Greater than the Sum of Its Parts: A Heterodinuclear Polymerization Catalyst

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S *Supporting Information*

ABSTRACT: Homodinuclear catalysts have good precedent for epoxide and carbon dioxide/anhydride copolymerizations; in contrast, so far pure heterodinuclear catalysts are unknown. The synthesis and properties of a heterodinuclear Zn(II)/Mg(II) complex coordinated by a symmetrical macrocyclic ligand are reported. It shows high polymerization selectivity, control, and significantly greater activity compared to either of the homodinuclear analogues or any combinations of them. Indeed, compared to a 50:50 mixture of the homodinuclear complexes, it shows 5 times (CO_2/epoxide) or 40 times (anhydride/epoxide) greater activity.

Figure 1. "Chain shuttling" mechanism for CO_2/epoxide copolymerization by a dinuclear catalyst.

Heterometallic cooperativity is an attractive means to enhance catalyst reactivity and selectivity. Mixed metal or heterometallic complexes have shown better performances in a range of organic and small-molecule transformations, including metal–halogen exchange[1] and C–H bond activation reactions.[2] In olefin polymerization catalysis, significantly improved rates are observed for mixed metal complexes, as pioneered by Marks (with Ti/Cr and Ti/Zr systems), Roesky (Ti/Zr and Al/Zr), and Harder (Al/Zr),[3] among others. Heterometallic catalysts have also shown higher activities in the synthesis of oxygenated polymers, from ε-caprolatone,[4] lactide,[5] and trimethylene carbonate monomers.[6] Using abundant, low-toxicity main-group/first-row transition metals in catalysis, e.g., magnesium/zinc, is also attractive from both an economic and environmental perspective. However, the preparation of mixed Mg/Zn catalysts is challenging due to their similar physical and chemical properties and kinetic lability. There are encouraging reports of successes using such heterodinuclear catalysts;[7] for example, Trost et al. demonstrated enhanced selectivity in asymmetric Michael reactions using a heterodinuclear catalyst, formed in situ by reaction between a Pro-phenol compartmental ligand and both organo-Zn and organo-Mg precursors.[8]

Ring-opening copolymerization (ROCOP) of epoxides and heterocumulenes, such as cyclohexene oxide (CHO)/anhydride with carbon dioxide, is a useful, controlled method to prepare polycarbonates/esters. In particular, using carbon dioxide to prepare polycarbonate polyols is an attractive means to "add value" to CO_2 and to recycle it into a range of useful materials, such as polyurethanes. ROCOP requires a catalyst, and some of the most successful have included dinuclear or dimeric homogeneous complexes or bimetallic heterogeneous surfaces.[9] Both types of catalyst are proposed to operate by polymerization routes that require bot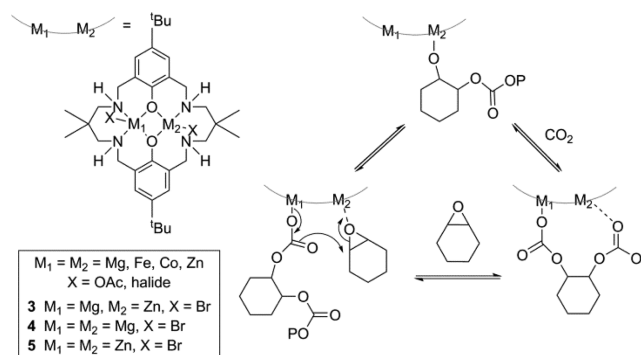h metals. Surprisingly, there are not yet any reports of heterodinuclear catalysts, although there are hints that when they are present as part of mixtures, enhanced performance can result.[10]

Previously, we reported a range of high-activity homodinuclear catalysts, coordinated by a symmetrical macrocycle (Figure 1), for ROCOP of epoxides/anhydrides/CO_2.[9d,i,11] Kinetic, DFT, and spectroscopic studies led to a proposed "chain shuttling" copolymerization pathway (Figure 1).[9h,11a,12] Accordingly, each of the two metals has a distinct role in catalysis, and the growing polymer chain "shuttles" between the metals with each insertion. Kinetic studies showed that the rate-limiting step corresponded to the epoxide coordination at one center and attack by a carbonate bound at the other metal.[12] One implication of such a pathway is that heterodinuclear catalysts might be expected to show better activities if the distinct roles of coordination and insertion could be optimized.

There are only a few examples of heterodinuclear complexes coordinated by the broader class of bis(phenolate) macrocycles, and in all cases these require the use of asymmetric macrocycles, which leads to complex and lower-yielding syntheses.[13] Our goal was to use the symmetrical ligand, prepared in near-quantitative yield, and to target a Zn/Mg heterodinuclear complex. One of the challenges in developing the synthetic route is that the ancillary ligand, **1**, is symmetrical, so there is no differentiation in coordination environment for the metals. We previously reported that mixing organo-Zn and organo-Mg reagents with the macrocycle resulted in the formation of a mixture of products, one of which included the desired heterodinuclear complex.[10d] However, the separation of the mixture was

extremely challenging, and so far isolation of the desired species using this synthetic method has not been possible. Here, a new synthetic route, using the symmetrical ligand and sequential metalation reactions, allows the preparation of a pure heterodinuclear complex.

The mono-metalation was achieved by reacting the ligand **1** with just 1 equiv of Et_2Zn, in THF. The reaction was monitored using ^1H NMR spectroscopy, which suggested that the mono-metallic complex LZn, **2**, formed after 24 h. The NMR spectrum (Figure S1) showed the complete disappearance of the resonances assigned to the starting materials, including for **1** and Zn-coordinated ethyl groups, together with the formation of ethane (0.85 ppm). The signals for **2** were highly broadened indicative of various fluxional processes and/or conformers in solution. Low-temperature ^1H NMR (193 K) spectroscopy showed four separate aromatic and at least seven methylene resonances, consistent with the formation of a low-symmetry complex (Figure S2). The ^1H NMR spectrum in d_5-pyridine (298 K) was better resolved and showed single, broadened signals for the aromatic and methylene protons, consistent with an average/coalesced spectrum being obtained (Figure S3). One interpretation is that the mono-Zn complex is labile, with the Zn center becoming "locked" into one of the two available phenolic pockets at low temperature. However, other processes including exchange between aggregation states and conformational isomers cannot be discounted. Indeed, DOSY NMR spectroscopy (298 K) suggested that **2** has a dimeric structure in d_6-benzene (Figure S4), while in pyridine the observed diffusion coefficient lies intermediate between monomer/dimer (Figure S5), indicative of rapid equilibration. Mass spectrometry confirmed the formation of **2**, with the molecular ion being observed as the base peak at 615 amu (Figure S6), and elemental analysis results were in line with expected values.

Reaction conditions were carefully selected on the basis that **2** showed a predominantly monomeric structure at low temperatures in coordinating solvents; this would likely be desirable to increase the yield of the hetero complex. Accordingly, a magnesium bromide solution was added to **2**, in a mixed pyridine/THF solvent system cooled to −78 °C (Scheme 1).

Scheme 1. Synthesis of Heterodinuclear Complex 3[a]
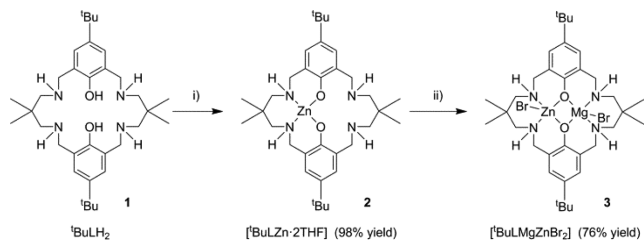
[a]Reagents and conditions: (i) Et_2Zn, THF, 25 °C, 24 h; (ii) $MgBr_2$, pyridine, THF, −78 to 25 °C, 1 h.

Incorporation of $MgBr_2$ selectively generated the new, heterodinuclear species, **3**, isolated in 76% yield. The ^1H NMR spectrum is sharp at room temperature and shows eight distinct benzylic and methylene resonances, consistent with the formation of a heterodinuclear complex (Figure 2). The resonances of **3** were assigned using COSY and HSQC experiments (Figures S7 and S8), which showed that the highest chemical shift peak at 5.07 ppm was attributed to one of the diastereotopic benzylic protons adjacent to the N atom coordinated to the Zn center. The other diastereotopic proton
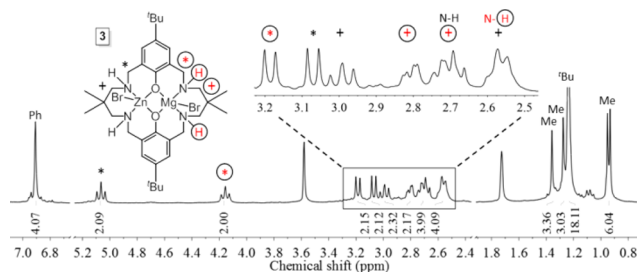
Figure 2. ^1H NMR spectrum for heterodinuclear complex **3** in d_8-THF at 298 K. The low-intensity signals at 1.1 ppm are assigned to methyl groups from a minor (<5%) conformer (they show the same diffusion coefficient in DOSY).

was observed at 3.07 ppm. The methylene bridging protons, associated with the 2,2-dimethylpropylene bridge, are also diastereotopic, and again, the protons adjacent to the N atoms coordinated to Zn were observed at higher chemical shifts (2.99 ppm), consistent with the greater electron affinity of Zn vs Mg. COSY experiments showed that these benzylic and methylene resonances are connected through the Zn-coordinated NH resonance at 2.76 ppm. Similarly, the second set of diastereotopic benzylic and methylene signals are connected through the bridging, Mg-coordinated NH resonance at 2.56 ppm. To be sure that the spectrum observed for **3** was distinct from those of the two homodinuclear complexes, these species were also synthesized and their ^1H NMR spectra compared (Figure S9; X-ray data were obtained for **5**, Figure S10). The signals observed for **3** are clearly distinct from those for either **4** or **5**.

By comparison of the signals of **3** to those of **4** and **5**, the benzylic, methylene, and NH resonances could be assigned as those adjacent to Zn and those next to Mg. ^1H DOSY spectroscopy of **3** (Figure S11) suggested its structure is mononuclear in THF solution; further, all peaks were attributed to a single species. The ^{13}C NMR spectrum of **3** also showed distinct peaks for all four benzylic and methylene C atoms (Figure S12). Through HSQC experiments, the resonances at 58.1 and 56.4 ppm were identified as benzylic carbons adjacent to the N atom, coordinated to Zn and Mg, respectively. The MALDI-TOF mass spectrum showed the molecular ion at 671 amu, although peaks attributable to the di-Zn and di-Mg complexes were also observed and are proposed to form during ionization (Figure S13).

To further probe the solution-state behavior of **3** under polymerization conditions, a d_8-THF solution of **3** was heated at 80 °C for 24 h. The ^1H NMR spectrum remained constant, suggesting that the catalyst composition was not thermally altered. In contrast, heating an equimolar mixture of **4** and **5** led to the formation of ^1H NMR resonances attributable to **3**, although in low yields (25% after 48 h, Figure S14). The slow formation of **3** suggests that it is thermodynamically favored over its homodinuclear analogues but that redistribution of the metal centers is slow to occur once a dinuclear complex has formed. It thus seems plausible that the key stage for determining the heterodinuclear content is the incorporation of the second metal center into mono-Zn species **2**.

The catalytic activity of **3** was compared to the homodinuclear **4** and **5** for the ROCOP of CO_2/CHO, using conditions under which the homodinuclear catalysts had previously performed well. The polymerizations were run at 0.1 mol% catalyst loading (vs the epoxide, CHO), using just 1 bar of CO_2 (Table 1, entries 1−4). The activity of the heterodinuclear catalyst **3** is more than

Table 1. CHO/CO$_2$ ROCOP Data for Catalysts 3, 4, and 5

entry	cat. (mol%)	TON^a	TOF^b (h^{-1})	CO$_2{}^c$ (%)	M_n [Đ]^d
1^e	**2** (0.1)	0±0	0±0	0	-
2^e	**3** (0.1)	344±40	34±4	>99	3100 [1.14]
3^e	**4** (0.1)	151±18	15±2	>99	800 [1.13]
4^f	**5** (0.1)	0±0	0±0	0	-
5^e	1:1 **4:5** (0.1)	72±9	7±1	>99	<500
6^g	**3** (0.01)	3053±149	180±9	>99	32 600 [1.03] 13 800 [1.06]
7^h	**3** (0.01)	3118±152	624±30	>99	18 000 [1.05] 7300 [1.10]
8^{i,j}	**A** (0.05)	1300	1300	95	23 000 [1.09]
9^{i,k}	**B** (0.2)	500	21	>99	14 500 [1.13]
10^{i,l}	**C** (0.1)	420	210	>99	8800 [1.14]

^{a}Turnover number (TON) = number of moles of cyclohexene oxide consumed/number of moles of catalyst. ^{b}Turnover frequency (TOF) = TON/time. ^{c}Expressed as the percentage CO$_2$ uptake vs the theoretical maximum (100%), determined by comparison of 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; distribution is given in brackets. ^{e}10 h, 1 bar, 80 °C. ^{f}24 h, 1 bar, 80 °C. ^{g}17 h, 50 bar, 90 °C. ^{h}5 h, 50 bar, 120 °C. ^{i}Catalyst structures shown in Figure S15. ^{j}1 h, 35 bar, 80 °C; ref 14a. ^{k}24 h, 50 bar, 80 °C; ref 14b. ^{l}2 h, 13 bar, 70 °C; ref 14c.

5 times greater than that obtained using a 1:1 molar ratio of **4** and **5**. Further, **3** is more than twice as active as di-Mg **4**, while di-Zn **5** is completely inactive. **3** also exhibits excellent selectivity, with high uptake of CO$_2$, forming polymers with >99% of carbonate linkages. Only trace amounts of cyclic carbonates are observed, even at elevated temperature. The polymer molecular weights are within the range expected for this type of polymerization,[9b,i,15] and the distributions are narrow in all cases, indicative of controlled polymerizations. At lower catalyst loadings there is an increase in MW, once again highlighting the high degree of control. The MW distributions are bimodal, a feature commonly observed in this type of polymerization using a range of different catalysts, and previously shown to be due to the presence of 1,2-cyclohexanediol, which functions as a chain-transfer agent, leading to the formation of telechelic polymers.[9b,i,14b,15] Catalyst **3** is able to operate under low loadings and showed a TOF of 624 h^{-1}, which is competitive with other catalysts with halide initiating groups (Table 1, entries 7–10).[14,16] Compared to the (salalen)chromium chloride catalyst (entry 10), **3** shows a TOF ~3 times higher while operating a lower catalyst loading. On the other hand, catalyst **A** (entry 8, Figure S15) shows a higher TOF (>1000 h^{-1}) but operates at a higher catalyst loading.

Ring-opening copolymerization of epoxides/anhydrides offers a controlled route to prepare polyesters.[17] Given the better rates already observed for polymerizations using CHO/CO$_2$, the next step was to investigate catalyst **3** in ROCOP using CHO/phthalic anhydride (PA). Reactions were performed at 1 mol% catalyst loading, 100 °C, and using excess epoxide as the solvent, as these are typical conditions for catalysts in this field. Once again, catalyst **3** showed superior activity compared to either of the homodinucear complexes **4** and **5** (Table 2). It shows a TOF 20 times greater than that of the di-Mg **4** and 10 times greater

Table 2. CHO/PA ROCOP Data for Catalysts 3, 4, and 5^a

cat.	time (h)	TON^b	TOF (h^{-1})	ester linkage^c (%)	M_n [Đ]^d
3	0.5	94±6	188±12	>99	10 900 [1.04] 5000 [1.09]
4	6	52±6	9±1	91	3600 [1.04] 1400 [1.11]
5	3	52±3	17±0	99	7400 [1.03] 3000 [1.10]
1:1 **4:5**	6	30±2	5±0	66	1500 [1.12]

^{a}Reactions were conducted at 100 °C with a 1:100:800 molar ratio of catalyst:PA:CHO. Refer to Table S1 for further data. ^{b}Determined by ^{1}H NMR spectroscopy (CDCl$_3$) by integrating the normalized resonances for PA (7.97 ppm) and the phenylene signals in polyester (7.30–7.83 ppm). ^{c}Determined by ^{1}H NMR spectroscopy (CDCl$_3$) by integrating the normalized resonances for ester linkages (3.22–3.64 ppm). ^{d}Determined by SEC in THF using narrow-M_n polystyrene standards to calibrate the instrument; distribution is given in brackets.

than that of the di-Zn **5**. Compared to an equimolar mixture of **4:5**, it showed ~40 times higher activity. In all cases, the ROCOP occurred with high degrees of alternating enchainment, giving >90% ester linkages. The polyesters showed moderate MWs, with bimodal distributions. As discussed for CO$_2$/CHO ROCOP, the distributions are commonly observed for other catalysts in this area of copolymerization and are due to chain transfers with 1,2-cyclohexanediol.[9b,11b,15d,18]

A pure heterodinuclear Mg/Zn complex (**3**), coordinated by a symmetrical macrocyclic ligand, was synthesized using a route that enables mono-metalation of the ligand, followed by addition of the second metal center. The synthesis is notable as it was recently shown that zinc carboxylates and magnesium alkyls undergo complete ligand exchange and that mixed or heterodinuclear complexes are not isolated.[19] Catalyst **3** significantly out-performs either of the homodinuclear complexes in the ring-opening copolymerizations of epoxide/CO$_2$ and epoxide/anhydride. It shows an activity that is greater than "the sum of its parts", suggesting there is a synergic relationship between the metals. To rationalize this behavior, it is relevant to consider common mechanistic hypotheses in this field of catalysis. Nozaki et al. developed a DFT model, using planar, mono-metallic catalysts, revealing that two significant processes dominate rates: epoxide coordination and metal–carbonate attack.[20] We previously conducted complete DFT calculations using homodinuclear catalysts as well as detailed structure–activity and spectroscopic studies, showing that the metal carbonate attack on the coordinated epoxide is rate limiting.[9h,12] In the case of **3**, it is proposed that a closely related mechanism operates but that the enhancement in activity results from the two different metals mediating each other's reactivity and adopting distinct roles in the catalysis. It is tentatively proposed that the Lewis acidic Zn may enhance epoxide coordination and the labile magnesium carbonate accelerates carbonate attack. Significantly, this synergy also enhances the ability of the bromide co-ligand to initiate polymerization, as homodinuclear di-Zn **5** is completely inactive for the same reaction. In the case of epoxide/anhydride ROCOP, a closely related mechanism is proposed whereby Zn and Mg synergic interactions accelerate metal carboxylate attack on coordinated epoxide. The ability to significantly increase the activity by combining metals in this

manner is rather unusual but points to a new design strategy for this area of catalysis. Application of the method more generally to prepare other catalysts, e.g., for processes where the catalyst combines both Lewis acidity and labile M−OR bonds, also warrants further investigation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b09913.

> Experimental procedures and characterization data for **2**−**5** and copolymers (PDF)
> X-ray crystallographic data for **5** (CIF)

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Notes

The authors declare the following competing financial interest(s): C.K.W. is a director and CSO of Econic Technologies.

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