

Copolymerization of Cyclohexene Oxide with CO₂ by Using Intramolecular Dinuclear Zinc Catalysts

Youli Xiao, Zheng Wang, and Kuiling Ding*^[a]

Abstract: The intramolecular dinuclear zinc complexes generated in situ from the reaction of multidentate semi-aza-crown ether ligands with Et₂Zn, followed by treatment with an alcohol additive, were found to promote the copolymerization of CO₂ and cyclohexene oxide (CHO) with completely alternating polycarbonate selectivity and high efficiency. With this type of novel initiator, the copolymerization could be accomplished under mild conditions at 1 atm pressure of CO₂, which represents a significant advantage over most catalytic systems developed for this reaction so far. The copolymerization reaction was demonstrated to be a living process as a result of the narrow polydispersities and the linear increase in the molecular weight with conversion of CHO. In addition, the solid-state

structure of the dinuclear zinc complex was characterized by X-ray crystal structural analysis and can be considered as a model of the active catalyst. On the basis of the various efforts made to understand the mechanisms of the catalytic reaction, including MALDI-TOF mass analysis of the copolymers' end-groups, the effect of alcohol additives on the catalysis and CO₂ pressure on the conversion of CHO, as well as the kinetic data gained from in situ IR spectroscopy, a plausible catalytic cycle for the present reaction system is outlined. The copolymer-

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ization is initiated by the insertion of CO₂ into the Zn–OEt bond to afford a carbonate–ester-bridged complex. The dinuclear zinc structure of the catalyst remains intact throughout the copolymerization. The bridged zinc centers may have a synergistic effect on the copolymerization reaction; one zinc center could activate the epoxide through its coordination and the second zinc atom may be responsible for carbonate propagation by nucleophilic attack by the carbonate ester on the back side of the *cis*-epoxide ring to afford the carbonate. The mechanistic implication of this is particularly important for future research into the design of efficient and practical catalysts for the copolymerization of epoxides with CO₂.

Introduction

CO₂ is not only an inexpensive and abundant one-carbon chemical feedstock, but also an atmospheric greenhouse gas that contributes to global warming. Thus, the development of efficient catalytic processes that employ this nontoxic carbon source with the simultaneous reduction of its environmental impact is of great interest and has been a long-standing goal for chemists.^[1] One of the most promising

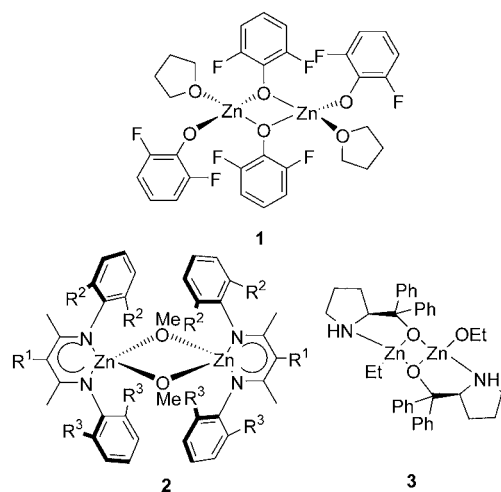
ways to effectively utilize CO₂, the synthesis of polycarbonates through metal-catalyzed coupling reactions of CO₂ and epoxides, was first reported by Inoue et al. in 1969^[2] and has attracted much attention over the past few decades.^[3,4] A wide variety of catalytic systems, including both heterogeneous catalyst mixtures^[5] and homogeneous discrete metal complex catalysts,^[6–14] have been developed over the past decade with the latter being the focus of most current research owing not only to their high activities, but also to their well-defined structures that allow mechanistic investigations.

Among the metal complex catalysts developed so far for CO₂/epoxide copolymerization, zinc complexes have been of considerable interest.^[9,11,12,14] Mechanistic studies of the catalyzed copolymerization reactions involving these complexes suggest that various dimeric zinc complexes formed by the bridging of two zinc monomers are the effective catalysts and that a bimetallic epoxide enchainment mechanism often

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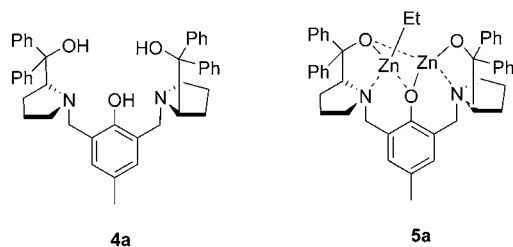
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dominates the polymerization process.^[9d,11c,11e,14b] For example, Darensbourg et al. showed that dimeric zinc–phenolate complex **1** could promote CO₂/cyclohexene oxide (CHO) copolymerization efficiently.^[9d] An elegant kinetic study per-



formed by Coates and co-workers on the copolymerization of CO₂ with CHO catalyzed by a zinc β -diimine complex revealed that dimeric zinc complex **2** is involved in the transition state of the epoxide ring-opening event.^[11e] In 1999, Nozaki et al. reported the first example of the asymmetric copolymerization of CO₂/CHO using a mixture of ZnEt₂ and (*S*)- α,α -diphenyl(pyrrolidin-2-yl)methanol, which affords the polycarbonate in excellent yields and with moderate enantioselectivity.^[14a] Further mechanistic studies demonstrated that a dimeric zinc complex **3** might be the active species and that the copolymerization was initiated by CO₂ insertion into the Zn–OEt bond of the complex.^[14b] All these studies have demonstrated that it is highly likely that catalysts that contain intramolecular dinuclear zinc complexes with multidentate ligands could be designed for the copolymerization of olefin epoxide with CO₂.

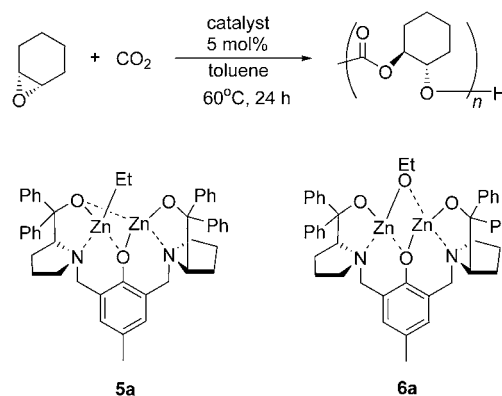
Trost's dinuclear zinc complex **5a**, easily prepared from the multidentate semi-azacrown ether ligand **4a** and Et₂Zn, has been successfully applied to the catalysis of a variety of enantioselective reactions.^[15] On the basis of the mechanistic understanding described above, we envisioned that this complex may serve as a promising catalyst for the copolymerization of CO₂ and epoxide owing to its intramolecular dinuclear zinc structure. It is reasonable to believe that **4a** can



bring the two metal centers sufficiently close together to allow for a synergistic effect of the two metallic centers in CO₂/CHO copolymerization. In this report, we describe our results of a novel use of intramolecular dinuclear zinc complexes in the catalysis of CO₂/CHO copolymerization under mild conditions with good activity and excellent chemoselectivity.

Results and Discussion

This research was initiated by testing the potential catalytic activity of Trost's zinc complex **5a** in the copolymerization of CO₂ and CHO (Scheme 1). Complex **5a** was prepared by



Scheme 1. Copolymerization of cyclohexene oxide with CO₂ in the presence of a dinuclear zinc complex as catalyst.

the in situ reaction of two equivalents of Et₂Zn with one equivalent of ligand **4a**. Although the exact structure of this complex has not been confirmed yet owing to the difficulties associated with its isolation and structural characterization, we prefer the structure of **5a** proposed by Trost et al., since it is well supported by the stoichiometric evolution of ethane in the complex formation,^[15a,c,g] ESI-MS spectrometric studies,^[15b] as well as MM2 force field calculations.^[15a] In the presence of complex **5a** (5 mol %), the copolymerization reaction was carried out under 30 atm of CO₂ in toluene at 60°C for 24 h. It was found that this catalytic system exhibited good activity in the CO₂/CHO copolymerization reaction, affording poly(cyclohexene carbonate) (PCHC) in a quantitative yield (>99%) and with a high *M_n* value of 44 100 g mol⁻¹ and a relatively narrow polydispersity (*M_w*/*M_n* ratio) of 1.82. The chemoselectivity was excellent as shown by the ¹H NMR spectroscopic analysis. The completely alternating nature (>99% carbonate linkage) of the copolymerization reaction was reflected in the presence of the methine proton peak at δ = 4.63 ppm (for carbonate) and the absence of a methine proton peak at around δ = 3.45 ppm (which can be attributed to the formation of polyether in the homopolymerization of CHO; Figure 1). The enantioselectivity of the copolymerization reaction was evaluated by following the procedure described by Nozaki et al.^[14a] After

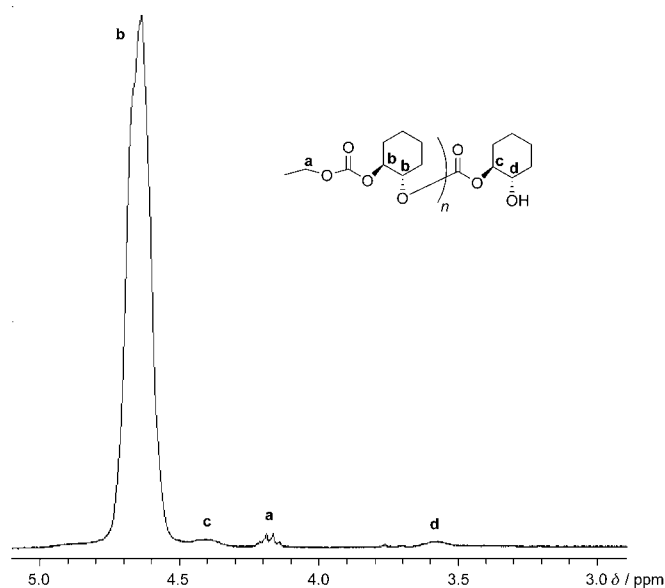


Figure 1. ^1H NMR spectrum of poly(cyclohexene carbonate).

hydrolysis of the polycarbonate with aqueous NaOH, the enantiomeric excess (*ee*) of the resulting cyclohexane-1,2-diol was determined by chiral GC to be only 18% with an *S,S* configuration.

The completely alternating structure of the poly(cyclohexene carbonate) obtained rendered MALDI-TOF mass spectrometry the ideal tool for end-group analysis to probe the active species responsible for the initiation of the polymerization reaction.^[16] As shown in Figure 2a, at least two series

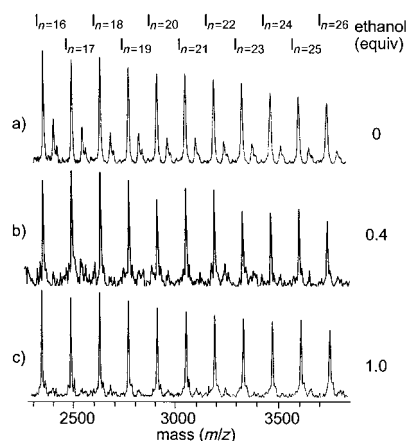


Figure 2. MALDI-TOF mass spectra of the copolymers obtained by using in situ prepared complex **5a** in combination with a) 0, b) 0.4, and c) 1.0 equivalent of ethanol additive.

of signals with regular repeat intervals (repeating units of 142.2 mass units) were observed in the mass spectra. The mass values within the series of the stronger signals match $[142.2n \text{ (repeating unit)} + 45.1 \text{ (ethoxy group)} + 1.0 \text{ (H)} + 23.0 \text{ (Na}^+ \text{ ion)}]$, while the values for the weaker ones match

$[142.2n \text{ (repeating unit)} + 99.1 \text{ (cyclohexyloxy group)} + 1.0 \text{ (H)} + 23.0 \text{ (Na}^+ \text{ ion)}]$. Therefore, the set of stronger signals can be assigned to copolymer **I** and the set of weaker signals to copolymer **II** (Figure 3). It can be deduced from this mass

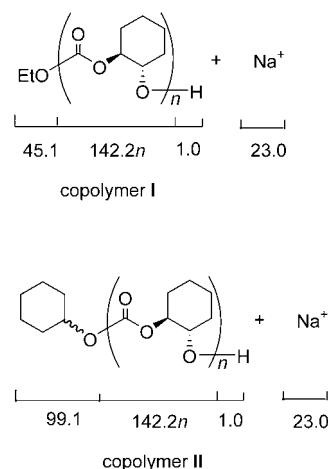


Figure 3. Structures of copolymers **I** and **II** with the ethoxy or cyclohexyloxy moiety as the initiating group.

spectrum (Figure 2a) that the copolymerization reaction was initiated by insertion of CO_2 into a Zn–alkoxide bond of the catalytic species, either an ethoxy or a cyclohexyloxy group attached to a zinc center, and terminated by protolysis to give the corresponding copolymers **I** or **II**, respectively. The ethoxy initiation hypothesis was also supported by the ^1H NMR spectrum of the copolymers (Figure 1). The signal at $\delta = 4.18$ ppm, which can be assigned to methylene protons, clearly indicates the presence of an ethoxy group in the structure of the copolymer obtained.^[14c] Thus, the in situ generated dinuclear zinc complex **5a** probably acts as a catalyst precursor. The alkoxy-containing active species, such as **6a**, was probably produced in the reaction of ligand **4a** with an impurity present in the Et_2Zn reagent, probably EtZnOEt .^[14b,17] The ligand-exchange reaction of the labile ethyl group of complex **5a** with a trace amount of cyclohexanol, presumably formed by the reduction of cyclohexene oxide with unreacted diethylzinc, gave the minor cyclohexyloxy-zinc active species.

On the basis of the investigation described above, it has been recognized that the dinuclear zinc complex **6a** might be the major active species in the catalytic reaction. An increase in the concentration of the ethoxide-containing zinc species was expected to have a favorable impact on its catalytic performance. Accordingly, the effect of ethanol additive on the catalysis of the copolymerization reaction was examined. The addition of 0.2–0.4 equivalents (relative to ligand **4a**) of ethanol to the in situ prepared complex **5a** improved the yields of the copolymers and led to a simultaneous decrease in the molecular weight (Figure 4). Addition of 0.4 equivalents of ethanol was found to be optimal, affording the copolymer with a molecular weight of $2.32 \times$

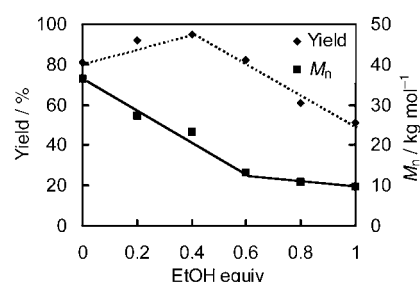


Figure 4. The effect of ethanol additive on the yield (dashed line) and molecular weight (solid line) of copolymers (the data were obtained for the reactions in 6 h).

10^4 g mol^{-1} ($M_w/M_n=1.43$) in 95 % yield. MALDI-TOF mass spectrometric analysis of the resulting copolymers at this stage showed that the relative intensities of the signals corresponding to copolymer **I** (Figure 2b) had been dramatically enhanced with respect to those in Figure 2a. This is in good agreement with the expectation that an increase in the concentration of ethanol would result in a higher portion of polymer **I** with the simultaneous suppression of the competing pathway. However, addition of further ethanol resulted in a decrease in catalytic activity, while the molecular weight distribution (polydispersity) was found to remain in the range of 1.18–1.28, and addition of two equivalents of ethanol completely inhibited the reaction. MALDI-TOF mass spectrometric analysis of the copolymers attained upon addition of 1 equivalent of ethanol (Figure 2c) suggests an overwhelming predominance of Zn-ethoxide as the initiator.

An investigation of the impact of CO_2 pressure on its copolymerization with epoxide might provide some useful information about the catalytic mechanism. To examine the effect of CO_2 pressure on the reaction, the copolymerization reactions of CHO and CO_2 at CO_2 pressures of 1–20 atm were performed by using in situ prepared **5a** (5 mol%) in the presence of 2 mol% ethanol at 60°C . All the reactions tested were complete within 6 h and the results are summarized in Table 1. Remarkably, the conversion was found to be independent of CO_2 pressure and the copolymerization proceeds smoothly even under 1 atm of CO_2 without significant loss of conversion (97%) or degree of CO_2 incorpora-

tion (>99% polycarbonate by ^1H NMR spectroscopy). This is a very interesting result, since most copolymerization systems developed so far employ much higher CO_2 pressure.^[7–14] Only very recently the first example of ambient-pressure CHO/ CO_2 copolymerization using a porphyrin/ MnOAc catalytic system was reported by Sugimoto et al., although the turnover frequency (TOF) was somewhat modest (ca. 3 h^{-1}).^[6] Mechanistically, the independence of CHO conversion on the CO_2 pressure indicates that the insertion of CO_2 into the Zn-alkoxide bond is not the rate-determining step of the reaction.

To gain some preliminary kinetic information about the copolymerization reaction performed under 1 atm pressure of CO_2 , the reaction was monitored under the conditions specified above by in situ IR spectroscopy, by analysis of the emerging carbonyl stretch at 1752 cm^{-1} ($\nu(\text{CO})$ for the polycarbonate).^[8d,e,11e,18] The spectra and the plot of absorbance versus time are shown in Figure 5. As shown in the bottom

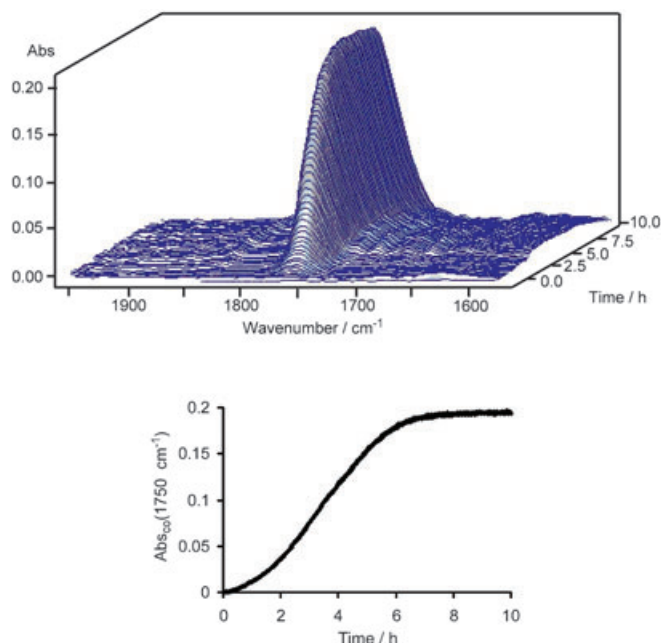


Figure 5. Top: Three-dimensional stack plot of the IR spectra collected every 2 min for the reaction of cyclohexene oxide and CO_2 under 1 atm pressure. Bottom: Time profile of the absorbance at 1752 cm^{-1} (corresponding to the formation of poly(cyclohexene carbonate)).

Table 1. The effect of CO_2 pressure on the conversion of cyclohexene oxide and the molecular weight of the copolymer.^[a]

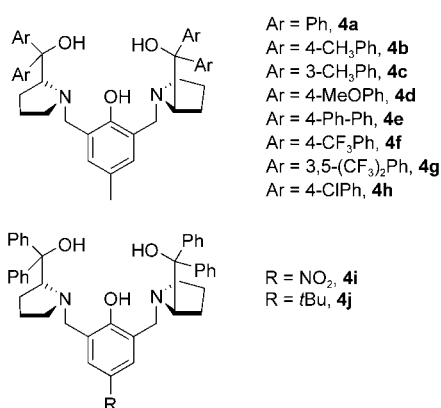
	$p(\text{CO}_2)$ [atm]	Conv. of CHO [%] ^[b]	Carbonate linkages [%] ^[b]	M_n [kg mol^{-1}] ^[c]	M_w/M_n ^[c]
1	20	>99	>99	16.9	1.35
2	10	97	>99	19.3	1.55
3	5	98	>99	20.9	1.51
4	1	97	>99	19.2	1.56

[a] All the copolymerization reactions of CHO (1 M in toluene) and CO_2 were performed using in situ prepared **5a** (5 mol%) in the presence of 2 mol% of ethanol additive at 60°C for 6 h. [b] Determined by ^1H NMR spectroscopy. [c] Determined by gel-permeation chromatography (GPC) and calibrated with polystyrene standards in tetrahydrofuran.

half of Figure 5, apart from the small lag within the initial 0.5 h, the carbonyl absorbance increased steadily in a nearly linear fashion over the next 5 h and remained constant after 6 h. This result indicates that the rate of polycarbonate formation was a little slow in the initiation stage, but then increased somewhat and remained almost constant in the following hours until completion, suggesting a constant concentration of propagating species leading to a smooth overall reaction under 1 atm of CO_2 . The initiation period shown in Figure 5 (bottom) may be the time required to activate the catalyst; presumably not all of the catalyst molecules are ini-

tiated simultaneously in the early stages leading to a small lag in the initial reaction rate. This phenomenon has also been reported for the salen/Cr system by Darensbourg et al.^[8e] Since the reaction was performed under 1 atm of pressure, the time needed for CO₂ saturation to reach equilibrium in solution^[11e] might be responsible for the catalyst activation period.

Tuning the steric and electronic features of ligands in metal-catalyzed epoxide/CO₂ copolymerization reactions often has a profound effect on the catalytic efficiencies.^[9,11] Thus, to probe the substituent effects of the dinucleating ligand, a series of phenol-bridged bis(α,α -diarylprolinol) ligands (**4a–4j**) with different stereoelectronic features were synthesized following a modified version of Trost's procedure, in which the corresponding dichlorides were used as the starting materials instead of the dibromides.^[15f] The cata-



lytic performance of these ligands in zinc-catalyzed CHO/CO₂ copolymerization was then investigated under an ambient pressure of CO₂ by using in situ prepared catalyst precursors [ligand **4** (5 mol %)+Et₂Zn (10 mol %) in toluene] in the presence of ethanol additive (2 mol %) at 80 °C. The results of the polymerization are summarized in Table 2. It was found that the presence of electron-donating groups (ligands **4b** and **4d**), as well as a phenyl group (ligand **4e**) or chlorine (ligand **4h**) at the *para*-positions of the α,α -diaryl moieties of the prolinol led to slightly decreased CHO conversions and considerably lower yields (entries 2, 4, 5, and 8) than those obtained with ligand **4a** (entry 1). On the other hand, the introduction of strongly electron-withdrawing groups into the α,α -diaryl moieties of the prolinol ligands (ligands **4f** and **4g**) either reduced the yield (entry 6) or had a disastrous effect on the chemoselectivity (entry 7). The high percentage of polyether linkages obtained when utilizing catalyst **4g** is probably partly due to the homopolymerization of the epoxide prior to the addition of carbon dioxide. The ¹H NMR spectra indicate that 6% CHO was converted to polyether within five minutes prior to the introduction of CO₂. The *meta*-substituted methyl group (ligand **4c**) resulted in a significantly lower yield (entry 3). Modifications to the bridging phenolic part of the ligand

Table 2. Stereoelectronic effect of ligands on Zn-catalyzed CHO/CO₂ copolymerization.^[a]

Ligand 4	Conv. of CHO [%] ^[b]	Yield [%] ^[c]	Carbonate linkages [%] ^[b]	<i>M</i> _n [kg mol ⁻¹] ^[d]	<i>M</i> _w / <i>M</i> _n ^[d]
1 4a	> 99	> 99	> 99	24.9	1.63
2 4b	92	79	> 99	24.8	1.58
3 4c	77	19	> 99	6.33	1.54
4 4d	87	71	> 99	16.3	1.49
5 4e	93	63	> 99	7.73	1.32
6 4f	94	70	> 99	11.5	1.34
7 4g	> 99	> 99	22	18.4	1.75
8 4h	94	70	> 99	21.1	1.72
9 4i	89	41	> 99	5.85	1.94
10 4j	95	88	> 99	48.5	1.84

[a] All the copolymerization reactions of CHO (1.0 M in toluene) and CO₂ (1 atm) were carried out by using in situ prepared catalyst precursor (ligand **4** (5 mol %)+Et₂Zn (10 mol %) in toluene) in the presence of ethanol additive (2 mol %) at 80 °C for 48 h. [b] Determined by ¹H NMR spectroscopy. [c] Isolated yield. [d] Determined by GPC and calibrated with polystyrene standards in tetrahydrofuran.

backbone (ligand **4i** and **4j**) led to an unsatisfactory yield (entry 9) and molecular weight distribution (entries 9 and 10). In summary, ligand **4a** turns out to be the best choice for this catalytic system.

From an environmental viewpoint, solvent-free processes are ideal.^[19] Moreover, the concentrations of both catalyst and substrate can be significantly increased under solvent-free conditions, which allows a further decrease in the catalyst loading and improvements in the efficiency of the catalysis. Thus, CHO/CO₂ copolymerization was carried out in neat CHO with a lower catalyst loading (0.5 mol %) under 20 atm of CO₂ pressure at 80 °C for 2 h. As shown in Table 3, the polymerization proceeded smoothly to give poly(cyclohexene carbonate) with good carbonate selectivity (94 %) and molecular weight distribution (*M*_w/*M*_n=1.30) in moderate yield (entry 1). Since the ethanol additive has a significant impact on the catalysis of the polymerization, as disclosed above, a variety of protonic additives, such as alcohols, phenols, and acetic acid, were then screened (Table 3, entries 2–13). Under the experimental conditions, alcohol additives were found to be superior to the phenolic and acidic additives in terms of both activity and chemoselectivity, as well as the molecular weight control (entries 1–3 versus 4–13). Of the three alcohols tested, ethanol appears to be the best additive for copolymerization.

Further optimization of the catalyst loading showed that, in conjunction with ethanol as additive, the copolymerization proceeded smoothly even when the catalyst loading was as low as 0.1 mol % of **5a** and that the activity remained essentially unchanged (Table 4). In neat CHO, the catalytic system exhibited good activity with a TOF of 142 h⁻¹ at a catalyst loading level of 0.2 % (entry 2), and thus is one of the most efficient catalysts reported so far.^[3d,e,7d,11]

To probe the nature of the copolymerization reactions, polymerization experiments were performed in neat CHO at 80 °C under 20 atm of CO₂ pressure in the presence of 0.5 mol % of **6a** generated from the reaction of **5a** with

Table 3. The catalysis of CHO/CO₂ copolymerization using **5a** in the presence of various additives under solvent-free conditions.^[a]

	Additive	Conv. of CHO [%] ^[b]	Yield [%] ^[c]	Carbonate linkages [%] ^[b]	M_n [kg mol ⁻¹] ^[d]	M_w/M_n ^[d]
1	EtOH	79	55	94	16.9	1.30
2	MeOH	69	43	93	13.0	1.23
3	<i>n</i> BuOH	69	45	88	10.3	1.21
4	HOAc	59	30	76	12.5	1.18
5	PhOH	66	39	86	11.9	1.24
6	4-O ₂ NPhOH	44	16	68	3.6	1.63
7	4- <i>t</i> BuPhOH	39	16	64	4.8	1.27
8	4-MeOPhOH	3.4	1.1	35	N.D.	N.D.
9	2,4-(<i>t</i> Bu) ₂ PhOH	19	4.2	49	4.0	1.98
10	2,6-(<i>t</i> Bu) ₂ PhOH	64	42	90	2.0	1.37
11	2,6-(<i>i</i> Pr) ₂ PhOH	20	4.3	66	7.0	1.22
12	2,6-Me ₂ PhOH	24	5.2	40	4.8	1.73
13	4-BrPhOH	11	1.8	34	5.5	1.40

[a] All the copolymerization reactions were performed in neat CHO (1.0 mL, 10.0 mmol) under 20 atm of CO₂ pressure at 80°C for 2 h in the presence of **5a** (0.5 mol %) and various additives (0.5 mol %). [b] Determined by ¹H NMR spectroscopy. [c] Isolated yield. [d] Determined by GPC and calibrated with polystyrene standards in tetrahydrofuran.

Table 4. Effect of catalyst loading on CHO/CO₂ copolymerization under solvent-free conditions.^[a]

	5a [mol %]	<i>t</i> [h]	Conv. of CHO [%] ^[b]	TON ^[c]	TOF [h ⁻¹] ^[d]	Carbonate linkages [%] ^[b]	M_n [kg mol ⁻¹] ^[e]	M_w/M_n ^[e]
1	0.5	2	80	160	80	94	16.9	1.30
2	0.2	2	57	285	142	92	21.0	1.28
3	0.1	2	26	260	130	91	19.2	1.29
4	0.1	3	36	360	120	93	22.4	1.28

[a] All the copolymerization reactions were performed in neat CHO under 20 atm of CO₂ pressure at 80°C using **5a** and an equimolar amount of EtOH. [b] Determined by ¹H NMR spectroscopy. [c] Turnover number; moles of CHO consumed per mole of ligand. [d] Turnover frequency; moles of CHO consumed per mole of ligand per hour. [e] Determined by GPC and calibrated with polystyrene standards in tetrahydrofuran.

EtOH. Samples were withdrawn periodically from the reaction mixture and analyzed by ¹H NMR spectroscopy and GPC. The data obtained were used to construct a plot of molecular weight (M_n) and polydispersity (M_w/M_n) versus conversion of cyclohexene oxide (Figure 6). A linear increase in the molecular weight of the copolymer with the conversion of CHO was observed within a reaction time of 2 h. The linear nature of the M_n plot combined with the narrow polydispersities ($M_w/M_n < 1.30$) suggest that the

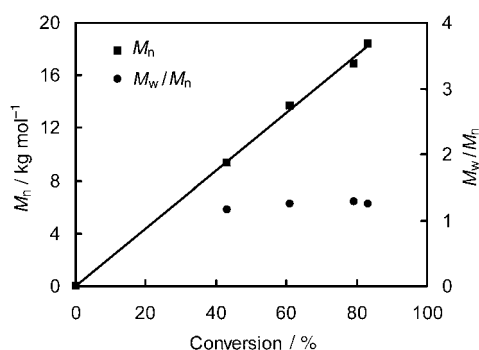
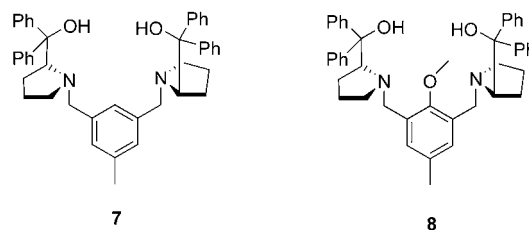


Figure 6. Plot of M_n (versus polystyrene standards) and polydispersity (M_w/M_n) for poly(cyclohexene carbonate) as a function of the conversion of cyclohexene oxide with a mixture of **5a** (0.5 mol %) and EtOH (0.5 mol %).

CHO/CO₂ copolymerization is a living process when catalyzed by the dinuclear zinc complex **6a**. However, for the copolymerization reactions carried out in toluene, considerably higher M_n values were observed based on the amount of monomer consumed per complex **5a** (Table 1, Figure 4, and the data obtained in the absence of alcohol). This seemingly abnormal phenomenon can be rationalized in terms of the incomplete transformation of **5a** to the real active species **6a** owing to the substoichiometric amount of ethanol used (0.4 equiv based on ligand **4a**, or none) and (or) the partial decomposition of the active species **6a** caused by contaminants, such as trace amounts of water, in these systems.^[8d]

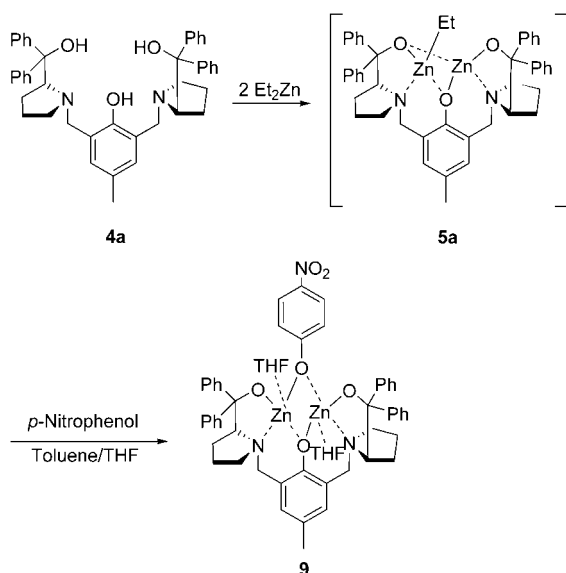
To examine the effect of the bridging phenolic hydroxy group in the ligand on the catalytic activity of the zinc complex, two new bis(diarylprolinol) ligands **7** and **8**, in which the hydroxy group was either removed or blocked with a

methyl group, were designed and synthesized. However, we did not isolate any polymers by using the zinc catalysts derived from **7** and **8** under the same experimental conditions. The dramatic difference in catalytic activity caused by the subtle modification of the structure of these ligands prompted us to investigate the underlying structural reasons for this behavior. The ¹H NMR spectra of the zinc complexes were recorded after mixing pure Et₂Zn and the ligands **4**, **7**, or **8** (ligand/Et₂Zn = 0.5:1) in [D₆]benzene at room temperature (see Figure S4 of the Supporting Information). For the **4a**/Et₂Zn mixture, a well-resolved spectrum was obtained, suggesting that the resulting complex **5a** has a well-defined structure, although at this moment it is still difficult to give an unambiguous assignment of the peaks. In contrast, extensive broadening of the ¹H NMR signals was observed for



the two complexes formed from **7**/ Et_2Zn and **8**/ Et_2Zn , indicating the intermolecular polymeric or oligomeric nature of these complexes. The importance of the hydroxy group in the linker of the bis-prolinol ligand **4a** in the copolymerization reaction, combined with the structural features disclosed by the ^1H NMR spectra of the zinc complexes generated from ligands **4a**, **7**, and **8**, demonstrate that it is critical for the zinc complex to have an intramolecular dinuclear structure for the activation of the substrates probably due to the cooperative effect of the two zinc cations during the catalysis.

Numerous attempts to isolate **6a** from the as-synthesized 1:1 mixture of **5a** and EtOH in toluene or other solvents proved to be unsuccessful. Fortunately, the structure of a closely related complex **9**, which may serve as a structural model of **6a**, could be elucidated by single-crystal X-ray analysis. Treatment of the in situ prepared **5a** with one equivalent of *p*-nitrophenol in toluene/THF resulted in a pale yellow solution of complex **9**. The resulting solution was left to stand for several days in order for the dinuclear zinc complex **9** to form pale yellow crystals in 50% yield (Scheme 2). A single crystal was selected for X-ray analy-



Scheme 2. Synthesis of complex **9**.

sis.^[20] As shown in Figure 7, the structure is indeed a dinuclear one as expected. The coordination sphere around each zinc atom is approximately square pyramidal with the two bridging phenoxo oxygen atoms (O1 and O2) and the nitrogen and oxygen atoms of the chelating prolinol moieties forming the base and a THF molecule at the apex. The geometries around the Zn1 and Zn2 atoms are very similar to each other with the THF rings pointing in opposite directions. The four-membered Zn_2O_2 core is almost planar (e.s.d. 0.002 Å), with the nonbonding Zn–Zn distance fixed at 3.1776(12) Å. A similar Zn_2O_2 core with similar bond parameters can be found in other μ -hydroxo- or μ -alkoxo-

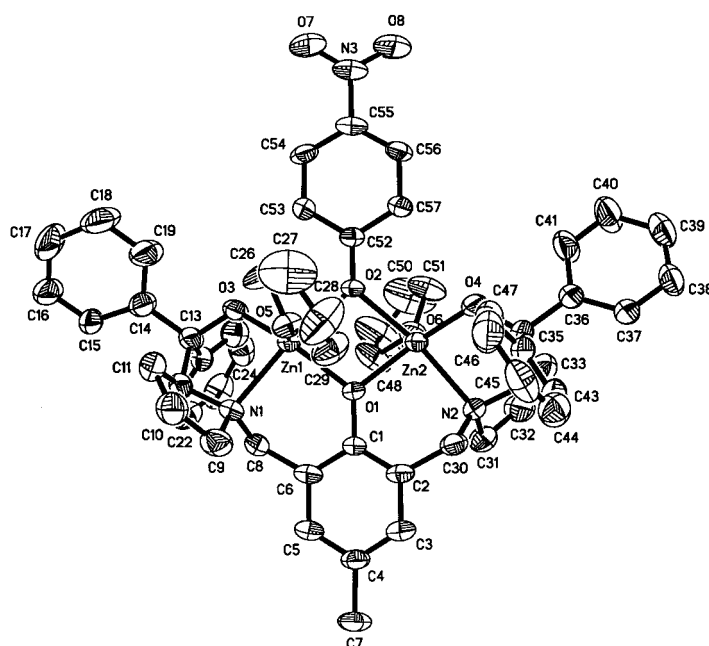
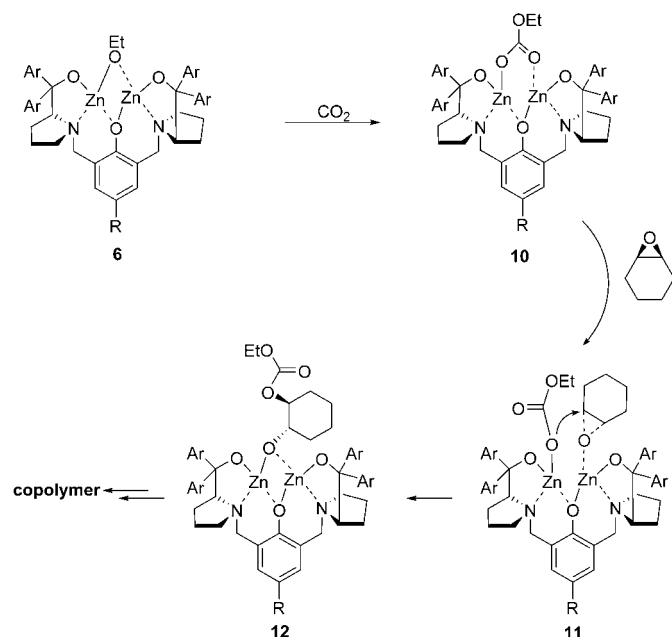


Figure 7. ORTEP drawing of complex **9** with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (degrees): Zn1–O1 2.005(6), Zn1–O2 2.081(5), Zn1–O3 1.902(5), Zn1–N1 2.190(6), Zn1–O5 2.096(6), Zn2–O1 2.000(6), Zn2–O2 2.091(5), Zn2–O4 1.896(5), Zn2–O6 2.096(6), Zn2–N2 2.203(6); O1–Zn1–O2 77.9(2), O1–Zn2–O2 77.8(2), Zn1–O1–Zn2 105.1(3), Zn1–O2–Zn2 99.3(2).

bridged intramolecular homodinuclear zinc complexes^[21] suggesting that the propensity of the zinc atoms to form this core locks the complex in the conformation described herein. This may in part explain the marked difference in the catalytic activities exhibited by bis-prolinol ligands **4a**, **7**, and **8**. The active dinuclear species **6a**, with a structure similar to that of **9**, is easily formed upon addition of Et_2Zn and EtOH to ligand **4a** owing to the presence of the phenolic hydroxy group. However, in the case of ligands **7** and **8**, the absence of this bridging hydroxy group hindered the formation of similar zinc complexes.

Based on these observations and the mechanistic information reported previously by others,^[9,11,14] we have proposed a plausible mechanism for the catalytic system described in this work (Scheme 3). Upon the addition of ethanol to the zinc complex generated in situ by the reaction of ligand **4** with diethylzinc, the ethoxy-bridged dinuclear zinc species **6** can be formed as a result of ligand exchange with EtOH. Complex **6** may adopt a structure similar to that of **9** and serve as the catalytically active species in the system described herein. The copolymerization reaction is initiated by the insertion of CO_2 into the Zn–OEt bond to afford the carbonate–ester-bridged complex **10**.^[8f,11a,14b] The two zinc centers should be situated sufficiently close to each other in complex **10** to allow a synergistic effect in the copolymerization, that is, one zinc center may activate the epoxide through its coordination, like that of the THF molecule in complex **9**, and the second zinc atom might be responsible

Experimental Section



Scheme 3. Proposed mechanism for the Zn-catalyzed copolymerization of cyclohexene oxide and CO₂ using ligand **4**.

for carbonate propagation by nucleophilic attack by the carbonate ester on the back side of the *cis*-epoxide ring in a co-operative manner (**11**) to afford **12**. It is evident that the dinuclear zinc structure of the catalyst remains intact throughout the catalysis of the copolymerization reaction. Subsequent alternating enchainment of CO₂ and CHO completes the catalytic cycle.

Conclusions

In summary, we have demonstrated a novel use of intramolecular dinuclear zinc complexes of multidentate ligands **4a–j** as catalysts in the copolymerization of cyclohexene oxide and CO₂ to afford completely alternating polycarbonates with good activity. With this type of novel initiator, copolymerization can be accomplished under mild conditions at 1 atm pressure of CO₂, which represents a significant advantage over most catalytic systems developed for this reaction so far. In addition, the solid-state structure of a dinuclear zinc complex with ligand **4a** was characterized, providing valuable information about the mechanism of the catalytic polymerization reaction. This strategy allows considerable scope for ligand modification, and thus might lead to the design of new, efficient, and practical catalysts for the copolymerization of epoxides with CO₂. Future work will be directed towards further mechanistic studies of these intramolecular CHO/CO₂ copolymerization reactions catalyzed by dinuclear zinc complexes and the simplification of the multidentate ligands, as well as the extension of this strategy to a broad range of metal-catalyzed epoxide/CO₂ copolymerization reactions.

General considerations: All air- and/or water-sensitive compounds were manipulated under dry nitrogen using a Braun Labmaster glove box or standard Schlenk line techniques. NMR spectra were recorded in deuteriochloroform with a Varian Mercury 300 (¹H: 300 MHz; ¹³C: 75 MHz; ¹⁹F: 282 MHz) spectrometer. Chemical shifts are reported in ppm relative to an internal standard: tetramethylsilane ($\delta = 0$ ppm) for ¹H NMR and deuteriochloroform ($\delta = 77.0$ ppm) for ¹³C NMR spectroscopy. Mass spectra (ESI) were recorded with a Mariner LC-TOF spectrometer. MALDI-TOF mass spectra were recorded with a PerSeptive Biosystems Voyager DE-STR spectrometer equipped with a 337 nm nitrogen laser, with α -cyano-4-hydroxycinnamic acid (α -CHCA) as the matrix and sodium trifluoroacetate as the ionizing agent. Elemental analyses were performed with an Elemental VARIO EL apparatus. Optical rotations were measured with a Perkin-Elmer 341 automatic polarimeter; [α]_D values are given in units of 10⁻¹ deg cm² g⁻¹. Infrared spectra were obtained with a BIO-RAD FTS-185 Fourier transform spectrometer in KBr pellets. The three-dimensional stack plot of the IR spectra was collected on a Mettler-Toledo ReactIR 4000 Reaction Analysis System. The molecular weights and molecular distributions were measured with a Waters 150C gel-permeation chromatograph equipped with microstyragel columns (HR1, HR3, and HR4) and an RI detector at 35 °C using polystyrene as the calibration standard and THF as the eluent (flow rate: 1.0 mL min⁻¹). All the solvents were dried and purified before use following standard procedures under argon. Cyclohexene oxide was distilled over CaH₂ before use. Diethylzinc was purchased from Aldrich and used as received. The purity of carbon dioxide was 99.999% and used as received.

Ligand synthesis: Ligands **4a–j** were prepared by following a modified version of Trost's procedure.^[15f]

(S,S)-2,6-Bis[2-(hydroxydiphenylmethyl)pyrrolidin-1-ylmethyl]-4-methylphenol (4a**):** 2,6-Bis(chloromethyl)-4-methylphenol (0.615 g, 3.00 mmol) was added in one portion to a stirred solution of (S)-diphenyl(pyrrolidin-2-yl)methanol (1.672 g, 6.60 mmol) and K₂CO₃ (3.649 g, 26.40 mmol) in dry DMF (20 mL) at 0 °C. The resulting solution was stirred at room temperature for 12 h before being diluted with water (70 mL) and Et₂O (70 mL). The organic phase was separated and the aqueous phase was extracted with Et₂O (3 × 50 mL). The combined organic phases were washed with water (2 × 50 mL) and brine and then dried with Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (20:1 to 5:1) as the eluent to yield **4a** (1.793 g, 94%) as a white amorphous solid. [α]_D²⁰ = +46.3 (*c* = 1.10 in CHCl₃) [Lit.: ^[15f]] [α]_D²⁵ = +49.8 (*c* = 3.0 in CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ = 1.43–1.63 (m, 4H), 1.75–1.82 (m, 2H), 1.97–2.04 (m, 2H), 2.14 (s, 3H), 2.33–2.41 (m, 2H), 2.76–2.83 (m, 2H), 3.21 (d, *J* = 12.3 Hz, 2H), 3.36 (d, *J* = 12.6 Hz, 2H), 3.94 (dd, *J* = 4.5, 9.3 Hz, 2H), 6.58 (s, 2H), 7.10–7.32 (m, 12H), 7.55 (d, *J* = 8.4 Hz, 4H), 7.68 ppm (d, *J* = 8.4 Hz, 4H); ¹³C NMR (75.5 MHz, CDCl₃): δ = 20.38, 24.01, 29.61, 54.99, 57.77, 71.36, 78.88, 123.98, 125.93, 125.98, 126.38, 126.60, 127.12, 127.95, 128.19, 128.82, 146.40, 146.98, 152.61 ppm; FTIR (KBr): $\tilde{\nu}$ = 3350, 3058, 2960, 2922, 1598, 1480, 1449, 1033 cm⁻¹; ESI-MS: *m/z*: 639.3 [*M*⁺ + H].

(S,S)-2,6-Bis[2-(hydroxydi-4-tolylmethyl)pyrrolidin-1-ylmethyl]-4-methylphenol (4b**):** Following a similar procedure to that described for the preparation of **4a**, the reaction of 2,6-bis(chloromethyl)-4-methylphenol with (S)-di-4-tolyl(pyrrolidin-2-yl)methanol afforded **4b** in 66% yield. [α]_D²⁰ = +58.8 (*c* = 1.00 in CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃): δ = 1.48–1.80 (m, 6H), 1.94–2.01 (m, 2H), 2.14 (s, 3H), 2.22 (s, 3H), 2.28 (s, 3H), 2.32–2.40 (m, 2H), 2.76–2.82 (m, 2H), 3.22 (d, *J* = 12.9 Hz, 2H), 3.39 (d, *J* = 13.2 Hz, 2H), 3.90 (dd, *J* = 4.2, 9.3 Hz, 2H), 6.58 (s, 2H), 7.06–7.11 (m, 8H), 7.42 (d, *J* = 8.4 Hz, 4H), 7.53 ppm (d, *J* = 8.1 Hz, 4H); ¹³C NMR (75.5 MHz, CDCl₃): δ = 20.37, 20.91, 20.96, 23.95, 29.60, 54.97, 57.50, 71.20, 78.56, 124.10, 125.67, 127.08, 128.66, 128.81, 128.90, 135.71, 135.88, 143.79, 144.32, 152.65 ppm; FTIR (KBr): $\tilde{\nu}$ = 3325, 3023, 2920, 2869, 1614, 1509, 1479, 1447, 1098 cm⁻¹; ESI-MS: *m/z*: 695.4 [*M*⁺ + H]; elemental analysis calcd (%) for C₄₇H₅₄N₂O₃: C 81.23, H 7.83, N 4.03; found: C 80.80, H 8.10, N 3.80.

(S,S)-2,6-Bis[2-(hydroxydi-3-tolylmethyl)pyrrolidin-1-ylmethyl]-4-methylphenol (4c): Following a similar procedure to that described for the preparation of **4a**, the reaction of 2,6-bis(chloromethyl)-4-methylphenol with (S)-di-3-tolyl(pyrrolidin-2-yl)methanol afforded **4c** in 48% yield. $[\alpha]_D^{20} = +86.4$ ($c = 1.03$ in CH_2Cl_2); ^1H NMR (300 MHz, CDCl_3): $\delta = 1.56\text{--}1.83$ (m, 6H), 1.96–2.03 (m, 2H), 2.14 (s, 3H), 2.28 (s, 3H), 2.33 (s, 3H), 2.35–2.42 (m, 2H), 2.80–2.86 (m, 2H), 3.19 (s, 4H), 3.89 (dd, $J = 4.5$, 9.6 Hz, 2H), 6.56 (s, 2H), 6.90 (d, $J = 7.2$ Hz, 2H), 7.00 (d, $J = 7.2$ Hz, 2H), 7.12–7.22 (m, 4H), 7.33–7.41 (m, 6H), 7.52 ppm (s, 2H); ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 20.42$, 21.68, 21.72, 24.10, 29.66, 55.13, 57.27, 71.50, 78.69, 122.82, 122.97, 123.96, 126.38, 126.59, 127.03, 127.12, 127.26, 127.79, 127.98, 128.73, 137.59, 137.65, 146.33, 146.95, 152.49 ppm; FTIR (KBr): $\tilde{\nu} = 3305$, 2948, 2919, 2868, 1604, 1304, 1149, 1091, 1000 cm^{-1} ; ESI-MS: m/z : 695.5 $[M^+ + H]$; elemental analysis calcd (%) for $\text{C}_{47}\text{H}_{54}\text{N}_2\text{O}_3$: C 81.23, H 7.83, N 4.03; found: C 80.89, H 8.15, N 3.72.

(S,S)-2,6-Bis[2-(hydroxybis(4-methoxyphenyl)methyl)pyrrolidin-1-ylmethyl]-4-methylphenol (4d): Following a similar procedure to that described for the preparation of **4a**, the reaction of 2,6-bis(chloromethyl)-4-methylphenol with (S)-bis(4-methoxyphenyl)(pyrrolidin-2-yl)methanol afforded **4d** in 63% yield. $[\alpha]_D^{20} = +36.0$ ($c = 1.87$ in CH_2Cl_2); ^1H NMR (300 MHz, CDCl_3): $\delta = 1.27\text{--}1.66$ (m, 6H), 1.80–1.87 (m, 2H), 2.01 (s, 3H), 2.17–2.25 (m, 2H), 2.61–2.67 (m, 2H), 3.08 (d, $J = 13.8$ Hz, 2H), 3.36 (d, $J = 12.9$ Hz, 2H), 3.58 (s, 6H), 3.62 (s, 6H), 3.71 (dd, $J = 4.5$, 9.3 Hz, 2H), 6.47 (s, 2H), 6.66–6.72 (m, 8H), 7.42 (d, $J = 8.7$ Hz, 4H), 7.55 ppm (d, $J = 8.7$ Hz, 4H); ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 20.38$, 23.96, 29.55, 54.97, 55.05, 55.12, 57.90, 71.27, 78.38, 113.22, 113.44, 124.11, 127.07, 128.86, 139.00, 139.50, 152.75, 157.84, 158.00 ppm; ESI-MS: m/z : 759.4 $[M^+ + H]$; FTIR (KBr): $\tilde{\nu} = 3398$, 2952, 2835, 1608, 1510, 1248, 1177, 1035 cm^{-1} ; elemental analysis calcd (%) for $\text{C}_{47}\text{H}_{54}\text{N}_2\text{O}_3$: C 74.38, H 7.17, N 3.69; found: C 74.26, H 7.10, N 3.29.

(S,S)-2,6-Bis[2-(hydroxy(biphenyl-4-yl)methyl)pyrrolidin-1-ylmethyl]-4-methylphenol (4e): Following a similar procedure to that described for the preparation of **4a**, the reaction of 2,6-bis(chloromethyl)-4-methylphenol with (S)-biphenyl-4-yl(pyrrolidin-2-yl)methanol afforded **4e** in 80% yield. $[\alpha]_D^{20} = +93.3$ ($c = 0.88$ in CH_2Cl_2) [Lit.: 151] $[\alpha]_D^{25} = +86.5$ ($c = 1.58$ in CH_2Cl_2); ^1H NMR (300 MHz, CDCl_3): $\delta = 1.50\text{--}1.64$ (m, 4H), 1.83–1.86 (m, 2H), 2.00–2.05 (m, 2H), 2.13 (s, 3H), 2.38–2.43 (m, 2H), 2.79–2.84 (m, 2H), 3.24 (d, $J = 12.6$ Hz, 2H), 3.58 (d, $J = 12.6$ Hz, 2H), 4.02 (dd, $J = 4.5$, 9.6 Hz, 2H), 6.60 (s, 2H), 7.24–7.43 (m, 14H), 7.52–7.59 (m, 14H), 7.67 (d, $J = 8.4$ Hz, 4H), 7.82 ppm (d, $J = 8.7$ Hz, 4H); ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 20.38$, 23.84, 29.62, 54.97, 57.86, 71.19, 78.68, 124.02, 126.34, 126.42, 126.76, 126.99, 127.07, 127.20, 128.60, 128.67, 129.05, 139.15, 139.32, 140.59, 140.74, 145.50, 146.17, 152.79 ppm; FTIR (KBr): $\tilde{\nu} = 3330$, 3028, 2962, 2870, 1600, 1485, 1403, 1007 cm^{-1} ; ESI-MS: m/z : 943.5 $[M^+ + H]$.

(S,S)-2,6-Bis[2-(hydroxybis(4-trifluoromethylphenyl)methyl)pyrrolidin-1-ylmethyl]-4-methylphenol (4f): Following a similar procedure to that described for the preparation of **4a**, the reaction of 2,6-bis(chloromethyl)-4-methylphenol with (S)-bis(4-trifluoromethylphenyl)(pyrrolidin-2-yl)methanol afforded **4f** in 77% yield. $[\alpha]_D^{20} = +35.3$ ($c = 1.02$ in CH_2Cl_2); ^1H NMR (300 MHz, CDCl_3): $\delta = 1.54\text{--}1.73$ (m, 6H), 1.95–2.02 (m, 2H), 2.14 (s, 3H), 2.39–2.42 (m, 2H), 2.79–2.80 (m, 2H), 3.18 (d, $J = 12.6$ Hz, 2H), 3.45 (d, $J = 12.6$ Hz, 2H), 4.01 (dd, $J = 3.6$, 9.4 Hz, 2H), 6.57 (s, 2H), 7.58–7.60 (m, 8H), 7.71 (d, $J = 8.1$ Hz, 4H), 7.87 ppm (d, $J = 7.8$ Hz, 4H); ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 14.12$, 20.28, 22.69, 23.65, 29.36, 29.54, 29.66, 29.70, 30.27, 31.92, 54.92, 57.96, 70.85, 78.51, 122.21, 122.26, 123.58, 125.21, 125.26, 125.34, 125.39, 125.54, 125.82, 125.86, 126.10, 126.37, 127.59, 128.77, 128.95, 129.09, 129.20, 129.39, 129.63, 129.82, 149.67, 150.45, 152.70 ppm; ^{19}F NMR (282 MHz, CDCl_3): $\delta = -62.87$, -62.81 ppm; FTIR (KBr): $\tilde{\nu} = 3340$, 2973, 2877, 2828, 1617, 1482, 1416, 1326, 1166, 1125, 1070, 1017 cm^{-1} ; ESI-MS: m/z : 911.3 $[M^+ + H]$; elemental analysis calcd (%) for $\text{C}_{47}\text{H}_{42}\text{F}_{12}\text{N}_2\text{O}_3$: C 61.98, H 4.65, N 3.08; found: C 62.02, H 4.74, N 2.83.

(S,S)-2,6-Bis[2-(hydroxybis[3,5-bis(trifluoromethyl)phenyl]methyl)pyrrolidin-1-ylmethyl]-4-methylphenol (4g): Following a similar procedure to that described for the preparation of **4a**, the reaction of 2,6-bis(chloromethyl)-4-methylphenol with (S)-bis[3,5-bis(trifluoromethyl)phenyl](pyrrolidin-2-yl)methanol afforded **4g** in 81% yield. $[\alpha]_D^{20} = +43.6$ ($c = 1.04$ in

CH_2Cl_2); ^1H NMR (300 MHz, CDCl_3): $\delta = 1.62\text{--}1.77$ (m, 6H), 1.90–1.99 (m, 2H), 2.11 (s, 3H), 2.44–2.52 (m, 2H), 2.79–2.84 (m, 2H), 3.16 (d, $J = 12.6$ Hz, 2H), 3.24 (d, $J = 12.6$ Hz, 2H), 4.00 (dd, $J = 3.6$, 9.4 Hz, 2H), 6.55 (s, 2H), 7.76 (s, 2H), 7.79 (s, 2H), 8.07 (s, 4H), 8.18 ppm (s, 4H); ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 20.10$, 23.26, 29.26, 54.90, 57.91, 71.39, 77.87, 117.78, 121.30, 121.39, 121.43, 121.54, 123.18, 125.01, 125.05, 125.68, 126.10, 128.07, 128.63, 128.67, 129.63, 131.18, 131.26, 131.62, 131.70, 132.06, 132.14, 132.50, 132.59, 147.63, 148.85, 152.78 ppm; ^{19}F NMR (282 MHz, CDCl_3): $\delta = -63.23$, -63.20 ppm; FTIR (KBr): $\tilde{\nu} = 3320$, 3103, 2979, 2882, 1626, 1484, 1371, 1279, 1172, 1134 cm^{-1} ; ESI-MS: m/z : 1183.3 $[M^+ + H]$; elemental analysis calcd (%) for $\text{C}_{51}\text{H}_{38}\text{F}_{24}\text{N}_2\text{O}_3$: C 51.79, H 3.24, N 2.37; found: C 51.95, H 3.29, N 2.18.

(S,S)-2,6-Bis[2-(hydroxybis(4-chlorophenyl)methyl)pyrrolidin-1-ylmethyl]-4-methylphenol (4h): Following a similar procedure to that described for the preparation of **4a**, the reaction of 2,6-bis(chloromethyl)-4-methylphenol with (S)-bis(4-chlorophenyl)(pyrrolidin-2-yl)methanol afforded **4h** in 90% yield. $[\alpha]_D^{20} = +50.4$ ($c = 1.03$ in CH_2Cl_2); ^1H NMR (300 MHz, CDCl_3): $\delta = 1.43\text{--}1.75$ (m, 6H), 1.94–2.01 (m, 2H), 2.15 (s, 3H), 2.33–2.42 (m, 2H), 2.76–2.82 (m, 2H), 3.20 (d, $J = 12.6$ Hz, 2H), 3.51 (d, $J = 12.6$ Hz, 2H), 3.87 (dd, $J = 4.2$, 9.0 Hz, 2H), 6.60 (s, 2H), 7.26–7.29 (m, 8H), 7.45 (d, $J = 8.4$ Hz, 4H), 7.59 ppm (d, $J = 8.4$ Hz, 4H); ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 20.36$, 23.82, 29.52, 54.96, 58.07, 70.97, 78.30, 123.76, 127.29, 127.42, 128.25, 128.43, 128.96, 132.47, 132.68, 144.61, 145.24, 152.68 ppm; FTIR (KBr): $\tilde{\nu} = 3326$, 2952, 2870, 1488, 1403, 1094, 1013 cm^{-1} ; ESI-MS: m/z : 777.2 $[M^+ + H]$; elemental analysis calcd (%) for $\text{C}_{43}\text{H}_{42}\text{Cl}_4\text{N}_2\text{O}_3$: C 66.50, H 5.45, N 3.61; found: C 66.43, H 5.62, N 3.24.

(S,S)-2,6-Bis[2-(hydroxydiphenylmethyl)pyrrolidin-1-ylmethyl]-4-nitrophenol (4i): Following a similar procedure to that described for the preparation of **4a**, the reaction of 2,6-bis(bromomethyl)-4-nitrophenol with (S)-diphenyl(pyrrolidin-2-yl)methanol afforded **4i** in 74% yield. $[\alpha]_D^{20} = +68.6$ ($c = 1.02$ in CH_2Cl_2); ^1H NMR (300 MHz, CDCl_3): $\delta = 1.60\text{--}1.71$ (m, 4H), 1.82–1.89 (m, 2H), 2.01–2.12 (m, 2H), 2.34–2.42 (m, 2H), 2.82–2.88 (m, 2H), 3.31 (d, $J = 13.5$ Hz, 2H), 3.39 (d, $J = 13.5$ Hz, 2H), 4.00 (dd, $J = 4.8$, 9.6 Hz, 2H), 7.10–7.36 (m, 12H), 7.56 (d, $J = 7.5$ Hz, 4H), 7.67 (d, $J = 7.8$ Hz, 4H), 7.70 ppm (s, 2H); ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 24.10$, 29.56, 55.24, 57.18, 71.21, 79.00, 123.86, 124.59, 125.91, 125.95, 126.68, 126.73, 128.17, 128.22, 139.01, 146.26, 146.42, 162.02 ppm; FTIR (KBr): $\tilde{\nu} = 3380$, 3058, 2958, 2872, 1595, 1492, 1466, 1449, 1334, 1290 cm^{-1} ; ESI-MS: m/z : 670.3 $[M^+ + H]$; elemental analysis calcd (%) for $\text{C}_{42}\text{H}_{43}\text{N}_3\text{O}_3$: C 75.31, H 6.47, N 6.27; found: C 75.09, H 6.74, N 5.82.

(S,S)-2,6-Bis[2-(hydroxydiphenylmethyl)pyrrolidin-1-ylmethyl]-4-tert-butylphenol (4j): Following a similar procedure to that described for the preparation of **4a**, the reaction of 2,6-bis(bromomethyl)-4-tert-butylphenol with (S)-diphenyl(pyrrolidin-2-yl)methanol afforded **4j** in 74% yield. $[\alpha]_D^{20} = +56.6$ ($c = 1.03$ in CH_2Cl_2); ^1H NMR (300 MHz, CDCl_3): $\delta = 1.22$ (s, 9H), 1.48–1.64 (m, 4H), 1.75–1.82 (m, 2H), 1.97–2.04 (m, 2H), 2.35–2.44 (m, 2H), 2.76–2.81 (m, 2H), 3.25 (d, $J = 12.9$ Hz, 2H), 3.40 (d, $J = 12.6$ Hz, 2H), 3.97 (dd, $J = 4.8$, 9.3 Hz, 2H), 6.00 (s, 2H), 7.09–7.21 (m, 4H), 7.26–7.32 (m, 8H), 7.55 (d, $J = 8.4$ Hz, 4H), 7.69 ppm (d, $J = 7.2$ Hz, 4H); ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 24.10$, 29.62, 31.56, 33.78, 55.03, 57.99, 71.33, 78.88, 123.47, 125.33, 125.90, 125.93, 126.38, 126.61, 127.98, 128.23, 140.80, 146.37, 147.04, 152.48 ppm; FTIR (KBr): $\tilde{\nu} = 3350$, 3058, 2961, 2870, 1589, 1485, 1449, 1303, 1214 cm^{-1} ; ESI-MS: m/z : 681.4 $[M^+ + H]$; elemental analysis calcd (%) for $\text{C}_{46}\text{H}_{52}\text{N}_2\text{O}_3$: C 81.14, H 7.70, N 4.11; found: C 80.98, H 7.72, N 3.90.

(S,S)-1,3-Bis[2-(hydroxydiphenylmethyl)pyrrolidin-1-ylmethyl]-5-methylbenzene (7): Following a similar procedure to that described for the preparation of **4a**, the reaction of 1,3-bis(bromomethyl)-5-methylbenzene with (S)-diphenyl(pyrrolidin-2-yl)methanol afforded **7** in 83% yield. $[\alpha]_D^{20} = +115.3$ ($c = 1.02$ in CH_2Cl_2); ^1H NMR (300 MHz, CDCl_3): $\delta = 1.63\text{--}1.80$ (m, 6H), 1.94–2.01 (m, 2H), 2.23 (s, 3H), 2.30–2.35 (m, 2H), 2.86–2.91 (m, 2H), 2.95 (d, $J = 12.3$ Hz, 2H), 3.17 (d, $J = 12.9$ Hz, 2H), 3.98 (dd, $J = 4.5$, 9.3 Hz, 2H), 5.00 (s, 2H), 6.60–6.64 (d, $J = 12.0$ Hz, 2H), 7.08–7.34 (m, 12H), 7.61 (d, $J = 7.5$ Hz, 4H), 7.77 ppm (d, $J = 8.4$ Hz, 4H); ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 21.25$, 24.15, 29.79, 55.48, 60.41, 70.58, 77.86, 125.53, 125.63, 125.76, 126.20, 126.34, 127.90, 128.06, 128.14, 137.36, 139.40, 146.68, 148.07 ppm; FTIR (KBr): $\tilde{\nu} = 3280$, 3059, 2942,

2793, 1606, 1489, 1449, 1391, 1106 cm⁻¹; ESI-MS: m/z : 639.3 [$M^+ + H$]; elemental analysis calcd (%) for C₄₃H₄₆N₂O₂: C 82.92, H 7.44, N 4.50; found: C 82.83, H 7.38, N 4.30.

(S,S)-2-Methoxy-1,3-bis[2-(hydroxydiphenylmethyl)pyrrolidin-1-ylmethyl]-5-methylbenzene (8): Following a similar procedure to that described for the preparation of **4a**, the reaction of 1-methoxy-2,6-bis(bromomethyl)-4-methylbenzene with (S)-diphenyl(pyrrolidin-2-yl)methanol afforded **8** in 81% yield. [α]_D²⁰ = +9.0 (c = 1.00 in CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃): δ = 1.50–1.72 (m, 6H), 1.84–1.91 (m, 2H), 2.26 (s, 3H), 2.27–2.36 (m, 2H), 2.80–2.87 (m, 2H), 3.15 (s, 3H), 3.18 (s, 4H), 3.94 (dd, J = 3.3, 8.7 Hz, 2H), 5.22 (s, 2H), 6.82 (s, 2H), 7.03–7.29 (m, 12H), 7.54 (d, J = 8.7 Hz, 4H), 7.70 ppm (d, J = 8.4 Hz, 4H); ¹³C NMR (75.5 MHz, CDCl₃): δ = 20.99, 23.57, 29.68, 54.45, 55.09, 61.23, 70.51, 77.47, 125.53, 125.67, 126.08, 126.26, 127.89, 128.03, 129.14, 131.89, 132.96, 146.83, 148.09, 154.06 ppm; FTIR (KBr): $\tilde{\nu}$ = 3343, 3058, 2945, 2872, 1597, 1491, 1449, 1381, 1212 cm⁻¹; ESI-MS: m/z : 653.4 [$M^+ + H$]; elemental analysis calcd (%) for C₄₄H₄₈N₂O₃: C 80.95, H 7.41, N 4.29; found: C 80.91, H 7.85, N 3.98.

A typical procedure for the copolymerization of cyclohexene oxide and CO₂ in toluene: In a glove box, a solution of diethylzinc (0.10 mL, 1.0 M in hexane, 0.10 mmol) was added to a solution of **4a** (0.032 g, 0.05 mmol) in toluene (1.0 mL). The mixture was stirred at room temperature for 30 min. A solution of ethanol (0.02 mL, 1.0 M in toluene, 0.02 mmol) was then added to the mixture. The solution was stirred at room temperature for an additional 15 min. This solution was transferred into an autoclave and then cyclohexene oxide (0.1 mL, 1.0 mmol) was introduced. The vessel was pressurized to 30 atm with carbon dioxide. After stirring at 60°C for the necessary reaction time, the mixture was cooled to ambient temperature and the CO₂ pressure was slowly released. The mixture was diluted with CH₂Cl₂ (30 mL) and washed with aqueous HCl (1 M, 2 × 10 mL) and brine (2 × 10 mL). The organic layer was dried with Na₂SO₄ and concentrated to 3 mL by vacuum evaporation. The copolymer was precipitated by adding MeOH (30 mL), collected by filtration, and dried in vacuo to a constant weight.

A typical procedure for the copolymerization of cyclohexene oxide and CO₂ at atmospheric pressure: In a Schlenk tube, a solution of diethylzinc (0.10 mL, 1.0 M in hexane, 0.10 mmol) was added to a solution of **4a** (0.032 g, 0.05 mmol) in toluene (1.0 mL) under argon. The mixture was stirred at room temperature for 30 min. Then a solution of ethanol (0.02 mL, 1.0 M in toluene, 0.02 mmol) was added to the mixture. The solution was stirred at room temperature for an additional 15 min and then cyclohexene oxide (0.1 mL, 1.0 mmol) was introduced. Carbon dioxide was bubbled into the solution whilst stirring at 60°C for the necessary reaction time. Copolymer work up was carried out following the same procedure as that described above.

A typical procedure for the copolymerization of cyclohexene oxide and CO₂ in neat CHO: In a glove box, a solution of diethylzinc (0.10 mL, 1.0 M in hexane, 0.10 mmol) was added to a solution of **4a** (0.032 g, 0.05 mmol) in CH₂Cl₂ (1.0 mL). The mixture was stirred at room temperature for 30 min. Following the addition of ethanol (0.05 mL, 1.0 M in toluene, 0.05 mmol), the solution was stirred at room temperature for an additional 15 min and then the solvent was removed in vacuo. The resulting white residue was dissolved in cyclohexene oxide (1.0 mL, 10.0 mmol). This solution was transferred into an autoclave. The vessel was pressurized to 20 atm with carbon dioxide. After stirring at the desired temperature for the specified reaction time, the mixture was cooled to ambient temperature and the CO₂ pressure was slowly released. A small sample of the crude material was removed for characterization, the product was dissolved in methylene chloride (5 mL), and the polymer was precipitated from methanol (50 mL). The product was then dried in vacuo to constant weight.

Preparation and X-ray crystal structural analysis of complex 9: In a glove box, a solution of diethylzinc (1.0 mL, 1.0 M in hexane, 1.0 mmol) was added to a solution of **4a** (0.320 g, 0.5 mmol) in toluene (5.0 mL). The mixture was stirred at room temperature for 30 min. *p*-Nitrophenol (0.0696 g, 0.5 mmol) was added to this solution and some solid was precipitated. THF (5.0 mL) was added and the resulting homogeneous solution was stirred for an additional 15 min. The solvent was concentrated

under reduced pressure, filtered, and left to stand at room temperature for several days before the zinc complex **9** was obtained as pale yellow block crystals. The crystals were vacuum-dried before characterization. Yield: 50%. ¹H NMR (300 MHz, CDCl₃): δ = 1.04–1.54 (m, 6H), 1.70–1.90 (m, 10H), 2.11 (s, 3H), 2.36 (s, 3H, toluene-CH₃), 2.40–2.70 (m, 4H), 3.66–3.91 (m, 14H), 6.67 (s, 2H), 7.01–7.08 (m, 4H), 7.11–7.28 (m, 13H, of which 5H can be assigned to the aromatic protons of toluene), 7.81 (s, J = 6.3 Hz, 4H), 7.99 (s, J = 7.5 Hz, 4H), 8.34–8.37 (m, 2H), 8.78 ppm (s, 2H); ¹³C NMR (75.5 MHz, CDCl₃): δ = 19.71, 20.02, 21.44 (toluene-CH₃), 25.25, 28.72, 55.65, 60.38, 69.20, 72.34, 76.57, 120.41, 124.48, 125.15, 125.28, 125.52, 125.59, 125.81, 126.50, 127.54, 127.58, 128.21, 129.02, 131.11, 137.79, 153.10, 153.30, 156.50, 173.49 ppm; FTIR (KBr): $\tilde{\nu}$ = 2976, 2876, 1584, 1493, 1475, 1446, 1298, 1166, 1109, 1063, 864, 707, 698 cm⁻¹; elemental analysis calcd (%) for **9**·toluene (C₆₄H₇₁N₃O₈Zn₂): C 67.37, H 6.27, N 3.68; found: C 66.62, H 6.61, N 3.68.

A single crystal suitable for X-ray analysis was picked out from the mother liquor and sealed in a capillary tube. The X-ray diffraction data were collected with a Bruker Smart APEX diffractometer at 20°C by using MoK α radiation (λ = 0.71069 Å) with a ω –2 θ scan mode. Crystal data: C₆₉H₈₇N₃O₁₁Zn₂, M_r = 1265.16, trigonal, space group $P3_2$, a = 17.6424(6), b = 17.6424(6), c = 19.4741(10) Å, α = 90, β = 90, γ = 120°, V = 5249.3(4) Å³, Z = 3, ρ_{calcd} = 1.201 g cm⁻³, $F(000)$ = 2010, $\mu(\text{MoK}\alpha)$ = 0.742 mm⁻¹. Data collection and refinement: Diffraction data measured to $2\theta_{\text{max}}$ = 2.66–53.98°. A total of 12664 unique reflections with positive intensities were recorded. The final refinement, based on F^2 , converged at R = 0.0697 (wR_2 = 0.1814) for 3284 observations with $I_0 > 2\sigma(I_0)$ and R = 0.1059 (wR_2 = 0.1983) for all data. At convergence, S = 0.734 and $\Delta\rho$ = –0.323 e Å⁻³. A detailed list of the crystal data and data collection parameters is given in the Supporting Information.

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- [1] For comprehensive reviews on the uses of CO₂, see: a) H. Arakawa, M. Areata, J. N. Armor, M. A. Barteau, E. J. Beckman, A. T. Bell, J. E. Bercaw, C. Creutz, E. Dinjus, D. A. Dixon, K. Domen, D. L. DuBois, J. Eckert, E. Fujita, D. H. Gibson, W. A. Goddard, D. W. Goodman, J. Keller, G. J. Kubas, H. H. Kung, J. E. Lyons, L. E. Manzer, T. J. Marks, K. Morokuma, K. M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielsen, W. M. H. Sachtler, L. D. Schmidt, A. Sen, G. A. Somorjai, P. C. Stair, B. R. Stults, W. Tumas, *Chem. Rev.* **2001**, *101*, 953–996; b) W. Leitner, *Angew. Chem.* **1995**, *107*, 2391–2405; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2207–2221; c) G. Musie, M. Wei, B. Subramaniam, D. H. Busch, *Coord. Chem. Rev.* **2001**, *219*, 789–820; d) P. G. Jessop, T. Ikariya, R. Noyori, *Chem. Rev.* **1995**, *95*, 259–272; e) D. H. Gibson, *Chem. Rev.* **1996**, *96*, 2063–2095; f) A. I. Cooper, *J. Mater. Chem.* **2000**, *10*, 207–234.
- [2] S. Inoue, H. Koinuma, T. Tsuruta, *J. Polym. Sci. Part B: Polym. Lett.* **1969**, *7*, 287–292.
- [3] For reviews on epoxide/CO₂ copolymerization reactions, see: a) D. J. Darensbourg, M. W. Holtcamp, *Coord. Chem. Rev.* **1996**, *153*, 155–174; b) M. S. Super, E. J. Beckman, *Trends Polym. Sci.* **1997**, *5*, 236–240; c) A. Rokicki, W. Kuran, *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **1981**, *C21*, 135–186; d) G. W. Coates, D. R. Moore, *Angew. Chem.* **2004**, *116*, 6784–6806; *Angew. Chem. Int. Ed.* **2004**, *43*, 6618–6639; e) H. Sugimoto, S. Inoue, *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42*, 5561–5573.
- [4] For the properties of these polymers that make them attractive as materials, see: a) M. Okada, *Prog. Polym. Sci.* **2002**, *27*, 87–133; b) S. Y. Yang, X. G. Fang, L. B. Chen, *Polym. Adv. Technol.* **1996**, *7*, 605–608.

- [5] For examples of heterogeneous catalysis of epoxide/CO₂ copolymerization reactions, see: a) J. H. Jung, M. Ree, T. Chang, *J. Polym. Sci. Part A: Polym. Chem.* **1999**, *37*, 1863–1876; b) J. H. Jung, M. Ree, T. Chang, *J. Polym. Sci. Part A: Polym. Chem.* **1999**, *37*, 3329–3336; c) C. S. Tan, T. J. Hsu, *Macromolecules* **1997**, *30*, 3147–3150; d) B. Y. Liu, X. J. Zhao, X. H. Wang, F. S. Wang, *J. Polym. Sci. Part A: Polym. Chem.* **2001**, *39*, 2751–2754.
- [6] H. Sugimoto, H. Ohshima, S. Inoue, *J. Polym. Sci. Part A: Polym. Chem.* **2003**, *41*, 3549–3555.
- [7] For use of supercritical CO₂ as both reactant and solvent in metal-complex-catalyzed copolymerization of CO₂ with epoxides, see: a) M. S. Super, E. Berluche, C. Costello, E. J. Beckman, *Macromolecules* **1997**, *30*, 368–372; b) T. Sarbu, J. Beckman, *Macromolecules* **1999**, *32*, 6904–6912; c) T. Sarbu, T. Styranec, E. J. Beckman, *Nature* **2000**, *405*, 165–168; d) S. Mang, A. I. Cooper, M. E. Colclough, N. Chauhan, A. B. Holmes, *Macromolecules* **2000**, *33*, 303–308; e) L. M. Stamp, S. A. Mang, A. B. Holmes, K. A. Knights, Y. R. de Minuel, I. F. MaConvey, *Chem. Commun.* **2001**, 2502–2503.
- [8] For examples of CO₂/epoxide copolymerization with homogeneous metal complexes other than zinc, see: a) Z. Qin, C. M. Thomas, S. Lee, G. W. Coates, *Angew. Chem.* **2003**, *115*, 5642–5645; *Angew. Chem. Int. Ed.* **2003**, *42*, 5484–5487 and references therein; b) X.-B. Lu, Y. Wang, *Angew. Chem.* **2004**, *116*, 3658–3661; *Angew. Chem. Int. Ed.* **2004**, *43*, 3574–3577; c) W. J. Kruper, D. V. Dellar, *J. Org. Chem.* **1995**, *60*, 725–727; d) D. J. Darensbourg, J. C. Yarbrough, *J. Am. Chem. Soc.* **2002**, *124*, 6335–6342; e) D. J. Darensbourg, J. C. Yarbrough, C. Ortiz, C. C. Fang, *J. Am. Chem. Soc.* **2003**, *125*, 7586–7591; f) D. J. Darensbourg, S. A. Niezgoda, J. D. Draper, J. H. Reibenspies, *J. Am. Chem. Soc.* **1998**, *120*, 4690–4698; g) D. J. Darensbourg, J. R. Wildeson, S. J. Lewis, J. C. Yarbrough, *J. Am. Chem. Soc.* **2002**, *124*, 7075–7083; h) M. H. Chisholm, Z. Zhou, *J. Am. Chem. Soc.* **2004**, *126*, 11030–11039; see also references [7d,e].
- [9] a) D. J. Darensbourg, M. W. Holtcamp, *Macromolecules* **1995**, *28*, 7577–7579; b) D. J. Darensbourg, M. W. Holtcamp, G. E. Struck, M. S. Zimmer, S. A. Niezgoda, P. Rainey, J. B. Robertson, J. D. Draper, J. H. Reibenspies, *J. Am. Chem. Soc.* **1999**, *121*, 107–116; c) D. J. Darensbourg, M. S. Zimmer, P. Rainey, D. L. Larkins, *Inorg. Chem.* **2000**, *39*, 1578–1585; d) D. J. Darensbourg, J. R. Wildeson, J. C. Yarbrough, J. H. Reibenspies, *J. Am. Chem. Soc.* **2000**, *122*, 12487–12496.
- [10] D. J. Darensbourg, P. Rainey, J. Yarbrough, *Inorg. Chem.* **2001**, *40*, 986–993.
- [11] a) M. Cheng, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **1998**, *120*, 11018–11019; b) M. Cheng, D. R. Moor, J. J. Reczek, B. M. Chamberlain, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2001**, *123*, 8738–8749; c) D. R. Moor, M. Cheng, E. B. Lobkovsky, G. W. Coates, *Angew. Chem.* **2002**, *114*, 2711–2714; *Angew. Chem. Int. Ed.* **2002**, *41*, 2599–2602; d) S. D. Allen, D. R. Moore, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2002**, *124*, 14284–14285; e) D. R. Moor, M. Cheng, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2003**, *125*, 11911–11924; f) C. M. Byrne, S. D. Allen, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2004**, *126*, 11404–11405.
- [12] For zinc β -diiminate catalyzed copolymerization of CO₂ and epoxides with ethyl sulfinate as the initiating group, see: a) R. Eberhardt, M. Allmendinger, G. A. Luinstra, B. Rieger, *Organometallics* **2003**, *22*, 211–214; b) R. Eberhardt, M. Allmendinger, M. Zintl, C. Troll, G. A. Luinstra, B. Rieger, *Macromol. Chem. Phys.* **2004**, *205*, 42–47.
- [13] a) H. S. Kim, J. J. Kim, B. G. Lee, O. S. Jung, H. G. Jang, S. O. Kang, *Angew. Chem.* **2000**, *112*, 4262–4264; *Angew. Chem. Int. Ed.* **2000**, *39*, 4096–4098; b) H. S. Kim, J. J. Kim, S. D. Lee, M. S. Lah, D. Moon, H. G. Jang, *Chem. Eur. J.* **2003**, *9*, 678–686.
- [14] a) K. Nozaki, K. Nakano, T. Hiyama, *J. Am. Chem. Soc.* **1999**, *121*, 11008–11009; b) K. Nakano, K. Nozaki, T. Hiyama, *J. Am. Chem. Soc.* **2003**, *125*, 5501–5510; c) K. Nakano, K. Nozaki, T. Hiyama, *Macromolecules* **2001**, *34*, 6325–6332.
- [15] a) B. M. Trost, H. Ito, *J. Am. Chem. Soc.* **2000**, *122*, 12003–12004; b) B. M. Trost, H. Ito, E. R. Silcoff, *J. Am. Chem. Soc.* **2001**, *123*, 3367–3368; c) B. M. Trost, E. R. Silcoff, H. Ito, *Org. Lett.* **2001**, *3*, 2497–2500; d) B. M. Trost, V. S. C. Yeh, *Org. Lett.* **2002**, *4*, 3513–3516; e) B. M. Trost, V. S. C. Yeh, *Angew. Chem.* **2002**, *114*, 889–891; *Angew. Chem. Int. Ed.* **2002**, *41*, 861–863; f) B. M. Trost, V. S. C. Yeh, H. Ito, N. Bremeyer, *Org. Lett.* **2002**, *4*, 2621–2623; g) B. M. Trost, L. R. Terrell, *J. Am. Chem. Soc.* **2003**, *125*, 338–339; h) B. M. Trost, T. Mino, *J. Am. Chem. Soc.* **2003**, *125*, 2410–2411; i) B. M. Trost, A. Fettes, B. T. Shireman, *J. Am. Chem. Soc.* **2004**, *126*, 2660–2661.
- [16] S. D. Hanton, *Chem. Rev.* **2001**, *101*, 527–570.
- [17] Trace amounts of oxygen in the reaction system could oxidize the ethyl zinc species to ethyl peroxide, which might be reduced to ethoxy zinc species, see: a) J. Lewinski, Z. Ochal, E. Bojarski, E. Tratkiewicz, I. Justyniak, J. Lipkowski, *Angew. Chem.* **2003**, *115*, 4791–4794; *Angew. Chem. Int. Ed.* **2003**, *42*, 4643–4646; b) D. Enders, J. Zhu, L. Kramps, *Liebigs Ann./Recl.* **1997**, 1101–1113.
- [18] D. J. Darensbourg, S. J. Lewis, J. L. Rodgers, J. C. Yarbrough, *Inorg. Chem.* **2003**, *42*, 581–589.
- [19] For examples of solvent-free catalysis, see: a) M. Tokunaga, J. F. Larrow, F. Kakiuchi, E. N. Jacobsen, *Science* **1997**, *277*, 936–938; b) N. K. Anand, E. M. Carreira, *J. Am. Chem. Soc.* **2001**, *123*, 9687–9688; c) T. Shibata, N. Tashida, K. Takagi, *J. Org. Chem.* **2002**, *67*, 7446–7450; d) J. Long, J. Hu, X. Shen, B. Ji, K. Ding, *J. Am. Chem. Soc.* **2002**, *124*, 10–11; e) Y. Yuan, X. Zhang, K. Ding, *Angew. Chem.* **2003**, *115*, 5636–5638; *Angew. Chem. Int. Ed.* **2003**, *42*, 5478–5480.
- [20] CCDC-255984 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [21] For examples of intramolecular homodinuclear zinc complexes with two alkoxo bridges, see: a) H. Adams, N. A. Bailey, P. Bertrand, C. O. R. de Barbarin, D. E. Fenton, S. Gou, *J. Chem. Soc. Dalton Trans.* **1995**, 275–279; b) C. Bazzicalupi, A. Bencini, A. Bianchi, V. Fusi, L. Mazzanti, P. Paoletti, B. Valtancoli, *Inorg. Chem.* **1995**, *34*, 3003–3010.

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