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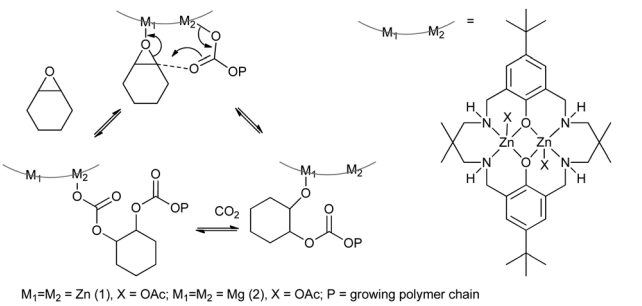
Dinuclear metal catalysts: improved performance of heterodinuclear mixed catalysts for CO_2–epoxide copolymerization†

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Some of the most active catalysts for carbon dioxide and epoxide copolymerization are dinuclear metal complexes. Whilst efficient homodinuclear catalysts are known, until now heterodinuclear catalysts remain unreported. Here, a facile, *in situ* route to a catalyst system comprising a mixture of homo- and heteronuclear Zn–Mg complexes is presented. This catalyst system shows excellent polymerization control and exhibits significantly higher activity than the homodinuclear catalysts alone or in combination.

Making polymers from carbon dioxide is an attractive means to add value to waste gases and to improve the sustainability of commodity polymer manufacture.[1] The reaction between epoxides and carbon dioxide, in the presence of a suitable catalyst, yields aliphatic polycarbonates whose mass is 30–50% derived from CO_2.[2] Low molecular weight (M_n), di-hydroxyl terminated, polycarbonates or 'polycarbonate polyols' are particularly important as replacements for polyether polyols, which are widely used in polyurethane manufacture.[3] Efficient polymer production from CO_2 is critically dependent on the activity and selectivity of the catalyst.[1]

Some promising homogeneous catalysts include complexes of Zn-β-diiminates [(BDI)Zn], Co(III)/Cr(III)(salens), Al/Co(III)/Cr(III) porphyrins.[1] Whether these catalysts exist as mono- or dinuclear structures, especially under the conditions of the polymerizations, remains a central, if controversial, question. On the one hand, the porphyrin catalysts are most likely mononuclear complexes,[4] whilst on the other, the most active β-diiminate zinc[5] and Co/Cr salen species, in the absence of a co-catalyst, likely exist as dimers.[6] Metal salen/porphyrin catalysts show much better activities when co-catalysts (*e.g.* ionic species or non-nucleophilic bases) are applied.[7] The best salen catalysts are bi-component where the salen ligand binds both the metal and the ionic co-catalyst(s).[8] In contrast, the Zn catalysts require no such co-catalyst additives. We, and others, have deliberately targeted dinuclear complexes leading to higher activities, particularly at low catalyst loadings (when dimerization would be entropically disfavoured).[6a,9] Thus, our group have introduced various homodinuclear complexes, ligated by a diphenolate tetraamine macrocyclic ligand, of Zn(II) (**1**), Mg(II) (**2**), Co(II/III) and Fe(III) (Fig. 1).[10] These catalysts are highly active and operate at low pressures of carbon dioxide (*e.g.* 1 bar). Indeed, the di-Mg complex (**2**) shows equivalent activity to the best Co(III) salen systems, but operates at a fraction of the CO_2 pressure and obviates the need for co-catalyst.[10a] The polymerization kinetics, studied using a di-zinc catalyst (**1**), revealed a second order rate law, dependent on both the concentration of epoxide and catalyst, but independent of CO_2 pressure (1–40 bar range).[10b,c] It is proposed that the rate limiting step is the attack by the metal–carbonate species on the metal-bound-epoxide. Detailed kinetic, computational and spectroscopic studies have led to our current mechanistic hypothesis: Dinuclear Chain Shuttling.[10b] According to this pathway the growing polymer chain 'shuttles' between the two metal (*e.g.* Zn) centres *twice* per complete cycle of monomer additions (*i.e.* epoxide and CO_2 addition) as illustrated in Fig. 1.



M_1=M_2 = Zn (1), X = OAc; M_1=M_2 = Mg (2), X = OAc; P = growing polymer chain

Fig. 1 Illustrates the proposed chain shuttling pathway for CO_2–epoxide copolymerization by dinuclear catalysts **1** and **2**.

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† Electronic supplementary information (ESI) available: Experimental section, attempted heterodinuclear catalyst preparation routes (Table S1), Fig. S1–S4: MALDI-ToF spectra, Fig. S5–S7: ^{1}H NMR, SEC and MALDI ToF spectra of the PCHC, Fig. S8: structures of reference catalysts, Table S2 and Fig. S9: effect of adding 16 eq. of water, Table S3: PO/CO_2 copolymerizations. See DOI: 10.1039/c3cc49158g

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A key implication of the mechanistic hypothesis is that heterodinuclear catalysts are expected to be more active.[10b] However, to date there are no studies examining the influence of such mixed metal catalysts using any homogeneous catalyst. It is, perhaps, notable that some of most effective heterogeneous catalysts (double metal cyanides) have bimetallic surfaces, *e.g.* Zn/Co or Zn/Fe.[11]

Thus, our goal was to investigate heterodinuclear analogues of our previously successful dinuclear catalysts. In so doing it is essential to maintain the same ancillary ligand; modification of the ligand is known to exert a significant influence over catalytic activity and selectivity.[10f,12] Numerous unsuccessful attempts were made to prepare the heterodinuclear Zn/Mg analogue as outlined in the ESI† (Table S1). Unfortunately, none were yet successful, due in part to the difficulties in differentiating between Zn and Mg metal centres, the propensity to form homo-dinuclear complexes and the challenges associated with efficient macrocycle (*vs.* polymer) formation (Table S1, ESI†). The strategy was, therefore, adapted to investigate whether the macrocyclic ligand, L, could be induced to coordinate a single metal ion. All attempts to prepare a mono-metallic complex *via* the addition of a single equivalent of zinc/magnesium acetate to H_2L resulted only in the formation of the respective homodinuclear complexes and excess ligand. However, the reaction of H_2L with one equivalent of diethyl zinc followed by the addition of equivalent of magnesium acetate resulted in the formation of a white powder, which was isolated in 85% yield (Fig. 2). The characterization data for the product was quite different from either that for $LZn_2(OAc)_2$ (**1**) or $LMg_2(OAc)_2$ (**2**).

The ^{1}H NMR spectrum of the product showed the complete consumption of the zinc bound ethyl group and the formation of broadened ligand resonances which are consistent with metal coordination.[10a,g] These broad signals could not be resolved either by changing solvent (*e.g.* benzene, toluene, tetrachloroethane) or by high/low temperature experiments (−50 to 80 °C). This is in contrast to the homodinuclear complexes which both show clearly resolved peaks at elevated temperatures.[10a,g] Elemental analysis showed that the product contained equal quantities of Zn and Mg, as expected. The MALDI-ToF spectrum (Fig. 3) showed a peak at 697 amu, corresponding to the heterodinuclear cation $[LZnMg(O_2CCH_3)]^+$. The presence of both homodinuclear complexes **1** and **2**, was evidenced by the peaks at 657 and 739 amu, due to $[LMg_2(O_2CCH_3)]^+$ and $[LZn_2(O_2CCH_3)]^+$, respectively. In order to rule out the possibility

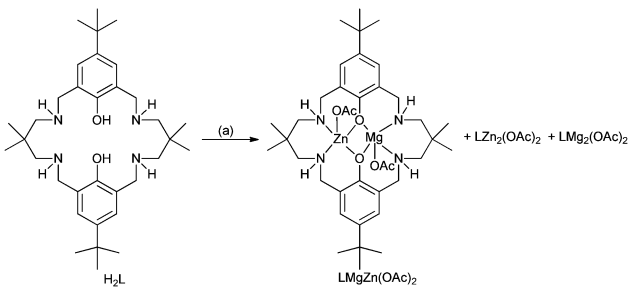


Fig. 2 Illustrates the synthesis of the catalyst system, **3**. (a) Reagents and conditions: (i) 1 eq. Et_2Zn, THF −40 °C to 25 °C, 2 h; (ii) 1 eq. $Mg(OAc)_2$, THF 25 °C, 16 h.

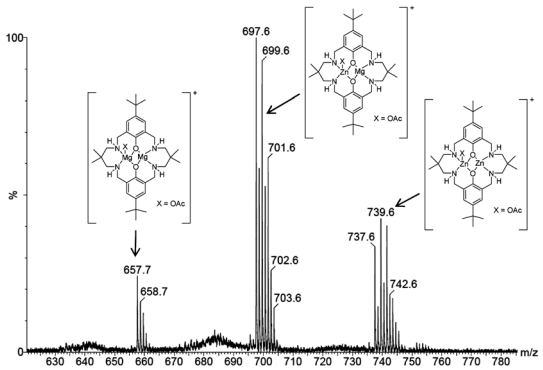


Fig. 3 Part of the MALDI-ToF mass spectrum for the catalyst system, with the structures for the molecular ions illustrated. The full spectrum is available in the ESI† (Fig. S1).

of the mixed metal species being formed only during the MALDI-ToF experiments, an equimolar mixture of $[LZn_2(OAc)_2]$ and $[LMg_2(OAc)_2]$ was compared (Fig. S2, ESI†). The equimolar mixture shows only homodinuclear complex ions (*i.e.* **1** and **2**); there is no evidence for any heterodinuclear cations. Furthermore, when the equimolar mixture was heated at 80 °C for 16 h (equivalent conditions as during polymerization), the spectrum remained the same (Fig. S3, ESI†). The mass spectrometry data, therefore, suggested that catalyst system **3** contains a new heterodinuclear complex as well as the two homodinuclear complexes (**1**, **2**). It was not yet possible to quantify the mixture composition due to the broad NMR signals, although the expected stoichiometry would be 1 : 2 : 1 ($LZn_2(OAc)_2$: $LMgZn(OAc)_2$: $LMg_2(OAc)_2$) in line with the elemental analysis results. All attempts to separate the mixture by selective crystallisation were unsuccessful: such a separation is likely to be highly challenging due to the similarities between the complexes. Instead, the mixed catalyst system was itself investigated for CO_2–epoxide copolymerization.

Its activity for the copolymerization of cyclohexene oxide and carbon dioxide was evaluated using 0.1 mol% of catalyst (*vs.* epoxide, assuming a 1 : 2 : 1 composition), 1 bar pressure of CO_2, at 80 °C and over a 6 hour run, as these conditions had previously proved most effective for **1**.[10g] Catalyst system **3** was compared with the two homodinuclear catalysts (**1**, **2**) and with the equimolar mixture (1 : 1 molar ratio of compounds **1** : **2**) (Table 1). It is clearly

Table 1 Shows the catalytic activity, productivity, selectivity and molecular weight data for runs using catalysts **1–3**

Catalyst	TON[a]	TOF[b] (h^{-1})	CO_2[c] (%)	M_n[d] (g mol^{-1})	PDI[d]
1 ($LZn_2(OAc)_2$)	99 ± 11	17 ± 2	>99	1300	1.23
2 ($LMg_2(OAc)_2$)	309 ± 34	52 ± 5	>99	5600	1.04
3	476 ± 31	79 ± 5	>99	5200	1.12
50 : 50; **1** : **2**	239 ± 36	40 ± 6	>99	2900	1.18

All copolymerizations were conducted in a Schlenk tube at 0.1% catalyst loading (*vs.* CHO), 80 °C, 1 bar CO_2 for 6 h. [a] The turn over number (TON) = number of moles of cyclohexene oxide consumed/number of moles of catalyst. [b] The turn over frequency (TOF) = TON/6. [c] Expressed as the percentage carbon dioxide uptake *vs.* the theoretical maximum (100%). This is determined by comparing the relative integrals of the ^{1}H NMR resonances due to carbonate (δ: 4.65 ppm) and ether (δ: 3.45 ppm) linkages in the polymer backbone. [d] Determined by SEC, in THF, using narrow M_n polystyrene standards as the calibrant.

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significantly more active than either **1** or **2**; indeed, it has nearly twice the activity of **2**, which is itself a notably high activity catalyst. Furthermore, it shows considerably higher activity than the equimolar mixture. The equimolar mixture has productivity (TON) and activity (TOF) values that closely match those expected on the basis of the mixture composition: *i.e.* $TON_{mixture} = (TON_{\mathbf{1}} + TON_{\mathbf{2}})/2$. This is in line with the mass spectrometry studies that indicated there was no substantial metal exchange between the two catalysts. In contrast, **3** exerts significantly greater activity than the sum of its parts. This finding further supports the presence of the heterodinuclear complex and attests to the much improved activity and productivity of this species. These findings also provide indirect support for the chain shuttling mechanism.

Catalyst **3** shows excellent selectivity, with near theoretical uptake of carbon dioxide into the polymer backbone and a very low quantity of ether linkages in the resulting polymer (Table 1 and Fig. S4, ESI†). All the catalysts yield low M_n polycarbonates ($M_n < 6000$ g mol^{-1}), due to efficient chain transfer reactions with protic impurities (alcohols).[3b,10c,13] Such M_n values are highly desirable for the target application as polyols for higher polymer synthesis.[3a] Furthermore, using catalyst **3** the polydispersity index of the resulting polycarbonate is narrow, indicative of a high degree of polymerization control (Fig. S5, ESI†). The MALDI-ToF spectrum shows two series of chains, both with >99% carbonate linkages, and differing according to the chain end groups: one series is α-acetyl-ω-hydroxyl and the other is α,ω-di-hydroxyl end-capped polycyclohexene carbonate (Fig. S6, ESI†).

In order to better compare the activity of catalyst **3** with other catalysts, experiments were conducted under a range of conditions (Table 2). Under all conditions, **3** shows very high degrees of polymerization control, as evidenced by the linear increases in molecular weight with the decreasing catalyst concentration. Furthermore, there is no difference in activity, at a fixed catalyst concentration, by changing the CO_2 pressure which is consistent with the earlier finding, using a zinc catalyst, that the rate is independent of its pressure.[10c] On the other hand, as expected increasing the temperature significantly improves the activity, whilst maintaining a very high selectivity for carbonate linkages. This system displays equivalent or higher productivities and activities to one of the most active cobalt catalysts.[14] Compared to a di-Mg catalyst, it is 2.5 times faster whilst operating at 5 times lower loading.[9d]

The poly(cyclohexene carbonate) (PCHC) shows monomodal molecular weight distributions and narrow polydispersity indices (Fig. S5, ESI†). This is, at first sight, somewhat surprising as there are three different catalysts present in the mixture. However, the rapid rate of chain transfer, *vs.* propagation, leads to the narrow distribution in chain lengths and rapid interconversion between all chains with all the catalysts present.[15] Lee and co-workers have recently pioneered mixed homogeneous/heterogeneous catalyst systems.[11c] Our approach highlights the improvements such systems can offer to activity.

It is important that catalyst **3** retains its high activity even when 16 equivalents of H_2O (*vs.* catalyst) are added to the reaction (Table S2, ESI†). This remarkable tolerance to water is advantageous, particularly as it obviates complex and difficult drying of epoxides and CO_2 whilst at the same time improving the selectivity for the desired polyol product. The addition of protic reagents, such as water, results in chain transfer *via* the formation of cyclohexane diol from which telechelic dihydroxyl terminated polymers are produced.[10c] Thus, when 16 equivalents of water are added to polymerizations catalysed by **3**, the M_n of polycarbonate reduces to 1300 g mol^{-1}, whilst the PDI remains narrow (1.14) (Table S2, ESI†). Importantly, the α,ω-di-hydroxyl end-capped PCHC chains are produced as the major product, with almost complete suppression of the mono-hydroxyl terminated chains (Fig. S8, ESI†). This selectivity for di-hydroxyl terminated chains is important as such 'polyols' are key reagents for the manufacture of polyurethanes/polyesters.[3]

Table 2 Shows the catalytic activity, productivity, selectivity and molecular weight data for runs using catalyst **3**

3 : CHO (molar ratio)	Time (h), temp (°C), pressure (bar)	TON[a]	TOF[b] (h^{-1})	CO_2[c] (%)	M_n[d] (g mol^{-1})	PDI[d]
1 : 1000	6, 80, 1	476	79	>99	5200	1.12
1 : 2000	6, 80, 1	246	41	>99	2600	1.12
1 : 10 000	6, 80, 1	196	33	>99	800	1.12
1 : 10 000	6, 80, 50	196	33	>99	710	1.19
1 : 10 000	6, 90, 50	1379	230	>99	2900	1.09
1 : 1000	3, 90, 50	875	292	>99	15 400	1.03
Ref. 9*d* (di-Mg) 1 : 200	6, 60, 1	194	32	>99	42 800	1.56
Ref. 14[e] (Co salen) 1 : 5000	5, 50, 1	1315	263	>99	48 000	1.16

[a] The turn over number (TON) = number of moles of cyclohexene oxide consumed/number of moles of catalyst. [b] The turn over frequency (TOF) = TON/reaction period. [c] Expressed as the percentage carbon dioxide uptake *vs.* the theoretical maximum (100%). This is determined by comparing the relative integrals of the ^{1}H NMR resonances due to carbonate (δ: 4.65 ppm) and ether (δ: 3.45 ppm) linkages in the polymer backbone. [d] Determined by SEC, in THF, using narrow M_n polystyrene standards. [e] Structures of the reference catalysts illustrated in Fig. S7 (ESI).

Catalyst **3** was also tested for the copolymerization of propylene oxide (PO)–CO_2. It displayed a moderate productivity and activity for poly(propylene carbonate) PPC production, showing a TON of 248 and a TOF of 11 h^{-1} (Table S3, ESI†). Under the conditions tested, the selectivity for PPC was low (<10%) with the major product being the five-membered ring cyclic propylene carbonate (PC), the thermodynamic product of the reaction (Table S3, ESI†). However, it is rather remarkable that catalyst **3** functions at all in this context, particularly given that the equimolar mixture shows no formation of PPC under identical conditions.

In conclusion, we report the first example of a heterodinuclear, mixed catalyst system, for the copolymerization of carbon dioxide and epoxides. The catalyst, prepared by straightforward coordination chemistry, is a mixture of the two known homodinuclear (Zn–Zn and Mg–Mg) complexes and a new heterodinuclear (Zn–Mg) complex. It displays considerably better performance than either homodinuclear catalyst, either alone or mixed together. It is a particularly effective catalyst in the presence of excess water (16 eq.), where a high selectivity for polycarbonate polyols results which is useful for higher polymer synthesis. These findings illustrate the significant potential for both *new heterodinuclear catalysts and*

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mixed catalyst systems. Further investigation into other combinations of metals and catalysts are certainly warranted and would be expected to maximise performance.

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