Inorganic Chemistry
Award Article

Inorg. Chem. **2010**, *49*, 10765–10780 **10765**
DOI: 10.1021/ic101800d

Chemistry of Carbon Dioxide Relevant to Its Utilization: A Personal Perspective

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Received September 2, 2010

This presentation provides a review of the author's research group's contributions to the organometallic chemistry of carbon dioxide with a focus on incorporating this information into the development of an effective means for producing chemicals from this greenhouse gas. The types of chemistry addressed include insertion reactions of CO_2 into M−H, M−C, and M−O bonds as well as seminal contributions related to the copolymerization reactions of CO_2 and cyclic ethers. Relevant to this latter subject, efforts were made to place the author's achievements into perspective with the accomplishments of other investigators, but these efforts were not meant to be exhaustive.

Introduction

The use of carbon dioxide as a building block for the synthesis of useful chemicals and as a fluid in numerous applications can serve to contribute to a sustainable chemical industry and concomitantly reduce CO_2 emissions into the atmosphere.[1−8] Nevertheless, because of the enormity of the total anthropogenic CO_2 emissions of ~25 Gton per year, other technologies for the capture and disposal of CO_2 must play major roles in reducing CO_2 emissions. The current industrial uses of CO_2 are rather limited. That is, the major processes involving the conversion of CO_2 into chemicals include the synthesis of urea, salicylic acid, inorganic carbonates, ethylene/propylene carbonates, and polycarbonates and the use as an additive to CO for the synthesis of methanol.[9] Relevant to this issue is the fact that the worldwide consumption of fuels is approximately 100 times greater than that of chemicals. Hence, chemical recycling of CO_2 to components of the fuel pool would be more effective at reducing CO_2 emissions significantly. The widespread use of CO_2 as a C_1 feedstock generally requires a major input of energy and is therefore counterproductive when employing traditional energy sources. In order to accomplish a sustainable conversion of CO_2 to liquid fuels, solar energy would appear to be the best option in the long term, although there are biological routes such as microalgae. In addition, because CO_2 is such an inert molecule, in most instances, its reactivity will need to be greatly enhanced by the judicious choice of catalysts. In this regard, metal complexes as catalysts play a pivotal role in advancing the utilization of CO_2 as a source of chemical carbon. This report chronicles the path my research program has taken, leading to our current efforts to develop and understand mechanistically single-site metal catalysts for the copolymerization of CO_2 and cyclic ethers, i.e., oxiranes and oxetanes, to provide polycarbonates.

The Early Years

In the mid-1970s, we became interested in the organometallic chemistry of CO_2 during our studies encompassing the nucleophilic addition of bases at the carbon center of metal carbonyls. Our curiosity with the reactivity of CO_2 stemmed from mechanistic studies involving the use of group 6 metal hexacarbonyls as homogeneous catalysts for the mildly exothermic ($\Delta G^{298} = -28.6\ \mathrm{kJ\ mol^{-1}}$) water−gas shift reaction (eq 1).[10,11]

$$CO + H_2O \overset{\text{cat}}{\rightleftharpoons} CO_2 + H_2 \qquad (1)$$

Earlier in collaborative studies with Professor Marcetta Darensbourg, our groups established a relationship between the CO stretching force constants in metal carbonyl complexes and the rate and regiospecificity of nucleophiles,

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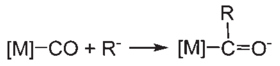
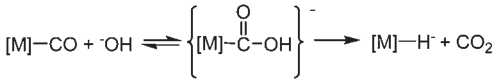
specifically main-group metal alkyls, adding to the carbon center (eq 2).[12]



$$\mathrm{[M]{-}CO + R^- \longrightarrow [M]{-}\overset{R}{\overset{|}{C}}{=}O^-} \qquad (2)$$

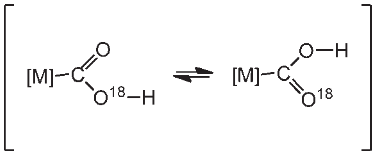
These studies revealed that CO ligands with high CO stretching force constants, which are associated with more positive character at the carbon center, were more susceptible to attack by nucleophiles.[13] A similar reaction profile accounts for the production of metal hydride and ultimately dihydrogen production when OH^- interacts with metal carbonyls (eq 3).[14]



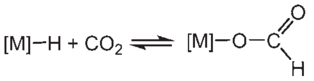
$$\mathrm{[M]{-}CO + {}^-OH \rightleftharpoons \left\{[M]{-}\overset{O}{\overset{\|}{C}}{-}OH\right\}^- \longrightarrow [M]{-}H^- + CO_2} \qquad (3)$$

It is also well-established that the reaction between metal carbonyl and ^-OH is reversible, as is evident by the scrambling of the oxygen atoms subsequent to rapid proton transfer, when isotopically labeled H_2O is employed (Scheme 1).[15−19]

Scheme 1



During this time period, the concurrent development of good synthetic methods for the isolation of well-characterized group 6 metal carbonyl hydride complexes allowed us the opportunity to pursue our first in-depth mechanistic study of CO_2 insertion reactions into metal−hydride bonds.[20,21] As depicted in eq 4, the product of this reaction is the corresponding metal formate derivative. That is, CO_2 insertion into the metal−hydride bond to provide the metalloformate species is a more facile process than the reverse reaction of the decarboxylation process illustrated in eq 3.[22−24]



(4)

The CO_2 insertion reaction defined in eq 4 readily occurs with hydridic metal hydrides, especially anionic complexes such as $HCr(CO)_5^-$. This is best illustrated by the fact that, although $HCr(CO)_5^-$ rapidly reacts with atmospheric CO_2 at ambient temperature, the isoelectronic derivative $HMn(CO)_5$ displays no tendency to react with CO_2. Similarly, $HFe(CO)_4^-$ undergoes reactions with CO_2 to provide the corresponding formate, whereas the acidic hydride $HCo(CO)_4$ does not react with CO_2. The thus-formed formate complex, $HCO_2Cr(CO)_5^-$, easily undergoes decarboxylation, as is evidenced by its exchange reaction with $^{13}CO_2$ (eq 5).

$$\mathrm{Cr(CO)_5O_2CH^- + excess\ {}^{13}CO_2 \rightleftharpoons Cr(CO)_5O_2{}^{13}CH^- + CO_2} \qquad (5)$$

The insertion and deinsertion of CO_2 into anionic hydrides of chromium and tungsten have been well-studied themes in our laboratory. These processes are thought to be prototypical of carboxylation/decarboxylation reactions involving low-valent, saturated metal centers. There are no documented cases of CO_2 insertion into metal−hydride bonds to provide the metallocarboxylic acid isomeric form, although complexes of this type are afforded by the nucleophilic attack of hydroxide on metal-bound carbonyl ligands (eq 3). Mechanistic aspects of the CO_2 insertion reaction into $HCr(CO)_5^-$ were investigated by performing kinetic studies of the microscopically reverse deinsertion process using a large excess of $^{13}CO_2$.[25]

The process depicted in eq 5, and its tungsten analogue, were monitored by ^1H NMR, where the formate resonance at 8.28 ppm is split by ^{13}C ($J_{C-H} = 186$ Hz) upon $^{13}CO_2$ exchange. The reaction was shown to be first-order in the metal complex, zero-order in CO_2, and retarded by carbon monoxide. The transition state was proposed to involve an O,H-dihapto structure following the loss of CO in the rate-determining step, as indicated in Figure 1, subsequently leading to an O,O-dihapto structure as a reaction intermediate. The preference for CO_2 insertion into a M−H bond to

Donald J. Darensbourg was born in Baton Rouge, LA, in 1941 and received his B.S. and Ph.D. degrees from California State University at Los Angeles and the University of Illinois—Urbana, respectively. Following a 9-month period at the Texaco Research Center in Beacon, NY, he was on the faculties of State University of New York at Buffalo from 1969 to 1972 and Tulane University from 1973 to 1982. He has been at Texas A&M University since 1982, where he currently is a Distinguished Professor. His research interests have been in mechanistic inorganic/organometallic chemistry with an emphasis on catalytic processes. Presently, his focus is on the utilization of CO_2 as both a monomer and a solvent in copolymerization reactions with oxiranes and oxetanes, and the ring-opening polymerization of renewable monomers such as lactides.

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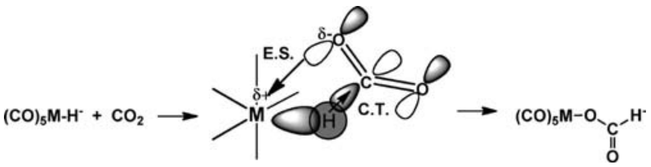


Figure 1. Charge-transfer interaction between metal hydride and CO_2. E.S. = electrostatic interaction; C.T. = charge-transfer interaction.

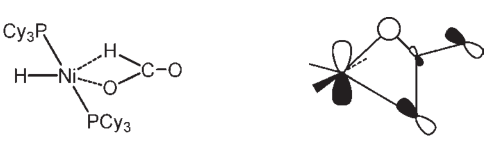


Figure 2. Orbital interaction between a low-lying empty orbital on nickel and the doubly occupied orbital of the formate unit.

afford a metal formate as opposed to a metallocarboxylic acid has been ascribed to a strong charge-transfer interaction between a hydridic M−H σ orbital and the π^* orbital of CO_2.[26] This interaction is supplemented by an attractive electrostatic interaction between $H\cdots CO_2$ and $O\cdots M$. The activation barrier of decarboxylation of the chromium derivative was determined to be 22.7 kcal mol^{-1}, and the barrier for CO dissociation in $HCO_2Cr(CO)_5^-$ was found to be 20.6 kcal mol^{-1}. Of importance, the decarboxylation reaction for $HCO_2Cr(CO)_5^-$ was not completely quenched at high CO pressures (>4.1 MPa). This behavior is indicative of an alternative, slightly higher in energy pathway for CO_2 extrusion/insertion that does not involve prior CO dissociation.

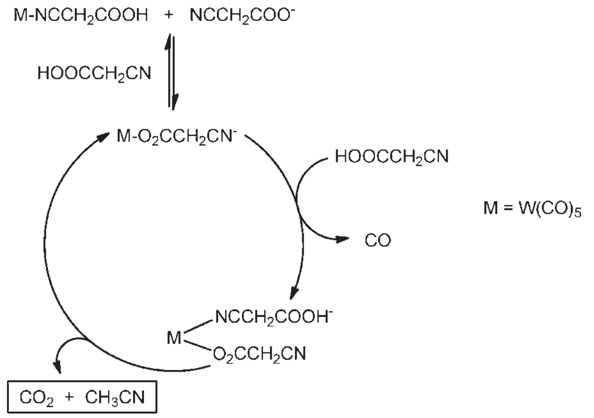
The lack of the need for ligand dissociation prior to decarboxylation of a metal-bound formate or the reverse process of CO_2 insertion into a metal hydride is best illustrated by the reactions of the square-planar nickel(II) complex, $HNi(O_2CH)(PCy_3)_2$ (eq 6). In this instance, CO_2 exchange was demonstrated to be first-order in the nickel formate complex and zero-order in CO_2.[27] This is consistent with a rate-determining step involving CO_2 extrusion to provide a metal dihydride intermediate, which undergoes a facile reinsertion of CO_2. Furthermore, the deinsertion/insertion process was found not to be retarded by added tricyclohexylphosphine. This behavior is to be expected for a d^8 metal complex, which possesses a low-lying empty p orbital for interaction with the doubly occupied orbital of the formate ligand (Figure 2).

$$\begin{aligned}&\mathrm{HNi(O_2CH)(PCy_3)_2}\\&+\ \text{excess}\ {}^{13}\mathrm{CO_2} \rightleftharpoons \mathrm{HNi(O_2{}^{13}CH)(PCy_3)_2 + CO_2}\end{aligned}\qquad(6)$$

The activation parameters determined for the isotope exchange reaction defined in eq 7 of $\Delta H^{\ddagger} = 22.0$ kcal mol^{-1} and $\Delta S^{\ddagger} = -4.8$ eu were found to be quite similar to those measured for the exchange reaction in eq 6, indicative of common reaction pathways. The intramolecular C−H/Ni−D exchange process displayed an equilibrium isotope effect of 1.47.

$$\mathrm{DNi(O_2CH)(PCy_3)_2 \rightleftharpoons HNi(O_2CD)(PCy_3)_2}\qquad(7)$$

Scheme 2



Anionic alkyl and aryl complexes of the group 6 metal carbonyl were similarly employed to probe the mechanistic aspects of CO_2 insertion into M−C bonds leading to C−C bond formation.[28,29] For the tungsten derivative, the rate of irreversible CO_2 insertion was shown to strongly depend on the nature of the W−C moiety, with more nucleophilic R groups undergoing CO_2 insertion more rapidly (eq 8).

$$\begin{gathered}\mathrm{RW(CO)_5^- + CO_2 \rightarrow RCO_2W(CO)_5^-}\\ \mathrm{R = CH_3CH_2 > CH_3 > PhCH_2 >> NCCH_2}\end{gathered}\qquad(8)$$

Correspondingly, upon an increase in the electron density at the metal center by replacement of a CO ligand with the sterically unencumbering PMe_3, an increase in the reaction rate for CO_2 insertion into the $W-CH_3$ bond of ~250 times was noted.[30] The reactions were found to be first-order in the metal complex and first-order in CO_2 and displayed activation parameters indicative of an associative interchange mechanism. For example, for $CH_3W(CO)_5^-$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for CO_2 insertion were determined to be 10.2 kcal mol^{-1} and −43.3 eu, respectively. Consistent with an I_a pathway, the stereochemistry about the α-carbon atom of the alkyl group was maintained during the CO_2 insertion process.[31] In addition, the second-order rate constant for CO_2 insertion into the M−R bond was found to be independent of added CO pressure, indicative of a transition state containing a coordinatively saturated metal center.

Although, in general, aliphatic carboxylic acids undergo a decarboxylation reaction at temperatures greater than 300 °C,[32] we have found the complex $NCCH_2CO_2W(CO)_5^-$ to catalyze the decarboxylation of cyanoacetic acid at modest temperatures.[33] A comprehensive kinetic analysis of the process strongly suggests a mechanism that is initiated by CO dissociation from the precursor complex $NCCH_2CO_2W(CO)_5^-$ with concomitant cyanoacetic acid binding via the nitrile group (Scheme 2). The free energies of activation for the decarboxylation and CO dissociation were found to be nearly identical at 23 kcal mol^{-1}. Upon elimination of the thermal barrier for CO dissociation by photolysis,

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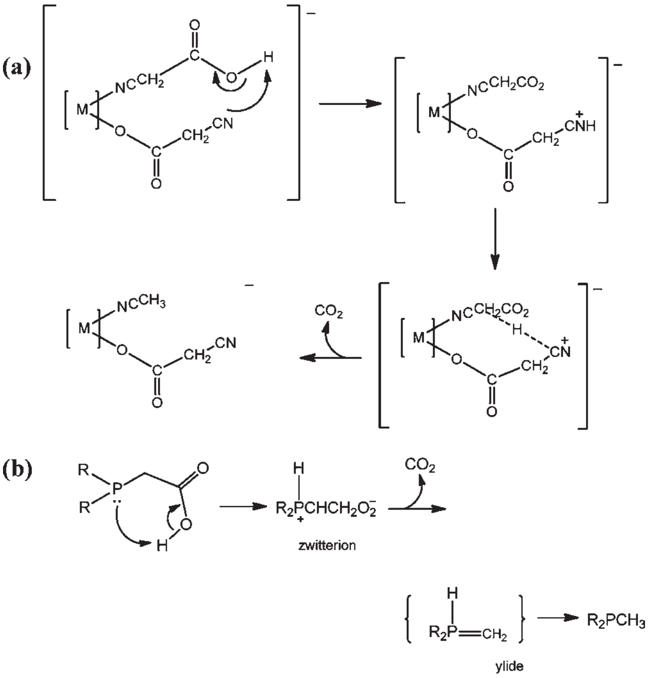
Scheme 3



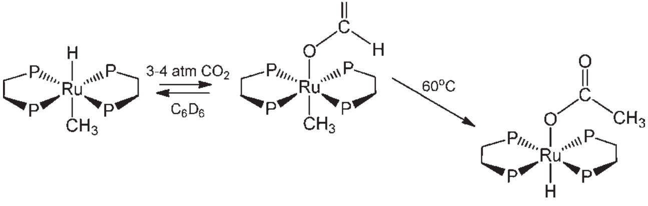
decarboxylation readily occurred. The process is thought to involve intramolecular proton transfer between the nitrogen-bound acid and the carboxylate ligand through its nitrile function. A similar process has been proposed for the facile decarboxylation of phosphinoacetic acid (Scheme 3).[34]

Pertinent to the issue of CO_2 fixation, it is important to note that CO_2 insertion into M−H bonds (eq 4) is considerably faster than its insertion into analogous M−R bonds (eq 8). Dedieu et al. have attributed the mechanistic differences of CO_2 insertion into M−H versus M−R bonds to a favorable interaction between the empty d_π orbital of the metal fragment and the doubly occupied valence orbital of the incipient HCO_2^- group (Figure 3A), whereas there is unfavorable overlap between the orbital of RCO_2^- and d_π (Figure 3B).[35]

Early on we attempted to compare the relative rates of CO_2 insertion into M−H versus M−R bonds at a single metal site, i.e., $RNi(H)(PCy_3)_2$, where R = CH_3 or Ph.[36] Although the methyl derivative was found to undergo a complicated reaction, possibly by a radical pathway, the phenyl complex underwent facile CO_2 insertion into the Ni−H bond to provide $PhNi(O_2CH)(Cy_3P)_2$. Hence, the kinetic product is clearly the anticipated result of CO_2 insertion into the M−H bond. However, because this process is reversible and the corresponding insertion into the M−R bond is not, it should be possible to obtain the alternative regioinsertion product. Indeed, very recently Field and co-workers have shown for a ruthenium(II) phosphine complex that insertion of CO_2 into the Ru−H bond occurs initially at ambient temperature, followed by a deinsertion of the formate complex with concomitant insertion into the Ru−CH_3 bond to afford the stable acetate derivative (Scheme 4).[37] This chemistry therefore offers the possibility of catalytically fixing CO_2 via C−C bond formation subsequent to C−H bond activation.

Figure 3. (A) Stabilizing interaction between the empty d_π orbital of the metal and the doubly occupied valence orbital of the incipient HCO_2^- ligand in the C−H bond-forming reaction. (B) Empty d_π orbital of the metal pointing toward the nodal plane of the p component of the alkyl carbon atom in the C−C bond-forming reaction.

Scheme 4



Finally, the mechanistic aspects of CO_2 insertion reactions involving M−O bonds were studied. As will soon become obvious, this reaction will comprise a pivotal step in processes that we are currently investigating for CO_2 incorporation into organic carbonate and polycarbonates. Unlike the relatively stable anionic group 6 metal carbonyl hydrides and alkyls discussed, $M(CO)_5OR^-$ complexes can be subject to two facile processes, which can complicate these studies. Namely, these derivatives can be unstable toward metal hydride formation with extrusion of the corresponding aldehyde or ketone (eq 9)[38] or aggregation as a result of their very rapid dissociation of CO ligands (eq 10).[39] The reverse process of the reaction depicted in eq 9 has been utilized in the catalytic hydrogenation of aldehyde or ketone by H_2 in the presence of anionic group 6 metal carbonyl hydrides.[40]

$$M(CO)_5OCHR_2^- \rightleftharpoons M(CO)_5H^- + R_2CO \qquad (9)$$

$$M(CO)_5OR^- \xrightarrow{-CO} \{(CO)_8M_2(\mu\text{-}OR)_2\}^{2-} \xrightarrow{-CO} [(CO)_3M(\mu\text{-}OR)]_4^{4-} \qquad (10)$$

The CO-labilizing property of alkoxide ligands is attributed to their ability to π-donate electron density to the metal center, thereby stabilizing the developing intermediate

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resulting from CO dissociation.[41] Hence, this facile CO dissociation can be moderated by the addition of electron-withdrawing substituents to the alkoxide ligand, e.g., changing $-\mathrm{OEt}$ to $-\mathrm{OCH_2CF_3}$.[42] Similarly, exchanging an alkoxide for an aryloxide ligand retards reaction (10) and eliminates reaction (9). Nevertheless, these secondary processes can be overcome, and the CO_2 insertion reaction into M−OR bonds to provide metal carbonates has been shown to occur under conditions where the metal remains electronically and coordinatively saturated (eq 11).[43]

$$\mathrm{M(CO)_5OR^- + CO_2 \rightleftharpoons M(CO)_5O_2COR^-} \qquad (11)$$

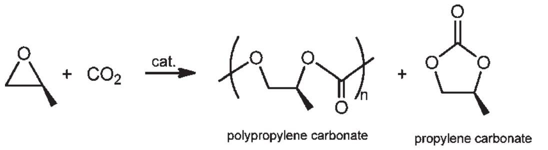
As with the metal hydride analogues, these processes are generally reversible. This is best illustrated for the reaction of CO_2 with the electron-rich manganese(I) complex, *fac*--$\mathrm{(CO)_3(dppe)MnOCH_3}$, where the very reactive methoxide ligand is sterically unencumbered.[44] The manganese(I) methoxide complex was shown not to undergo ligand-exchange processes at ambient temperature; however, it reacts with a low concentration of CO_2 at −78 °C during the time of mixing.[45] This observation further supports the mechanism of CO_2 insertion into metal−alkoxide bonds, where no coordination site for CO_2 binding is required. The reverse process, CO_2 extrusion from *fac*-$\mathrm{(CO)_3(dppe)MnO_2COCH_3}$, occurs much slower with activation parameters of $\Delta H^\ddagger = 31.1$ kcal mol^{-1} and $\Delta S^\ddagger = 29.1$ eu. Hence, in this instance the metal carbonate is much more stable than the corresponding metal alkoxide and CO_2 with an estimated ΔG value at −78 °C of less than −12 kcal mol^{-1}.

The reaction defined in eq 11 is reminiscent of the corresponding process involving CO_2 insertion into a M−OH bond, a key step in the catalytic cycle for the hydration of CO_2 by the zinc metalloenzyme, carbonic anhydrases (eq 12).[46] Indeed, Parkin and Vahrenkamp have performed excellent studies modeling this process with well-defined zinc(II) complexes.[47] In studies closely related to those reported for the reaction of $\mathrm{W(CO)_5OR^-}$ with CO_2, we have fully characterized the bicarbonate complex resulting from CO_2 insertion into the W−O bond of $\mathrm{W(CO)_5OH^-}$.[48]

$$\mathrm{CO_2 + 2H_2O \rightleftharpoons HCO_3^- + H_3O^+} \qquad (12)$$

The Intervening Years

We, like numerous other research groups, have incorporated some of the chemistry discussed here in fixing CO_2 into small molecules.[49−52] Recently, there have been significant gains made in these efforts by several research groups.[53] However, we decided early on to follow up on the pioneering efforts of Inoue et al.[54] and Rokicki and Kuran[55] and focus our attention on CO_2 coupling reactions with high-energy cyclic ether monomers to provide polycarbonates and cyclic carbonates (eq 13).



(13)

Our initial studies of this process were centered around attempts to understand the catalytic coupling of CO_2/propylene oxide (PO) using the most active catalysts available at the time, zinc carboxylates.[56] To better assess the role of these catalysts, we endeavored to define the solid-state structure of zinc glutarate. Although we were not able to obtain single crystals of this material, the structure of this polycrystalline compound was obtained from its powder pattern. It was shown to be a layered structure of zinc atoms with bridging dicarboxylates between the layers (Figure 4).[57,58] Subsequently, Zheng and co-workers were able to grow single crystals of zinc glutarate and confirm the structure.[59] Our early studies of the copolymerization process employing this catalyst revealed that supercritical CO_2 was a good, environmentally benign solvent replacement for the commonly used methylene chloride solvent.[60] Nevertheless, it was clear that our efforts would be better directed at exploring other potential catalysts for this important polymerization process.

Pursuing catalytic systems based on the bioinspired zinc(II) complexes, we examined several stable cadmium(II) analogues where epoxide binding occurred in the absence of subsequent facile ring-opening processes.[61,62] These studies report crystal structures of rarely observed metal-bound

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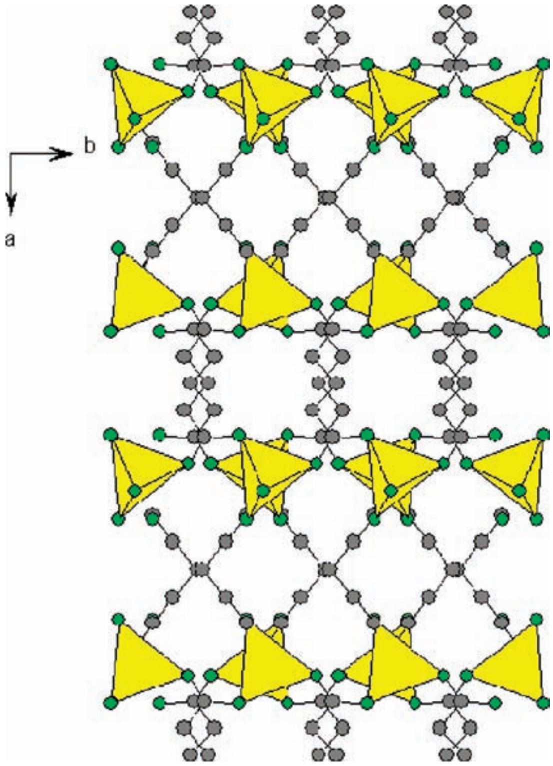

Figure 4. Crystal structure of zinc glutarate prepared from ZnO and glutaric acid in toluene. The structure was determined from the powder X-ray diffraction pattern (view along the *c* axis).[58].

epoxide derivatives, e.g., (η^3-HB(3-Phpz)$_3$)Cd^{II}(acetate)PO, where pz = pyrazolyl and PO = propylene oxide (Figure 5). The solid-state structure of the corresponding tetrahydrofuran (THF) and cyclohexene oxide (CHO) derivatives revealed the Cd−O bond distances to increase in the order THF < CHO ≤ PO.

This binding order was confirmed in methylene chloride by ^{113}Cd NMR spectroscopic studies, where the $\Delta G°$ values determined at 298 K for eq 14 were -1.00 kJ mol^{-1} for THF and $+3.73$ kJ mol^{-1} for CHO and PO. Furthermore, it was demonstrated that when a CHO solution of [Tp^{Ph}]Cd(O$_2$^{13}CCH$_3$)·CHO was refluxed, oligomerization of CHO occurred, initiated by ring opening of the epoxide by the acetate group, as revealed by ^{13}C NMR spectroscopy.

$$[\mathrm{Tp^{Ph}}]\mathrm{Cd^{II}(acetate)} + \text{cyclic ether} \overset{K_{eq}}{\rightleftharpoons} [\mathrm{Tp^{Ph}}]\mathrm{Cd^{II}(acetate)}\cdot \text{cyclic ether} \quad \mathrm{Tp^{Ph}} = \eta^3\text{-HB(3-Phpz)}_3 \text{ and pz} = \text{pyrazolyl} \tag{14}$$

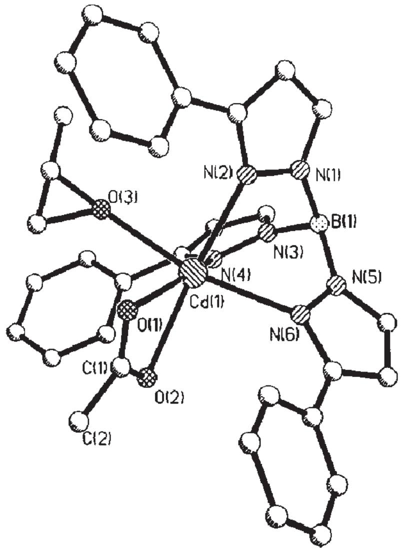

Figure 5. Molecular structure of the PO adduct of Tp^{Ph}Cd^{II}(acetate).

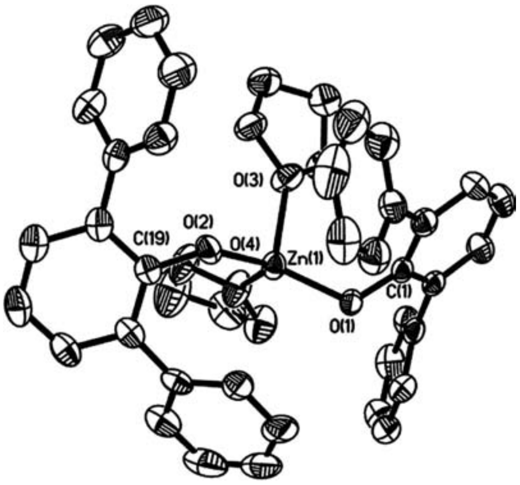

Figure 6. Molecular structure of the (2,6-Ph$_2$C$_6$H$_3$O)$_2$Zn(THF)$_2$ catalyst.

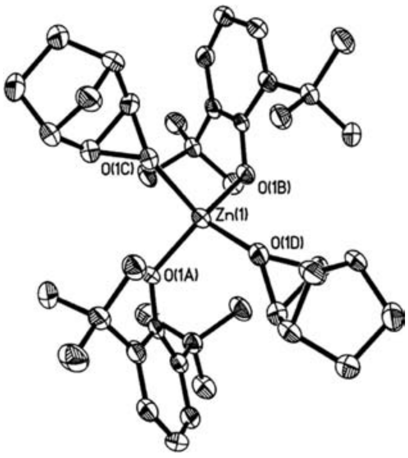

Figure 7. Epoxide adduct of the bis-phenoxide zinc complex, [Zn(O-2,6-*t*-Bu$_2$C$_6$H$_3$)$_2$](*exo*-2,3-epoxynorborane)$_2$.

Our most significant early breakthrough in the copolymerization of epoxides and CO$_2$ came when my graduate student Matt Holtcamp discovered that well-defined bis-phenoxide complexes of zinc were active catalysts for this process.[63,64] A series of four-coordinate zinc phenoxides of the general formula (2,6-R$_2$C$_6$H$_3$O)$_2$Zn(base)$_2$ [R = Ph, ^{t}Bu, ^{i}Pr; base = Et$_2$O, THF] were shown to afford high-molecular-weight polycarbonates from CHO and CO$_2$ at 80 °C and 5.17 MPa with a low level of ether linkages (eq 15 and Figure 6). The high polydispersity measured for these copolymers, greater than

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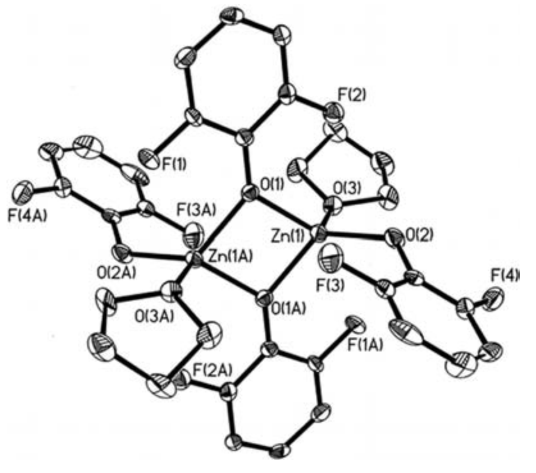
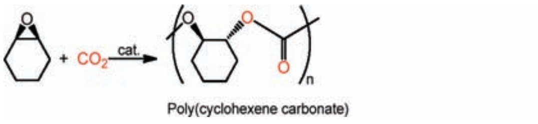


Figure 8. Molecular structure of the $[(2,6\text{-}F_2C_6H_3O)_2Zn(THF)]_2$ dimer.

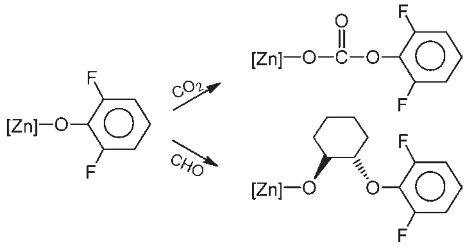
2.5, suggested that more than one zinc species were initiating the process. Under similar reaction conditions, the reaction between PO and CO_2 produced only propylene carbonate. However, upon a decrease of the temperature to 40 °C, poly(propylene carbonate) is slightly favored over propylene carbonate production. That is, the rate of propylene carbonate formation displayed a greater temperature dependence than the rate of copolymer formation. On the contrary, at 80 °C terpolymerization of PO/CHO/CO_2 resulted in a random mixture of polycarbonate linkages with little cyclic carbonate production. Epoxides such as *exo*-2,3-epoxynorbornane, which are reluctant to undergo ring opening, provided four-coordinate complexes of zinc much like the THF adducts (Figure 7).[65]



(15)

It is important to note here that these catalytic systems were carried out in the absence of an organic solvent; i.e., the catalysts were dissolved in the epoxide and pressurized with CO_2. Hence, CO_2 served as both a monomer and cosolvent in these copolymerization processes. When the phenoxide ligands in the bis-phenoxide complexes of zinc contained sterically less demanding substituents, e.g., fluoride groups, the zinc(II) derivatives were found to be dimeric both in the solid state and in solution (Figure 8).[66] In this instance, where the zinc center is more electrophilic, the catalysts are very active for homopolymerizing the epoxide prior to pressurizing the catalyst solution with CO_2. In these cases, a polyether polymer was shown to form prior to copolymer production.[67] Although homopolymerization of epoxide is very facile in the absence of CO_2, the copolymerization process was found to take place in a completely alternating manner, i.e., with essentially no ether linkages. This is presumably due to the presence of only one epoxide binding site per zinc center and supports a dimeric structure for the active catalyst. This latter conclusion was further bolstered by the lack of catalytic activity in the presence of 1 equiv of PCy_3 per zinc center, which was shown to strongly bind to the available metal binding site. The presence of the fluoride substituents on the phenoxide ligands of the zinc catalyst provided a probe for the initiation process. ^{19}F NMR spectroscopy suggested two initiation processes involving the nucleophilic addition of the zinc-bound phenoxide to an epoxide or CO_2 (Scheme 5).

Scheme 5



Following our preliminary report on the copolymerization of epoxides and CO_2 utilizing well-defined zinc metal complexes as catalysts, Beckman and Costello described a similar catalytic activity for the copolymerization of CHO and CO_2.[68] Although their zinc catalyst derived from a long-chain perfluorinated alcohol (tridecafluorooctanol) was not structurally defined, it was soluble in liquid or supercritical CO_2. A major flaw in the design of these and our zinc catalysts for the copolymerization reaction is that the polymer initiator is part of the metal's ancillary ligand system (Scheme 5). This is where Coates et al. made a great leap forward in catalyst development by utilizing zinc complexes that possessed an anionic initiator while its bidentate monoanionic ancillary ligand system remained intact during the copolymerization process.[69,70] This mimics the design protocol for effective olefin polymerization catalysts. Coates' group's use of these very effective β-diiminate zinc derivatives for the copolymerization of both CHO and PO with CO_2 provided well-controlled polymerization processes, affording a copolymer with a narrow molecular weight distribution. Furthermore, following a similar study by Nozaki's group's use of a chiral zinc catalyst derived from an amino alcohol,[71] Coates and co-workers utilized a chiral imineoxazoline zinc catalyst for the asymmetric alternating copolymerization of CHO and CO_2 to provide isotactic poly(cyclohexene carbonate) with an enantiomeric excess of about 70%.[72]

The Present Decade

As mentioned in the Introduction, because part of the strategies to curtail the emission of CO_2 into the atmosphere from various operations involves the capture of CO_2, much *renewed* interest has focused on utilizing CO_2 as a source of chemical carbon. However, because CO_2 is the end product

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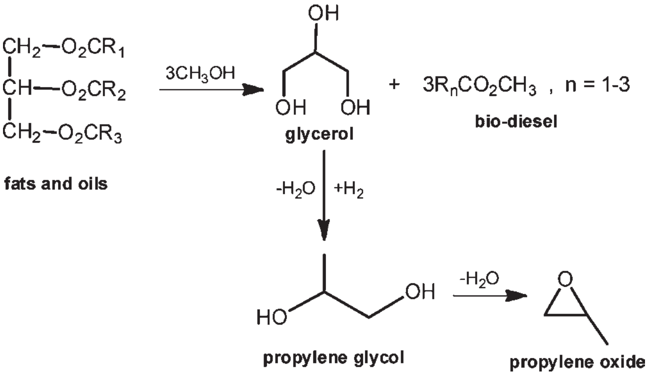
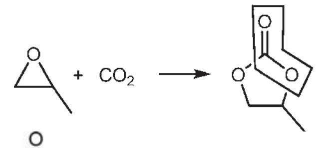
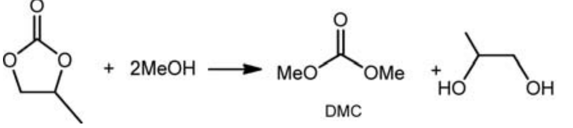
Scheme 6



of many energy-producing processes, its use generally requires a major input of energy. One way to minimize this energy requirement is to incorporate CO_2 *intact* into molecules of practical importance. The formation of cyclic carbonates from the coupling of epoxides and CO_2 represents one such process (eq 16). Organic carbonates can serve as solvents for a wide range of chemical processes; in particular, they are used in lithium batteries and other electrochemical applications.[73] Propylene and ethylene carbonates can be used as environmentally friendly reagents for the synthesis of dimethyl carbonate (DMC) via transesterification, where DMC is a "green" replacement for phosgene (eq 17). Hence, in addition to CO_2 utilization adding value to an otherwise waste, there are substantial *health and safety benefits* derived from toxic chemical substitution. It is also worth noting that PO can be synthesized from a nonpetroleum source, i.e., propylene glycol derived from bioglycerol (Scheme 6).[74]



$\Delta H_f^\circ = -70$ kJ/mol (16)



(17)

There are numerous catalysts for producing cyclic carbonates from epoxides and CO_2. These range from simple metal salts like $ZnCl_2$ and VCl_3 to chiral main-group or transition-metal complexes.[75] In general, any one of these catalysts is effective at coupling a large variety of epoxide substrates with CO_2 to provide cyclic organic carbonates. Pertinent to this presentation is the communication by Paddock and Nguyen, which reported that various (salen)CrCl derivatives, including Jacobsen's chiral catalyst (Figure 9),[76] in the presence of 4-(dimethylamino)pyridine were effective for the coupling of CO_2 and a wide range of aliphatic epoxides to provide cyclic carbonates.[77] In this manner, cyclic carbonates derived from the epoxides PO, epichlorohydrin, vinyl epoxide, and styrene oxide were obtained in near-quantitative yields. These reactions were carried out at 0.3 MPa CO_2 pressure and 75−85 °C, providing a turnover frequency (TOF) of 127−254 h^{-1}.

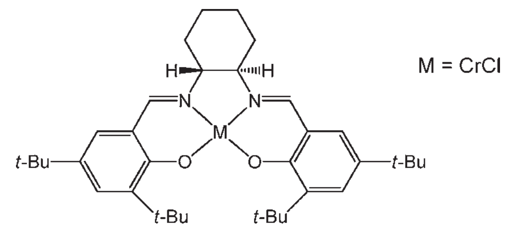
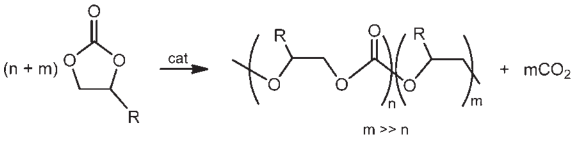


Figure 9. Enantioselective (salen)CrCl complex for epoxide ring opening.

During this time period, Jason Yarbrough, then a graduate student in my research group, was inspired by the studies of Jacobsen as well as related studies employing chromium(III) porphyrin complexes by Kruper and Dellar[78] and Holmes et al.[79] to investigate the copolymerization of epoxides and CO_2 utilizing (salen)CrCl catalysts. An article with the details of our investigations using Jacobsen's catalyst was published following an earlier release of our results at the Sixth International Conference on Carbon Dioxide Utilization in Breckenridge, CO, in July 2001.[80] It is important to note here that five-membered cyclic carbonates afforded from epoxides and CO_2 are more stable than their ring-opened polymers. Hence, ring-opening polymerization (ROP) of five-membered cyclic carbonates occurs with significant loss of CO_2 (eq 18).[81]



(18)

Utilizing the (salen)CrCl complex along with various initiators, we introduced investigations of these processes employing in situ IR spectroscopy. The ReactIR system used consists of a stainless steel Parr autoclave modified at its base with a 30-bounce silicon crystal, which allows for attenuated total reflectance Fourier transform IR spectroscopy.[82] The reaction analysis system along with typical data obtained for the copolymerization of CHO and CO_2 in the absence of a cosolvent is depicted in Figure 10. As indicated in Figure 10b, this procedure for in situ monitoring of the epoxide/CO_2 coupling reaction provides real-time data for the formation of both copolymer and cyclic carbonate reaction products. For the two commonly studied *alicyclic* and *aliphatic* epoxides,

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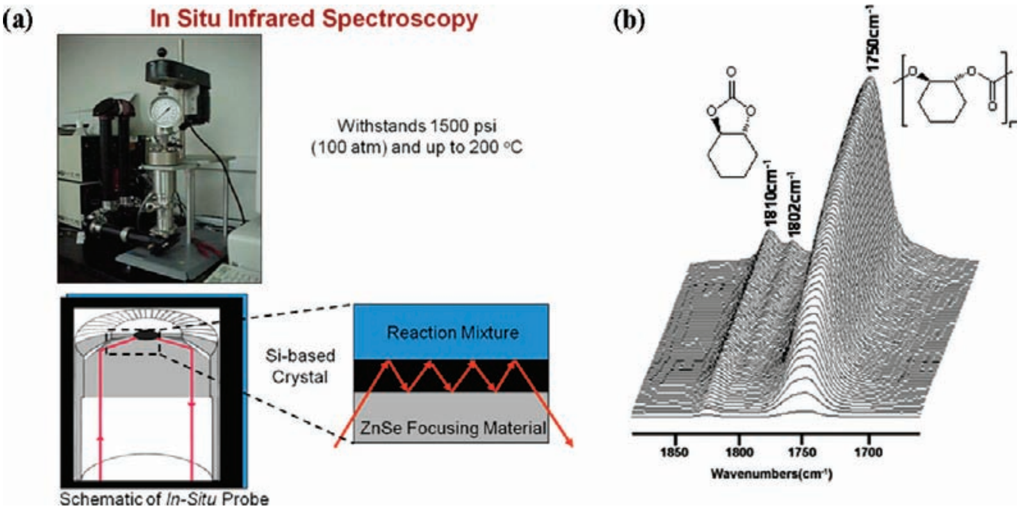
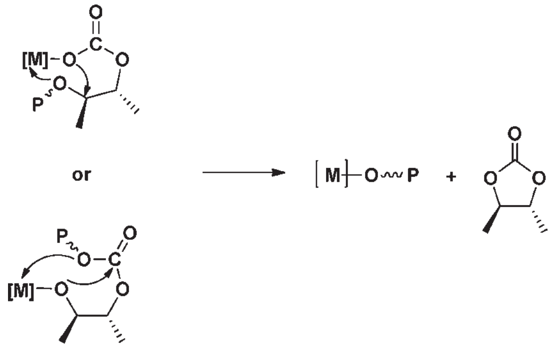


Figure 10. (a) ASI ReactIR 1000 reaction analysis system with a stainless steel Parr modified autoclave. (b) Typical 3D stack plot of the IR spectra collected every 3 min during the coupling reaction of CHO and CO_2 (80 °C and 55 bar pressure).

Scheme 7



CHO and PO, we established that, at the reaction conditions of 80 °C, the two epoxides were selective for affording poly(cyclohexylene carbonate) and propylene carbonate, respectively. Upon a decrease of the reaction temperature to 30 °C, the reaction between PO and CO_2 selectively provided poly(propylene carbonate). This is what we reported early on for the bis-phenoxide zinc catalyzed processes.

The production of cyclic carbonates is proposed to occur via a backbiting mechanism from either a carbonate or an alkoxide chain end during the coupling process, as indicated in Scheme 7. Kinetic studies of this process revealed that backbiting from an alkoxide chain end has a lower activation energy barrier than that occurring by way of a carbonate chain end.[83] This is consistent with cyclic carbonate production being inversely dependent on the CO_2 pressure.[84] In addition, dissociation of the growing polymer chain from the influence of the metal catalysts is thought to greatly enhance cyclic formation. This hypothesis is strongly supported by the highly selective production of poly(propylene carbonate) from PO and CO_2 using a (salen)CoOAc catalyst in the absence of an added onium salt,[85] and studies employing bifunctional (salen)cobalt(III) catalysts containing positively charged ligand systems independently by the groups of Nozaki et al.,[86] Lee et al.,[87] and Lu et al.[88] Figure 11 illustrates three of these very effective catalyst systems employed for the selective production of poly(propylene carbonate) from PO and CO_2.

Temperature-dependent rate data obtained via in situ IR spectroscopy studies for the coupling reactions of CHO or PO with CO_2 have provided energy profiles for the formation of the two products, copolymer versus cyclic carbonate.[89] As illustrated in Figure 12, it is apparent that, in order to avoid cyclic carbonate formation from the coupling of PO and CO_2 using the (salen)CrCl catalyst system, the reactions must be carried out at low temperature. This is a consequence of the activation barrier for cyclic carbonate production being only 32.9 kJ mol^{-1} higher in energy than that for copolymer formation. By way of contrast, the CHO/CO_2 coupling reactions have considerably different activation barriers, differing by 86.1 kJ mol^{-1}. We have attributed this large energy difference between the two consecutive processes to be associated with the ring strain imposed on the five-membered cyclic carbonate by the conformation requirement of the cyclohexyl ring, as seen in the boxed overlapped structures of the two cyclic carbonates.

The mechanistic aspects of copolymer formation involving (salen)CrX complexes as catalysts are presented in skeletal form in Scheme 8. As noted in the scheme, an initiator or cocatalyst is required in this process, which initially binds to the five-coordinate Cr^{III} center, leading to a six-coordinate intermediate. Several such six-coordinate complexes have been crystallographically characterized.[90] Various bases, including heterocyclic amines, phosphines, and anions, have

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(89) Darensbourg, D. J.; Yarbrough, J. C.; Ortiz, C. G.; Fang, C. *J. Am. Chem. Soc.* **2003**, *125*, 7586.

(90) (a) Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers, J. L. *J. Am. Chem. Soc.* **2005**, *127*, 14026. (b) Darensbourg, D. J.; Moncada, A. I. *Inorg. Chem.* **2008**, *47*, 10000.

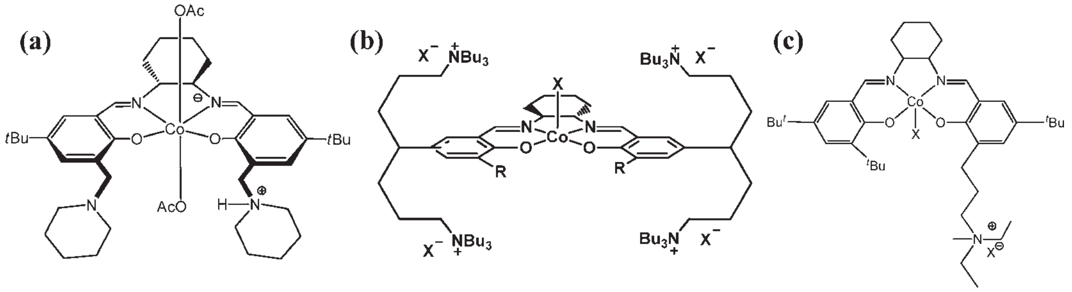


Figure 11. Bifunctional cobalt(III) salen catalysts for the copolymerization of PO and CO_2: (a) Nozaki et al.;[86] (b) Lee et al.;[87b] (c) Lu et al.[88].

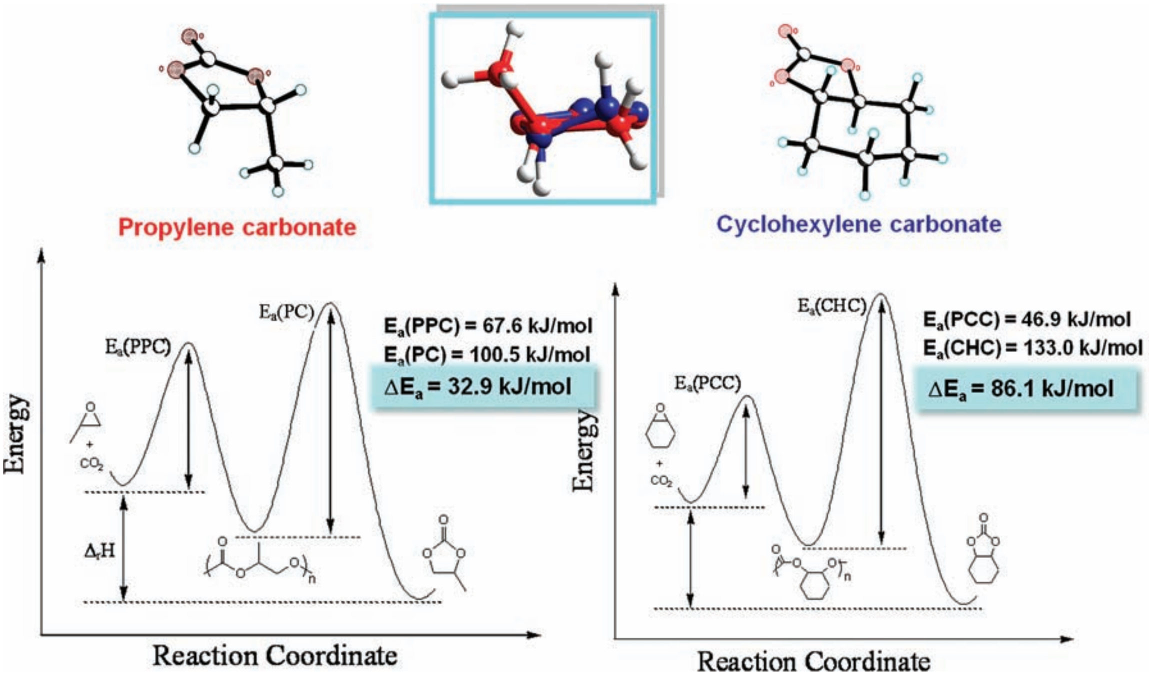
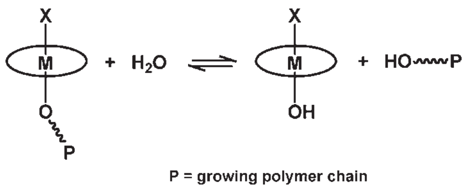


Figure 12. Reaction energy profiles for the coupling reactions of PO or CHO and CO_2.

been utilized as initiators. In general, anionic initiators have proven to be more effective at promoting this polymerization process. These free or weakly interacting anions serve to ring-open the activated (metal bound) epoxide in much the same manner as the metal-bound anion of the five-coordinate (salen)CrX complex ring-opens a metal-bound epoxide in the Jacobsen bimolecular in the metal complex mechanism.[76] We have optimized the catalytic activity for the copolymerization of CHO and CO_2 in the presence of (salen)CrX complexes by varying the substituents on the salicylaldimine ligand and the nature of the X group.[91,92] Sterically encumbering substituents on the diimine backbone were shown to greatly diminish the catalytic activity, whereas electron-donating substituents on the 3 and 5 positions of the phenolic ligands increased the rate of copolymerization. For example, an −OMe group in the 3 position and a *t*-Bu group in the 5 position provided a more active catalyst than the di-*tert*-butyl analogue. Changing X from chloride to azide enhanced the catalytic activity. The ultimate TOF for the copolymerization of CHO and CO_2 utilizing such a complex at 80 °C and 3.5 MPa was determined to be 1153 h^{-1}.[84]

It is generally observed for these copolymerization processes that the molecular weights of the purified copolymers are significantly less than expected based on the monomer/initiator. Nevertheless, the molecular weight distribution is rather narrow. This is thought to be due to a rapid and reversible chain-transfer process with trace quantities of water (eq 19). It has alternatively been suggested that this results from the simultaneous growth of two polymer chains from one metal center, as in the boxed area in the lower right-hand corner of Scheme 8. We designed an experiment to directly address this issue using the closely related (tmtaa)CrCl catalyst system, which had been previously demonstrated to behave mechanistically like its (salen)CrCl analogue.[93]



(19)

P = growing polymer chain

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[91] Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers, J. L.; Phelps, A. L. *Inorg. Chem.* **2004**, *43*, 1831.

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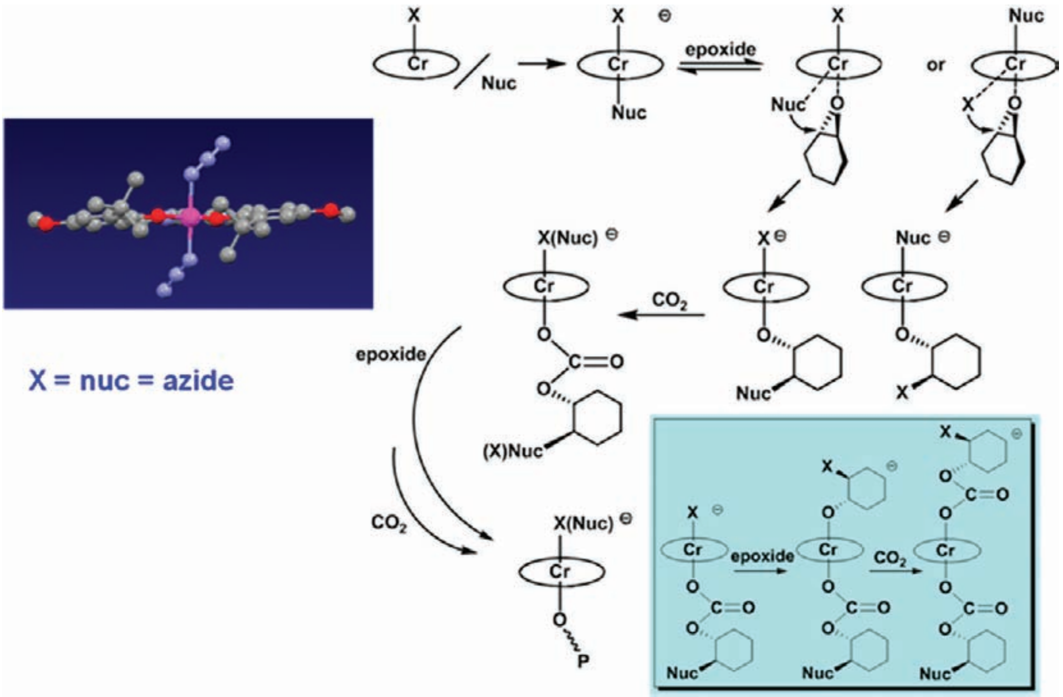
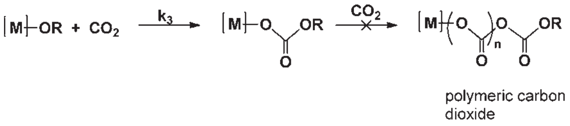
[93] (a) Darensbourg, D. J.; Fitch, S. B. *Inorg. Chem.* **2007**, *46*, 5474. (b) Darensbourg, D. J.; Fitch, S. B. *Inorg. Chem.* **2008**, *47*, 11868.

Scheme 8



In an effort to resolve the issue of simultaneous chain propagation from both sides of the (salen)Cr^{III} plane, two electronically identical tetramethyltetraazaannulene (tmtaa) complexes were synthesized. As illustrated in Figure 13, one of the tetradentate ligands is protected on the underside and the other has a flexible underside.[94] As is apparent from the crystal structure of the dimethyl sulfoxide (DMSO) adduct of the chromium complex containing the strapped ligand, there is no space for copolymer propagation on the protected face (Figure 14). The catalytic activities for the copolymerization of CHO and CO_2 using the two closely related (tmtaa)CrCl complexes carried out under the same reaction conditions (80 °C and 3.5 MPa CO_2) were determined to be the same (800 h^{-1}); see Figure 15. Furthermore, each catalyst system afforded the same high selectivity for copolymer formation, and the copolymers were of similar molecular weights ($M_n \approx 12\,000$) and polydispersities (1.10). This observation was taken as strong evidence for the lack of dual catalysis behavior at a single metal site, as depicted in Scheme 8. There are other uncertainties about some of the features of the steps in the catalytic cycle shown here. In particular, we are currently embarking on a collaborative theoretical study with Edwin Webster at The University of Memphis involving the interpretation of the dashed lines indicated in the epoxide ring-opening steps. That is, does the initiator and/or the carbonate function of the growing polymer chain dissociate from the metal center during the ring-opening process or is the process more akin to an associative interchange pathway?

Ordinarily, copolymerization of epoxides and CO_2 catalyzed by (salen)CrX and related complexes affords completely alternating copolymers, even at modest CO_2 pressures. This can be accounted for by two considerations. First, the carbonate function of the growing polymer chain is a better nucleophile than an alkoxide for ring opening of a weakly bound or activated epoxide (Scheme 9). On the other hand, for strongly bound (activated) epoxides resulting from binding to strong Lewis acids, e.g., some zinc-based catalysts, ring-opening reactions by alkoxide and carbonate are competitive. Second, consecutive CO_2 insertion reactions are unknown and presumably are thermodynamically unfavored (eq 20). It should, nevertheless, be noted that k_3 in eq 20 is dependent on the concentration of CO_2.[84]



(20)

(salen)CrX complexes in the presence of onium salts are not as effective for catalyzing the copolymerization of PO and CO_2 as their cobalt(III) analogues at the required low temperatures to avoid cyclic carbonate production.[95,96] However, (salan)CrX derivatives are more active and have been shown to provide poly(propylene carbonate) selectively at ambient temperature with a high degree of regioregularity.[97] Assignments of the ^{13}C NMR resonances in the carbonate region to define the microstructure characteristics of the regioselective ring opening of PO in these copolymerization reactions have been reported by Chisholm and coworkers.[98] The uniformity of the regiochemistry of the ring-opening process for PO and CO_2 copolymerization catalyzed by the (salan)CrCl/onium salt system is illustrated in Figure 16. Furthermore, (salalen)CrCl complexes and onium salts have

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(94) Darensbourg, D. J.; Fitch, S. B. *Inorg. Chem.* **2009**, *48*, 8668.

(95) Eberhardt, R.; Allmendinger, M.; Rieger, B. *Macromol. Rapid Commun.* **2003**, *24*, 194.

(96) Darensbourg, D. J.; Phelps, A. L. *Inorg. Chem.* **2005**, *44*, 4622.

(97) (a) Li, B.; Wu, G.-P.; Ren, W.-M.; Wang, Y.-M.; Rao, D.-Y.; Lu, X.-B. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6102. (b) Darensbourg, D. J.; Ulusoy, M.; Karroonnirun, O.; Poland, R. R.; Reibenspies, J. H.; Çetinkaya, B. *Macromolecules* **2009**, *42*, 6992.

(98) (a) Chisholm, M. H.; Navarro-Llobet, D.; Zhou, Z. *Macromolecules* **2002**, *35*, 6494. (b) Chisholm, M. H.; Zhou, Z. *J. Am. Chem. Soc.* **2004**, *126*, 11030.

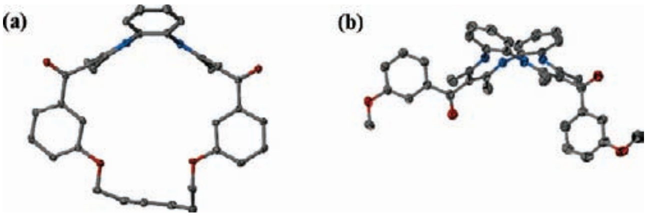


Figure 13. (a) X-ray crystal structure of the strapped tmtaa ligand. (b) X-ray crystal structure of the strapped mimic ligand, illustrating the flexibility of the anisole arms to the exposed underside of the ligand.

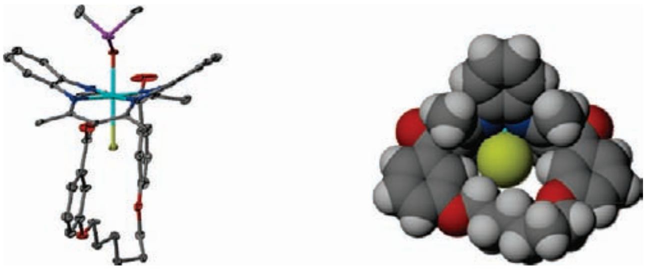


Figure 14. X-ray crystal structure of the DMSO adduct of the chromium complex containing the strapped tmtaa ligand, Cr(stmtaa)Cl, along with its space-filling model.

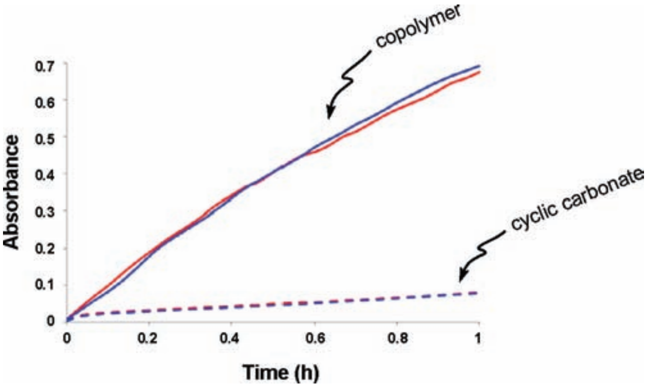
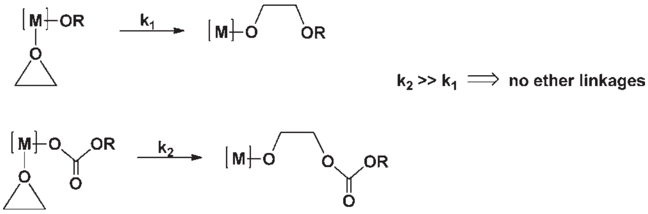


Figure 15. Reaction profiles for copolymer and cyclic carbonate formation using the strapped (red) and strapped mimic (blue) Cr(tmtaa)Cl complexes as catalysts.

Scheme 9



been demonstrated by Nozaki and co-workers to have high catalytic activity for the nearly perfectly alternating copolymerization of cyclohexene and CO_2 even under atmospheric CO_2 pressure.[99] It is not surprising that (salen)CrCl and its reduced analogues, (salalen)CrCl and (salan)CrCl, display different catalytic behavior in these copolymerization processes. That is, in general, (salen)CrCl complexes have a trans structure, as shown in Figure 17, whereas the salalen and salan derivatives have a cis arrangement.[100] Importantly, these latter Schiff base metal complexes allow for cis binding sites of the monomer and the growing polymer chain or can bind the growing carbonate polymer chain end in a bidentate fashion.[99]

Significant findings in the area of terpolymerization processes have aided in our understanding of the mechanistic aspects of the epoxide/CO_2 coupling reactions. In this regard, as previously mentioned, (salan)CrCl along with $[PPN]N_3$ was shown to be effective at copolymerizing PO and CO_2 at ambient temperature. However, higher temperatures (~60 °C) were required for copolymerizing CHO and CO_2. Most strikingly, the terpolymerization of PO/CHO/CO_2 occurred easily at ambient temperature with only modest selectivity for PO.[97b] A similar observation was also noted by Lu and co-workers.[101] This rate enhancement for the incorporation of CHO into the polycarbonate in the presence of PO can be ascribed to a faster rate for the ring opening of CHO by a propylene carbonate polymer chain end group (vide infra).

Because the CO_2 insertion step is fast at moderate CO_2 pressures, the composition of the terpolymer is dependent on the epoxide monomer reactivity ratios. Our results and others have shown that the monomer reactivity ratios are obtainable from Fineman−Ross plots.[102] These plots of the mole fraction of the monomer in feed and in terpolymer can be utilized to determine the reactivity ratios of the epoxide pairs at low conversion (Figure 18).[103] The linear plot depicted in Figure 18 was obtained from the relationship indicated in eq 21, where r_{PO} is k_{11}/k_{12}, as defined in Scheme 10. The relative reactivity of a carbonate unit ring-opening its component epoxide was found to be different from its reactivity for ring-opening the other epoxide. For example, for the limited number of (salen)MX or (salan)MX (M = Co or Cr) catalyst systems examined for PO and CHO, $k_{11}/k_{12} > 1$ and the analogous parameters for the cyclohexylene carbonate unit k_{22}/k_{21} is less than 1 (Scheme 10).[88,103,104]

$$\frac{f-1}{F} = -r_{PO}\frac{f}{F} + r_{CHO} \qquad (21)$$

Concerns for most homogeneously catalyzed processes utilizing metal catalysts are the issues of efficient catalyst separation from the product and subsequent catalyst recycling. A variety of homogeneous and heterogeneous catalyst systems have been designed for metal salen complexes with these matters of contention in mind.[105] The highly active Co(salen)-based catalyst with pendent ammonium salts shown in Figure 11b was found to be easily separated on silica and recycled several times with little loss in catalytic activity.[87b] Bergbreiter and co-workers have synthesized a chromium salen complex where the ligand was substituted with ~1000 Da poly(isobutylene) substituents to render the complex highly soluble in saturated hydrocarbon solvents (Figure 19).[106] This catalyst exhibited catalytic activity very similar to that of comparable (salen)CrCl complexes and

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(99) Nakano, K.; Nakamura, M.; Nozaki, K. *Macromolecules* **2009**, *42*, 6972.

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(101) Ren, W.-M.; Liu, Z.-W.; Wen, Y.-Q.; Zhang, R.; Lu, X.-B. *J. Am. Chem. Soc.* **2009**, *131*, 11509.

(102) Fineman, M.; Ross, S. D. *J. Polym. Sci.* **1950**, *5*, 259.

(103) Darensbourg, D. J.; Poland, R. Unpublished results.

(104) Seong, J. E.; Na, S. J.; Cyriac, A.; Kim, B.-W.; Lee, B. Y. *Macromolecules* **2010**, *43*, 903.

(105) Baleizão, C.; Garcia, H. *Chem. Rev.* **2006**, *106*, 3987.

(106) Hongfa, C.; Tian, J.; Andreatta, J. R.; Darensbourg, D. J.; Bergbreiter, D. E. *Chem. Commun.* **2008**, 975.

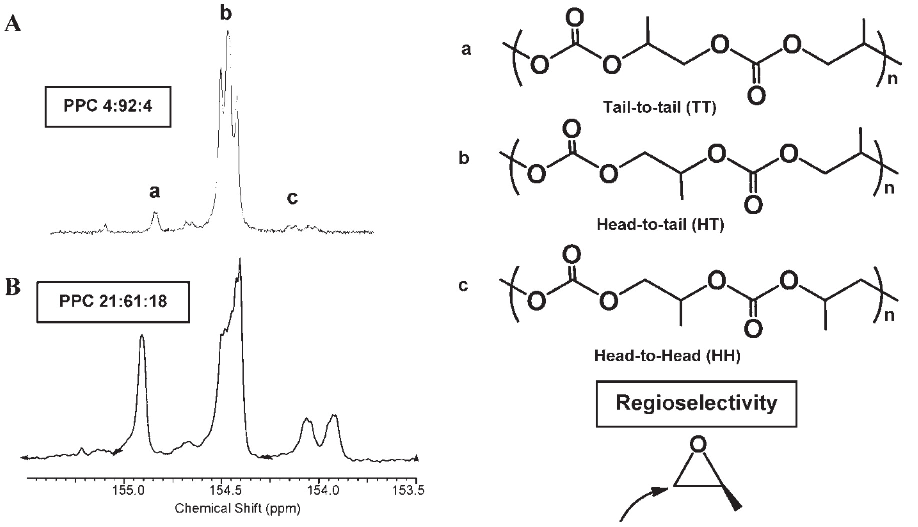


Figure 16. ^{13}C NMR spectra of poly(propylene carbonate) in the carbonate region: (A) copolymer produced from (salan)CrCl/[PPN]N_3 at ambient temperature;[97b] (B) regioirregular copolymer commercially available.

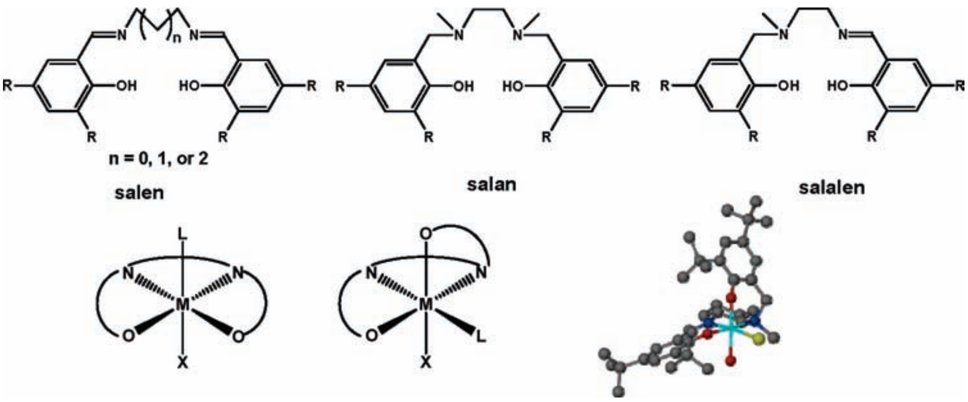
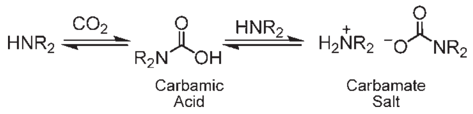


Figure 17. Structures of salen, salan, and salalen and their octahedral metal complexes. X-ray structure of a (salalen)CrCl(H_2O) complex.[100].

possessed the added capabilities of efficient separation from the copolymer and recyclability. An alternative approach to polymer/catalyst separation, which required *no* catalyst modification, was to employ a switchable polarity solvent developed by Jessop and co-workers.[107] The process involves the reaction of a volatile secondary amine, which reacts with CO_2 to *reversibly* form a carbamate salt, which is an ionic liquid at ambient temperature (eq 22). Upon dissolution of the polymer mixture in EtBuNH and the addition of atmospheric CO_2, the polymer precipitates from solution and can be isolated by filtration. The amine and CO_2 can be distilled off for catalyst recovery and easily recycled.



$$HNR_2 \underset{}{\overset{CO_2}{\rightleftharpoons}} R_2N\text{-}C(=O)\text{-}OH \overset{HNR_2}{\rightleftharpoons} H_2\overset{+}{N}R_2\ {}^{-}O\text{-}C(=O)\text{-}NR_2 \qquad (22)$$

Over this decade, numerous authoritative reviews covering the utilization of well-defined metal complexes as catalysts for the copolymerization of epoxides and CO_2 have appeared in the published literature.[108−117]

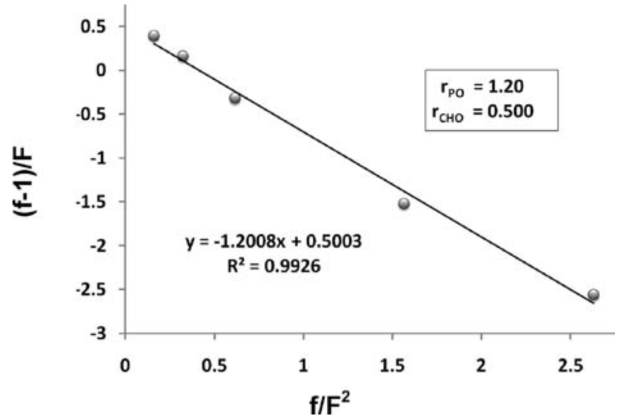


Figure 18. Data from CHO/PO/CO_2 terpolymerization with (salan)-CrCl/PPNN_3 catalyst. r_{PO} and r_{CHO} = reactivity ratios, F = fraction of CHO in the feed, and f = fraction of CHO in the polymer.

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(107) Pahn, L.; Andreatta, J. R.; Horvey, L. K.; Edie, C. F.; Luco, A.-L.; Michandani, A.; Darensbourg, D. J.; Jessop, P. G. *J. Org. Chem.* **2008**, *73*, 127.

(108) Coates, G. W.; Moore, D. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6618.

(109) Chisholm, M. H.; Zhou, Z. *J. Mater. Chem.* **2004**, *14*, 3081.

(110) Sugimoto, H.; Inoue, S. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5561.

(111) Darensbourg, D. J.; Mackiewicz, R. M.; Phelps, A. L.; Billodeaux, D. R. *Acc. Chem. Res.* **2004**, *37*, 836.

(112) Ochiai, B.; Endo, T. *Prog. Polym. Sci.* **2005**, *30*, 183.

(113) Darensbourg, D. J. *Chem. Rev.* **2007**, *107*, 2388.

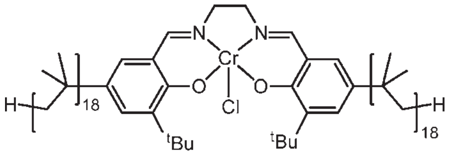
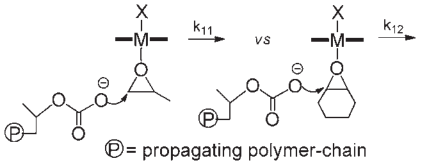
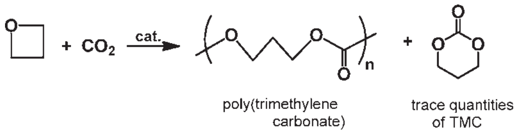


Figure 19. Cr(PIBsalen)Cl utilized for the copolymerization of CO_2 and CHO.

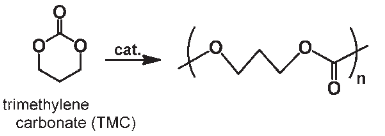
Scheme 10



More recently, we have undertaken investigations to compare the copolymerization reactions of oxetanes and CO_2 to those of the well-studied oxiranes (epoxides). Initially, our studies employing (salen)CrX complexes in the presence of onium salts have been centered on the other isomer of 1,2-PO, i.e., 1,3-PO (eq 23).[90b,118,119] Because the ring-strain energy in the two forms of PO do not differ greatly, 114.2 versus 106.7 kJ mol^{-1}, it would be anticipated that the same catalyst system would promote both processes. Although epoxides have higher ring strain, oxetane is a much better ligand for binding to metals, having a pK_b of 3.13 versus 6.94 for PO. For example, the X-ray crystal structure of a stable oxetane adduct of (salen)CrCl has been reported (Figure 20).[119] A major difference between the two copolymerization processes is that the five-membered cyclic carbonates afforded from epoxides and CO_2 are thermodynamically more stable than the copolymer; whereas, six-membered cyclic carbonates are thermodynamically less stable than their ring-opened polymer (eq 24).



(23)



(24)

Indeed, it was shown that the (salen)CrCl/[PPN]N_3 catalyst is effective at catalyzing the ROP of trimethylene carbonate (TMC) and the copolymerization of oxetane and CO_2 to afford poly(TMC) under similar reaction conditions.[119] The free energies of activation at 110 °C for the two processes, ROP of TMC and enchainment of oxetane and CO_2, were determined to be 101.9 and 107.6 kJ mol^{-1}, respectively. This raises the question of whether the copolymerization of CO_2 and oxetane proceeds all or, in part, via the ROP of preformed TMC (Scheme 11). A notable difference in the composition of the polymeric product from the two processes is observed. That is, the ROP of TMC leads to a polycarbonate with no ether linkages, whereas the enchainment of oxetane and CO_2 results in up to 10% ether linkages depending on the catalyst system (vide infra).

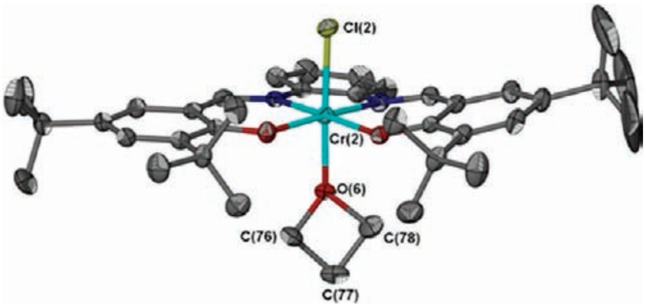
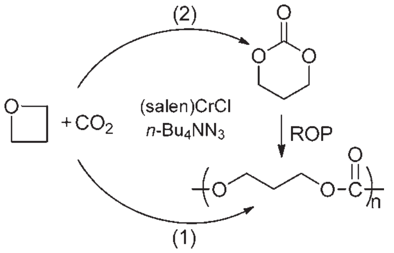


Figure 20. Thermal ellipsoid plot of (salen)CrCl·oxetane, where the salen ligand contains *t*-Bu substituents in the 3 and 5 positions of the phenolates, respectively, with a phenylenediamino backbone.

Scheme 11



We have observed by way of in situ IR spectroscopy monitoring of the copolymerization of oxetane and CO_2 that early in the process TMC is produced, which subsequently undergoes ROP to yield copolymer (Figure 21). From end-group analysis of the afforded copolymer, along with the extent of random ether linkages in the copolymer, we have been able to establish that the coupling of oxetane and CO_2 provides copolymer via both routes, i.e., the ROP of preformed TMC (route 2) and enchainment of oxetane and CO_2 (route 1). Hence, the overall catalytic cycle for the process can be presented by Scheme 12.

A close examination of the proposed pathways in Scheme 12, coupled with our general understanding of the backbiting process, suggests that it should be possible to optimize the intermediate formation of TMC on the way to copolymer production. This, in turn, would minimize or alleviate ether linkages in the polycarbonate thereby produced. Originally, we chose to examine (salen)Co^{II} complexes in the presence of onium salts containing anions that are good leaving groups as catalysts for this coupling process.[120] These systems have proven to be excellent catalysts for the coupling of epoxides and CO_2 to provide cyclic carbonates. This is presumably a consequence of the growing polymer chain having little affinity for binding to the less electrophilic metal

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(114) Nakano, K.; Kosaka, N; Hiyama, T.; Nozaki, K. *Dalton Trans.* **2003**, 4039.

(115) Darensbourg, D. J.; Andreatta, J. R.; Moncada, A. I. In *Carbon Dioxide as Chemical Feedstock*; Aresta, M., Ed.; Wiley-VCH: Weinheim, Germany, 2010; p 213.

(116) Darensbourg, D. J. In Synthetic Biodegradable Polymers. *Advances in Polymer Science*;Coates, G. W., Rieger, B., Eds.; Springer Publishers: Berlin, in press.

(117) Kember, M. R.; Buchard, A.; Williams, C. K. *Chem. Commun.* **2010**, DOI: 10.1039/C0CC02207A.

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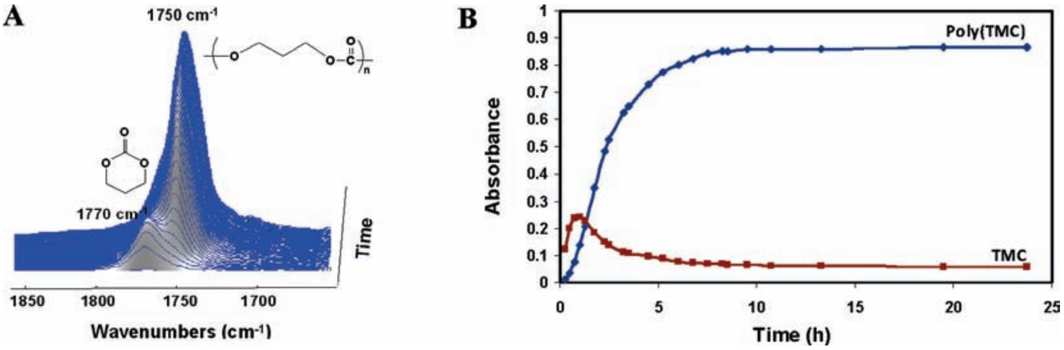
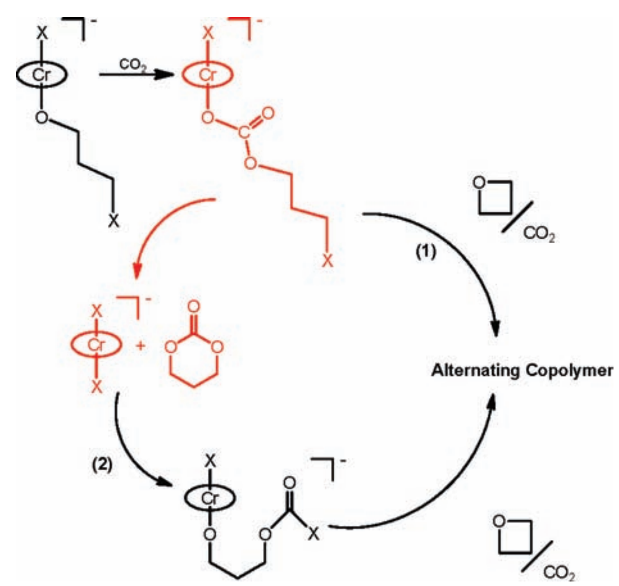


Figure 21. (A) 3D IR plot in the ν_{CO_2}region for the copolymerization of oxetane and CO_2 utilizing (salen)CrBr/*n*-Bu_4NBr at 110 °C. (B) Reaction profiles for the formation of poly(TMC) and TMC. IR spectra in part A were deconvoluted.

center, thereby leading to dissociation and rapid cyclic carbonate formation. In this manner, (salen)Co^{II} in the presence of *n*-Bu_4NBr afforded copolymers with low levels of ether linkages resulting from the ROP of preformed TMC by the onium salt. Next we returned to the (salen)CrX/onium salt system and examined the effects of good leaving groups as X and the reaction temperature.[121] This proved to be quite effective at reducing ether linkages in the copolymer. For example, the (salen)CrBr/*n*-Bu_4NBr catalyst system operating at the lower temperature of 70 °C, which is less than that normally employed, as in Figure 21, afforded copolymer with >99% carbonate linkages. Indeed, as revealed by in situ IR monitoring of the reaction, copolymer formation via the intermediary of TMC is evident (Figure 22).

Because polymers of TMC have numerous uses as copolymers with polyesters, such as lactides and ε-caprolactone, it would be of value to have a selective route to TMC from four-membered cyclic ethers and CO_2. This is particularly true because the chromium(III) and cobalt(II) catalyst systems described herein for CO_2/oxetane copolymerization are not competent catalysts for the ROP of lactides or ε-caprolactone. Furthermore, because the polymeric materials resulting from these processes are used in a variety of medical applications, it would be best to employ catalysts from biocompatible metals.[122] Relevant to this latter issue, homogeneous catalysts for these processes derived from calcium are ideally suitable for internal medical application.[123] For example, we have recently shown calcium complexes based on Schiff base ligands to be excellent single-site catalysts for the ROP of TMC and lactides.[124]

Scheme 12



It should be noted that TMC is traditionally prepared by reacting 1,3-propanediol with the highly poisonous gas phosgene or derivatives thereof. Alternatively, it can be synthesized by a greener route from 1,3-propanediol and DMC derived from CO_2-based propylene carbonate and methanol (eq 17). Furthermore, 1,3-propanediol is currently commercially produced by the fermentation of glycerol[125] or glucose.[126] We have initiated studies to efficiently synthesize TMC from oxetane and CO_2 at modest temperatures and pressures using catalysts derived from biocompatible metals. Attempts thus far have been fairly successful employing a simple commercially available vanadium(IV) complex, $VO(acac)_2$, where acac = acetylacetonato, in the presence of an onium salt as the cocatalyst.[127] For example, $VO(acac)_2$ and 1 equiv of *n*-Bu_4NBr quantitatively convert oxetane and CO_2 to TMC at 60 °C and 1.7 MPa pressure. Other oxetane derivatives were shown to selectively afford the corresponding cyclic carbonates upon coupling with CO_2.

Closing Remarks

The utilization of CO_2 as a feedstock for the production of chemicals and/or fuels represents a viable supplement to the various technologies for controlling its emission into the atmosphere. It is recognized that any such process must result in a *net* CO_2 emission reduction when using energy derived from petroleum sources. Nevertheless, some processes incorporating CO_2 can be advantageous from the standpoint of health and safety. Clearly, processes that utilize CO_2 to produce products that meet all of the requirements of safety, performance, and cost with respect to alternative

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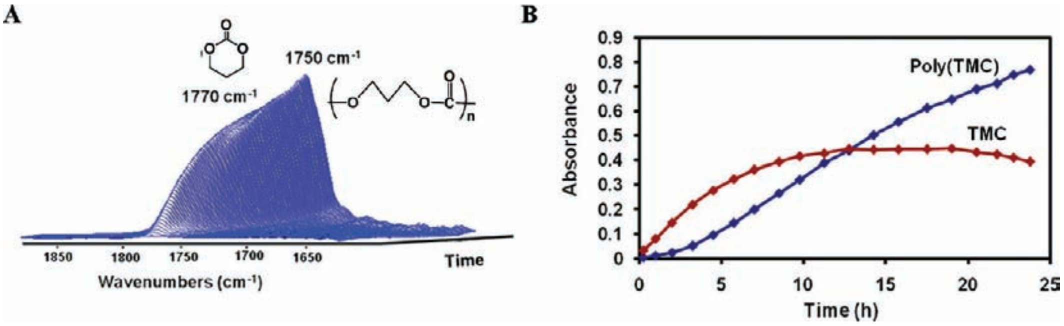

Figure 22. (A) 3D IR plot in the ν_{CO_3} region for the copolymerization of oxetane and CO_2 utilizing (salen)CrBr/*n*-Bu_4NBr at 70 °C. (B) Reaction profiles for the formation of poly(TMC) and TMC. IR spectra in part A were deconvoluted.

processes should be aggressively pursued. While the focus of this Award Article on CO_2 chemistry and utilization has been my research group's contributions to the area, it is acknowledged that numerous researchers around the world are making great strides in developing efficient synthetic routes to various bulk and specialty chemicals from CO_2. Indeed, this is currently a very vibrant area of research whose impact will only grow in the coming years. Developments in the effective utilization of CO_2 as a chemical feedstock are essential as fossil carbon sources are depleted. For example, in addition to the traditional uses of CO_2, more recently, there are commercial operations producing both specialty polymers (polycarbonates) and bulk chemicals (dimethylcarbonate) from CO_2.

Acknowledgment. D.J.D. gratefully acknowledges the long-standing financial support of the National Science Foundation and the Robert A. Welch Foundation (A-0923). He also is greatly appreciative of the many students and coworkers, most of whose names are mentioned in the references, who have carried out the research described herein. He thanks many researchers in the CO_2 utilization community for their stimulating interactions. In particular, he recognizes Professors Malcolm Chisholm, Geoffrey Coates, Kyoko Nozaki, and Xiao-Bing Lu for their significant influence to his contributions in the area of CO_2/epoxide copolymerization processes. He is most grateful and pleased to be recognized by the ACS Award in Inorganic Chemistry for 2010 sponsored by Aldrich Chemical Co.