

# Effective, Selective Coupling of Propylene Oxide and Carbon Dioxide to Poly(propylene Carbonate) Using (Salen)CrN<sub>3</sub> Catalysts

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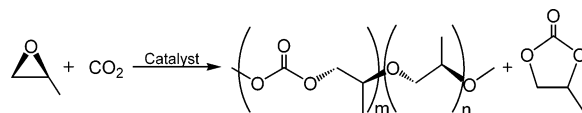
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The copolymerization of propylene oxide and CO<sub>2</sub> has been investigated employing Cr(salen)N<sub>3</sub> complexes as catalysts. Unfortunately the reaction could not be studied in real time via in situ IR spectroscopy, thereby obtaining detailed kinetic data, because of the copolymer limited solubility in most solvents. Investigations employing batch reactor runs concentrating on varying the cocatalyst, the equivalents of cocatalyst, and the steric and electronic structure of the catalyst through modification of the salen ligand were undertaken. It was discovered that the optimal catalyst for copolymer selectivity vs the monomeric propylene carbonate was one that contained a salen ligand with an electron-withdrawing phenylene backbone and electron-donating *tert*-butyl groups in the phenolate rings. This catalyst was used to investigate the effect of altering the nature of the cocatalyst and its concentration, the three cocatalysts being tricyclohexylphosphine (PCy<sub>3</sub>), PPN<sup>+</sup>N<sub>3</sub><sup>-</sup>, and PPN<sup>+</sup>Cl<sup>-</sup>, where PPN<sup>+</sup> is the large very weakly interacting bis(triphenylphosphoranylidene)ammonium cation. By utilization of more or less than 1 equiv of PCy<sub>3</sub> as cocatalyst, the yield of polymer was reduced. On the other hand, the PPN<sup>+</sup> salts showed the best activity when 0.5 equiv was employed, and produced only cyclic when using over 1 equiv.

## Introduction

The copolymerization of carbon dioxide and aliphatic epoxides, first reported by Inoue in the late 1960s, has currently been a topic of much interest.<sup>1</sup> Much of our past research and that of others have focused on the *alicyclic* epoxide, cyclohexene oxide, as the comonomer as it is easily studied mechanistically; however, the properties of the resulting polymer are inferior to the industrially produced polymer derived from the polycondensation of bisphenol-A and phosgene or diphenyl carbonate limiting its usefulness.<sup>2,3</sup> In contrast, the wide-scale production of poly(propylene carbonate) (PPC) from propylene oxide and carbon dioxide (Figure 1) would be highly desirable since this copolymer is currently industrially relevant. The uses of this material result from the copolymer features of a low *T*<sub>g</sub> (40 °C), a sharp, clean decomposition above 200 °C, and the environmental benefit of biodegradability. The two general application categories are destructive (evaporative pattern casting, ceramic binders) and nondestructive (adhesives and coatings).<sup>4</sup> However, the copolymerization process has been



**Figure 1.** Copolymerization of propylene oxide and carbon dioxide to form PPC with polyether and cyclic carbonate as side products.

plagued by low catalyst activity and the concomitant production of propylene carbonate (PC).

Recently, several different catalyst systems have been reported for this copolymerization process that have been able to increase the activity and selectivity for PPC. Coates

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and co-workers have reported an active ( $\beta$ -diiminato)ZnOAc complex which copolymerizes propylene oxide and CO<sub>2</sub> at 25 °C and 7 atm CO<sub>2</sub> with a turnover frequency (TOF) of 235 h<sup>-1</sup> and a selectivity for copolymer of 75%.<sup>5</sup> Rieger and co-workers reported the use of (salen)Cr(III)Cl employing varying equivalents of DMAP to give PPC and PC with modest turnover frequencies at 75 °C and 35 bar CO<sub>2</sub> pressure.<sup>6</sup> A recent communication from Coates' laboratories using a chiral Co(salen)OAc catalyst found selective production of PPC from propylene oxide and CO<sub>2</sub> at 25 °C,<sup>7</sup> whereas Shen and co-workers employing a similar cobalt(II) catalyst produced exclusively PC at 100 °C.<sup>8</sup> Similarly, Lu and Wang have utilized Co(salen)OAc in the presence of propylene oxide/CO<sub>2</sub> to afford a copolymer with >95% head-to-tail linkages and turnover frequencies approaching 290 hr<sup>-1</sup>.<sup>9</sup> Pertinent to these reports, it is noteworthy that catalytic processes carried out in our laboratory with Co(III) salen complexes, unlike with their Cr(III) analogues, at *elevated* temperatures generally provided Co(II) derivatives which were ineffective at producing copolymers.<sup>10</sup> Herein, we delineate the utilization of chromium salen complexes for the copolymerization of propylene oxide and carbon dioxide in the presence of various cocatalysts. Specifically, these studies will focus on the effects of both the nature and loading level of the cocatalysts, the electronic and steric structure of the salen ligand, and the reaction conditions for the selectivity for PPC vs PC formation.

## Experimental Section

**Reagents and Methods.** Unless otherwise specified, all syntheses and manipulations were carried out on a double-manifold Schlenk vacuum line under an atmosphere of argon or in an argon-filled glovebox. All solvents were freshly distilled from the appropriate reagents before use. Propylene oxide (Aldrich) was freshly distilled from CaH<sub>2</sub>. 2-(3,4-Epoxy cyclohexyl)-ethyltrimethoxysilane (TMSO) was vacuum-distilled from CaH<sub>2</sub>. Tricyclohexylphosphine was recrystallized from distilled ethanol before use. Bis(triphenylphosphoranylidene)ammonium chloride (PPN<sup>+</sup>Cl<sup>-</sup>) was recrystallized from dichloromethane/ether before use, and PPN<sup>+</sup>N<sub>3</sub><sup>-</sup> was prepared according to the published procedure.<sup>11</sup> Bone-dry carbon dioxide supplied in a high-pressure cylinder equipped with a liquid dip tube was purchased from Scott Specialty Gases. The corresponding salen ligands and chromium complexes were synthesized as previously described.<sup>12</sup> Unless otherwise stated, all other reagents were used

without further purification. <sup>1</sup>H and <sup>13</sup>C NMR spectra were acquired on Unity+ 300 MHz and VXR 300 MHz superconducting NMR spectrometers. IR spectra were recorded on a Mattson 6021 Fourier Transform (FT) IR spectrometer with a MCT detector. GPC molecular weight determinations (*M<sub>n</sub>* and *M<sub>w</sub>*) were carried out at the New Jersey Center for Biomaterials, Rutgers University. High-pressure reaction kinetic measurements were carried out using a stainless steel Parr autoclave modified with a silicon crystal to allow for FT attenuated total reflectance (ATR) IR spectroscopy (ASI ReactIR 1000 in situ probe).

**Copolymerization Reactions.** In a typical experiment, 50 mg of the catalyst and the appropriate amount of cocatalyst were dissolved in 20 mL of freshly distilled propylene oxide. This solution was then delivered via the injection port into a 300-mL stainless steel Parr autoclave reactor that was thoroughly dried overnight in vacuo at 80 °C. The reactor was then pressurized to 35 bar CO<sub>2</sub>, and the temperature was raised to 60 °C. The reaction was stopped after a 4-h time period, and the reactor was then cooled in a dry ice/acetone bath before venting the CO<sub>2</sub> pressure. A <sup>1</sup>H NMR spectrum was immediately taken to obtain the ratio of polymer:cyclic and the amount of polyether linkages present in the copolymer. The polymer was precipitated with 1 M HCl in MeOH and dried overnight in vacuo at room temperature and then weighed to obtain the turnover data.

**In Situ IR Monitoring of Epoxide Ring-Opening Reactions.** In a typical experiment, 10 mL of distilled dichloromethane was delivered via the injection port into a 300-mL stainless steel Parr autoclave reactor dried overnight in vacuo at 80 °C. The reactor is modified with a 30-bounce SiCOMP window to allow for the use of an ASI ReactIR 1000 system equipped with a MCT detector. The reactor was cooled to 6 °C with a cooling tower containing a 50:50 mix of ethylene glycol:water before the background solvent was injected. The solvent was allowed time to reach temperature, and a single 128-scan background spectrum was collected. The catalyst (~100 mg) was dissolved in 5 mL of dichloromethane and injected into the reactor, and the temperature was allowed to equilibrate. The spectrometer was started, collecting a 128 scan spectrum every 3 min. After one scan, the cooled propylene oxide was added and the reaction was monitored for changes in the  $\nu(\text{N}\equiv\text{N})$  region of the IR spectrum.

**Copolymerization Reactions Monitored by In Situ IR Spectroscopy.** In a typical experiment, 10 mL of distilled 2-(3,4-epoxy cyclohexyl)-ethyltrimethoxysilane (TMSO) was delivered via the injection port into a 300-mL stainless steel Parr autoclave reactor dried overnight in vacuo maintained at 80 °C temperature. The reactor is modified with a 30-bounce SiCOMP window to allow for the use of an ASI ReactIR 1000 system equipped with a MCT detector. In this manner, a single 128-scan background spectrum was collected. The catalyst and PPN<sup>+</sup>Cl<sup>-</sup> cocatalyst previously premixed in a 4:1 benzene:MeOH solution and dried overnight was dissolved in 10 mL of epoxide. This was then injected into the reactor followed by pressurization with 55 bar of CO<sub>2</sub> pressure. The IR spectrometer was set to collect one spectrum every 5 min over a 10-h period. Profiles of the absorbance at 1750 cm<sup>-1</sup> (polymer) with time were recorded after baseline correction and analyzed to provide initial reaction rates.

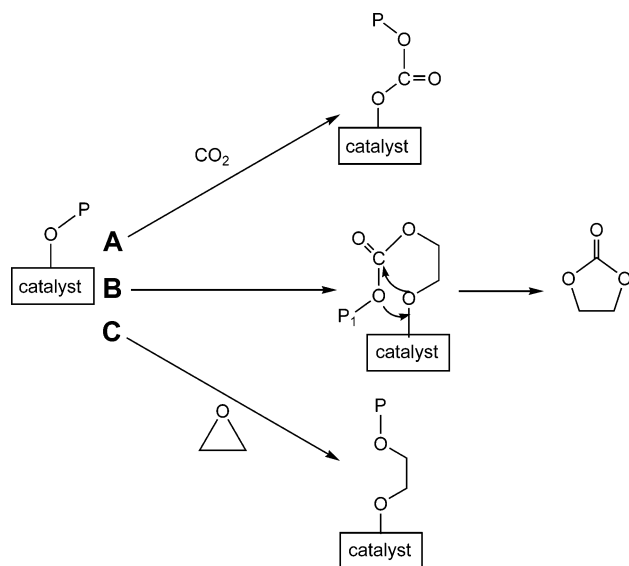
## Results and Discussion

As outlined in Scheme 1, there are three different pathways available during the CO<sub>2</sub>/epoxide polymerization process for

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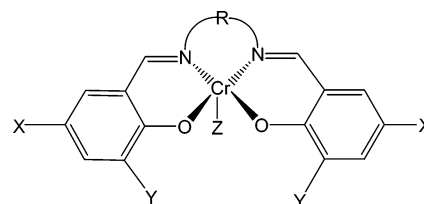
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Scheme 1



polymer reactivity. Pathway **A** involves CO<sub>2</sub> insertion to provide a polycarbonate linkage, pathway **B** involves a backbiting mechanism resulting in production of the monomeric byproduct cyclic carbonate, and pathway **C** involves consecutive epoxide enchainment to afford a polyether linkage. Now while we have been able to effectively optimize pathway **A** for the cyclohexene oxide/CO<sub>2</sub> coupling process, the small energy difference in pathways **A** and **B** for propylene oxide represents a significant challenge still unresolved.<sup>13</sup> Indeed, at 100 °C this process is selective for pathway **B**, the production of cyclic propylene carbonate, in the presence of (salen)CrCl and one equivalent of DMAP.<sup>14</sup> We have ascribed the greater selectivity for polycarbonate formation in the case of cyclohexene oxide to the increased strain in forming the five-membered carbonate ring imposed by the conformation of the cyclohexyl group. The adjacent cyclohexyl ring introduces a significant amount of twist in the five-membered carbonate ring, whereas propylene carbonate is unconstrained and perfectly planar, producing a lower energy of activation for the formation of propylene carbonate via the polymer degradation pathway (for pathway **B**,  $E_{\text{act}}^{\text{PC}} = 100.5 \text{ kJ/mol}$  vs  $E_{\text{act}}^{\text{CHC}} = 133.0 \text{ kJ/mol}$ ).<sup>13b</sup>

In situ IR spectroscopy has proven to be the most vital instrumental method to obtain kinetic and mechanistic information of these copolymerization reactions. An experimental obstacle to acquiring detailed mechanistic aspects of the CO<sub>2</sub> coupling reaction exists when utilizing propylene oxide as the comonomer, as PPC has a very low solubility in the propylene oxide/CO<sub>2</sub> reaction mixture, as well as in the presence of weakly interacting organic cosolvents.<sup>15</sup> This leads to precipitation of the copolymer onto the ATR crystal mounted at the bottom of the reactor; thereby useful in situ kinetic data is difficult to obtain. Hence, our analysis of the



- 1a: R=C<sub>6</sub>H<sub>4</sub>, X,Y=*t*-Bu, Z=Cl  
 1b: R=C<sub>6</sub>H<sub>4</sub>, X,Y=*t*-Bu, Z=N<sub>3</sub>  
 1c: R=C<sub>6</sub>H<sub>4</sub>, X=H, Y=*t*-Bu, Z=N<sub>3</sub>  
 2a: R=C<sub>6</sub>H<sub>10</sub>, X,Y=*t*-Bu, Z=N<sub>3</sub>  
 2b: R=C<sub>6</sub>H<sub>10</sub>, X=H, Y=*t*-Bu, Z=N<sub>3</sub>  
 3a: R=C<sub>2</sub>H<sub>4</sub>, X,Y=*t*-Bu, Z=N<sub>3</sub>  
 3b: R=C<sub>2</sub>H<sub>4</sub>, X=H, Y=*t*-Bu, Z=N<sub>3</sub>  
 4: R=C<sub>2</sub>H<sub>4</sub> or C<sub>6</sub>H<sub>4</sub>, X,Y=Cl, Z=N<sub>3</sub>  
 5: R=C<sub>2</sub>H<sub>4</sub> or C<sub>6</sub>H<sub>4</sub>, X=H, Y=Ph, Z=N<sub>3</sub>

**Figure 2.** Skeletal representation of the Cr(III)salen catalysts used in the copolymerization of propylene oxide and CO<sub>2</sub>.

propylene oxide/CO<sub>2</sub> coupling reaction has been performed with bulk reactor studies, where only the end result of the reaction was observed. Nevertheless, in our limited in situ studies done under controlled conditions, it was apparent that at low temperature (30 °C) only PPC was produced which upon raising the temperature (80 °C) degraded to cyclic carbonate.<sup>13</sup> Indeed, this phenomenon has been demonstrated to be a general one for a variety of metal catalyst systems.<sup>2a,2b,16</sup>

The main objective of our efforts involving propylene oxide/CO<sub>2</sub> coupling has been directed at optimizing copolymer production and minimizing or totally excluding the production of cyclic carbonate. As with previously reported cyclohexene oxide studies, many factors must be taken into consideration in order to optimize formation of the polycarbonate.<sup>12</sup> These variables include: electronic and steric effects of the salen ligand, cocatalyst, initiator, CO<sub>2</sub> pressure, and an additional concern, temperature. Herein, we have focused our attention on Cr(salen)N<sub>3</sub> derivatives (Figure 2) in the presence of tricyclohexylphosphine (PCy<sub>3</sub>) or bis-(triphenylphosphoranylidene)ammonium chloride and azide (PPN<sup>+</sup>X<sup>-</sup> where X = Cl or N<sub>3</sub>) salts as cocatalysts for an optimization of this CO<sub>2</sub> coupling process with propylene oxide to selectively afford PPC.

Copolymerization reactions were carried out employing a catalyst loading of ~0.05 mol % in 20 mL of propylene oxide and 1 equiv of cocatalyst at 60 °C and 35 bar CO<sub>2</sub> pressure for 4 h. A comprehensive summary of the data obtained for this copolymerization process using various (salen)CrN<sub>3</sub> derivatives as catalysts in the presence of several cocatalysts is provided in Table 1. The salen diimine backbone and the substituents in the 5 position on the phenolate group were varied, with the *tert*-butyl substituent in the 3 position kept constant to aid in solubility (Figure 2, complexes **1b–3b**). Each chromium catalyst was investigated in the presence of three common cocatalysts we have previously utilized in these copolymerization reactions, namely, PCy<sub>3</sub>, PPN<sup>+</sup>N<sub>3</sub><sup>-</sup>, and PPN<sup>+</sup>Cl<sup>-</sup>. From these data, it is apparent that the electronic effect of the salen ligand of the chromium complex on the catalytic activity for polycarbonate production is different for propylene oxide as compared to cyclohexene

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**Table 1.** TOF and Selectivity for Copolymer Formation for the Various Catalyst Systems<sup>a</sup>

	backbone	5 position	cocatalyst	TOF <sup>b</sup>	polymer:cyclic <sup>c</sup>	% carbonate <sup>d</sup>
<b>1b</b>	phenylene	<i>t</i> -Bu	PCy <sub>3</sub> <sup>e</sup>	149 <sup>f</sup>	91:9	96
	phenylene	<i>t</i> -Bu	PPN <sup>+</sup> N <sub>3</sub> <sup>-</sup>	190 <sup>g</sup>	84:16	96
	phenylene	<i>t</i> -Bu	PPN <sup>+</sup> Cl <sup>-</sup>	192	93:7	99
<b>1c</b>	phenylene	H	PCy <sub>3</sub>	144	93:7	97
	phenylene	H	PPN <sup>+</sup> N <sub>3</sub> <sup>-</sup>	194	84:16	94
	phenylene	H	PPN <sup>+</sup> Cl <sup>-</sup>	177	94:6	99
<b>3a</b>	ethylene	<i>t</i> -Bu	PCy <sub>3</sub>	21	72:28	90
	ethylene	<i>t</i> -Bu	PPN <sup>+</sup> N <sub>3</sub> <sup>-</sup>	76	35:65	97
	ethylene	<i>t</i> -Bu	PPN <sup>+</sup> Cl <sup>-</sup>	75	62:38	96
<b>3b</b>	ethylene	H	PCy <sub>3</sub>	52	89:11	95
	ethylene	H	PPN <sup>+</sup> N <sub>3</sub> <sup>-</sup>	90	93:7	99
	ethylene	H	PPN <sup>+</sup> Cl <sup>-</sup>	91	73:27	97
<b>2a</b>	cyclohexylene	<i>t</i> -Bu	PCy <sub>3</sub>	11	65:35	90
	cyclohexylene	<i>t</i> -Bu	PPN <sup>+</sup> N <sub>3</sub> <sup>-</sup>	91	58:42	98
	cyclohexylene	<i>t</i> -Bu	PPN <sup>+</sup> Cl <sup>-</sup>	109	60:40	98
<b>2b</b>	cyclohexylene	H	PCy <sub>3</sub>	124	82:18	96
	cyclohexylene	H	PPN <sup>+</sup> N <sub>3</sub> <sup>-</sup>	163	85:15	94
	cyclohexylene	H	PPN <sup>+</sup> Cl <sup>-</sup>	169	87:13	87

<sup>a</sup> Each reaction was performed with 50 mg of catalyst, 20 mL of propylene oxide, 1 equiv of cocatalyst, 60 °C, and 34 bar CO<sub>2</sub> for 4 h.

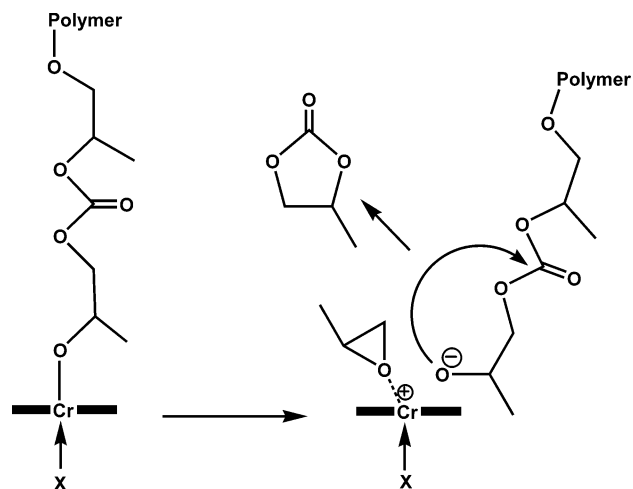
<sup>b</sup> The TOF was determined by weighing the polymer after precipitating in 1 M HCl in MeOH, washing with MeOH, and thoroughly drying in a vacuum oven and is reported as mol epoxide consumed per mol Cr·h.

<sup>c,d</sup> Determined from <sup>1</sup>H NMR spectroscopy. <sup>e</sup> An identical run carried out in the presence of 2 equiv of PCy<sub>3</sub> afforded a TOF of 99 with a polymer:cyclic ratio of 84:16. <sup>f</sup> *M*<sub>n</sub> = 13 200 with a PDI of 1.07. <sup>g</sup> *M*<sub>n</sub> = 26 100 with a PDI of 1.11.

oxide. That is, while the copolymerization of CO<sub>2</sub> and cyclohexene oxide is enhanced by electron-donating groups on the diimine backbone (complexes **2** and **3**), in the case of propylene oxide a large quantity of cyclic carbonate is produced. On the other hand, the complex containing the electron-withdrawing phenylene diimine backbone (complex **1b**) afforded predominantly copolymer under the same reaction conditions. As was observed for the cyclohexene oxide/CO<sub>2</sub> copolymerization reaction, electron-withdrawing substituents on the phenolate moieties (complexes **4** and **5**) led to decreased activity for formation of either CO<sub>2</sub>/propylene oxide coupled product. From this we concluded propylene oxide is much more sensitive to the electronic environment around the chromium center than cyclohexene oxide, requiring a catalyst with a “middle of the road” electronic structure, e.g., an electron-withdrawing backbone and electron-donating groups on the phenolate rings.

Before further examination of the results summed up in Table 1, it should be noted that these experiments at first presented a difficulty in obtaining accurate TON and TOF values. There are two methods commonly employed for determining these quantities: (1) <sup>1</sup>H NMR allows for an analysis of the unreacted epoxide or (2) weighing out the dried isolated copolymer. We found following several successive trials employing both procedures that TOF assessed via the <sup>1</sup>H NMR method gave inflated values.<sup>17</sup> Therefore, it was decided that weighing the polymer after thoroughly drying it in a vacuum oven overnight was the more accurate method of reporting these data. As it is

(17) For example, the TOFs reported in Table 1 using catalysts **1c** with PCy<sub>3</sub> and PPN<sup>+</sup>Cl<sup>-</sup> as cocatalysts if done by <sup>1</sup>H NMR were found to be higher at 192 and 329, respectively. This is undoubtedly due to the fact that our experiments are carried out in neat epoxide, where at the termination of the copolymerization process free epoxide is the dominant signal in the NMR spectrum.



**Figure 3.** Growing polymer dissociates from an electron-rich metal center leading to the formation of cyclic carbonate.

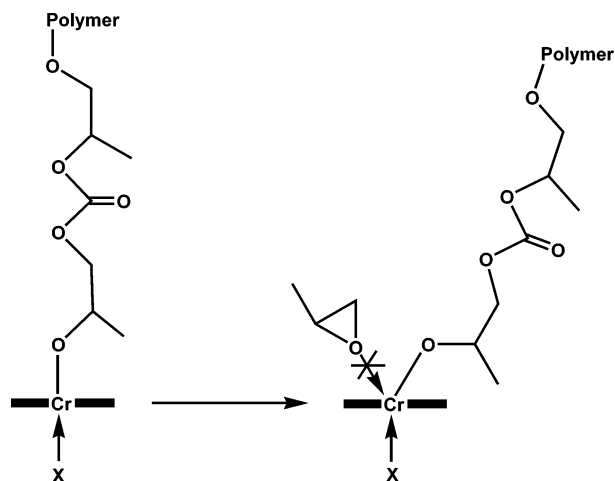
difficult to isolate the high-boiling cyclic carbonate from the copolymer, the amount of cyclic formed is reported as the ratio of polymer to cyclic derived from an integration of the appropriate peaks in the <sup>1</sup>H NMR taken directly upon completion of the reaction. It should be noted that these copolymerization reactions are only partially complete under the conditions employed; hence, relative TOFs are a good measure of relative reaction rates.

It should first be noted that little polyether is produced in these polymerization reactions, that is, pathway **C** (Scheme 1), is minimized employing these (salen)CrN<sub>3</sub> catalysts. In contrast to cyclohexene oxide, there is a fine balance between the catalyst electronic and steric structure for maximizing PPC. The most optimal catalysts thus far utilized are ones that contain the electron-withdrawing phenylene backbone and either an electron-donating *t*-Bu group or neutral H group on the phenolate ring, giving TOF values in the range of 190 mol epoxide consumed/mol Cr·h and little cyclic carbonate. When the backbone is changed to the electron-donating ethylene backbone, the TOF greatly decreases with a concomitant increase in the amount of cyclic compared to copolymer. A possible explanation for this is depicted in Figure 3. That is, the reaction might proceed through a mechanism with a great deal of ionic character in the epoxide ring-opening step, thereby allowing the polymer chain more easily to backbite upon itself to afford cyclic carbonate.

On the other hand, if the catalyst contains a ligand structure that has electron-withdrawing groups (complexes **4** and **5**), the chromium oxygen bond will be strengthened, not allowing the polymer chain to ring open the epoxide, thereby decreasing or shutting down activity all together (Figure 4).

The selectivity for producing PPC vs cyclic carbonate is also a function of the pressure of CO<sub>2</sub> as would be predicted by Scheme 1; that is, pathway **A** is dependent on the [CO<sub>2</sub>] and pathway **B**, which is unimolecular with regard to the growing polymer chain, is not.<sup>18</sup> A polymerization performed with only 6.9 bar of CO<sub>2</sub> led to an increased amount of cyclic carbonate produced.

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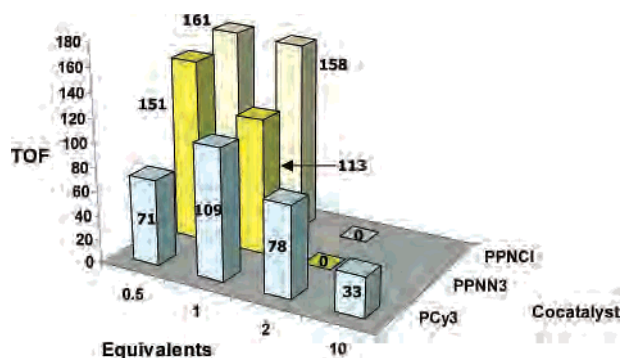
**Figure 4.** Chromium–alkoxide bond strengthened by an electron-withdrawing ligand structure, leading to little or no polymer formation.

**Table 2.** Effect of Different Cocatalysts and Their Equivalents on the Copolymerization of PO and CO<sub>2</sub> with Catalyst **1b**<sup>a</sup>

entry	cocatalyst (equiv)	TOF <sup>b</sup>	% carbonate <sup>c</sup>
1	PCy <sub>3</sub> (0.5)	71	89
2	PCy <sub>3</sub> (1)	109	94
3	PCy <sub>3</sub> (2)	76	96
4	PCy <sub>3</sub> (10)	33	95
5	PPN <sup>+</sup> N <sub>3</sub> <sup>-</sup> (0.5)	151	93
6	PPN <sup>+</sup> N <sub>3</sub> <sup>-</sup> (1)	113	98
7	PPN <sup>+</sup> N <sub>3</sub> <sup>-</sup> (2)	0	
8	PPN <sup>+</sup> Cl <sup>-</sup> (0.5)	161	94
9	PPN <sup>+</sup> Cl <sup>-</sup> (1)	158	97
10	PPN <sup>+</sup> Cl <sup>-</sup> (2)	0	

<sup>a</sup> All reactions were carried out with 50 mg of catalyst ( $7.9 \times 10^{-5}$  mol), 20 mL of racemic propylene oxide, 35 bar CO<sub>2</sub>, and at 53 °C for 4 h.

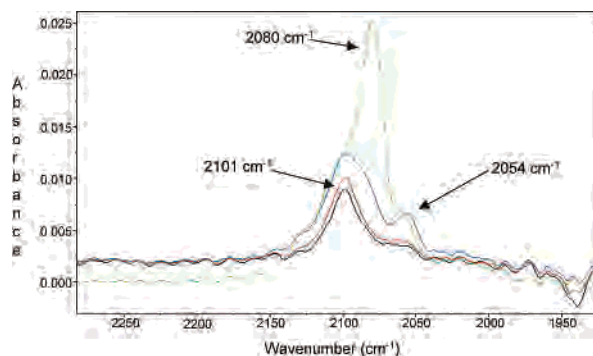
<sup>b</sup> Moles of epoxide consumed/mol Cr·h. <sup>c</sup> Determined by <sup>1</sup>H NMR spectroscopy.



**Figure 5.** TOF as a function of cocatalyst loading.

Focusing on the most active catalyst (**1b**) for selectively producing PPC, we have investigated the dependence of the process on the nature and number of equivalents of the cocatalyst. The data from these studies are provided in Table 2 and also depicted in the bar graph in Figure 5. It is worth noting here that all the studies throughout this publication produced PPC that was regioirregular with head-to-head, head-to-tail, and tail-to-tail junctions.<sup>19</sup> As previously noted for the cyclohexene oxide/CO<sub>2</sub> study, the TOFs for polycarbonate production increases as the donating ability of the

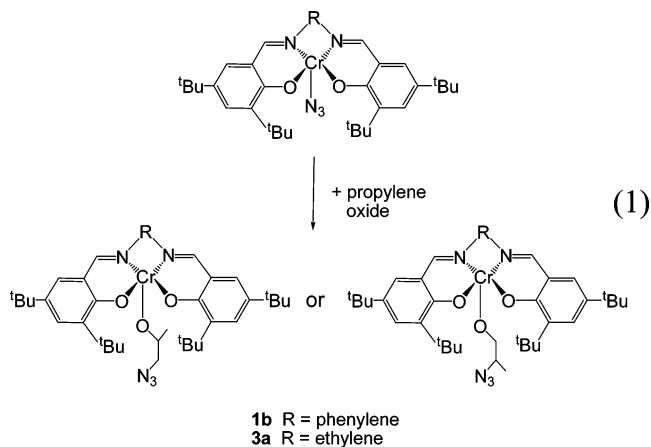
(19) Byrnes, M. J.; Chisholm, M. H.; Hadad, C. M.; Zhou, Z. *Macromolecules* **2004**, *37*, 4139–4145.



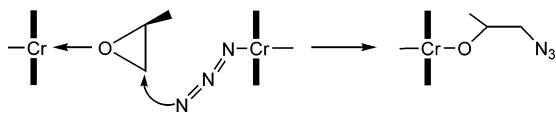
**Figure 6.** IR spectra of complex **3a** before and after addition of 200 equiv of propylene oxide in which the intermediate six-coordinate species is observed.

cocatalyst increases, with little cyclic carbonate produced in any instance. One of the most striking differences in the propylene oxide/CO<sub>2</sub> copolymerization process as compared to that involving cyclohexene oxide is that in the case of PCy<sub>3</sub> addition a cocatalyst loading beyond 1 equiv retards copolymer formation (entries 3 and 4 in Table 2); however, as indicated in footnote e of Table 1, no attendant increase in cyclic carbonate formation was concomitantly observed. A similar decrease in copolymer production in the presence of cocatalyst loading beyond 1 equiv was seen by Rieger for a (salen)CrCl/DMAP-catalyzed reaction.<sup>6</sup> Hence, the difference in behavior of the CHO/CO<sub>2</sub> and PO/CO<sub>2</sub> systems in the presence of PCy<sub>3</sub> cocatalyst is mostly attributed to the ease of copolymer degradation to cyclic carbonate in the latter instance.

It is *important* to note here that the initiation step of epoxide ring-opening depicted in eq 1 in the absence of a cocatalyst occurs rapidly even below ambient temperature. That is, upon determining the IR spectrum of a 0.015 M solution of catalyst **3a** in methylene chloride at 6 °C, the  $\nu_{N_3}$  stretching vibration was observed at 2080 cm<sup>-1</sup>, which corresponds to that of the five-coordinate complex. When 25 equiv of propylene oxide were added to the solution, the azide stretching vibration immediately shifted from the five-coordinate species to the ring-opened organic azide metal derivative at 2101 cm<sup>-1</sup> as depicted in Figure 6. However, upon addition of 200 equiv of propylene oxide the presumed *intermediate* six-coordinate propylene oxide bound species could be observed for one scan at 2054 cm<sup>-1</sup> (Figure 6),



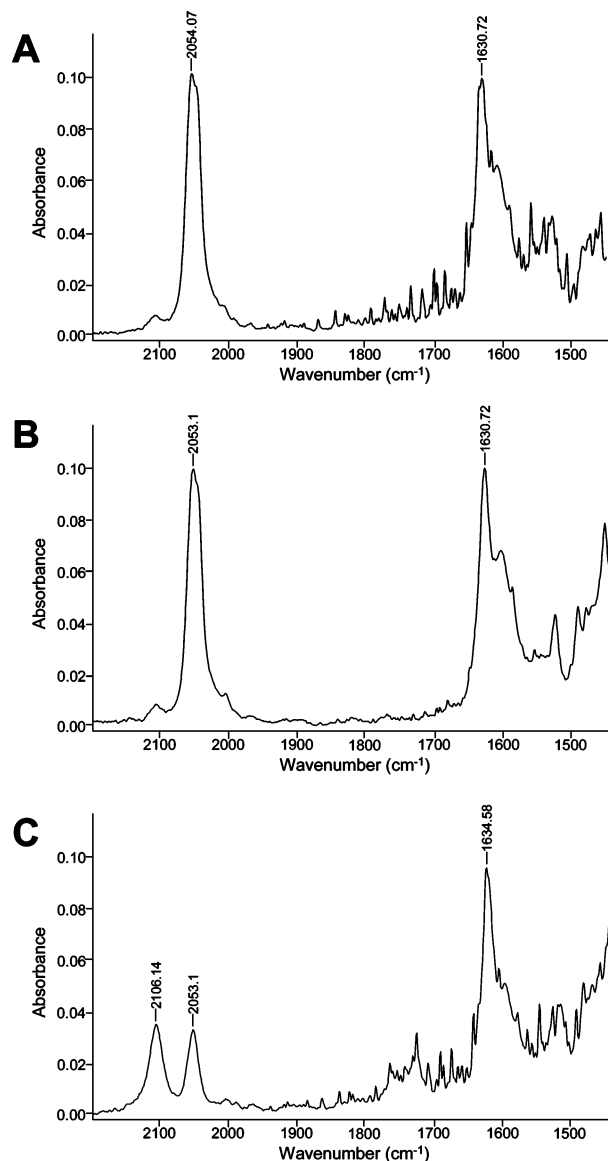
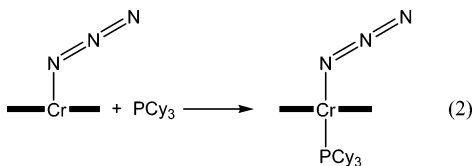
Scheme 2



immediately followed by a shift to all of the chromium complex existing as the organic azide derivative. A similar experiment involving complex **1b** and 1000 equiv of propylene oxide failed to observe any intermediate epoxide-bound metal species prior to the formation of the ring-opened azide derivative, indicative of a stronger epoxide binding or activation by the less electron-rich metal complex in this instance.

Jacobsen and co-workers have demonstrated the epoxide ring-opening reactions described in eq 1, specifically involving cyclopentene oxide, occurs via a process second order in  $(\text{salen})\text{CrN}_3$  concentration.<sup>20</sup> As skeletally illustrated in Scheme 2, this behavior is proposed to arise from an azide on one chromium center serving to nucleophilically attack an activated epoxide bound to a second chromium center. Consistent with this suggestion when the reaction outlined in eq 1 was carried out in the presence of 1 equiv of a  $\text{PPN}^+\text{X}^-$  cocatalyst, where the  $(\text{salen})\text{CrN}_3$  complex exists as an anionic six-coordinate derivative, the ring-opening reaction is greatly retarded at ambient temperature. For example, as shown in Figure 7, the ring-opening performed in the presence of the readily IR-monitored  $\text{PPN}^+\text{OAc}^-$  cocatalyst is only partially complete after several hours at ambient temperature as indicated by the attendant organic azide ( $2106\text{ cm}^{-1}$ ) and metal-bound azide ( $2053\text{ cm}^{-1}$ ) stretching frequencies. Concomitantly, the unidentate-bound acetate  $\nu_{\text{CO}_2}$  asymmetric stretch is only slightly shifted from  $1630$  to  $1635\text{ cm}^{-1}$  following azide ring-opening of the propylene oxide.

As indicated, the anions furnished by the  $\text{PPN}^+\text{X}^-$  salts which serve as cocatalysts for these  $\text{CO}_2/\text{epoxide}$  coupling reactions readily afford six-coordinate anionic  $(\text{salen})\text{CrN}_3$  derivatives, where the  $\text{PPN}^+$  counterion is solvent separated. On the other hand, the sterically encumbering  $\text{PCy}_3$  ligand upon addition to a toluene solution of  $(\text{salen})\text{CrN}_3$  is slowly interacting with the chromium center at ambient temperature (eq 2). That is, there is a significant barrier to  $\text{PCy}_3$  binding which occurs at a slow rate in the presence of 1 equiv of  $\text{PCy}_3$  at ambient temperature (Figure 8), with higher  $\text{PCy}_3$  concentrations driving reaction 2 to the right. However, upon heating a solution of  $(\text{salen})\text{CrN}_3$  and  $\text{PCy}_3$  to temperatures of  $60\text{--}80\text{ }^\circ\text{C}$ , a six-coordinate derivative forms more readily. Although there is some degree of  $\text{PCy}_3$  binding at the chromium center, especially at elevated temperatures, we have evidence from our kinetically monitored studies involving cyclohexene oxide and  $\text{CO}_2$  in the presence of  $\text{PCy}_3$  that the most effective cocatalyst present in solution is a phos-



**Figure 7.** IR spectra in  $\nu_{\text{N}_3}$  and  $\nu_{\text{CO}_2}$  stretching regions for complex **3a** in the presence of 1 equiv of  $[\text{PPN}][\text{OAc}]$  in methylene chloride. (A) Spectrum prior to the addition of epoxide. (B) After stirring the solution for 15 min in the presence of 25 equiv of propylene oxide at ambient temperature. (C) After carrying out the process in B for an additional 14 h.

phonium zwitterionic species resulting from phosphine ring opening of the epoxide.<sup>21,22</sup>

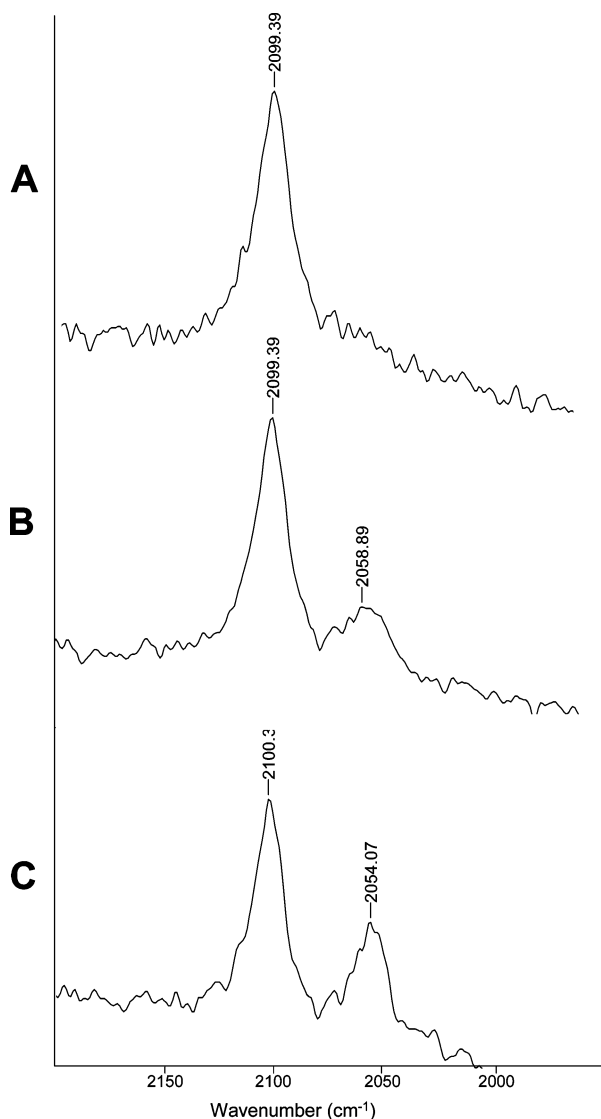
Because of the numerous studies demonstrating the superior properties of *N*-heterocyclic carbene ligands (NHC) in place of traditional phosphine ligands in organometallic catalysis, it was of interest to explore the use of these as cocatalysts for the copolymerization process.<sup>23</sup> Initially we utilized the stable, sterically encumbering 1,3-dicyclohexyl-

(20) Jacobsen, E. N. *Acc. Chem. Res.* **2000**, *33*, 421–431 and references therein.

(21) Dr. Ryan Mackiewicz in our laboratory has shown via  $^{31}\text{P}$  NMR and kinetic studies that the active cocatalyst is a phosphonium zwitterion or inner salt formed from phosphine and epoxide or carbonate monomer or oligomer formed therefrom. That is, the origin of the reported initiation step in the presence of phosphines is this autocatalytic process.<sup>22</sup>

(22) Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers, J. R.; Phelps, A. L.; *Inorg. Chem.* **2004**, *43*, 1831–1833.

(23) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290.

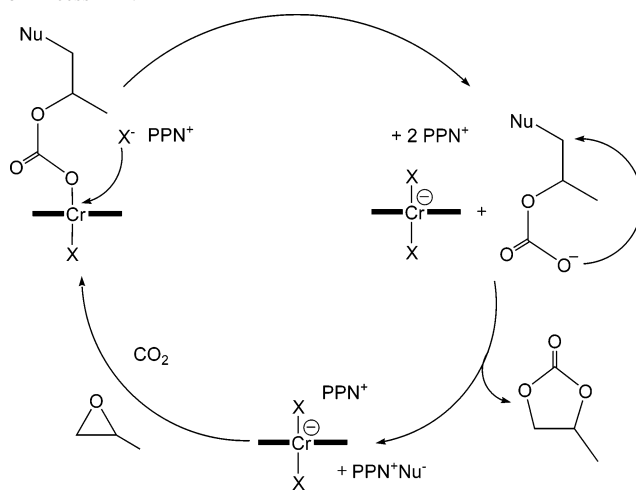


**Figure 8.** IR spectra in  $\nu_{N_3}$  stretching region for complex **1b** in toluene. (A) Pure sample of **1b**. (B) **1b** in the presence of 1 equiv of  $PCy_3$ . (C) Solution in **B** heated to 80 °C.

imidazol-2-ylidene derivative as a potential cocatalyst in the presence of complex **3a**. We assumed the lack of catalytic activity observed in this instance to be the result of steric hindrance. Hence, we went to great lengths to synthesize the smaller 1,3,4,5-tetramethylimidazol-2-ylidene derivative which similarly was ineffective as a cocatalyst.<sup>24</sup> Recently, it has become quite apparent why NHCs fail in these experiments in that they react with  $CO_2$  to afford stable adducts at temperatures less than 100 °C and thus are not available for serving as cocatalysts.<sup>25</sup>

Another significant difference between propylene oxide vs cyclohexene oxide emerged when using the  $PPN^+X^-$  salts as cocatalysts. When more than 1 equiv of  $PPN^+X^-$  is utilized with cyclohexene oxide as the monomer, there is an increase in the amount of cyclic carbonate produced but not

**Scheme 3.** Exclusive Production of Cyclic Carbonate in the Presence of Excess  $PPN^+X^-$



to a major extent. On the other hand, when more than 1 equiv of the  $PPN^+X^-$  salts are used with propylene oxide as the monomer, the only product formed is cyclic carbonate.<sup>26</sup> The mechanism depicted in Scheme 3 may account for this behavior. Indeed, we have isolated and crystallographically characterized a  $[(salen)Cr(N_3)_2][PPN]$  salt.<sup>27</sup> The excess anion could displace the alkoxide from the chromium center, forming a catalyst with two nucleophiles bound thereby dissociating the copolymer chain. The polymer chain then backbites on itself, forming cyclic. An experiment was conducted where  $PPN^+N_3^-$  and propylene oxide were subjected to the polymerization conditions in the absence of catalyst **1b**, and it was found that no cyclic was produced under these conditions, ruling out the possibility of the excess salt ring opening the PO and forming cyclic carbonate. Another experiment to determine if the free anion degrades the polymer without catalyst present to cyclic was performed where previously synthesized PPC was stirred in solution with  $PPN^+Cl^-$  at elevated temperatures. Over a period of several days, no PC formation was observed as evinced via IR. These results rule out the possibility of the excess salt ring opening the PO and forming cyclic carbonate or attacking the polymer chain in random places and degrading it to PC.

It was also observed that 0.5 equiv of the  $PPN^+X^-$  salts gave a higher TOF than 1 equiv (entries 5, 6, 8, and 9 in Table 2). This same effect is seen when utilizing other epoxides such as TMSO.<sup>28</sup> As we are unable to adequately monitor the PO/ $CO_2$  coupling in situ, by IR spectroscopy, the effect of varying the number of equivalents of  $PPN^+Cl^-$  with TMSO was studied in the presence of catalyst **1a**. Figure 9 shows the absorbance vs time profiles of these reactions

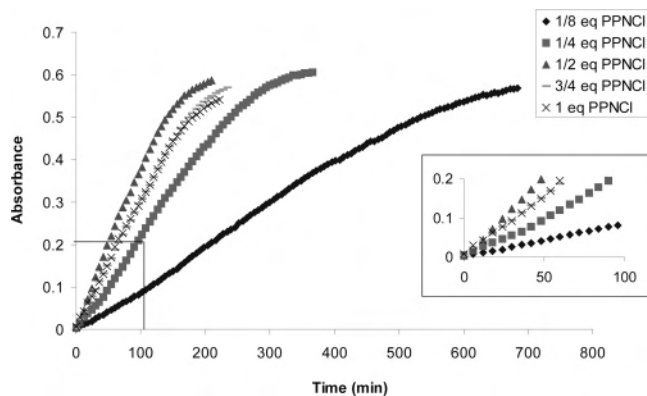
(26) Consistent with this is the observation that, when an identical copolymerization run was carried out in the presence of 2 equiv of the more ion paired  $n-Bu_4NCl$  salt as cocatalyst, there was some copolymer isolated (polymer:cyclic ratio was 25:75).

(27) Bis(triphenylphosphoranylide)ammonium][ $N, N'$ -bis(3,5-di-*tert*-butylsalicylidene)-1,2-ethylene-diiminechromium(III)*bis*-azide] has been isolated and crystallographically characterized in our laboratory by Ryan M. Mackiewicz.

(28) Darensbourg, D. J.; Rodgers, J. L.; Fang, C. C. *Inorg. Chem.* **2003**, *42*, 4498–4500.

(24) Arduengo, A. J., III; Rasika Dias, H. V.; Dixon, D. A.; Harlow, R. L.; Klooster, W. T.; Koetzle, T. F. *J. Am. Chem. Soc.* **1994**, *116*, 6812–6822.

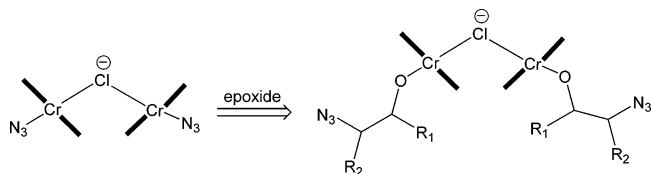
(25) Duong, H. A.; Tekavec, T. N.; Arif, A. M.; Louie, J. *Chem. Commun.* **2004**, 112–113.



**Figure 9.** Absorbance vs time profiles of the growth of copolymer with varying equivalents of  $\text{PPN}^+\text{Cl}^-$ . Conditions used were 100 mg of catalyst **3a** except where  $Z = \text{Cl}$ , 20 mL of epoxide, 80 °C, and 55 bar of  $\text{CO}_2$ .

where it is obvious that when using 0.5 equiv of the cocatalyst the reaction does indeed proceed at a slightly faster rate.

Presently, we do not have a definitive explanation for this complex  $\text{PPN}^+\text{X}^-$  rate behavior. It is however of importance to note that  $\text{PPN}^+\text{X}^-$  salts are insoluble in epoxides. Hence, the catalyst system ( $\text{salenCrX}$  and  $\text{PPN}^+\text{X}^-$ ) must be dissolved in a common organic solvent to form the six-coordinate anionic chromium complex which upon vacuum drying is soluble in the epoxide. It might be possible that chloride can serve as a bridging ligand to two chromium centers, thereby, producing an active catalytic species as depicted in Figure 10. The lone pairs on the chloride allow electron donation to both metal centers while concurrently reducing the amount of anions in solution. However, repeated attempts to crystallize this species have not met with success.



**Figure 10.** Possible catalyst complex when 0.5 equiv of the  $\text{PPN}^+\text{X}^-$  salts are used.

### Summary

In this report, we have optimized the selective production of PPC from propylene oxide and carbon dioxide in the absence of an organic solvent utilizing ( $\text{salen}$ ) $\text{CrX}$  catalysts. That is, employing a salen ligand with a phenylene backbone and *tert*-butyl substituents in the 3 and 5 positions of the phenolate rings along with an anionic cocatalyst, TOFs for copolymer production close to  $200 \text{ h}^{-1}$  at 60°C have been achieved. Furthermore, it was demonstrated that *in this instance* 0.5 equiv of the costly  $\text{PPN}^+\text{X}^-$  cocatalyst was preferable over 1 equiv, and the presence of excess anionic cocatalyst strongly favors the formation of the cyclic derivative, PC. There is still a tremendous need for the design of metal catalysts that will selectively and efficiently produce polycarbonate from a wide variety of *alicyclic* and *aliphatic* epoxide monomers, especially those derived from sustainable resources.

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