Group 1, 2 and Zn(II) Heterodinuclear Catalysts for Epoxide/CO_2 Ring Opening Copolymerization

Arron C. Deacy,[a] *Christopher B. Durr,*[a] *Jennifer A. Garden,*[b‡] *Andrew J. P. White*[b] *and*

Charlotte K. Williams[a]*

[a]Department of Chemistry, University of Oxford, Chemistry Research Laboratory, 12 Mansfield Road, Oxford, OX1 3TA, U.K.

[b]Department of Chemistry, Imperial College London, London SW7 2AZ, U.K.

‡ Current address: School of Chemistry, University of Edinburgh, Joseph Black Building, Edinburgh EH9 3FJ, U.K.

Keywords: Heterodinuclear, Zinc, Carbon Dioxide, Polymerization, Copolymerization, Epoxide

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 reaction products; the only exception is the Na(I)/Zn(II) complex which are 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_2 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.[1-2] Synergic interactions between two different metals has been proposed as responsible for enhanced activity in homogeneous catalysis ranging from metallation,[3] CH bond activation,[4-6] and CF bond activation,[7-9] lactone ring opening polymerization (ROP),[10-12] olefin polymerization[13-17] and, relevant to this work, the ring opening copolymerization (ROCOP) of CO_2 and epoxides.[18-22]

Here, new heterodinuclear complexes are applied as catalysts for the ring opening copolymerization (ROCOP) of epoxides with CO_2. 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_2 to produce a commercially viable material.[23-26] The structures of the resulting polycarbonates influence their applications. Low molar mass hydroxyl-telechelic polycarbonates are used to prepare polyurethanes which show equivalent or better properties than those using polyether or polyester polyols.[25, 27-30] Additionally the CO_2-containing polyurethanes result in significant reductions in greenhouse gas emissions and fossil depletion compared to conventional products.[31-33] Higher molar mass CO_2-derived polycarbonates may be applied as packaging plastics, engineering polymers, coatings, elastomers and adhesives.[34-36] The viability of CO_2/epoxide ROCOP depends on the selection of the metal catalyst which, in turn, controls rates, polymer molar mass and polymer composition (selectivity).[37-40] Amongst the highest performing catalysts are dinuclear, dimeric or bicomponent metal complexes.[35, 41-47] For many highly active dinuclear catalysts it is proposed that one metal activates the epoxide while the other provides the attacking nucleophile.[40] 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 (Fig. 1). These complexes which show promising activities and high selectivity for polymer at 1 bar carbon dioxide pressure (i.e. at low pressure).[48-51] Detailed kinetic, mechanistic and theoretical studies suggest a ‘chain shuttling’ mechanism where the rate-limiting step is metal-carbonate attack on coordinated epoxide (Fig. 1).[52-53] Applying this mechanistic hypothesis a Zn(II)/Mg(II) heterodinuclear catalyst was isolated and showed a 5-fold higher rate than either di-zinc or di-magnesium counterparts or combinations of them.[19] This promising result highlights the potential to increase performance using mixed metal complexes but, so far, there are very few examples of heterodinuclear catalysts for this polymerization.

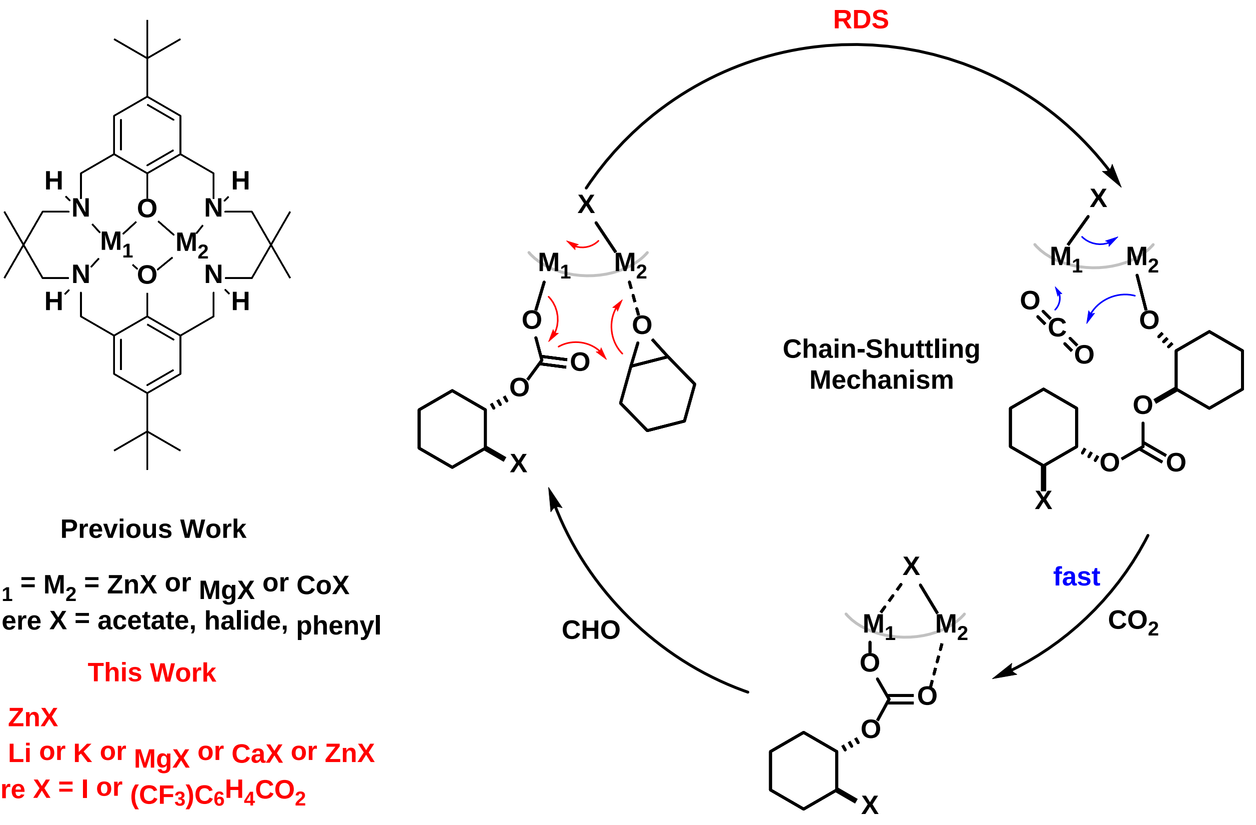
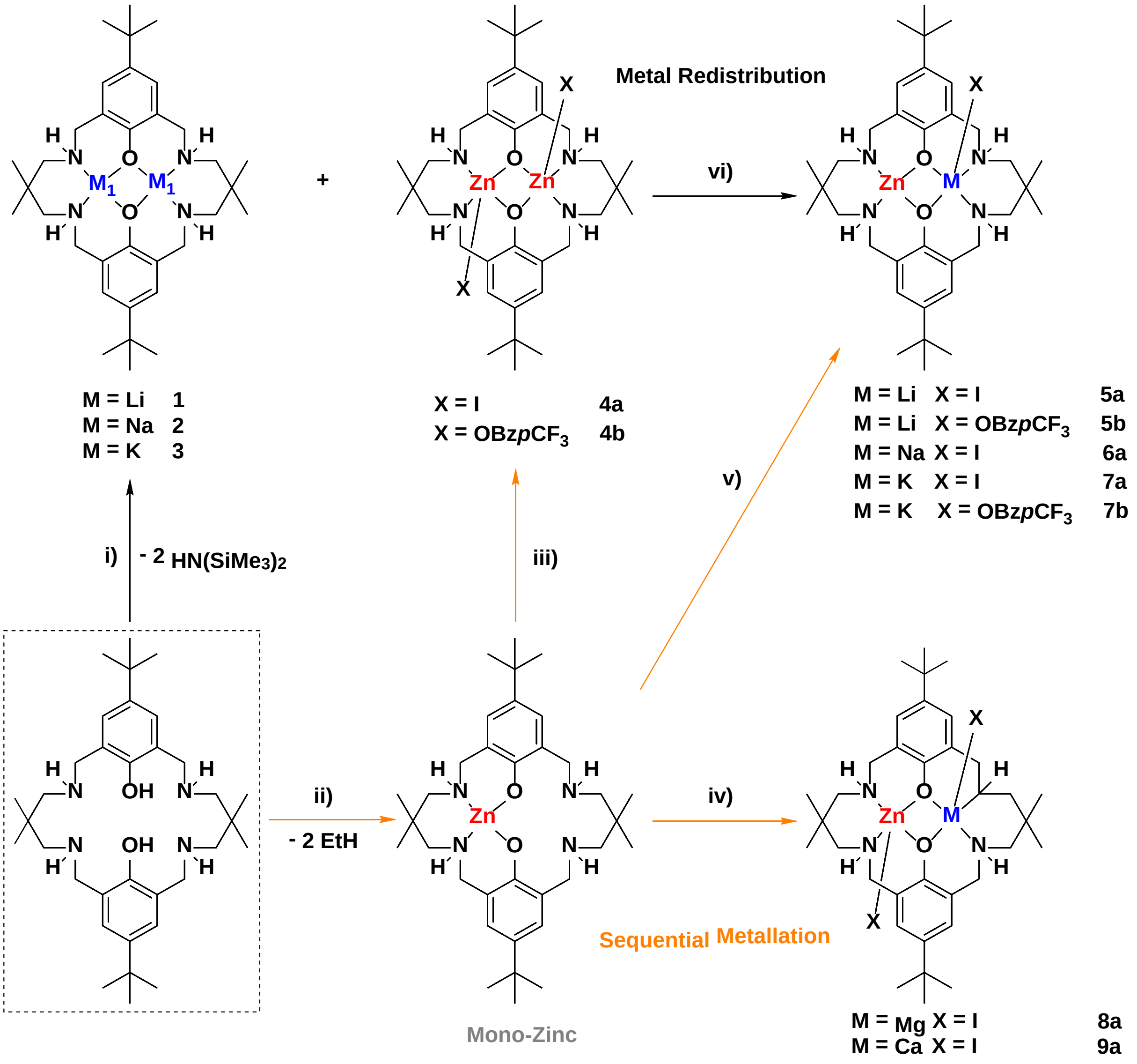


Figure 1: Heterodinuclear complexes described in this work alongside the proposed ‘chain-shuttling’ mechanism.

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.[41, 44, 48, 54-56] Although there are a few reports of testing of alkaline earth metal catalysts, specifically Ca(II), for epoxide/CO_2 polymerizations none were found to be active.[57-59] 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. In this work both synthetic methods are applied to evaluate the complex stabilities and to assess the best synthetic routes to heterodinuclear complexes (Scheme 1). The selection of co-ligands was motivated by an initial NMR study screening a series of acetates, benzoates and halides where iodide and para-CF_3 substituted benzoate displayed the sharpest NMR spectra to unambiguously assign the heterodinuclear nature of the complexes.



Scheme 1: Synthesis of complexes **1**-**9**. i) $M(N(Si(CH_3)_2)$, THF, 25 °C, 16 h, > 75 %. ii) $ZnEt_2$, THF, 25 °C, 1 h. iii) MX_2 (where M = Zn and X = I, $OBz\textit{p}CF_3$), THF, 25 °C, 16 h. > 70 %. iv) MX_2 (where M = Mg, Ca and X = I, $OBz\textit{p}CF_3$), THF, 100 °C, 24 h. > 70 %. v) MX (where M = Li, Na, K and X = I, $OBz\textit{p}CF_3$), 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. 2, S14-S15). In the solid state both **1** and **2** are dimeric and **1** displays a distorted cubane (Li_4O_4) structure where each lithium centre adopts a tetrahedral geometry. For **1** both Li(1) and Li(2) atoms favour bonding to phenoxide-oxygen centres over amine-nitrogens centres, whereas 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 (τ = 0.02) forming a cubane structure (N_4O_4) where bonding to each donor atom is fulfilled (Fig. S14-S15). 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).

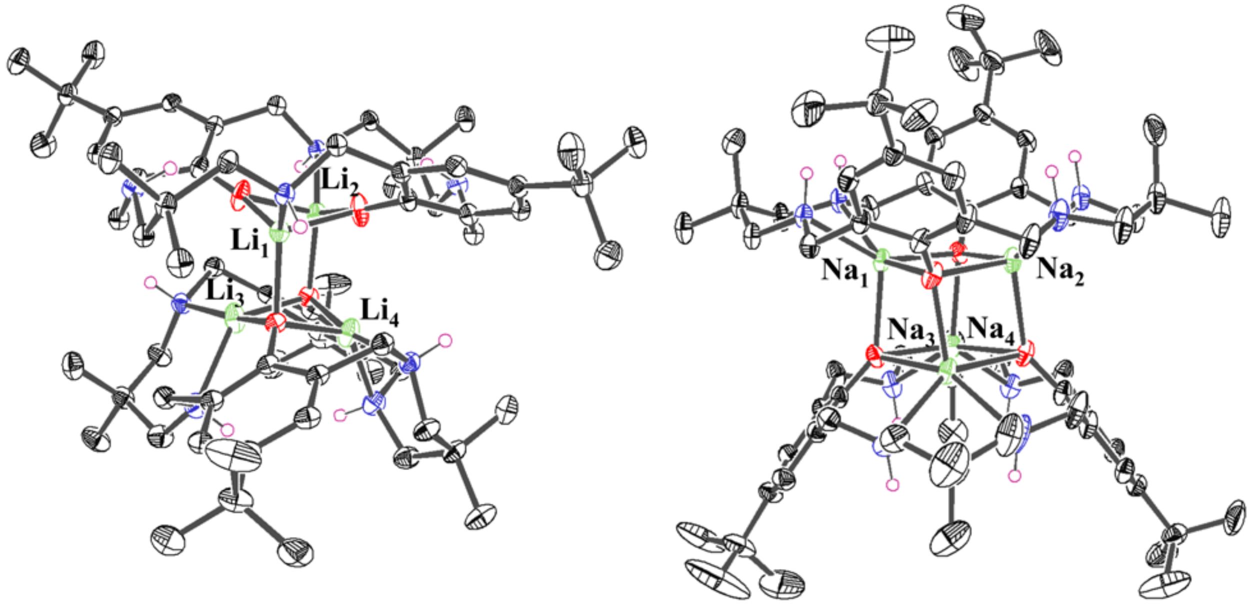


Figure 2: ORTEP representations of the molecular structures of complexes **1** (LHS) and **2** (RHS) obtained by single crystal X-ray diffraction. Disorder and H-atoms (excluding NH) have been omitted for clarity, with thermal ellipsoids represented at 40 % probability (For complete structures see Fig. 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 ^1H NMR spectra, determined in d_8-THF, are complex and show many coupled, broadened resonances. This is in-line with previously reported di-zinc complexes using this macrocycle with other co-ligands and could be due to ligand conformational disorder.[48, 60] 2D DOSY NMR experiments in d_8-THF display a single diffusion coefficient of -9.142 log(m^2s^{-1}) and -9.215 log (m^2s^{-1}) for **4a** and **4b**. The DOSY NMR data are consistent with a monomeric species in solution (Fig. S26/S27). In contrast to the spectra in THF, the ^{1}H NMR spectra determined in tetrachloroethane (TCE) at 403 K are straightforward to assign. The HT NMR spectra 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. Single crystals of **4a** and **4b** were obtained via vapour diffusion of an anti-solvent (**4a**: methanol, **4b**: pentane) into a saturated solution of the complex in THF at -40 °C (Fig. 3). Both complexes are monomeric in the solid state with **4a** adopting a 'bowl' and **4b** an 'S-shape' conformation. Intermetallic separation was measured at 3.10(0) Å and 3.19(2) Å for **4a** and **4b**, respectively.

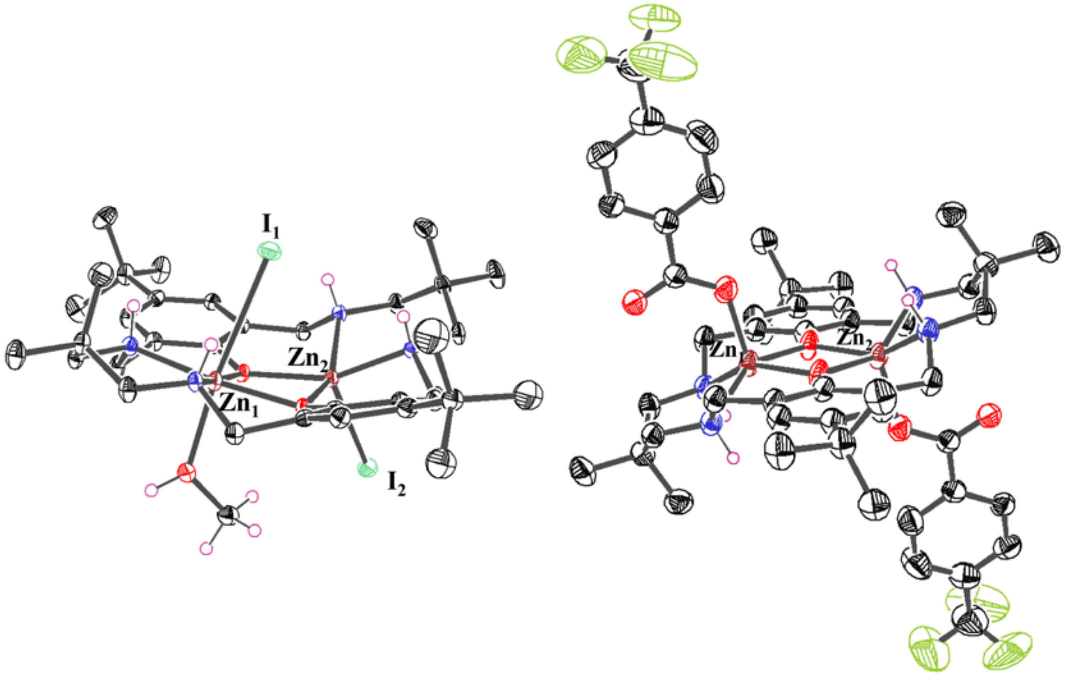


Figure 3: ORTEP representation of the molecular structures of complexes **4a** (LHS) and **4b** (RHS), obtained by single crystal X-ray diffraction. Disorder and H-atoms (excluding N-H) have been omitted for clarity with thermal ellipsoids represented at 40 % probability (for complete structural data 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}H NMR spectroscopy. For 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 whereas the homodinuclear precursors each show only one resonance (Fig. S34). The broad proton resonances observed for **7a** limited the utility of COSY NMR in establishing heterodinuclear complex formation. The reaction between the di-sodium and di-zinc complexes (**2** and **4a**) showed no change to the ^{1}H NMR spectrum even after prolonged heating, at 100 °C for 48 h (Fig. S35).

Next, the sequential metalation synthesis was investigated by reaction of the ligand with diethyl zinc to generate a mono-zinc intermediate.[19] 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}H and 2D NMR spectra of the products 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}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 only 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**; they were characterised by multinuclear NMR spectroscopy (Fig. S44-S51) and mass spectrometry (Fig. S52-S55). Single crystals of **5b** were isolated via crystallization from a DMSO solution and structural elucidation showed the complex was monomeric in the solid state (Fig. 3, S56). The ligand adopts an unusual ‘crown-shape’ conformation where the NH bonds alternate in their direction around the macrocycle. The metal centres in the structure cannot be assigned as zinc or lithium due to their positional disorder, although heterodinuclear character is strongly indicated as only one coligand is present whereas the di-lithium complex is dimeric with no coligands (Fig. 2) and the di-zinc complex has two coligands (Fig. 3). 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 κ_2 chelating benzoate ligand. The intermetallic separation is 2.86(1) Å.

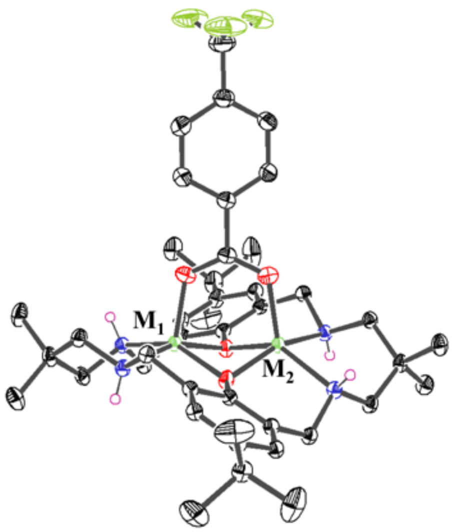


Figure 4: ORTEP representation of the molecular structure of complex **5b**, obtained by single crystal X-ray diffraction. Disorder and H-atoms (excluding N-H) have been omitted for clarity with thermal ellipsoids represented at 40 % probability (for further information see SI and Fig. S56).

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 and in > 70 % yield. Complexes **8a** and **9a** were characterized by multinuclear NMR spectroscopy (Fig. S57-66), mass spectrometry (Fig. S67 – S68), X-ray crystallography (Fig. S69-S70) and bulk purity was confirmed by elemental analysis. The ^{1}H NMR spectra each show ten resonances, between 2.0 and 5.2 ppm, assigned to the diastereotopic benzylic and methylene protons. The resonances are assigned to the zinc side of the macrocycle by noting common chemical shifts for **8a** and **9a**. For **9a** all resonances are significantly broader compared to those for **8a** which is perhaps due to a weaker complexation of the larger ionic radius calcium compared to magnesium (*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 °C, under nitrogen. Both structures confirm the formation of discrete heterodinuclear complexes in the solid state (Fig. 5). 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 but for **9a** an 'S-shaped' conformation with only two NH substituents on the same face. The zinc atoms are all pentacoordinate and adopt a slightly distorted square based pyramidal coordination geometry (**8a**: $\tau = 0.09$, **9a**: $\tau = 0.06$). They 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. The THF molecule coordinates to the magnesium centre which 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) Å, from the ligand coordination plane (formed by N(3)N(4)O(1)O(2)) which is particularly different to the analogous magnesium centre in complex **8a**, 0.15(3) Å. 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.[49, 55, 61]

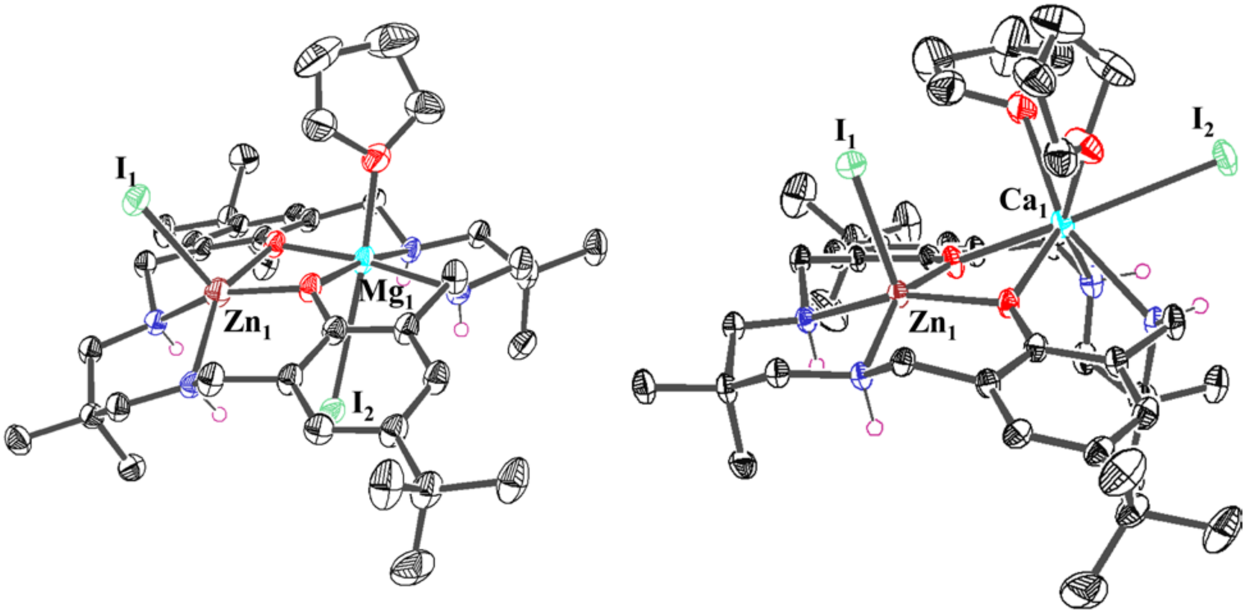


Figure 5: ORTEP representation of crystallographic structures of complexes **8a** (LHS) and **9a** (RHS), obtained by single crystal X-ray diffraction. Disorder and H-atoms (excluding N-H) have been omitted for clarity with thermal ellipsoids represented at 40 % probability (for further information see SI and Fig. S69 and S70).

Ring Opening Copolymerization of CO_2 and Cyclohexene Oxide (CHO)

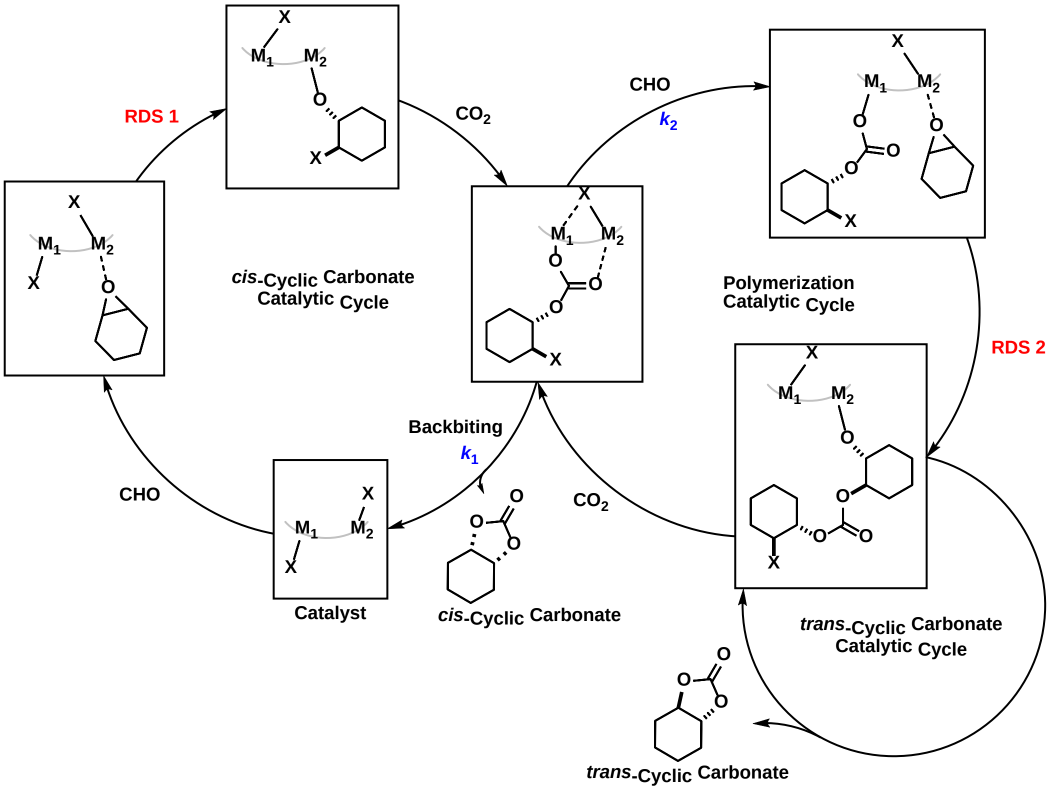
Di-zinc complexes, **4**, and the new heterodinuclear complexes, **5-9**, were each tested in the ROCOP of CO_2 with CHO (Table 1). The polymerizations were carried out at 80 °C, using a 0.1 mol % catalyst loading and at 1 bar CO_2 pressure. Complexes **1-3** were totally inactive which is probably due to their lacking an initiating group. The lack of activity is more interesting than it may appear as it rules out the likelihood of any initiation from the ligand.

Table 1: ROCOP of CO_2/CHO with catalysts **4a - 9a.**[a]

(M/M)	Cat.	Time (d)	TON[b]	TOF[c] (h^{-1})	CO_2[d] (%)	Polymer[e] (%)	Cyclic Carbonate	M_n [Đ][f]
(Zn/Zn)	**4a**	3	441	11	> 99	96	*4% Trans*	9800 [1.05] 4000 [1.09]
	4b	1	470	20	> 99	> 99	*<1% Trans*	11,300 [1.05] 4900 [1.13]
(Zn/Li)	**5a**	3	20	0.4	> 99	0	*>99% Cis*	*n.d*
	5b	3	281	10	> 99	98	*2% Trans*	11,000 [1.08] 4400 [1.13]
(Zn/K)	**7a**	3	27	0.6	> 99	0	*>99% Cis*	*n.d*
	7b	3	138	4	> 99	96	*4% Trans*	5600 [1.06] 2100 [1.11]
(Zn/Mg)	**8a**	0.25	430	72	> 99	99	*1% Trans*	17,700 [1.03] 7600 [1.12]
(Zn/Ca)	**9a**	3	35	0.5	> 99	0	*>99% Cis*	*n.d*

[a] *Copolymerization conditions: cat : CHO 0.1 mol %, 1 bar CO_2.* [b] *Turnover number (TON) = number of moles of cyclohexene oxide consumed / number of moles of catalyst.* [c] *Turnover frequency (TOF) = TON / Time (h) for the final 24 h of reaction.* [d] *Expressed as a percentage of CO_2 uptake vs the theoretical maximum (100 %), determined by comparison of the relative integrals of the ^1H NMR resonances due to carbonate (δ 4.65 ppm) and ether (δ 3.45 ppm) linkages in the polymer backbone.* [e] *Expressed as a percentage of polymer formation vs. the theoretical maximum (100 %), determined by comparison of the relative integrals of the ^1H 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).* [f] *Determined by SEC, in THF, using narrow-M_n polystyrene standards as the calibrant; dispersity is given in brackets.*

All catalysts (**4a-9a)** display excellent selectivity towards CO_2 (> 99 %) with no ether linkages observed by ^1H 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**. The activity finding is in line with previous observations made using a heterodinuclear complex featuring bromide co-ligands.[19] 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.[27, 48, 51, 56, 62-68]



Scheme 2: Proposed catalytic cycles rationalizing formation of *cis*-cyclic carbonate, *trans*-cyclic carbonate and/or poly(cyclohexene oxide). Where M_1 = Li(I), K(I), Mg(II), Ca(II) and M_2 = Zn(II); X = I or OBz*p*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 favored 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 favored by: (1) highly Lewis acidic metals and (2) covalent metal-oxygen bonds. This hypothesis is substantiated by the observation that 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 subsequently 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. It has been proposed that ionic or metal-dissociated polymer chains undergo faster back-biting reactions in ROCOP catalysis.[30, 38-39, 69-70] Hetero-complexes **5b** and **7b** are very selective for polycarbonate formation and show a high uptake of CO_2 in the backbone with no detectable ether linkages (Table 1). 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. The Zn(II)/Mg(II) combination leads to both the highest rates and selectivity for polymer formation. It also shows a solid state structure with THF coordination at magnesium and it is proposed that during catalysis 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 of a symmetrical macrocycle whereby Zn(II) is coordinated with Li(I), K(I), Mg(II) or Ca(II) 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.[71] For epoxide/CO_2 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 and is followed by the zinc carbonate attacking it. Catalytic reactivity trends highlight the subtle factors controlling rate as indicated by the replacement of magnesium with any other Lewis acidic metals reducing the 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. Overall, these stable heterodinuclear complexes warrant investigation for other catalytic transformations and 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 polymerizations (PDF) and Single crystal X-ray structural information in CIF format (CIF).

Author Information

Corresponding Author

*E-mail: charlotte.williams@chem.ox.ac.uk

Funding Sources

The EPSRC (EP/K014668/1; EP/L017393/1), EIT Climate KIC (EnCO$_2$re) and econic technologies (AD) are acknowledged for research funding.

Notes

CKW declares she is a director of econic technologies.

References

1. van der Vlugt, J. I., Cooperative Catalysis with First-Row Late Transition Metals, *Eur. J. Inorg. Chem.*, **2012,** 363.
2. Mata, J. A.; Hahn, F. E.; Peris, E., Heterometallic complexes, tandem catalysis and catalytic cooperativity, *Chem. Sci.*, **2014,** *5*, 1723.
3. Hevia, E.; Chua, J. Z.; García-Álvarez, P.; Kennedy, A. R.; McCall, M. D., Exposing the hidden complexity of stoichiometric and catalytic metathesis reactions by elucidation of Mg-Zn hybrids, *P.N.A.S.*, **2010,** *107*, (12), 5294.
4. Andrikopoulos, P. C.; Armstrong, D. R.; Barley, H. R. L.; Clegg, W.; Dale, S. H.; Hevia, E.; Honeyman, G. W.; Kennedy, A. R.; Mulvey, R. E., Sodium Dialkyl-amidozincates: Alkyl or Amido Bases? An Experimental and Theoretical Case Study, *J. Am. Chem. Soc.*, **2005,** *127*, (17), 6184.
5. Mulvey, R. E.; Mongin, F.; Uchiyama, M.; Kondo, Y., Deprotonative Metalation Using Ate Compounds: Synergy, Synthesis, and Structure Building, *Angew. Chem. Int. Ed.*, **2007,** *46*, (21), 3802.
6. Martínez-Martínez, A. J.; Kennedy, A. R.; Mulvey, R. E.; O'Hara, C. T., Directed ortho-meta′- and meta-meta′-dimetalations: A template base approach to deprotonation, *Science*, **2014,** *346*, (6211), 834.
7. Bakewell, C.; White, A. J. P.; Crimmin, M. R., Reactions of Fluoroalkenes with an Aluminium(I) Complex, *Angew. Chem. Int. Ed.*, **2018,** *57*, (22), 6638.

8. Bakewell, C.; Ward, B. J.; White, A. J. P.; Crimmin, M. R., A combined experimental and computational study on the reaction of fluoroarenes with Mg–Mg, Mg–Zn, Mg–Al and Al–Zn bonds, *Chem. Sci.*, **2018,** *9*, (8), 2348.
9. Coates, G.; Ward, B. J.; Bakewell, C.; White, A. J. P.; Crimmin, M. R., Reactions of Fluoroalkanes with Mg−Mg Bonds: Scope, $sp^3C{-}F/sp^2C{-}F$ Coupling and Mechanism, *Chem. Eur. J.*, **2018,** doi:10.1002/chem.201804580.
10. Chen, H.-Y.; Liu, M.-Y.; Sutar, A. K.; Lin, C.-C., Synthesis and Structural Studies of Heterobimetallic Alkoxide Complexes Supported by Bis(phenolate) Ligands: Efficient Catalysts for Ring-Opening Polymerization of l-Lactide, *Inorg. Chem.*, **2010,** *49*, (2), 665.
11. Maudoux, N.; Roisnel, T.; Carpentier, J.-F.; Sarazin, Y., Aluminum, Indium, and Mixed Yttrium–Lithium Complexes Supported by a Chiral Binap-Based Fluorinated Dialkoxide: Structural Features and Heteroselective ROP of Lactide, *Organometallics*, **2014,** *33*, (20), 5740.
12. Char, J.; Brulé, E.; Gros, P. C.; Rager, M.-N.; Guérineau, V.; Thomas, C. M., Synthesis of heterotactic PLA from *rac*-lactide using hetero-bimetallic Mg/Zn–Li systems, *J. Organomet. Chem.*, **2015,** *796*, 47.
13. Kuwabara, J.; Takeuchi, D.; Osakada, K., Early-late heterobimetallic complexes as initiator for ethylene polymerization. Cooperative effect of two metal centers to afford highly branched polyethylene, *Chem. Commun.*, **2006,** (36), 3815.
14. Li, H.; Marks, T. J., Nuclearity and cooperativity effects in binuclear catalysts and cocatalysts for olefin polymerization, *P.N.A.S.*, **2006,** *103*, (42), 15295.
15. Delferro, M.; Marks, T. J., Multinuclear Olefin Polymerization Catalysts, *Chem. Rev.*, **2011,** *111*, (3), 2450.
16. Liu, S.; Motta, A.; Delferro, M.; Marks, T. J., Synthesis, Characterization, and Heterobimetallic Cooperation in a Titanium–Chromium Catalyst for Highly Branched Polyethylenes, *J. Am. Chem. Soc.*, **2013,** *135*, (24), 8830.
17. Mandal, S. K.; Roesky, H. W., Assembling Heterometals through Oxygen: An Efficient Way To Design Homogeneous Catalysts, *Acc. Chem. Res.*, **2010,** *43*, (2), 248.
18. Saini, P. K.; Romain, C.; Williams, C. K., Dinuclear metal catalysts: improved performance of heterodinuclear mixed catalysts for CO_2-epoxide copolymerization, *Chem. Commun.*, **2014,** *50*, (32), 4164.
19. Garden, J. A.; Saini, P. K.; Williams, C. K., Greater than the Sum of Its Parts: A Heterodinuclear Polymerization Catalyst, *J. Am. Chem. Soc.*, **2015,** *137*, (48), 15078.
20. Garden, J. A.; White, A. J. P.; Williams, C. K., Heterodinuclear titanium/zinc catalysis: synthesis, characterization and activity for CO_2/epoxide copolymerization and cyclic ester polymerization, *Dalton Trans.*, **2017,** *46*, (8), 2532.
21. Qin, J.; Xu, B.; Zhang, Y.; Yuan, D.; Yao, Y., Cooperative rare earth metal–zinc based heterometallic catalysts for copolymerization of CO_2 and cyclohexene oxide, *Green Chem.*, **2016,** *18*, (15), 4270.
22. Nagae, H.; Aoki, R.; Akutagawa, S.; Kleemann, J.; Tagawa, R.; Schindler, T.; Choi, G.; Spaniol, T. P.; Tsurugi, H.; Okuda, J.; Mashima, K., Lanthanide Complexes Supported by a Trizinc Crown Ether as Catalysts for Alternating Copolymerization of Epoxide and CO_2: Telomerization Controlled by Carboxylate Anions, *Angew. Chem. Int. Ed.*, **2018,** *57*, (9), 2492.
23. Poland, S. J.; Darensbourg, D. J., A quest for polycarbonates provided via sustainable epoxide/CO_2 copolymerization processes, *Green Chem.*, **2017,** *19*, (21), 4990.

24. Artz, J.; Müller, T. E.; Thenert, K.; Kleinekorte, J.; Meys, R.; Sternberg, A.; Bardow, A.; Leitner, W., Sustainable Conversion of Carbon Dioxide: An Integrated Review of Catalysis and Life Cycle Assessment, *Chem. Rev.*, **2018,** *118*, (2), 434.
25. Chapman, A. M.; Keyworth, C.; Kember, M. R.; Lennox, A. J. J.; Williams, C. K., Adding Value to Power Station Captured CO_2: Tolerant Zn and Mg Homogeneous Catalysts for Polycarbonate Polyol Production, *ACS Catal.*, **2015,** *5*, (3), 1581.
26. Zhu, Y.; Romain, C.; Williams, C. K., Sustainable polymers from renewable resources, *Nature*, **2016,** *540*, 354.
27. Nakano, K.; Nakamura, M.; Nozaki, K., Alternating Copolymerization of Cyclohexene Oxide with Carbon Dioxide Catalyzed by (salalen)CrCl Complexes, *Macromolecules*, **2009,** *42*, (18), 6972.
28. Na, S. J.; S, S.; Cyriac, A.; Kim, B. E.; Yoo, J.; Kang, Y. K.; Han, S. J.; Lee, C.; Lee, B. Y., Elucidation of the Structure of a Highly Active Catalytic System for CO_2/Epoxide Copolymerization: A salen-Cobaltate Complex of an Unusual Binding Mode, *Inorg. Chem.*, **2009,** *48*, (21), 10455.
29. Noh, E. K.; Na, S. J.; S, S.; Kim, S.-W.; Lee, B. Y., Two Components in a Molecule: Highly Efficient and Thermally Robust Catalytic System for CO_2/Epoxide Copolymerization, *J. Am. Chem. Soc.*, **2007,** *129*, (26), 8082.
30. Darensbourg, D. J.; Wei, S.-H., Depolymerization of Polycarbonates Derived from Carbon Dioxide and Epoxides to Provide Cyclic Carbonates. A Kinetic Study, *Macromolecules*, **2012,** *45*, (15), 5916.
31. von der Assen, N.; Bardow, A., Life cycle assessment of polyols for polyurethane production using CO2 as feedstock: insights from an industrial case study, *Green Chem.*, **2014,** *16*, (6), 3272.
32. Paul, S.; Zhu, Y.; Romain, C.; Brooks, R.; Saini, P. K.; Williams, C. K., Ring-opening copolymerization (ROCOP): synthesis and properties of polyesters and polycarbonates, *Chem. Commun.*, **2015,** *51*, (30), 6459.
33. Lee, S. H.; Cyriac, A.; Jeon, J. Y.; Lee, B. Y., Preparation of thermoplastic polyurethanes using in situ generated poly(propylene carbonate)-diols, *Polym. Chem.*, **2012,** *3*, (5), 1215.
34. Hauenstein, O.; Reiter, M.; Agarwal, S.; Rieger, B.; Greiner, A., Bio-based polycarbonate from limonene oxide and CO_2 with high molecular weight, excellent thermal resistance, hardness and transparency, *Green Chem.*, **2016,** *18*, (3), 760.
35. Stößer, T.; Li, C.; Unruangsri, J.; Saini, P. K.; Sablong, R. J.; Meier, M. A. R.; Williams, C. K.; Koning, C., Bio-derived polymers for coating applications: comparing poly(limonene carbonate) and poly(cyclohexadiene carbonate), *Polym. Chem.*, **2017,** *8*, (39), 6099.
36. Luinstra, G. A., Poly(Propylene Carbonate), Old Copolymers of Propylene Oxide and Carbon Dioxide with New Interests: Catalysis and Material Properties, *Polym. Rev.*, **2008,** *48*, (1), 192.
37. Trott, G.; Saini, P. K.; Williams, C. K., Catalysts for CO_2/epoxide ring-opening copolymerization, *Phil. Trans. R. Soc. A.*, **2016,** *374*, (2061), 1.
38. Darensbourg, D. J., Making Plastics from Carbon Dioxide: Salen Metal Complexes as Catalysts for the Production of Polycarbonates from Epoxides and CO_2, *Chem. Rev.*, **2007,** *107*, (6), 2388.
39. Lu, X.-B.; Ren, W.-M.; Wu, G.-P., CO_2 Copolymers from Epoxides: Catalyst Activity, Product Selectivity, and Stereochemistry Control, *Acc. Chem. Res.*, **2012,** *45*, (10), 1721.

40. Romain, C.; Thevenon, A.; Saini, P. K.; Williams, C. K., Dinuclear Metal Complex-Mediated Formation of CO_2-Based Polycarbonates. In *Carbon Dioxide and Organometallics*, (Lu, X.-B.) Topics in Organometallic Chemistry, 53, pp 101, Cham, Switzerland, Springer International **2016**.

41. Lehenmeier, M. W.; Kissling, S.; Altenbuchner, P. T.; Bruckmeier, C.; Deglmann, P.; Brym, A.-K.; Rieger, B., Flexibly Tethered Dinuclear Zinc Complexes: A Solution to the Entropy Problem in CO_2/Epoxide Copolymerization Catalysis?, *Angew. Chem. Int. Ed.*, **2013,** *52*, (37), 9821.

42. Kissling, S.; Lehenmeier, M. W.; Altenbuchner, P. T.; Kronast, A.; Reiter, M.; Deglmann, P.; Seemann, U. B.; Rieger, B., Dinuclear zinc catalysts with unprecedented activities for the copolymerization of cyclohexene oxide and CO_2, *Chem. Commun.*, **2015,** *51*, (22), 4579.

43. Moore, D. R.; Cheng, M.; Lobkovsky, E. B.; Coates, G. W., Mechanism of the Alternating Copolymerization of Epoxides and CO_2 Using β-Diiminate Zinc Catalysts: Evidence for a Bimetallic Epoxide Enchainment, *J. Am. Chem. Soc.*, **2003,** *125*, (39), 11911.

44. Nakano, K.; Nozaki, K.; Hiyama, T., Asymmetric Alternating Copolymerization of Cyclohexene Oxide and CO_2 with Dimeric Zinc Complexes, *J. Am. Chem. Soc.*, **2003,** *125*, (18), 5501.

45. Peña Carrodeguas, L.; González-Fabra, J.; Castro-Gómez, F.; Bo, C.; Kleij, A. W., AlIII-Catalysed Formation of Poly(limonene)carbonate: DFT Analysis of the Origin of Stereoregularity, *Chem. Eur. J.*, **2015,** *21*, (16), 6115.

46. González-Fabra, J.; Castro-Gómez, F.; Kleij, A. W.; Bo, C., Mechanistic Insights into the Carbon Dioxide/Cyclohexene Oxide Copolymerization Reaction: Is One Metal Center Enough?, *ChemSusChem*, **2017,** *10*, (6), 1233.

47. Thevenon, A.; Cyriac, A.; Myers, D.; White, A. J. P.; Durr, C. B.; Williams, C. K., Indium Catalysts for Low-Pressure CO_2/Epoxide Ring-Opening Copolymerization: Evidence for a Mononuclear Mechanism?, *J. Am. Chem. Soc.*, **2018,** *140*, (22), 6893.

48. Kember, M. R.; Knight, P. D.; Reung, P. T. R.; Williams, C. K., Highly Active Dizinc Catalyst for the Copolymerization of Carbon Dioxide and Cyclohexene Oxide at One Atmosphere Pressure, *Angew. Chem. Int. Ed.*, **2009,** *48*, (5), 931.

49. Kember, M. R.; White, A. J. P.; Williams, C. K., Highly Active Di- and Trimetallic Cobalt Catalysts for the Copolymerization of CHO and CO_2 at Atmospheric Pressure, *Macromolecules*, **2010,** *43*, (5), 2291.

50. Buchard, A.; Kember, M. R.; Sandeman, K. G.; Williams, C. K., A bimetallic iron(III) catalyst for CO_2/epoxide coupling, *Chem. Commun.*, **2011,** *47*, (1), 212.

51. Kember, M. R.; Williams, C. K., Efficient Magnesium Catalysts for the Copolymerization of Epoxides and CO_2; Using Water to Synthesize Polycarbonate Polyols, *J. Am. Chem. Soc.*, **2012,** *134*, (38), 15676.

52. Jutz, F.; Buchard, A.; Kember, M. R.; Fredriksen, S. B.; Williams, C. K., Mechanistic Investigation and Reaction Kinetics of the Low-Pressure Copolymerization of Cyclohexene Oxide and Carbon Dioxide Catalyzed by a Dizinc Complex, *J. Am. Chem. Soc.*, **2011,** *133*, (43), 17395.

53. Buchard, A.; Jutz, F.; Kember, M. R.; White, A. J. P.; Rzepa, H. S.; Williams, C. K., Experimental and Computational Investigation of the Mechanism of Carbon Dioxide/Cyclohexene Oxide Copolymerization Using a Dizinc Catalyst, *Macromolecules*, **2012,** *45*, (17), 6781.

54. Inoue, S.; Koinuma, H.; Tsuruta, T., Copolymerization of carbon dioxide and epoxide, *J. Polym. Sci., Part A: Polym. Lett.,*, **1969,** *7*, (4), 287.
55. Moore, D. R.; Cheng, M.; Lobkovsky, E. B.; Coates, G. W., Electronic and Steric Effects on Catalysts for CO_2/Epoxide Polymerization: Subtle Modifications Resulting in Superior Activities, *Angew. Chem. Int. Ed.,* **2002,** *41*, (14), 2599.
56. Lee, B. Y.; Kwon, H. Y.; Lee, S. Y.; Na, S. J.; Han, S.-i.; Yun, H.; Lee, H.; Park, Y.-W., Bimetallic Anilido-Aldimine Zinc Complexes for Epoxide/CO_2 Copolymerization, *J. Am. Chem. Soc.,* **2005,** *127*, (9), 3031.
57. Xiao, Y.; Wang, Z.; Ding, K., Intramolecularly Dinuclear Magnesium Complex Catalyzed Copolymerization of Cyclohexene Oxide with CO_2 under Ambient CO_2 Pressure: Kinetics and Mechanism, *Macromolecules,* **2006,** *39*, (1), 128.
58. Piesik, D. F. J.; Range, S.; Harder, S., Bimetallic Calcium and Zinc Complexes with Bridged β-Diketiminate Ligands: Investigations on Epoxide/CO_2 Copolymerization, *Organometallics,* **2008,** *27*, (23), 6178.
59. Range, S.; Piesik, D. F. J.; Harder, S., Binuclear Magnesium, Calcium and Zinc Complexes Based on Bis(salicylaldimine) Ligands with Rigid Bridges, *Eur. J. Inorg. Chem.,* **2008,** 3442.
60. Zhu, Y.; Romain, C.; Williams, C. K., Selective Polymerization Catalysis: Controlling the Metal Chain End Group to Prepare Block Copolyesters, *J. Am. Chem. Soc.,* **2015,** *137*, (38), 12179.
61. Klaus, S.; Lehenmeier, M. W.; Anderson, C. E.; Rieger, B., Recent advances in CO_2/epoxide copolymerization—New strategies and cooperative mechanisms, *Coord. Chem. Rev.,* **2011,** *255*, (13), 1460.
62. Lu, X.-B.; Darensbourg, D. J., Cobalt catalysts for the coupling of CO_2 and epoxides to provide polycarbonates and cyclic carbonates, *Chem. Soc. Rev.,* **2012,** *41*, (4), 1462.
63. Wu, G.-P.; Darensbourg, D. J., Mechanistic Insights into Water-Mediated Tandem Catalysis of Metal-Coordination CO_2/Epoxide Copolymerization and Organocatalytic Ring-Opening Polymerization: One-Pot, Two Steps, and Three Catalysis Cycles for Triblock Copolymers Synthesis, *Macromolecules,* **2016,** *49*, (3), 807.
64. Sugimoto, H.; Kuroda, K., The Cobalt Porphyrin−Lewis Base System: A Highly Selective Catalyst for Alternating Copolymerization of CO_2 and Epoxide under Mild Conditions, *Macromolecules,* **2008,** *41*, (2), 312.
65. Nakano, K.; Kobayashi, K.; Nozaki, K., Tetravalent Metal Complexes as a New Family of Catalysts for Copolymerization of Epoxides with Carbon Dioxide, *J. Am. Chem. Soc.,* **2011,** *133*, (28), 10720.
66. Nakano, K.; Kobayashi, K.; Ohkawara, T.; Imoto, H.; Nozaki, K., Copolymerization of Epoxides with Carbon Dioxide Catalyzed by Iron–Corrole Complexes: Synthesis of a Crystalline Copolymer, *J. Am. Chem. Soc.,* **2013,** *135*, (23), 8456.
67. Kember, M. R.; Copley, J.; Buchard, A.; Williams, C. K., Triblock copolymers from lactide and telechelic poly(cyclohexene carbonate), *Polym. Chem.,* **2012,** *3*, (5), 1196.
68. Decortes, A.; Haak, R. M.; Martín, C.; Belmonte, M. M.; Martin, E.; Benet-Buchholz, J.; Kleij, A. W., Copolymerization of CO_2 and Cyclohexene Oxide Mediated by Yb(salen)-Based Complexes, *Macromolecules,* **2015,** *48*, (22), 8197.
69. Darensbourg, D. J.; Moncada, A. I.; Wei, S.-H., Aliphatic Polycarbonates Produced from the Coupling of Carbon Dioxide and Oxetanes and Their Depolymerization via Cyclic Carbonate Formation, *Macromolecules,* **2011,** *44*, (8), 2568.

70. Wu, G.-P.; Wei, S.-H.; Ren, W.-M.; Lu, X.-B.; Li, B.; Zu, Y.-P.; Darensbourg, D. J., Alternating copolymerization of CO_2 and styrene oxide with Co(III)-based catalyst systems: differences between styrene oxide and propylene oxide, *Energy Environ. Sci.*, **2011,** *4*, (12), 5084.

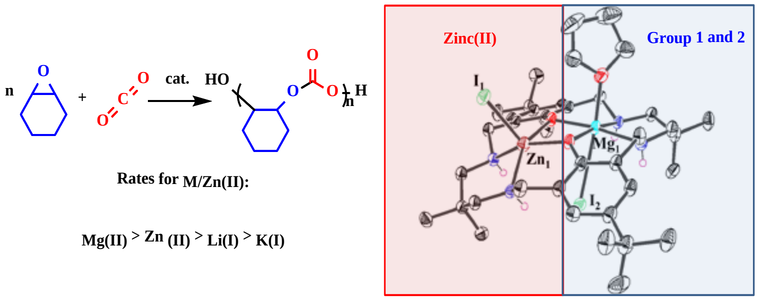
71. Butler, M. J.; Crimmin, M. R., Magnesium, zinc, aluminium and gallium hydride complexes of the transition metals, *Chem. Commun.*, **2017,** *53*, (8), 1348.

Table of Contents Entry for:

Group 1, 2 and Zn(II) Heterodinuclear Catalysts for Epoxide/CO_2 Ring Opening Copolymerization

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

Charlotte K. Williams



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_2/epoxide Ring-opening copolymerization follows the order: Mg(II) > Zn(II) > Li(I) > K(I).