Intramolecularly Dinuclear Magnesium Complex Catalyzed Copolymerization of Cyclohexene Oxide with CO_2 under Ambient CO_2 Pressure: Kinetics and Mechanism

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ABSTRACT: The intramolecularly dinuclear magnesium complexes generated in situ from the reaction of multidentate semi-azacrown ether ligands with *n*-Bu_2Mg followed by treatment with alcohol additive were found to be efficient catalysts for the copolymerization of CO_2 and cyclohexene oxide (CHO), affording the completely alternating poly(cyclohexene carbonate) (PCHC) under extremely mild conditions (1 atm pressure of CO_2, temperatures ranging from 20 to 60 °C). Ligand substituent effects were observed to dramatically influence both the activity and the chemoselectivity of the catalysis, exemplifying the fine-tunability of this type of ligands. With regard to the mechanistic studies, end-group analysis of the copolymer by MALDI-TOF mass spectroscopy revealed the predominance of the butoxy-initiated CO_2/CHO copolymerization process. The butoxy-containing catalytically active species in the present system was proposed to possess a dinuclear structure similar to an isolated model Mg complex which was characterized by X-ray crystal structural analysis. Rate studies performed on the copolymerization using the in situ prepared catalyst (molar ratio of **5a**:*n*-Bu_2Mg:*n*-BuOH = 1:2:0.4) at 60 °C demonstrate a zero-order dependence on CO_2 pressure and approximately first-order dependence on CHO and the catalyst concentration. Furthermore, the relative propensity of polycarbonate vs cyclic carbonate formation in the present system was evaluated by a comparative kinetic study of the temperature effect using the in situ IR technique. On the basis of these findings, a plausible bimetallic mechanism was tentatively proposed for the present reaction system.

Introduction

The development of efficient catalytic processes employing nontoxic carbon dioxide with the simultaneous reduction of its environmental impact is of great interest and has been a long-standing goal for chemists.[1] As one of the very promising way for the effective utilization of CO_2, synthesis of polycarbonates via metal-catalyzed coupling reactions of CO_2 with epoxides has attracted a great deal of attention over the past several decades[2,3] since the first report by Inoue et al. in 1969.[4] A wide variety of catalytic systems, including both heterogeneous catalyst mixtures[5] and homogeneous discrete metal complex catalysts,[6−17] have been developed with the later being the focus of most current research owing not only to their high activities but also to their well-defined structures for mechanistic investigations.

Among various homogeneous catalysts developed so far for the CO_2/epoxides copolymerization, a variety of metal complexes of Co,[8] Cr,[9] Cd,[10] Al,[11] and Zn[12−17] have shown significant activities for the copolymerization of CO_2 and epoxides under high CO_2 pressure.[7−16] Furthermore, the elegant mechanistic investigations carried out independently by Darensbourg,[9c,d,12f] Coates,[13e] Chisholm,[11b] among others,[15b,18,19] have provided valuable insights into the corresponding processes. Particularly, it was found that a bimetallic epoxide enchainment mechanism often dominates the process of polymerization in zinc-based catalysis (**1**−**3**, Chart 1).[12d,13c,e,15b] On the basis of this mechanistic understanding, Lee's and our groups recently have demonstrated that intramolecularly dinuclear zinc complexes **4**[16] and **6**[17] could also serve as efficient catalysts for the copolymerization of CO_2/CHO. In particular, Lee's bimetallic anilido-aldimine−zinc complexes **4** exhibited extremely high activity for the copolymerization, affording the corresponding polymers with molecular weight of up to 284 000 (M_n) at a catalyst loading of [Zn]/[monomer] = 1:16800.[16] Despite the successes of these catalyst systems, the copolymerization under mild conditions, such as ambient pressure of CO_2, is still a challenge for chemists. Coates and co-workers have shown that poly(cyclohexene carbonate) could also be produced at CO_2 pressures of roughly 1 atm (∼20 psi) using analogous Zn complex to **2**.[13e] Only very recently, Sugimoto and co-workers realized the first example of ambient-pressure cyclohexene oxide (CHO)/CO_2 copolymerization using a porphyrin−MnOAc with low TOF values (ca. 3 h^{-1}).[6] We also demonstrated that CHO/CO_2 copolymerization could proceed smoothly via the catalysis of **6** under 1 atm of CO_2 with similar catalytic activity.[17]

In contrast to the zinc complexes, the Lewis acidic main group magnesium-containing catalysts have received much less attention in the title reaction, despite their obvious potential catalytic activities.[20] To the best of our knowledge, only two examples of magnesium-catalyzed epoxide/CO_2 copolymerization ($Mg(OAc)_2$ and $MgEt_2$−H_2O) have been reported so far, both of which exhibited very poor activity (TOF ≤ 0.1 h^{-1}).[20b,c] Recently, Coates and Chisholm have shown that magnesium−diiminate complexes are efficient catalysts for the ring-opening polymerization of lactides.[20d−f] In comparison with Zn^{2+}, Mg^{2+} can be considered a harder Lewis acidic metal and is more oxophilic,[21] which might make it more effective for epoxides activation. Although both of them share some similar properties including formation of M^{2+} salts and similar ionic radii, just how this affects their chemical behavior is hardly predictable. In the present work, we will report our results on the first

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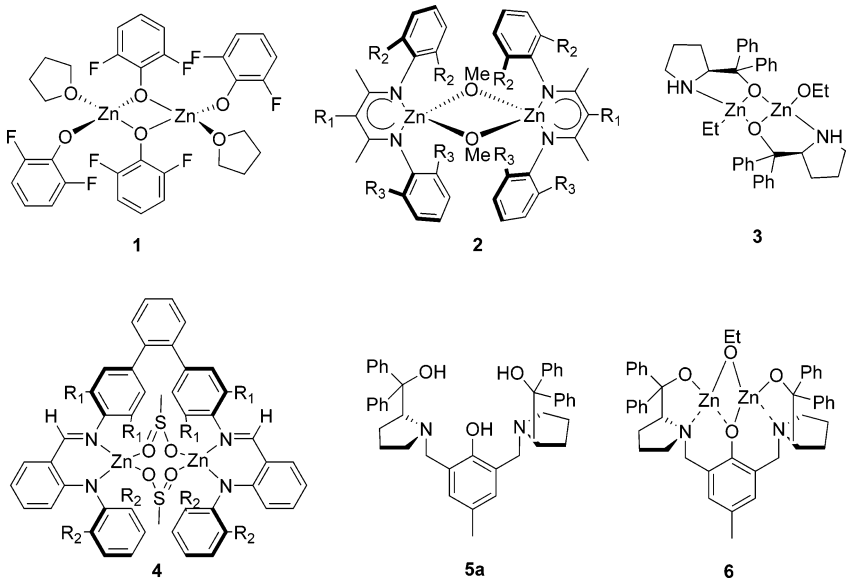
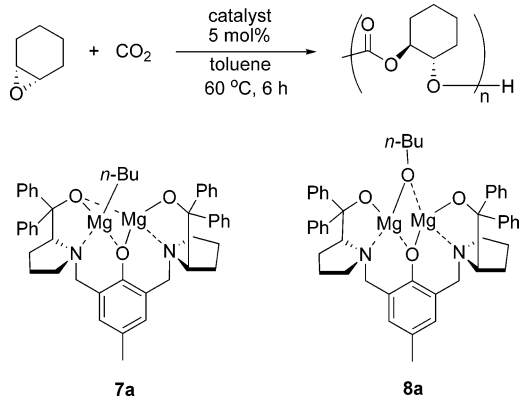
Chart 1. Dinuclear Zinc Complexes Used for Epoxide/CO_2 Copolymerization



Scheme 1. Copolymerization of Cyclohexene Oxide with CO_2 under the Catalysis of Dinuclear Magnesium Complexes



example of using magnesium complexes for the catalysis of CO_2/CHO copolymerization under mild conditions (1 atm of CO_2) and the mechanistic investigations of the copolymerization.

Results and Discussion

Preliminary Examination of CHO/CO_2 Copolymerization Catalyzed by in Situ Prepared [Mg−5a] Complex. On the basis of our previous finding in the dinuclear Zn complexes promoted CHO/CO_2 copolymerization, it is reasonable to assume that the semicrown dinucleating ligand **5a** may also be capable of bringing the two magnesium centers to a sufficiently close proximity and hence may allow for a synergistic effect of two metallic centers and exert profound influence on the CO_2/epoxide copolymerization. To test this hypothesis, the work began with a preliminary examination of the potential catalytic activity of the magnesium complex **7a**, formed in situ by reaction of 2 equiv of *n*-Bu_2Mg with 1 equiv of ligand **5a** in toluene. The copolymerization was carried out under 30 atm of CO_2 in toluene at 60 °C in the presence of 5 mol % of complex **7a** for 6 h (Scheme 1). To our delight, it was found that this catalyst system indeed was active for the CHO/CO_2 copolymerization, yielding an alternated poly(cyclohexene carbonate) (PCHC) in good conversion of CHO (88%) with a M_n value of 16900 g mol^{-1} and a molecular weight distribution (M_w/M_n ratio) of 1.61 (Table 1, entry 1). The chemoselectivity was excellent as determined by the ^1H NMR analyses. The completely alternating nature (>99% carbonate linkage) of the

Table 1. Copolymerization of CO_2 and Cyclohexene Oxide with the Catalysis of Mg(II) Complexes of 5a[a]

entry	*n*-BuOH (equiv to **5a**)	P_{CO_2} (atm)	conv (%)[b]	yield (%)[c]	carbonate linkages (%)[b]	M_n (kg/mol)[d]	M_w/M_n[d]
1	0.0	30	88	77	>99	16.9	1.61
2	0.4	30	>99	87	>99	23.7	1.73
3	1.0	30	90	84	>99	9.67	1.50
4	0.4	20	>99	92	>99	32.3	1.73
5	0.4	10	98	87	>99	47.6	2.02
6	0.4	5	99	81	>99	36.2	2.00
7	0.4	1	97	94	>99	42.8	1.51
8	0.0	1	94	82	>99	20.3	1.64
9	0.2	1	95	87	>99	36.9	1.65
10	0.6	1	94	90	>99	35.4	1.66
11	0.8	1	93	85	>99	29.2	1.75
12	1.0	1	94	81	>99	25.4	1.67
13	1.2	1	94	76	>99	21.2	1.61
14[e]	0.4	1	>99	>99	>99	30.2	1.69

[a] All the copolymerization of CHO (1 M in toluene) and CO_2 was performed using in situ prepared **7a** (5 mol %) at 60 °C for 6 h with or without *n*-butanol additive. [b] Determined by ^1H NMR. [c] Isolated yields. [d] Determined by gel permeation chromatography (GPC) and calibrated with polystyrene standards in tetrahydrofuran. [e] Reaction time was 8 h.

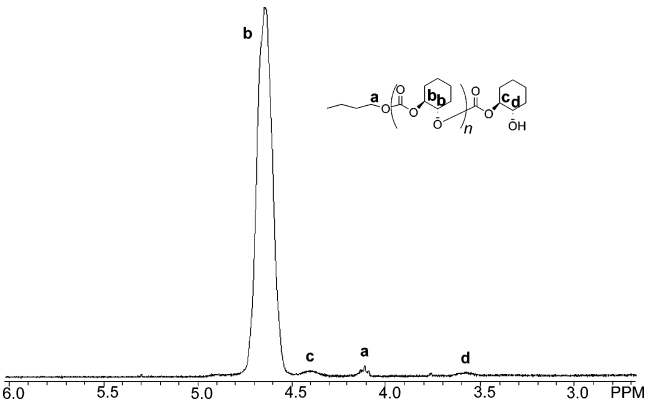


Figure 1. ^1H NMR spectrum of poly(cyclohexene carbonate).

PCHC was confirmed by the predominance of methine proton peak at δ 4.63 (for carbonate) and the absence of methine proton peak around δ 3.45 (assignable to polyether from homopolymerization of the CHO) (Figure 1). However, the level of the asymmetric induction in the copolymerization was low. After hydrolysis of the polycarbonate with aqueous NaOH, the

enantiomeric excess (*ee*) of the resulting cyclohexane-1,2-diol was measured by chiral GC to be 8% with *S*,*S* configuration.[15a]

A MALDI-TOF mass spectrometric analysis[15b,22] of the obtained poly(cyclohexene carbonate) indicated that the predominant ending group in the polymer was butoxy group (see Figure S1 in the Supporting Information), which provided a valuable clue on the mechanism of the chain initiation step. Evidently, the copolymerization was initiated by CO_2 insertion into a Mg−alkoxide bond of a catalytic species, predominantly [Mg]−butoxide, and terminated by protolysis to give the corresponding copolymers. On the other hand, the coexistence of multiple much weaker sets of unidentified peaks suggests the involvement of other less important parallel reaction paths. The butoxy initiation pathway was further supported by ^{1}H NMR spectrum of the copolymers (Figure 1). The signal **a** at 4.12 ppm (triplet), which is assignable to methylene protons, clearly indicated the presence of a butoxy group in the structure of the copolymer obtained. Thus, for this preliminary test reaction, the in situ generated magnesium alkyl complex **7a** presumably acted as a catalyst precursor. The active butoxide containing species **8a** for initiating the CO_2/CHO copolymerization might be produced by the O−O cleavage of its alkyl peroxide complex formed via the reaction of **7a** with the adventitious dioxygen present in the reaction system.[23] An alternatively possible pathway for the formation of **8a** might be the direct reaction of ligand **5a** with the butoxy impurities present in the *n*-Bu_2Mg reagent.[24]

Control experiments were then performed in order to further probe the nature of the butoxy-containing initiating species. When a 1:1 (molar ratio) mixture of *n*-BuOH and *n*-Bu_2Mg was used under either 1 or 20 atm pressure of CO_2, no CHO conversion could be detected. Moreover, using the α,α-diphenyl-substituted prolinol as the ligand, which can be viewed as a single arm of the dinucleating ligand **5a**, only resulted in very low CHO conversion with negligible isolated yield of the copolymer. Thus, the dinucleating ligand **5a** seemed to play a crucial role in the magnesium-catalyzed CO_2/CHO copolymerization. These observations are also consistent with the above discussion that **8a** might serve as the catalytically active species in the copolymerization.

On the basis of these investigations, it can be deduced that the butoxy-containing dinuclear Mg complex **8a** might be the major active species responsible for the catalysis. An enhancement of the concentration of butoxide-containing Mg species in the catalytic system was expected to be beneficial to the catalysis. Accordingly, the effect of *n*-butanol additive on the catalysis of the copolymerization was subsequently investigated. Copolymerizations were run by addition of 0.4 or 1.0 equiv (relative to ligand **5a**) of *n*-butanol to the in situ prepared complex **7a**, while keeping the other reaction conditions identical to those of the preliminary test reaction. The addition of 0.4 and 1.0 equiv (relative to ligand **5a**) of *n*-butanol to the in situ prepared complex **7a** indeed changed the conversion and the yields of the copolymers (Table 1, entries 2 and 3). Addition of 0.4 equiv of *n*-butanol was found to be optimal in terms of both CHO conversion and the copolymer yield, affording the copolymer with molecular weight of 2.37×10^4 g mol^{-1} ($M_w/M_n = 1.73$) with complete conversion of CHO and in 87% isolated yield. However, addition of more *n*-butanol resulted in a slight decrease of catalytic activity (Table 1, entry 3). Given that some amount of butoxy-containing **8a** has already been present in the reaction system prior to the addition of any *n*-butanol as discussed above, it is not surprising that an optimization of the polymerization conditions led to only addition of 0.4 equiv (instead of 1 equiv) of *n*-butanol to the in situ generated **7a**.

Pressure Dependence of the Magnesium Complex Catalyzed CHO/CO_2 Copolymerization. The investigation of the pressure dependence of CO_2/CHO copolymerization can be considered as one of the useful probes for understanding of the catalytic mechanism.[13e,17] We then set up a series of experiments to examine the impact of CO_2 pressure on its copolymerization with CHO. The CO_2/CHO copolymerizations were performed using in situ prepared **7a** (5 mol %) in the presence of 2 mol % n-butanol at 60 °C with CO_2 pressure ranging from 20 to 1 atm (Table 1, entries 4−7). All the tested reactions were completed within 6 h. Interestingly, the conversion was found to be independent of CO_2 pressure, and the copolymerization proceeded smoothly even under 1 atm of CO_2 without significant loss of conversion (97%) or degree of CO_2 incorporation (>99% polycarbonate by ^{1}H NMR). This result is remarkable since most copolymerization systems developed so far employed much higher pressure of CO_2.[7−16] Similar behavior has also been observed by us in dinuclear Zn complex **6** catalyzed CHO/CO_2 copolymerization,[17] suggesting that the intramolecularly bimetallic nature of the complexes may indeed have some kind of synergistic effect on the catalysis to render this reaction to proceed under extremely mild conditions. As far as the mechanism is concerned, the independence of CHO conversion on the CO_2 pressure implied that the insertion of CO_2 into the Mg−alkoxide bond should be a facile step in the whole catalytic cycle.

With these leading results in hand, the amount of additive (*n*-BuOH) was reoptimized for the copolymerization at ambient pressure of CO_2. As shown in Table 1 (entries 7−13), addition of 0.4 equiv of *n*-BuOH (relative to **5a**) was again found to be optimal, although the CHO conversion was less influenced by the amount of *n*-BuOH additive. When the reaction time was extended to 8 h, nearly quantitative isolated yield of the copolymer could be achieved under the optimized conditions (entry 14).

Effects of Alcoholic or Phenolic Additives. As we disclosed above, the copolymerization was predominantly initiated by the butoxide-containing Mg complex of **5a**. Thus, a change in the butoxide moiety of Mg complex into other types of alkoxides or phenoxides is also expected to influence the catalytic behavior in the polymerization. Consequently, a variety of protonic additives including alcohols and phenols were then screened as the additives for **7a** (*n*-Bu_2Mg/**5a**) catalyzed CHO/CO_2 copolymerization under 1 atm of CO_2 pressure (Table 2). Except for a more acidic alcohol, CF_3CH_2OH (entry 6), all the alcoholic additives exhibited comparable catalytic performances in terms of both CHO conversion and copolymer yields (entries 1−5 and 7). On the other hand, with the exception of one case (2,6-di-*tert*-butylphenol, entry 15), almost all of the phenol additives were found to give consistently poorer yields of the copolymer than the alcoholic additives (entries 8−16). *n*-BuOH turns out to be the best additive among those examined for the copolymerization. Although so far we do not know exactly how and why the more acidic phenolic additives retard the CHO/CO_2 copolymerization, the insertion of CO_2 into the phenoxy−Mg bond might become tougher than that into the alkoxy−Mg bond at the initiation step under the experimental conditions.

Substituent Effects of Ligand on the Catalytic Behaviors. In the metal-catalyzed epoxide/CO_2 copolymerizations, the steric and electronic features of the substituents on the ligands often exert a significant influence upon the course of the polymerizations.[12,13,15−17] Thus, we then investigated the sub-

Table 2. Effect of Various Additives on CHO/CO_2 Copolymerization[a]

entry	additive	conv (%)[b]	yield (%)[c]	carbonate linkages (%)[b]	M_n (kg/mol)[d]	M_w/M_n[d]
1	*n*-BuOH	97	94	>99	42.8	1.51
2	MeOH	95	87	>99	33.7	1.73
3	EtOH	98	87	>99	36.0	1.88
4	*i*-PrOH	97	92	>99	33.3	1.52
5	*n*-BnOH	94	88	>99	28.6	1.57
6	CF_3CH_2OH	89	55	>99	17.8	1.89
7	*t*-BuOH	93	86	>99	23.3	1.63
8	PhOH	92	58	>99	5.46	1.71
9	4-MePhOH	86	64	>99	7.11	1.86
10	4-*t*-BuPhOH	92	78	>99	6.60	2.24
11	4-BrPhOH	89	74	>99	4.94	1.28
12	2,4-(*t*-Bu)$_2$PhOH	82	56	>99	5.00	1.26
13	2,6-Me_2PhOH	87	67	>99	6.49	1.29
14	2,6-(*i*-Pr)$_2$PhOH	73	48	>99	7.82	1.71
15	2,6-(*t-Bu*)$_2$PhOH	92	91	>99	16.8	2.10
16	4-O_2NPhOH	25	12	91	15.7	1.41

[a] All the copolymerization reactions of CHO (1 M in toluene) and CO_2 (1 atm) were carried out using in situ prepared catalyst precursor (5 mol % ligand **5a** + 10 mol % *n*-Bu_2Mg in toluene) in the presence of various additives (2 mol %) at 60 °C for 6 h. [b] Determined by ^{1}H NMR. [c] Isolated yields. [d] Determined by gel permeation chromatography (GPC) and calibrated with polystyrene standards in tetrahydrofuran.

Chart 2. Phenol-Bridged Bis(α,α-diarylprolinol) Ligands (5a−5o) Tested for the Magnesium-Catalyzed Copolymerization of CO_2 and Cyclohexene Oxide

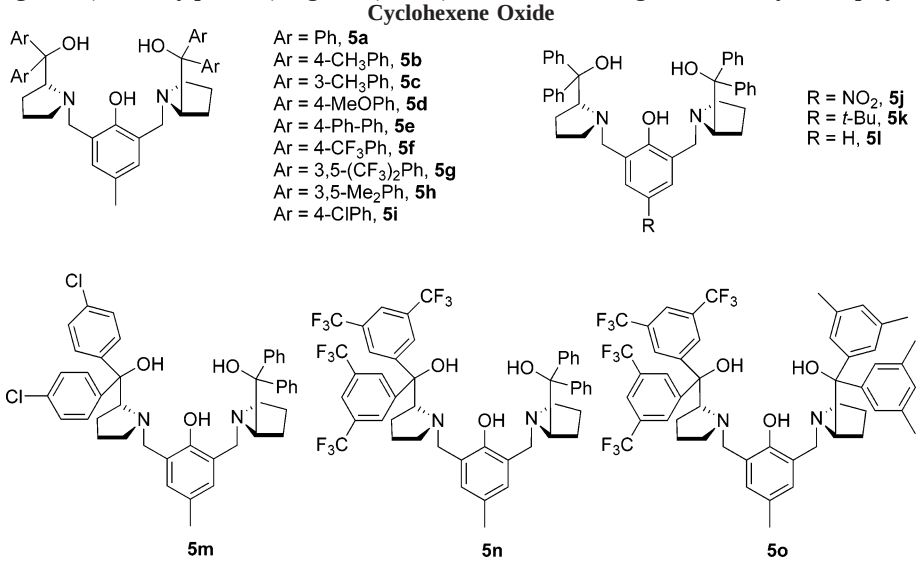


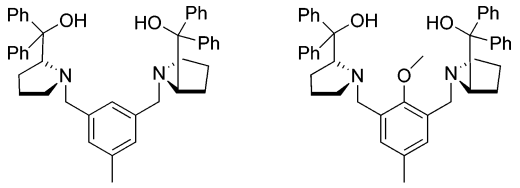
Table 3. Stereoelectronic Effect of Ligands on Magnesium-Catalyzed CHO/CO_2 Copolymerization[a]

entry	ligand **5**	conv (%)[b]	yield (%)[c]	carbonate linkages (%)[b]	M_n (kg/mol)[d]	M_w/M_n[d]
1	**5a**	90	77	>99	25.4	1.85
2	**5b**	79	58	99	34.0	1.97
3	**5c**	44	20	88	16.4	1.73
4	**5d**	41	23	97	30.4	1.58
5	**5e**	78	62	>99	38.1	2.42
6	**5f**	86	79	84	60.4	1.94
7	**5g**	95	51	<1	25.5	1.61
8	**5h**	12	trace	28	N.D.	N.D.
9	**5i**	82	50	77	22.6	2.51
10	**5j**	2	1.6	75	N.D.	N.D.
11	**5k**	74	62	97	22.4	1.76
12	**5l**	82	56	93	24.5	1.79
13	**5m**	83	70	90	21.1	2.57
14	**5n**	37	trace	<1	N.D.	N.D.
15	**5o**	30	trace	<1	N.D.	N.D.

[a] All the copolymerization reactions of CHO (1 M in toluene) and CO_2 (1 atm) were carried out using in situ prepared catalyst precursor (5 mol % ligand **5** + 10 mol % *n*-Bu_2Mg in toluene) in the presence of butanol additive (2 mol %) at 60 °C for 2 h. [b] Determined by ^{1}H NMR. [c] Isolated yields. [d] Determined by gel permeation chromatography (GPC) and calibrated with polystyrene standards in tetrahydrofuran.

stituent effect of the ligands on the catalyst activities of their Mg complexes. To this end, a series of Trost-type bis(α,α-diarylprolinol) ligands[25] (**5a**−**5o**, Chart 2) with different stereoelectronic features were submitted to Mg(II)-catalyzed CHO/CO_2 copolymerization under ambient pressure of CO_2 in the presence of 2 mol % of *n*-BuOH additive at 60 °C. The results are summarized in Table 3. As can be seen from this table, the ligand series showed a marked substituent effect, both the CHO conversion and the copolymer yield, as well as the chemoselectivity (as reflected by the percent of carbonate linkage) are sensitive to the subtle changes in the ligand structure. First, it was found that structural modifications made on the α,α-diaryls of the prolinol moieties (ligands **5b**−**i**) usually led to decreased CHO conversions and/or lowered copolymer

Chart 3. Bis(diarylprolinol) Ligands without the Bridging Phenoxo Hydroxyl Group



9 **10**

yields as compared with their prototype ligand **5a** (entries 2−9 vs entry 1). Especially, the presence of the 3,5-disubstituents in the α,α-diaryls of the prolinol moieties in ligands **5g** and **5h** exhibits a detrimental effect on the chemoselectivity for PCHC, yielding products with very low carbonate linkages (1% and 28%, respectively, entries 7 and 8). The large percentage of polyether linkages when utilizing catalyst **5g** (entry 8) can be attributed to the competing homopolymerization of the epoxide.[26] Next, altering the substituents on the phenolate ring of the ligand backbone (ligand **5j**, **5k**, and **5l**) leads to either the unsatisfactory CHO conversion or low copolymer yield (entries 10−12). Finally, for the series of unsymmetrical ligands **5m**−**5o**, none of them exhibits comparable catalytic result as that of **5a**. In particular, it was noted that for ligands bearing strong electron-withdrawing CF_3 substituents at meta positions (**5g**, **5n**, and **5o**) the copolymers were obtained in very high ether linkages (entries 14 and 15). This is not surprising in that binding of the **5n** and **5o** with strong electron-withdrawing substituents would significantly increase the Lewis acidity (electrophilicity) of the magnesium centers and concomitantly enhancing their affinity with epoxide and ring-opening rate of epoxides, a competing pathway to CO_2 enchainment, hence leading to a high percentage of polyether linkages in the formed copolymer. Upon this ligand screening, **5a** proved to be the most effective ligand for the magnesium-catalyzed CHO/CO_2 copolymerization process.

Furthermore, as an extension of the above work, two other bis(diarylprolinol) ligands **9** and **10** (Chart 3) were also screened for their activities in Mg-catalyzed CO_2/CHO copolymerization. Despite their striking structural similarities with that of ligand **5a**, the magnesium complex derived from **9** and **10** did not show any catalytic activity for CHO conversion under 1 or 20 atm of CO_2. This observation reinforces the above discussions that subtle modifications of ligand architecture may result in drastic changes in the catalytic activity. It should be noted that similar phenomenon has also been observed in our previous work on the Zn complex **6** catalyzed CO_2/CHO copolymerization, which was attributed to the key structural role of the phenolic hydroxyl group of **5a** in bridging the two zinc centers to form a catalytically active dinuclear species.[17]

Structural Aspects of 8a As Revealed by a Model Complex. Detailed structural information on the proposed active species **8a** would be very helpful in elucidating the mechanism of the present reaction. However, meaningful ^1H or ^{13}C NMR spectral probe for this complex in solution is still unavailable because of the poor quality of the spectra. After many futile attempts to isolate **8a** from the as-synthesized 1/1 mixture of **7a** and *n*-BuOH in toluene or other solvents, we finally succeeded in clarifying the solid-state structure of an intimately related compound **11**, which may well serve as a structural model of **8a**. By treatment of the in situ prepared **7a** with 1 equiv of *p*-nitrophenol in toluene/THF and keeping the resulting solution for several days (Scheme 2), the Mg complex **11** was precipitated out as pale yellow single crystals. X-ray crystallographic analysis of this complex[27] revealed that it is indeed dinuclear and virtually isostructural to its zinc analogue, [(THF)Zn(μ-**5a**)(μ-*p*-nitrophenol)Zn(THF)],[17] with only slightly different geometrical parameters. The solid-state structure of **11** is displayed in Figure 2. The dinuclear magnesium complex exhibited a distorted square-pyramidal geometry around each magnesium center, with the two bridging phenoxo oxygens [O(1) and O(2)] and N and O of the chelating prolinol moieties forming the basal plane and a terminal THF ligand in the apical position. The structure consists of a planar parallelogrammical [Mg_2O_2] core, and the Mg(1)−Mg(2) separation is 3.102(3) Å.

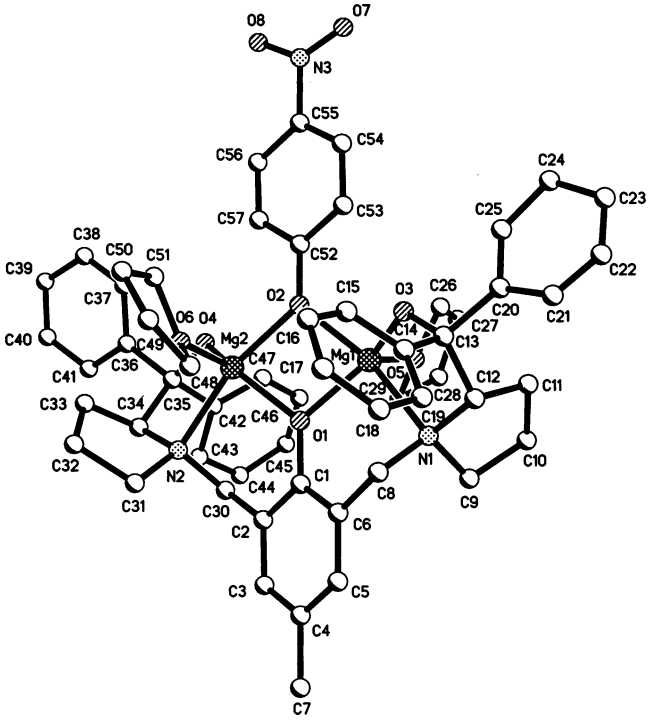
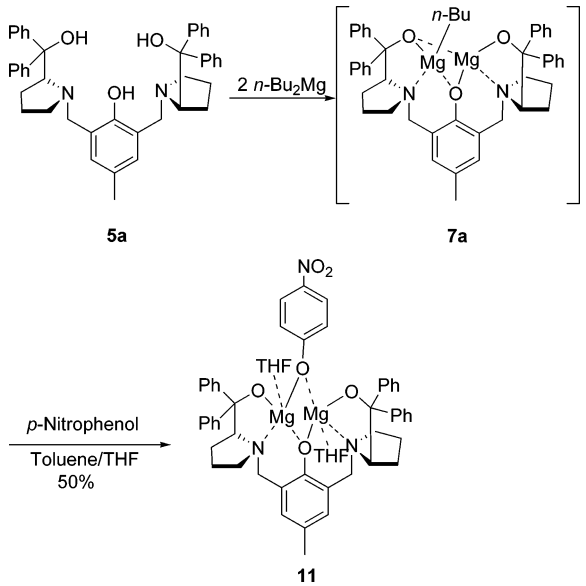


Figure 2. PLUTO drawing of complex **11**. Hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (deg): Mg(1)−O(1) 1.991(6), Mg(1)−O(2) 2.031(6), Mg(1)−O(3) 1.894(6), Mg(1)−N(1) 2.252(7), Mg(1)−O(5) 2.041(6), Mg(2)−O(1) 1.979(6), Mg(2)−O(2) 2.016(6), Mg(2)−O(4) 1.878(6), Mg(2)−O(6) 2.031(6), Mg(2)−N(2) 2.238(7); O(1)−Mg(1)−O(2) 78.3(2), O(1)−Mg(2)−O(2) 78.9(2), Mg(2)−O(1)−Mg(1) 102.8(2), Mg(2)−O(2)−Mg(1) 100.1(2).

Scheme 2. Synthesis of Complex 11



CDV

By way of comparison, the distance between the metal centers (Zn−Zn) in [(THF)Zn(μ-**5a**)(μ-*p*-nitrophenol)Zn(THF)] is 3.1776(12) Å.[17] It is also worth noting that a similar [Mg_2O_2] arrangement with closely matched bond parameters has also been found in other μ-hydroxo-bridged or μ-alkoxo-bridged homodinuclear magnesium complexes,[28] suggesting that the propensity to form this core by the magnesium atoms fixed the complex in its present conformation. It could be readily envisioned that, upon the addition of *n*-Bu_2Mg and *n*-BuOH to ligand **5a** in a noncoordinating solvent such as toluene, the active dinuclear species **8a** with a structure similar to that of **11** but without the two coordinating THF molecules (and thus adequate vacant sites for substrate binding and activation) could be easily formed and is ready for CO_2 insertion, hence initiating a copolymerization event by further alternating enchainment of CHO/CO_2. In contrast, for ligand **9** or **10**, the bridging phenol hydroxy group is either removed or blocked and thus no longer available for the dinuclear complex formation, resulting in no catalytic activity for the reaction. Combined with the information presented on the control experiment part, it could be inferred that the inherently dinucleating nature of ligand **5** seemed to play a key role in the titled copolymerization.

We have tried to use the isolated 4-nitrophenol complex **11** for the CO_2/CHO copolymerization reaction. Surprisingly, this complex was shown to be inactive as a catalyst for the copolymerization process. Presumably, the magnesium centers are coordinatively saturated by the THF ligands, and when exposed to the toluene solution of CHO substrate, they cannot undergo ligand exchange reactions with CHO owing to their different affinities or steric hindrance to the metal centers, thereby avoiding a consecutive epoxide ring-opening process. This can be further supported by the observation that even when **8a** is used, the copolymerization can still be effectively inhibited when THF is employed as solvent (see the Supporting Information). Recall that the THF ligands in the model compound **11** are absent in our proposed active species **8a**, thus leaving a vacant site on magnesium for CHO binding and activation. It should also be noted that model complexes for catalysts need not necessarily themselves be catalytically active.[12g]

Kinetic Studies of the CHO/CO_2 Copolymerization Catalyzed by in Situ Prepared 8a. Owing to the dinuclear nature of the catalyst complex, it can be easily envisioned that a synergistic effect might be present for the two proximal magnesium centers in the catalysis of copolymer production, and thus a bimetallic mechanism may be operative for **8a**-catalyzed copolymerization. In an effort to better assess the mechanistic aspects of the reaction at a molecular level, we have carried out some preliminary kinetic studies of this system as a function of the pressure of carbon dioxide, initial CHO concentration, and catalyst concentration with ^{1}H NMR and in situ IR techniques. To this end, rate studies were conducted on a series of copolymerization reactions at 60 °C. First, to investigate the rate dependence on the CO_2 pressure, the copolymerization of CHO (1.0 M in toluene) and CO_2 from 1 to 20 atm was performed in the presence of the in situ prepared **8a** (50 mM in toluene), and the samples were withdrawn periodically from the reaction mixture and analyzed by ^{1}H NMR (Figure S2 in the Supporting Information). As is evident from Figure 3, the rates of the cyclohexene oxide conversion exhibit essentially no dependence on CO_2 pressure. Thus, all the rest kinetic studies were performed under 1 atm pressure of CO_2, and the progress of the reaction was monitored by in situ IR spectroscopy through the emerging carbonyl stretch at 1752 cm^{-1} (ν(C═O) for the polycarbonate).[9c,d,13e] Comparative kinetic measurements of the copolymerization performed at 1 atm pressure of CO_2 by using ^{1}H NMR and in situ IR spectroscopy indicated that both can reliably be used to monitor the reaction process, yielding essentially the same results (Figure S3 in Supporting Information).

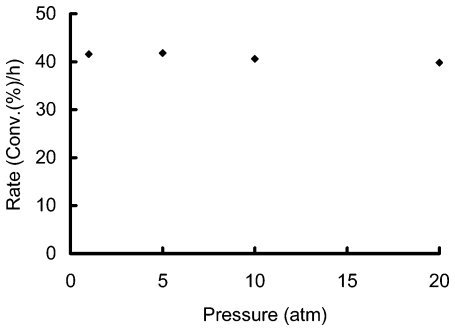


Figure 3. Plots of reaction rate with CO_2 pressure using [**8a**] (0.05 M) at 60 °C (1.0 M CHO in toluene).

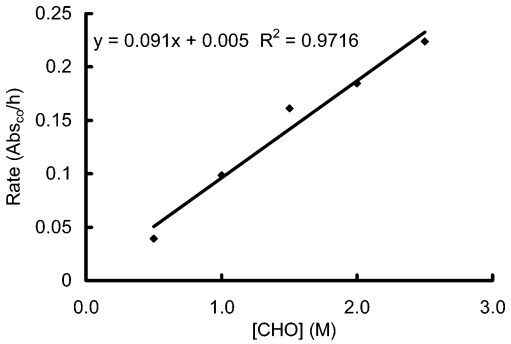


Figure 4. Impact of CHO concentration (from 0.5 to 2.5 M in toluene) on the reaction rate of copolymerization with CO_2 (1 atm) using [**8a**] (0.05 M) at 60 °C.

Subsequently, five different reactions with various concentrations of CHO (0.5−2.5 M in toluene) were carried out under 1 atm of CO_2 using **8a** (0.05 M in toluene) at 60 °C in order to examine the rate dependence on the epoxide monomer. The in situ IR reaction profiles at 1752 cm^{-1} indicated the polycarbonate carbonyl stretch intensities increased with higher CHO concentration, with slower initiation rate observed in the early stages of the polymerization as evidenced by the presence of an inflection point in reaction profiles (Figure S4 in Supporting Information). This is suggestive of the presence of an early initiation period in the reaction, which may be the time required to activate the catalyst. This phenomenon has also been reported for the salen−Cr system by Darensbourg.[9d] Since the reaction was performed under 1 atm pressure by bubbling CO_2 into the system, the time needed for equilibrium of CO_2 saturation in solution might be responsible for the initial catalyst activation period,[13e] leading to the slower initiation rate observed in the early stages of the polymerization. Figure 4 depicts the plot of initial rate of copolymer formation vs [CHO] (conversion range 5−15%), which clearly demonstrates the rate law for the process is approximately first order in CHO.

Finally, the rate dependence with respect to the concentration of in situ prepared catalyst **8a** (0.03−0.1 M) was also evaluated, using the copolymerization of 1.0 M CHO in toluene with 1 atm of CO_2 at 60 °C (Figure S5 in Supporting Information). Interestingly, an approximately linear correlation between the copolymerization rate vs [**8a**] was obtained (Figure 5), reflecting a nearly first-order dependence on catalyst. Therefore, the copolymerization of CHO and CO_2 using **8a** at 60 °C proceeds

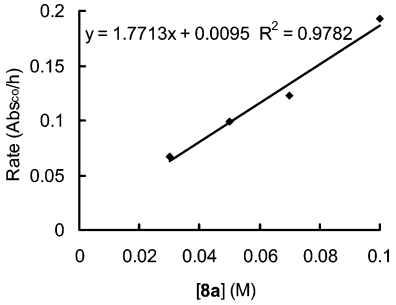


Figure 5. Copolymerization of CHO (1.0 M in toluene) + CO_2 (1 atm) using [**8a**] (0.03−0.1 M) at 60 °C (CHO conversion: 5%−15%).

by approximately following the overall kinetic law shown in eq 1:

$$d[PCHC]/dt \propto k_p[CO_2]^0[CHO]^1[\mathbf{8a}]^1 \quad (1)$$

where k_p is the apparent propagation rate constant.

Since CO_2 is not included in the rate equation (1), CO_2 insertion is a fast step. The approximately linear dependence of the reaction rate on catalyst **8a** and CHO could most logically be explained by a bimetallic transition state for the rate-determining epoxide ring-opening step. Owing to the intramolecularly dinucleating nature of ligand **5a**, the bimetallic intermediates with structures analogous to that of **11** are presumably present throughout the whole alternating enchainment of CO_2 and CHO catalytic cycle.

Polycarbonate vs Cyclic Carbonate Formation: Temperature Dependence. When the **8a**-catalyzed CHO/CO_2 copolymerizations was performed at 70 °C in toluene, in situ IR indicated that there was minor amount of cyclic cyclohexyl carbonate formed as the byproduct accompanying with the polycarbonate production, as evidenced by the IR peak of 1825 cm^{-1} (C═O stretching vibration of the cyclic carbonate) in Figure 6a.[12f] Cyclic carbonates have been reported to be a common byproduct during the CO_2/epoxides copolymerization[29] and are generally thought to be generated by the depolymerization of a growing polycarbonate chain via the backbiting of a metal alkoxide into an adjacent carbonate linkage, in which the cyclic carbonate is released with the rest propagating chain coordinating itself to the metal center.[2a,9c,d] Although cyclic carbonate formation is less important for alicyclic epoxides as compared to aliphatic epoxides, it is often much more temperature-dependent than chain propagation;[2a] therefore, an evaluation of the activation barriers for the two competing pathways (substrate enchainment vs cyclic carbonate release) is still highly desirable for achieving a full optimization and a better understanding of the present process. To this end, we have performed a comparative kinetic study of the temperature effect on the rates of polycarbonate vs cyclic carbonate production for the titled reaction. Experimental runs were carried out employing identical reaction condition in 1.0 M CHO with 0.05 M **8a** in toluene at the temperature range from 20 to 80 °C under 1 atm of CO_2, and the initial rates for production of polycarbonate and cyclic carbonate were simultaneously monitored by the in situ IR technique (Figure S6 in Supporting Information). Figure 6 demonstrates the typical reaction profiles for the CHO/CO_2 copolymerization process, in which the peak around 1825 cm^{-1} indicates the increases of cyclic carbonate formation with the temperature. It should be noted that the copolymerization indeed proceeded smoothly at 20 °C under 1 atm of CO_2 using catalyst **8a** to give the PCHC selectively, albeit the reaction rate was not yet satisfactory (Figure 6b). This is probably the mildest

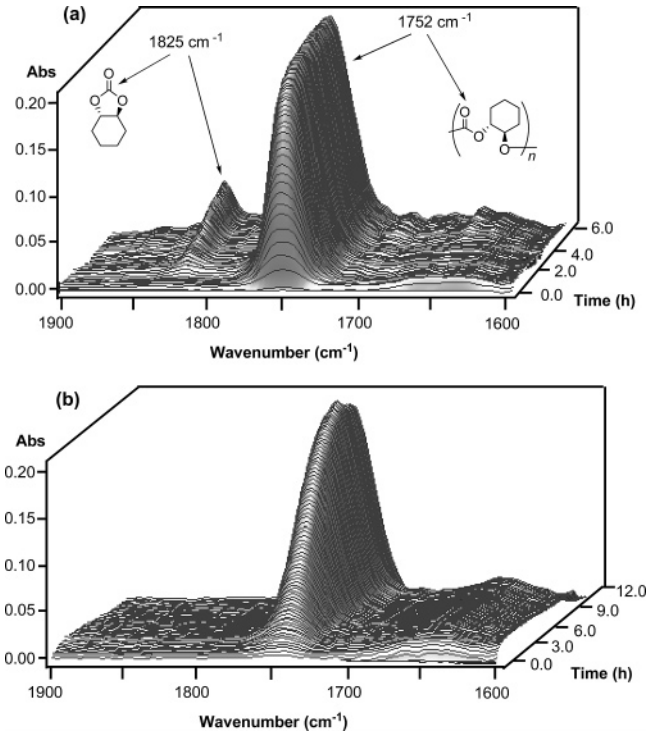


Figure 6. Three-dimensional in situ IR stack plots of the copolymerization of CHO/CO_2 at (a) 70 °C and (b) 20 °C, respectively, using 5 mol % of **8a**.

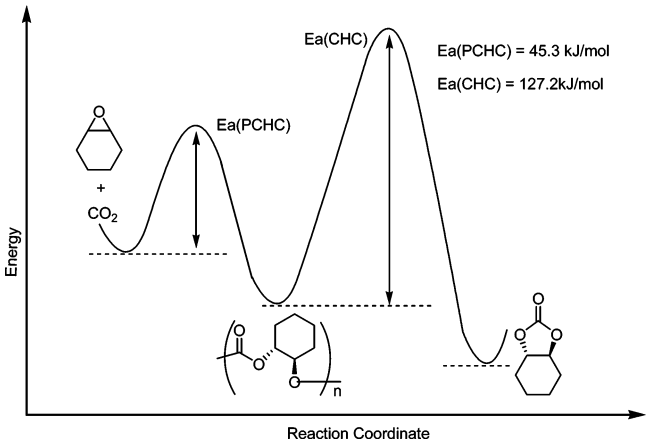


Figure 7. Reaction coordination diagram of the coupling of CO_2 and CHO.

reaction conditions reported so far for the copolymerization of CO_2 with epoxide.[2]

The initial rates of polycarbonate vs cyclic carbonate formation were calculated from the in situ IR data and were listed as the function of temperature (20−80 °C) (Table S3 in Supporting Information). From these kinetic data the activation energies for copolymer and cyclic carbonate formation were determined to be 45.3 and 127.2 kJ mol^{-1}, respectively, via the Arrhenius plots (Figure S7 in Supporting Information). Using these activation energy values in combination with the unimolecular depolymerization mechanism for cyclic carbonate formation as discussed above, we tentatively depicted reaction diagrams for the two competing processes in Figure 7. The significant energy difference of 81.9 kJ mol^{-1} is comparable to that of Darensbourg's Salen−Cr system for the same substrates (CHO and CO_2),[9d] rationalizing the origin of the predominant formation of poly(cyclohexene carbonate) at lower temperatures.

The Possible Mechanism for Intramolecularly Dinuclear Mg Complex-Catalyzed CHO/CO_2 Copolymerization. On the

Scheme 3. Proposed Mechanism for the Mg-Catalyzed Copolymerization of Cyclohexene Oxide with CO_2 Using 8

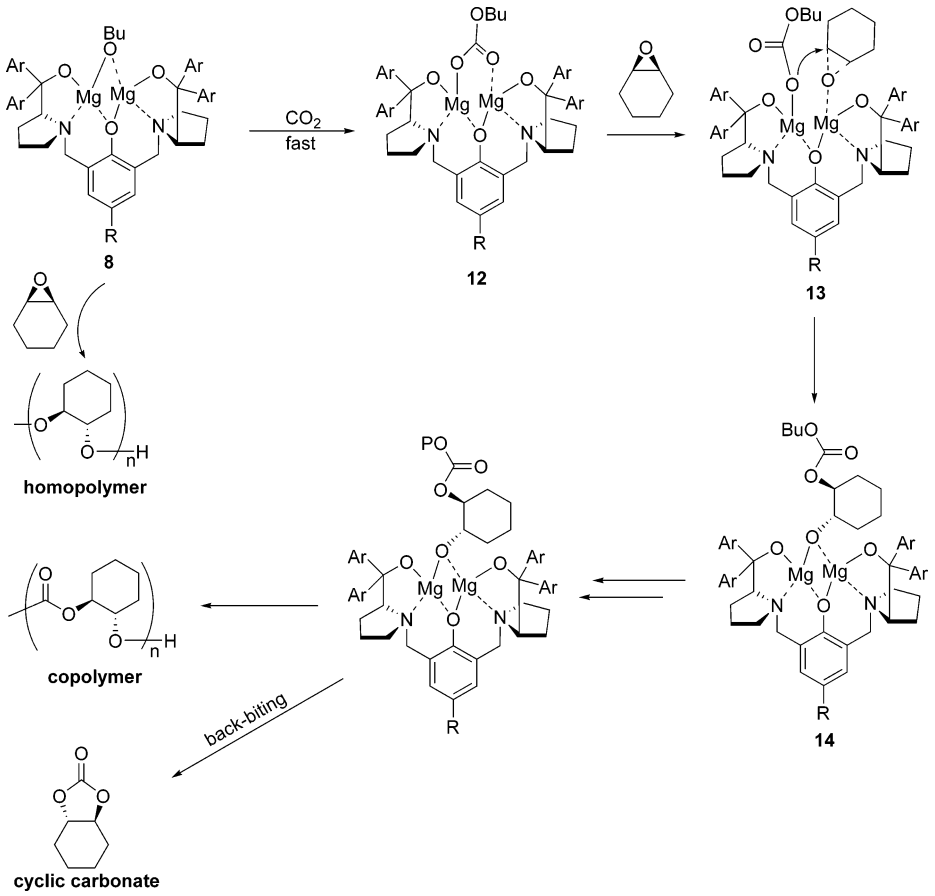


Table 4. Effect of the Various Catalyst Loading on the CHO/CO_2 Copolymerization under a Fixed Catalyst Concentration (0.05 M)[a]

entry	**5a** (mol %)	vol_{CHO} (mL)	vol_{PhMe} (mL)	[CHO] (M)	conv (%)[b]	TOF (h^{-1})	yield (%)[c]	carbonate linkages (%)[b]
1	5	0.10	1.0	0.9	90	9	77	>99
2	2	0.25	0.75	2.5	48	12	10	93
3	1	0.50	0.50	5.0	34	17	6.3	82
4	0.71	0.70	0.30	7.0	45	32	12	85
5[d]	0.67	0.75	0.25	7.5	57	43	26	94
6	0.62	0.80	0.20	8.0	42	34	15	75
7	0.56	0.90	0.10	9.0	34	31	16	72
8	0.50	1.00	0.10	9.1	24	24	11	64
9	0.50	1.00	free	10.0	20	20	6.3	66

[a] All the copolymerization reactions of CHO and CO_2 (1 atm) were carried out using in situ prepared catalyst (ligand **5a**:*n*-Bu_2Mg:butanol = 1:2:0.4, in toluene) at 60 °C for 2 h. [b] Determined by ^1H NMR. [c] Isolated yields. [d] M_n = 12.6 kg/mol, M_w/M_n = 1.29 (determined by GPC).

basis of the information presented thus far, we tentatively proposed a plausible mechanism for the present catalytic system as summarized in Scheme 3. Generated in situ by ligand exchange reactions, the butoxy-bridged magnesium complex **8** might adopt a dinuclear structure quite similar to that of **11** and act as the initiating species in the catalytic cycle. Since the copolymerization rate was found to be independent of the CO_2 pressure, CO_2 insertion into the *n*-BuO−Mg bond is a fast step, affording the carbonate ester-bridged complex **12**. The two magnesium centers in **12** might act in a bimetallic fashion; i.e., one magnesium center may serve as a Lewis acidic center for epoxide binding and activation (like that of THF molecule in complex **11**), while another magnesium delivers the (poly)-carbonate for a backside nucleophilic attack on the neighboring *cis*-epoxide ring through **13** to **14**. Since the overall rate law exhibits an approximately first-order dependence on both [catalyst] and [CHO], it can be deduced that either the epoxide binding to the catalyst complex (**12** to **13**) or epoxide ring-opening by intramolecular nucleophilic attack (**13** to **14**) should be the rate-determining step. Subsequent alternating enchainment of CO_2 and CHO affords the alternating polycarbonate. Cyclic carbonate could be produced through the backbiting degradation of the growing polymer−catalyst complex. It should also be noted if the Lewis acidity of the magnesium is rendered too strong, consecutive epoxide enchainment would lead to a high percentage of ether linkage in the resulting polymer. It is evident that over the whole catalytic cycle the dinuclear feature of the intermediates will persist, owing to the nature of ligand **5**.

Further Improvement of the Activity of 8a for 1 atm CO_2/CHO Copolymerization. Finally, the copolymerization process at 1 atm pressure of CO_2 has been optimized using our most efficient catalyst **8a**, by tuning the volume ratio of substrate (CHO) and solvent (toluene), while keeping a constant concentration of the catalyst (Table 4). A TOF up to 43 h^{-1} (entry 5) could be reached with 0.67 mol % of the catalyst loading for ambient pressure CHO/CO_2 copolymerization. When the reaction was carried out in (quasi) solvent-free conditions, the chemoselectivity degraded significantly as evidenced by the considerable increase of the (poly)ether linkages in the resulting copolymer (entries 7−9). This observation suggested that there

probably exists a competition between the completely alternating CHO/CO_2 copolymerization and the consecutive CHO enchainment sequence, with the latter pathway becoming gradually conspicuous at high CHO concentrations. Indeed, when the reaction was performed at 60 °C with [CHO] = 7.5 M in toluene and [**8a**] = 0.05 M but without CO_2 pressure, there is 34% CHO conversion to polyether over 30 min reaction period. However, when the reaction was carried out with [CHO] = 1.0 M under the otherwise identical conditions, no polyether formation was detected after 24 h.

Conclusions

Intramolecularly dinuclear maganesium complexes of the type **8** are first demonstrated to be efficient catalysts for the alternating copolymerization of CHO and CO_2, affording the polycarbonate under extremely mild conditions. These catalysts showed good activity for atmospheric pressure copolymerization, which represents a rare and valuable feature among all the catalysts developed so far for the reaction. Moreover, excellent chemoselectivity for completely alternating enchainment of the CHO and CO_2 could be accomplished by judicious choice of the substituents in ligand backbone. The dinuclear structures of the magnesium catalysts were also revealed by solid-state structural characterization of the model complex **11**. Preliminary kinetics studies performed on the copolymerization demonstrate a zero-order dependence on CO_2 and an approximately first-order dependence on both CHO and the catalyst concentrations. On the basis of these facts, a bimetallic mechanism in which the two magnesium centers in **8** act in synergy to promote the copolymerization was tentatively proposed. Furthermore, a comparative kinetic study focusing on the effect of temperature was also undertaken to assess the relative propensity of polycarbonate vs cyclic carbonate formation in the present system. The strategy of using intramolecularly dinucleating ligands leaves large space for both ligand and metal variations and thus may provide new inspirations for design of more efficient and practical catalysts for epoxides/CO_2 copolymerization under mild conditions.

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Supporting Information Available: Experimental details, including synthetic procedures, spectral data of the copolymer, solvent and temperature effects on the copolymerization, rate studies, and crystal structural data. This material is available free of charge via the Internet at http://pubs.acs.org.

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