Making Plastics from Carbon Dioxide: Salen Metal Complexes as Catalysts for the Production of Polycarbonates from Epoxides and CO$_2$

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Contents

1. Introduction

Because carbon dioxide is an abundant, inexpensive, and nontoxic biorenewable resource, it is an attractive raw material for incorporation into important industrial processes. Eminent on the list of processes that are technologically viable is the use of CO$_2$ as both a monomer and a solvent in the manufacturing of biodegradable copolymers, most notably, polycarbonates. This process is illustrated in eq 1 for the copolymerization of cyclohexene oxide and CO$_2$ to afford poly(cyclohexene carbonate). As indicated in eq 1, in general, this process is accompanied by the production of varying quantities of five-membered cyclic carbonates. There appears to be some confusion among members of the scientific community who object to referring to the use of CO$_2$ as a raw material for generating useful chemicals as "green chemistry". It has been apparent to most of us working in the area of CO$_2$ utilization that the small quantity of CO$_2$ consumed in these processes is likely always to be a very small fraction of the total CO$_2$ produced from fossil fuel combustion and other sources. Although this consumption would have a minimal effect on global warming, its use is considered "green chemistry" in the context of providing more environmentally benign routes to producing chemicals otherwise made utilizing reagents detrimental to the environment.
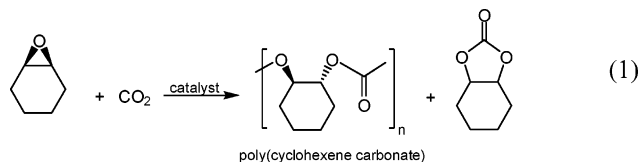
$$\text{(1)}$$

poly(cyclohexene carbonate)

Donald J. Darensbourg was born in 1941 in Baton Rouge, Louisiana, where he received his primary/secondary education. Subsequent to earning a B.S. degree in Chemistry at California State University at Los Angeles, he obtained his Doctor of Chemistry degree from the University of Illinois in 1968 with a dissertation on infrared intensities of CO stretching modes in metal carbonyls under the direction of Theodore L. Brown. Following a brief stay in industry at the Texaco Research Center in Beacon, NY, he began his independent academic career at the State University of New York at Buffalo. In 1973, he relocated his research program to Tulane University to join his wife, Marcetta Darensbourg, who was at that time a faculty member in Tulane's Chemistry Department. He assumed his current position of Professor of Chemistry at Texas A&M University in the summer of 1982. He has published over 300 scientific publications in the general area of mechanistic/catalytic inorganic/organometallic chemistry. Presently, his research activities focus on catalysis of the copolymerization of carbon dioxide and oxiranes or oxetanes and the ring-opening polymerization of six-membered cyclic carbonates to provide polycarbonates. Additional studies are directed at developing biocompatible metal catalysts for the copolymerization of six-membered cyclic carbonates and lactides or caprolactone to afford biomaterials for medical applications.

Both the monomeric and the polymeric products provided from the coupling of CO$_2$ and epoxides have important industrial applications. Polycarbonates possess outstanding properties, which include strength, lightness, durability, high transparency, heat resistance, and good electrical insulation; in addition, they are easily processed and colored.[1] Hence, these materials have wide-scale uses in electronics, optical media, glazing and sheeting, the automotive industry, the medical and healthcare industry, and many other consumable goods. On the other hand, cyclic carbonates find numerous applicabilities, most importantly as high boiling and flash point solvents with low odor/toxicity in degreasing, paint stripping, and cleaning processes.[2] These monomeric compounds are also extensively employed as reactive intermediates.

The early discoveries in this copolymerization process have been broadly and excellently covered in the comprehensive review of this area by Coates and Moore and will not be

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duplicated herein.[3] However, I will reiterate some of the more important advances in chronological order based on a personal perspective. The origin of the metal-catalyzed copolymerization of carbon dioxide and epoxides can best be traced back to the early efforts of Professor Inoue and co-workers at Kyoto University, where the enantioselective homopolymerization of racemic propylene oxide by a catalyst produced from the reaction of diethyl zinc and an optically active alcohol was first reported.[4] A few years later, Inoue and co-workers, now at the University of Tokyo, employed a closely related heterogeneous catalyst system derived from a 1:1 mixture of diethyl zinc and H_2O to provide the first example of the production of a copolymer from CO_2 and epoxides.[5,6] Although the activity of this initial catalyst system investigated was low (~0.10 mol of epoxide consumed/ mol Zn h) at 80 °C and at an elevated pressure of CO_2 (20−50 bar), these early studies have inspired the development of this important area of polymer science. Subsequent to Inoue's report, the late Professor Kuran and co-workers at Warsaw University of Technology investigated a group of related catalysts derived from diethyl zinc and di- and triprotic sources such as pyrogallol.[7] These systems exhibited a slight improvement over the initial studies of Inoue for the production of poly(propylene carbonate) from propylene oxide and CO_2.

The next major breakthrough in the area of propylene oxide and CO_2 copolymerization came with the uncovering of air-stable dicarboxylic acid derivatives of zinc by Soga and co-workers.[8] These catalysts were prepared by the reaction of zinc hydroxide or zinc oxide with dicarboxylic acids in toluene. Although the zinc glutarate analogue was found to be catalytically most active, producing significant quantities of polypropylene carbonate from propylene oxide and CO_2, the percent of active zinc sites on this heterogeneous catalyst was quite low (<5%). Hence, catalyst loadings were generally very high; in addition, reproducibility was often a factor. This latter behavior was most likely attributed to excess glutaric acid in the catalyst sample. Nevertheless, this catalyst system is patented[9] and, because of its inexpensive starting materials, forms the basis for a commercial process for the production of poly(ethylene carbonate) and poly(propylene carbonate).[10] We initially investigated this catalyst system for the copolymerization of propylene oxide and CO_2 in supercritical carbon dioxide (scCO$_2$) and found it to be a fitting and environmentally friendly replacement for the organic solvents usually employed for this process.[11] In an effort to better assess the role of this catalyst, we attempted to grow single crystals of zinc glutarate, but all of our efforts failed. Nevertheless, we were able to obtain the structure of this polycrystalline material from its powder pattern and found it to be a layered structure of zinc atoms with bridging dicarboxylates between the layers (see Figure 1).[12,13]

Concurrently, Zheng and co-workers determined the crystal structure of zinc glutarate from single crystals obtained from a sample synthesized from $ZnCO_3$ and glutaric acid in water.[14] Subsequently, we have demonstrated that the structure of the bulk material is identical to that of the single crystal.[13] The structure of the zinc glutarate has also been confirmed by Rieger and co-workers,[15] as well as by Ree and co-workers.[16] Studies of the interactions of both monomers, propylene oxide and CO_2 with polycrystalline zinc glutarate, have been carried out by Ree and co-workers employing near edge X-ray absorption fine structure.[17] These
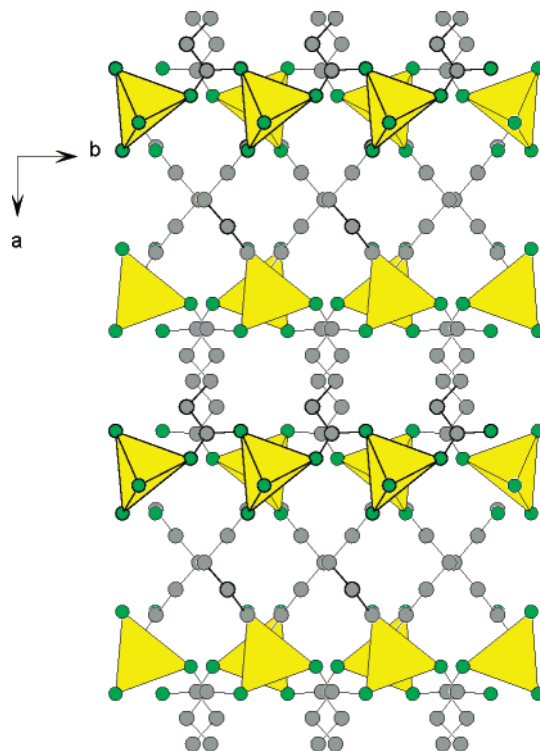

Figure 1. Crystal structure of zinc glutarate prepared from ZnO and glutaric acid in toluene. The structure was determined from the X-ray powder pattern (view along the c-axis).[12]

investigations reveal that propylene oxide and CO_2 reversibly bind to the catalyst surface, with propylene oxide binding initiating copolymerization followed by CO_2 insertion into the thus formed Zn−O bond. This latter observation is consistent with closely related chemistry involving well-characterized organometallic derivatives.[18]

The next milestone in the area of CO_2/epoxide copolymerization was the discovery by Inoue and co-workers in 1986 of the first single-site catalyst for this process.[19] In this instance, the catalyst system employed was a tetraphenylporphyrin derivative of aluminum, (tpp)AlCl, in the presence of a quaternary organic salt or triphenylphosphine. At ambient temperature and a relatively high catalyst loading, reaction rates were slow, generally requiring 12−23 days and thereby affording rather low molecular weight polymers. Nevertheless, copolymers from ethylene oxide, propylene oxide, or cyclohexene oxide and carbon dioxide with very narrow molecular weight distributions (1.06−1.14) were isolated. Approximately a decade later, Kruper and Dellar investigated the use of (tpp)CrX complexes in the presence of 4−10 equiv of nitrogen donors, such as N-methylimidazole (N-MeIm) or (4-dimethylamino)pyridine (DMAP), for the coupling of a wide variety of epoxides and carbon dioxide to provide cyclic carbonates.[20] For example, propylene oxide readily afforded propylene carbonate at 50 bar of CO_2 pressure with a turnover frequency (TOF) of 158 h^{-1} at 80 °C. Conversely, cyclohexene oxide and CO_2 yielded predominantly copolymer under similar reaction conditions. The reasons for the general discrepancy in product selectivity for propylene oxide and cyclohexene oxide coupling with carbon dioxide will be discussed in detail for the (salen)CrX catalyst system where mechanistic information is available. In more recent studies, Holmes and co-workers have reported the copolymerization of cyclohexene oxide and CO_2 in the presence of a fluorinated (tpp)CrCl catalyst (Figure 2) along
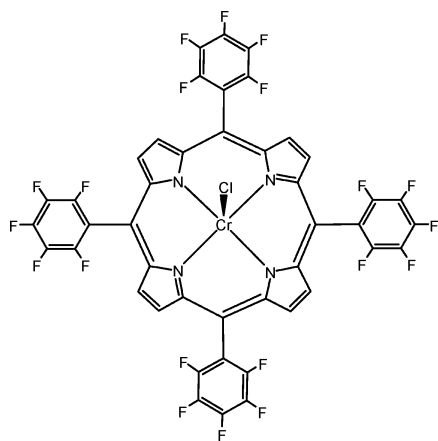
Figure 2. Fluorinated porphyrin derivative of chromium(III) chloride.[21]

with a cocatalyst such as DMAP.[21] TOFs greater than 150 h^{-1} were observed for reactions performed at 110 °C in scCO$_2$ (225 bar) where the catalyst solubility is greatly enhanced over its (tpp)CrCl analogue, with the resulting copolymers having a high percentage of carbonate linkages (>97%) and narrow polydispersities (PDIs).

The rapid advances currently being experienced in the copolymerization of cyclohexene oxide and carbon dioxide were fueled by our development of a series of discrete zinc phenoxide derivatives as catalysts in 1995.[22,23] A typical *bis*(phenoxide)Zn(THF)$_2$ complex (where THF = tetrahydrofuran) used in these studies is illustrated in Figure 3,
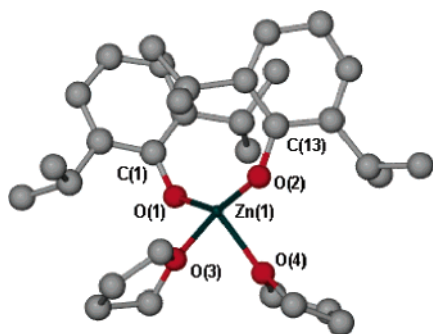

Figure 3. Monomeric zinc-*bis*(phenoxide) complex for the copolymerization of cyclohexene oxide and CO$_2$. The phenoxide ligand is 2,6-diisopropylphenoxide.

where the steric bulk of the phenoxide ligands limits aggregate formation. These catalysts were extremely effective for homopolymerizing epoxides to polyether; hence, the CO$_2$ content of the copolymer provided by this method was generally ~90% even though the reactions were carried out at high CO$_2$ pressures.[24,25] The copolymerization processes were performed in the absence of an organic solvent at 55 bar CO$_2$ pressure and 80 °C. Bulk polymerization reactions were run over a 24 h period, providing minimum values of TOFs of ~10 h^{-1} with catalytic activity varying slightly as a function of the substituents on the phenoxide ligands. Although the coupling reaction of propylene oxide and CO$_2$ provided predominantly propylene carbonate at 80 °C, at 40 °C, the reaction selectivity switched mainly to copolymer formation. This temperature dependence of product selectivity is a general phenomenon observed for most catalyst systems investigated and will be discussed in more detail later. Terpolymers with up to 20% propylene oxide content were produced from reaction mixtures of propylene oxide/cyclo-

hexene oxide and carbon dioxide. More moisture-tolerant dimeric zinc derivatives (Figure 4) containing the less
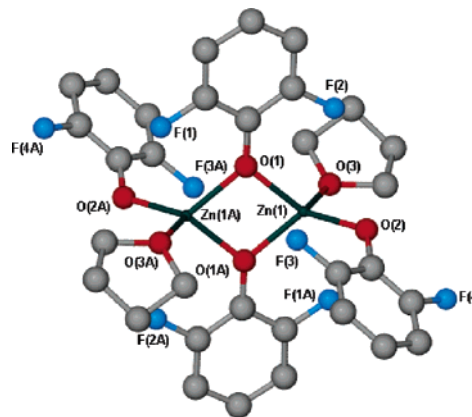

Figure 4. Dimeric zinc-*bis*(phenoxide) complex for the copolymerization of cyclohexene oxide and CO$_2$. The phenoxide ligand is 2,6-difluorophenoxide.

sterically encumbering 2,6-difluorophenoxide were later also shown to be quite active for the copolymerization process.[26] Unfortunately, these first generation homogeneous catalysts utilized the phenoxide ligand as the polymerization initiators. This was demonstrated in the instance of the difluorophenoxide derivative, where the fluorinated phenoxide was found as one of the end groups of the growing polymer chain by ^{19}F NMR and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS).[26,27] Hence, the active zinc species are ill-defined leading to broad molecular weight distributions (PDI > 4.0). Later studies by Coates' research group utilizing β-diminate zinc catalyst overcame this catalyst inadequacy (vide infra).[28]

Shortly following our report, Beckman and co-workers published upon the utilization of a fluorinated carboxylic acid zinc complex (Figure 5) derived from a monoester of maleic
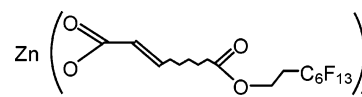

Figure 5. Highly fluorinated zinc carboxylate catalyst for the copolymerization of CO$_2$ and cyclohexene oxide in scCO$_2$.

acid as a catalyst for the coupling of CO$_2$ and cyclohexene oxide to produce poly(cyclohexene carbonate).[29] The copolymerization reactions were performed in the absence of organic solvent under scCO$_2$ conditions at 135 bar CO$_2$ pressure and 100 °C providing TOFs of about 9.0 h^{-1}. A significant breakthrough in zinc catalyst design for the copolymerization of cyclohexene oxide and CO$_2$ came from the research laboratory of Geoffrey Coates at Cornell University.[28] These catalysts were found to be highly active at low CO$_2$ pressure and provided copolymers of very narrow PDIs. A typical dimeric zinc β-diiminate catalyst is illustrated in Figure 6. Dramatic changes in catalytic activities for cyclohexene oxide/CO$_2$ copolymerization were noted for minor variations in the electronic and steric character of the (β-diiminate)ZnOR complex.[30] For example, for the zinc species where R^1 = H and R^2 and R^3 = Et, a rather typical TOF of 239 h^{-1} at 50 °C and 6.9 bar was obtained. However, upon changing R^1 to CN and R^2 and R^3 to Me and ^{i}Pr, respectively, the TOF increases to 2290 h^{-1} under the same reaction conditions. Alternatively, whereas zinc derivatives as shown in Figure 6 are poor copolymerization catalysts
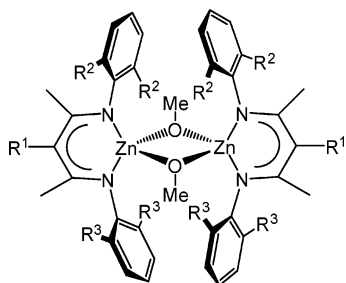
Figure 6. Highly active β-diiminate zinc catalyst for cyclohexene oxide/CO_2 copolymerization. A typical example is where $R^1 = H$ and R_2 and $R_3 = i$-propyl.
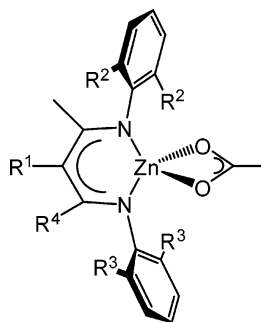

Figure 7. β-Diiminate zinc catalyst for propylene oxide/CO_2 copolymerization, where $R^1 = H$, $R^2 = Et$, $R^3 = {}^iPr$, and $R^4 = CF_3$.

for propylene oxide/CO_2, the complex depicted in Figure 7 is an effective catalyst for copolymerizing propylene oxide and CO_2 to poly(propylene carbonate) at 25 °C and 6.9 bar with a TOF of 235 h^{-1}.[31]

The mechanism of the copolymerization of epoxides and CO_2 as catalyzed by β-diiminate derivatives of zinc has been extensively investigated by Coates and co-workers employing in situ infrared techniques.[32] The transition state for the epoxide ring-opening step is proposed to take place by way of a bimetallic process illustrated in Figure 8. In closely
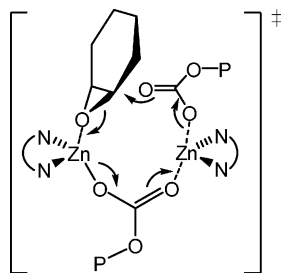

Figure 8. Transition state of the epoxide ring-opening step ($P =$ growing polymer chain).

related studies, Chisholm and co-workers have found that β-diiminate derivatives of zinc containing sterically encumbering initiators, such as O^{t}Bu or OSiPh$_3$, are monomeric and, as would be anticipated, are effective catalysts for the copolymerization of cyclohexene oxide and CO_2.[33,34] In these instances, the initial ring-opening step involving the bulky alkoxide initiators probably proceeds via a monometallic transition state.

2. Focus of Review

The focus of this review is to provide a comprehensive chronicle of the coupling reactions of oxiranes and carbon dioxide catalyzed by salicylaldimine (salen)-metal derivatives

in the presence of appropriate cocatalysts, with the emphasis being on polycarbonate production.[35-39] In addition to surveying catalytic activities for the various metal catalyst systems, special attention will be directed at a thorough and unifying discussion of the mechanistic aspects of these processes. The majority of investigations involve the readily available epoxide monomers, cyclohexene oxide and propylene oxide; however, references to other monomers will be made when relevant to the discussion. This review will be organized according to the metal centers, which include Cr, Co, Al, and others. Comparisons with the closely related metal porphyrin catalysts will be incorporated when appropriate. The information used in this review mainly comes from the available scientific publications, with patent literature only occasionally cited.

3. Elementary Reactions Relevant to Epoxide/CO_2 Coupling Utilizing (salen)MX Catalyst Systems

Before surveying the specific (salen)MX catalyst systems, it would be useful at this point to describe the elementary steps that may be involved in these instances for the alternating copolymerization reaction of epoxides and CO_2. In general, these processes catalyzed by (salen)MX complexes require a cocatalyst. These cocatalysts include Lewis bases such as *N*-heterocyclic amines or phosphines, in addition to quaternary organic salts. At this point, I will refer to all of these cocatalysts as Nuc, bearing in mind that Nuc may be the active species, either anionic or neutral, derived from the initially added cocatalyst. A detailed analysis of the nature of the cocatalyst will be provided later on in this review (vide infra). The present discussion will assume that Nuc = cocatalyst added, for example, an azide derived from a weakly interacting cation such as *n*-Bu$_4$N$^+$ and PPN$^+$ [*bis*(triphenylphosphoranylidene)ammonium cation], and will focus on chromium(III) derivatives where the most definitive data are available. Presumably, as has been shown in several instances, similar reaction pathways are available to the other analogous active metal complexes.

Upon the dissolution of a typical five-coordinate (salen)-CrX derivative in the presence of a cocatalyst (Nuc) in a weakly interacting solvent, the formation of a six-coordinate complex is evident. For example, the X-ray structure of the complex resulting from addition of [PPN][N$_3$] to (salen)-CrN$_3$, (salen)Cr(N$_3$)$_2{}^-$ as its PPN$^+$ salt, has been described.[40] Furthermore, solution infrared data in the $\nu_{N_3^-}$ stretching vibration region of (salen)CrN$_3$ in toluene reveal its five-coordination geometry, which shifts to six-coordination upon adding epoxide or Nuc.[41] Indeed, X-ray structures of the THF analogues of the six-coordinate epoxide complex, (salen)-Cr(N$_3$)THF, have been reported.[42,43] Hence, the (salen)CrX/Nuc catalyst system in a large excess of epoxide monomer exists as a equilibrium mixture greatly favoring the neutral epoxide adduct (eq 2). This reaction constitutes the epoxide activation step in the process. Recently, we have clearly established that (salen)CrCl derivatives in the presence of excess *n*-Bu$_4$NN$_3$ readily afford (salen)Cr(N$_3$)$_2{}^-$ species.[44] Furthermore, this process is irreversible upon subsequent addition of excess chloride ions.


$$\text{(2)}$$
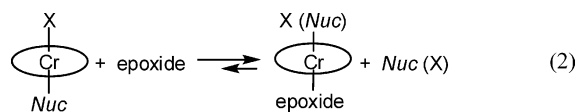
The initiation step of the copolymerization reaction can proceed via either a monometallic or bimetallic pathway.

Reaction 3 employs a specific epoxide, propylene oxide, to address regiochemistry. Although ring opening is favored at the least sterically hindered C−O bond as illustrated below, attack at either carbon center is generally observed leading to regioirregularity.[45] As indicated in eqs 3 and 4, either X or Nuc may serve as the initiator group and, hence, the polymer chain end group.

monometallic

$$(3)$$

bimetallic

$$(4)$$
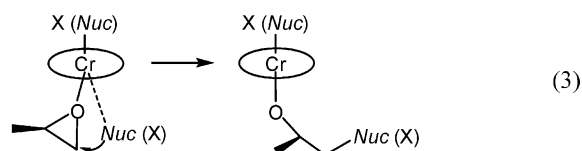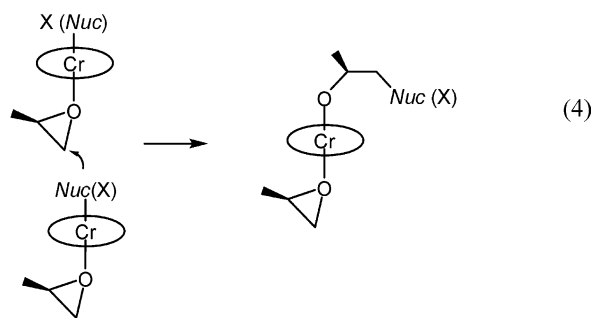
The intermolecular bimetallic pathway for epoxide ring opening is the pivotal step of Jacobsen's asymmetric nucleophilic ring opening of epoxides catalyzed by chiral (salen)CrX derivatives in the absence of a cocatalyst.[42] Indeed, for the chiral (salen)CrX complex [H$_2$salen = *N,N′*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexenediamine], a "head-to-tail" orientation of the two metal complexes in the transition state is required for enantioselectivity.[46] An X-ray structure of the THF adduct of the product derived from the reaction of (salen)CrN$_3$ with cyclopentene oxide by way of eq 4 has been reported.[42]

The subsequent step in the copolymerization reaction involves CO$_2$ insertion into the metal−oxygen bond generated upon epoxide ring opening (eq 5). This reaction has been extensively investigated from a mechanistic standpoint utilizing low-valent organometallic compounds containing metal−alkoxide or metal−aryloxide moieties.[18,47] These studies have unambiguously established that the CO$_2$ insertion process does not require an open coordination site on the metal center. Furthermore, the rate of CO$_2$ insertion increases as the electronic and steric availability of the lone pairs on the oxygen atom of the alkoxide or aryloxide increases, thereby allowing for better interaction with the poorly electrophilic carbon center of CO$_2$. That is, the more nucleophilic and less sterically encumbered M−OR centers are more reactive. In general, complexes meeting these requirements are quite reactive toward CO$_2$ insertion. Concomitantly, decarboxylation of these afforded metal−alkyl or aryl carbonates is comparatively slow.[18c] The thus formed carbonate serves as the nucleophile to propagate monomer enchainment.

$$(5)$$
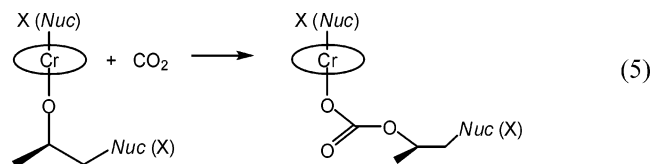
Side reaction pathways that are detrimental to completely alternating copolymer formation include (i) consecutive epoxide ring opening (reaction 6) and (ii) backbiting leading to cyclic carbonate production (reaction 7). The former process is not terribly important for (salen)MX catalytic systems; that is, the afforded copolymers are generally completely alternating. However, for the stronger Lewis acid catalysts, such as Zn(II) complexes, this can be a significant occurrence (vide supra).

(i) Consecutive epoxide ring opening:

$$(6)$$
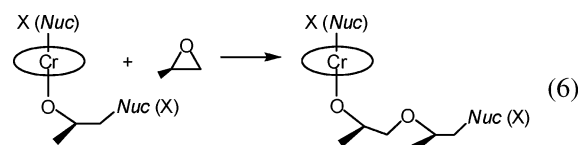
(ii) Backbiting reaction leading to cyclic carbonate:

$$(7)$$
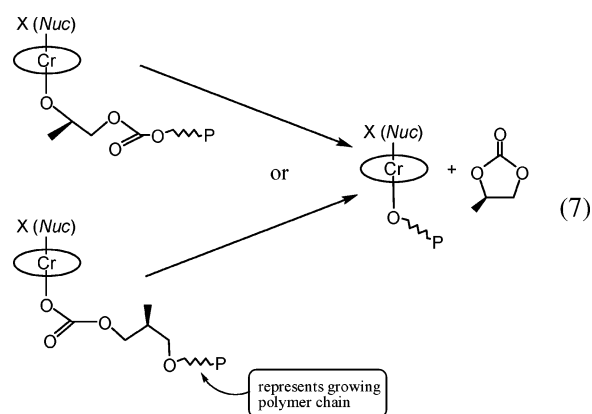
This process is responsible for the production of the undesirable cyclic carbonate product. For aliphatic epoxides, this reaction generally is very significant and is favored at higher temperatures. Alternatively, the growing polymer chain may dissociate from the metal center (can be aided by the presence of a large [cocatalyst]), thereby more easily leading to cyclic carbonate production. That is, the process described in Figure 9 should have a much lower barrier for
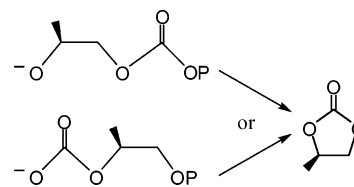
Figure 9. Formation of cyclic carbonate through the "free" anionic polymer chain.

cyclic carbonate formation when compared with its "metal-bound" analogue (eq 7).

4. Chromium Salen Catalysts

In 2000, we began efforts to uncover well-defined transition metal coordination complexes as catalysts for the coupling of CO$_2$ and epoxides to selectively provide polycarbonates. Jason Yarbrough, then a graduate student in my research group, was inspired by the elegant studies of Jacobsen and co-workers on the use of chiral Cr(III) catalysts for the asymmetric ring opening of epoxides (Figure 10).[48] Hence, we thought that it might be possible to generate stereoregular copolymers from the copolymerization of CO$_2$ and cyclo-
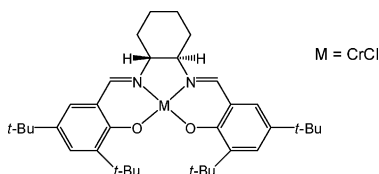
Figure 10. Complex **1**, the most reactive and enantioselective (salen)M^{III}X catalyst for epoxides ring opening.[48]

hexene oxide employing Jacobsen's catalyst. Unknown to us at the time, Jacobsen and co-workers had reported in a 2000 patent that the (*R,R*)-enantiomer of **1** in the presence of one atmosphere CO_2 selectively reacted with the (*S*)-enantiomer of racemic 1,2-epoxyhexane to afford polycarbonate.[49,50] Our studies were as well encouraged by the success of the related reports of Kruper[20] and Holmes[21] utilizing Cr-(III) porphyrin derivatives as copolymerization catalysts.

Our initial results using complex **1** as a catalyst for the copolymerization of CO_2 and cyclohexene oxide in the presence of *N*-MeIm were reported in 2001.[51] Concurrent with our studies, Paddock and Nguyen communicated on the use of various (salen)CrCl derivatives, including complex **1**, in the presence of DMAP for the effective coupling of CO_2 and a variety of terminal aliphatic epoxides to provide cyclic carbonates in nearly quantitative yields and 100% selectivity.[52] Among the epoxides examined were propylene oxide, epichlorohydrin, vinyl epoxide, and styrene oxide. These reactions were carried out at approximately 3 bar CO_2 pressure and 75−85 °C in the presence of 1−2 equiv of DMAP with TOFs ranging from 127 to 254 h^{-1}. An increase in the number of equivalents of DMAP to 4 greatly retarded the process. These researchers also indicated in a footnote that alicyclic epoxides, such as cyclohexene oxide, couple with CO_2 to selectively provide polycarbonates.

In early 2002, a detailed account of our investigations utilizing complex **1** as a catalyst for the copolymerization of cyclohexene oxide and CO_2 was published.[53] In this study, the X-ray structure of Jacobsen's pervasive five-coordinate chiral catalyst, **1**, was described and shown to contain a nearly planar N_2O_2 ligand core about the chromium center with an axial chloride group (Figure 11).[54] At 80 °C and
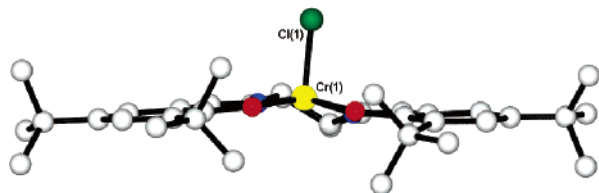

Figure 11. Ball-and-stick drawing of complex **1** defined by X-ray crystallography.[53]

58.5 bar CO_2 pressure, complex **1** alone copolymerized cyclohexene oxide and carbon dioxide to poly(cyclohexylene carbonate), void of polyether linkages, with a TOF of 10.4 h^{-1}. Under these reaction conditions, there was an extended initial period of no catalytic activity, which in part accounts for the relatively low TOF observed. Presumably, this incubation time provides a endogenous source of cocatalyst to initiate the copolymerization process, for it is well-established that complex **1** is capable of readily ring opening cyclohexene oxide to provide the species
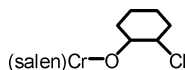
in the absence of a cocatalyst.[48,55] The number average (M_n) molecular weight of the copolymer produced as determined by gel permeation chromatography (GPC) was found to be 8900 g/mol, which is considerably smaller than that predicted by theory. This latter observation is suggestive of chain-transfer processes occurring, although efforts were made to ensure anhydrous conditions.

As anticipated, on the basis of the copolymerization process involving the analogous chromium(III) porphyrin complex,[21] the addition of an organic base such as *N*-MeIm to complex **1** resulted in enhanced catalytic activity. For example, in the presence of 5 equiv of *N*-MeIm, an increase in TOF to 32.2 h^{-1} at 80 °C was achieved. Levels of *N*-MeIm much greater than this were detrimental to copolymer production (vide infra). Although we had hoped to provide stereocontrol by a site-control mechanism using the chiral catalyst **1**, the resulting copolymers were found to be completely atactic as revealed by ^{13}C NMR (see Figure 12).[56]
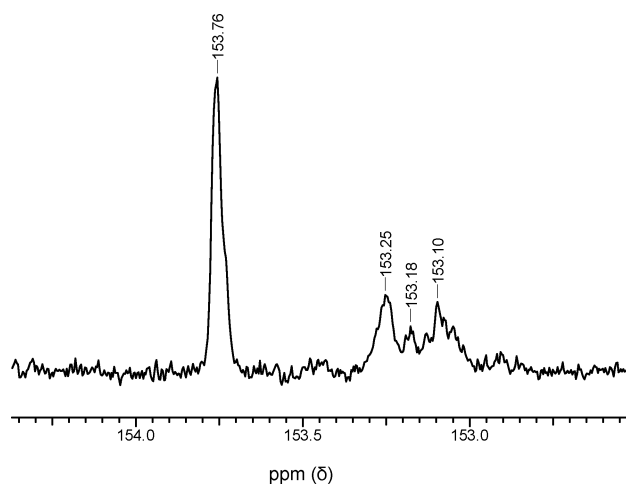

Figure 12. ^{13}C NMR spectrum of poly(cyclohexylene carbonate) in the carbonate region produced from cyclohexene oxide and CO_2 (60 bar) catalyzed by *R,R*-version of complex **1** in the presence of a cocatalyst at 80 °C. The m-centered tetrads (isotactic) appearing at 153.7 ppm and the r-centered tetrads (syndiotactic) at 153.1 ppm integrate equally. For an analogous process performed at 21 bar of CO_2 and 40 °C, the copolymer isolated was slightly enhanced in m-centered tetrads (unpublished observations by E. B. Frantz and D. J. Darensbourg).

At this time, we also investigated the mechanistic aspects of this process by in situ infrared spectroscopy. These experiments were performed using a stainless steel Parr autoclave modified with a silicon crystal, which allows for FT attenuated total reflectance (ATR) infrared spectroscopy.[57] The ATR crystal is permanently fixed to the bottom of the reactor, and the infrared beam, after passing through several connecting arms reflected by mirrors at each junction, enters the crystal. Signal enhancement is achieved by repetitive reflections (30) along the length of the ATR crystal prior to returning to the MCT detector via the connection arms (see Figure 13). Since our original report, this spectroscopic technique for monitoring these copolymerization reactions has been utilized worldwide, thereby contributing greatly to our understanding of these processes.[32,58]

Figure 14 illustrates a typical reaction profile obtained while monitoring the coupling reaction of CO_2 and cyclohexene oxide, where the infrared absorbance at 1750 cm^{-1} corresponds to the asymmetric ν_{CO_2} vibrational mode and

In-Situ Infrared Spectrometry

Withstands 1500 psi
(100 atm) and up to 200 °C

Reaction Mixture

Si-based
Crystal

ZnSe Focusing Material
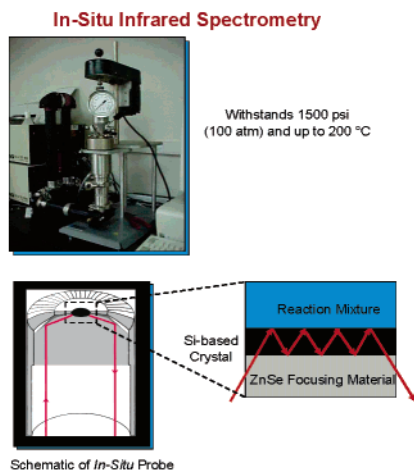
Schematic of *In-Situ* Probe

Figure 13. ASI ReactIR 1000 reaction analysis system with a stainless steer Parr-modified autoclave.
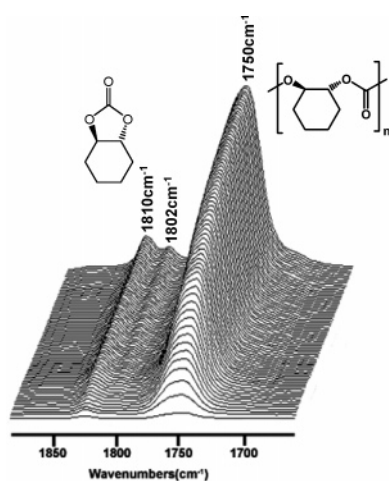

Figure 14. Typical three-dimensional stack plot of the infrared spectra collected every 3 min during the coupling reaction of cyclohexene oxide and CO_2 (80 °C and 55 bar pressure).

the bands at 1810 and 1802 cm^{-1} correspond to the *trans*-cyclic carbonate. These early kinetic measurements on the (salen)CrX-catalyzed reaction of CO_2 and cyclohexene oxide in the presence of *N*-MeIm revealed copolymer formation, i.e., the chain propagation step, to be first-order in metal catalyst and epoxide concentrations at a CO_2 pressure of 55 bar in the presence of 2 equiv of *N*-MeIm. An important observation noted during these studies was that although the copolymerization process was greatly enhanced in the presence of *N*-MeIm, the reaction profile displayed a sigmoidal shape suggestive of an initiation period (Figure 15). Furthermore, additional increases in *N*-MeIm concentration revealed an extension of this initiation period as depicted in Figure 15. A similar dependence on DMAP concentration was previously reported by Paddock and Nguyen for the coupling of aliphatic epoxides and CO_2 to afford cyclic carbonates (vide supra).[52] Our initial thoughts were that this phenomenon was simply due to an inhibition of the primary epoxide ring-opening step depicted in eq 3 or 4 by the organic base preferentially coordinating the five-coordinate metal center, thereby repressing epoxide binding and activation. A more comprehensive analysis of the role of various cocatalysts will follow shortly.

Temperature-dependent rate data for the formation of both copolymer and cyclic carbonate products from the reaction of cyclohexene oxide and CO_2 were obtained in the presence
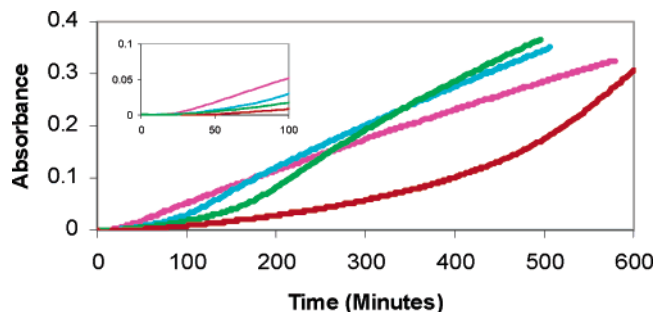

Figure 15. In situ infrared monitoring of complex **1**-catalyzed formation of poly(cyclohexylene carbonate) from cyclohexene oxide and CO_2 at different *N*-MeIm concentrations. Pink line, 2.25 equiv; teal line, 6 equiv; green line, 10 equiv; and red line, 33 equiv.

of complex **1** without the intervention of a cocatalyst.[59] The linear portion of the sigmoidal reaction profiles of product formation vs time was utilized in the kinetic analysis.[60] The energies of activation for poly(cyclohexylene carbonate) and cyclohexene carbonate formation were derived from these kinetic data and were determined to be 46.9 and 133.0 kJ mol^{-1}, respectively. Analogous comparative data for the coupling of propylene oxide and CO_2 will be discussed later. Using these activation parameters, the reaction coordinate diagram for these competitive processes is depicted in Figure 16. As is apparent from Figure 16, the activation barrier for
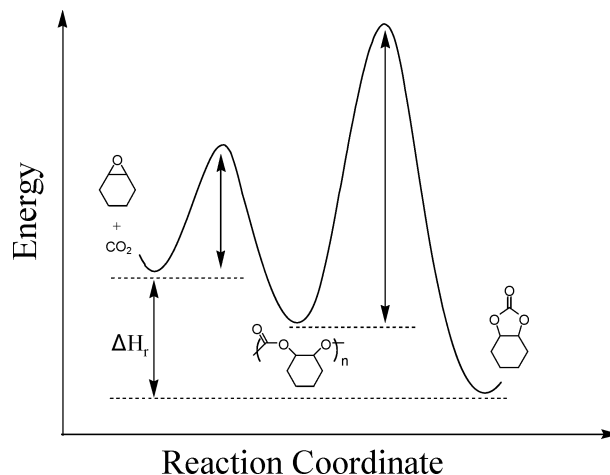

Figure 16. Reaction coordinate diagram of the coupling reaction of CO_2 and cyclohexene oxide. ΔH_r is estimated to be −34 kJ mol^{-1}.

cyclic carbonate production via the backbiting mechanism is some 86 kJ mol^{-1} higher in energy than that of the copolymer formation. This is consistent with the generally observed low level of cyclohexene carbonate production during CO_2/cyclohexene oxide copolymerization processes. A similar analysis of rate data for this process utilizing a dinuclear magnesium catalyst revealed the Arrhenius-derived activation parameters to differ by 81.9 kJ mol^{-1}.[58] We have rationalized this large energy difference between the two consecutive processes to be associated with the ring strain imposed on the five-membered carbonate grouping resulting from the conformation requirement of the alicyclic cyclohexyl ring.

In an effort to optimize the catalytic activity of the (salen)-CrX derivatives (Figure 17) toward the copolymerization of cyclohexene oxide and CO_2 in the presence of a common cocatalyst (*N*-MeIm), the reaction was investigated as a function of the various substituents on the salicylaldimine
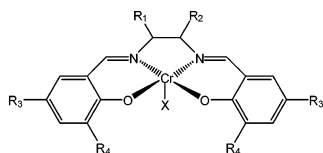
Figure 17. General structure of chromium(III) salen catalysts used in the copolymerization reactions.

ligand and the nature of the X nucleophile.[55] The synthetic accessibility of salen ligands readily provides a plethora of (salen)CrX derivatives possessing a wide range of steric and electronic properties. Steric variations in the diimine substituents (R_1 and R_2) of the (salen)CrCl complex while maintaining the R_3 and R_4 groups as t-butyls dramatically altered the effectiveness of these catalysts for the copolymerization process. That is, if R_1 and R_2 are the sterically encumbering t-butyl substituents (Figure 18), the catalytic
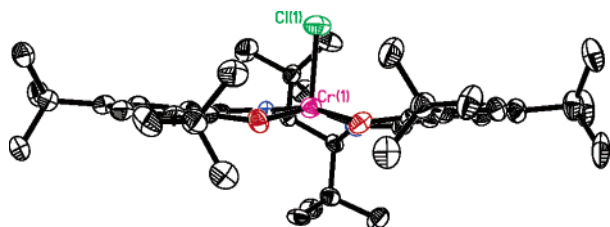

Figure 18. Thermal ellipsoid plot of (salen)CrCl (**2**) complex, where H_2salen $= N,N$-bis-(3,5-di-$tert$-butylsalicylidene)-1,2-di-$tert$-butylethylenediimine.

activity was greatly diminished, with a measured TOF of 0.8 h^{-1} at 80 °C as compared to a value of 35.7 h^{-1} for the $R_1 = R_2 = $ H analogue. Similarly, when R_1 and R_2 are phenyl substituents, which must both be axial or equatorial, the chromium derivative with phenyl groups in the sterically demanding axial conformation is much less catalytically effective than the complex with phenyl groups in the equatorial conformation, that is, 7.0 vs 72.8 h^{-1}. Surprisingly, even relatively less bulky substituents on the diimine backbone ($R_1 = $ H, $R_2 = $ Me) decrease the catalytic activity by more than half that as compared to the $R_1 = R_2 = $ H derivatives, 14.9 vs 35.7 h^{-1}. Conversely, changes in the electronic character of the R_1 and R_2 substituents displayed little to no effect on the rate of the copolymerization process. For example, the catalytic activities for the ethylene, phenylene, and R,R-cyclohexylene backbones were 35.7, 36.2, and 35.5 h^{-1}, respectively.

The dramatic impact of steric-encumbering substituents in the diimine backbone is consistent with the lack of an open face for the approaching monomer to interaction with the metal center as illustrated in the simplistic model catalysts in Figure 19. In this instance, the space-filling model of complex **2** (skeletonized in Figure 19A) is one of the few available for a (salen)CrCl derivative defined by X-ray crystallography (see Figure 20). It should be emphasized here that in the absence of at least two of the bulky t-butyl groups on the phenolic ligands, there is little solubility of these metal complexes in the weakly interacting CO_2-expanded epoxide solvents.

Upon maintaining a common sterically nonencumbering diimine structure while increasing the electron-donating substituents in the 3,5-positions of the phenolic ligands, an increase in the rate of copolymerization was observed. For example, (salen)CrCl containing an ethylene diimine backbone with $R_3 = $ OMe and $R_4 = t$-Bu is significantly more
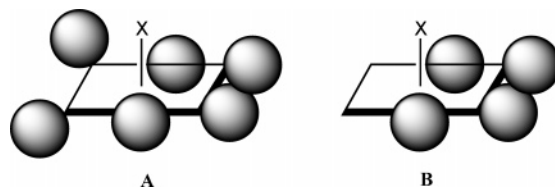

Figure 19. (A) (salen)CrX complex with bulky t-butyl substituents inhibiting all faces for monomer approach (see Figure 18 for the structure derived from X-ray analysis). (B) (salen)CrX complex without sterically encumbering substituents on the diimine backbone structure, thereby possessing an open face for monomer enchainment as in complex **1**.
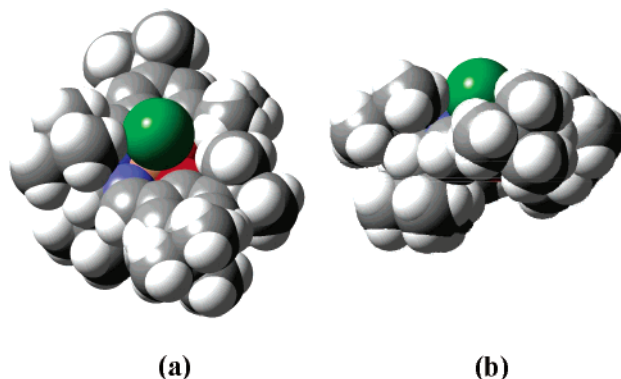

Figure 20. Space-filling models of complex **2**: (a) top view and (b) side view.

active catalytically than its di-t-butyl analogue, 56.7 vs 35.7 h^{-1}. Interestingly, unlike for its di-t-butyl analogue, this increase in catalytic activity observed for the $R_3 = $ OMe and $R_4 = t$-Bu complex varies slightly with changes in the diimine structure, that is, R,R-cyclohexylene (65.6 h^{-1}) > ethylene (56.7 h^{-1}) > phenylene (45.7 h^{-1}). Again, employing our simplistic model of the catalyst, it is readily apparent that the metal center for the (salen)CrCl ($R_3 = $ OMe and $R_4 = t$-Bu) derivative (Figure 21) is more accessible than that

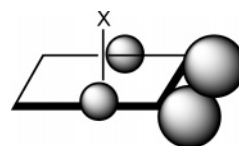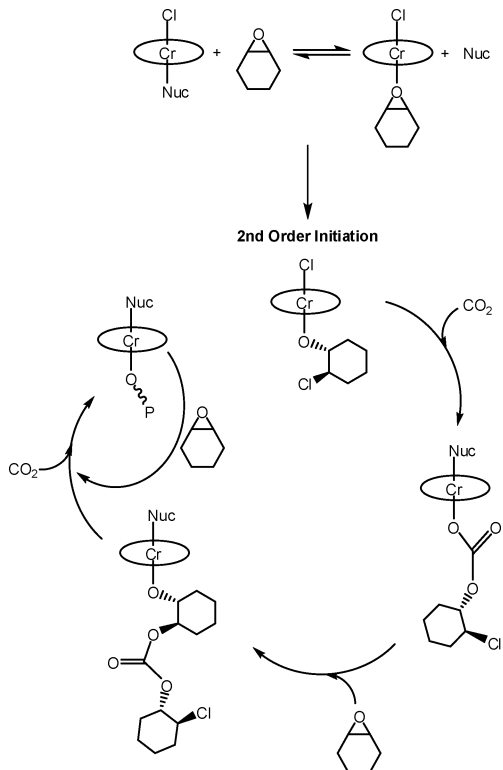**Figure 21.** Model for the (salen)CrCl catalyst, where $R_3 = $ OMe and $R_4 = t$-Bu with a sterically nonencumbering diimine backbone structure.

in complex **1** (Figure 19B), which may account for some of the increase in catalytic activity noted.

In all cases, changing the X ligand from chloride to azide enhanced the catalytic activity of the (salen)CrCl derivative. For example, (salen)CrX where $R_1 = R_2 = $ H and $R_3 = $ OMe, $R_4 = t$-Bu, and X $= $ azide has a TOF at 80 °C of 46.9 vs 35.7 h^{-1} for the comparable complex with X $= $ chloride. This is the result of a more rapid initiation step (epoxide ring opening by X) when X $= N_3$, as has been noted by in situ infrared studies. Hence, the optimal (salen)CrX derivative for the copolymerization of CO_2 and cyclohexene oxide in the presence of N-MeIm as cocatalyst was observed to be that containing a cyclohexylene diimine backbone with $R_3 = $ OMe, $R_4 = t$-Bu, and X $= N_3$. Finally, this study also revealed the importance of the nature of the cocatalyst on the rate of the copolymerization reaction, where DMAP was shown to be much more effective than N-MeIm as a cocatalyst (vide infra).

The preliminary mechanism that we proposed for the copolymerization of cyclohexene oxide and carbon dioxide by complex **1** and related catalysts in the presence of *N*-heterocyclic amine cocatalyst based on initial observations is summarized in Scheme 1. An increase in the *N*-MeIm

Scheme 1. Preliminary Mechanism for the Copolymerization of Cyclohexene Oxide and CO_2 Catalyzed by 1 in the Presence of Cocatalyst (Nuc = *N*-Heterocyclic Amine)
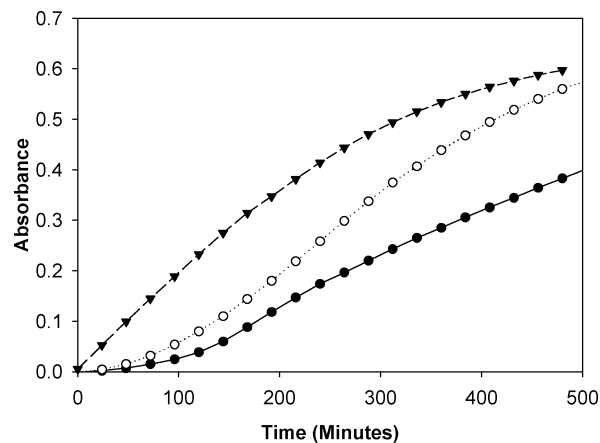

Figure 22. Comparison of in situ infrared profiles of copolymer production from CO_2 and cyclohexene oxide utilizing catalyst **1** and the three classes of cocatalysts: PPN^+Cl^- (▼), PCy_3 (○), and *N*-MeIm (●).

The comparable catalytic activity for the copolymerization of cyclohexene oxide and CO_2 in the presence of the (salen)-CrX catalyst (**3**) ($R_1 = R_2 = H$, $R_3 = R_4 = t$-Bu, and X = N_3) at 55 bar of CO_2 and 80 °C as a function of anionic cocatalysts is provided in Table 1. As is apparent in Table

Table 1. Catalytic Activity for the Copolymerization of Cyclohexene Oxide and CO_2 in the Presence of 1 equiv of PPNX Cocatalyst[a]
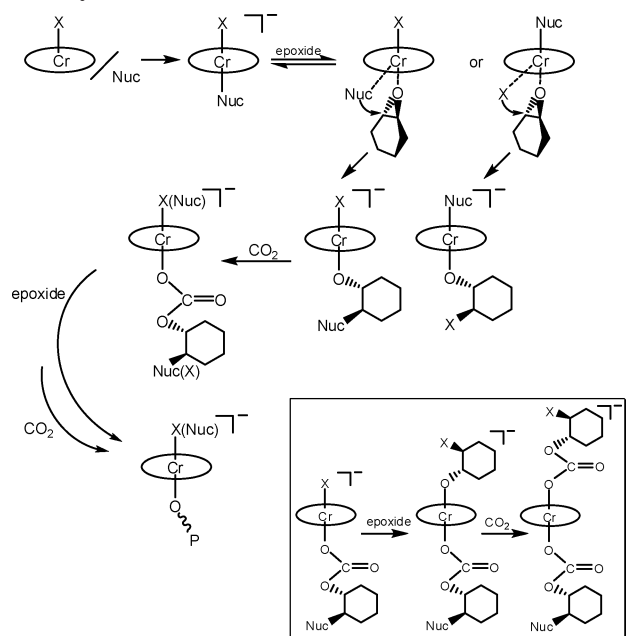
X	TOF[b]
N_3	608
Cl	494
Br	420
I	360
OAc	350
HCO_3	280

[a] The carbonate content of all copolymers isolated was greater than 99%. [b] Mol of epoxide consumed/mol of catalyst h.

concentration was proposed to retard the second-order initiation step (a la Jacobsen[42]) via inhibiting epoxide binding and concomitant activation. At the same time, monomer enchainment, shown to be first-order in both epoxide and metal catalyst, is enhanced in the presence of a strongly binding cocatalyst, which leads to a more reactive metal−oxygen bond on the growing polymer chain. Related studies of axial ligation of (salen)CrCl by neutral ligands to afford a six-coordinate complex have shown the Cr−Cl bond to be destabilized as revealed by X-ray data.[55]

Despite the notable increases in catalytic activity displayed by (salen)CrX derivatives for the copolymerization of cyclohexene oxide and CO_2 achieved by varying the salen ligand and X group, the most dramatic influence on the effectiveness of this catalyst system has been found to depend on the nature and concentration of the cocatalyst.[40,61] We have examined the three classes of cocatalysts generally employed in these and closely related catalyst systems, namely, *N*-heterocyclic amines, phosphines, and anions derived from PPN^+ or tetraalkylammonium$^+$ salts. The cadre of anionic cocatalysts are overwhelmingly more effective than the neutral ones and will be discussed first. The most striking feature of these anionic cocatalysts is the lack of an initiation period, that is, the copolymerization reactions displayed ideal kinetic behavior as compared to their neutral counterparts. See Figure 22 for the in situ infrared reaction profiles for the formation of poly(cyclohexylene carbonate) from cyclohexene oxide and CO_2 catalyzed by **1** in the presence of the three general types of cocatalysts.

1, the azide anion is again found to be most effective, with Cl > Br > I. Anions derived from PPN^+ are more competent than those originating from *n*-Bu_4N^+, albeit generally not greater than 20%. The superior activity of PPN^+ salts is probably due to the fact that they are hydrophobic and easily isolated in pure form, whereas tetraalkylammonium salts require multiple recrystallizations to ensure minimal water content. Furthermore, these latter counterions are more interactive with anions than their PPN^+ analogues.

More comprehensive kinetic studies employing complex **3** in the presence of anionic cocatalysts (Nuc) reveal the mechanistic aspect represented in Scheme 2, where X and Nuc may be the same anion or different anions.[40] Nevertheless, it is clear that whether one starts with (salen)CrCl and 1 equiv of $PPNN_3$ or (salen)CrN_3 and 1 equiv of PPNCl, the rate of formation of copolymer is the same.[62] Furthermore, rate studies demonstrate that anionic six-coordinate intermediates are more effective at both the epoxide ring opening and the CO_2 insertion steps than their neutral six-coordinate analogues (vide infra). Both Nuc and X are found as copolymer end groups by MALDI-TOF-MS on low molecular weight copolymers. However, these observations are not quantified; hence, it is not known currently which of the two initiation pathways is favored. Similarly, it is not definitively established where two polymer chains propagate from one metal center as indicated in the boxed section of

Scheme 2. Mechanistic Aspects of Cyclohexene Oxide/CO_2 Copolymerization in the Presence of (Salen)CrX and Cocatalyst (Nuc = Anion)

Table 2. Copolymerization of Cyclohexene Oxide and CO_2 Catalyzed by Complex 3 in the Presence of Amine Cocatalysts[a]

| cocatalyst[b]	TOF
DMAP	270
pyridine	55.6
Et$_3$N	trace
4-PYP[c]	323
DBU[d]	130

[a] CO_2 pressure of 55 bar at 80 °C. [b] Cocatalyst loading of 3 equiv. [c] 4-(Pyrrolidin-l-yl)pyridine. [d] 18-Diazabicyclo[5.4.0]undec-7-ene.

Scheme 2. There is some support for this latter behavior based on molecular weight data for polycarbonates produced by these and related catalytic systems.[63,64] Some caveats to Scheme 2 worthy of note in the presence of excess quantities of cocatalyst (Nuc) are that (i) the initial form of the catalyst system can be (salen)Cr(Nuc)$_2^-$-dependent on the nature of Nuc and that (ii) more rapid displacement of the growing polymer chain can occur with concomitant enhancement of cyclic carbonate production (Figure 9).

Our earlier explanation with regard to the role of *N*-heterocyclic amines as cocatalysts appears at odds with more recent observations, which clearly show that the second-order initiation step is not significantly retarded at 80 °C in the presence of these cocatalysts. Furthermore, it was also apparent that tertiary amines such as triethylamine or pyridines were not very effective as cocatalysts (Table 2). Infrared spectroscopy along with X-ray crystallography have led us to conclude that the heterocyclic nitrogen base cocatalysts are activated in two steps, initially interacting

with CO_2 in the presence of (salen)CrX to afford a weak zwitterionic carbamic complex, followed by a reaction with cyclohexene oxide to provide a stabilized zwitterion. Scheme 3 summarizes the catalytic cycle for the activation process, which is consistent with an increase in the initiation period with increasing cocatalyst precursor. These studies clearly revealed a strong correlation between the disappearance of the infrared band at 1599 cm^{-1} due to "free DMAP" and the maximum rate of copolymer production. That is, these zwitterions serve as cocatalyst analogues to anions derived from organic salts.

A modified catalytic cycle for the copolymerization of cyclohexene oxide and carbon dioxide utilizing (salen)CrX/heterocyclic nitrogen base systems, which accounts for the new mechanistic information, is shown in Scheme 4. As seen in Scheme 4, two alternative pathways for copolymer production are proposed to occur at different rates, which may account for the bimodal distributions of molecular weights with narrow PDIs commonly observed in these systems. Alternatively, this bimodal distribution of molecular weights may arrive from trace water contaminants.

Relevant to the catalytic cycle proposed in Scheme 4, Kim and co-workers have isolated and structurally characterized an intermediate (**4**) in the catalytic coupling of propylene oxide and CO_2 to afford propylene carbonate with a TOF > 300 h^{-1} at 100 °C and 35 bar CO_2 pressure (Scheme 5).[65,66] In this instance, pyridine bases were found to ring open propylene oxide with 100% selectivity at the least hindered carbon to provide dimeric pyridinium alkoxy zinc derivatives. As might be anticipated, pyridines containing electron-donating substituents exhibited greater reactivity than those containing electron-withdrawing groups. Contradictory to this latter report, Scheme 4 incorporates CO_2 insertion into the electron-rich Cr−N bond prior to epoxide ring opening by

Scheme 3. Catalytic Cycle for the Activation of *N*-Heterocyclic Amines, Illustrated Specifically for DMAP

X-ray structure of complexes where X = N$_3$
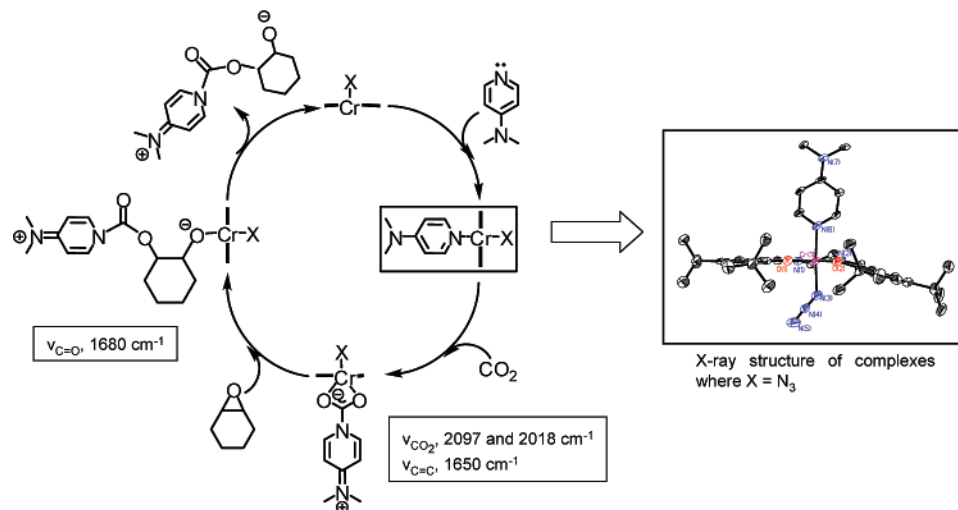
Scheme 4. Catalytic Cycle for Copolymerization of Cyclohexene Oxide and CO₂ in the Presence of (salen)CrX/ N-Heterocyclic Amine Catalysts
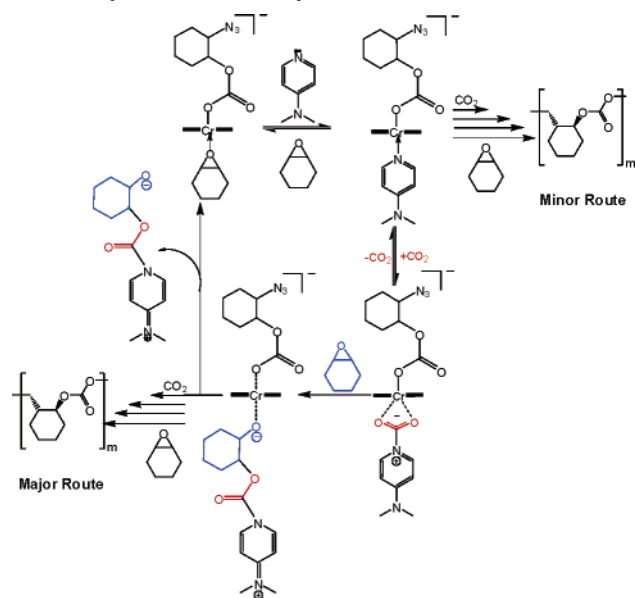
Scheme 5. Proposed Catalytic Cycle for the Synthesis of Propylene Carbonate Using (Pyridine)₂ZnBr₂ Catalysts
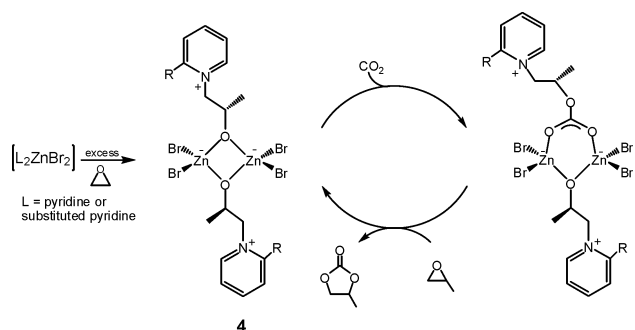
a carbamate group. This was proposed to be consistent with the observation that the process was highly influenced by CO_2 pressure. Nevertheless, we cannot unequivocally rule out a similar reaction pathway occurring here as well. Indeed, when employing phosphine ligands as cocatalysts, ring opening of epoxides by phosphines to provide phosphonium zwitterions is proposed to be a pivotal step in the copolymerization process.

As mentioned above, sterically encumbering phosphines (Tolman cone angles 145−185°)[67] were found to be effective cocatalysts for (salen)CrX complexes, generally more so than the best N-heterocyclic nitrogen bases. See Table 3 for the catalytic activities of the more effective phosphine ligands for the copolymerization of cyclohexene oxide and CO_2 at 80° and 55 bar CO_2. As illustrated in Figure 23, contrary to what is observed for N-heterocyclic nitrogen base-cocatalyzed processes, an increase in phosphine concentration decreases the initiation period, eventually reaching saturation kinetics. Importantly, these bulky phosphines in the presence of excess cyclohexene oxide do not readily bind to the metal center as revealed by infrared spectroscopy in the ν_{N_3} region of complex 3.

Consistent with this kinetic behavior, we proposed a direct attack on the metal-bound epoxide by basic phosphines leading to phosphonium zwitterions, which serve in the same capacity as anions derived from organic salts (Scheme 6).

Table 3. Effect of Various Phosphines on the Rate of Copolymerization of Cyclohexene Oxide and CO₂ Catalyzed by Complex 3[a]

phosphine	cone angle (deg)	TON[b]	TOF[c]
P[C(CH₃)₃]₃	182	1277	638
P(2,4,6-tri-CH₃OC₆H₂)₃	185	1417	354
P(C₆H₁₁)₃	170	1318	329
P(p-CH₃OC₆H₄)₃	145	1293	323
P(o-CH₃OC₆H₄)₃	153	1170	292
P(p-CH₃C₆H₄)₃	145	1301	325

[a] Each experiment was performed with 3 equiv of phosphine. Cone angles were derived utilizing the Tolman method.[67] All active catalyst systems produced copolymer with >97% carbonate content. [b] Measured in mol CHO consumed/mol Cr. [c] Measured in mol CHO consumed/ mol Cr h.
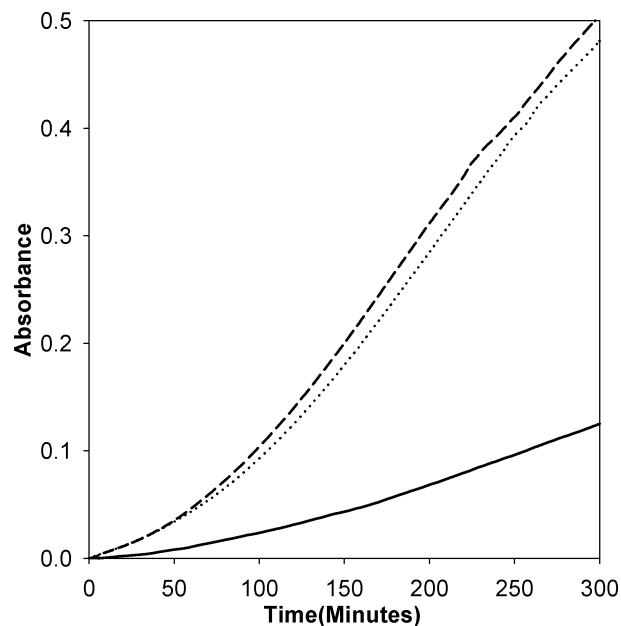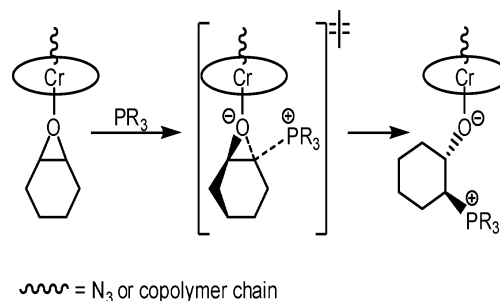

Figure 23. Effect of [tricyclohexylphosphine] on the rate of copolymerization as monitored by in situ infrared spectroscopy: solid line, 1 equiv; dotted line, 3 equiv; and dashed line, 5 equiv.

Scheme 6. Activation of Phosphines by Formation of Phosphonium Zwitterions

⌇⌇⌇ = N₃ or copolymer chain

The lack of interactions of these large phosphines with the metal center does not retard active cocatalyst formation as is observed for N-heterocyclic nitrogen bases. Inoue and co-workers have previously proposed in their copolymerization studies catalyzed by aluminum porphyrin derivatives in the presence of PPh₃ the formation of phosphonium salts.[19,68,69] Interestingly, small basic phosphines, for example, n-Bu₃P, initially served as effective cocatalysts, presumably via a similar pathway to that of sterically bulky ones. However, eventually, these phosphines are consumed by an alternative route that is detrimental to copolymer production. In summary, a consolidated pathway for (salen)CrX-catalyzed

copolymerization of cyclohexene oxide and CO_2 is proposed, which involves anionic initiators originating from organic salts or *N*-heterocyclic nitrogen bases or phosphine precursors.

Finally, in efforts to further optimize the rate of selective copolymer formation from cyclohexene oxide and CO_2 in the presence of the (salen)CrX/cocatalyst systems, a detailed examination of the CO_2 pressure dependence of this process was performed.[43] Figure 24 displays the pressure dependence
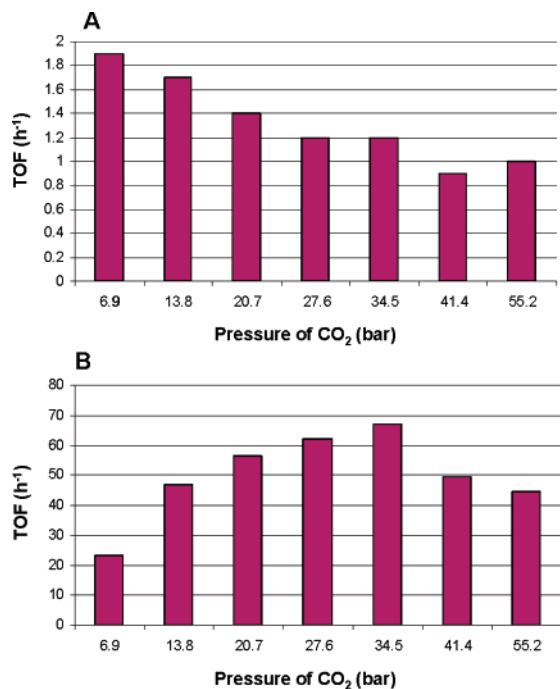

Figure 24. Pressure dependence of CO_2/cyclohexene oxide-coupling reaction catalyzed by complex **3** in the presence of 2.25 equiv of *N*-MeIm. (A) Cyclic carbonate production and (B) polycarbonate production.

of the TOFs for both cyclic carbonate and polycarbonate production utilizing complex **3** in the presence of *N*-MeIm as a cocatalyst. As is evident from Figure 24, there is a decrease in cyclic carbonate production with an increase in CO_2 pressure, whereas polycarbonate formation is significantly enhanced reaching a maximum at 34.5 bar with a subsequent decrease at higher CO_2 pressures. The decrease in cyclohexylene carbonate production with increasing CO_2 pressure is consistent with a reduction in the lifetime of the chromium–alkoxy intermediate (boxed in Scheme 7), which is thought to be favored over its CO_2 insertion intermediate in the backbiting mechanism leading to cyclic carbonate (eq 7). The decrease in the rate of copolymer formation at pressures of $CO_2 > 35$ bar was ascribed to a catalyst/epoxide dilution effect in the cyclohexene oxide-enriched liquid phase.[70,71] This is the consequence of a significant volumetric expansion of the gas-expanded liquid at high CO_2 pressures.[72,73] The ultimate TOF for the copolymerization of cyclohexene oxide and CO_2 was achieved utilizing the complex in Figure 17, where R_1, $R_2 = (1R,2R)$-C_4H_8−, R_3 = OCH_3, $R_4 = t$-Bu, and X = N_3, in the presence of one equivalent of $PPNN_3$, where a TOF of 1153 h^{-1} at 80° was observed at a CO_2 pressure of 35 bar.

Currently, studies aimed at catalyst design for the selective production of completely alternating copolymers from cyclohexene oxide and carbon dioxide have reached a high level of maturity. Nevertheless, it has been adequately

Scheme 7. Catalytic Pathways to Copolymer (A) vs Cyclic Carbonate (B) Formation
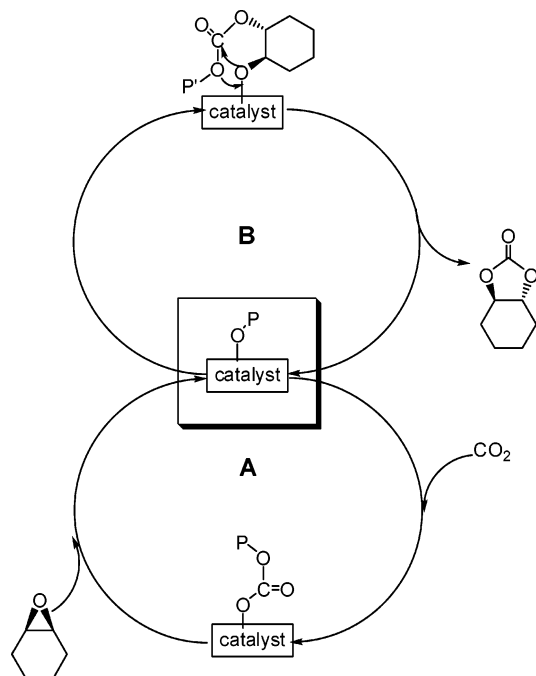
demonstrated that poly(cyclohexylene carbonate), with its T_g value of 115 °C, has inferior mechanical and physical properties as compared to those of the widely applied polycarbonate derived from bisphenol A and phosgene or diphenylcarbonate.[25,74] Hence, because of the limited uses of the copolymer derived from cyclohexene oxide, it is desirable to pursue other monomers for the CO_2 copolymerization reaction, in particular other alicyclic epoxides where the available catalysts are generally quite selective toward copolymer production. In this regard, our most successful efforts have involved utilization of the epoxy functionalized silane, [2-(3,4-epoxycyclohexyl)ethyl]trimethoxysilane (**5**) (Figure 25).[75]
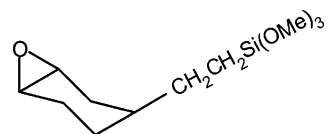

Figure 25. [2-(3,4-Epoxycyclohexyl)ethyl]trimethoxysilane (**5**), TMSO, obtained as a mixture of *cis* and *trans* isomers from Gelest, Inc.

The copolymerization of monomer **5** with CO_2 was found to afford completely alternating copolymers with only trace quantities of unwanted cyclic carbonate side product. The rates of copolymerization catalyzed by (salen)CrX/cocatalyst systems were determined to be essentially the same as the corresponding parameters for the cyclohexene oxide/CO_2 process under identical reaction conditions. An important difference noted is that there is only one CO_2-expanded liquid phase when utilizing monomer **5** vs cyclohexene oxide, thereby providing homogeneous solutions for accurate kinetic measurements.[70,71] Indeed, much of the kinetic information about the copolymerization process involving alicyclic epoxides we have compiled using monomer **5**. In addition to the trimethoxysilane functionality in **5** affording both the reactant monomer and the product copolymer good solubility in liquid carbon dioxide, it is possible to isolate the metal-

free polycarbonate via high-pressure CO_2 extraction following hydrolytic cleavage from the metal center. Of most significance, monomer **5** provides copolymers capable of being hydrolytically cross-linked via silsesquioxane units (Si−O−Si), thereby greatly altering the physical properties of the copolymer. Unfortunately, copolymers produced entirely from monomer **5** and CO_2 readily cross-link after prolonged standing in moist air or upon heating to yield a completely insoluble, nonprocessable material. In an effort to increase the shelflife and provide more tractable copolymers, we have been exploring terpolymers of cyclohexene oxide/TMSO/CO_2. Because the rates of incorporating cyclohexene oxide or TMSO into the polymer chain are comparable, terpolymers of desired composition, for example, 1−10% monomer **5**, are easily synthesized.

Other alicyclic epoxides examined as comonomers for copolymerization with carbon dioxide with very limited success employing the (salen)CrX/cocatalyst systems, as well as second generation zinc phenoxide catalysts,[76] include 1,4-dihydronapthalene oxide (**6**),[77] *exo*-norbornene oxide (**7**), (+)-limonene oxide (**8**), and α-pinene oxide (**9**). Importantly, these latter two monomers (**8** and **9**) are of particular interest since these are derived from sustainable resources. Coates and co-workers have reported some encouraging results at copolymerizing *trans*- or *cis*-(*R*)-limonene oxide with CO_2 to produce poly(limonene carbonate).[78] These latter studies utilized β-diiminate zinc acetate catalysts, for example, the derivative where $R_1 = H$, $R_2 = R_3 = Et$, $R_4 = CH_3$ in Figure 7, where a TOF of 33 h^{-1} was obtained under mild reaction conditions (35 °C and 6.9 bar CO_2 pressure). Thus far, no copolymers have been reported resulting from the copolymerization of CO_2 and epoxides **7** and **9**.
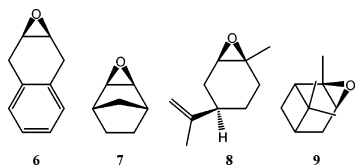
Other than cyclohexene oxide, the most widely studied monomer for copolymerization with CO_2 is the aliphatic epoxide, propylene oxide. In contrast to the copolymer derived from cyclohexene oxide, poly(propylene carbonate) is currently industrially extremely relevant due to its low T_g (40 °C), sharp, clean decomposition above 200 °C, and the environmental benefit of biodegradability. The two general application categories are destructive (evaporative pattern casting and ceramic binders) and nondestructive (adhesives and coating).[10] However, as was mentioned earlier, this process is plagued by the accompanying formation of sizable quantities of propylene carbonate. Nevertheless, recently, several advances toward more selective production of poly(propylene carbonate) from propylene oxide and CO_2 have been reported involving (salen)metal catalysts. The most important catalysts of this type comprise cobalt-based complexes, which will be elaborated upon later.

Pertinent to the employment of the (salen)CrX catalysts for the copolymerization of propylene oxide and CO_2, we initially demonstrated utilizing complex **1** that copolymer formation was favored over cyclic carbonate production at temperatures near ambient.[53] As the temperature was raised, cyclic carbonate was produced with a concomitant degradation of the poly(propylene carbonate). Figure 26 illustrates this temperature effect via the in situ infrared traces as a
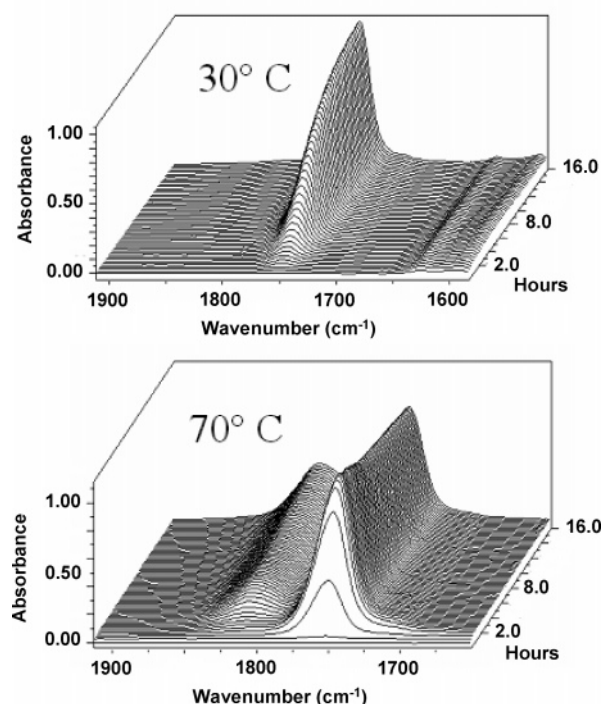

Figure 26. In situ infrared traces of the copolymerization reaction of propylene oxide and CO_2 at two different temperatures.

function of time at two different temperatures.[59,79] An Arrhenius analysis of the temperature-dependent rate data revealed activation parameters of 67.6 and 100.5 kJ/mol for poly(propylene carbonate) and propylene carbonate production, respectively. Hence, as is depicted in the reaction coordinate diagram in Figure 27, unlike the sizable barrier differ-
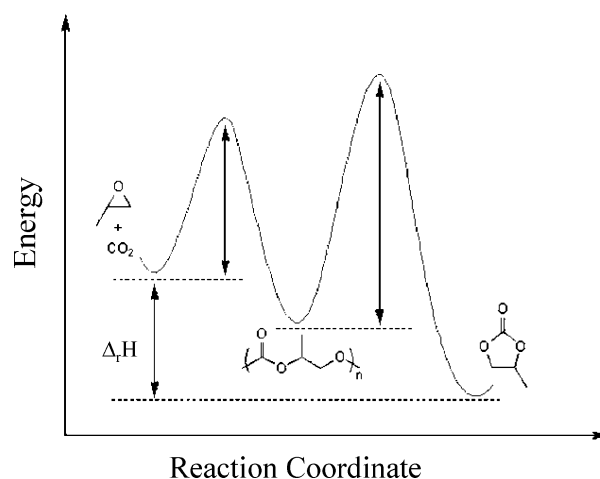
Figure 27. Reaction coordinate diagram for the coupling reaction of CO_2 and propylene oxide. ΔH_r is estimated to be −54 kJ/mol.

ence for degradation of poly(cyclohexylene carbonate) to cyclohexylene carbonate (86 kJ/mol), the difference in activation barriers for poly(propylene carbonate) to propylene carbonate is only 33 kJ/mol. The low barrier for cyclic carbonate formation is to be anticipated for aliphatic derivatives since there is no ring strain in forming the five-membered cyclic product. This observation explains the propensity to produce significant quantities of propylene carbonate from the coupling of propylene oxide and CO_2 at elevated temperatures.

Therefore, to effectively and selectively produce poly(propylene carbonate) from propylene oxide and CO_2, it is

necessary to uncover new catalysts or cocatalysts that have high activity at lower temperatures, that is, <80 °C.[80] With this in mind, Rieger and co-workers have reported that the (salen)CrX derivative bearing a phenylenediimine backbone (R_1, $R_2 = C_6H_4$ and $R_3 = R_4 = t$-Bu in Figure 17, complex **10**) displays TOFs for copolymer formation between 154 and 159 h^{-1} at 75 °C and 13 bar CO_2 pressure in the presence of 0.5−1.0 equiv of DMAP.[81] The copolymer produced had 96% carbonate linkages, with selectivity toward copolymer formation increasing with an elevation of CO_2 pressure to 35 bar. On the other hand, at 2 equiv of DMAP under identical conditions, 80% of the propylene oxide was converted exclusively to propylene carbonate in 2 h (TOF = 602 h^{-1} at 75 °C). This latter observation is ascribed to DMAP-assisted dissociation of the growing polymer chain as depicted in Scheme 8. The greater selectivity for copoly-

Scheme 8. Formation of Cyclic Carbonate Via "Backbiting" of Dissociated Alkoxy Chain in the Presence of Excess DMAP
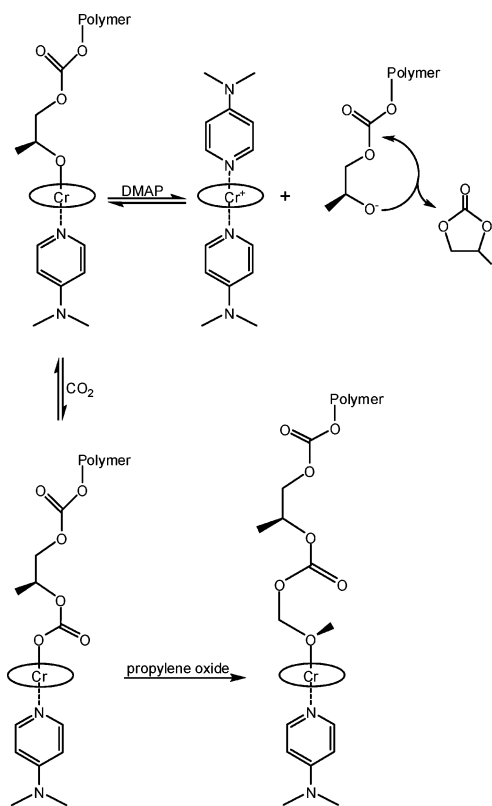
mer formation observed utilizing complex **10** as a catalyst vs complex **1** is thought to result from enhanced dissociation of the growing polymer chain for the latter more electron-rich complex.

In the meantime, we examined the copolymerization of propylene oxide and CO_2 employing various (salen)CrX catalysts along with PCy$_3$ or PPN$^+$ azide and chloride salts as cocatalysts.[82] Of the chromium complexes investigated, complex **10** and its analogue, where the t-Bu substituents in the 3-positions were replaced with hydrogen atoms, were found to be most effective at selectively producing poly-(propylene carbonate) at 60 °C and 34 bar CO_2 pressure. The thus provided copolymers were of high molecular weight with a narrow molecular weight distribution (PDI = 1.07−1.11). TOFs in the presence of 1 equiv of cocatalyst spanned the range 144−194 h^{-1} at 60 °C, with selectivity for copolymer formation of 84−94%. Focusing on the most

Scheme 9. Stereochemical Preference for Producing the Head-to-Head Carbonate Linkages in the Formation of Poly(propylene carbonate) as Catalyzed by (R,R-salen)CrCl
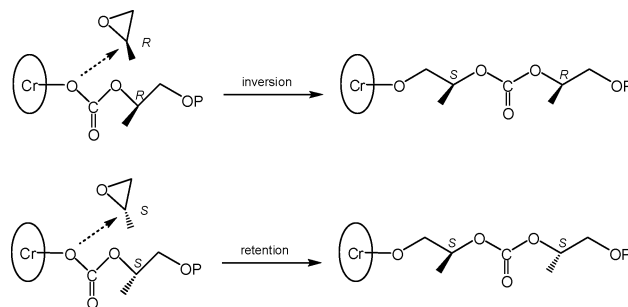
active complex, **10**, a detail study of the dependence of the propylene oxide/CO_2 coupling process on the nature and number of equivalents of cocatalyst provided the results summarized in the bar graphs in Figure 28. As is apparent
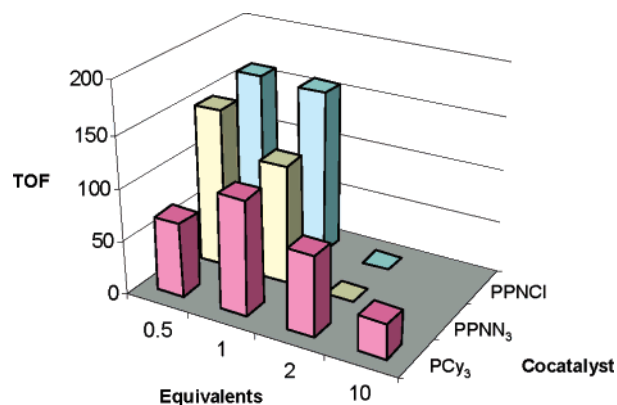

Figure 28. TOF for poly(propylene carbonate) production catalyzed by complex **10** at 60 °C and 34 bar CO_2 pressure as a function of cocatalyst loading.

from Figure 28, when the number of equivalents of anionic cocatalysts doubled from 1 to 2, the systems went from highly selective for copolymer formation to solely providing propylene carbonate. It should be noted parenthetically that the optimal anionic cocatalyst loading was 0.5 equiv with a slight decrease in the rate of copolymer formation occurring at 1.0 equiv. Similarly, the addition of more than 1 equivalent of PCy$_3$ was observed to greatly retard the TOF for copolymer formation. These observations are consistent with those reported by Rieger and co-workers when utilizing DMAP as a cocatalyst.[81]

Although our studies utilizing the achiral complex **10** as catalyst for the copolymerization of propylene oxide and CO_2 did not allow for an assessment of the stereoregularity of the resulting poly(propylene carbonate), Chisholm and Zhou have determined the microstructure of the copolymer from the copolymerization of rac-/(S)-/(R)-propylene oxide and CO_2 employing the chiral analogue, complex **1**.[83] These researchers clearly established by ^{13}C NMR spectroscopy that the (R,R-salen)CrCl catalyst prefers to ring open the propylene oxide monomer to afford the primary alkoxide of S stereochemistry by attack at the methine carbon center as illustrated in Scheme 9.

Subsequent to their initial contribution in this area,[81] Rieger and co-workers have published a comprehensive computational and experimental account on the formation of aliphatic polycarbonates from CO_2/epoxides catalyzed by (salen)CrCl in the presence of anionic and DMAP activators.[84] The

theoretical studies addressed the ΔE of reaction and $\Delta E^{\neq}$ of activation for the various reactions outlined in Section 3 of this review. Although most computations were performed using a reduced model for (salen)CrCl as shown in Figure 29, a key step, the epoxide ring-opening process was carried out on the intact complex **10**. Interestingly, we have investigated the use of (*t*-butylacacen)CrCl (Figure 30) as a catalyst for the copolymerization of cyclohexene oxide and CO_2 and found it to behave mechanistically analogous to its (salen)CrCl analogs.[85] Both coordination of ethylene oxide to the chromium center and backside attack of the bound epoxide by the external nucleophile (OAc⁻, Cl⁻, or DMAP) to provide the Cr−alkoxy intermediate were found to be highly exothermic with little to no energy of activation barriers. However, CO_2 insertion into the six-coordinate chromium−alkoxy intermediate (eq 5) was found to proceed via a more complex pathway. That is, dissociation of a phenolate ligand was required to provide a coordination site for CO_2 interaction prior to the insertion process and attendant phenolate recoordination. Such a mechanism is in stark contrast with experimental observations, which have unambiguously demonstrated in low-valent organometallic alkoxides that CO_2 insertion proceeds by a concerted process at coordinatively saturated metal centers.[18,47] Alternatively, the insertion of CO_2 into a five-coordinate (salen)Cr−OR species resulting from anion dissociation was computed to be highly favored with an energy of reaction of −24 kJ/mol and an activation energy of 45 kJ/mol. Finally, chain growth was calculated to take place by way of the thus-formed metal-bound alkyl carbonate attacking a metal-coordinated epoxide, that is, a bimolecular process similar to that observed by Jacobsen for the ARO of epoxides.[48] Again, this proposed mechanism for chain growth is inconsistent with experimental results showing the chain growth process to be first-order in metal complex.[53,59] Nevertheless, Rieger and co-workers point out that the bimolecular chain growth pathway is congruous with the experimentally observed parabolic dependency of the selectivity for poly-(propylene carbonate) formation on the concentration of the cocatalyst.
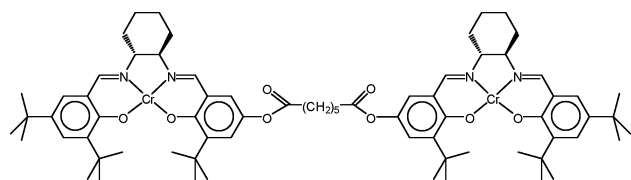
11

In a related experimental study, Chen and co-workers have examined the gas-phase polymerization reaction of propylene oxide in the presence of mononuclear (**1**) and dinuclear (**11**) (salen)CrCl complexes.[86] Whereas the mononuclear cation did not polymerize propylene oxide in the gas phase, the dicationic dinuclear species was an active catalyst for the process. This led the authors to conclude a dinuclear cationic mechanism for the polymerization reactions as indicated in Scheme 10.

Theoretical investigations have also revealed that metal-centered cyclic carbonate production has a high activation barrier, with backbiting via the alkoxy end group being disfavored over the carbonate end group (eq 7). Interestingly, the computed $\Delta E^{\neq}$ for propylene carbonate formation from

Scheme 10. Dinuclear (salen)Cr Dication as Catalyst for the Polymerization of Propylene Oxide in the Gas Phase
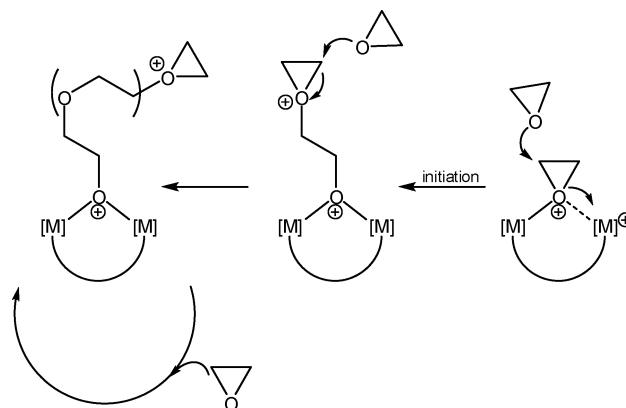

the metal-bound carbonate of 95 kJ/mol is strikingly close to the experimentally determined of $\Delta E^{\neq}$ 100.5 kJ/mol.[59] The conclusion that cyclic carbonate formation is favored from the metal carbonate species vs the metal alkoxide species appears counterintuitive based on the fact that cyclic carbonate production increases with decreasing CO_2 pressure.[43,81] Of significance, these researchers find that decomposition of free chains to cyclic carbonate was found to occur with a small energy of activation, again with the carbonate chain end being favored with $\Delta E^{\neq} = 35$ kJ/mol (Figure 9).

Finally, Garcia and co-workers have described a chromium salen derivative, which was covalently anchored to a silicon support via a linker that resulted from a nucleophilic substitution reaction between an amino-modified silica and a chloromethyl-substituted in the 3-position of one of the phenolate groups (**12**).[87] This catalyst system operating under supercritical conditions (100 bar and 80 °C) was found to be recyclable and exhibited 100% selectivity for cyclic carbonate production at 70% styrene oxide conversion.

5. Cobalt Salen Catalysts

He and co-workers have reported upon utilizing various tetradentate Schiff base metal catalysts in the presence of quaternary salts as cocatalysts for the coupling of ethylene oxide and CO_2 to provide ethylene carbonate.[88] Although this communication primarily dealt with (salen)AlX catalysts (vide infra), comparative studies were performed using a range of (salen)metal derivatives, including (salen)CrCl or (salen)Co and 1 equiv of *n*-Bu₄NBr at 15−16 MPa of CO_2
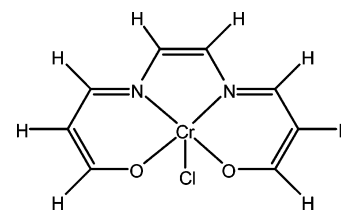
Figure 29. Reduced model complex used in the calculations.
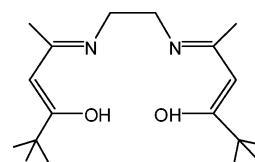
Figure 30. Skeletal representation of *t*-butylacacenH₂.
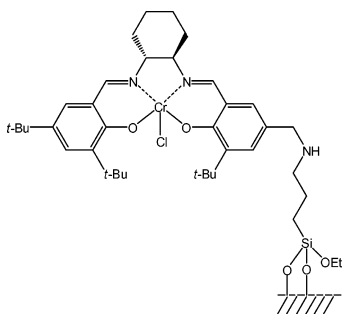
12

pressure at 110 °C with TOFs of 2140 and 1320 h^{-1}, respectively. In a closely related study, Shi and co-workers have described the production of various cyclic carbonates from the corresponding epoxides and CO_2 employing binaphthyldiamino salen type catalysts, including the Co(II) complex depicted in Figure 31.[89] Specifically, in this instance,
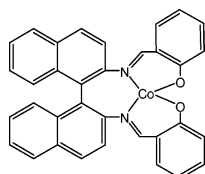

Figure 31. Cobalt(II) binaphthyldiamino salen type complex.

reaction 8 afforded propylene carbonate in isolated yields of 80 and 91% for reactions carried out with 2 equiv of the cocatalysts DMAP and Et$_3$N, respectively.[90,91] On the basis of the stereochemistry of the cyclic carbonate product (**13**) afforded from *trans*-deuterioethene oxide, a mechanistic pathway as that portrayed in Scheme 11 was proposed to be

Scheme 11. [M] = Metal(II) Binaphthyldiamino Salen Catalyst for Cyclic Carbonate Formation
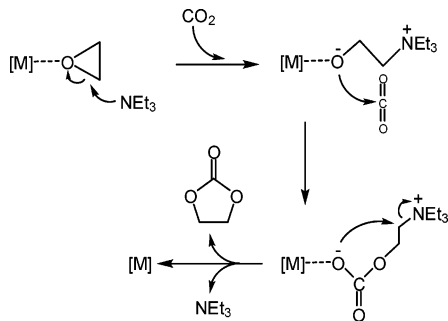
operative. This is to be contrasted with a pathway involving amine activation of CO_2 and subsequent epoxide ring opening by the resulting zwitterion leading to **14**.


13 **14**
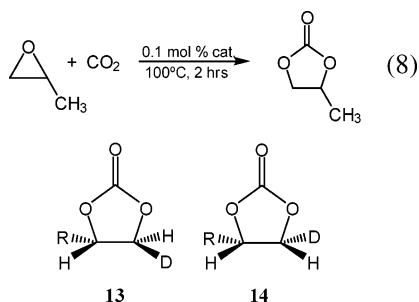
Lu and co-workers have described the preparation of optically pure cyclic carbonates from racemic epoxides by
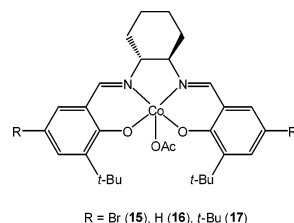
R = Br (15), H (16), *t*-Bu (17)

Figure 32. Effective (salen)CoOAc catalysts for the selective coupling of propylene oxide and CO_2 to poly(propylene oxide).

a catalytic kinetic resolution process involving chiral (salen)-CoX complexes in the presence of quaternary ammonium halides.[92] For example, employing the cobalt(III) analogue of complex **1** along with *n*-Bu$_4$NBr in neat propylene oxide, propylene carbonate was produced with a TOF of 120 h^{-1} at 25 °C with an enantiomeric excess of 39.8% or k_{rel} = 3.3. For a similar reaction in the presence of the chiral chromium complex, **1**, although a TOF of 44 h^{-1} was observed, the ee of the resulting propylene carbonate was only 2.9% or k_{rel} = 1.1. More recently, Berkessel and Brandenburg have reported a binary catalyst system composed of a chiral (salen)CoX complex [salen = *N,N'-bis*(3,5-di-*tert*-butylsali-cylidene)-1,2-diaminocyclohexane] and [PPN]Y at −10 °C and atmospheric pressure for the production of enantiomerically enriched propylene carbonate.[93] For example, the most impressive result was obtained utilizing the cobalt(III) derivative, where X = O$_2$CCF$_3$, and 2 equiv of [PPN]F, where a 40% conversion was obtained in 18 h at a catalyst loading of 0.1 mol %. Under these conditions, a selectivity factor, **S**, of 19 was achieved as compared to the corresponding **S** value of 9 previously reported by Lu and co-workers.[92,94] Notwithstanding, enhanced selectivity factors as high as 48.4 have been achieved by Yamada and co-workers employing a chiral (salen)Co and Et$_2$NSiMe$_3$ catalyst system for the coupling of CO_2 and *N,N'*-diphenyl-aminomethyloxirane to the corresponding cyclic carbonate (eq 9).[95] Upon optimization of this selectivity by kinetic resolution, the cyclic carbonate and unreacted epoxide were obtained in 49% yield and recovery with ee values of 86 and 87%, respectively.

(9)
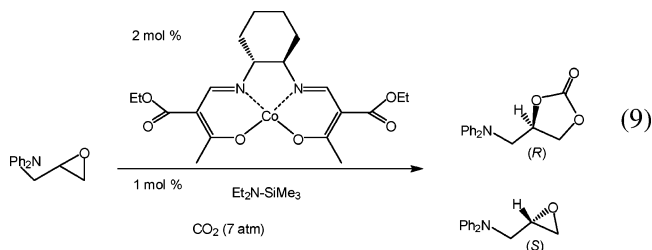
The most significant development involving the use of (salen)CoX catalysts was disclosed in 2003 by Coates and co-workers on the effective and selective production of poly-(propylene carbonate) from the copolymerization of *rac*-propylene oxide and carbon dioxide.[96] Complexes **15**−**17** were found to provide poly(propylene carbonate) in >99% selectivity with 90−99% carbonate linkages at a CO_2 pressure of 55 bar and ambient temperature (Figure 32). TOFs, in the absence of a cocatalyst to optimize activity, extended over a range of 17−81 h^{-1}, dependent on reaction conditions and the R substituent on the salen ligand. Complex **15** was shown to be the most active of the derivatives examined. Interestingly, prior to Coates report, we examined the cobalt(III) analogue of complex **1** for catalytic activity

for the cyclohexene oxide/CO_2 copolymerization process at an elevated temperature (80 °C) and found that it degraded to a Co(II) derivative, which was ineffective at producing copolymers.[97]

Subsequent to the original report by Coates, Lu and Wang found that the catalytic activity of complex **17** for the copolymerization of propylene oxide and CO_2 was enhanced in the presence of 1 equiv of n-Bu$_4$NBr at ambient temperature and 20 bar CO_2 pressure, with a TOF for polycarbonate and cyclic carbonate of 228 h^{-1}.[98] However, the selectivity for polycarbonate was greatly diminished at only 3% but with greater than 99% carbonate linkages. This is to be contrasted with Coates' results with **17** alone at 55 bar and 25 °C, where TOFs of 42 and 59 h^{-1} were observed with >99% selectivity for poly(propylene carbonate) with 99% carbonate linkages. However, upon altering the axial acetate ligand for phenolates containing electron-withdrawing $-NO_2$ substituents, these (salen)CoX catalysts in the presence of quaternary ammonium halides were highly active for the selective production of poly(propylene carbonate) (78−99%), with >99% carbonate linkages. Furthermore, the chiral $(1R,2R)$-(t-Bu)$_2$salenCoX binary catalyst system preferentially reacted with (S)-PO over (R)-PO with k_{rel} = 2.8−3.5. In addition, this catalyst system was highly regioselective, affording a copolymer with a head-to-tail content of >95% as revealed by ^{13}C NMR (Figure 33).
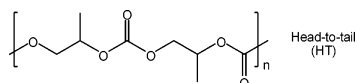
Figure 33. Regiochemistry of poly(propylene carbonate) produced from propylene oxide and CO_2.

When utilizing (salen)CoOAc [salen = N,N'-bis(3,5-di-$tert$-butylsalicylidene-1,2-benzenediamine)] and **18** as a catalyst for the copolymerization of propylene oxide and CO_2, the resulting copolymer was noted to contain both polyether and polycarbonate chains. Importantly, the poly-(propylene oxide) chains were shown to be highly isotactic with >99% mm-triads. This observation was exploited by Coates and co-workers for the preparation of rac-isotactic poly(propylene oxide) with [mm] >99%.[99,100] This catalyst represents the most active and stereoselective for isospecific rac-propylene oxide polymerization thus far discovered (eq 10).
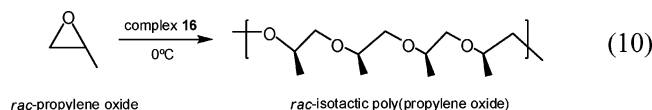
Directly after the Lu and Wang publication,[98] Paddock and Nguyen reported that a (salen)CoX/Lewis base catalyst system selectively provides poly(propylene carbonate) from propylene oxide and CO_2 under mild reaction conditions.[101] That is, a series of chiral (salen)CoX complexes, such as complex **17** where X covers a wide range of anions, in the presence of DMAQ (N,N-dimethylaminoquinoline, **18**) at 10−24 bar CO_2 pressure and ambient temperature, provided poly(propylene carbonate) in >99% selectivity with >99% carbonate linkages. The PDIs of the resulting polycarbonates were very narrow (<1.1), and the k_{rel} for preferential reaction of (S)-PO was found to be as high as 5.4. The most active catalyst system contained X = NO_3 along with 2 equiv of DMAQ (TOF = 97 h^{-1}) at a CO_2 pressure of 10 bar. TOFs dropped off with greater than 2 equiv of DMAQ with only

slight decreases in polycarbonate selectivity. Similar to the analogous result reported by Lu and Wang,[98] the (salen)-CoOTs/DMAQ catalyst system was observed to be highly regioselective with a head-to-tail content of 96%.
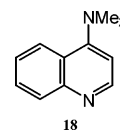
Coates and co-workers followed their preliminary report on the subject of the propylene oxide/carbon dioxide copolymerization process catalyzed by (salen)CoX derivatives with a comprehensive analysis of the system.[64] Recall that in their early study these researchers demonstrated that complex **17** alone was effective at copolymerizing rac- or (S)-propylene oxide and CO_2 selectively to poly(propylene carbonate) with TOFs generally less than 80 h^{-1} at 25 °C. Complex **17** and several of its analogues containing various axial ligands (complexes **19−22**) as catalysts were found to provide copolymers of narrow molecular weight distributions (1.14−1.24) with high degrees (>80%) of regioregularity (head-to-tail) and essentially 100% carbonate linkages. Of special interest in this investigation, care was taken for drying and maintaining anaerobic conditions for the cobalt catalysts and rac-propylene oxide/CO_2, which revealed that the copolymers produced exhibited experimental M_n values much closer to the theoretical values than those afforded under ambient conditions. This observation supports the generally held belief that the significant difference in measured and calculated M_n values is due to chain transfer processes involving adventitious water.

X = OBzF$_5$ (**19**), Cl (**20**), Br (**21**), I (**22**)
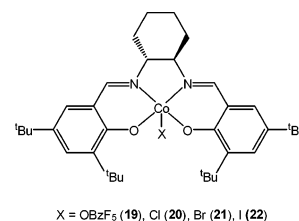
The TOFs for poly(propylene carbonate) production at ambient temperature and 55 bar CO_2 pressure varied with the nature of X in (salen)CoX derivatives in the order I < Cl < OAc ≈ OBzF$_5$(pentafluorobenzoate) < Br, with the latter derivative exhibiting a TOF of 90 h^{-1}. This relative trend is assumed to arise from a parallel order in the rates of initiation prior to polymer chain propagation. The initiation process is thought to proceed via a bimolecular pathway as first described by Jacobsen and co-workers.[42,102,103] Similar to the earlier report by Lu and Wang,[98] the activity as well as stereo- and regioselectivities of these Co(III) catalysts were greatly enhanced in the presence of anionic cocatalysts, in this instance, [PPN]Cl and [PPN][OBzF$_5$]. For example, the addition of 1 equiv of [PPN]Cl resulted in a TOF increase from 80 to 520 h^{-1} at a low CO_2 pressure (13.8 bar), with head-to-tail linkages increasing from 82 to 93%. On the basis of molecular weight data, it was proposed that two polymer chains were simultaneously propagated from either side of the (salen)Co plane. Although the copolymerization of rac-propylene oxide and CO_2 in the presence of complex **21** afforded atactic poly(propylene carbonate), under identical conditions except using (S)-propylene oxide as substrate, isotactic poly(propylene carbonate) was produced with a greater activity and regioselectivity (90 vs 120 h^{-1} and 82

vs 93% head-to-tail connectivity) (eq 11). Similarly, the copolymerization of *rac*-propylene oxide and CO_2 in the presence of (*R,R*)-**19** and [PPN]Cl provided a TOF of 620 h^{-1} at 22 °C and 13.8 bar pressure for formation of isotactic-enriched poly(propylene carbonate) with 94% head-to-tail connectivity, whereas employing (*S*)-propylene oxide as the monomer under identical reaction conditions, a TOF of 1100 h^{-1} for isotactic poly(propylene carbonate) with 96% head-to-tail linkages was observed. This represents the most efficient catalyst system for the formation of poly(propylene carbonate) uncovered to date.
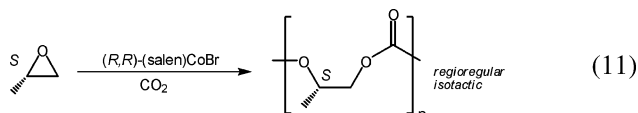
Lu and co-workers have subsequently more extensively examined the asymmetric alternating copolymerization of *rac*-propylene oxide and CO_2 in the presence of chiral (salen)CoX with *n*-Bu$_4$NX′ or PPNX′ salts or a strong nitrogen base as cocatalysts.[104] Following a detailed assessment of the effects of varying the salen ligand, X ligand, and cocatalyst on the activity, selectivity for copolymer formation, and enantio- and stereoselectivities, the best binary catalyst system was found to consist of a bulky chiral (salen)-CoX complex containing a poor X leaving group and a cocatalyst composed of an X′ anion with poor leaving ability or a sterically encumbering strong organic base with low metal-binding ability. With such a binary catalyst system, for example, the *R,R*-version of complex **17** where OAc is replaced by O_2CCCl_3 and 1 equiv of [PPN]Cl, *rac*-propylene oxide and 15 bar CO_2 at 25 °C afforded poly(propylene carbonate) with a TOF of 568 h^{-1} with >99% selectivity for copolymer and 96% head−tail linkages with $k_{rel} = 5.0$ or 54.5% ee. This (salen)CoX/cocatalyst system was also observed to asymmetrically copolymerize cyclohexene oxide and CO_2 to provide a copolymer with >99% carbonate linkages and 36.6% ee at ambient temperature. Electron ionization mass spectrometry was employed in monitoring the copolymer chain growth process, which was initiated primarily by the cocatalyst.

In an additional contribution, Cohen and Coates have reported that complexes **19** and **20** exhibited TOFs up to 720 h^{-1} at 22 °C for *rac*-propylene oxide/CO_2 copolymerization in the presence of [PPN]Cl or [PPN]OB$_z$F$_5$.[105] Furthermore, for a reaction carried out at −20 °C and 6.8 bar CO_2 pressure catalyzed by complex (*R,R*)-**19**/[PPN]Cl, a very regioregular (98% head-to-tail) and highly isoenriched copolymer was obtained, with a selectivity for poly(propylene carbonate) >99%. Concomitantly, the process showed a preference for enchainment of (*S*)- over (*R*)-propylene oxide with a k_{rel} of 9.7. The use of 1,2-dimethoxyethane enhanced the yield of polycarbonate significantly, presumably due to the increase in the reaction mixture's viscosity with an increase in monomer conversion.

A novel communication on this subject has been described by Nozaki and co-workers involving the highly selective formation of poly(propylene carbonate) from propylene oxide and CO_2.[106] These researchers have utilized a (salen)-Co(OAc)$_2$$^-$ derivative, which employs a salen ligand containing a piperidinium end-capping arm, complex **23**. As illustrated in Scheme 12, the piperidinium arm controls the formation of cyclic carbonate by protonating the anionic polymer chain when it dissociates from the cobalt center.

Scheme 12. Catalyst Design for the Highly Selective Production of Poly(propylene carbonate) from Propylene Oxide and Carbon Dioxide
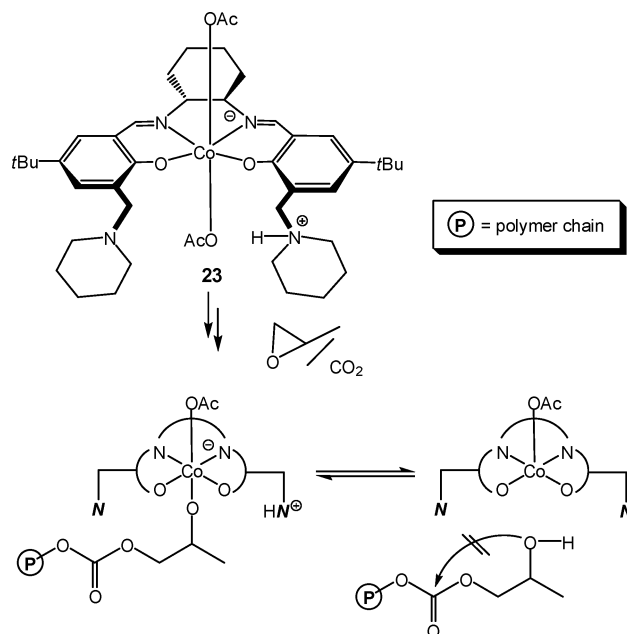
This phenomenon has allowed the reaction to be carried out at a temperature of 60 °C with only a small percentage (∼10%) of cyclic carbonate production. As previously noted by Cohen and Coates, the presence of added solvents, such as DME, allows for higher conversion of epoxide to polycarbonate without sacrificing selectivity.[105] In this manner, the Nokaki group achieved quantitative conversion of propylene oxide to copolymer, which allowed for the production of block terpolymers. For example, the block terpolymer of propylene oxide/1-hexene oxide and CO_2 was obtained in this manner with high conversion and selectivity, and a $M_w/M_n = 1.17$.

Coates and co-workers have also investigated these (salen)-CoX complexes as catalysts for the asymmetric alternating copolymerization of cyclohexene oxide and CO_2.[107] Although Nozaki and co-workers[108−111] and Coates' group[112] have described zinc complexes that afford isotactic poly(cyclohexene carbonate) with ee ∼70%, this recent study summarizes the production of previously unreported syndiotactic poly(cyclohexene carbonate) (Figure 34). For example,
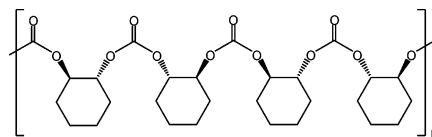
Figure 34. Syndiotactic poly(cyclohexene carbonate).

rac(salen)CoBr [salen = *N,N′-bis*(3,5-di-*tert*-butylsalicylidene)-1,2-diaminopropane] alone at 22 °C and 54.4 atm CO_2 was effective at providing syndiotactic poly(cyclohexene carbonate) with a TOF of 98 h^{-1} and 81% r-centered tetrads as revealed by ^{13}C NMR spectroscopy (Figure 35). There was observed a dramatic increase in catalytic activity (TOF) and syndiospecificity with an increase in carbon dioxide pressure. Interestingly, enantiomerically pure, racemic, and achiral (salen)CoX catalysts all provided some degree of syndiospecificity in the copolymer produced from cyclohexene oxide and CO_2, observations attributed to a chain-end-controlled mechanism. The best catalyst for the production
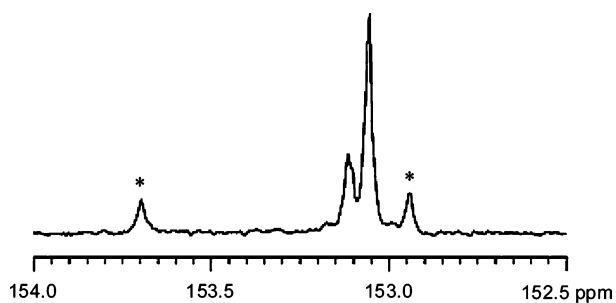
Figure 35. ^{13}C NMR spectrum of syndiotactic-enriched poly-(cyclohexene carbonate). Most downfield and upfield signals marked by asterisks correspond to m-centered tetrads with other signals assigned to r-centered tetrads.

of copolymer noted in this study was (R,R)-(salen)CoOBzF$_5$, which afforded a TOF of 440 h^{-1} at 70 °C and 6.8 bar pressure in the presence of 1 equiv of [PPN]Cl. The presence of a [PPN]Cl cocatalyst, however, resulted in a loss in syndiospecificity.

Lu and co-workers have also reported the asymmetric copolymerization of cyclohexene oxide and CO$_2$ under rather mild reaction conditions, generally 25 °C and 15 bar, employing chiral (salen)CoX catalysts (Figure 36) in the

24 R$_1$ and R$_2$ = (1R,2R)-trans-(CH$_2$)$_4$-, X = OOCCCl$_3$;
25 R$_1$ and R$_2$ = (1R,2R)-trans-(CH$_2$)$_4$-, X = 2,4-dinitrophenoxy ;
26 (1R,2R)-trans, R$_1$ = R$_2$ = Ph , X = OOCCCl$_3$;
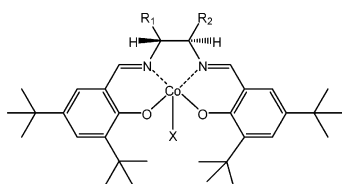**27** R$_1$ = (R)-CH$_3$, R$_2$ = H ; X = OOCCCl$_3$;

Figure 36. Schiff base cobalt(III) complexes with several different chiral diamine backbones.

presence of [PPN][Cl as a cocatalyst.[113] As indicated in eq 12, in this instance, isotactic-enriched poly(cyclohexene carbonate) was produced, where its enantioselectivity of 38% ee at 25 °C decreasing to 28% at 80 °C was determined from the cyclohexene-1,2-diol produced upon hydrolysis of the copolymer as measured by chiral GC. This stereoselectivity was also consistent with the ^{13}C NMR spectrum of the copolymer in the carbonate region. By way of contrast with Coates' earlier observation in the absence of [PPN]Cl, an increase in CO$_2$ pressure from 15 to 52 bar with this binary catalyst system led to a dramatic decrease in catalytic activity as well as a decrease in enantioselectivity. Utilizing complex **24** and 1 equiv of [PPN]Cl over the temperature range 25−80 °C, the TOF increased from 89 to 825 h^{-1} with little change in the enantioselectivity. Furthermore, this catalyst system was demonstrated to be very effective at the terpolymerization of cyclohexene oxide/propylene oxide/CO$_2$ to afford a terpolymer with a narrow molecular weight distribution (PDI = 1.24) and >99% carbonate linkages. The terpolymer was observed to have only one glass transition temperature, which was adjustable between 50 and 100 °C by controlling the relative proportions of cyclohexene oxide and propylene oxide.

(12)
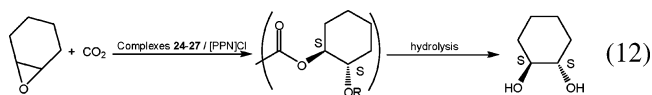
6. Aluminum and Other Metal Salen Catalysts

The relative affinity of the Lewis acidic metal cationic center in (tpp)MCl (M = Al, Ga, Cr, and Co) and (salen)-MCl (M = Al, Cr) derivatives toward propylene oxide has been determined in the gas phase by electrospray tandem mass spectrometry.[114] The chromium(III) and aluminum(III) metal centers were found to most effectively bind propylene oxide, with the (tpp)M$^+$ complexes more strongly coordinating propylene oxide than their (salen)M$^+$ [salen = (R,R)-N,N′-di-tert-butylsalicylidene)-1,2-cyclohexenediamine] analogues. Of particular interest herein, the (R,R-salen)AlCl complex was observed to ring open S-propylene oxide to afford as the major product (90%) (R,R-salen)AlOCHMe-(S)CH$_2$Cl (Figure 37). As evident in Figure 37, the aluminum
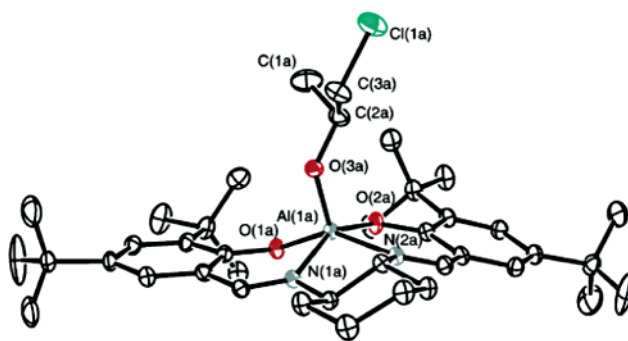

Figure 37. Thermal ellipsoid drawing of (R,R-salen)AlOCHMe-(S)CH$_2$Cl complex, where the solid-state structure of the free S-propylene oxide solvate was also obtained. The minor product (10%) of the ring-opening reaction was (R,R-salen)AlOCH$_2$CHMe-(R)Cl.

complex remains five-coordinate even though the crystals were grown in S-propylene oxide. The propensity of the aluminum center to remain five-coordinate in the presence of an excess of a sixth ligand was demonstrated as well for (salen)Al(acetate), where crystals grown in pure pyridine were shown to display square pyramidal geometry. A series of (salen)GaX analogues have also been shown to possess a distorted square pyramidal geometry in the solid state by X-ray crystallography. These gallium(III) complexes were found to be ineffective at copolymerizing CO$_2$ and cyclohexene oxide.[115]

By way of contrast, David Atwood and co-workers have characterized cationic (salen)Al complexes containing two neutral ligands by X-ray crystallography.[116,117] These derivatives were prepared from (salen)AlCl in protic solvents (H$_2$O or MeOH) where the chloride anion is readily dissociated. The role of these cationic complexes in the polymerization of oxiranes was discussed in this report.

Several recent studies have reported upon the use of (salen)AlX derivatives with tetraalkylammonium salts as catalysts for the coupling of CO$_2$ and epoxides to provide cyclic carbonates. For example, He and co-workers have examined their reaction employing ethylene oxide as monomer in supercritical carbon dioxide at 110 °C, where TOFs of 1200−3100 h^{-1} were achieved.[118] The high rates observed were ascribed to rapid diffusion of the substrate to the catalytic center as well as greater epoxide miscibility in scCO$_2$. Similar results were accounted for by these researchers elsewhere.[88] In related investigations, Lu and co-workers have described the reaction of a variety of terminal epoxide substrates, for example, ethylene oxide, propylene oxide, and styrene oxide, with CO$_2$ catalyzed by (salen)AlX/n-Bu$_4$NY

binary systems at 6 bar pressure and 25 °C to afford cyclic carbonates in good yield and 100% selectivity.[119] Additionally, these researchers have found that the (salen)AlEt/18-crown-6-KI binary catalyst reacts with (S)-propylene oxide to provide (S)-propylene carbonate in >99% ee.[120]

As intimated earlier in this review, the mechanistic aspects of the CO_2/epoxide copolymerization process catalyzed by Schiff base and porphyrin complexes have much in common. Although this was apparent from the pioneering efforts of Inoue and co-workers,[19] it has become much clearer with the comprehensive studies reported by Chisholm and Zhou involving the catalyst, (tpp)AlX, where X = Cl, $O(CH_2)_9$-CH_3, and $O_2C(CH_2)_6CH_3$.[83] From their studies, it was concluded that the rate of ring opening of propylene oxide followed the order Cl > OR > O_2CR, but in the presence of a Lewis base cocatalyst, DMAP, O_2CR > OR. Furthermore, consistent with our (salen)CrX-catalyzed copolymerization investigation of the cyclohexene oxide/CO_2 reaction, the (tpp)AlX catalyst system was shown to be first-order in metal complex concentration, with the role of DMAP being to enhance the nucleophilicity of the *trans*-Al−X bond and to promote CO_2 insertion into the Al−O growing polymer chain. A summary of Chisholm and Zhou's mechanistic conclusion from their kinetic studies is contained in Scheme 13.

Scheme 13. Proposed Mechanism for the Propylene Oxide/CO_2 Copolymerization Process Catalyzed by (tpp)AlX, Where Nu Represents the DMAP Cocatalyst

(ether linkage)

(carbonate linkage)

(ether linkage)

(carbonate linkage)
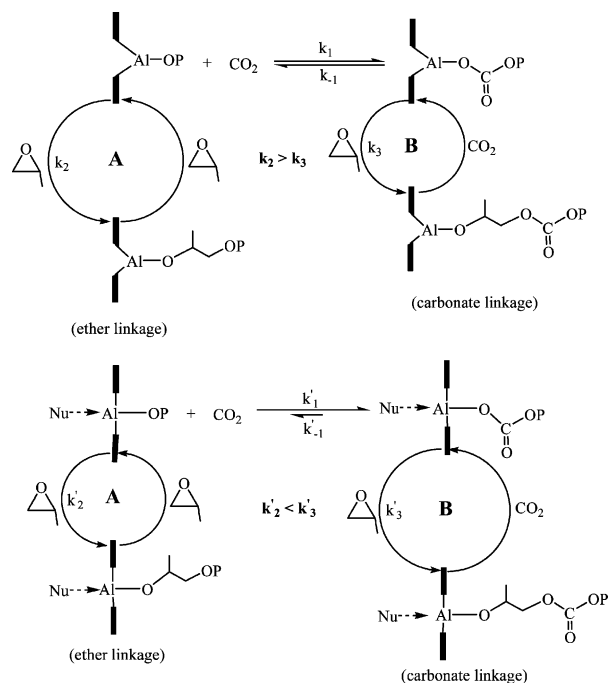
Shortly thereafter, in 2005, we published an investigation of the closely related (salen)AlX complexes as catalysts for the copolymerization of cyclohexene oxide and CO_2 in the presence of various neutral and ionic cocatalysts.[121] Importantly, the salen ligands represent less expensive and more easily derivatized alternatives to porphyrin ligands and generally provide more active metal catalyst than their porphyrin analogues. Upon examining a variety of salen derivatives of aluminum, we observed that electron-withdrawing substituents on the salen ligands afforded the most active metal catalysts. This is to be contrasted with our earlier studies, which revealed that (salen)CrX complexes

were more active when the salen ligands contained electron-donating substituents. Moreover, in all instances of altering the salen ligand, apical group (X), and cocatalyst, these (salen)AlX catalysts were found to be much less active than their (salen)CrX analogue under identical reaction conditions, with TOFs ranging from 5.2 to 35.4 h^{-1}. It is also worthy of reiterating that the (salen)GaX analogues were found to be completely ineffective at catalyzing the copolymerization of cyclohexene oxide and CO_2.[115]

Sugimoto, Ohtsuka, and Inoue have also recently examined this (salen)AlX-alkylammonium salt binary catalyst system for its ability to catalyze the copolymerization of cyclohexene oxide/CO_2 to provide poly(cyclohexene carbonate).[122] In addition, this study revealed a half-salen dimethylaluminum catalyst to be inferior to the (salen)AlX system, being much less active and affording a copolymer with a broad molecular weight distribution. As noted elsewhere for various (salen)-MX catalyst systems, a bimodal distribution was observed in the GPC profiles of these copolymers. However, upon scrupulously drying reagents and apparatus, the copolymer produced exhibited a unimodal distribution with a low PDI.

Correspondent to their previous studies involving supported (salen)CrX reusable catalysts,[87] García and co-workers have carried out an analysis of the use of polymer-bound (salen)AlX catalyst systems.[123] Two forms of the polymer-supported (salen)AlX catalyst were studied for the coupling of styrene oxide and CO_2 to afford styrene carbonate. These included partially cross-linked polystyrene and poly(ethylene glycol bismethacrylate) derivatives. These supported catalysts displayed similar activities at 80 °C and 100 bar CO_2 pressure to their unsupported analogues. The polystyrene-supported (salen)AlX catalyst exhibited greater stability, but somewhat lower activity, than the poly(ethylene glycol bismethacrylate)-bound system. As previously noted for unsupported (salen)AlX catalysts, the addition of Lewis bases such as DMAP significantly enhanced the catalytic activity of these polymeric (salen)AlX catalysts.

As described earlier in this review for Co(II) derivatives, binaphthyldiamino salen type complexes of copper(II) and zinc(II), see Figure 31, have been shown to be effective at catalyzing the coupling of CO_2 and various epoxides to provide in nearly quantitative yields the corresponding cyclic carbonate.[89] Finally, we have examined the use of half-salen, that is, *bis*-salicylaldiminato, derivatives of zinc as catalysts for the copolymerization of cyclohexene oxide and CO_2.[124] These complexes exhibited modest catalytic activity for providing poly(cyclohexene carbonate) with a high percentage of CO_2 linkages but broad molecular weight distributions.

7. Conclusion and Comments

It is apparent from this coverage that Schiff base complexes in conjunction with suitable cocatalysts represent some of the most robust metal catalysts for the selective coupling of CO_2 and epoxides to provide either polycarbonates or cyclic carbonates. Although these catalysts are very effective for the production of cyclic carbonates for a wide variety of epoxides, the range of epoxides that couples with CO_2 to selectively afford completely alternating copolymers still remains quite limited. That is, these latter reports remain focused on propylene oxide and cyclohexene oxide. Nevertheless, with regard to these latter monomers, (salen)CoX catalyst systems have been demonstrated to yield regioregular and/or stereoregular copolymers, and it will be of great interest to examine in detail the physical properties of these

materials. Hopefully, over the next few years, efficient catalysts for the formation of copolymers from CO_2 and other easily available epoxides, such as styrene oxide and limonene oxide, will be discovered.

Thus far, these studies have revealed that Cr(III) and Co(III) are the most effective catalysts for polycarbonate synthesis, with Al(III) derivatives being less active. Notwithstanding, the lower activity of these (salen)AlX analogues has allowed for obtaining more kinetic information with regard to some of the individual steps in the copolymerization process. The effectiveness of the intermediate six-coordinate Cr(III) and Co(III) species generated during the copolymerization reaction relative to other first-row transition metals is most likely due to the fact that d^3 Cr(III) and low-spin d^6 Co(III) are substitutionally inert. Concomitantly, the high spin d^4 Mn(III) derivative is substitutionally labile and (salen)MnX analogues are ineffective at copolymerizing cyclohexene oxide and CO_2.[125−127] Collectively, we have put our initial mechanistic interpretation to the test, where we have critically probed all of our current thinking of how this process proceeds. At the same time, we cannot be ashamed of admitting some shortness of insight for there is no way of avoiding misinterpretation in the absence of a prolonged exploration of the process. However, when attempting to discover how such a complicated process takes place, we must be fully prepared to commit mistakes, later making every effort to correct them. Of importance, computational methods have contributed to our understanding of the mechanistic aspects of the copolymerization reactions. It is anticipated that this approach will be of greater significance in the not too distant future.

Finally, despite the fact that (salen)MX catalysts provide completely alternating copolymers of high molecular weights and low PDIs, an issue that is currently receiving much attention from various research groups is that of achieving better control of molecular weight. The two main concerns that must be resolved in this regard are (i) does polymer chain growth occur from both sides of the (salen)M plane and (ii) how to avoid a chain transfer reaction involving adventitious water. The use of MALDI-TOF-MS measurements will greatly aid in defining different initiation, propagation, and termination reactions.[27,128]

8. Acknowledgments

9. Note Added after ASAP Publication

This paper was published ASAP on April 21, 2007, with an incorrect page number for ref 106. The corrected version was posted on April 24, 2007.

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