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# Catalytic Coupling of Cyclopentene Oxide and $CO_2$ Utilizing Bifunctional (salen)Co(III) and (salen)Cr(III) Catalysts: Comparative Processes Involving Binary (salen)Cr(III) Analogs

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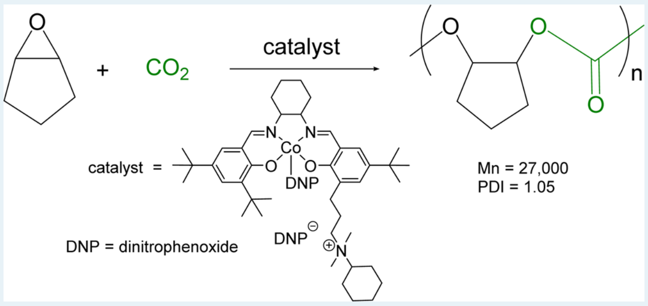
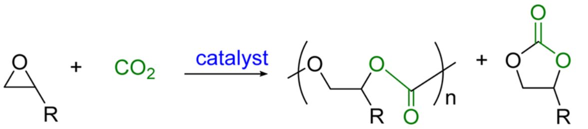


**ABSTRACT:** Previously, the polycarbonate produced from the alternating copolymerization of cyclopentene oxide and carbon dioxide has been demonstrated to readily be recyclable to its monomers, hence affording a sustainable route to the production of this polymeric material. This, in turn, necessitates the development of effective synthetic methods for this copolymer. Coupling reactions of the alicyclic epoxides, cyclohexene oxide (CHO) and cyclopentene oxide (CPO), with $CO_2$ were shown to provide grossly different product selectivities utilizing *binary* (salen)CrX/PPNX catalyst systems. That is, whereas the coupling of CHO/$CO_2$ affords >99% selectivity for completely alternating copolymers, under identical conditions, CPO/$CO_2$ yields >99% selectivity for *cis*-cyclopentene carbonate. By way of contrast, employing *bifunctional* (*R*,*R*)-(salen)M(III) catalysts (M = Cr and Co) for the coupling reactions of cyclopentene oxide and carbon dioxide results in the highly selective synthesis of well-controllable, narrowly distributed molecular weights copolymers. Although the chromium catalyst was found to be less active than its cobalt analog, it was shown to be thermally more stable, and hence, the reaction could be carried out at higher temperatures with little sacrifice in selectivity for copolymer production. The $T_g$ of the resulting poly(cyclopentene carbonate) was determined to be 84.5 °C.

**KEYWORDS:** *carbon dioxide, cyclopentene oxide, alternating copolymerization, cobalt, chromium*

## INTRODUCTION

The coupling of carbon dioxide and oxiranes (epoxides) to afford either linear polycarbonates or five-membered cyclic carbonates represents encouraging technologies for $CO_2$ utilization (eq 1).[1] Of importance, these processes designed



(1)

for carbon dioxide capture and utilization (CCU) involve carboxylation reactions that are less energy-intensive than $CO_2$ reduction processes.[2] Each of these processes has the potential for significantly contributing to a sustainable chemical industry. The selectivity of the reaction depicted in eq 1 for linear or cyclic product can presently be tuned by the appropriate selection of catalyst or reaction conditions. Until recently, cyclohexene oxide has been the oxiranes monomer of choice by researchers for nearly every catalyst screening for the copolymerization process. That is, researchers have typically used this cyclic ether monomer as a benchmark to demonstrate the viability of their catalyst for the $CO_2$/epoxide copolymerization reaction. Cyclohexene oxide is an inexpensive, easy-to-handle material that yields high selectivity for polycarbonate over cyclic carbonate for most catalyst systems under a broad range of reaction conditions. As such, many researchers have incorrectly generalized their catalyst's high selectivity for production of poly(cyclohexene carbonate) to be translatable to all other potential monomers.

Computational studies have shown this low preference for carbonate chain-end backbiting to produce cyclohexene carbonate in this instance is due to the linear polycarbonate having to undergo an endergonic conformational change (chair to boat) of 4.7 kcal-mol$^{-1}$ before traversing the activation barrier of 21.1 kcal mol$^{-1}$ for cyclic carbonate formation.[3] Thus, this high selectivity for copolymer formation is not necessarily typical, even for all alicyclic oxiranes. Indeed, the product selectivity for the coupling of $CO_2$ with cyclohexene oxide and cyclopentene oxide with (salen)CrCl and an onium salt catalyst system is starkly different, although the monomers differ by only one methylene group.[3−5] Herein, we show that cyclohexene oxide and $CO_2$ will combine to form poly(cyclohexene carbonate) with 99% selectivity (<1% *trans*-cyclohexene carbonate byproduct); cyclopentene oxide and $CO_2$ will instead form *cis*-cyclopentene carbonate with 100% selectivity (Scheme 1).

There are a few published reports for the production of poly(cyclopentene carbonate) from the completely alternating copolymerization of cyclopentene oxide and $CO_2$ involving zinc-based catalysts.[6,7] Recently, Lu and co-workers published the successful synthesis of isotactic poly(cyclopentene carbonate) employing

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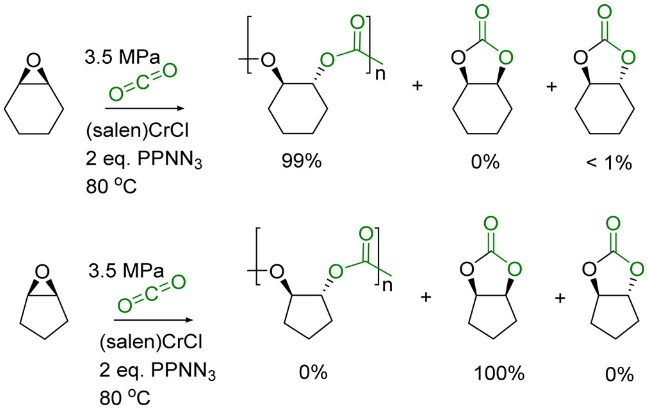
**Scheme 1**



chiral dinuclear cobalt(III) complexes as catalysts.[8] Because of the significant improvements in catalytic activity, we and others have experienced using bifunctional (salen)Co(III) catalysts for selectively providing copolymers over cyclic carbonates, we choose to investigate herein the preparation of poly(cyclopentene carbonate) utilizing these catalyst systems.[9] Lu and coworkers have shown that bifunctional catalysts such as that illustrated in Figure 1 exhibit a larger difference in the energies of activation for cyclic vs copolymer formation than their binary (salen)Co(III)/onium salt counterparts.[10]

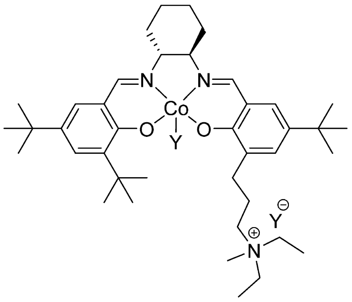


**Figure 1.** Asymmetric bifunctional (salen)Co(III) catalysts developed by Lu and co-workers.[10]

An added interest in developing good synthetic methods for the preparation of poly(cyclopentene carbonate) stems from the fact that this copolymer can be easily depolymerized to its monomers, cyclopentene oxide and $CO_2$.[4,5] Although most polycarbonates derived from carbon dioxide and epoxides can be degraded to their corresponding cyclic carbonate, copolymers capable of undergoing depolymerization that lead to a regeneration of their monomers represent the ideal method for recycling these materials. Indeed, depolymerization pathways of this type greatly enhance the sustainability of the process.

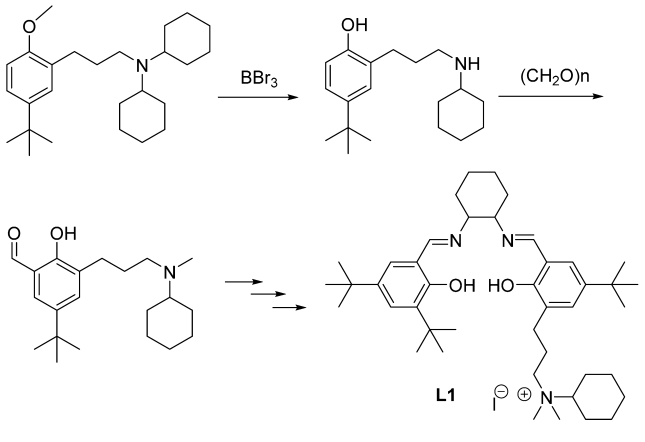
## ■ EXPERIMENTAL SECTION

**1. General Information.** All manipulations involving air- or water-sensitive compounds were carried out in a glovebox under an argon atmosphere or with standard Schlenk techniques under dry nitrogen. Toluene was distilled from sodium/benzophenone and stored in an argon-filled glovebox. Cyclopentene oxide (GL Biochem (Shanghai), Ltd.) was stirred over $CaH_2$, distilled, and stored in an argon-filled glovebox. Tetra-*n*-butylammonium chloride (Aldrich) was recrystallized from acetone/diethyl ether before use and stored in an argon-filled glovebox. (*R*,*R*)-*N*,*N*′-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminochromium(III) chloride, (salen)CrCl, was purchased from Strem, stored in an argon-filled glovebox, and used as received. Research grade 99.999% carbon dioxide supplied in a high-pressure cylinder and equipped with a liquid dip tube was purchased from Airgas. The $CO_2$ was further purified by passing through two steel columns packed with 4 Å molecular sieves that had been dried under vacuum at ≥200 °C. High-pressure reaction monitoring measurements were performed using an ASI ReactIR 1000 reaction analysis system with a 300 mL stainless steel Parr autoclave modified with a permanently mounted ATR crystal (SiComp) at the bottom of the reactor (purchased from Mettler Toledo). Infrared spectra were recorded on a Bruker Tensor 37 spectrometer in $CaF_2$ solution cells with a 0.1 mm path length.

**2. X-ray Crystal Study.** For the crystal structure of *cis*-cyclopentene carbonate, a Bausch & Lomb 10× microscope was used to identify suitable crystals. A single crystal sample was coated in mineral oil, affixed to a Nylon loop, and placed under streaming $N_2$ (110 K) in a single-crystal APEXii CCD or Bruker GADDS/Histar diffractometer. X-ray diffraction data were collected by covering a hemisphere of space upon combination of three sets of exposures. The structure was solved by direct methods. H atoms were placed at idealized positions and refined with fixed isotropic displacement parameters, and anisotropic displacement parameters were employed for all non-hydrogen atoms. The following programs were used: for data collection and cell refinement, APEX2;[11] data reductions, SAINTPLUS, version 6.63;[12] absorption correction, SADABS;[13] structure solutions, SHELXS-97;[14] structure refinement, SHELXL-97.[15]

**3. Synthesis of Bifunctional Catalysts.** *Asymmetric Salen Ligands (**L1**).* Asymmetric bifunctional ligand **L1** was synthesized following the literature.[16] However, instead of bearing two cyclohexyl groups and one methyl group on ammonium, the ligand obtained had one cyclohexyl group and two methyl groups. In the deprotection step to convert a methoxyl group to a hydroxyl group on the phenyl ring using $BBr_3$, one cyclohexyl group on the amine was shown to be replaced by hydrogen, making a secondary amine, as outlined below. In the following formylation step, this secondary amine reacted with formaldehyde and underwent reductive amination to give a tertiary amine with one methyl group and one cyclohexyl group. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.34 (s, 1H), 8.29 (s, 1H), 7.32 (d, 1H, $J$ = 3 Hz), 7.18 (d, 1H, $J$ = 3 Hz), 7.07 (d, 1H, $J$ = 3 Hz), 7.00 (d, 1H, $J$ = 3 Hz), 3.52 (m. 3H), 3.29−2.41 (m, 2H), 3.24 (s, 3H), 3.19 (s, 3H), 2.72 (m, 2H), 2.09 (m, 4H), 1.89 (m, 6H), 1.75−1.63 (m, 4H), 1.40 (br s, 15H), 1.24 (s, 9H), 1.22 (s, 9H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 165.54, 165.17, 157.96, 141.40, 140.06, 136.54, 130.40, 126.86, 126.81, 126.12, 126.10, 125.82, 72.91, 72.28, 71.77, 62.22, 48.94, 34.96, 34.07, 33.91, 33.50, 32.98, 31.44, 31.37, 29.37, 27.32, 26.29, 25.18, 24.61, 24.31, 24.17, 22.27 ppm. MS for (**L1** − $I^-$): $m/z$ = 658.5011.

*Bifunctional Chromium Catalyst **1**.* Bifunctional chromium catalyst **1** was synthesized via a modified literature procedure.[17] A 103 mg portion of ligand **L1** (0.131 mmol, 1 equiv) and 19.5 mg of chromium(II) chloride (0.158 mmol, 1.2 equiv) were dissolved in THF and stirred for 1 day under Ar and another day under air. After being washed by $NH_4Cl$ and NaCl aqueous solutions, the reaction mixture was dried, redissolved in acetonitrile, and transferred to a Schlenk flask charged with 51.4 mg of $AgBF_4$ (0.263 mmol, 2 equiv). After 1 day of stirring



L1

in the dark, the reaction mixture was filtered into another Schlenk flask with 51.4 mg of sodium azide (0.788 mmol, 6 equiv) and stirred for 1 day. Subsequently, the solvent was removed in vacuo, and the mixture was redissolved in dichloromethane. After being washed by NaCl aqueous solution, the solvent was removed in vacuo overnight, affording 61.3 mg of chromium catalyst **1** (0.0773 mmol, 58.8% yield). MS for (**1** − $N_3^-$), $m/z$ = 750.4571; for (**1** − 2($N_3^-$)), $m/z$ = 354.2231. Anal. Calcd. for $C_{43}H_{66}CrN_9O_2$: C, 65.1; H, 8.39. Found: C, 64.33; H, 8.38.

*Bifunctional Cobalt Catalyst* **3**. This complex was synthesized following the literature procedure starting from 29.6 mg of cobalt(II) acetate (0.165 mmol, 1.3 equiv) and 99.9 mg of **L1** (0.127 mmol, 1 equiv). The yield of complex **3** was 81.9 mg (0.0757 mmol), or 59.5%.

**4. Coupling of Cyclopentene Oxide and $CO_2$ Using Binary Chromium Catalyst.** A 72.5 mg portion of (salen)-CrCl (114.7 μmol) and 133.4 mg of $PPNN_3$ (229.2 μmol, 2 equiv) were charged into a vial, dissolved in dry $CH_2Cl_2$, and allowed to stir at room temperature under argon for ∼30 min to activate the catalyst. The solvent was thoroughly removed in vacuo, and the vial was charged with 15.0 mL of dry cyclopentene oxide (171.9 mmol, 1500 equiv). The homogeneous solution was cannulated into a 300 mL stainless steel autoclave with a permanently mounted SiComp crystal. The reactor was pressurized with 3.5 MPa $CO_2$ and heated to 80 °C. The course of the reaction was monitored for 3 h. The system was cooled to room temperature and depressurized, and both $^1$H NMR and FT-IR spectra were obtained from the crude reaction mixture; 56% conversion to *cis*-cyclopentene carbonate was observed from $^1$H NMR.

**5. *cis*-Cyclopentene Carbonate.** Following the completion of the coupling of CPO and $CO_2$, the mixture was concentrated in vacuo, redissolved in dichloromethane, and passed through a short column of silica gel to remove residual catalyst and cocatalyst. Clear, slightly colored crystals were grown from slow evaporation of the resulting solution. $^1$H NMR (300 MHz, $CDCl_3$): δ 3.39 (s, 2H), 1.94 (dd, 2H, $J$ = 5.1, 7.8 Hz), 1.45−1.54 (m, 3H), 1.23−1.34 (m, 1H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): δ 155.6, 82.0, 33.2, 21.6 ppm. FT-IR $\nu_{CO_3}$1796 cm$^{-1}$ ($CH_2Cl_2$); 1838sh, 1807 cm$^{-1}$ ($C_7H_8$). Anal. Calcd. for $C_6H_8O_3$: C, 56.24; H, 6.29. Found: C, 56.22; H, 6.15.

**6. Coupling of Cyclohexene Oxide and $CO_2$.** A 62.5 mg portion of (salen)CrCl (98.8 μmol) and 115.0 mg of $PPNN_3$ (197.7 μmol, 2 equiv) were charged into a vial, dissolved in dry $CH_2Cl_2$, and allowed to stir at room temperature under argon for ∼30 min to activate the catalyst. The solvent was thoroughly removed in vacuo, and the vial was charged with 15.0 mL of dry cyclohexene oxide (148.3 mmol, 1500 equiv). The homogeneous solution was cannulated into a 300 mL stainless steel autoclave with a permanently mounted SiComp crystal. The reactor was pressurized with 3.5 MPa $CO_2$ and heated to 80 °C. The course of the reaction was monitored for 3 h. The system was cooled to room temperature and depressurized, and both $^1$H NMR and FT-IR spectra were obtained of the crude reaction mixture. A 64% conversion to poly(cyclohexene carbonate), 0.7% conversion to *trans*-cyclohexene carbonate, and 0.2% ether linkages were observable from $^1$H NMR.

**7. Poly(cyclohexene carbonate).** The crude reaction mixture from the coupling of CHO and $CO_2$ was added dropwise to acidified methanol (∼5% HCl). The off-white polymer precipitate was collected by filtration, redissolved in dichloromethane, and reprecipitated using the same method. The resulting white solid was dried under vacuum with heating. $^1$H NMR (300 MHz, $CDCl_3$): δ 4.64 (br s, 2H), 2.10 (br s, 2H), 1.70 (br s, 2H), 1.23−1.55 (br m, 4H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): broad peaks centered at δ 153.4, 29.5, 22.8 ppm. FT-IR $\nu_{CO_3}$ 1750 ($CH_2Cl_2$); 1751 ($C_7H_8$). Anal. Calcd. for $(C_7H_{10}O_3)_n$: C, 59.14; H, 7.09. Found: C, 59.21; H, 7.09.

**8. Kinetic Measurements for the Direct Coupling of Cyclopentene Oxide and $CO_2$ Utilizing (salen)CrCl/*n*-$Bu_4$NCl.** In an argon-filled glovebox, 90.2 mg of (salen)CrCl (0.142 mmol), 79.3 mg of *n*-$Bu_4$NCl (0.285 mol, 2 equiv), 6.00 g of cyclopentene oxide (71.3 mmol, 500 equiv), and 5.22 g of toluene (6 mL) were charged into a vial. The reactants were cannulated into a 300 mL stainless steel Parr autoclave modified with a permanently mounted ATR crystal (SiComp) at the bottom of the reactor. This initial mixture served as the background signal for the measurements. $CO_2$ (3.4 MPa) was charged into the system, and the reactor was heated to the desired temperature (43, 53, 63, 73 °C). Infrared spectra were taken periodically throughout the course of the reaction, and the reaction's progress was monitored through the growth of cyclic carbonate peak at 1804 cm$^{-1}$. No activity was ever observed at 1750 cm$^{-1}$, indicating that polymer formation did not take place or was not appreciable. The reaction was followed to 100% completion.

**9. Coupling of Cyclopentene Oxide and $CO_2$ Utilizing Bifunctional Catalysts.** The copolymerization reactions of cyclopentene oxide and $CO_2$ were carried out in a similar manner utilizing either of the metal complexes **1**−**4** as catalyst. For example, 6.2 mg of the bifunction cobalt catalyst **2** (5.7 μmol) and 0.50 mL of cyclopentene oxide (5.77 mmol or 1000 equiv) were charged in a 12 mL stainless steel autoclave reactor that had previously been dried at 170 °C for six hours. The reactor was pressurized to the appropriate pressure (1.0−2.5 MPa) and heated to the desired temperature in an oil bath with magnetic stirring. After the required reaction time, the reactor was cooled to 0 °C, depressurized, and a $^1$H NMR spectrum of the crude reaction mixture was obtained.

**10. Poly(cyclopentene carbonate).** The crude reaction mixture from coupling of cyclopentene oxide and $CO_2$ was dissolved in $CH_2Cl_2$ and added to about 1 M HCl/methanol solution to quench the reaction and precipitate the copolymer. The supernatant HCl/methanol solution was removed, and the polymer precipitate was redissolved in dichloromethane and reprecipitated from methanol. The resulting copolymer was obtained by removing the supernatant and subsequently dried

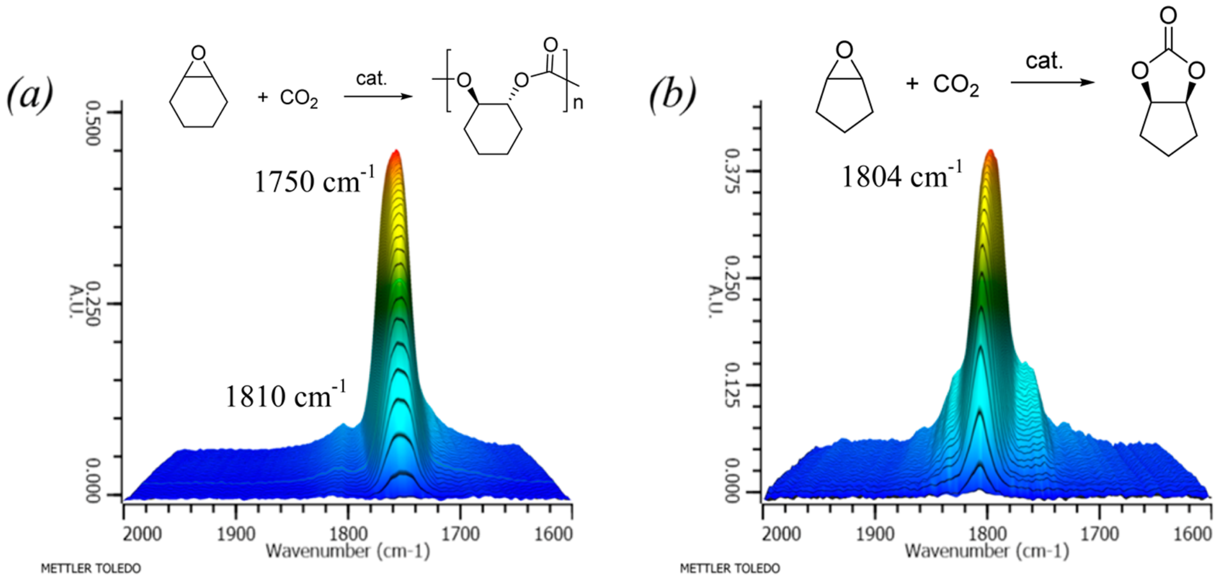
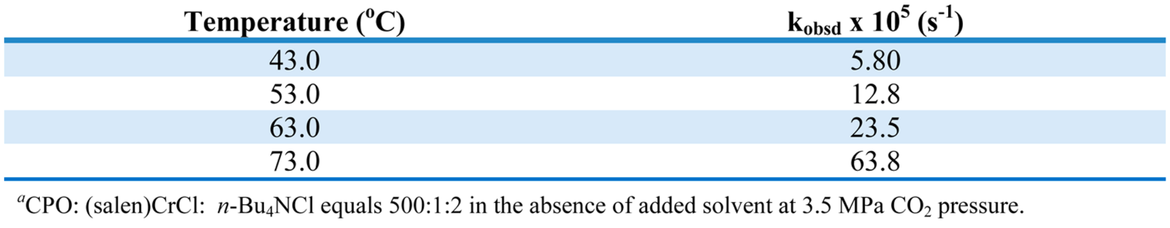


**Figure 2.** Product growth traces for the coupling of the alicyclic epoxides (CHO and CPO) and $CO_2$ utilizing in situ ATR-FTIR spectroscopy. (a) 99% selective PCHC growth at 1750 cm$^{-1}$ and <1% *trans*-CHC at 1810 cm$^{-1}$, as confirmed by $^1$H NMR. (b) 100% selectivity for CPC at 1804 cm$^{-1}$, as confirmed by $^1$H NMR. Reaction conditions: 500 equiv epoxide (15 mL), 1 equiv (salen)CrCl, 2 equiv $PPNN_3$, 3.5 MPa $CO_2$, 80 °C, 3 h.

**Table 1. Observed Rate Constants for the Coupling of Cyclopentene Oxide and $CO_2$ To Afford *cis*-Cyclopentene Carbonate**[a]



| Temperature (°C) | $k_{obsd} \times 10^5$ ($s^{-1}$) |
|---|---|
| 43.0 | 5.80 |
| 53.0 | 12.8 |
| 63.0 | 23.5 |
| 73.0 | 63.8 |

[a]CPO: (salen)CrCl: *n*-$Bu_4NCl$ equals 500:1:2 in the absence of added solvent at 3.5 MPa $CO_2$ pressure.

[a]CPO/(salen)CrCl/*n*-$Bu_4NCl$ equals 500:1:2 in the absence of added solvent at 3.5 MPa $CO_2$ pressure.

in vacuo at 50 °C for further analysis by GPC and DSC. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$5.00 (br s, 2H), 2.13 (br s, 2H), 1.84−1.77 (br m, 4H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$153.5, 82.3, 30.0, 21.2 ppm.

## ■ RESULTS AND DISCUSSION

As noted earlier in Scheme 1, comparative coupling reactions of cyclohexene oxide/$CO_2$ and cyclopentene oxide/$CO_2$ were carried out in the presence of (salen)CrCl (salen = (*R*,*R*′)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene-1,2-cyclohexanediamino) and 2 equiv of $PPNN_3$ at 80 °C and 3.5 MPa. The preformed (salen)Cr(III) complex under these reaction conditions is anionic, containing two azide ligands.[18] The reactions were monitored by in situ infrared spectroscopy in the carbonate stretching region, as depicted in Figure 2. This study clearly contracts the two processes, with cyclohexene oxide/$CO_2$ coupling highly favoring copolymer formation, and cyclopentene oxide/$CO_2$ coupling leading exclusively to cyclic carbonate production.

In a separate series of experiments, the catalytic coupling of cyclopentene oxide and $CO_2$ to afford *cis*-cyclopentene carbonate using (salen)CrCl and *n*-$Bu_4NCl$ was monitored by in situ infrared spectroscopy at several temperatures. The observed rate constants ($k_{obsd}$) found in Table 1 were determined from plots of $\ln[(A_i - A_t)/A_i]$ versus time in seconds, where $A_i$ is the absorbance of cyclic carbonate at time = infinity and $A_t$ is the absorbance of cyclic carbonate at 1804 cm$^{-1}$ at time = *t* (Figure 3).

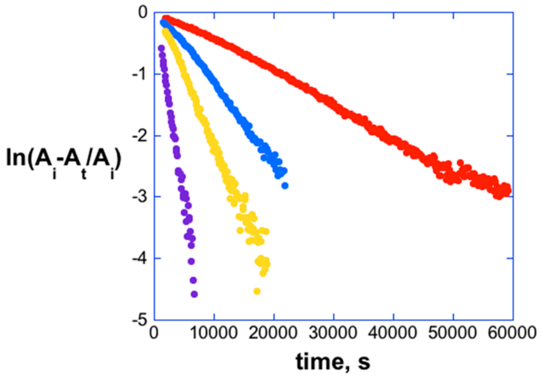


**Figure 3.** Kinetic plots of $\ln[(A_i - A_t)/A_t]$ vs time for *cis*-cyclopentene carbonate production. Red, 43.0 °C; blue, 53.0 °C; yellow, 63.0 °C; and purple, 73.0 °C.

The activation energy ($E_A$) of the coupling reaction was determined from the slope of the corresponding Arrhenius plot (Figure 4). The direct coupling of cyclopentene oxide and $CO_2$ to form *cis*-cyclopentene carbonate utilizing (salen)CrCl has an activation barrier of 72.9 ± 5.2 kJ/mol. The cis nature of the product was confirmed both by $^1$H NMR and X-ray diffraction analysis of single crystals grown from the final product mixture (Figure 5). Separate attempts were made to produce *trans*-cyclopentene carbonate from *trans*-1,2-cyclopentanediol and ethyl chloroformate, but these were unsuccessful. This is due to

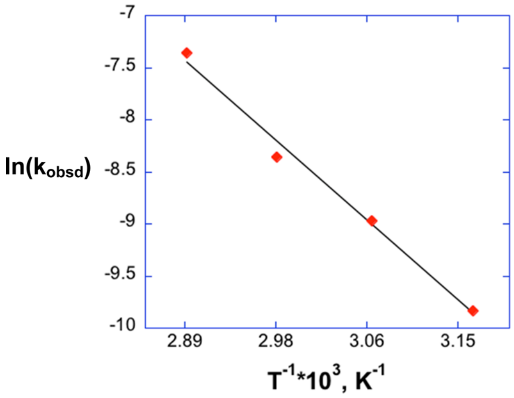


**Figure 4.** Arrhenius plot of *cis*-cyclopentene carbonate production in the presence of (salen)CrCl/*n*-$Bu_4NCl$. $R^2$ = 0.989.

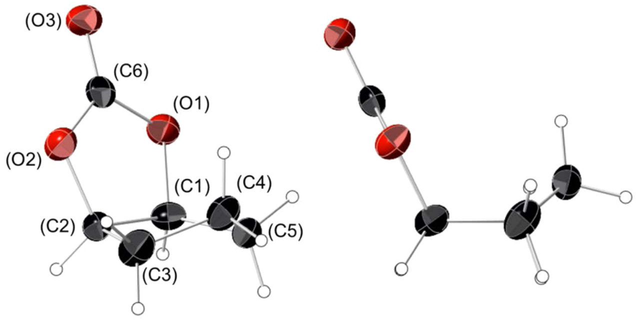
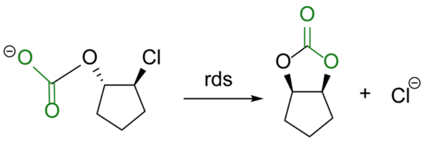


**Figure 5.** Thermal ellipsoid representation of *cis*-cyclopentene carbonate with ellipsoids at 50% probability surfaces. At right, looking down the plane created by C2−C1−C3−C5 to show the near-planarity of the cyclic carbonate ring (O1−C1−C2−O2 = 0.347°).

the extreme angle strain at the bridgehead carbons linking the fused 5-membered rings;[3,5] trans isomers are possible for the corresponding trithiocarbonate, however.[4,19,20]

The reaction pathway for the formation of cyclopentene carbonate in the presence of $CO_2$ (3.5 MPa) is proposed to proceed via backbiting by a free carbonate end group following epoxide ring-opening by chloride and carboxylation (eq 2).

 (2)

This pathway is most likely since *no* copolymer chain growth was observed during cyclic carbonate formation. Furthermore, it has been shown by experimental and computational studies that the activation barrier for the backbiting process involving the displacement of the carbonate polymer chain is significantly higher than that for the process illustrated in eq 2, that is, where $Cl^-$ is replaced by the copolymer tail.[3,5] High level ab initio calculations reveal this pathway to have a $\Delta G^\ddagger$ of 57.3 kJ/mol, which is consistent with the activation energy measured herein when considering the positive entropy of activation expected for the process in eq 2.

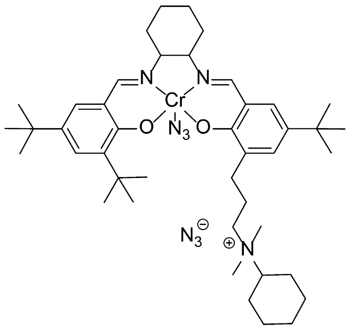


**Figure 6.** Asymmetric bifunctional (*R*,*R*)-(salen)$CrN_3$ catalyst, **1**.

By way of contrast, we have initiated studies utilizing the bifunctional (salen)Cr(III) analog of the binary system used in the preceding coupling reaction of cyclopentene oxide and $CO_2$. The (salen)Cr(III) complex (**1**) depicted in Figure 6 was shown to be selective for copolymer formation, even at elevated temperatures. Although we have not optimized the reaction conditions, for a 5 h reaction of cyclopentene oxide and 2.0 MPa $CO_2$ at 100 °C, the TOF for copolymer production was 50.3 $h^{-1}$ with 94.3% selectivity. For an epoxide/catalyst loading of 1000/1, the afforded poly(cyclopentene carbonate) following 25.1% conversion displayed a $M_n$ of 11900 with a PDI of 1.10.

The bifunctional (salen)Cr(III) catalyst system shown in Figure 6 shows the azide anion ion-paired with the ammonium cation. Unfortunately, we have thus far been unable to obtain single crystals for X-ray structural analysis; however, the solution structure clearly indicates the azide ion is bound to the chromium center, similar to what is observed in the binary catalyst system both in the solid state and in weakly interacting solvents.[18] That is, the infrared spectrum in dichloromethane of complex **1**, like its binary analog complex **2**, was shown to have *no* free azide band at 2000 $cm^{-1}$ and metal bound azide bands at 2044 $cm^{-1}$ with a shoulder at 2060 $cm^{-1}$, as illustrated in Figure 7. This is an important observation, for it indicates the metal is the preferred site for anion binding, where, during the polymerization reaction, the anion is the growing polymer chain. Furthermore, the infrared spectra of complexes **1** and **2** (see Figure 8) in pure cyclopentene oxide clearly show that under identical reaction conditions, the initial azide epoxide ring-opening step is faster in the binary catalytic process. It is important to note, however, that this step is not rate-limiting in the copolymerization process, which is, in the presence of high $CO_2$ pressures, ring-opening of the metal bound epoxide by the growing polymeric carbonate chain.

As anticipated, on the basis of copolymerization studies involving other epoxides, the (*R*,*R*)-cobalt(III) analog of the bifunctional chromium(III) catalyst, complex **3**, was found to be significantly more active for selective production of copolymer from cyclopentene oxide and $CO_2$ than complex **1**.[1i] For example, for a 5 h reaction carried out at 70 °C and 2.0 MPa, the corresponding TOFs were 56.5 vs 2.20 $h^{-1}$ (Tables 2 and 3). Table 2 lists the effects of temperature, $CO_2$ pressure, reaction time, and catalyst loading for the copolymerization of cyclopentene oxide and $CO_2$ in the presence of complex **3** (eq 3). As noted in Table 2, upon increasing the reaction temperature from 40 to 70 °C (entries 1−3), the catalytic activity increased along with the molecular weight of the copolymer. However, a further increase in temperature to 100 °C (entry 4) led to a significant decrease in catalytic activity, concomitantly with a decrease in selectivity for copolymer production (62% selectivity), as compared with >99% selectivity at the lower temperatures. The drop in reactivity is the result of catalyst instability at this elevated temperature. Although there is a slight increase in copolymer production with increasing $CO_2$ pressure

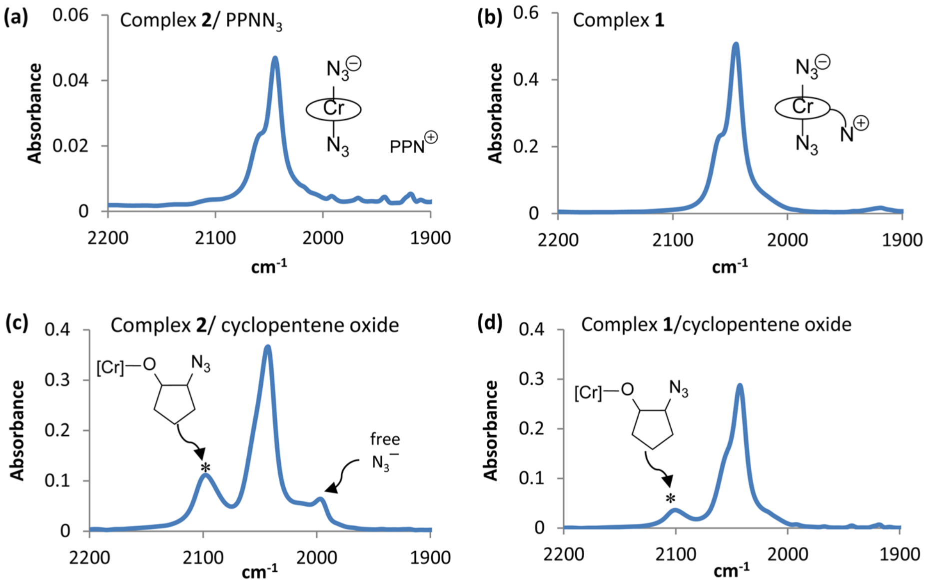
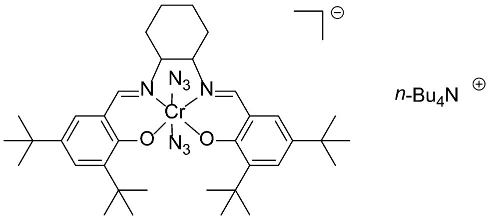


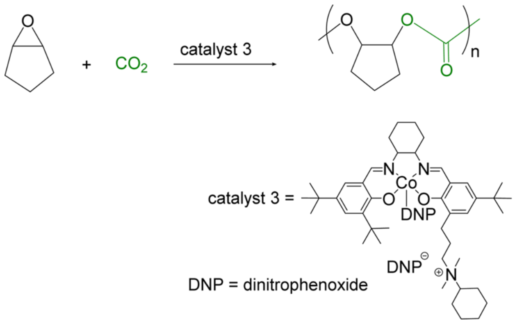
**Figure 7.** IR spectra in the $\nu_{N_3}$ region of (a) binary bis-azide chromium catalyst **2** in dichloromethane, (b) bifunctional chromium catalyst **1** in dichloromethane, (c) binary bis-azide chromium catalyst **2** in cyclopentene oxide after 40 min at ambient temperature, and (d) bifunctional chromium complex **1** in cyclopentene oxide after 40 min at ambient temperature. The asterisk (*) in parts c and d represents the $\nu_{N_3}$ vibration in the ring-opened epoxide.



**2**

**Figure 8.** Binary ($R$,$R$)-(salen)CrN$_3$/$n$-Bu$_4$NN$_3$ catalytic system.

(entries 5–7), clearly, the process can be performed successfully at a modest pressure of 1.0 MPa with little loss in activity. There was good molecular weight control, as indicated in entries 3, 8, and 9, where an increase in reaction time led to an increase in percent conversion and corresponding $M_n$ values. Furthermore, although the copolymers exhibited a bimodal molecular weight distribution (Figure 9), the measured molecular weights were not grossly different from those calculated on the basis of each



(3)

**Table 2. Effects of Variables on the Catalyzed Copolymerization of Cyclopentene Oxide and CO$_2$ Utilizing Complex 3**[a]

| Entry | Temp (°C) | Pressure (MPa) | Time (h) | Conversion (%) | TOF (h$^{-1}$) | $M_n$[b] (Da) | PDI |
|---|---|---|---|---|---|---|---|
| 1 | 40 | 2.0 | 5 | 9.43 | 18.9 | 5680 (6035) | 1.04 |
| 2 | 50 | 2.0 | 5 | 20.9 | 41.8 | 9380 (13376) | 1.10 |
| 3 | 70 | 2.0 | 5 | 28.2 | 56.5 | 19300 (18048) | 1.10 |
| 4 | 100 | 2.0 | 5 | 10.8 | 21.6 | 7410 (10432) | 1.20 |
| 5 | 70 | 1.0 | 5 | 30.5 | 61.0 | 17620 (19520) | 1.08 |
| 6 | 70 | 1.5 | 5 | 28.0 | 56.0 | 15250 (17920) | 1.13 |
| 7 | 70 | 2.5 | 5 | 36.8 | 73.5 | 20450 (23552) | 1.06 |
| 8 | 70 | 2.0 | 2 | 21.6 | 108 | 12220 (13824) | 1.06 |
| 9 | 70 | 2.0 | 10 | 44.1 | 44.1 | 27000 (28224) | 1.05 |
| 10 | 70 | 2.0 | 5 | 18.3 | 73.3[c] | 18100 (23424) | 1.06 |

[a] Catalyst loading = 1000/1. Polycarbonate selectivity over cyclic carbonate for all entries is >99%, except for entry 4, which is 62%. [b] Theoretical values provided in parentheses. [c] Catalyst loading = 2000/1.

Table 3. Coupling of Cyclopentene Oxide and $CO_2$ Catalyzed by Different Bifunctional Catalysts[a]

| entry | catalyst | temp (°C) | conv (%)[b] | TOF ($h^{-1}$)[b,c] | $M_n$[d] | PDI[d] | polymer selectivity (%)[b,e] |
|---|---|---|---|---|---|---|---|
| 1 | **3** | 70 | 28.2 | 56.5 | 19300 | 1.10 | >99 |
| 2 | **1** | 70 | 1.1 | 2.2 | N/A | N/A | >99 |
| 3 | **1** | 100 | 25.1 | 50.3 | 11900(16064)[f] | 1.10 | 94.3 |
| 4[g] | **1** | 100 | 19.4 | 38.8 | 8550 | 1.13 | 92.6 |
| 5 | **1** | 120 | 26.7 | 53.5 | 15400 | 1.16 | 75.8 |
| 6 | **4** | 70 | 38.3 | 76.6 | 18500 | 1.12 | 88.5 |
| 7 | **5** | 70 | 0.3 | 0.6 | N/A | N/A | >99 |

[a] CPO/catalyst = 1000/1, $CO_2$ 2.0 MPa. Reaction time = 5 h. [b] Determined by $^1$H NMR. [c] Moles of CPO converted/mol of catalyst/time. [d] Determined by GPC. [e] Polycarbonate/(polycarbonate + cyclic carbonate). [f] Calculated value. [g] $CO_2$ 1.5 MPa.

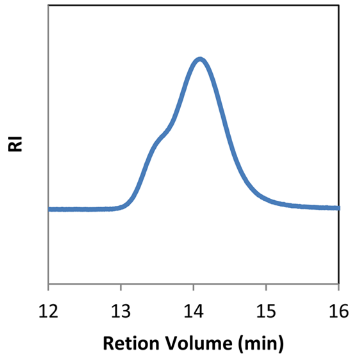


**Figure 9.** GPC trace of poly(cyclopentene carbonate) from Table 2, entry 9. Deconvolution of the two overlapping peaks revealed the smaller peak to account for 10% of the total area.

cobalt center averaging two polymer chains. It is thought that adventitious water can lead to reduced molecular weights of copolymers as a result of rapid and reversible chain transfer processes.[21,22] This phenomenon results in two copolymers, one with an X and OH chain ends and a second with two hydroxyl chain end groups. In addition, a decrease in catalyst loading (entry 10) had no negative effect on TOFs or $M_n$ and PDI. The $T_g$ of the high molecular weight copolymer (entry 9) was found to be 84.5 °C, considerably lower than the 116 °C value reported for its cyclohexene oxide derived analog.[23] The $^{13}$C NMR spectrum of the synthesized poly(cyclopentene carbonate) is shown in Figure 10 and is indicative of an atactic copolymer, as previously reported by Lu and co-workers utilizing similar catalysts.[8]

For comparative purposes, we have examined the coupling of cyclopentene oxide and $CO_2$ with various catalyst systems under similar reaction conditions. These are tabulated in Table 3, where complexes **4** and **5** are illustrated in Figure 11. As seen in entries 3−5, the bifunctional chromium catalyst (**1**) is thermally more stable than complex **3**, maintaining good catalytic activity at 120 °C. Nevertheless, as would be expected, there is a loss in copolymer selectivity at this elevated temperature. Finally, it is noted, as previously reported, that there is a correlation between the bulkiness of the ligand tethered ammonium ion and cat-

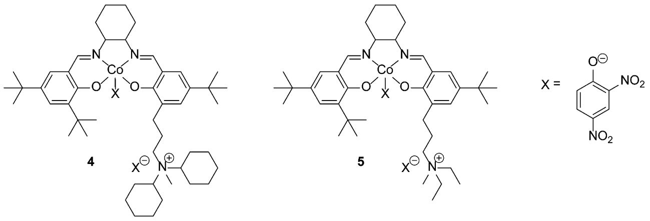


**Figure 11.** Asymmetric bifunctional (salen)Co(III) catalysts developed by Lu and co-workers.[10]

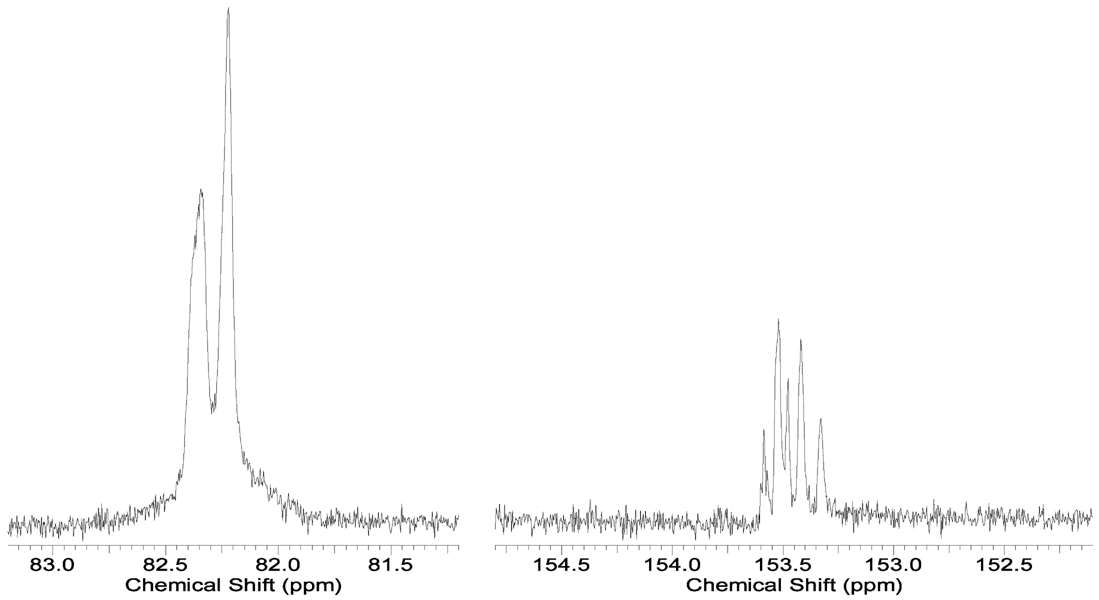


**Figure 10.** $^{13}$C NMR spectrum of poly(cyclopentene carbonate) from Table 2, entry 9. Methine region (left) and carbonate region (right).

alytic activity (entries 1, 6, and 7), with greater steric bulk leading to greater reactivity.[24]

## CONCLUDING REMARKS

Herein, we have successfully prepared high-molecular-weight poly(cyclopentene carbonate) from the completely alternating copolymerization of cyclopentene oxide and carbon dioxide utilizing bifunctional (salen)M(III) catalysts (M = Cr, Co). The copolymers were synthesized in a very selective manner with little to no production of cyclic carbonate byproduct. By way of contrast, it was demonstrated that, whereas under identical reaction conditions (80 °C/3.5 MPa) in the presence of the binary (salen)$CrN_3$/$PPNN_3$ catalyst system, the coupling of cyclohexene oxide and $CO_2$ produces poly(cyclohexene carbonate) with >99% selectivity, the corresponding reaction of the alicyclic cyclopentene oxide and $CO_2$ affords >99% selectivity for *cis*-cyclopentene carbonate. This cyclic carbonate was structurally characterized by X-ray crystallography. Kinetic studies for *cis*-cyclopentene carbonate formation revealed an activation energy of 72.9 ± 5.2 kJ/mol proceeding via backbiting of the anionic carbonate species generated in the initial epoxide ring-opening process subsequent to carboxylation, consistent with theoretical predictions.

For reactions carried out at 70 °C employing the bifunctional Co(III) catalyst in 0.1% catalyst loading at 2.0 MPa $CO_2$ pressure, 44% conversion to poly(cyclopentene carbonate) occurred within 10 h, leading to a copolymer with a $M_n$ value of 27 000 (PDI = 1.05). Although the analogous chromium catalyst is less active, it is thermally more stable, and hence, coupling reactions can be carried out at higher temperatures while maintaining a high selectivity for copolymer production. The $T_g$ of the resulting atactic poly(cyclopentene carbonate) was determined to be 84.5 °C. Importantly, these polycarbonates have been shown to be depolymerized to their comonomers, cyclopentene oxide and $CO_2$, thereby making their production from epoxide and $CO_2$ sustainable.

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### Notes

The authors declare no competing financial interest.

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