of CO<sub>2</sub>/CHO with catalysts **4a** - **9a**.<sup>a</sup>

(M/M)	Cat.	Time (d)	TON <sup>b</sup>	TOF <sup>c</sup> (h <sup>-1</sup> )	CO <sub>2</sub> <sup>d</sup> (%)	Polymer <sup>e</sup> (%)	Cyclic Carbonate	M <sub>n</sub> [Đ] <sup>f</sup>
(Zn/Zn)	<b>4a</b>	3	441	11	> 99	96	4% Trans	9800 [1.05] 4000 [1.09]
	<b>4b</b>	1	470	20	> 99	> 99	<1% Trans	11,300 [1.05] 4900 [1.13]
(Zn/Li)	<b>5a</b>	3	20	0.4	> 99	0	>99% Cis	<i>n.d</i>
	<b>5b</b>	3	281	10	> 99	98	2% Trans	11,000 [1.08] 4400 [1.13]
(Zn/K)	<b>7a</b>	3	27	0.6	> 99	0	>99% Cis	<i>n.d</i>
	<b>7b</b>	3	138	4	> 99	96	4% Trans	5600 [1.06] 2100 [1.11]
(Zn/Mg)	<b>8a</b>	0.25	430	72	> 99	99	1% Trans	17,700 [1.03] 7600 [1.12]
(Zn/Ca)	<b>9a</b>	3	35	0.5	> 99	0	>99% Cis	<i>n.d</i>

<sup>a</sup>Copolymerisation conditions: cat : CHO 0.1 mol %, 1 bar CO<sub>2</sub>. <sup>b</sup>Turnover number (TON) = number of moles of cyclohexene oxide consumed / number of moles of catalyst. <sup>c</sup>Turnover frequency (TOF) = TON / Time (h) for the final 24 h of reaction. <sup>d</sup>Expressed as a percentage of CO<sub>2</sub> uptake vs the theoretical maximum (100 %), determined by comparison of the relative integrals of the <sup>1</sup>H NMR resonances due to carbonate (δ 4.65 ppm) and ether (δ 3.45 ppm) linkages in the polymer backbone. <sup>e</sup>Expressed as a percentage of polymer formation vs. the theoretical maximum (100 %), determined by comparison of the relative integrals of the <sup>1</sup>H NMR proton resonances due to polymer (4.65 ppm), cis-cyclic carbonate (4.68 ppm) and trans-cyclic carbonate (4.00 ppm) (Fig. S71-S72). <sup>f</sup>Determined by SEC, in THF, using narrow-M<sub>n</sub> polystyrene standards as the calibrant; dispersity is given in brackets.

All catalysts (**4a-9a**) display excellent selectivity towards CO<sub>2</sub> (> 99 %) with no ether linkages observed by <sup>1</sup>H NMR spectroscopy. Catalysts **4a**, **4b**, **8a** and **8b** also show a high selectivity for polycarbonate formation (> 96 %). Overall, heterodinuclear complex **8a** is six times more active than di-zinc **4a**, a finding that is in line with previous observations made using a heterodinuclear complex featuring bromide co-ligands.<sup>19</sup> The polycarbonates have lower molar masses than theoretically calculated and show bimodal distributions; these findings are exactly in line with many other catalysts in the literature and are rationalized by initiation from both iodide and 1,2-cyclohexanediol groups, the latter forming by hydrolysis of the epoxide.<sup>27, 48, 51, 59-66</sup>



Scheme 2: Proposed catalytic cycles rationalizing formation of *cis*-cyclic carbonate, *trans*-cyclic carbonate and/or poly(cyclohexene oxide). Where  $M_1 = \text{Li(I)}, \text{K(I)}, \text{Mg(II)}, \text{Ca(II)}$  and  $M_2 = \text{Zn(II)}$ ;  $X = \text{I}$  or  $\text{OBz}p\text{CF}_3$ ; and the macrocyclic ligand is abbreviated to a light grey 'bowl' shape, as commonly observed in the solid state structures. Where RDS stands for rate determining step.

A mechanistic hypothesis can be proposed to rationalize the formation of both *cis*-cyclic carbonate and poly(cyclohexene carbonate) products (Scheme 2). Accordingly, the reaction selectivity of depends upon the relative rates of the backbiting reaction ( $k_1$ ) vs. binding of epoxide ( $k_2$ ). The backbiting reaction is favoured by: (1) more ionic metal-oxygen bonds and (2) the presence of a good leaving group (X). On the other hand, epoxide binding and subsequent copolymerization is favoured by: (1) highly Lewis acidic metals and (2) covalent metal-oxygen bonds. In line with this hypothesis, heterodinuclear complexes **5a**, **7a** and **9a** are selective for *cis*-cyclic carbonate formation (> 99 %). This selectivity results from the iodide ligand, which initiates ring-opening but sequently becomes a good leaving group and accelerates the back-biting reaction. An

additional driver may be the increased ionic character to the metal carbonate bonds which may result in partial dissociation of the growing chain from the metal centre. In the ROCOP catalysis field, it has previously been proposed that ionic/metal-dissociated carbonate/alkoxide-polymer chains undergo faster back-biting reactions.<sup>30, 38-39, 67-68</sup> On the other hand, hetero-complexes **5b** and **7b** are very selective for polycarbonate formation and show a high uptake of CO<sub>2</sub> in the backbone, with no detectable ether linkages (Table 2). Indeed, complexes **4b**, **5b**, **7b** and **8b** all show high selectivity for polymer formation (> 96 %) which clearly demonstrates the importance of co-ligand selection. In addition to the altered selectivity, the activity of **5b** and **7b** is also significantly greater than the analogous complexes featuring iodide ligands, **5a** and **7a**. This is proposed to result from a change in the rate limiting step from nucleophilic attack by an iodide on the epoxide (RDS 1) to metal-carbonate attack on coordinated epoxide in the propagation cycle for the benzoate co-ligands (RDS 2) (Scheme 2). The activity is also higher for the lighter homologues in both Group 1 and Group 2 (i.e. for Li and Mg) perhaps due to increased Lewis acidity and optimised coordination geometries (CN 5/6) for the rate determining epoxide ring-opening transition states. Considering the best catalysts in the series, Zn(II)/Mg(II) combinations lead to both the highest rates and selectivity for polymer formation. One of the best catalysts shows a solid state structure with THF coordination at magnesium and thus it is proposed that the Mg(II) centre coordinates the epoxide (Lewis acid) which is attacked by a zinc-carbonate intermediate.

## Conclusions



The efficient synthesis of a series of stable heterodinuclear complexes whereby Zn(II) is coordinated with Li(I), K(I), Mg(II) or Ca(II), by a symmetrical macrocycle, were reported. The complexes were isolated either by a sequential metalation synthesis or by heating the homodinuclear analogues for extended periods. Both approaches indicate that the heterodinuclear complexes are more thermodynamically stable than the homodinuclear counterparts. Such findings are in line with recent results demonstrating unexpected stability for other heteronuclear transition metal/main group combinations.<sup>69</sup> In terms of epoxide/CO<sub>2</sub> polymerisation catalysis, the most active and selective catalyst features Mg(II)/Zn(II) and all the other hetero-combinations are much less active. The solid state structure of the Mg(II)/Zn(II) catalyst suggests epoxide coordination may occur at the magnesium centre, with the zinc carbonate attacking it. Catalytic reactivity trends highlight the subtle factors controlling rate, since replacing magnesium with any other Lewis acidic metals reduces rate. There is a clear opportunity for more detailed study of other Mg(II)/Zn(II) complexes and to moderate selectivity through appropriate co-ligand selection. More generally, these stable heterodinuclear complexes warrant investigation for other catalytic transformations, particularly those with mechanisms requiring substrate activation by a Lewis acidic site and subsequent labile metal-heteroatom bond attack. For example, these complexes could be of interest as catalysts for lactone ring-opening polymerizations, phosphate ester hydrolysis or even hydroamination/etherification reactions. An additional incentive for their development for catalysis is the relatively high abundance, low cost and low toxicity of the alkali or alkaline earth metals.

### **Supporting Information.**

The Supporting Information (SI) is available free of charge on the ACS Publications website at DOI:

It contains complete experimental and characterization data for all compounds and polymerisations (PDF) and Single crystal X-ray structural information in CIF format(CIF).

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### Notes

CKW declares she is a director of eonic technologies.

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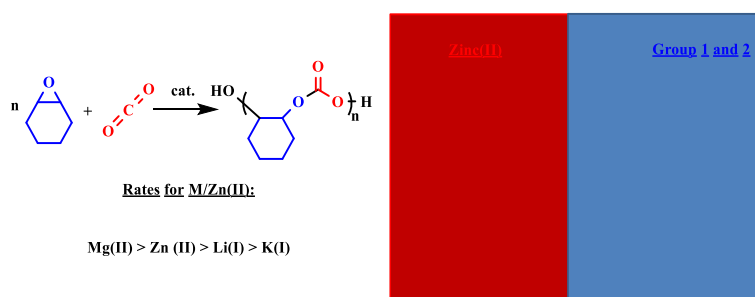
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**Table of Contents Entry for:**

**Group 1, 2 and Zn(II) Heterodinuclear Catalysts for Epoxide/CO<sub>2</sub> Ring Opening  
Copolymerization**

Arron C. Deacy, Christopher B. Durr, Jennifer A. Garden, Andrew J. P. White and

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A series of heterodinuclear Zn(II) complexes with elements from Group 1 or Group 2 were prepared using a sequential metalation strategy. The activity for CO<sub>2</sub>/epoxide Ring-opening copolymerization follows the order: Mg(II) > Zn(II) > Li(I) > K(I).