

# Efficient Magnesium Catalysts for the Copolymerization of Epoxides and CO<sub>2</sub>; Using Water to Synthesize Polycarbonate Polyols

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**S** Supporting Information

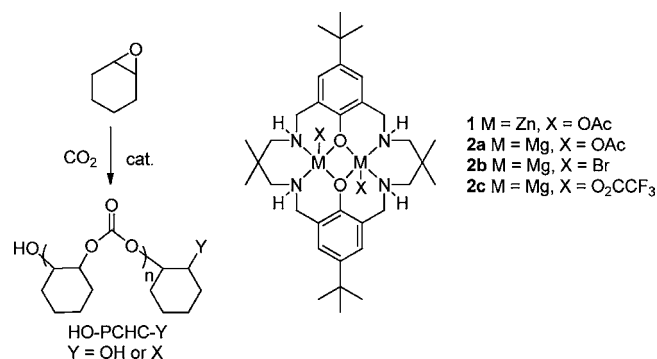
**ABSTRACT:** The synthesis and characterization of three highly active dimagnesium catalysts for the copolymerization of cyclohexene oxide and carbon dioxide, active under just 1 atm of carbon dioxide pressure, are reported. The catalysts have turnover numbers up to 6000 and turnover frequencies of up to 750 h<sup>-1</sup>. These values are, respectively, 75 and 20 times higher than those of the other three known magnesium catalysts. Furthermore, the catalysts operate at 1/500th the loading of the best reported magnesium catalyst. The catalyst selectivities are excellent, yielding polymers with 99% carbonate repeat units and >99% selectivity for copolymer. Using a dimagnesium bis(trifluoroacetate) catalyst, and water as a renewable chain transfer reagent, poly(cyclohexene carbonate) polyols are synthesized with high selectivity.

The use of carbon dioxide as a renewable raw material for the production of materials is an area of high interest, as CO<sub>2</sub> is nontoxic and the waste product of many industries. Several processes have been developed that overcome the thermodynamic stability of CO<sub>2</sub>;<sup>1</sup> in particular, copolymerization with epoxides is attractive as a more sustainable route to polycarbonates. Aliphatic polycarbonates have been proposed as alternatives to petrochemicals in applications such as films, packaging, and rigid plastics.<sup>2</sup> In particular, the commercialization of aliphatic polycarbonates is currently being initiated in several countries.<sup>3</sup> A key component of such developments is the use of low molecular weight polycarbonate polyols as macromonomers for polyurethane/other copolymer production.<sup>4,5</sup>

So far, only a few highly active homogeneous catalysts have been reported for the copolymerization, the development of which has been extensively reviewed recently.<sup>6–8</sup> The most active catalysts reported to date are ‘single component’ cobalt salen complexes bearing ammonium or nucleophilic substituents on pendant arms, which show high activity and selectivity using various epoxides.<sup>9–13</sup>

We have previously reported dinuclear complexes, coordinated by macrocyclic ancillary ligands, with Zn(II), Co(II/III), or Fe(III) metal centers (Scheme 1). The catalysts are notable in that they show good activities, and high selectivities, at carbon dioxide pressures as low as 1 bar.<sup>14–16</sup> The dicobalt complexes show the best activities; they are approximately 20 times faster than dizinc analogues; however, cobalt is rather expensive, toxic, and of relatively low abundance.

**Scheme 1. Copolymerization of Epoxides and Carbon Dioxide Using Dinuclear Catalysts**



Therefore, we were motivated to explore lower toxicity, cheaper, and more earth-abundant metals. Given the analogous chemistries of magnesium and zinc, including a common tendency to +II oxidation states and closely related ionic radii, and as magnesium is the eighth most abundant element on earth, biocompatible, and cheap, we targeted magnesium complexes for development. To our knowledge, there are only three other examples of Mg catalysts in the literature,<sup>17,18</sup> the most active of which has a TOF of 40 h<sup>-1</sup> and requires rather high catalyst loadings (5 mol %).<sup>17</sup>

Two new di-Mg catalysts were prepared by deprotonation of the macrocyclic pro-ligand, using KH, followed by a salt metathesis reaction with 2 equiv of the appropriate Mg precursor (Mg(OAc)<sub>2</sub> or MgBr<sub>2</sub>). A third catalyst was made by metathesis of **2b** with 2 equiv of KO<sub>2</sub>CCF<sub>3</sub>. Catalyst **2a** was isolated in 86% yield. Its <sup>1</sup>H NMR spectrum showed broadened signals at room temperature; however, at 100 °C, in d<sub>2</sub>-tetrachloroethane, a well resolved spectrum showed just one aromatic environment, four distinct methylene environments, and two distinct environments for the methyl substituents on the amine backbone.<sup>15</sup> LSI-MS showed a daughter peak corresponding to [LMg<sub>2</sub>OAc]<sup>+</sup>, and IR spectroscopy showed acetate group carbonyl stretching modes at 1592 and 1434 cm<sup>-1</sup>. The purity was confirmed by elemental analysis.

**2a** was tested for the copolymerization using cyclohexene oxide (CHO) and 1 atm of CO<sub>2</sub> pressure (Table 1). It was interesting to note that, at 80 °C and 1:1000 loading, the catalyst showed an activity (35 h<sup>-1</sup>) twice that of the dizinc analogue, **1** (18 h<sup>-1</sup>). At 100 °C the activity was six times

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Table 1. Copolymerization of CHO and CO<sub>2</sub> Using 2a<sup>a</sup>

cat.	T (°C)	TON <sup>b</sup>	TOF <sup>c</sup>	% Poly <sup>d</sup>	M <sub>n</sub> (g mol <sup>-1</sup> ) <sup>e</sup>	PDI <sup>e</sup>
1	80	439	18	96	6200	1.19
2a	80	522	35	>99	13,300/6800	1.03/1.05
1	100	527	25	94	7400	1.21
2a	100	458	152	>99	11,800/5900	1.03/1.06
2a <sup>g</sup>	100	3300	165	>99	14,600/3500	1.02/1.08
2a <sup>g</sup>	100	6100	97	98	7200	1.09
2a <sup>f,g</sup>	100	3660	730	>99	16,800	1.21

<sup>a</sup>All polymers were produced with >99% carbonate linkages. <sup>b</sup>TON = mol of epoxide consumed/mol of catalyst. <sup>c</sup>TOF = TON/h. <sup>d</sup>Selectivity for polycarbonate vs cyclic carbonate, determined by <sup>1</sup>H NMR spectroscopy. <sup>e</sup>Determined by SEC. <sup>f</sup>Copolymerization carried out at 12 atm of CO<sub>2</sub>. <sup>g</sup>Copolymerization carried out at 1:10000 loading.

higher, at 152 h<sup>-1</sup>, which is among the highest reported at this pressure using any metal center. Decreasing the catalyst loading to 1:10 000 led to a significant increase in the TON, to over 3000, with the same activity and no loss of selectivity. Increased time allowed TONs to exceed 6000, at just 1 atm of CO<sub>2</sub> pressure; this is approximately 75 times greater than that of the previous best magnesium catalyst, and is achieved at 500 times lower catalyst loadings.<sup>17</sup> Using an autoclave, the pressure was increased to 12 atm, at 100 °C and 1:10000 loading. A significant increase in activity and a maximum TOF of 730 h<sup>-1</sup> was observed; this activity is 20 times greater than that for the previous magnesium catalysts, again at 1/500 the catalyst loading. Kinetic studies have shown that, for **1**, the rate-determining step involves the nucleophilic attack and ring opening of a bound epoxide by the metal carbonate species.<sup>14</sup> We tentatively attribute the increased activity (compared to **1**) to the decreased Lewis acidity<sup>19</sup> and electronegativity<sup>20</sup> of magnesium, resulting in a more nucleophilic metal carbonate bond.

The catalysts' selectivities are all excellent: the copolymers have >99% carbonate linkages. In contrast to **1**, which produced 4–6% cyclic carbonate at 100 °C, no evidence of cyclic carbonate production was observed, even at elevated temperatures, using **2a–c**. The significant difference in selectivity of the two metals suggests that the backbiting reaction responsible for cyclic carbonate production, which can occur at the end of the free or metal-bound polymer,<sup>21</sup> predominantly occurs on the metal bound copolymer and is suppressed by replacing Zn with Mg.

The polymerizations are well controlled, with the polymer molecular weight increasing linearly with conversion and yielding polymers with narrow polydispersity indices (≤1.2). The polymers showed bimodal molecular weight distributions, observable by both SEC and MALDI-ToF, due to chain transfer reactions with trace amounts of protic impurities (water). This generates two polymer series differing according to the chain end groups, HO–PCHC–OH and HO–PCHC–OAc (see Scheme 1 and Figure S4). This chain transfer is endemic to CO<sub>2</sub>/epoxide copolymerization, with such bimodal distributions reported for most known catalysts, with experimental M<sub>n</sub> values generally significantly lower than theoretical values.<sup>7,9,14,22</sup>

The TON/TOF (g/g) of **2a** compare well with those of the best catalysts in the literature, in particular the single component cobalt salen complexes (Table 2, Figure S3 for the structures of **3** and **4**). **2a** shows excellent productivity

Table 2. Catalyst 2a Compared with Active Cobalt Catalysts

cat.	TON <sup>a</sup> (g/g)	TOF (h <sup>-1</sup> )	M <sub>n</sub> <sup>b</sup>	PDI
2a	725 <sup>c</sup>	145	16 800	1.21
3 <sup>12</sup>	311 <sup>d</sup>	622	43 800	1.20
4 <sup>13</sup>	284 <sup>e</sup>	284	92 000	1.23

<sup>a</sup>TON (g/g) = (TON (mol/mol) × 142.15)/RMM catalyst. <sup>b</sup>Determined by SEC, g mol<sup>-1</sup>. <sup>c</sup>Copolymerization conditions: 100 °C, 12 atm, 5 h, 1:10 000. <sup>d</sup>100 °C, 25 atm, 0.5 h, 1:5000. <sup>e</sup>75 °C, 20 atm, 1 h, 1:100 000.

(TON), albeit at longer reaction times than in the case of **3** and **4**, and its activity (TOF) was on the same order of magnitude as the activity of these highly active catalysts. This illustrates the considerable potential for improving catalyst performance on substituting heavier metals with magnesium.

Furthermore, the facile, high yielding synthesis of **2a**, which is isolated in 70% overall yield (unoptimized) in three steps from commercial reagents, is a desirable feature if compared with the lengthy syntheses, which exceed eight steps,<sup>10</sup> required for the most active cobalt catalysts. The ease of synthesis, combined with the much lower cost of magnesium (which is 2500 times more earth-abundant than cobalt), makes **2a** an attractive catalyst.

A promising application for aliphatic polycarbonates lies in the production of low molecular weight polyols, i.e. dihydroxyl terminated chains (HO–PC–OH). These polyols are used for the production of polyurethanes and other higher polymers.<sup>5,23</sup> Typically, their formation requires the addition of an excess of a diol or diacid, which serves as a chain transfer reagent. We were interested in using water as a cheap, renewable reagent for chain transfer, allowing selective formation of polyol. We have previously shown that a dizinc trifluoroacetate complex produces PCHC polyols.<sup>23</sup> Thus, catalysts **2b**, with bromide coligands, and **2c**, with trifluoroacetate coligands, were synthesized and showed comparable characterization data to **2a**. The copolymerization catalysis was monitored with and without exogenous water as a chain transfer agent (Table 3).

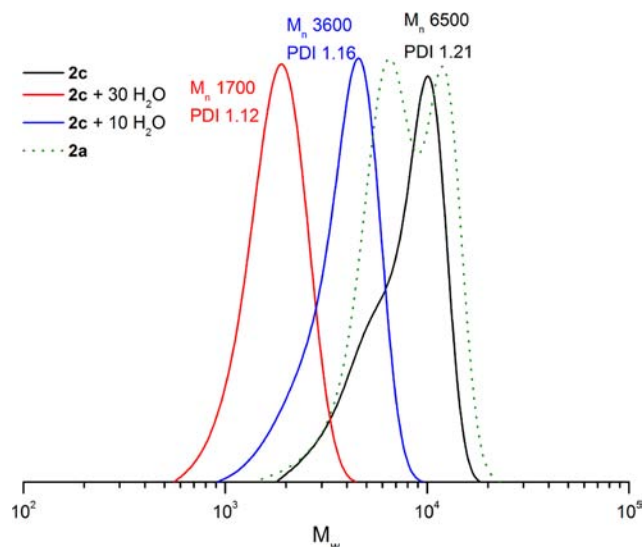
Table 3. Copolymerization Data for 2a–c<sup>a</sup>

cat.	T (°C)	cat./H <sub>2</sub> O	TON <sup>c</sup>	TOF <sup>d</sup>	M <sub>n</sub> <sup>e</sup>	PDI
2a	80	1:0	522	35	13 300/6800	1.03/1.05
2b	80	1:0	426	24	5500	1.21
2c	80	1:0	497	31	6500	1.21
2c <sup>b</sup>	100	1:0	3000	750	24 500/5300	1.03/1.10
2c	100	1:10	360	103	3600	1.16
2c	100	1:30	350	80	1700	1.12

<sup>a</sup>Copolymerization reactions carried out in neat CHO at 1 atm of CO<sub>2</sub> pressure and 1:1000 loading for 3–18 h. <sup>b</sup>Copolymerization run at 12 atm CO<sub>2</sub> and 1:10000 loading. <sup>c</sup>Mol of CHO consumed/mol of cat. <sup>d</sup>TON/time (h). <sup>e</sup>By SEC in g mol<sup>-1</sup>.

Catalyst **2c** showed excellent activity, comparable to that of catalyst **2a** at 80 °C and 1 atm CO<sub>2</sub>, while **2b** showed slightly reduced activity, presumably because bromide is a less effective initiating group (Table 3). It is remarkable that the magnesium halide catalyst showed any activity, as the zinc halide analogues showed no catalytic activity. Another notable observation was that, at 12 atm of CO<sub>2</sub> pressure and 100 °C, **2c** showed almost identical activity to **2a**, but with a significant increase in molecular weight.

The copolymers formed with **2c** were analyzed by MALDI-ToF mass spectrometry (see Figures S5–S7) and SEC (see Figure 1), which showed terminal groups from both chain



**Figure 1.** Distributions of molecular weights, determined using SEC, for PCHC produced by **2a–c** in the presence of water.

transfer and initiation reactions ( $Y = \text{OH}$  and  $\text{O}_2\text{CCF}_3$ ; respectively). In the case of **2c**, a significant reduction in  $\text{HO-PCHC-O}_2\text{CCF}_3$  (a monohydroxyl peak) was observed by SEC analysis compared the copolymer produced by **2a** (see Figures 1 and S4–S5). This indicated that **2c** might show enhanced selectivity for polyol formation. In order to promote selective polyol formation, the copolymerization was run using water, 10 and 30 equiv versus **2c**, as a chain transfer agent. These experiments showed that water is an effective chain transfer reagent, reducing the molecular weight and producing narrower weight distributions by SEC (Table 3, Figure 1).

Almost complete suppression of  $\text{O}_2\text{CCF}_3$  end group was observed when 30 equiv of water were added (Figures 1, S7). The  $^1\text{H}$  NMR spectrum of the copolymer shows a resonance at 3.77 ppm which is assigned to the methyne proton adjacent to the  $\text{O}_2\text{CCF}_3$  end group. By comparing the relative integrals of this resonance and the resonances assigned to the methyne protons adjacent to the hydroxyl end groups (Figures S8, S9), it was estimated that **2c** produces approximately 50% polyol in the absence of additional water. Upon addition of 30 equiv of water, the selectivity for polyol increases to  $\sim 85\%$ . Even using excess water, **2c** still shows good catalytic activity (cf. **2a** under the same conditions without water, Table 1, entry 4).

Furthermore, even in the presence of excess water, **2c** maintains a high selectivity for copolymer formation ( $>99\%$  carbonate linkages,  $>99\%$  selectivity for copolymer by  $^1\text{H}$  NMR; see Figure S9). This is particularly remarkable, as other catalysts (e.g., **4**) are deactivated by water, leading to complete suppression of catalytic activity.<sup>8,22,24</sup> Such a high tolerance to excess water is especially relevant for the integration of this process with carbon capture because water is a common contaminant of captured carbon dioxide, including typical concentrations of  $\sim 2\%$  in carbon dioxide captured from flue gases from coal combustion.

In conclusion, we report the first examples of highly active epoxide/ $\text{CO}_2$  copolymerization catalysts based on complexes with nontoxic, inexpensive, and highly abundant magnesium.

The catalysts are highly active under just 1 atm of  $\text{CO}_2$  pressure and produced poly(cyclohexene carbonate) with  $>99\%$  selectivity and carbonate linkages. The optimum activities and productivities compete with the very best cobalt catalysts reported for this polymerization. Furthermore, they can be used with up to 30 equiv (3 mol %) of water to efficiently produce polycarbonate polyols. The activity of these new magnesium catalysts with other epoxides (e.g., propylene oxide) is currently under investigation.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

This describes the experimental procedures, characterization data, and the structures of **3** and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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