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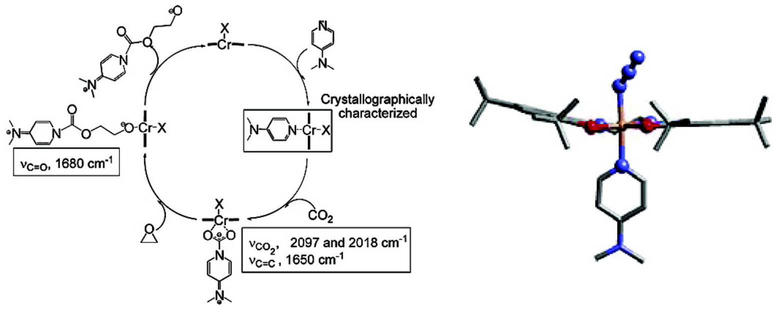

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Role of the Cocatalyst in the Copolymerization of CO_2 and Cyclohexene Oxide Utilizing Chromium Salen Complexes

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Abstract: The mechanism of the copolymerization of cyclohexene oxide and carbon dioxide to afford poly-(cyclohexylene)carbonate catalyzed by (salen)CrN_3 (H_2salen = N,N,′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-ethylene-diimine) in the presence of a broad range of cocatalysts has been studied. We have previously established the rate of copolymer formation to be very sensitive to both the electron-donating ability of the salen ligand and the [cocatalyst], where N-heterocyclic amines, phosphines, and ionic salts were effective cocatalysts. Significant increases in the rate of copolymerization have been achieved with turnover frequencies of ~1200 h^{-1}, thereby making these catalyst systems some of the most active and robust thus far uncovered. Herein we offer a detailed explanation of the role of the cocatalyst in the copolymerization of CO_2 and cyclohexene oxide catalyzed by chromium salen derivatives. A salient feature of the N-heterocyclic amine- or phosphine-cocatalyzed processes is the presence of an initiation period prior to reaching the maximum rate of copolymerization. Importantly, this is not observed for comparable processes involving ionic salts as cocatalysts, e.g., PPN^+X^-. In these latter cases the copolymerization reaction exhibits ideal kinetic behavior and is proposed to proceed via a reaction pathway involving anionic six-coordinate (salen)$Cr(N_3)X^-$ derivatives. By way of infrared and ^{31}P NMR spectroscopic studies, coupled with in situ kinetic monitoring of the reactions, a mechanism of copolymerization is proposed where the neutral cocatalysts react with CO_2 and/or epoxide to produce inner salts or zwitterions which behave in a manner similar to that of ionic salts.

Introduction

The use of transition metal catalysts for the coupling of CO_2 and epoxides producing either cyclic or polymeric carbonates has become an area widely studied by inorganic and organic chemists alike.[1] This chemistry has its roots in Inoue's discovery that zinc derivatives were viable catalysts for this copolymerization reaction.[2] However, due to zinc's high Lewis acidity, the balancing of the epoxide ring opening and carbon dioxide insertion processes proved to be a difficult task, with these catalysts producing low turnover frequencies (TOF = ~1 mol of epoxide consumed/mol of catalyst·h) and inconsistent carbonate contents. For the next 20 years, zinc catalysts design was centered around Inoue's chemistry exploiting heterogeneous mixtures of diethyl zinc and various protic sources. It was not until the mid-1990s that our group produced the first homogeneous zinc catalyst containing phenoxide ligands with bulky groups at the 2 and 6 positions.[3] These catalysts proved to be a significant improvement over the heterogeneous systems for the copolymerization of CO_2 and cyclohexene oxide, with turnover frequencies of up to 10 h^{-1} and up to >99% CO_2 incorporation. Soon thereafter, a homogeneous catalyst soluble in supercritical carbon dioxide produced from the reaction of zinc oxide with a perfluoronated long-chain monoester of a dicarboxylic acid was described by Beckman and co-workers which provided similar activity.[4] Zinc catalysts reached a pinnacle when Coates discovered that β-diiminate ligands formed highly active dimeric complexes for the production of poly(cyclohexylene carbonate), with a maximum TOF of 2300 h^{-1} and ~90% CO_2 incorporation.[5] However apparent that this type of chemistry had reached a plateau, the long-term instability of these zinc catalysts, and the fact that poly(cyclohexylene

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10.1021/ja053544f CCC: $30.25

carbonate) lacked viable industrial properties, left much to be desired in this area of research.[6]

Our use of chromium salen derivatives was inspired by several published studies involving organometallic complexes in tetradentate ligand environments. In the early 1980s, Inoue and co-workers showed that aluminum porphyrinates were successful, albeit slow, catalysts for the formation of polycarbonates.[7] A decade later, Kruper and Dellar, by applying chromium porphyrinates to this chemistry, showed that butylene oxide formed cyclic carbonate at a much higher rate than that of the corresponding aluminum catalysts.[8a] Subsequently, Mang and co-workers utilized a fluorinated chromium porphyrinate catalyst which was soluble in supercritical CO_2 to produce copolymer from cyclohexene oxide with $>95\%$ CO_2 incorporation and a polydispersity index of <1.2.[8b] Common to all of these tetradentate ligand complexes is that catalytic activity is significantly enhanced in the presence of a cocatalyst, either quaternary ammonium salts or heterocyclic nitrogen Lewis bases.

The most significant influence on our studies is the work of Jacobsen and co-workers, wherein chiral chromium salens were shown to be effective catalysts for the asymmetric ring opening of epoxides, with $>90\%$ enantomeric excess.[9] Thus, by combining these elegant studies, our initial research with Jacobsen's catalyst was very successful in that high rates of polymerization, up to 32.2 turnovers h^{-1}, high CO_2 incorporation, $>99\%$, and low polydispersities, PDI of ~ 1.2, were achieved.[10] Mechanistic studies into the effect of altering the salen structure found that electron-donating groups increased the rate of copolymer production to 81.9 h^{-1}.[11]

We have also reported the effect of changing the cocatalyst and altering the CO_2 pressure during copolymerization.[12] These studies have resulted in significant increases in the rate of copolymerization up to ~ 1200 turnovers h^{-1}. Prior to this point many of these results have remained poorly understood. Herein we will provide details of mechanistic studies into the copolymerization of CO_2 and cyclohexene oxide catalyzed by the chromium salen/cocatalyst system. These mechanistic conclusions represent the dénouement of the chromium salen studies and will unite the evolving theories as to how these systems operate.

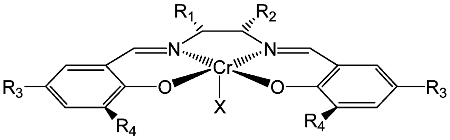
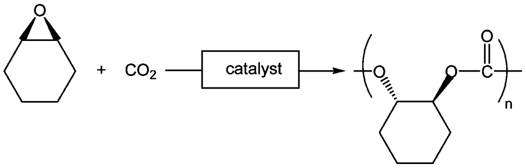


Figure 1. General structure of chromium salen catalysts utilized for the copolymerization reaction.

Results and Discussion

Previously, publications from our laboratory have demonstrated the sensitivity of the copolymerization reaction depicted in eq 1 on the nature of the (salen)CrX catalyst (Figure 1).[11] In



(1)

these reports we have established that by altering virtually every aspect of the metal complex from the diimine backbone (R_1 and R_2) and the phenolate moieties (R_3 and R_4) to the apical nucleophile (X), the rate of copolymerization can be modified greatly from nearly zero to over 1100 h^{-1}. Concurrently, we have shown that this catalytic system operates effectively at atmospheric carbon dioxide pressure.[12] Despite the benefits of these structural changes on reaction rates, by far the most important aspect of this and other closely related catalyst systems has been the effect of the cocatalyst, which has not been fully understood. Within this report we will offer a detailed interpretation of the role of the cocatalyst in the copolymerization of CO_2 and cyclohexene oxide catalyzed by chromium salen derivatives. Presumably, these mechanistic aspects of the CO_2/epoxide coupling reaction should apply to other closely related catalytic systems.

Reactivity Studies of the Copolymerization of CO_2 and Cyclohexene Oxide Utilizing the Chromium Salen/Anionic Cocatalyst System. Although chronologically out of order, we will first describe our findings employing *anionic* cocatalysts for reaction 1, for these were eventually shown to be the most effective. Initially, our studies utilized PPN^+X^- derivatives, for these salts are easily prepared anhydrously and the bis(triphenylphosphorylidine)ammonium(PPN) cation is rather noninteracting even in weakly polar solvents such as epoxides. As illustrated in Table 1, when these salts are combined with catalyst **1** (R_1, R_2 = H, R_3, R_4 = *tert*-butyl, and X = N_3), the rates of copolymer production are quite significant, and this system represents one of the most active catalyst known to date for this copolymerization process. Comparative studies done with several different anions show $PPN^+N_3^-$ to be the most effective cocatalyst, producing copolymer at a rate of 608 turnovers h^{-1} (Table 1).

Other less expensive salts such as phosphonium and ammonium were also utilized as cocatalysts (Table 2). These salts produce slightly smaller turnover numbers than those observed for their PPN analogues with $Bu_4N^+Cl^-$ producing copolymer

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Table 1. Turnover Data for the Copolymerization of Cyclohexene Oxide and CO_2 Utilizing Complex **1** and 1 equiv of Various PPN Salt Cocatalysts[a]

PPN salt	TON[b]	TOF[c]
N_3	2432	608[d]
Cl	1977	494[e]
Br	1683	420
I	1441	360
OAc	1400	350
HCO_3	1120	280

[a] Copolymerization reactions were conducted with 50 mg of catalyst **1** at 80 °C and under 55 bar of CO_2 pressure for 4 h. [b] Mol of epoxide consumed/mol of catalyst. [c] Mol of epoxide consumed/mol of catalyst·h. Note: The carbonate content of all copolymers obtained was 99% or greater. [d] $M_n = 14\,000$ with a PDI of 1.54. [e] $M_n = 10\,000$ with a PDI of 1.26.

Table 2. Turnover Data for the Copolymerization of Cyclohexene Oxide and CO_2 Utilizing Complex **1** and 1 equiv of Other Anionic Cocatalysts[a]

cocatalyst	TON[b]	TOF[c]
tetrabutylammonium salts		
Bu_4NCl	1655	414
phosphonium salts		
PPh_4Cl	1367	342

[a] Copolymerization reactions were conducted with 50 mg of catalyst **1** at 80 °C and under 55 bar of CO_2 pressure for 4 h. [b] Mol of epoxide consumed/mol of catalyst. [c] Mol of epoxide consumed/mol of catalyst·h. Note: The carbonate content of all copolymers obtained was 99% or greater.

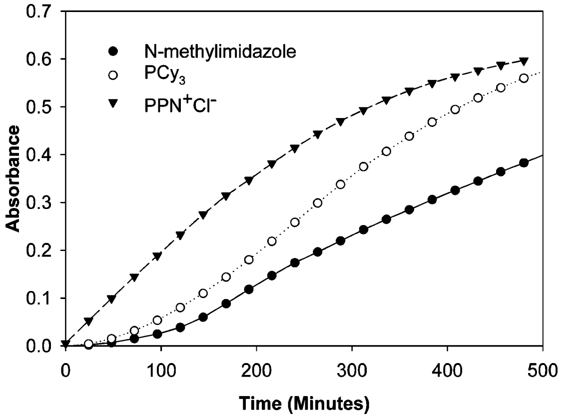


Figure 2. Comparison of in situ infrared profiles of copolymer production from CO_2 and cyclohexene oxide utilizing catalyst **1** and the three classes of cocatalysts.

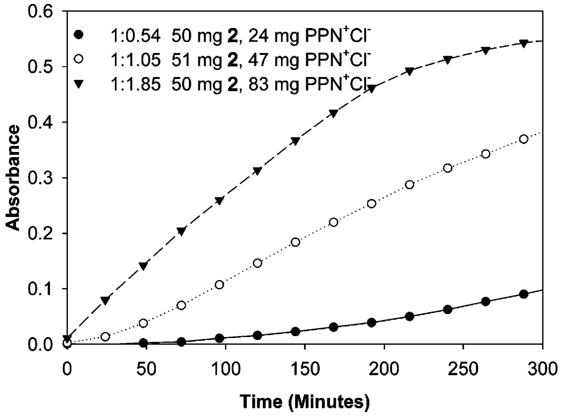


Figure 3. In situ infrared study done by varying the amount of cocatalyst during the copolymerization of TMSO (2-(3,4-epoxycyclohexyl)trimethoxysilane) and CO_2 catalyzed by complex **2** and PPN^+Cl^-.

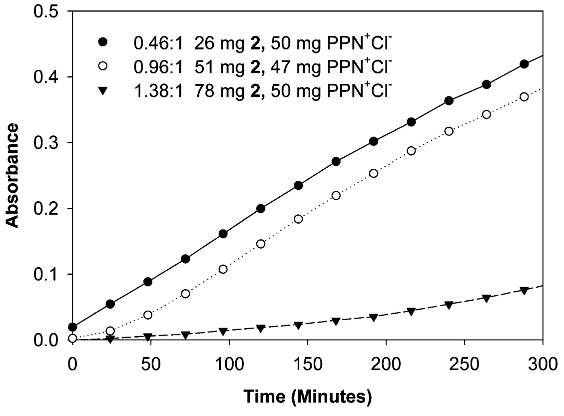


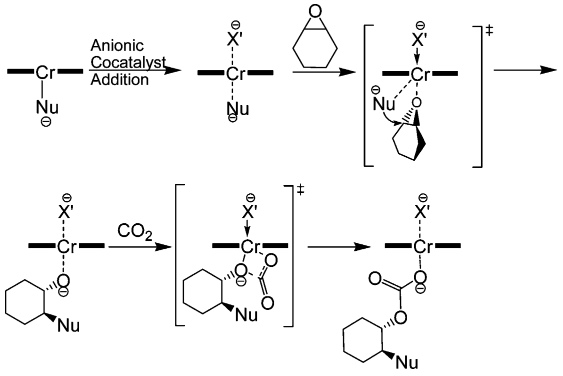
Figure 4. In situ infrared study varying the [catalyst] while maintaining a constant [cocatalyst] during the copolymerization of TMSO and CO_2 catalyzed by complex **2** and PPN^+Cl^-.

at 414 turnovers h^{-1} as compared to 494 h^{-1} for PPN^+Cl^-. The main difference between these cocatalysts is their properties toward water. PPN salts are very hydrophobic and thus are easily recrystallized and isolated in a highly purified form, while ammonium and phosphonium salts must be recrystallized several times and may still contain significant quantities of water. This is important because water could have detrimental effects on the anionic copolymerization including low catalytic activity, low molecular weight copolymer, and high PDI. In addition, alkylammonium cations are more interactive with hard anions than are their PPN counterparts.

As mentioned earlier, anionic cocatalysts derived from PPN^+X^- salts are significantly more competent at catalyzing reaction 1 than other cocatalyst precursors we and others have examined, e.g., heterocyclic nitrogen bases or bulky phosphines (vide infra). This is best seen from the reaction profiles obtained during in situ monitoring of the copolymer formation by way of its ν(C=O) stretch at 1750 cm^{-1} (Figure 2). Most importantly, it can clearly be seen from Figure 2 that when utilizing anionic cocatalysts *no* initiation period is seen as compared with other cocatalysts or cocatalyst precursors. That is, the reaction shows ideal kinetic behavior and does not decrease in rate until the reaction mixture becomes highly viscous and the [epoxide] is sufficiently depleted, making copolymerization controlled by the rate of mass transfer. This behavior alone explains why this class of cocatalysts produces significantly enhanced turnovers, as the other catalyst systems are initially slowed by the initiation period.

Interestingly, the copolymerization reaction proceeds at its maximum rate when the anion (both the cocatalyst and initiator (X)) and metal are present in approximate 2:1 ratio. This is best shown by in situ infrared experiments, where both the anion and catalyst concentrations were altered. As depicted in Figure 3, and employing catalyst **2** (R_1, R_2 = H, R_3, R_4 = *tert*-butyl, and X = BF_4), when the concentration of the anion, in this case provided by PPN^+Cl^-, is increased the maximum rate is distinctly observed at ~2 equiv of anion with *no* change in the rate of catalysis above this concentration. Also found in this study is that if the amount of cocatalyst is kept constant and the amount of catalyst is increased, the rate of copolymer formation significantly decreases (Figure 4). That is, the ratio of metal to anion is more important than the actual amount of metal present in the reaction mixture. The conclusion that can

Scheme 1



be drawn from these results is that 2 equiv of anions play an important role in the mechanism of catalysis and thus controls the rate of copolymerization.

These studies, taken together, suggest that in order to achieve the maximum rate of catalysis, the metal center prefers an electron-rich environment. To explain this we believe that following the addition of the anionic cocatalyst to the metal center, the chromium nucleophile bond is weakened with the amount of electron density around the metal center dictating the degree of elongation (represented by a dashed bond in Scheme 1). This destabilization then allows for the epoxide to interact or be activated by the metal center. As the epoxide interacts, the adjacent metal anion bond is weakened while the other metal anion bond is strengthened, allowing for a rapid, concerted epoxide ring opening. Following this step, the dianion species is regenerated again weakening the chromium anion bonds, allowing for facile CO_2 insertion and the generation of the initial carbonate complex.

Relevant to this proposal we have isolated and characterized the chromium salen anionic derivative obtained from the addition of $PPN^+N_3^-$ to complex **1**.[13] As illustrated in Figure 5 the bis azide derivative is quite symmetric with the salen ligand adopting a stairlike structure to accommodate the two azide groups with folding angles (φ_+ and φ_-) of 127° and 128°.[14] A detailed report of the structure may be found in the Supporting Information.

The major complication with this proposed mechanism is why would the other anion (in Scheme 1 designated X′) not undergo a similar process, i.e., ring-opening an epoxide followed by CO_2 insertion? For this not to be the case the carbonate species would have to be significantly faster at the chain propagation step than the other anion. This is highly unlikely given the high rate of ring opening we have observed for an azide anion.[11b] Hence, if we assume the other anion is also activated, the catalyst would chain propagate from both sides of the salen ligand, ending up as detailed in Scheme 2. Similar proposals have been put forth by Aida and Inoue for aluminum porphyrin catalysts with ammonium and phosphonium salts[15] and more recently by Cohen and co-workers for cobalt salen derivatives along with PPN^+X^- cocatalysts.[16] It should be noted, however, that many salen ligands are able to undergo significant distortion without necessarily disrupting the N_2O_2 metal plane. Concomitantly, these distortions could make it sterically hindering toward polymer chain growth on one side of the salen ligand. This could lead to monomer enchainment inhibition on one side of the chromium center, or at least result in different rates of enchainment on the two chromium sites. This latter process could lead to a bimodal molecular weight distribution, much like that generally observed in these copolymerization reactions. The success of this catalytic system and the proposed mechanistic pathway raise questions as to how the other neutral cocatalyst systems operate. The following sections will address these issues and attempt to establish a common thread among these catalytic processes.

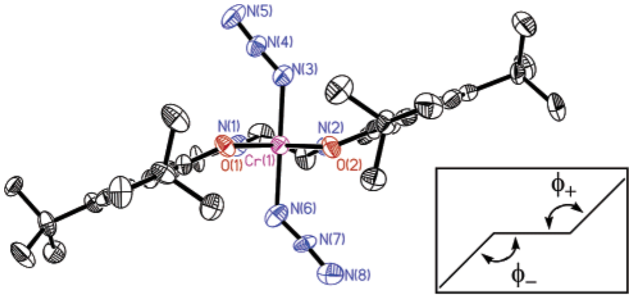
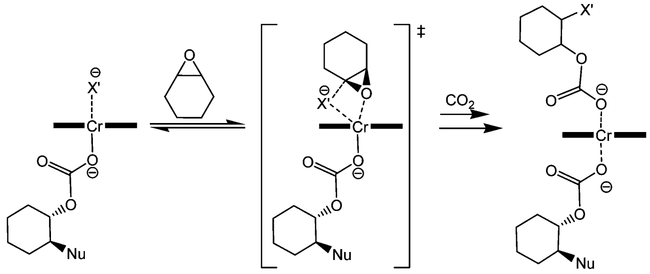


Figure 5. Six-coordinate complex formed from the reaction of complex **1** with $PPN^+N_3^-$.

Scheme 2



Reactivity Studies of the Copolymerization of CO_2 and Cyclohexene Oxide Utilizing Heterocyclic Nitrogen Lewis Base Cocatalysts. While our previous studies involving heterocyclic nitrogen Lewis base cocatalysts have focused on *N*-methylimidazole (*N*-MeIm), 4-(dimethylamino)pyridine (DMAP) has proven to be much more effective. Catalyst **1** and 1 equiv of DMAP produced copolymer at a turnover frequency of 270 h^{-1}, or ~5 times that observed with 1 equiv of *N*-MeIm under identical conditions (Table 3). DMAP-cocatalyzed reactions also exhibit a very large decrease in the amount of copolymer produced at high cocatalyst loadings (31 equiv), producing turnover frequencies of only 84.4 h^{-1}, almost 4 times slower than at 5 equiv, accompanied by a dramatic increase in the polyether and cyclic carbonate content. By comparison with the *N*-MeIm system, a trend starts to appear whereby both cocatalysts operate in the same manner but at very different rates.

Other pyridine derivatives were also examined for their efficacy as serving as cocatalysts along with complex **1** for the copolymerization of cyclohexene oxide and CO_2 under similar reaction conditions (Table 4). Initially, pyridines with bulky groups at the 2 and 6 position were employed but produced very little ring opened product. These latter pyridines were previously found to be very effective as cocatalysts for zinc-

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(13) This complex crystallized with two PPN^+ cations and a perchlorate anion, in addition to solvent molecules, and we were only able to refine it to an *R* value of 13.15%. Nevertheless, the geometry about the chromium center is well-defined.

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Table 3. Copolymerization Activities of Complex **1** at Different 4-Dimethylamino Pyridine Loadings[a]

equiv of cocatalyst	TOF[b]	% carbonate linkages[c]
0	trace	N/A
0.5	128	98.2
1	270	98.1[d]
3	270	98.4
5	311	98.2
10	249	96.1
31	84.4	68.9[e]

[a] Copolymerization conditions: 50 mg of catalyst **1** (0.04 mol %), 20 mL of cyclohexene oxide, 55 bar of CO_2, 80 °C, over a 4 h reaction time. [b] Measured in mol of CHO consumed/mol of Cr•h. [c] Estimated based on ^{1}H NMR. [d] $M_n = 31\,500$ with a PDI of 1.12. [e] $M_n = 1600$ with a PDI of 1.40.

Table 4. Copolymerization Activities of Catalyst **1** Utilizing Different Heterocyclic Amine Cocatalysts[a]

cocatalyst	TOF[b]	% carbonate linkages[c]
2,6-dimethoxy pyridine	trace	N/A
2,4,6-tri-*tert*-butyl pyridine	trace	N/A
Pyridine	55.6	91.3
4-*tert*-butylpyridine	63.8	91.7
4-methoxypyridine	50.4	92.4
Et_3N	trace	N/A
PYP	323	99
DBU	130	99

[a] Copolymerization conditions: 50 mg of catalyst **1** (0.04 mol %), 3 equiv of cocatalyst, 20 mL of cyclohexene oxide, 55 bar of CO_2, 80 °C, 4 h reaction time. [b] Measured in mol of CHO consumed/mol of Cr•h. [c] Estimated based on ^{1}H NMR.

catalyzed copolymerization processes.[17] On the basis of this result, several other pyridines substituted only in the 4-position were used as cocatalysts. This approach was more effective but still not nearly as successful as DMAP and only slightly better than unsubstituted pyridine. Other amine complexes similar to DMAP, which will be discussed latter in more detail, including 4-(pyrrolidin-1-yl)pyridine (4-PYP) and 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU), produced polycarbonate at 323 h^{-1} and 130 h^{-1}, respectively. The former is very closely related to DMAP and thus as expected exhibited very similar catalytic activity, while the latter has very different steric properties and showed a significant decrease in polymer production. *It is important to note here that tertiary amines such as triethylamine are completely ineffective as cocatalysts for the copolymerization process* (entry 6 in Table 4).

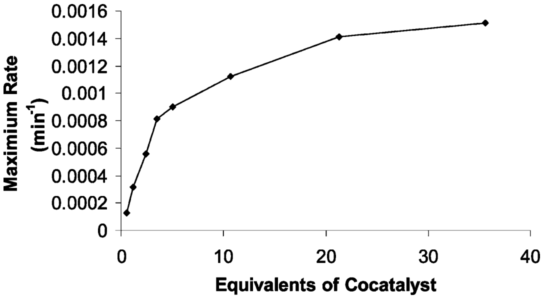


Figure 6. Graphical representation showing the effect of increasing [cocatalyst] while maintaining a constant [catalyst] upon the maximum rate of catalysis for complex **1** in the presence of *N*-methylimidazole.

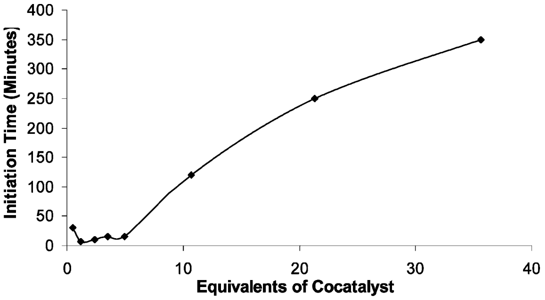
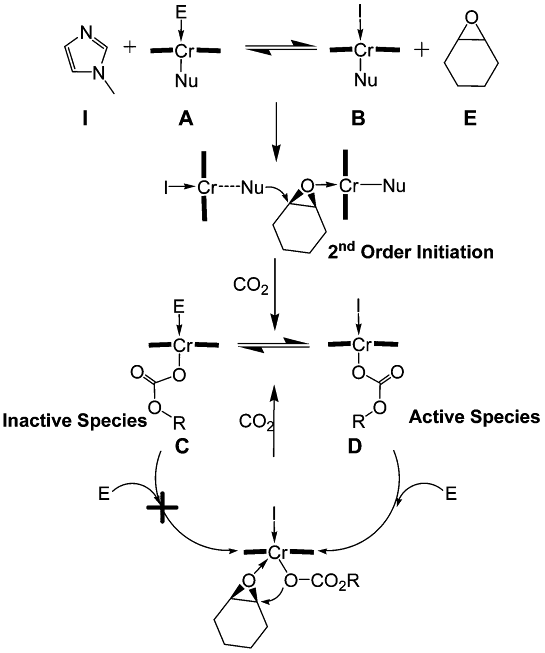


Figure 7. Graphical representation showing the effect of increasing [cocatalyst] while maintaining a constant [catalyst] upon the initiation time for the copolymerization of CO_2 and cyclohexene oxide catalyzed by complex **1** and *N*-methylimidazole.

Scheme 3



Prior to delineating our recent findings involving heterocyclic nitrogen bases as cocatalysts for the copolymerization of cyclohexene oxide and carbon dioxide, we wish to summarize our observations utilizing complex **1** and *N*-MeIm, some of which have been previously published. In this instance upon keeping the [catalyst] constant and varying the [cocatalyst] two phenomena were observed. That is, the maximum rate of copolymerization and the initiation time increased steadily until at high cocatalyst loadings (>30 equiv) a leveling off effect starts to become apparent for both kinetic features (Figures 6 and 7). Taken together, these observations suggest that an equilibrium exists between epoxide and cocatalyst binding trans to the propagating chain. The lack of activity when the cocatalyst is absent indicates that the cocatalyst-bound chromium complex is much more active than the corresponding epoxide-bound complex.

These data led to our mechanistic proposal that the rate of copolymerization was dependent on two separate equilibria (Scheme 3). The first equilibrium was thought to control the bimetallic initiation step, which requires the catalyst be present in both cocatalyst-bound (**B**) and epoxide-bound (**A**) forms, making the initiation very sensitive to [catalyst], [epoxide], and [cocatalyst]. The propagation step is susceptible to a similar equilibrium; however, it prefers that the catalyst be present with

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(17) Darensbourg, D. J.; Lewis, S. J.; Rodgers, J. L.; Yarbrough, J. C. *Inorg. Chem.* **2003**, *42*, 581−589.

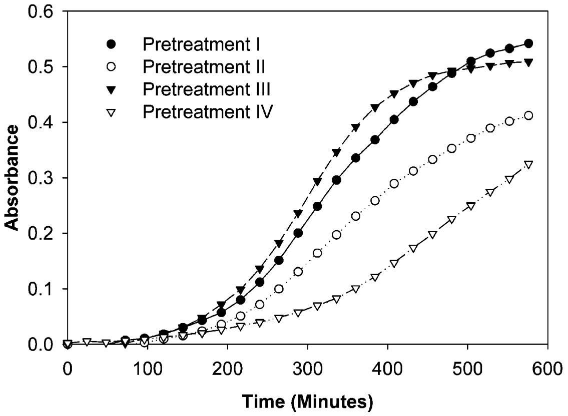

Figure 8. In situ infrared results of the pretreatment study, preformed by heating several components (catalyst, cocatalyst, CO_2, and epoxide) of the copolymerization of CO_2 and cyclohexene oxide to 80 °C for several hours before in situ monitoring of CO_2/cyclohexene oxide coupling.

the active cocatalyst-bound species (**D**) rather than the less active epoxide-bound analogue (**C**). Thus, this step benefits from excess cocatalyst. In the case of high *N*-MeIm loadings, the majority of the catalyst is present as species **B** and **D**, resulting in a lengthening of the initiation time, but also increasing the rate of propagation.

Throughout our kinetic studies of this copolymerization reaction the origin of the S-shaped reaction profile observed for many cocatalysts has been difficult to fully explain. Obviously, it was somehow related to the time necessary to generate the active catalytic species. As pointed out earlier, anionic cocatalysts do not display this initiation period and thus the active species must be rapidly generated in these instances. The heterocyclic nitrogen base cocatalysts, however, exhibit a long initiation period; depending on the [cocatalyst] this could be on the order of hours. In an attempt to identify the reactive catalytic species several "pretreatment" studies were conducted, with the goal of these experiments being to generate the active catalytic species prior to performing the copolymerization reaction. This preformed catalyst would then display ideal kinetic behavior and achieve the maximum overall rate of copolymer formation for this particular system. The conditions for pretreatment of the catalyst are described in detail in the Supporting Information and in abbreviated form here: I (no pretreatment), II (**1**/30 equiv of *N*-MeIm/*e*poxide), III (**1**/2 equiv of epoxide/CO_2/toluene), IV (**1**/30 equiv of *N*-MeIm/toluene/CO_2). As shown in Figure 8, the rate of copolymerization for these reactions varied to some degree, but all still showed a significant initiation time, meaning that all attempts to generate the active species failed.

Our previous mechanism identified the active species as a chromium salen containing a coordinated cocatalyst and the initial carbonate species **D**. However, experiment II should have generated the alkoxide species **D**-CO_2 and experiment III should have generated the carbonate complex **D** (Figure 9). From this we conclude that our initial assessment of the active species was incorrect, and this calls into question the validity of our preliminary mechanistic interpretation.

To better assess these mechanistic inconsistencies we have examined the copolymerization reaction using several heterocyclic nitrogen bases as cocatalysts. For these studies we have employed 2-(3,4-epoxycyclohexyl)trimethoxysilane(TMSO) as the epoxide monomer because of its, and its resulting copolymer,

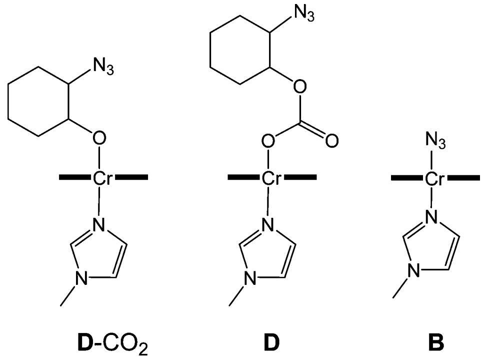

Figure 9. Probable species generated by the above pretreatment experiments that can now be discounted as the active species during copolymerization.

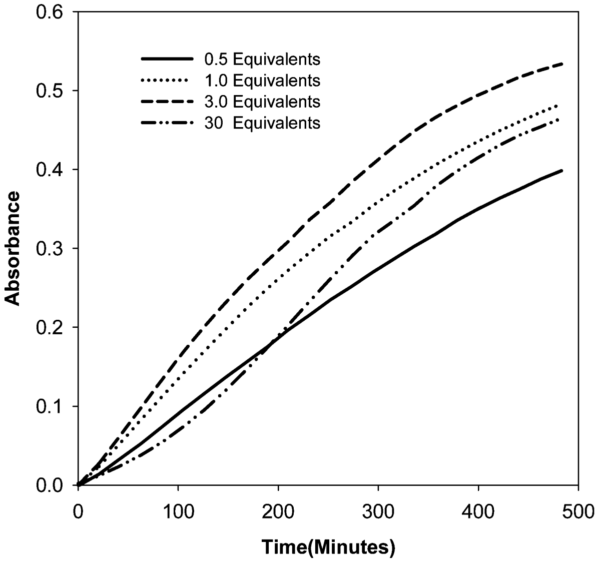

Figure 10. In situ infrared monitoring of complex **1** catalyzed formation of the poly(TMSO-carbonate) at different DMAP concentrations.

enhanced miscibility with carbon dioxide.[18] Although investigations involving complex **1** with varying concentrations of the cocatalyst DMAP afforded data with trends similar to that obtained for *N*-MeIm, there were several key rate differences (Figure 10). First, the rate of copolymer production increased rather dramatically upon increasing the DMAP loading from 0.5 to 1 equiv, followed by a slight enhancement until the maximum rate was observed at 3 equiv of cocatalyst. Recall that it took ∼10 equiv of *N*-MeIm to maximize the rate of copolymer formation. Second, at low cocatalyst loadings (<3 equiv) there is a short initiation time, <10 min, and at 30 equiv the activity decreases slightly with concomitant lengthening of the initiation time, up to approximately 3 h; however, the observed initiation time is appreciably less than that observed for *N*-MeIm (∼6 h).

Cyclic carbonate formation accelerates with increasing [DMAP] (Figure 11), again similar to *N*-MeIm, but at drastically increased rates. Additional kinetic studies for complex **1** and DMAP show this copolymerization process to exhibit a [catalyst] dependence much closer to first-order than with *N*-MeIm, 1.11 versus 1.38, respectively. Hence, it has become abundantly clear that DMAP behaves very similar to *N*-methylimidazole; however, all processes occur at an increased rate, including the production

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[18] Darensbourg, D. J.; Rodgers, J. L.; Fang, C. C. *Inorg. Chem.* **2003**, *42*, 4498−4500.

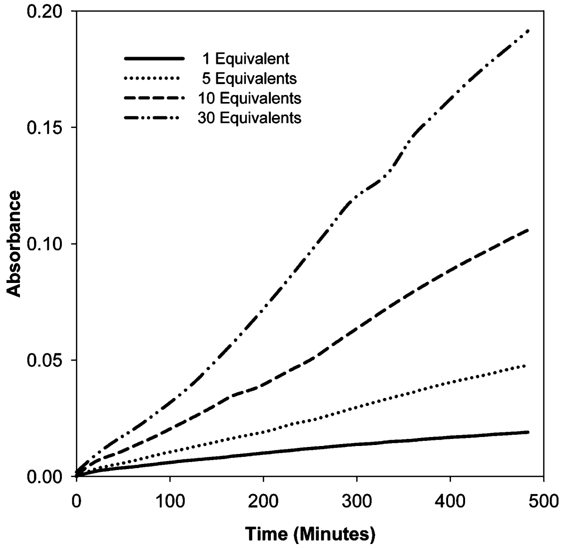


Figure 11. In situ infrared monitoring of complex **1** catalyzed formation of monomeric TMSO carbonate at different DMAP concentrations.

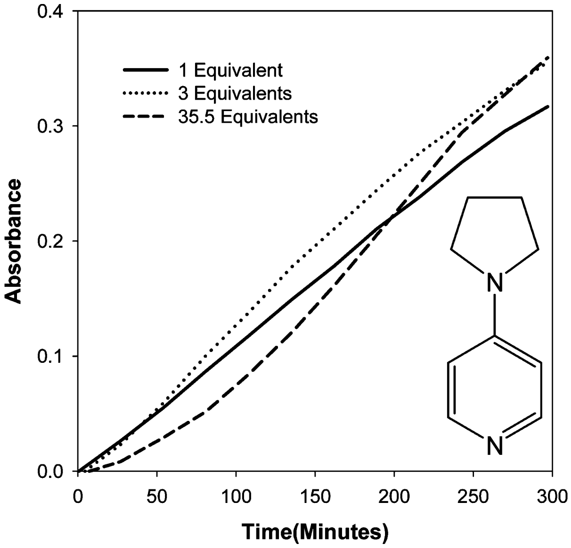


Figure 12. In situ infrared monitoring of the copolymerization of TMSO and CO_2 with catalyst **1** and 4-(pyrrolidin-1-yl)pyridine as a cocatalyst.

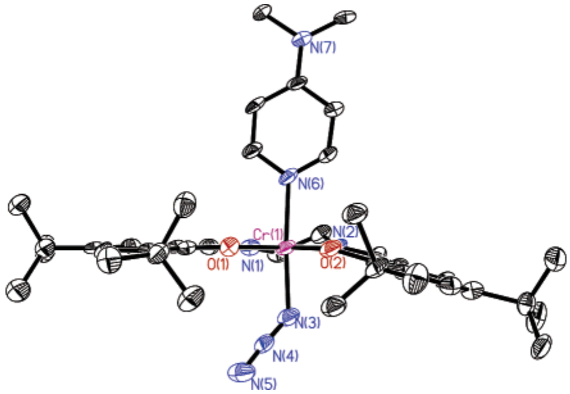


Figure 13. Molecular structure of **1·DMAP**. Ellipsoids are shown at 50% probability level, with hydrogens omitted for clarity. Selected distances (Å) and angles (deg): Cr(1)−O(1), 1.925(6); Cr(1)−O(2), 1.935(6); Cr(1)−N(1), 2.021(7); Cr(1)−N(2), 2.016(7); Cr(1)−N(3), 2.042(7); Cr(1)−N(6), 2.090(7); N(3)−N(4), 1.205(11); N(4)−N(5), 1.148(11); Cr(1)−N(3)−N(4), 124.4(6); N(3)−N(4)−N(5), 175.5(9).

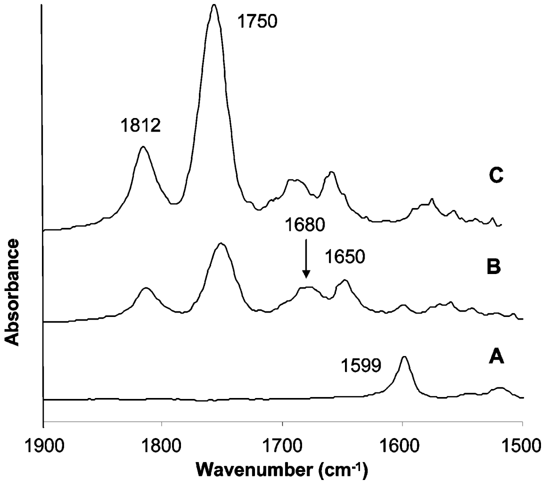


Figure 14. In situ infrared monitoring of TMSO/CO_2 copolymerization utilizing complex **1** and 30 equiv of DMAP, showing the transformation from "free DMAP", observed at 1599 cm^{-1}, to the "activated DMAP", observed at 1680 and 1650 cm^{-1}. Peaks at 1812 and 1750 cm^{-1} correspond to cyclic carbonate and polycarbonate, respectively; (A) $t = 0$, (B) $t = 2$ h, and (C) $t = 4$ h.

of the unwanted product cyclic carbonate. Further inspection showed a first-order dependence on [cocatalyst] for both copolymer formation and cyclic carbonate formation, with a decreasing dependence as the [catalyst] increased (as seen in Figure 7 for *N*-MeIm). In addition, as previously mentioned when catalyst **1** was employed with 4-(pyrrolidin-1-yl)pyridine as the cocatalyst, turnover frequencies slightly smaller than those obtained with DMAP were observed. In situ infrared spectroscopy confirms that the rate of polymer production was slightly less than DMAP at both 1 and 3 equiv, respectively (Figure 12). However, at 35.5 equiv this cocatalyst was shown to have an initiation time of <2 h, significantly less than those of *N*-methylimidazole and DMAP, which have initiation times of 6 and 3 h, respectively.

Our endeavors to define the most catalytically active species when employing *N*-MeIm as cocatalyst ruled out species **B**; nevertheless, we have observed spectroscopically and kinetically that the binding of heterocyclic nitrogen bases to (salen)CrX derivatives occurs readily. Indeed, such a six-coordinate metal complex was isolated from the reaction of complex **1** and DMAP, and its molecular structure was determined by X-ray crystallography. A thermal ellipsoid representation of **1·DMAP** is depicted in Figure 13. As seen in this drawing, only a slight deformation of the salen ligand is necessary in order to accommodate the sterically unencumbering DMAP ligand.

Therefore, it is clear from these studies that heterocyclic nitrogen bases are somehow transformed during the copolymerization process. An analysis of the infrared spectra collected during the in situ monitoring of copolymer formation revealed a peak corresponding to a ν(C=N) stretching frequency in DMAP at 1599 cm^{-1} that can be observed at high DMAP loading (>30 equiv). This infrared signal at 1599 cm^{-1} allows a spectroscopic method for monitoring the cocatalyst during the copolymerization reaction (Figure 14). This DMAP peak was observed to gradually decrease to zero, while two new infrared signals concurrently appeared at 1650 and 1680 cm^{-1}. Similar infrared spectroscopic data were observed by Inoue for his aluminum porphyrinate/*N*-MeIm system, where it was hypothesized that these infrared bands resulted from an aluminum

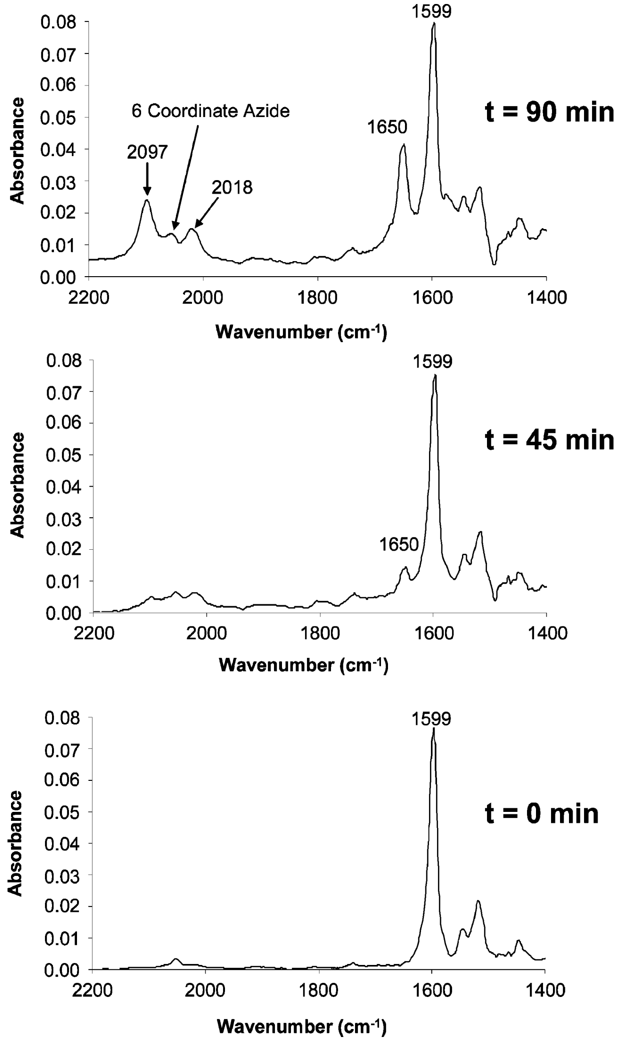


Figure 15. In situ infrared experiment showing the CO$_2$/DMAP interaction performed with 50 mg of catalyst **1**, 50 equiv of DMAP in 20 mL of toluene and 55 bar of CO$_2$ pressure at ambient temperature; (A) $t = 0$, (B) $t = 45$ min, and (C) $t = 90$ min.

carbonate species and unidentified "activated" CO$_2$ complex.[7] Nguyen and co-workers similarly suggested the possibility of a CO$_2$-activated DMAP species and proposed it to hinder propylene oxide/CO$_2$ copolymerization.[19] Ultimately, this transformation was thought to be the reason for decreased propylene carbonate formation at high CO$_2$ pressures. So, the question remains as to whether the observed change is indeed DMAP interacting with CO$_2$ and is such an interaction beneficial to catalysis?

To ascertain answers to these questions, several control experiments were conducted. When DMAP is reacted under copolymerization conditions, except for the absence of the metal complex, *no* change in the DMAP infrared spectrum occurs. Similarly, when excluding CO$_2$ *no* change in the infrared spectrum is observed. However, when epoxide is excluded from the reaction and CO$_2$ pressure is added to a toluene solution of catalyst **1** and 50 equiv of DMAP, the appearance of several new bands at 1650, 2097, and 2018 cm^{-1} is observed (Figure 15). Contrary to what is seen during the copolymerization process, the parent DMAP peak only slightly decreases in intensity, indicating that this reaction is stoichiometric rather than catalytic. Further experiments at different catalyst/DMAP concentrations showed that the intensity of the interaction is directly dependent on the catalyst/cocatalyst ratio.

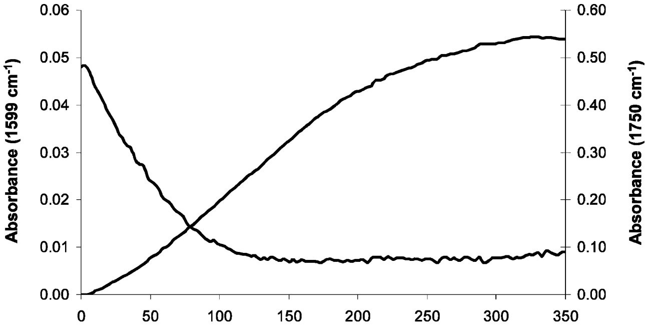
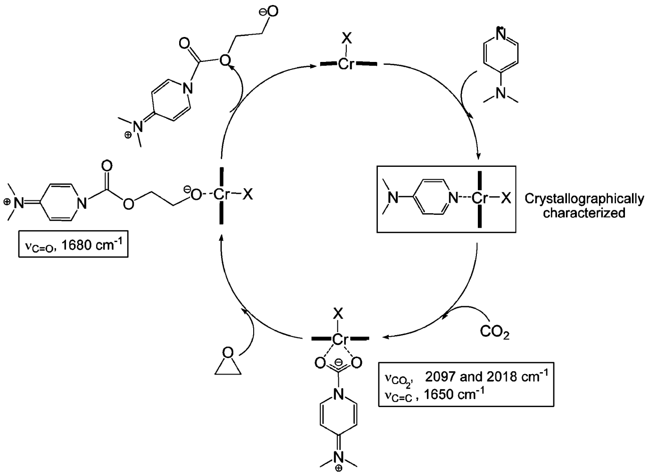


Figure 16. Peak profiles for both the "free DMAP" (1599 cm^{-1}, decreasing) and the polycarbonate (1750 cm^{-1}, increasing) peaks as observed during the copolymerization of CO$_2$ and cyclohexene oxide utilizing the catalyst **1**/DMAP system.

Scheme 4



The rate of this reaction was also shown to be dependent on CO$_2$ pressure, with high CO$_2$ pressures resulting in a very rapid reaction. In addition, the intensity of the 1650 and 1680 cm^{-1} peaks observed during copolymerization were found to be dependent on [DMAP] and *not* [catalyst], hence, precluding the possibility of representing a metal-bound carbonate species. Additional inspection of the copolymerization reaction indicated that the initiation time, ~150 min, ends when a majority of the "free DMAP" peak has disappeared, i.e., the decrease in intensity of the "free DMAP" peak relates directly to the initiation time observed for the formation of copolymer (Figure 16). It is of importance to note that beyond the initiation period, where copolymer formation is maximized, the infrared signals at 2097 and 2018 cm^{-1} assigned to CO$_2$ insertion into a metal−amide bond disappear with only the infrared peaks at 1650 and 1680 cm^{-1} remaining (see Scheme 4 for infrared band assignments).

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), an alternative heterocyclic nitrogen base, has been utilized for its intrinsic ability to absorb a molecule of CO$_2$, thereby serving as a quantitative method for CO$_2$ addition.[20] Hence, because of the obvious parallels between DBU and DMAP, we have examined DBU as a cocatalyst for the copolymerization of CO$_2$ and cyclohexene oxide. In situ infrared experiments clearly dem-

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(19) (a) Paddock, R. L.; Hiyama, Y.; McKay, J. M.; Nguyen, S. T. *Tetrahedron Lett.* **2004**, *45*, 2023−2026. (b) Paddock, R. L.; Nguyen, S. T. *Chem. Comm.* **2004**, 1622−1623.

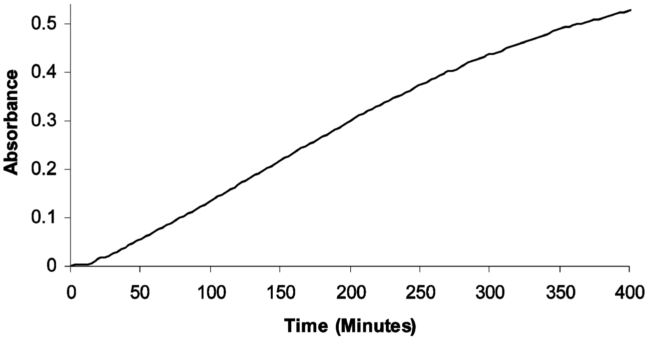


Figure 17. In situ infrared profile of the polycarbonate peak at 1750 cm^{-1} for the copolymerization of CO_2 and cyclohexene oxide utilizing catalyst **1** and 30 equiv of DBU as a cocatalyst.

onstrated that DBU absorbs CO_2 at ambient conditions and relatively low CO_2 pressure (6.9 bar). However, upon increasing the temperature to 80 °C this zwitterionic interaction was reversible, with no adduct formation being noted even at elevated CO_2 pressures. Consistent with the DMAP system, in the presence of the (salen)CrX complex an interaction was observed via infrared spectroscopy (2097, 2020, 1649 cm^{-1}). Copolymerization reactions carried out with the DBU cocatalyst exhibited very little initiation time, even at high cocatalyst loadings (>30 equiv, Figure 17). A comparison of the initiation times displayed by the different heterocyclic nitrogen base cocatalysts showed a clear trend of decreasing initiation period in proceeding from *N*-MeIm < DMAP < 4-PYP < DBU. Hence, this order is not correlated with the nitrogen pK_a's but rather with their ability to resonance stabilize negative charge on the nitrogen atom and thereby interact with CO_2.

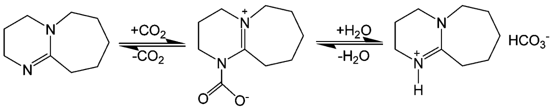
From these studies we can conclude that the heterocyclic nitrogen base cocatalysts are activated in two steps, first interacting with CO_2 in the presence of (salen)CrX to afford a weak zwitterionic carbamic complex (ν_{CO_2} at 2097 and 2018 cm^{-1}), followed by a reaction with cyclohexene oxide to provide a stabilized zwitterion. The weakness of the CO_2−nitrogen base interaction is reflected in the high frequencies of the ν_{CO_2} infrared bands, i.e., in isolatable metal carbamates these vibrational modes typically occur at 1600−1480 cm^{-1}.[21] Scheme 4 depicts the catalytic cycle for the activation process where ethylene oxide is employed for simplicity. These zwitterions serve as cocatalysts in an analogous manner as the PPN^+X^- salts, except less effectively. This process involving heterocyclic nitrogen base activation explains the production of copolymer being a sigmoidal function of time.

In Scheme 4 we have represented the weak CO_2 adduct of DMAP as being stabilized by the (salen)CrX complex in a bidentate fashion. This is consistent with the difference in the ν_{CO_2}(asym) and ν_{CO_2}(sym) vibrations, i.e., 2097 and 2018 cm^{-1}, respectively, being less than 100 cm^{-1}.[22] It should be reiterated here that the instability of the CO_2 interaction is reflected in the small vibrational shift (∼290 cm^{-1}) of the average ν_{CO_2} value from that of free CO_2 (2349 cm^{-1}). In an attempt to definitively characterize this CO_2 interaction we endeavored to isolate crystals from the DBU/CO_2 reaction. As was previously reported by Franco and co-workers,[20] we isolated single crystals of the bicarbonate salt of DBU which result from the presence of adventitious water.[23] That is, water transforms the carbamic zwitterion into its bicarbonate salt (eq 2).

Table 5. Copolymerization of CO_2 and Cyclohexene Oxide Utilizing Catalyst **1** and 3 equiv of DMAP with Added Water[a]

equiv of H_2O	TON[b]	TOF[c]
0	1071	268
5	873	218
50	132	33

[a] Copolymerization conditions: 50 mg of catalyst **1** (0.04 mol %), 20 mL of cyclohexene oxide, 55 bar of CO_2, 80 °C, over a 4 h reaction time. [b] Measured in mol of CHO consumed/mol of Cr. [c] Measured in mol of CHO consumed/mol of Cr•h.



(2)

On the other hand, Heldebrant and co-workers have recently reported that they were unable to spectroscopically observe adduct formation between DBU and CO_2 at moderate CO_2 pressure (10−20 bar) and ambient temperature.[24]

Relevant to this latter point, as was listed earlier in Table 2, the [PPN][HCO_3] salt serves as a cocatalyst for the copolymerization of cyclohexene oxide and CO_2 in the presence of catalyst **1**. Hence, although every effort has been made to keep our copolymerization reactions anhydrous, we were concerned that trace quantities of water might be present thereby allowing the heterocyclic nitrogen bases to proceed via an anionic bicarbonate cocatalyst. Notwithstanding the lack of cocatalyst activity noted for triethylamine (Table 2), which should as well provide bicarbonate ions in the presence of CO_2/H_2O, we have deliberately added known quantities of water to our DMAP catalytic system. The results of this study are summarized in Table 5, where water is shown to have a deleterious effect on copolymer production. We conclude from these data that bicarbonate generated by adventitious water is not likely the cocatalyst in these instances. This is particularly true for reactions carried out in large excesses of DMAP.

The catalytic cycle for activation of DMAP shown in Scheme 4 accounts for the observed increase in the initiation period with increasing cocatalyst loading. That is, the inactive DMAP-bound complex is present in significant concentrations as long as "free" DMAP is available. Once all the DMAP has reacted only the catalytically active cocatalyst is present, as is best shown by the direct correlation between the disappearance of the ν(C=N) in "free" DMAP and the time until the maximum rate of catalysis is achieved (Figure 16). It is suggested herein that this scheme applies to all heterocyclic nitrogen bases studied, with different bases undergoing these reactions at various rates.

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(20) (a) Peàez, E. R.; Odnicki da Silva, M.; Costa, V. C.; Rodrigues-Filho, U. P.; Franco, D. W. *Tetrahedron Lett.* **2002**, *43*, 4091−4093. (b) Pérez, E. R.; Santos, R. H. A.; Gambardella, M. T. P.; de Macedo, L. G. M.; Rodrigues-Filho, U. P.; Launay, J.-C.; Franco, D. W. *J. Org. Chem.* **2004**, *69*, 8005−8011.

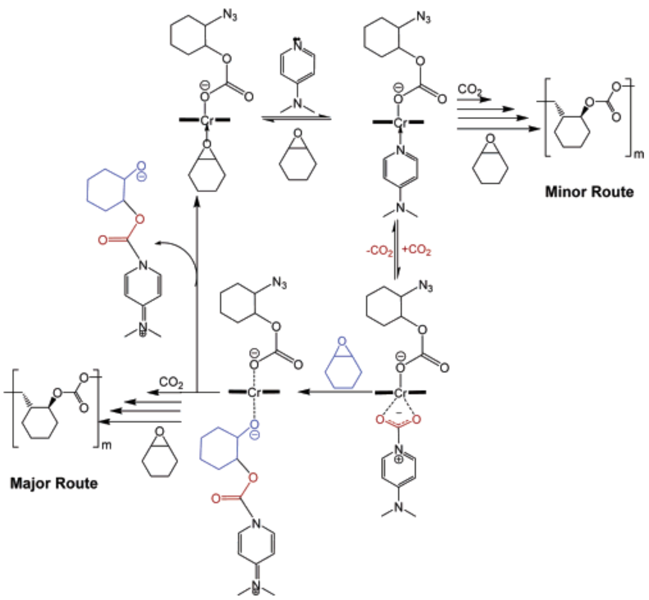
(21) Caudle, M. T.; Benedict, J. B.; Mobley, C. K.; Straessler, N. A.; Groy, T. L. *Inorg. Chem.* **2002**, *41*, 3183−3190.

(22) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley and Sons: New York, 1986; p 231.

(23) Crystals for $HDBU^+HCO_3^-$: $C_{10}H_{18}N_2O_3$ (214.26), monoclinic, *P*2(1)/*n*, $a = 7.129(8)$, $b = 18.34(2)$, $c = 8.149(9)$ Å, $\beta = 91.93(2)°$, $V = 1065(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.337$ mg/m^3, Mo Kα radiation, $\lambda = 0.710\,73$ Å, $T = 110(2)$ K, 4628 measured reflections, 1507 unique, $\mu = 0.099$ mm^{-1}, R1[$I > 2\sigma(I)$] = 0.0420, wR2 = 0.1045, GOF = 0.997, no. of parameters = 141.

(24) Heldebrant, D. J.; Jessop, P. G.; Thomas, C. A.; Eckert, C. A.; Liotta, C. L. *J. Org. Chem.* **2005**, *70*, 5335−5338.

Scheme 5



A more comprehensive mechanistic description of the copolymerization of CO_2 and cyclohexene oxide utilizing (salen)-CrX/heterocyclic nitrogen base systems can now be put forth as detailed in Scheme 5, specifically for DMAP. The initial epoxide ring opening occurs via a second-order process as described by Jacobsen and co-workers.[9] This step has previously been shown to take place immediately upon dissolving (salen)-CrN_3 in cyclohexene oxide at ambient temperature prior to cocatalyst addition and is not rate limiting.[25] The insertion of CO_2 into the chromium alkoxide species thereby produced also is rapid at high CO_2 pressures.[12] Also, we have demonstrated the chain propagation step to be first-order in metal catalyst concentration.[10a] In the presence of the cocatalyst an equilibrium is established between epoxide-bound and cocatalyst-bound (salen)Cr(alkoxide) derivative. CO_2 addition to this latter chromium complex then allows for the formation of another equilibrium, an activation that is stabilized by both the high $[CO_2]$ and the subsequent epoxide ring-opening step. This species represents the most active species during copolymerization but is not entirely stable as excess cocatalyst will displace the zwitterionic species and repeat the cycle until [DMAP] is sufficiently depleted. At this point the parallels between the ionic cocatalysts and the heterocyclic nitrogen Lewis base cocatalysts should be obvious, as these cocatalysts catalytically form zwitterions, which represent the active catalyst species, very similar to the ionic system.

Reactivity Studies of the Copolymerization of CO_2 and Cyclohexene Oxide Utilizing Phosphine Cocatalysts. Originally, we examined the phosphines, PPh_3 and PCy_3, for their efficacy to serve as cocatalysts for the copolymerization of cyclohexene oxide and carbon dioxide in the presence of catalyst **1**. These results are tabulated in Table 6, and display an increase in the rate of copolymer production with increasing phosphine/catalyst ratio up to about 7 equiv. Beyond this ratio there was no significant effect (increase or decrease) on copolymer production. As is apparent from the TOFs listed in Table 6, the bulkier, more nucleophilic phosphine, PCy_3, is considerably more effective as a cocatalyst or cocatalyst precursor than PPh_3. Kinetic studies carried out employing the epoxide TMSO were consistent with the bulk cyclohexene oxide runs, with one such representative series of experiments involving varying quantities of PCy_3 being depicted in Figure 18. Similar to kinetic traces of copolymer production when utilizing DMAP as cocatalyst, this reaction exhibits a sigmoidal shape as a function of time. However, contrary to the DMAP-catalyzed copolymerization reactions, in this instance the initiation period decreases with increasing phosphine concentration.

Table 6. Effect of Phosphine Cocatalyst Concentration on the Rate of Copolymerization of Cyclohexene Oxide and CO_2 Catalyzed by Complex **1**[a]

phosphine (equiv)	TON[b]	TOF[c]
PPh_3 (1)	288	72
PPh_3 (3)	420	105
PPh_3 (5)	403	101
PPh_3 (7)	408	102
PCy_3 (1)	354	89
PCy_3 (3)	1318	329
PCy_3 (5)	1306	326
PCy_3 (7)	1482	371

[a] Copolymerization conditions: 50 mg of catalyst **1** (0.04 mol %), 20 mL of cyclohexene oxide, 55 bar of CO_2, 80 °C, over a 4 h reaction time. Note: all catalysts produced copolymers with at least 99% carbonate content. [b] Measured in mol of CHO consumed/mol of Cr. [c] Measured in mol of CHO consumed/mol of Cr·h.

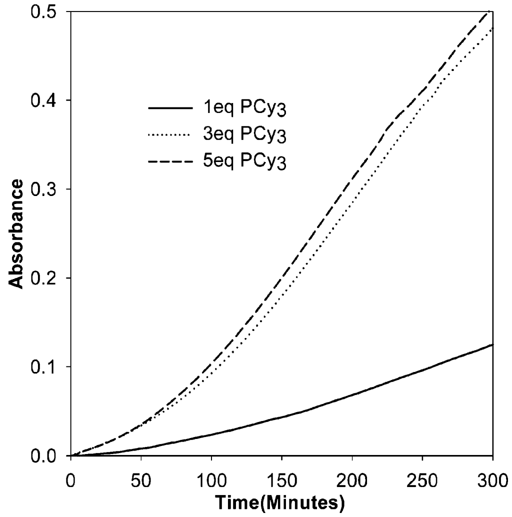


Figure 18. Effect of [tricyclohexylphosphine] on the rate of copolymerization as monitored by in situ infrared spectroscopy.

A summary of the other phosphines surveyed for their effectiveness as cocatalysts is presented in Table 7. To decipher a trend in these data both the steric and electronic properties of the various phosphines must be considered.[26] For example, an examination of triphenylphosphine derivatives revealed the sterically demanding and nucleophilic tris(2,4,6-trimethoxyphenyl)phosphine is somewhat more effective than PCy_3. Other substituted triphenylphosphine derivatives, all very similar in size, showed a slight decrease in reactivity as the location of the substituents changed, following a direct trend based on the predicted electron-donating ability. On the other hand substituted trialkyl phosphines show a very different reactivity trend, i.e., comparing the *n*-butyl, *iso*-propyl, and *tert*-butyl derivatives,

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(25) The process is slower in the presence of a cocatalyst; hence, if (salen)-CrN_3 and DMAP are simultaneously dissolved in epoxide this reaction is not rapid at ambient temperature.[11b]

(26) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348.

Table 7. Effect of Different Phosphines on the Rate of Copolymerization of Cyclohexene Oxide and CO_2 Catalyzed by Complex **1**[a]

phosphine	cone angle (deg)	TON[b]	TOF[c]
$P(C(CH_3)_3)_3$[d]	182	1277	638[e]
$P(2,4,6\text{-tri-}CH_3OC_6H_2)_3$	185	1417	354[f]
$P(C_6H_{11})_3$	170	1318	329[g]
$P(p\text{-}CH_3OC_6H_4)_3$	145	1293	323
$P(o\text{-}CH_3OC_6H_4)_3$	153	1170	292
$P(p\text{-}CH_3C_6H_4)_3$	145	1301	325
$P(C_6H_5)_3$	145	420	105
$Fe(CpPC_6H_5)_2$		1084	271

[a] Each experiment was performed with 3 equiv of phosphine. Cone angles were derived utilizing the Tolman method.[26] All active catalyst systems produced copolymer with >97% carbonate content. Copolymerization conditions: 50 mg of catalyst **1** (0.04 mol %), 20 mL of cyclohexene oxide, 55 bar of CO_2, 80 °C, over a 4 h reaction time. [b] Measured in mol of CHO consumed/mol of Cr. [c] Measured in mol of CHO consumed/mol of Cr·h. [d] Reaction carried out for 2 h. [e] M_n = 29 000 with a PDI of 1.16. [f] M_n = 21 000 with a PDI of 1.79. [g] M_n = 11 000 with a PDI of 1.54.

which all have similar electronic properties but vary in steric requirements, it was found that the smaller *n*-butyl and *iso*-propyl phosphines were only marginally effective as cocatalysts. However, the bulky tri(*tert*-butyl)phosphine derivative was highly effective, producing copolymer at a rate of 638 mol of epoxide consumed/mol of catalyst·h, clearly demonstrating that donating ability is not the only factor when determining what makes an effective cocatalyst. Other small donating trialkylphosphines, such as trimethyl- and triethylphosphine, produced very little copolymer, which is believe to be due to their low boiling points that prevent their being present in sizable quantities in the catalyst-rich liquid phase of the reaction. The least active of the phosphines, tri(*o*-tolyl)phosphine, is both weakly donating and has a very large cone angle, possibly prohibiting any type of reaction. Another attractive alternative involves the use of substituted ferrocene derivatives. One such derivative is that of $Fe(CpPPh_2)_2$, which when utilized as a cocatalyst produced slightly higher turnover numbers than that of PPh_3. These results lead us to draw two conclusions: first, that the phosphine needs to be highly nucleophilic in nature, and second, an effective phosphine cocatalyst must also be very large in size; and only with a combination of the two is catalytic activity optimized.

Because trace quantities of phosphine oxides are often present in phosphine samples, especially for trialkylphosphines, we examined several phosphine oxides for their ability to serve as cocatalysts for the copolymerization reaction. These were all extremely ineffective at producing copolymer when combined with catalyst **1**. Nevertheless, phosphine oxides readily afforded six-coordinate complexes with (salen)CrX catalysts. One such complex containing $Cy_3P{=}O$, **3·O═PCy₃**, was isolated in crystalline form and its structure determined by X-ray crystallography. A thermal ellipsoid representation of this complex is depicted in Figure 19, along with selected bond distances. It should be stated parenthetically that all attempts to grow single crystals of adducts of catalytically active phosphines with **1** were unsuccessful. Similarly, in a recent report efforts to grow single crystals of chromium(III) octaehtylporphyrin, Cr(OEP)Cl, with PPh_3 failed, whereas crystals of its $OPPh_3$ adduct were readily obtained from $OPPh_3$ and its molecular structure was determined.[27]

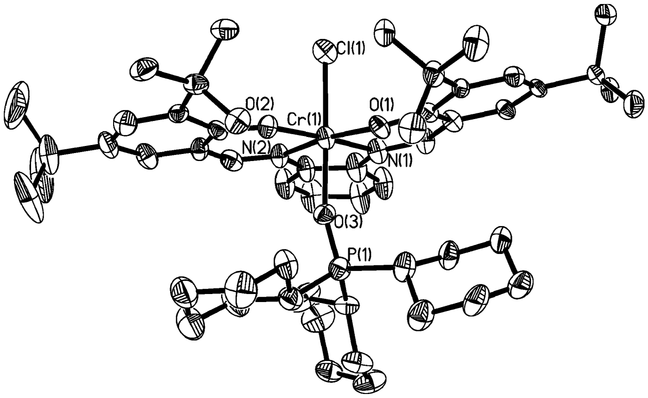

Figure 19. X-ray crystal structure of **3·O═PCy₃**. Thermal ellipsoids are shown at the 50% probability level with hydrogens omitted for clarity. Selected distances (Å): Cr(1)−Cl(1), 2.3260(19); Cr(1)−O(3), 2.007(4); Cr(1)−O(1), 1.912(4); Cr(1)−O(2), 1.913(5); Cr(1)−N(1), 2.002(5); Cr(1)−N(2), 2.013(5);

As discussed earlier *N*-heterocyclic amines readily bind to the metal center in $(salen)CrN_3$ catalysts in weakly interacting solvents as revealed by a shift in the ν_{N_3} infrared stretching frequency from 2082 cm^{-1} in the five-coordinate complex to 2054 cm^{-1} in the thus formed six-coordinate derivative.[11b] Furthermore, as would be anticipated based on the second-order pathway in [catalyst] for epoxide ring opening, the addition of ligand to the vacant axial chromium site greatly retards the initial ring-opening process, which otherwise occurs rapidly at ambient temperature. Parallel studies with phosphines showed that upon adding 1 equiv of Ph_3P to complex **1** in toluene *no* shift in the ν_{N_3} vibration was initially observed, indicative of *no* phosphine $(salen)CrN_3$ interaction. However, after this solution stood for 20 min at 80 °C, a shift in the ν_{N_3} from 2082 to 2054 cm^{-1} was partly observed, with a significant amount of the 2082 cm^{-1} parent peak remaining. The shift to the six-coordinate complex was intensified upon continued exposure of the solution to elevated temperatures or upon adding more triphenylphosphine. Similar studies employing the more nucleophilic, however sterically more demanding, PCy_3 ligand exhibited an enhanced interaction with $(salen)CrN_3$ complexes.

Overall, these results suggest that, while the phosphine binding in noncoordinating solvents is thermodynamically favored, it is kinetically slow, and some deformation of the salen ligand is necessary to incorporate it into the coordination sphere of the metal center, creating a significant activation energy barrier. This implies that epoxide coordination to the catalyst, especially when it is used as the solvent, should be kinetically favored over phosphine binding. Proof of this is seen in copolymerization reactions where both catalyst and cocatalyst are dissolved in cyclohexene oxide simultaneously. Infrared spectroscopy shows that the metal center produces the organic azide species instantaneously, a reaction that does not occur without the epoxide binding to the metal.

These observations imply that, analogous to *N*-heterocyclic Lewis bases, phosphine cocatalysts are not innocent as previously thought and instead react in a catalytic fashion to generate the predominant active species. Indeed, ^{31}P NMR spectra of catalytic active copolymerization processes cocatalyzed by phosphines display a strong signal at ~40 ppm. Inoue and co-

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(27) Inamo, M.; Matsubara, N.; Nakajima, K.; Iwayama, T. S.; Okimi, H.; Hoshino, M. *Inorg. Chem.* **2005**, *44*, 6445−6455.

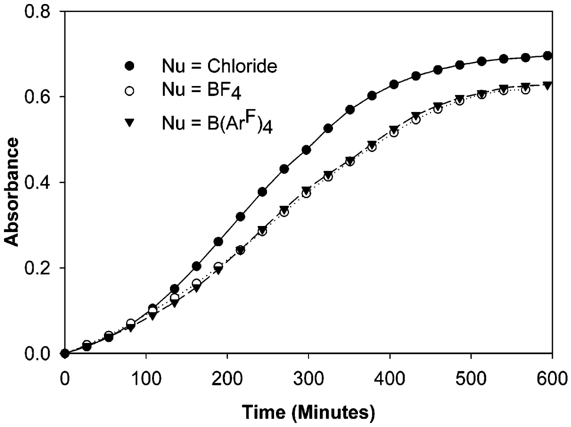
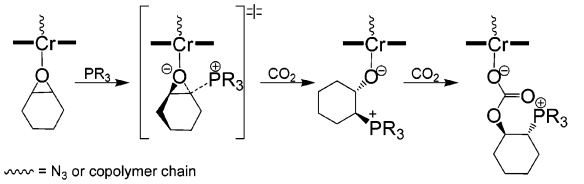


Figure 20. Copolymer formation profiles for TMSO/CO_2 reaction in the presence of (salen)CrX catalysts (X = Cl, BF_4, BAr_4^F) and *three equiv* of Cy_3P.

Scheme 6



workers observed a similar ^{31}P resonance in their copolymerization reaction catalyzed by aluminum porphyrin derivatives in the presence of PPh_3, which they attributed to formation of a phosphonium salt.[7] Further support for this behavior is revealed in copolymerization studies involving catalyst **1**, where the anionic axial azide group is replaced by the weakly or noninteracting BF_4 or BAr_4^F anions. Copolymerization reactions performed with these catalysts in the presence of 3 equiv of PCy_3 exhibited only small decreases in catalytic activity compared to the analogous catalyst containing an axial chloride ligand bound to chromium under identical reaction conditions. That is, in situ infrared monitoring of these copolymerization processes has shown that when equal [catalyst] are utilized, nearly identical copolymer formation profiles are observed (Figure 20).

At this point it should be reiterated that, for cocatalysts such as *N*-MeIm or DMAP, the initiation time is extended as the [cocatalyst] increases. Hence, the catalytic system does not proceed at maximum rate until all of the catalyst precursor is consumed, or in other words, not until all of the cocatalyst is activated. The difference in behavior between the phosphine-cocatalyzed system and that of *N*-heterocyclic amines lies in the fact that these latter bases readily bind to the (salen)CrN_3 center, thereby stabilizing a less reactive catalytic species. The sterically demanding nucleophilic phosphines do not compete with epoxide for the apical chromium binding site; therefore, the equilibria such as those depicted in Scheme 5 are unimportant in this instance. Instead, phosphine activation occurs in a rather facile step, reacting with the activated epoxide molecule producing a phosphonium inner salt or zwitterion. As is apparent in Scheme 6, this reaction step is more straightforward than the process for *N*-heterocyclic base activation and readily explains the saturation in [cocatalyst] kinetics observed. In the case of the amine cocatalysts, the small size and donating ability of the neutral cocatalyst allowed it to displace the zwitterionic cocatalyst, hindering copolymerization until all of the cocatalyst was activated; however, phosphines lack this binding ability and following the activation of 1 equiv of phosphine maximum catalytic activity is achieved. Indeed ionic cocatalysts have been shown to obtain their maximum rate with 1 equiv of cocatalyst, and the very similar phosphonium inner salt should behave in a like manner. The phosphonium inner salt would also interact with the metal much easier than its bulky phosphine precursors and be more donating than the epoxide, making it highly competitive for binding to chromium. This pathway of ring opening leads to the process being second-order overall, first-order in both [catalyst] and [cocatalyst]. The time necessary for the generation of these zwitterions, i.e., the cocatalyst active species, would also account for the initiation time that is observed during most of the phosphine reactions.

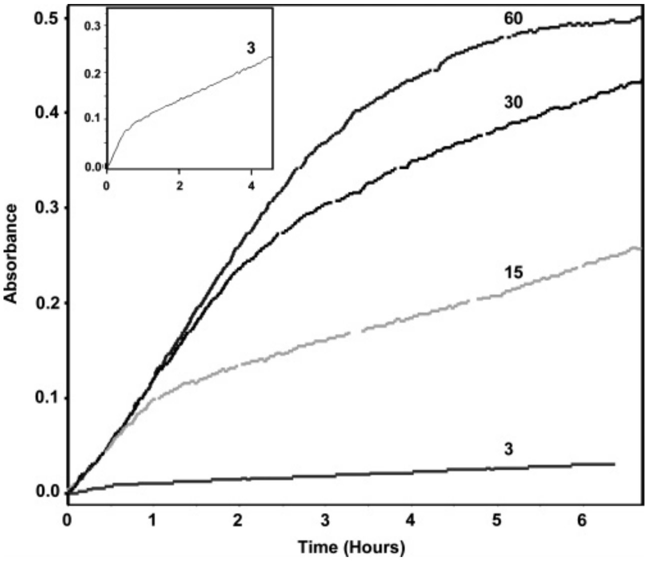


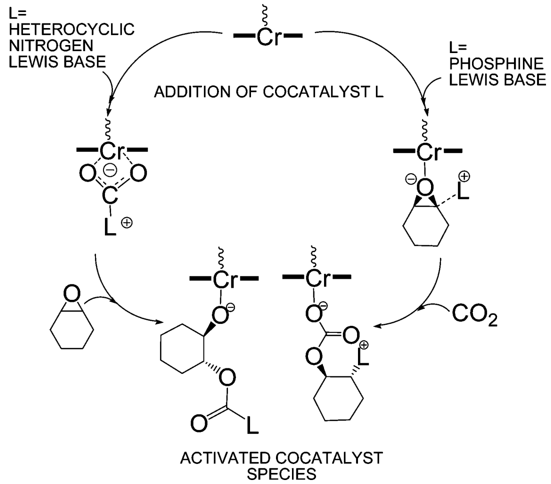
Figure 21. In situ infrared trace of the ν(C═O) at 1750 cm^{-1} corresponding to the polycarbonate product from the copolymerization of TMSO and CO_2 utilizing catalyst **1** and varying equivs of tri(*n*-butyl)phosphine. The inset illustrates the sharp drop off in production of copolymer at 3 equiv of *n*-Bu_3P.

The main disconnect in this unifying mechanistic proposal is why less sterically encumbering, nucleophilic phosphines are not effective as cocatalysts for the copolymerization reaction. Close examination of one such phosphine, *n*-Bu_3P, by in situ infrared monitoring of the process showed the incipient activity is indeed greater than that seen in other catalytically active phosphines. However, after a brief time of high activity, catalytic activity falls off sharply. The time period before activity decline is lengthened as the [*n*-Bu_3P] is increased. This is best illustrated in Figure 21, where the time profiles for copolymer formation are displayed as a function of [*n*-Bu_3P]. Currently, we are attempting to better understand the catalytic role of small, nucleophile phosphines in this copolymerization process, but it is likely that these very reactive bases are being consumed by reacting with the copolymer product or active chain end (vide infra).

Relevant to this latter point, an interesting aspect of these catalyst systems in general is that, based on the amount of epoxide consumed, the copolymer produced always has a molecular weight significantly lower than the theoretical molecular weight. Nevertheless, the polydispersity index (PDI) measured for these copolymer is always quite low (1.05−1.40). This is very apparent when employing a high loading of DMAP.

For example, in going from 1 to 31 equiv of DMAP as cocatalyst the molecular weight is reduced from 31 500 to 1600 g/mol and the carbonate content decreases from 99 to 70%. These activated cocatalysts may find the carbonate carbon an attractive reaction center leading to depolymerization reactions. Alternatively, each of the excess zwitterions initiates a polymer chain leading to shorter chains or lower molecular weights.[28] The best evidence for the depolymerization mechanism is found in the work of Hedrick and co-workers, wherein it was shown that phosphines and DMAP can act as organic catalysts for the ring-opening polymerization of lactides.[29] The molecular weights of the polymer obtained were found to be very sensitive to the [catalyst]. This sensitivity stems from the fact that polylactides, very similar to polycarbonates in most respects, can be depolymerized with DMAP. Interestingly, depolymerization was shown to be controllable and occurred with minimal change in the polydispersity index of the resulting polymer. The above observations are consistent with our results employing phosphine cocatalysts, where, as the steric requirements of the cocatalyst decrease while maintaining similar electronic properties, the molecular weight of the corresponding polycarbonate decreases. For example, tri-*tert*-butylphosphine and tricyclohexylphosphines produce copolymer with M_n values of 29 000 and 11 000 g/mol, respectively. However, the theoretical molecular weight is still never obtained, concluding that the depolymerization step or reaction of the zwitterions with the alkoxide active chain end cannot be totally discounted, but rather slowed. The molecular weight should then be maximized with the anionic cocatalysts where only 1 equiv of cocatalyst is added, limiting the possibilities of these processes occurring. However, in these latter instances copolymer growth can be occurring at both sides of the (salen)Cr center, concomitantly leading to lower molecular weight values. An alternative pathway which could account for the low molecular weights is the formation of large cyclic carbonates containing more than one carbonate group, as has been observed during long-running polycondensation reactions.[30] We have observed that by going from a five-membered cyclic ring to a six-membered cyclic carbonate that the ν(C=O) stretching frequency decreases (1825 cm^{-1} versus 1760 cm^{-1}),[31] thereby appearing quite close to that of the linear polymer (1750 cm^{-1}). Hence, it is quite conceivable that a large cyclic carbonate would appear in the same ν_{CO_2} infrared region as a linear copolymer and thus would go unnoticed by way of infrared monitoring. Currently, MALDI-TOF-MS studies are underway to better define different initiation, propagation, and termination reactions.[32,33]

Scheme 7



Conclusions

The skeletal cartoon in Scheme 7 summarizes the proposed complex activation modes required for achieving maximum catalytic activity when utilizing neutral Lewis bases as cocatalysts for the copolymerization of epoxide and CO_2 in the presence of (salen)CrX catalysts. These cocatalyst activation processes, which involved the production of zwitterions, account for the sigmoidal profiles observed for the formation of polycarbonate as a function of time in these systems. Hence, a unifying mechanism emerges, where *N*-heterocyclic amines and phosphines provide inner salts or zwitterions, which behave in a manner similar to that of anions as cocatalysts for copolymerization reactions catalyzed by (salen)CrX derivatives. Presumably, these mechanistic considerations apply to other metal complexes which serve as catalysts for this process and contain tetradentate ligand systems, e.g., metal porphyrins.

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Supporting Information Available: Complete details for the crystallographic studies, of **1·DMAP**, **1·[PPN][N$_3$]**, and **3·O-PCy$_3$**. This material is available free of charge via the Internet at http://pubs.acs.org.

JA053544F

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[28] We are grateful to acknowledge one of the reviewers of this contribution for this latter suggestion.

[29] (a) Nederberg, F.; Connor, E. F.; Glausser, T.; Hedrick, J. L. *Chem. Commun.* **2001**, 2066−2067. (b) Nederberg, F.; Connor, E. F.; Möller, M.; Glauser, T.; Hedrick, J. L. *Angew. Chem. Int. Ed.* **2001**, *40*, 2712−2715.

[30] An example of which can be found here: Kricheldorf, H. R.; Böhme, S.; Schwarz, G.; Schultz, C. L. *Macromolecules*, **2004**, *37*, 1742−1748.

[31] Darensbourg, D. J.; Ganguly, P.; Billodeaux, D. *Macromolecules* **2005**, *38*, 5406−5410.

[32] van Meerendonk, W. J.; Duchateau, R.; Koning, C. E.; Gruter, G.-J. M. *Macromolecules*, **2005**, *38*, 7306−7313.

[33] Initial mass spectral observations involving a low-molecular-weight copolymer (~3000) produced from cyclohexene oxide and CO_2 in the presence of (salen)CrN$_3$ and PPN$^+$Cl$^-$ reveal both chloride and azide end-groups in the polycarbonates formed.