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Mechanistic Aspects of the Copolymerization Reaction of Carbon Dioxide and Epoxides, Using a Chiral Salen Chromium Chloride Catalyst

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Abstract: The air-stable, chiral (salen)$Cr^{III}Cl$ complex (**3**), where H_2salen = *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexene diamine, has been shown to be an effective catalyst for the coupling of cyclohexene oxide and carbon dioxide to afford poly(cyclohexenylene carbonate), along with a small quantity of its trans-cyclic carbonate. The thus produced polycarbonate contained >99% carbonate linkages and had a M_n value of 8900 g/mol with a polydispersity index of 1.2 as determined by gel permeation chromatography. The turnover number (TON) and turnover frequency (TOF) values of 683 g of polym/g of Cr and 28.5 g of polym/g of Cr/h, respectively for reactions carried out at 80 °C and 58.5 bar pressure increased by over 3-fold upon addition of 5 equiv of the Lewis base cocatalyst, *N*-methyl imidazole. Although this chiral catalyst is well documented for the asymmetric ring-opening (ARO) of epoxides, in this instance the copolymer produced was completely atactic as illustrated by ^{13}C NMR spectroscopy. Whereas the mechanism for the (salen)Cr^{III}-catalyzed ARO of epoxides displays a squared dependence on [catalyst], which presumably is true for the initiation step of the copolymerization reaction, the rate of carbonate chain growth leading to copolymer or cyclic carbonate formation is linearly dependent on [catalyst]. This was demonstrated herein by way of in situ measurements at 80 °C and 58.5 bar pressure. Hence, an alternative mechanism for copolymer production is operative, which is suggested to involve a concerted attack of epoxide at the axial site of the chromium(III) complex where the growing polymer chain for epoxide ring-opening resides. Preliminary investigations of this (salen)Cr^{III}-catalyzed system for the coupling of propylene oxide and carbon dioxide reveal that although cyclic carbonate is the main product provided at elevated temperatures, at ambient temperature polycarbonate formation is dominant. A common reaction pathway for alicyclic (cyclohexene oxide) and aliphatic (propylene oxide) carbon dioxide coupling is thought to be in effect, where in the latter instance cyclic carbonate production has a greater temperature dependence compared to copolymer formation.

Introduction

The use of well-defined coordination complexes as catalysts or catalyst precursors for the coupling of carbon dioxide and epoxides to provide cyclic carbonates or polycarbonates is the focus of much current research. This is in part due to the economic and environmental benefits of carbon dioxide utilization as a C_1 feedstock.[1] These considerations are accentuated in the context of polycarbonate synthesis because of the hazardous and expensive production process currently in place industrially, which involves the interfacial polycondensation of phosgene and diols (most commonly bisphenol-A).[2] The feasibility of preparing high molecular weight polycarbonates from carbon dioxide and epoxides was first demonstrated by Inoue employing heterogeneous zinc catalysts derived from diethylzinc and water.[3] Subsequently, we and others have made excellent gains using soluble, for the most part, fully characterized zinc derivatives to synthesize polycarbonates from *alicyclic* epoxides,[4] including copolymers with a high degree of stereoregularity.[5]

In addition there have been a variety of complexes of other metals which have been, to a lesser extent, investigated as potential catalysts for the coupling reaction of carbon dioxide

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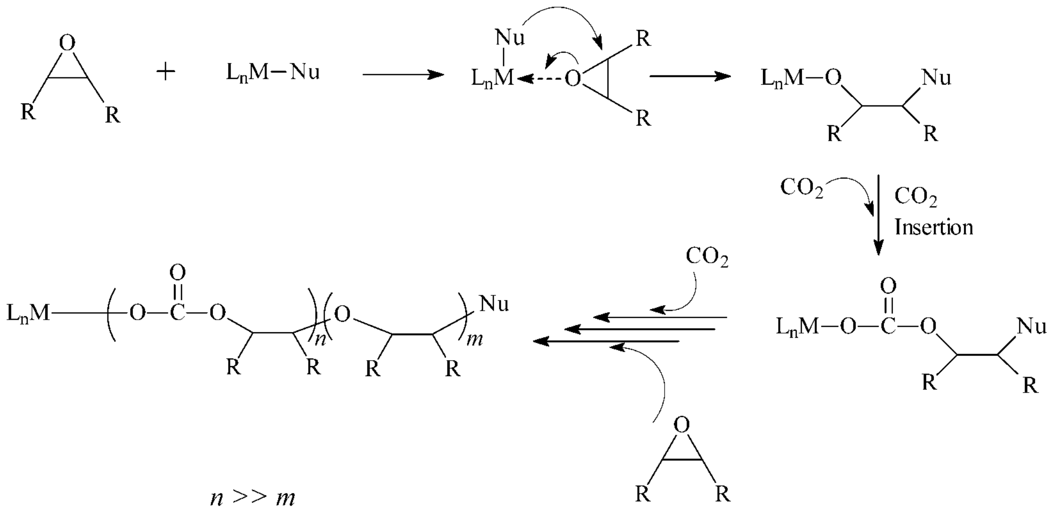
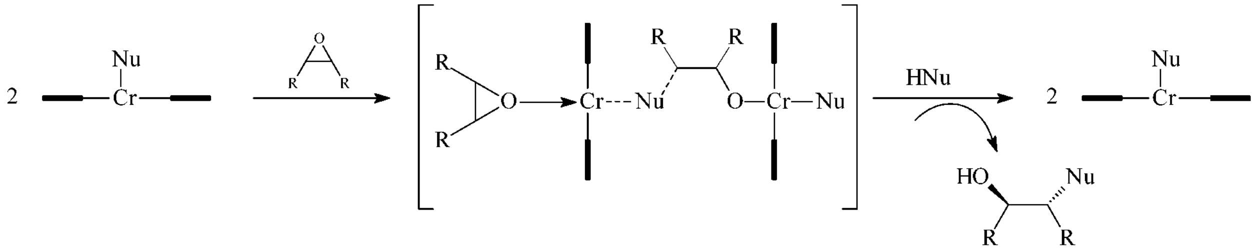
Scheme 1



Scheme 2



and epoxides to afford polycarbonates. Examples in the literature which are particularly relevant to the results presented herein include the studies of Inoue and co-workers, who have investigated the use of Al(III) porphyrinate and salen complexes as catalysts in this copolymerization process.[6] Similarly, Kruper and Dellar have examined chromium porphyrin derivatives for the formation of copolymers and cyclic carbonates.[7] A further contribution to this copolymerization process is the work of Mang and Holmes utilizing sc-CO_2 soluble perfluorotetraphenyl porphyrinate Cr(III) chloride complexes as catalysts.[8]

Interestingly, these latter catalyst systems are not readily accommodated by the previously proposed mechanism (Scheme 1) for the ring opening of epoxides (the rate determining step in these processes).[4,9] That is, because these catalysts have square-pyramidal geometries, it is difficult to imagine a situation where the epoxide can be bound and thereby activated by the metal center for ring opening by a neighboring initiator ligand. A possible answer to the question of mechanism comes from the work of Jacobsen. In 1995 his group reported the use of a chiral Cr(III) chloride salen-type complex for the asymmetric ring-opening of epoxides.[10] This was followed quickly in 1996 with a more comprehensive study in which kinetic details were elucidated, indicating there was a second-order rate dependence on catalyst loading.[11] Thus Jacobsen proposed a mechanism that proceeded through a dinuclear transition state (Scheme 2). This is not unlike the proposal of Kuran and Listos with regard to cooperativity in Zn alkoxide catalysts.[12]

It is the purpose of this study to investigate whether Jacobsen-type catalysts, e.g., (salenCr(III)Cl), are capable of facilitating repetitive epoxide ring opening accompanied by CO_2 insertion to produce polycarbonate. Further, it is our intention to address the ability of this catalyst to asymmetrically incorporate the epoxide into the polymer backbone, thus producing a stereoregular copolymer.[13] Pertinent to our study, Nguyen has very recently proposed a cooperative mechanism for propylene oxide/CO_2 coupling to cyclic carbonate to proceed via a mechanism involving two different metal species derived from (salenCr(III)Cl) and DMAP(4-(dimethylamino)pyridine).[14]

Experimental Section

Methods. Unless otherwise specified, all syntheses and manipulations were carried out on a double manifold Schlenk vacuum line under an atmosphere of argon or in an argon-filled glovebox. ^1H and ^{13}C NMR spectra were acquired on Unity+ 300 MHz and VXR 300 MHz superconducting NMR spectrometers. Infrared spectra were recorded on a Mattson 6021 FTIR spectrometer with DTGS and MCT detectors. The syntheses of the diammonium tartrate salt (**1**),[15] *N*,*N*′-bis(3,5-di-*tert*-butyl-salicylidene)-1,2-cyclohexane diamine (H_2salen, **2**),[15] and the chromium catalyst (**3**)[11] were performed as described in the literature. Crystals of **2** and **3** suitable for X-ray analysis were obtained by slow solvent evaporation from a methylene chloride solution of **2** or **3**, and X-ray data were collected on a Bruker Smart 1000 CCD diffractometer.[16−20] Details may be found in the Supporting Information.

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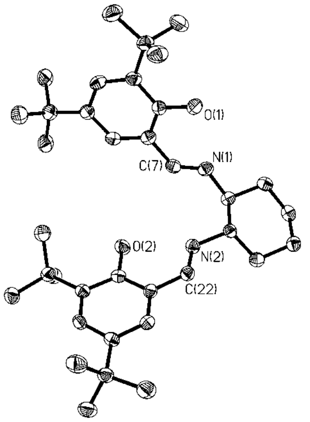

Figure 1. Thermal ellipsoid representation of *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexane diamine (H_2salen, **2**).

Copolymerization of Cyclohexene Oxide and Carbon Dioxide. A typical polymerization experiment was carried out as follows: Approximately 50 mg of complex **3** (0.040 mol %) was dissolved in 20 mL of neat cyclohexene oxide. The solution was then loaded via injection port into a 300-mL autoclave that had been previously under vacuum overnight at 80 °C. The autoclave was placed under 48.3 bar of CO_2 and heated to 80 °C (approximately 60 bar at reaction temperature). The reaction was allowed to stir for 24 h at which time stirring was discontinued and the autoclave allowed to return to room temperature. The polymer was extracted as a methylene chloride solution and subjected to repeated precipitation with methanol.

The collected polycarbonate copolymers were analyzed by ^{1}H NMR where protons adjacent to carbonate linkages afford a signal at 4.6 ppm while the absence of polyether linkages was verified by the absence of a signal at 3.5 ppm. Further, infrared spectra were collected to verify the presence of the $\nu(CO_2)$ stretch at 1750 cm^{-1}. To determine polymer tacticity, ^{13}C NMR spectroscopy was employed and analyzed as described recently by Nozaki and co-workers.[5a] Chemical shifts observed at 153.8, 153.4, and 153.2 ppm indicate the production of largely atactic polymer. The number average (M_n) and weight average (M_w) molecular weights, and concomitant the polydisperisty of the copolymer were obtained in THF by using gel permeation chromatography (calibrated with polystyrene standards) in the laboratories of Exxon-Mobil, Baytown, TX.

Copolymerization Reactions Monitored by IR Spectroscopy. In a typical experiment, 10 mL of neat cyclohexene oxide was delivered via the injection port into a 300-mL stainless steel Parr autoclave reactor. The reactor is modified with a ZnSe window to allow for the use of an ASI ReactIR 1000 in situ probe. In this manner, a single 128 scan background spectrum was collected. The catalyst (in 30 mL neat cyclohexene oxide) was then injected into the reactor via the injection port, resulting in a 40-mL reaction solution. The reactor was pressurized to 48.3 bar of CO_2 and heated to 80 °C as the IR probe began collecting scans. The probe was set up to collect 1 spectrum every 3 min over an 18 h period. Profiles of the absorbance at 1750 cm^{-1} ($\nu(CO_2)$ for the carbonate functionality) with time were recorded and used to provide initial reaction rates for analysis. (Note: Catalyst loading varied with experiment as described in the results and discussion section.)

Table 1. Crystallographic Data for Compounds **2** and **3**

	2	**3**
empirical formula	$C_{36}H_{54}N_2O_2$	$Cr_2Cl_{10}C_{76}H_{112}N_4O_4$
formula wt, g/mol	546.81	1604.20
temp (K)	110(2)	110(2)
wavelength	0.71073	0.71073
crystal system	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1$
a (Å)	6.6894(7)	12.593(3)
b (Å)	18.0963(18)	30.774(7)
c (Å)	27.195(3)	11.704(3)
β (deg)		110.880(5)
Cell volume (Å^3)	3292.1(6)	4238.0(17)
Z	4	2
density (calcd)	1.103	1.257
absorb coeff (mm^{-1})	1.847	0.618
obsd no. of reflcns	21065	22512
no. of unique reflcns ($I > 2\sigma$)	7744	13271
R,[a] % [$I > 2\sigma$]	6.29	10.79
R_w,[a] % [$I > 2\sigma$]	13.30	24.88

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg)

	2		
N(1)−C(7)	1.270(3)	N(1)−C(1)	1.472(4)
N(2)−C(22)	1.271(3)	N(2)−C(6)	1.472(4)
O(1)−C(9)	1.353(3)	O(2)−C(28)	1.365(3)
C(1)−N(1)−C(7)	118.6(2)	C(6)−N(2)−C(22)	118.7(2)
	3		
Cr(1)−Cl(1)	2.29(2)	Cr(1)−O(1)	1.880(14)
Cr(1)−O(2)	1.914(16)	Cr(1)−N(1)	1.975(16)
Cr(1)−N(2)	2.037(18)	N(1)−C(7)	1.302(19)
N(2)−C(22)	1.331(19)		
N(1)−Cr(1)−Cl(1)	84.5(7)	N(2)−Cr(1)−Cl(1)	79.0(7)
O(1)−Cr(1)−Cl(1)	81.6(7)	O(2)−Cr(1)−Cl(1)	80.8(7)
O(1)−Cr(1)−O(2)	94.1(7)	N(1)−Cr(1)−N(2)	80.8(7)

Results and Discussion

The *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexene diamine ligand (**2**) was readily synthesized by the deprotonation of the 1,2-cyclohexane diammonium L-tartrate salt and subsequent condensation of the diamine with 3,5-*tert*-butylsalicylaldehyde. Slow evaporation of solvent from a methylene chloride solution of the ligand yielded X-ray quality crystals. The molecular structure of **2** is depicted in the thermal ellipsoid representation shown in Figure 1, along with a partial atomic numbering scheme. Selected bond distances and angles are listed in Table 2. The N1−C7 and N2−C22 bond distances in compound **2** at 1.270(3) and 1.271(3) Å, respectively, are consistent with C═N imine bond lengths and are in agreement with the infrared spectrum for **2** where ν(CN) appears at 1629 cm^{-1}.[21]

The (salen)Cr(III)Cl catalyst (**3**) was readily synthesized from compound **2** as described in the literature.[11a] Upon binding **2** to the metal center, there was a slight shift of the ν(CN) vibration to lower frequency at 1625 cm^{-1}. X-ray quality crystals of complex **3** were obtained by slow evaporation of a methylene chloride solution of **3**. Figure 2 displays the thermal ellipsoid drawing of one of the two independent chromium molecules found in the asymmetric unit, along with a partial atomic numbering scheme. Selected bond distances and angles are tabulated in Table 2. As would be anticipated based on ν(CN) infrared data, there is not much change in the C═N bond distances upon formation of complex **3**, suggesting the ligand retains much of its imine character. The crystal structure of complex **3** exhibited disorder of the Cr−Cl bond over positions on opposing sites of the salen plane. Resolution of the disorder,

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(17) *17.SAINT-Plus*, version 6.02; Bruker: Madison, WI, 1999.
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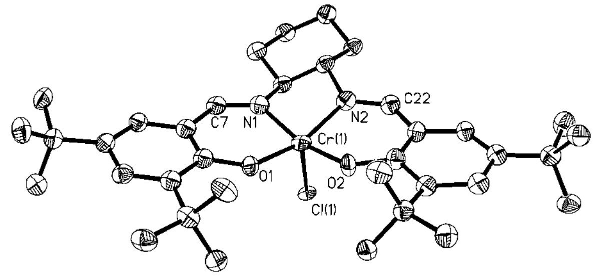

Figure 2. Thermal ellipsoid representation of (salen)Cr$^{(III)}$ chloride, complex **3**.

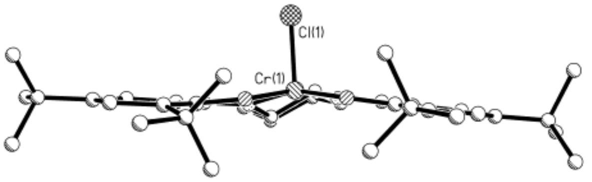

Figure 3. Ball-and-stick drawing of complex **3**, illustrating the position of the chromium center out of the plane of the N/O donors on the salen ligands.

Table 3. The Effect of *N*-Methyl Imidazole (*N*-MeIm) on Copolymer Yields[a]

run	equiv of *N*-MeIm	TON[b] (g of polym/g of Cr)	TOF[c] (g of polym/g of Cr/h)
1	0	683 (250)	28.5 (10.4)
2	2.25	1104 (404)	46.0 (16.8)
3	5.00	2116 (774)	88.2 (32.2)
4	7.00		

[a] All polymerizations were carried out over 24 h at 80 °C and 58.5 bar pressure. [b] Values in parentheses are in units of moles of CHO consumed/mole of Cr. [c] Values in parentheses are moles of CHO consumed/mole of Cr/hour.

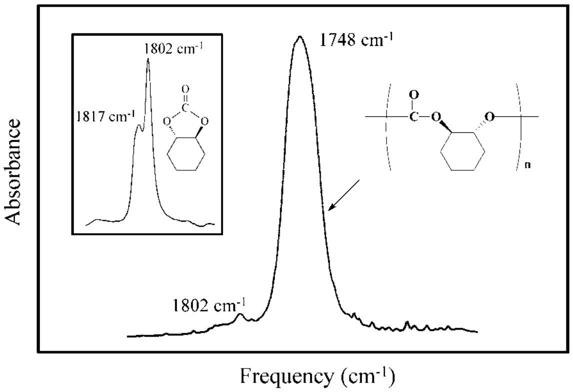

Figure 4. Infrared spectrum in the $\nu(CO_2)$ region in a methylene chloride solution of the reaction mixture from a typical copolymerization run of cyclohexene oxide and carbon dioxide. The insert displays the infrared spectrum of a pure sample of *trans*-7,9-dioxabicyclo[4.3.0]nonan-8-one in methylene chloride solution.

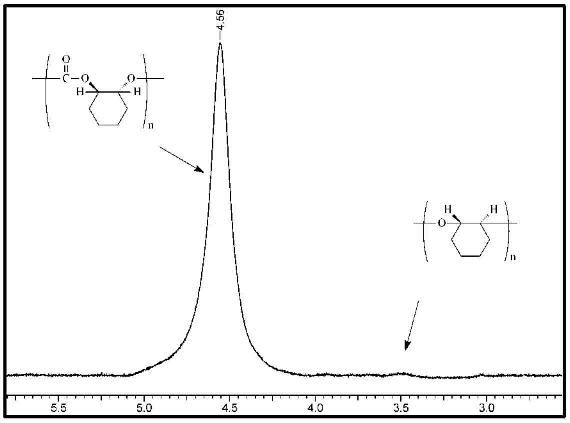

Figure 5. Proton NMR spectrum of the poly(cyclohexylene carbonate) copolymer produced from cyclohexene oxide and carbon dioxide, and catalyzed by complex **3**.

however, reveals the Cr$^{(III)}$ center is bound in a square-pyramidal geometry, as expected, with the metal sitting slightly out of the plane of the N/O donors of the salen ligand and in the direction of chloride ligand (Figure 3). Further, the absolute structure (Flack[22]) parameter (racemic twin)[19] was refined to a value of $-0.06(9)$, which is indicative of the correct stereochemistry.

It is important to note, with thought toward optimizing the communication between the chiral environment of the catalyst and the incoming epoxide substrate, that Jacobsen and co-workers have extensively studied the steric and electronic contributions of various ligand substituents,[23] and reported ligand **2** as optimum for these purposes. Thus we do not currently report any investigations into catalyst activity optimization through derivatization of the ligand backbone.

Copolymerization Reactions of Epoxides and Carbon Dioxide. Complex **3**, (salen)Cr(III)Cl, has been found to be an effective catalyst for coupling carbon dioxide and cyclohexene oxide to afford alternating copolymer, poly(cyclohexenylene carbonate). At 80 °C and 58.5 bar, complex **3** exhibited a turnover number (TON) of 683 g of polym/g of Cr for a rection period of 24 h, which translates into a turnover frequency (TOF) of 28.5 g of polym/g ofCr/h. (See Table 3.) Prior to isolation of the copolymer, an aliquot of the crude reaction mixture was dissolved in methylene chloride and subjected to infrared analysis in the $\nu(CO_2)$ region to ascertain the extent of cyclic carbonate formation (Figure 4). As is readily observed, the intense absorbance at approximately 1750 cm^{-1}, which corresponds to the asymmetric $\nu(CO_2)$ vibration of the polycarbonate copolymer, is the major absorbance in this area. A very weak absorption around 1802 cm^{-1} with a high energy shoulder indicates the production of a small quantity of trans-cyclic carbonate. The degree of CO_2 incorporation in the copolymer was determined to be essentially 100% by ^{1}H NMR spectroscopy (Figure 5), where only protons adjacent to carbonate linkages (4.6 ppm) were observed. This result is consistent with the related metal porphyrin catalyzed work of Inoue[6] and Holmes[8] that afforded polycarbonates exhibiting high levels of CO_2 incorporation. Analysis of the copolymer by gel permeation chromatography revealed the number and weight average molecular weights as $M_n = 8\,900$ g/mol and $M_w = 11\,000$ g/mol, respectively, yielding a polydispersity index (PDI) of 1.2. Thus, complex **3** has proven to be an active catalyst for cyclohexene oxide/CO_2 coupling, producing polymer with a narrow molecular weight distribution. Importantly, unlike most catalysts reported for this process, complex **3** is remarkably stable to air and moisture. The measured molecular weights are approximately an order of magnitude lower than those calculated for a living initiator based on the ratio of [monomer] to [catalyst]. This is suggestive of chain transfer processes occurring; although every effort is made to maintain anhydrous conditions during the copolymerization processes, high pressures

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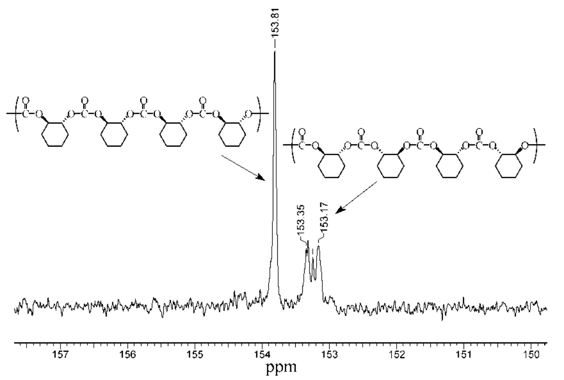


Figure 6. ^{13}C NMR spectrum of the poly(cyclohexylene carbonate) copolymer produced from cyclohexene oxide and carbon dioxide, and catalyzed by complex **3**.

of CO_2 necessarily introduce small quantities of water. Nevertheless, monomer consumption, polydispersity, and M_n values reported herein are consistent with those reported for similar systems in the literature.[6,8]

Studies by Inoue and co-workers,[6] and Kruper and Dellar[7] employing Al(III) and Cr(III) porphyrin derivatives, respectively, have reported significant increases in the catalytic activity of these derivatives for the CO_2/epoxide coupling process in the presence of neutral Lewis base cocatalysts, such as *N*-methyl imidazole (*N*-MeIm) and 4-dimethyl(amino)pyridine (DMAD). In and effort to enhance the catalytic activity for copolymerization utilizing complex **3**, we have investigated the addition of varying quantities of *N*-methyl imidazole. The results are tabulated in Table 3, where the TON and TOF are shown to increase by over 3-fold upon the addition of 5 equiv of *N*-MeIm. Presumably, binding of the *N*-MeIm ligand at the vacant axial site of (salen)CrCl increases the nucleophilicity about the metal center thereby enhancing the rate of epoxide ring-opening by the nucleophile as well as the subsequent CO_2 insertion process. Evidently, these processes are dominant over epoxide metal interaction prior to ring-opening, a reaction that should be retarded by a more electron-rich metal center. Nevertheless, a further increase in the concentration of added *N*-MeIm leads to a significant reduction in polymer formation, possibly as a consequence of imidazole interaction at the site required for the epoxide substrate binding in the initiation step.

An important goal of this study was to address the issue of asymmetric incorporation of the cyclohexene oxide substrate into the polymer backbone. Relevant to this point Nozaki and co-workers[5c] have recently characterized, by ^{13}C NMR spectroscopy, a series of cyclohexene carbonate tetramer models with varying tacticities. Their results make it possible to rudimentarily assess tacticity of this specific copolymer. They reported that the ^{13}C NMR signal for the carbonate carbon of m-centered tetrads ((mmm), (mmr), (rmr)) is observed at 153.7 ppm, whereas the signal for the carbonate carbon of r-centered tetrads ((rrr), (rrm), (mrm)) is observed at higher field (153.3−153.1 ppm). Similar conclusions were reached by Coates and co-workers based on the probability calculation of all tetrad configurations.[5b] ^{13}C NMR analysis of all copolymer produced in our study (see Figure 6) showed a signal at 153.8 ppm, plus signals at 153.3, 153.2, and 153.1 ppm, thus indicating a lack of stereocontrol in the ring-opening step. This observation might be indicative of significant deviation from the proposed mechanism of Jacobsen for epoxide ring opening during polymer chain growth (vide infra).

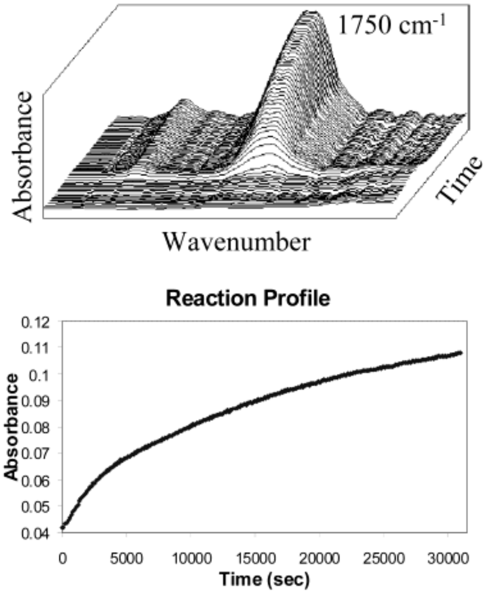


Figure 7. In situ infrared monitoring of the poly(cyclohexylene carbonate) formation as a function of time.

Mechanism of the Copolymerization Process. An important conclusion from Jacobsen's elegant mechanistic studies of the (salen)Cr-catalyzed asymmetric ring opening (ARO) reaction is that the chromium complex serves as a Lewis acid catalyst for epoxide binding/activation, and as a delivery agent for the nucleophile that ring opens the epoxide.[11] That is, there is a second-order dependence on the catalyst concentration in the rate law for the ARO process. Furthermore, it was established that upon linking two catalyst units in a bimetallic complex, enantioselectivity was principally noted for a catalyst system where head-to-tail arrangement of the salen ligands was possible. To examine this aspect of the (salen)Cr-catalyzed copolymerization reaction of cyclohexene oxide and carbon dioxide, we have carried out kinetic studies of this process as a function of catalyst loading. The copolymerization reactions were monitored in the $\nu(CO_2)$ region of the infrared spectrum of the polycarbonate utilizing an in situ ASI 1000 ReactIR probe fitted to a modified stainless steel Parr reactor. Each polymerization was performed in 40 mL of neat cyclohexene oxide at 80 °C and under 58.5 bar of carbon dioxide. Six different reactions were carried out and monitored in this fashion with varying amounts of catalyst, but always in the presence of 2 equiv of *N*-MeIm relative to catalyst loading. Figure 7 displays a typical reaction profile, where the asymmetric $\nu(CO_2)$ vibration of the polycarbonate is observed as a strong absorption at 1750 cm^{-1}. From these experiments we have obtained initial rates of copolymerization, which are listed in Table 4 along with their corresponding catalyst loadings. Figure 8 depicts the plot of initial rate of copolymer formation vs catalyst loading, which clearly shows the process to be linearly dependent on catalyst loading. Similarly, as depicted in Figure 9 the initial rate for the simultaneously produced trans-cyclic carbonate exhibits a linear dependence on catalyst loading. This observation is consistent with a back-biting mechanism for cyclic carbonate formation in which the propagating chain coordinates itself to the metal

Table 4. Catalyst Loadings and Initial Rates[a,b]

complex **3** (mg)	initial rate ($\times 10^6$) (abs/s)
42.4 (150)	4.39 (0.872)
50.0 (300)	5.47 (2.04)
71.0 (450)	5.49 (2.86)
80.0	6.51
160	13.6
249	21.0

[a] All reactions were carried out in the presence of 2 equiv of *N*-methyl imidazole in 40 mL of neat cyclohexene oxide at 80 °C, under 58.5 bar pressure. [b] Values in parentheses were obtained in an identical manner in the absence of added *N*-methyl imidazole.

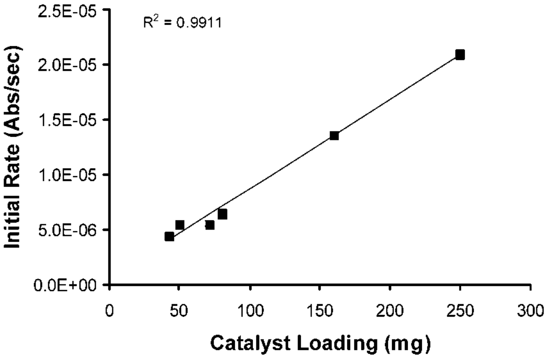


Figure 8. Plot of the initial rate of copolymer (poly(cyclohexylene carbonate)) formation as a function of catalyst (complex **3**) loading (or concentration) for copolymerization of cyclohexene oxide and carbon dioxide in the presence of 2 equiv of *N*-methyl imizadole. Initial rate intercept at zero catalyst loading is 0.56×10^{-6}.

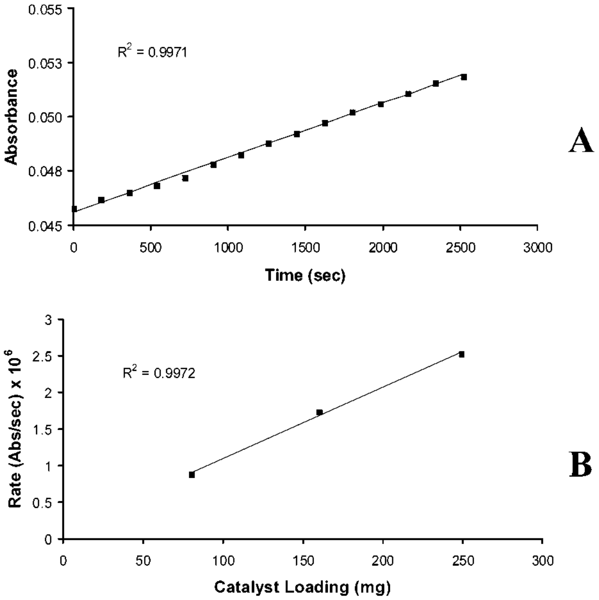


Figure 9. (A) Representative plot of absorbance vs time for the linear portion of trans-cyclic carbonate formation. (B) Plot of initial rate of trans-cyclic carbonate formation as a function of catalyst (complex **3**) loading (or concentration) for coupling of cyclohexene oxide and carbon dioxide in the presence of 2 equiv of *N*-methyl imizdazole. Initial rate intercept at zero catalyst loading is 0.13×10^{-6}.

center as suggested by Kuran.[24] Since all reactions are performed under identical conditions, catalyst loading is directly proportional to catalyst concentration.[25] To ensure that addition of the Lewis base, *N*-MeIm, does not play an unanticipated mechanistic role, rate studies were conducted on a series of copolymerization reactions in the absence of added *N*-MeIm. As Figure 10 illustrates, the initial rates were found to exhibit the same dependence on [catalyst], but catalytic activity was diminished significantly. It is of importance to note that our kinetic studies monitored the initial rate of carbonate chain growth which ultimately leads to copolymer or cyclic carbonate formation. That is, we are not following the initiation step that presumably occurs via Jacobsen's mechanism. On the basis of the information presented thus far, we propose the mechanistic model for copolymerization using the (salen)CrCl catalyst shown in Scheme 3.

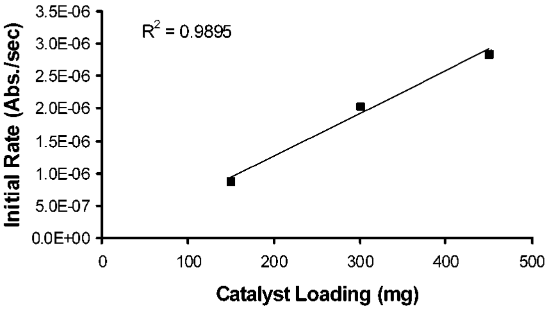
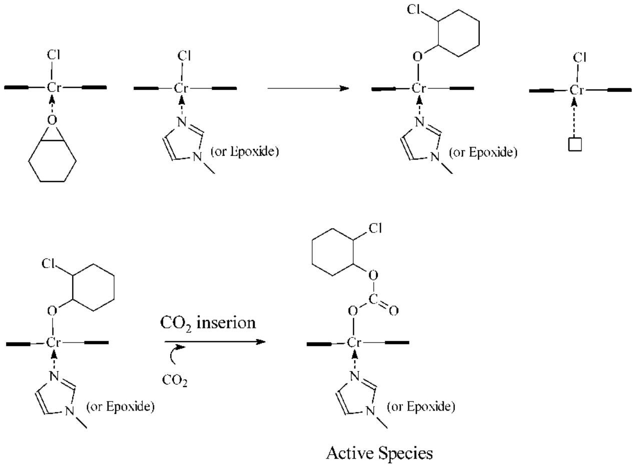


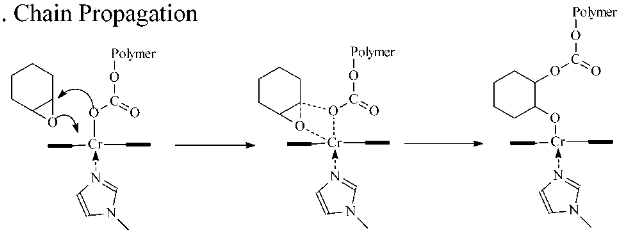
Figure 10. Plot of the initial rate of copolymer (poly(cyclohexylene carbonate)) formation as a function of catalyst (complex **3**) loading (or concentration) for copolymerization of cyclohexene oxide and carbon dioxide in the absence of added *N*-methyl imizadole. The initial rate intercept at zero catalyst loading is -0.62×10^{-7}.

Scheme 3

1. Initiation Process - Transition State illustrated in **Scheme 2**.



2. Chain Propagation



This concerted epoxide ring-opening mechanism is consistent with the observed enhancement of activity in the presence of a Lewis base cocatalyst. Further, it is supported by the work of

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(24) Rokicki, A.; Kuran, W. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1981**, *C21*, 135.

(25) From studies of the phase behavior of the cyclohexene oxide-CO_2 binary,[4c] at 58.5 bar CO_2 pressure there exists cyclohexene oxide-rich (X_{CHO}(@80 °C) ≈ 0.65) and cyclohexene oxide-poor phases, the former being where the catalyst mostly resides and is the phase monitored by our in situ infrared probe.

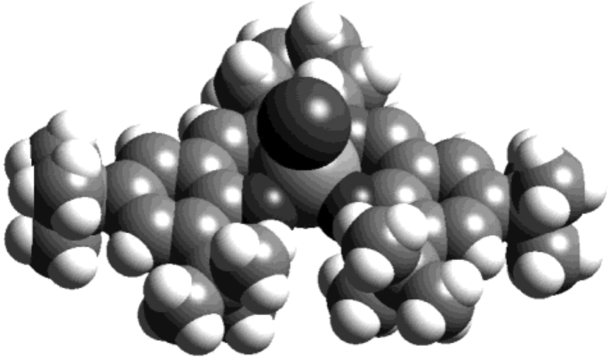

Figure 11. Space-filling model of complex **3**.

Mang et al., who demonstrated that a similar Cr(III) porphyrin complex was very sensitive to the effective concentration of epoxide through a series of phase behavior experiments.[8] It is readily evident from the space-filling model of complex **3** (Figure 11) that there is adequate space to accommodate an incoming epoxide substrate for interaction with the chromium center. Furthermore, the approach by cyclohexene oxide in the chain propagation, step 2, appears to be unhindered. Finally, the first-order behavior with regard to [catalyst] is in accord with the lack of stereoregular control observed in the produced copolymer. Notwithstanding, Scheme 3 contrasts considerably with the mechanistic proposal recently put forth by Paddock and Nguyen, which proposes a bimetallic pathway for production of cyclic carbonates from the coupling reaction of various terminally substituted aliphatic epoxides (e.g., propylene oxide) and carbon dioxide.[14] These authors have suggested a CO_2 molecule carbon bound to a (salen)Cr(I)·DMAP anion as the nucleophile that ring opens the epoxide ligand which is activated by binding to a (salen)Cr(III)Cl complex. Although a (salen)-Co(I) anion has been shown to react with CO_2, and has been crystallographically defined in the presence of alkali metal cations,[26] the most perplexing part of Nguyen's proposal is the origin of the reduced (salen)Cr·DMAP species, which is asserted to bind CO_2. In addition, these researchers report the (salen)-CrCl catalyst to be ineffective for the CO_2/epoxide coupling reaction in the *absence* of a cocatalyst (DMAP).

In an effort to better assess the mechanistic aspects of the propylene oxide/carbon dioxide coupling process, we have carried out preliminary studies of this system analogous to those described herein for cyclohexene oxide/carbon dioxide, except at much lower temperatures. Relevant to these investigations, our previous results have shown for zinc-based catalyzed coupling reactions of propylene oxide and carbon dioxide that although cyclic carbonate production is the predominant pathway at elevated temperatures (75−80 °C), copolymer formation is competitive at lower temperatures.[4f] Indeed, (salen)CrCl-catalyzed propylene oxide/carbon dioxide coupling occurs at 40 °C with greatly reduced activity to afford, in addition to propylene carbonate, a small quantity of completely alternating poly(propylene carbonate). On a *molar basis* much more cyclic carbonate is produced (probably 50−70 molar excess) as compared to polycarbonate; however, chain growth, i.e., ring-opening of epoxide and CO_2 insertion leading to copolymer, is competitive with release of a cyclic carbonate unit. Furthermore, the reaction proceeds, albeit somewhat slower, in the absence of a cocatalyst (*N*-methyl imidazole). Figure 12 illustrates the infrared spectra in the $\nu(CO_2)$ region of the reaction products, where cyclic carbonate and polycarbonate have bands at 1802 and 1750 cm^{-1} of approximately equal intensities, respectively. Although the cyclic carbonate yield is somewhat greater than that of chain growth at 40 °C, there is perhaps a slight enhancement of the relative rate of chain growth vs cyclic carbonate production with added *N*-methyl imidazole. This latter observation must be elaborated upon by varying the nature and concentration of the cocatalyst, but it suggests an electronic means of enhancing polycarbonate vs cyclic carbonate production. Upon further reduction in temperature to 25 °C in the absence of *N*-methyl imidazole, chain growth significantly exceeds that of the cyclic carbonate formation, with mostly copolymer being formed (Figure 12c). As noted for our zinc-catalyzed processes, the rate of cyclic carbonate formation apparently has a greater temperature dependence that the rate of copolymer production. This latter observation is consistent with a unimolecular pathway (back biting) for cyclic carbonate production. Detailed mechanistic studies to quantify the activation parameters for these two concurrent processes are underway.

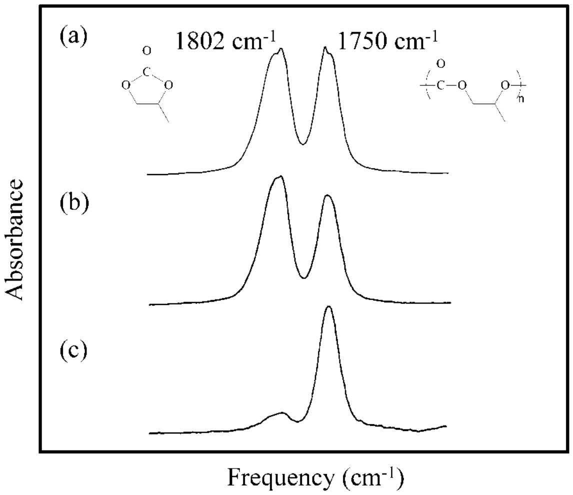

Figure 12. Infrared spectra in the $\nu(CO_2)$ region in CH_2Cl_2 of the reaction mixture from the complex **3** catalyzed propylene oxide/carbon dioxide coupling process. (A) Reaction carried out at 40 °C and 58 bar pressure in the presence of 3 equiv of *N*-methyl imizadole. (B) Reaction carried out at 40 °C and 58 bar pressure in the absence of added *N*-methyl imizadole. (C) Reaction carried out at 25 °C and 58 bar pressure in the absence of added *N*-methyl imizadole.

Concluding Remarks

The chiral (salen)CrCl complex has been shown to be an effective catalyst for the copolymerization of cyclohexene oxide and carbon dioxide. Kinetic studies of the carbonate chain growth process leading to formation of the major product (completely alternating copolymer) and minor product (trans-cyclic carbonate) were performed by way of in situ infrared spectroscopy and found to be linearly dependent on catalyst concentration. Whereas the initiation step in the copolymerization process must follow the mechanistic model documented by Jacobsen, after this epoxide ring-opening pathway and carbon dioxide insertion we propose the chain propagation step to proceed via a concerted insertion of epoxide into a metal−carbonate bond. This overall reaction pathway is consistent with the first-order dependence on [catalyst], the lack of stereocontrol

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(26) Gambarotta, S.; Arena, F.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1982**, *104*, 5082−5092.

in the ring-opening propagation step, as well as the enhanced activity of the complex in the presence of a neutral Lewis base (*N*-MeIm). It is also important to note that copolymerization inhibition in the presence of a large excess of added Lewis base is in agreement with a Jacobsen- type initiation step, where the Lewis base would retard binding/activation of the epoxide. Preliminary investigations of the coupling reaction of propylene oxide and carbon dioxide suggest a similar reaction pathway where cyclic carbonate production has a greater temperature dependence as compared to copolymerization. That is, at elevated temperature cyclic carbonate is the major product, whereas at ambient temperature polycarbonate is the major product.

Finally, although the use of solvent-free conditions for copolymer production results in complete “atom economy”, these conditions are not ideal for detailed mechanistic studies. Therefore, we are currently examining these reaction pathways in noninteracting organic solvents.

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Supporting Information Available: Complete details of the X-ray diffraction studies on complexes **2** and **3** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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