

# Mechanistic Insight into the Initiation Step of the Coupling Reaction of Oxetane or Epoxides and CO<sub>2</sub> Catalyzed by (salen)CrX Complexes

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The most active and robust current catalysts for the copolymerization of carbon dioxide and epoxides or oxetanes, (salen)CrX in conjunction with PPNX (PPN<sup>+</sup> = (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>) or *n*-Bu<sub>4</sub>NX (X = Cl, N<sub>3</sub>, CN, NCO), are characterized both in solution by infrared spectroscopy and in the solid-state by X-ray crystallography. All anions (X) afford six-coordinate chromium(III) PPN<sup>+</sup> or *n*-Bu<sub>4</sub>N<sup>+</sup> salts composed of *trans*-(salen)CrX<sub>2</sub><sup>-</sup> species. Of the X groups investigated in (salen)CrX, chloride is easily displaced by the others, that is, the reaction of (salen)CrCl with 2 equiv of N<sub>3</sub><sup>-</sup>, CN<sup>-</sup>, or NCO<sup>-</sup> quantitatively provide (salen)Cr(N<sub>3</sub>)<sub>2</sub><sup>-</sup>, (salen)Cr(CN)<sub>2</sub><sup>-</sup>, and (salen)Cr(NCO)<sub>2</sub><sup>-</sup>, respectively. On the other hand, addition of less than 2 equiv of azide to (salen)CrCl leads to a Schlenk (ligand redistribution) equilibrium of the three possible anions both in solution and in the solid-state as shown by X-ray crystallography and electrospray ionization mass spectrometry. It was further demonstrated that all *trans*-(salen)CrX<sub>2</sub><sup>-</sup> anions react with the epoxide or oxetane monomers in TCE (tetrachloroethane) solution to afford an equilibrium mixture containing (salen)CrX·monomer, with the oxetane adduct being thermodynamically more favored. The ring-opening steps of the bound cyclic ether monomers by X<sup>-</sup> were examined, revealing the rate of ring-opening of the epoxides (cyclohexene oxide and propylene oxide) to be much faster than of oxetane, with propylene oxide faster than cyclohexene oxide. Furthermore, both X anions in (salen)CrX<sub>2</sub><sup>-</sup> were shown to be directly involved in monomer ring-opening.

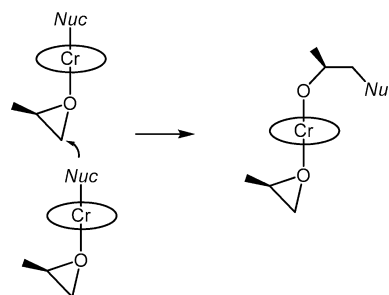
## Introduction

Since the discovery of the epoxide/CO<sub>2</sub> copolymerization process by Inoue and co-workers in 1969,<sup>1</sup> the scientific community exploring this area has directed much of its attention to finding discrete well-defined metal catalysts for this reaction.<sup>2</sup> Among the most effective, and importantly most robust, catalysts for these processes involve Schiff base complexes of M(III), where M = Cr, Co, or Al.<sup>3,4</sup> Jacobsen and co-workers have clearly shown that an intermolecular bimetallic pathway for asymmetric nucleophilic ring-opening of epoxides catalyzed by (salen)CrX derivatives is operative

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- (1) (a) Inoue, S.; Koinuma, H.; Tsuruta, T. *J. Polym. Sci., Part B: Polym. Phys.* **1969**, *7*, 287. (b) Inoue, S.; Koinuma, H.; Tsuruta, T. *Makromol. Chem.* **1969**, *130*, 210.
- (2) (a) Aida, T.; Ishikawa, M.; Inoue, S. *Macromolecules* **1986**, *19*, 8. (b) Kruper, W. J.; Dellar, D. D. *J. Org. Chem.* **1995**, *60*, 725. (c) Darensbourg, D. J.; Holtcamp, M. W. *Macromolecules* **1995**, *28*, 7577. (d) Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **1998**, *120*, 11018.
- (3) (a) Coates, G. W.; Moore, D. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6618. (b) Chisholm, M. H.; Zhou, Z. *J. Mater. Chem.* **2004**, *14*, 3081.
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## Scheme 1



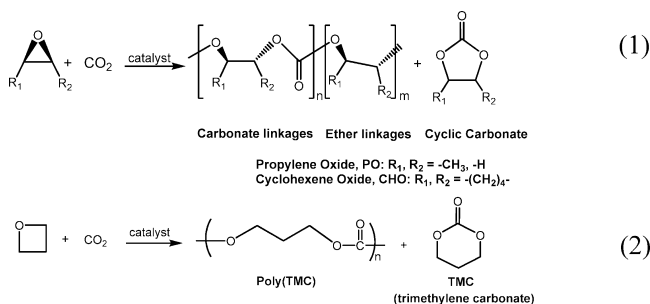
(Scheme 1).<sup>5</sup> However, in the absence of an added or endogenous source of cocatalyst these five-coordinate complexes are not effective catalysts for the copolymerization of CO<sub>2</sub> and epoxides. This is presumably a consequence of the metal center being too electrophilic to facilitate the CO<sub>2</sub> insertion reaction.<sup>6</sup> Relevant to this latter point, we have recently demonstrated the ring-opening reaction of epoxides

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to be second-order in the five-coordinate Schiff base complex of manganese(III), (tfacacen)MnN<sub>3</sub> (tfacacen = *N,N'*-bis-(trifluoroacetylacetonate)-1,2-ethylenediamine), and at the same time to be ineffective at catalyzing the copolymerization of epoxide and CO<sub>2</sub>.<sup>7</sup>

In the presence of various cocatalysts, for example, heterocyclic amines and anionic nucleophiles, however, (salen)MX (M = Cr and Co) are very reactive catalysts for the coupling of epoxides and CO<sub>2</sub>.<sup>4</sup> The chromium catalytic system has been similarly shown to be active for the copolymerization of oxetane and CO<sub>2</sub> via a closely related mechanistic pathway.<sup>8</sup> Anions derived from PPN<sup>+</sup>-((Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>) and tetraalkylammonium<sup>+</sup> salts are the most active cocatalysts discovered to date.

Herein, we wish to report on the structural characterization of complexes resulting from the reaction of (salen)CrX complexes with PPNX or *n*-Bu<sub>4</sub>NX salts which serve as catalysts for the copolymerization processes described in eqs 1 and 2. In addition, comparative monomer binding to the chromium center and subsequent ring-opening steps of epoxides and oxetanes will be discussed.



## 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. Toluene was freshly distilled from sodium/benzophenone. Ethanol was freshly distilled from Mg/I<sub>2</sub>. 1,1,2,2-tetrachloroethane was freshly distilled from CaH<sub>2</sub>. Diethyl ether, dichloromethane, pentane, and hexanes were purified by an MBraun Manual Solvent Purification System packed with Alcoa F200 activated alumina desiccant. Other chemicals employed in these studies, and their origin in parentheses, are provided below. Oxetane (Alfa Aesar) was freshly distilled from CaH<sub>2</sub> and stored in the freezer of the glovebox. Cyclohexene oxide (TCI) was freshly distilled from CaH<sub>2</sub> before use. PPNN<sub>3</sub>, PPNCN, and PPNCO (PPN<sup>+</sup> = (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>) were synthesized according to a published procedure.<sup>9</sup> Tetra-*n*-butylammonium bromide (Aldrich), tetra-*n*-butylammonium iodide (Eastman), and tetra-*n*-butylammonium chloride (TCI) were recrystallized from acetone/diethyl ether before use. Tetra-*n*-butylammonium azide (TCI) was stored in the freezer of the glovebox upon arrival. Bone-dry carbon dioxide supplied in a high-pressure cylinder and 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>10</sup>

IR spectra were recorded on a Mattson 6021 Fourier Transform (FT) IR spectrometer with a MCT detector. Analytical elemental analysis was provided by Canadian Microanalytical Services Ltd. High-pressure reaction kinetic measurements were performed using an ASI ReactIR 1000 reaction analysis system with a stainless steel Parr autoclave modified with a permanently mounted ATR crystal (SiComp) at the bottom of the reactor (purchased from Mettler Toledo).

**Cocatalyst, Substrate Binding, and Ring-Opening Steps Examined by Infrared Spectroscopy.** Cocatalyst, substrate binding, and ring-opening step studies were examined by solution infrared spectroscopy. The catalytic system used in these studies was a (salen)CrCl complex **1** (*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-ethylenediamino chromium(III) chloride) or a (salen)CrN<sub>3</sub> complex **2** (*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-ethylenediamino chromium(III) azide) in the presence of *n*-Bu<sub>4</sub>NN<sub>3</sub> or *n*-Bu<sub>4</sub>NCl as cocatalyst, and using TCE as the solvent.

**Statistical Deconvolution of FTIR Spectra.** Where noted FTIR spectra were deconvoluted using Peakfit, version 4.12 (Peakfit for Windows, v. 4.12; SYSTAT Software Inc., San Jose, CA, 2003). Statistical treatment was a residuals method utilizing a combination Gaussian–Lorentzian summation of amplitudes with a linear baseline and Savitsky–Golay smoothing.

**X-ray Structural Studies.** Single crystals of (salen)Cr(Cl)<sub>2</sub><sup>−</sup>*n*-Bu<sub>4</sub>N<sup>+</sup> (complex **3**) were obtained by layering hexanes into a saturated dichloromethane solution of the corresponding (salen)CrCl complex (*N,N'*-bis(3-*tert*-butyl-5-methoxysalicylidene)-1,2-phenylenediamino chromium(III) chloride) containing 2 equiv of *n*-Bu<sub>4</sub>NCl. Anal. Calcd for C<sub>47</sub>H<sub>72</sub>Cl<sub>4</sub>CrN<sub>3</sub>O<sub>4</sub>: C, 60.25; H, 7.15; N, 4.49. Found: C, 60.73; H, 7.91; N, 4.45.

Single crystals of (salen)Cr(N<sub>3</sub>)<sub>2</sub><sup>−</sup>*n*-Bu<sub>4</sub>N<sup>+</sup> (complex **4**) were obtained in a similar manner employing 2 equiv of *n*-Bu<sub>4</sub>NN<sub>3</sub>. Anal. Calcd for C<sub>46</sub>H<sub>70</sub>CrN<sub>9</sub>O<sub>4</sub>: C, 63.86; H, 8.16; N, 14.57. Found: C, 61.84; H, 7.96; N, 12.20. IR (TCE, cm<sup>−1</sup>): 2057 (sh) and 2047 (s, N<sub>3</sub><sup>−</sup>). Single crystals of (salen)Cr(CN)<sub>2</sub><sup>−</sup>PPN<sup>+</sup> (complex **5**) were obtained in a similar manner as above employing 2 equiv of PPNCN. Anal. Calcd for C<sub>68</sub>H<sub>64</sub>CrN<sub>5</sub>O<sub>4</sub>P<sub>2</sub>: C, 72.33; H, 5.71; N, 6.20. Found: C, 70.31; H, 6.01; N, 5.80. IR (TCE, cm<sup>−1</sup>): 2118 (w, CN<sup>−</sup>). Single crystals of (salen)Cr(NCO)<sub>2</sub><sup>−</sup>PPN<sup>+</sup> (complex **6**) were obtained in a similar manner as above employing 2 equiv of PPNCO. Anal. Calcd for C<sub>70</sub>H<sub>68</sub>Cl<sub>4</sub>CrN<sub>5</sub>O<sub>6</sub>P<sub>2</sub>: C, 63.16; H, 5.15; N, 5.26. Found: C, 63.12; H, 5.14; N, 5.20. IR (TCE, cm<sup>−1</sup>): 2211 (s, NCO<sup>−</sup>). Single crystals of (salen)Cr(Cl)<sub>x</sub>(N<sub>3</sub>)<sub>y</sub><sup>−</sup>PPN<sup>+</sup> (complex **7**) were obtained in a similar manner as above employing 1 equiv of PPNN<sub>3</sub>. ESI-MS: *m/z* 608.18 [(salen)Cr(Cl)<sub>2</sub>]<sup>−</sup>, 615.23 [(salen)Cr(Cl)(N<sub>3</sub>)]<sup>−</sup>, 622.20 [(salen)Cr(N<sub>3</sub>)<sub>2</sub>]<sup>−</sup>, and 632.23 [(salen)Cr(Cl)(OAc)]<sup>−</sup>. IR (TCE, cm<sup>−1</sup>): 2051 (b, N<sub>3</sub><sup>−</sup>).

For all the crystal structures, a Bausch and Lomb 10× microscope was used to identify suitable crystals. Each crystal was coated in paratone, affixed to a nylon loop, and placed under streaming nitrogen (110 K) on a Bruker-AXS Apex II three-circle, a Bruker-D8 Adv GADDS, or on a Bruker SMART 1000 CCD X-ray diffractometer. Space group determinations were made on the basis of systematic absences and intensity statistics. All crystal structures were solved by direct methods and were refined by full-matrix least-squares on *F*<sup>2</sup>. All hydrogen atoms were placed in idealized positions and refined with fixed isotropic displacement parameters equal to 1.2 (1.5 for methyl protons) times the equivalent isotropic

(6) Darensbourg, D. J.; Mueller, B. L.; Bischoff, C. J.; Chojnacki, S. S.; Reibenspies, J. H. *Inorg. Chem.* **1991**, *30*, 2418.

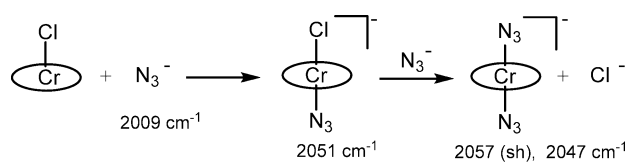
(7) Darensbourg, D. J.; Frantz, E. B. *Inorg. Chem.* **2008**, *47*, 4977.

(8) Darensbourg, D. J.; Moncada, A. I.; Choi, W.; Reibenspies, J. H. *J. Am. Chem. Soc.* **2008**, *130*, 6523.

(9) Demadis, K. D.; Meyer, T. J.; White, P. S. *Inorg. Chem.* **1998**, *37*, 3610.

(10) Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers, J. L.; Fang, C. C.; Billodeaux, D. R.; Reibenspies, J. H. *Inorg. Chem.* **2004**, *23*, 6024.

## Scheme 2



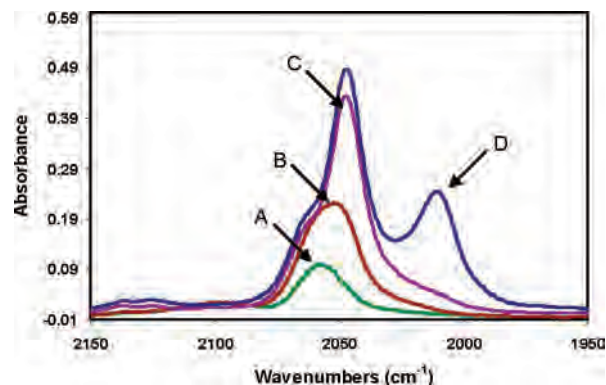
displacements parameters of the atoms to which they were attached. All non-hydrogen atoms were refined with anisotropic displacement parameters.

The following are the programs that were used: data collection and cell refinements, APEX II data collection software, FRAMBO Version 4.1.05 (GADDS)<sup>11</sup> or SMART WNT/2000 Version 5.632;<sup>12</sup> data reductions, APEX II data reduction software or SAINTPLUS Version 6.63;<sup>13</sup> absorption correction, SADABS;<sup>14</sup> structural solutions, SHELXS-97;<sup>15</sup> structural refinement, SHELXL-97;<sup>16</sup> molecular graphics and preparation of material for publication, SHELXTL,<sup>17</sup> version 6.14 and X-Seed, version 1.5.<sup>18</sup>

**Copolymerization Reactions Monitored by *in situ* IR Spectroscopy.** In a typical experiment, the catalyst (*N,N'*-bis(3,5-*tert*-butylsalicylidene)-1,2-cyclohexylenediamino chromium(III) chloride), (complex **8**) cocatalyst and oxetane (4 g) were dissolved in 10 mL of toluene and delivered via the injection port into a 300 mL stainless steel Parr autoclave reactor that was previously dried in vacuo overnight at  $80^\circ\text{C}$  and cooled down to room temperature before the reaction mixture was delivered into it. The autoclave 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 128-scan background spectrum was collected after the reaction mixture was heated to the temperature of the corresponding experiment, the autoclave was then pressurized with 35 bar of  $\text{CO}_2$ , and the infrared spectrometer was set to collect one spectrum every 3 min over a 12 or 24 h period. Profiles of the absorbance at  $1750 \text{ cm}^{-1}$  (polymer) with time were recorded after baseline correction, and analyzed to provide initial reaction rates. (Note: cocatalyst, cocatalyst loading, and temperature varied within each experiment and are described in the Results and Discussion section).

## Results and Discussion

Our first concern was to examine in detail the nature of the soluble catalytic species resulting from the addition of the salt containing the anionic initiator to the (salen)CrX complex. In a typical copolymerization experiment the (salen)CrCl complex is dissolved in neat epoxide or oxetane in the presence of 1–2 equiv of a salt cocatalyst. Anions derived from either the very bulky and less interacting  $\text{PPN}^+$  cation or the more interacting  $n\text{-Bu}_4\text{N}^+$  cation have been shown to be very effective initiators for these copolymeri-



**Figure 1.** Overlay of infrared spectra illustrating azide based cocatalyst dependence. 0.5 equiv of  $n\text{-Bu}_4\text{NN}_3$  (A), 1 equiv of  $n\text{-Bu}_4\text{NN}_3$  (B), 2 equiv of  $n\text{-Bu}_4\text{NN}_3$  (C), and 3 equiv of  $n\text{-Bu}_4\text{NN}_3$  (D).

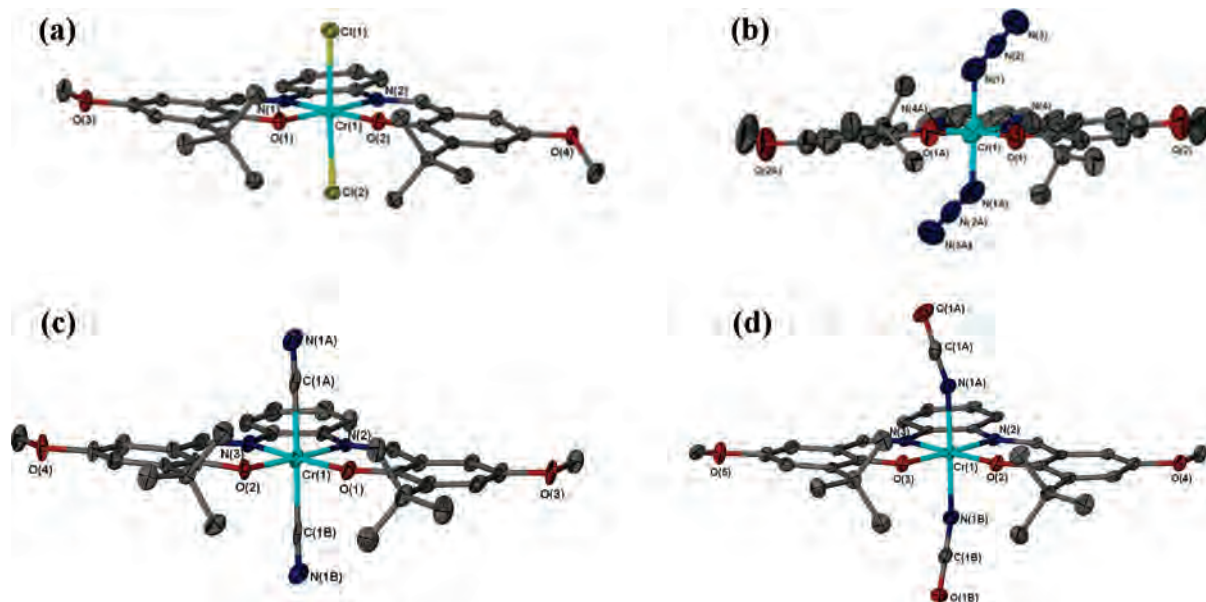
zation processes.<sup>8,19</sup> Although, the PPNX salts have the added desirable feature of being readily available in an anhydrous form, these salts are generally insoluble or very sparingly soluble in low polarity cyclic ethers. Hence, in these instances *pretreatment* of the (salen)CrX complex with PPNX is required to ensure maximum catalytic activity. This is achieved by dissolving the (salen)CrX complex and PPNX salt in a compatible solvent such as methylene chloride, followed by vacuum removal of the solvent prior to introducing the cyclic ether monomer.

The identity of the chromium derivative resulting from the addition of  $n\text{-Bu}_4\text{NX}$  to (salen)CrX was initially investigated by solution infrared spectroscopy for  $X = \text{azide}$  ion, where azide is strongly absorbing in the infrared region around  $2000 \text{ cm}^{-1}$ . The titration of (salen)CrCl (complex **1**) with  $n\text{-Bu}_4\text{NN}_3$  proceeded in a stepwise fashion as illustrated in Scheme 2 via monitoring the  $\nu_{\text{N}_3}$  stretching vibration as depicted in Figure 1. As noted the reaction proceeds all the way to the right, eventually forming an anionic bis-azide complex, (salen)Cr( $\text{N}_3$ )<sub>2</sub><sup>-</sup>. That is, the chloride ligand is easily displaced by an azide ligand in tetrachloroethane solution.<sup>20</sup> Furthermore, the process is irreversible upon subsequent addition of excess  $n\text{-Bu}_4\text{NCl}$ . It should also be pointed out that, as expected, the identical diazide complex can be prepared by the reaction of (salen)CrN<sub>3</sub> with 1 equiv of  $n\text{-Bu}_4\text{NN}_3$ .

The generality of Scheme 2 involving the reaction of (salen)CrCl in the presence of 2 equiv of  $X^-$  ligands other than azide (eq 3) was also noted as revealed by infrared spectral data and, more importantly, X-ray crystallography. Four such six-coordinate anionic chromium(III) complexes have been isolated and characterized as their  $\text{PPN}^+$  or  $n\text{-Bu}_4\text{N}^+$  salts, where  $X^- = \text{Cl}^-$ ,  $\text{N}_3^-$ ,  $\text{CN}^-$ , and  $\text{NCO}^-$  (Figure 2).<sup>21</sup> Crystallographic data pertaining to these crystal structures are provided in Table 1, with selected bond distances listed in Table 2. As anticipated, strong field ligands

(11) FRAMBO:FRAME Buffer Operation, v.41.05; Bruker AXS Inc.: Madison, WI.  
 (12) SMART, v.5.632; Bruker AXS Inc.: Madison, WI.  
 (13) SAINT, v.6.63; Bruker AXS Inc.: Madison, WI.  
 (14) Sheldrick, G. M. SADABS; Bruker AXS Inc.: Madison, WI.  
 (15) Sheldrick, G. M. SHELXS-97; Institut für Anorganische Chemie der Universität: Göttingen, Germany, 1997.  
 (16) Sheldrick, G. M. SHELXL-97; Institut für Anorganische Chemie der Universität: Göttingen, Germany, 1997.  
 (17) Sheldrick, G. M. SHELXTL, v.6.14; Bruker-Nonius Inc.: Madison, WI, 2000.  
 (18) Barbour, L. J. *J. Supramol. Chem.* **2001**, *1*, 189.

(19) (a) Darensbourg, D. J.; Mackiewicz, R. M. *J. Am. Chem. Soc.* **2005**, *127*, 14026. Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers, J. L. *J. Am. Chem. Soc.* **2005**, *127*, 17565.  
 (20) Darensbourg, D. J.; Fitch, S. B. *Inorg. Chem.* **2007**, *46*, 5474.  
 (21) The X-ray crystallographically defined structure of a six-coordinate anionic (salen)Cr( $\text{N}_3$ )<sub>2</sub><sup>-</sup> species has previously been reported by us as its  $\text{PPN}^+$  salt, but we were only able to refine it to an *R* value of 13.15%.<sup>19</sup>

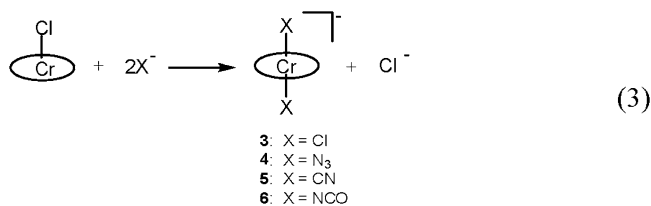


**Figure 2.** Thermal ellipsoid representations of (salen)CrX<sub>2</sub><sup>-</sup> anions, where the salen ligand contains -OMe and -*t*-Bu substituents in the 3,5-positions of the phenolates, respectively, with a phenylene diamino-backbone. H atoms omitted for clarity. Ellipsoids are at the 50% level. (a) *n*-Bu<sub>4</sub>N<sup>+</sup> salt, X = Cl. One molecule of dichloromethane was crystallized in the unit cell. (b) *n*-Bu<sub>4</sub>N<sup>+</sup> salt, X = N<sub>3</sub>. (c) PPN<sup>+</sup> salt, X = CN. Three molecules of dichloromethane were crystallized in the unit cell. (d) PPN<sup>+</sup> salt, X = NCO. Two molecules of dichloromethane were crystallized in the unit cell.

**Table 1.** Crystallographic Data for Complexes **3**, **4**, **5**, **6**, and **7**

	<b>3</b> ·[CH <sub>2</sub> Cl <sub>2</sub> ]	<b>4</b>	<b>5</b> ·[3(CH <sub>2</sub> Cl <sub>2</sub> )]	<b>6</b> ·[2(CH <sub>2</sub> Cl <sub>2</sub> )]	<b>7</b> ·[2(CH <sub>2</sub> Cl <sub>2</sub> )]
empirical formula	C <sub>47</sub> H <sub>72</sub> Cl <sub>4</sub> CrN <sub>3</sub> O <sub>4</sub>	C <sub>46</sub> H <sub>70</sub> CrN <sub>9</sub> O <sub>4</sub>	C <sub>71</sub> H <sub>70</sub> Cl <sub>6</sub> CrN <sub>5</sub> O <sub>4</sub> P <sub>2</sub>	C <sub>70</sub> H <sub>68</sub> Cl <sub>4</sub> CrN <sub>5</sub> O <sub>6</sub> P <sub>2</sub>	C <sub>67.50</sub> H <sub>67</sub> Cl <sub>3</sub> CrN <sub>6</sub> O <sub>4</sub> P <sub>2</sub>
fw	936.88	865.11	1383.96	1331.03	1215.59
temperature (K)	110(2) K	110(2) K	110(2) K	110(2) K	110(2) K
crystal system	triclinic	orthorhombic	triclinic	triclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>Pnna</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	13.039(3)	10.622(10)	12.104(3)	11.961(2)	12.447(2)
<i>b</i> (Å)	13.372(3)	25.105(2)	16.019(4)	15.876(3)	15.076(2)
<i>c</i> (Å)	14.703(3)	17.256(17)	19.970(7)	18.842(4)	18.509(3)
$\alpha$ (deg)	93.050(3)	90	66.377(15)	68.179(10)	70.026(8)
$\beta$ (deg)	101.587(3)	90	80.31(2)	79.346(12)	82.558(9)
$\gamma$ (deg)	104.698(3)	90	79.034(17)	88.643(11)	79.978(9)
<i>V</i> (Å <sup>3</sup> )	2414.4(9)	4602.0(7)	3464.4(18)	3260.5	3205.3(9)
<i>D</i> <sub>c</sub> (Mg/m <sup>3</sup> )	1.289	1.249	1.327	1.356	1.260
<i>Z</i>	2	4	2	2	2
abs coeff(mm <sup>-1</sup> )	0.502	0.301	4.33	3.867	3.261
reflections collected	28288	42139	24726	25681	21367
independent reflections	11323 [ <i>R</i> (int) = 0.0454]	5632 [ <i>R</i> (int) = 0.0986]	9069 [ <i>R</i> (int) = 0.0606]	9249 [ <i>R</i> (int) = 0.0409]	8449 [ <i>R</i> (int) = 0.0965]
data/restraints/ parameters	11323/0/544	5632/0/278	9069/0/810	9249/0/801	8449/565/821
GOF on <i>F</i> <sup>2</sup>	1.001	1.000	1.000	1.000	1.001
final <i>R</i> indices	<i>R</i> <sub>1</sub> = 0.0452	<i>R</i> <sub>1</sub> = 0.0822	<i>R</i> <sub>1</sub> = 0.0843	<i>R</i> <sub>1</sub> = 0.0504	<i>R</i> <sub>1</sub> = 0.0894
[ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>w</sub> = 0.1152	<i>R</i> <sub>w</sub> = 0.2018	<i>R</i> <sub>w</sub> = 0.2478	<i>R</i> <sub>w</sub> = 0.1663	<i>R</i> <sub>w</sub> = 0.2131
final <i>R</i> indices	<i>R</i> <sub>1</sub> = 0.0706	<i>R</i> <sub>1</sub> = 0.2139	<i>R</i> <sub>1</sub> = 0.1344	<i>R</i> <sub>1</sub> = 0.0657	<i>R</i> <sub>1</sub> = 0.1747
(all data)	<i>R</i> <sub>w</sub> = 0.1311	<i>R</i> <sub>w</sub> = 0.2536	<i>R</i> <sub>w</sub> = 0.3210	<i>R</i> <sub>w</sub> = 0.2110	<i>R</i> <sub>w</sub> = 0.2716

such as N<sub>3</sub><sup>-</sup>, CN<sup>-</sup>, and NCO<sup>-</sup> easily displace chloride at ambient temperature because of their greater trans effect.



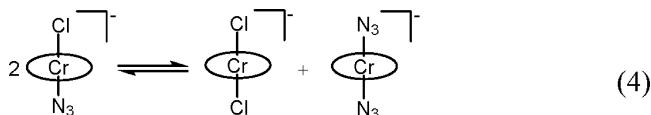
Pertinent to the copolymerization reaction it was of interest to determine the characteristics of the anionic species which forms upon treating (salen)CrCl with only 1 equiv of PPNN<sub>3</sub>. That is, we have demonstrated for cyclohexene oxide/CO<sub>2</sub> copolymerization processes that the rate of copolymer

formation is the same whether we employ (salen)CrCl and 1 equiv of PPNN<sub>3</sub> or (salen)CrN<sub>3</sub> and 1 equiv of PPNCI as catalysts. This observation suggests the differently derived catalyst systems are equivalent. To more definitively address this issue we first examined the infrared data observed in the ν<sub>N<sub>3</sub></sub> region upon treating (salen)CrCl with 1 equiv of *n*-Bu<sub>4</sub>NN<sub>3</sub>. As seen in Figure 1, a broad absorption at 2051 cm<sup>-1</sup> was observed which shifts to lower frequency upon addition of another equivalent of azide. At this point it is also noted that there is *no* free azide in solution as evident by the lack of a band at 2009 cm<sup>-1</sup>. X-ray quality crystals were grown upon layering a concentrated dichloromethane solution of (salen)CrCl and 1 equiv of PPNN<sub>3</sub> with hexanes. Surprisingly, four different anionic species were detected by

**Table 2.** Selected Bond Lengths for Complexes **3**, **4**, **5**, and **6**

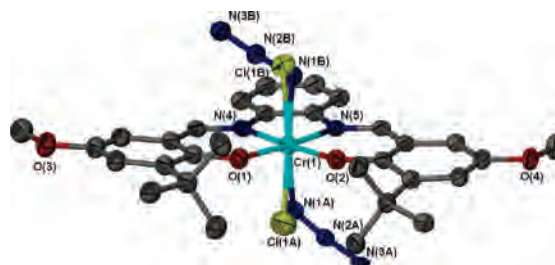
	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
Cr–O <sub>salen</sub> ligand	1.9245(15)	1.915(3)	1.907(5)	1.926(3)
	1.9220(15)		1.919(4)	1.928(3)
Cr–N <sub>salen</sub> ligand	2.0016(17)	2.007(4)	2.017(6)	2.020(3)
	2.0189(17)		2.026(5)	2.023(3)
Cr–N <sub>apical</sub> ligand		2.050(4)		2.016(4)
				2.025(3)
N–N <sub>apical</sub> ligand		1.174(5)		
		1.168(6)		
Cr–Cl <sub>apical</sub> ligand	2.3236(7)			
	2.3959(7)			
Cr–C <sub>apical</sub> ligand			2.104(9)	
			2.126(10)	
C–N <sub>apical</sub> ligand			1.155(10)	
			1.144(10)	
C–O <sub>apical</sub> ligand				1.210(5)
				1.206(5)

X-ray crystallography, that is, (salen)CrCl<sub>2</sub><sup>−</sup>, (salen)Cr(N<sub>3</sub>)<sub>2</sub><sup>−</sup>, and two different forms of (salen)Cr(N<sub>3</sub>)Cl<sup>−</sup> (see Table 1, Figure 3 and Supporting Information). The two forms of the mixed ligand complex results from the fact that the salen ligand is not completely planar. These crystals were further analyzed by electron-spray ionization mass spectroscopy (ESI-MS). The parent ions of (salen)CrCl<sub>2</sub><sup>−</sup>, (salen)Cr(N<sub>3</sub>)Cl<sup>−</sup>, and (salen)Cr(N<sub>3</sub>)<sub>2</sub><sup>−</sup> were observed in the negative mode of the ESI-MS spectrum at 608.18, 615.23, and 622.20 *m/z*, respectively. In addition the parent ion of (salen)Cr(Cl)(OAc)<sup>−</sup> was also detected which resulted from the reaction of (salen)CrCl<sub>2</sub><sup>−</sup> with acetic acid which is used in the mass spectral analysis experiment. These results from infrared spectroscopy, X-ray crystallography, and mass spectral analysis all suggest that when (salen)CrCl is treated with 1 equiv of azide, a Schlenk (ligand redistribution) equilibrium as shown in eq 4 is most likely formed.

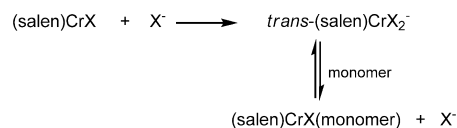
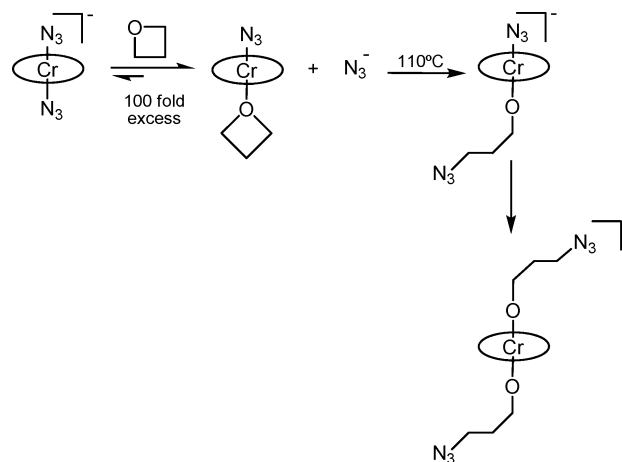


**Substrate Binding and Ring-Opening Step Studies as Examined by Solution Infrared Spectroscopy and *in situ* Infrared Techniques.** Subsequent to examining the nature of the catalyst system employed in these copolymerization reactions, our next challenge was to investigate in depth the monomer binding to the metal center and its consequent ring-opening via the anionic initiator. This was accomplished by adding X<sup>−</sup> to the five-coordinate chromium(III) complex in TCE to yield *trans*-(salen)CrX<sub>2</sub><sup>−</sup>. Upon adding an excess of the cyclic ether monomers, an equilibrium process was established as depicted in Scheme 3.

The equilibrium position and subsequent ring-opening reaction differ significantly with the nature of the monomer. For example, comparing propylene oxide and oxetane, these monomers have similar steric requirements, but the ring-strain energies of propylene oxide and oxetane have been calculated to be 27.3 and 25.5 kcal/mol, and their p*K*<sub>b</sub> values are 6.94 and 3.13, respectively.<sup>22</sup> To illustrate how these differences affect the binding of these monomers to the metal center and subsequent ring-opening step, we have examined



**Figure 3.** Thermal ellipsoid plot of complex **7**. Ellipsoids are at the 50% level. The salen ligand contains –OMe and *t*-Bu substituents in the 3,5 positions of the phenolates respectively, with a phenylene diamino backbone. H atoms and PPN<sup>+</sup> cation are omitted for clarity. Two dichloromethane molecules were crystallized in the unit cell and are omitted for clarity. Selected bond lengths (Å): Cr(1)–Cl(1A) = 2.319(8); Cr(1)–Cl(1B) = 2.363(7); Cr(1)–N(1A) = 2.01(2), Cr(1)–N(1B) = 2.04(3); N(1A)–N(2A) = 1.212(15); N(2A)–N(3A) = 1.218(12); N(1B)–N(2B) = 1.232(15); N(2B)–N(3B) = 1.201(13).

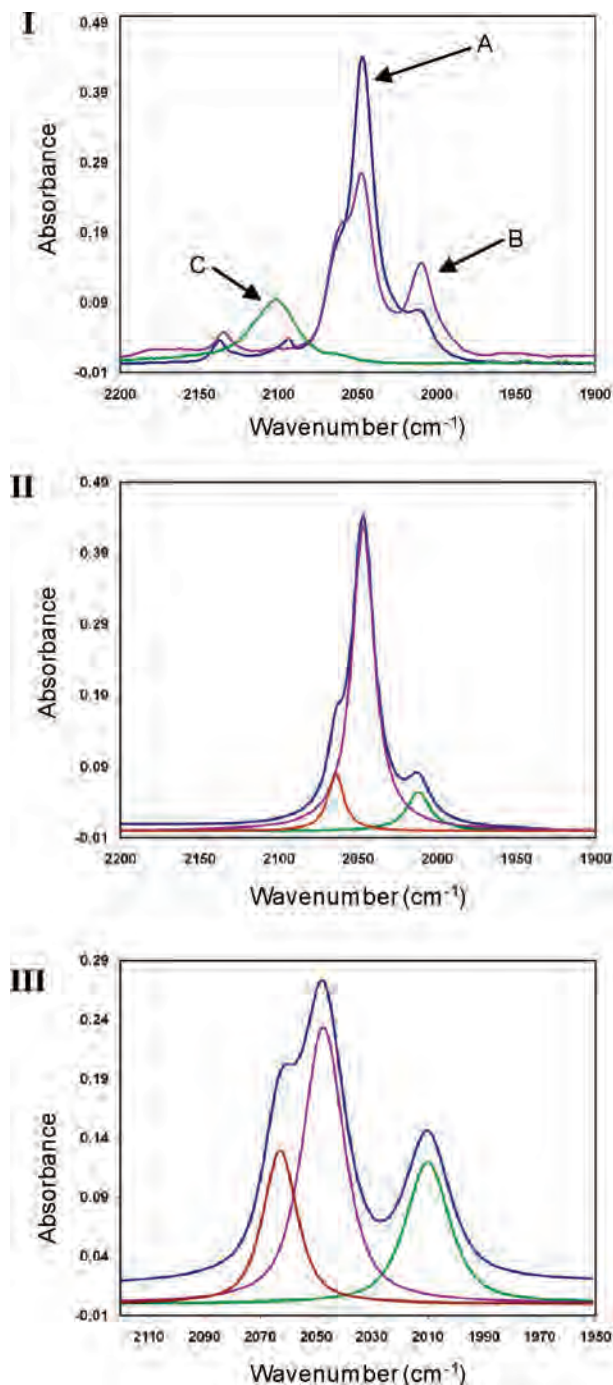
**Scheme 3****Scheme 4**

cyclohexene oxide, propylene oxide, and oxetane as substrates for these processes by solution infrared spectroscopy and by *in situ* infrared techniques.

For the solution infrared spectroscopy studies we utilized the (salen)CrX complexes (X = Cl or N<sub>3</sub>), where the salen ligand contained di-*tert*-butyl substituents in the 3,5-positions of the phenolate rings and an ethylene backbone for the diamine (complexes **1** and **2**). The azide anion derived from the very soluble *n*-Bu<sub>4</sub>NN<sub>3</sub> was employed in these studies since the ν<sub>N<sub>3</sub></sub> stretching vibration provides accessible probes for both anion binding and ring-opening steps. The results of studies involving oxetane as the monomer are presented first as depicted in Scheme 4 and Figure 4.

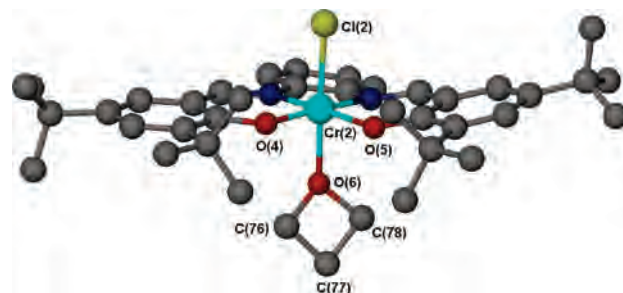
As indicated in Scheme 4 and revealed by the infrared spectrum **A** in Figure 4, upon addition of slightly more than 1 equiv of *n*-Bu<sub>4</sub>NN<sub>3</sub> to (salen)CrN<sub>3</sub>, the six-coordinate bis-azide complex (salen)Cr(N<sub>3</sub>)<sub>2</sub><sup>−</sup> forms at ambient temperature.

(22) (a) Pell, A. S.; Pilcher, G. *Trans. Faraday Soc.* **1965**, *61*, 71. (b) Yamashita, Y.; Tsuda, T.; Okada, M.; Iwatsuki, S. *J. Polym. Sci., Part A: Polym. Chem.* **1966**, *4*, 2121.



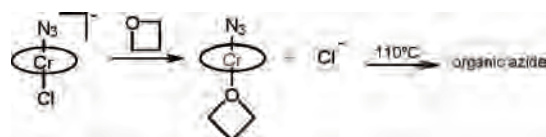
**Figure 4.** (I) Spectra of TCE solutions of chromium salen azide complex with 1 equiv of *n*-Bu<sub>4</sub>NN<sub>3</sub> (A), after addition of 100 equiv of oxetane at ambient temperature (B), and after heating the reaction solution at 110 °C for 3 h (C). Data taken from ref 8. (II) Deconvoluted spectrum of A. (III) Deconvoluted spectrum of B.

Subsequent addition of 100-fold excess of oxetane displaces some of the azide ligand as seen by an increase in the absorption at 2099 cm<sup>-1</sup> because of free azide with a concomitant decrease in the infrared band at 2047 cm<sup>-1</sup> of the (salen)Cr(N<sub>3</sub>)<sub>2</sub><sup>-</sup> species. In addition, a new ν<sub>N<sub>3</sub></sub> stretching band appears at 2061 cm<sup>-1</sup> which was assigned to (salen)Cr(N<sub>3</sub>)•oxetane, spectrum B in Figure 4. Confirmation of this assignment was made by the isolation of single crystals of the oxetane adduct suitable for analysis by X-ray crystallography (Figure 5). The ring-opening of the metal



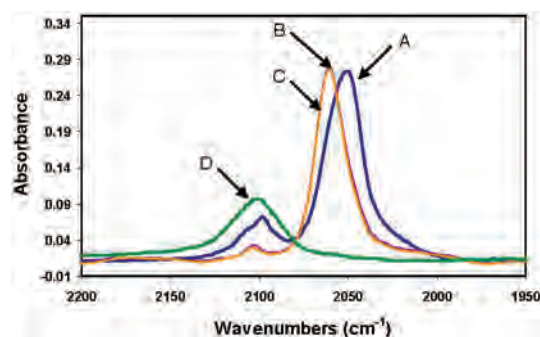
**Figure 5.** Ball-and-stick representation of the X-ray defined structure of (salen)CrCl•oxetane adduct, where the salen ligand contains *t*-Bu substituents in the 3,5 positions of the phenolates respectively, with a phenylene diimine backbone. Data taken from ref 8.

#### Scheme 5

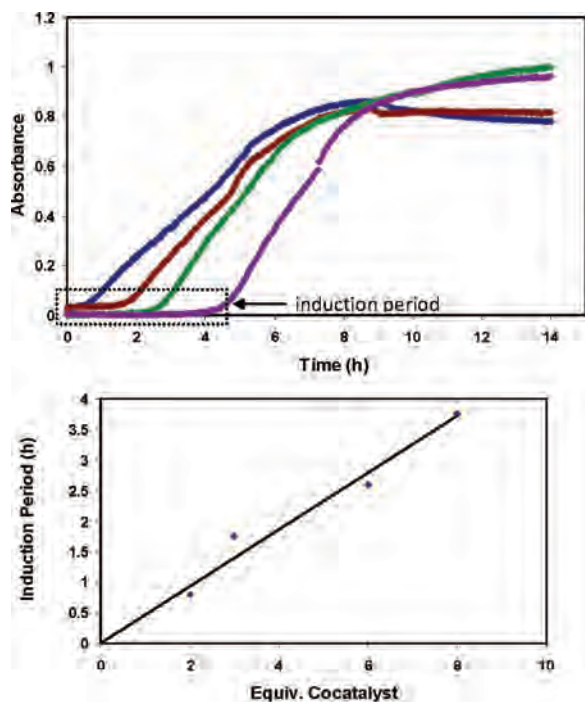


bound oxetane monomer by azide was not observed at ambient temperature. Indeed, only after heating the reaction solution for 3 h at 110 °C did the metal azide species disappear accompanied by the appearance of an organic azide infrared band at 2100 cm<sup>-1</sup> (spectrum C in Figure 4). That is, following the oxetane ring-opening process, the only ν<sub>N<sub>3</sub></sub> band present in the infrared spectrum C is that of the organic azide, with *no* observable free or metal bound azide ν<sub>N<sub>3</sub></sub> vibrations.

A similar series of experiments were carried out to further investigate the initial ring-opening step of oxetane employing the (salen)CrN<sub>3</sub> complex in the presence of 1 equiv of *n*-Bu<sub>4</sub>NCl. The results of this inquiry are shown in Scheme 5 and Figure 6. Consistent with our earlier observations, upon addition of *n*-Bu<sub>4</sub>NCl to (salen)CrN<sub>3</sub>, a mixed anionic six-coordinate species is formed at ambient temperature which displays a ν<sub>N<sub>3</sub></sub> absorption at 2051 cm<sup>-1</sup>. Further addition of 100-fold excess of oxetane leads to displacement of the chloride ligand as revealed by the appearance of a ν<sub>N<sub>3</sub></sub> band at 2061 cm<sup>-1</sup> corresponding to the (salen)Cr(N<sub>3</sub>)•oxetane adduct, as well as no ν<sub>N<sub>3</sub></sub> vibration for the free azide ion. Hence, the chloride ligand is selectively and quantitatively displaced by oxetane at an oxetane concentration where the



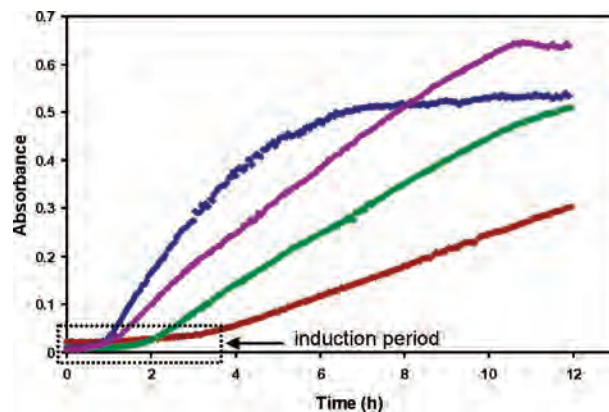
**Figure 6.** Spectra of TCE solutions of chromium salen azide complex with 1 equiv of *n*-Bu<sub>4</sub>NCl. (A), after addition of 100 equiv of oxetane at ambient temperature (B), after stirring the reaction solution for 24 h ambient temperature (C), and after heating the reaction solution for 3 h at 110 °C (D).



**Figure 7.** Time dependent reaction profiles depicting the growth of the copolymer at  $1750\text{ cm}^{-1}$  from oxetane and  $\text{CO}_2$ , utilizing  $(\text{salen})\text{CrCl}$  with different equivalents of *n*-Bu<sub>4</sub>NN<sub>3</sub> at  $110\text{ }^\circ\text{C}$ : 2 equiv of *n*-Bu<sub>4</sub>NN<sub>3</sub> (blue line), 3 equiv of *n*-Bu<sub>4</sub>NN<sub>3</sub> (red line), 6 equiv of *n*-Bu<sub>4</sub>NN<sub>3</sub> (green line), 8 equiv of *n*-Bu<sub>4</sub>NN<sub>3</sub> (purple line).

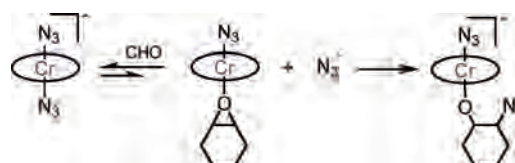
azide ligand is only partially displaced in the  $(\text{salen})\text{Cr}(\text{N}_3)_2^-$  species (see Figure 4, spectrum **B**). Oxetane ring-opening was detected in this instance after heating the reaction solution for 3 h at  $110\text{ }^\circ\text{C}$ , which lead to the appearance of an organic azide band at  $2100\text{ cm}^{-1}$  (Figure 6, spectrum **D**). Of importance to note here, is that oxetane ring-opening occurs by the azide ligand, which as stated before supports the fact that the azide ligand in  $(\text{salen})\text{Cr}(\text{N}_3)(\text{O}-(\text{CH}_2)_3-\text{N}_3)^-$  also ring-opens an oxetane monomer.

Additional studies of the initiation step for the coupling reaction of oxetane and carbon dioxide were undertaken using *in situ* infrared techniques.<sup>23</sup> In these studies a slightly modified  $(\text{salen})\text{CrCl}$  complex was employed, that is one containing di-*tert*-butyl substituents in the 3,5-positions of the phenolates with a cyclohexylenediamino backbone, along with *n*-Bu<sub>4</sub>NN<sub>3</sub> as anion source. We have previously shown this to be the most active catalyst system we have thus far investigated for this copolymerization process. As evident in Figure 4, upon the addition of 100-fold excess of oxetane to the catalyst system in solution an equilibrium is established between the bis-azide complex,  $(\text{salen})\text{Cr}(\text{N}_3)_2^-$ , and the oxetane adduct,  $(\text{salen})\text{Cr}(\text{N}_3)\cdot\text{oxetane}$ . This equilibrium process greatly favors the neutral oxetane adduct in pure oxetane solution. On the other hand, in the presence of a large excess of azide ion initiator it favors the bis-azide species, and hence should retard the initial ring-opening step of the copolymerization process. Figure 7 depicts the reaction profiles for copolymer formation during the copolymerization of oxetane and  $\text{CO}_2$  utilizing  $(\text{salen})\text{CrCl}$  in the presence of



**Figure 8.** Temperature dependent reaction profiles depicting the growth of the copolymer at  $1750\text{ cm}^{-1}$  for oxetane and  $\text{CO}_2$ , utilizing  $(\text{salen})\text{CrCl}$  with 2 equiv of *n*-Bu<sub>4</sub>NN<sub>3</sub>: Reaction temperature =  $80\text{ }^\circ\text{C}$  (red line), reaction temperature =  $90\text{ }^\circ\text{C}$  (green line), reaction temperature =  $100\text{ }^\circ\text{C}$  (purple line), and reaction temperature =  $110\text{ }^\circ\text{C}$  (blue line).

#### Scheme 6



varying quantities of *n*-Bu<sub>4</sub>NN<sub>3</sub>. As is readily observed in Figure 7, an induction period is evident for the copolymerization process which increases as the numbers of equivalents of *n*-Bu<sub>4</sub>NN<sub>3</sub> increases (see inset). This induction period is attributed to an inhibition of oxetane binding in the presence of excess azide ions which preferentially coordinate to the chromium(III) center thereby retarding the ring-opening process.

A brief induction period of several minutes is generally observed for the copolymerization of oxetane and  $\text{CO}_2$  carried out at  $110\text{ }^\circ\text{C}$  during the addition of carbon dioxide where the temperature temporarily drops by  $20\text{ }^\circ\text{C}$ . This would be anticipated since we have demonstrated earlier that the oxetane ring-opening step is relatively slow at  $110\text{ }^\circ\text{C}$  (Figure 4). We have further investigated the temperature dependence of this initial oxetane ring-opening step during the copolymerization reaction employing  $(\text{salen})\text{CrCl}$  and 2 equiv of *n*-Bu<sub>4</sub>NN<sub>3</sub> in the temperature range  $80\text{--}110\text{ }^\circ\text{C}$ . As observed in Figure 8, the induction period is lengthened as the reaction temperature is lowered, being most significant in the  $80\text{--}90\text{ }^\circ\text{C}$  temperature range. The induction period is not greatly different in the temperature range  $100\text{--}110\text{ }^\circ\text{C}$ . Nevertheless, it *must* be pointed out at this time that the selectivity for cyclic carbonate versus copolymer formation is also temperature dependent; hence, the difference noted in Figure 8 cannot be ascribed to temperature alone.

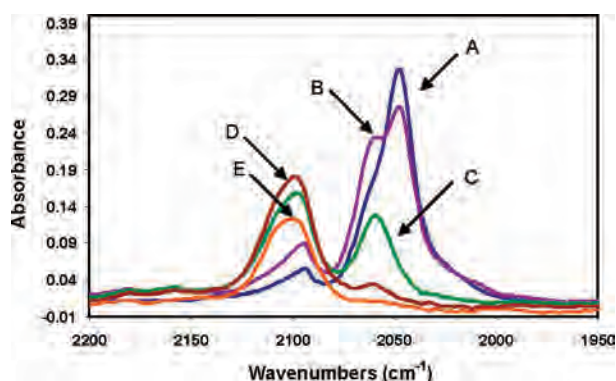
In an analogous manner we have examined the initial ring-opening steps for cyclohexene oxide (CHO) and propylene oxide in the presence of the  $(\text{salen})\text{CrCl}/n\text{-Bu}_4\text{NN}_3$  catalyst system. This study was designed to provide a semiquantitative comparison of processes involving three- and four-membered cyclic ethers. Scheme 6, along with Figures 9 and 10 summarize our findings. As expected, on the basis of their relative ring strain energies, the three-membered cyclic

(23) Darensbourg, D. J.; Rodgers, J. L.; Mackiewicz, R. M.; Phelps, A. L. *Catal. Today* **2004**, *98*, 485.

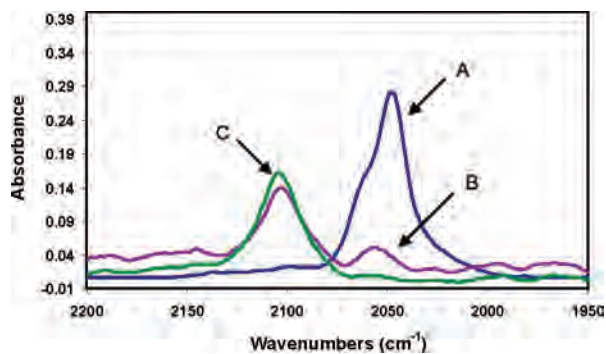
ethers, cyclohexene oxide, and propylene oxide undergo ring-opening under much milder conditions than their four-membered counterpart, oxetane. A bit more unanticipated was the significantly greater ease with which propylene oxide was ring-opened by azide compared to cyclohexene oxide.

Other information apparent from these experiments (Figures 4 and 9) is that the equilibrium reaction between (salen)Cr(N<sub>3</sub>)<sub>2</sub><sup>-</sup> and 100-fold excess of oxetane proceeded further to completion than the comparable process involving cyclohexene oxide with formation of (salen)Cr(N<sub>3</sub>)•cyclohexene oxide ( $\nu_{N_3}$  @ 2058 cm<sup>-1</sup>). That is, the infrared spectra in Figure 9 reveal a smaller decrease in the bis-azide complex at 2047 cm<sup>-1</sup> than seen in Figure 4, as well as a lack of initial formation of free azide ions at 2009 cm<sup>-1</sup>. This is consistent with the lower basicity of three-membered versus four-membered cyclic ethers. As previously noted for the oxetane ring-opening process, both inorganic azide ligands are converted to organic azides.

In a similar manner the initial ring-opening step of the cyclohexene oxide/CO<sub>2</sub> copolymerization process was investigated employing a (salen)CrN<sub>3</sub> complex and 1 equiv of *n*-Bu<sub>4</sub>NCl. The results of this study are quite comparable to that for the oxetane/CO<sub>2</sub> process as seen in Scheme 7, with the only difference being that ring-opening of cyclohexene oxide occurs at ambient temperature.

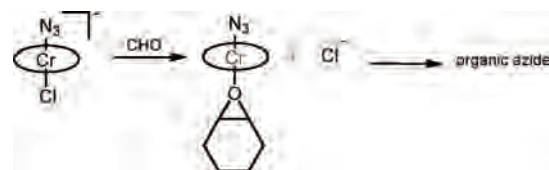


**Figure 9.** Spectra of TCE solutions of chromium salen chloride complex with 2 equiv of *n*-Bu<sub>4</sub>NN<sub>3</sub> (A), after addition of 100 equiv of cyclohexene oxide at ambient temperature (B), after stirring the reaction solution for 2 h at ambient temperature (C), after stirring the reaction solution for 4 h at ambient temperature (D), and after stirring the reaction solution for 24 h at ambient temperature (E).



**Figure 10.** Spectra of TCE solutions of (salen)CrCl with 2 equiv of *n*-Bu<sub>4</sub>NN<sub>3</sub> (A). Immediately after addition of 100 equiv of propylene oxide at ambient temperature (B). Reaction solution stirred for 15 min at ambient temperature (C).

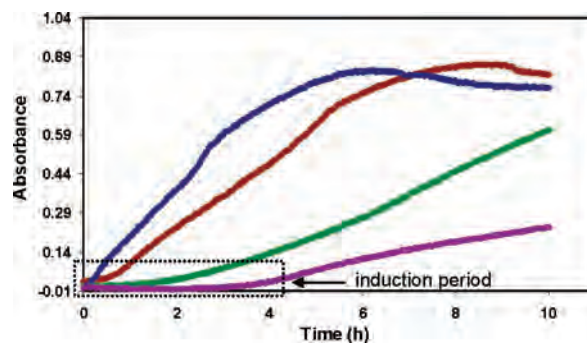
**Scheme 7**



### Nature of Anionic Initiator (Cocatalyst) on the Initial Ring-Opening Step of the Copolymerization Process.

As previously noted, the formation of the anionic six-coordinate species of the form *trans*-(salen)CrX<sub>2</sub><sup>-</sup> readily occurs upon treating (salen)CrCl with 2 equiv of a salt of X<sup>-</sup> (eq 3). The next step in the process involves binding and subsequent ring-opening of the cyclic ether monomer, which in the case of oxetane is a highly energetic process. Hence, based on the nature of the anion X<sup>-</sup>, there should be a significant variation in the initiation step which is a function of both its binding ability to chromium(III) and its propensity for ring-opening monomer. To investigate this dependence the copolymerization of oxetane/CO<sub>2</sub> was examined by *in situ* infrared spectroscopy utilizing (salen)CrCl and 2 equiv of *n*-Bu<sub>4</sub>NX. Figure 11 depicts the reaction profiles for the formation of poly(trimethylene carbonate) involving either 2 equiv of *n*-Bu<sub>4</sub>NN<sub>3</sub> or *n*-Bu<sub>4</sub>NCl. As evident in Figure 11 a short induction period is seen when using *n*-Bu<sub>4</sub>NN<sub>3</sub>, and *no* induction period was detected when employing *n*-Bu<sub>4</sub>NCl as cocatalyst. This observation is consistent with our earlier findings where oxetane more easily replaces a chloride ligand from chromium(III) than an azide ligand. The following copolymerization reaction (monomer enchainment) processes as expected are not affected.

The initiation step for the copolymerization of oxetane and carbon dioxide was also examined in the presence of (salen)CrCl and other anions containing intense absorptions in the infrared, namely, CN<sup>-</sup> and NCO<sup>-</sup>. These anions, like azide, exhibit induction periods for copolymer formation (see Figure 11). This is consistent with the observation that CN<sup>-</sup> and NCO<sup>-</sup> readily displace Cl<sup>-</sup> from (salen)CrCl, and at the same time are more difficult to be replaced by oxetane. Finally, it should be noted here that because of the ease of cyclohexene oxide ring-opening, *no* induction period is observed for the copolymerization reaction of cyclohexene oxide and CO<sub>2</sub> employing either



**Figure 11.** Reaction profiles depicting the growth of the copolymer at 1750 cm<sup>-1</sup> from oxetane and CO<sub>2</sub> at 110 °C, utilizing (salen)CrCl with 2 equiv of *n*-Bu<sub>4</sub>NN<sub>3</sub> (red line), 2 equiv of *n*-Bu<sub>4</sub>NCl (blue line), 2 equiv of *n*-Bu<sub>4</sub>NNCO (green line), and 2 equiv of *n*-Bu<sub>4</sub>NCN (purple line).



PPNX or  $n\text{-Bu}_4\text{NX}$  ( $X = \text{Cl}^-$  or  $\text{N}_3^-$ ) as cocatalyst along with  $(\text{salen})\text{CrX}$  complexes.

### Concluding Remarks

The addition of salts of PPNX or  $n\text{-Bu}_4\text{NX}$  to  $(\text{salen})\text{CrX}$  complexes yield [*trans*- $(\text{salen})\text{CrX}_2$ ][PPN or  $n\text{-Bu}_4\text{N}$ ] complexes which have been crystallographically defined for  $\text{salen} = N,N'$ -bis(3-*tert*-butyl-5-methoxysalicylidene)-1,2-phenylenediamino and  $X = \text{Cl}, \text{N}_3, \text{CN},$  and  $\text{NCO}$ . The latter three derivatives are readily synthesized by the addition of 2 equiv of  $\text{PPN}^+$  or  $n\text{-Bu}_4\text{N}^+$  salts of  $\text{N}_3^-$ ,  $\text{CN}^-$ , and  $\text{NCO}^-$  to  $(\text{salen})\text{CrCl}$ . On the other hand, the addition of 1 equiv of  $n\text{-Bu}_4\text{NN}_3$  to  $(\text{salen})\text{CrCl}$  leads initially to *trans*- $(\text{salen})\text{Cr}(\text{N}_3)\text{Cl}^-$  which exists in TCE solution in a Schlenk equilibrium with the corresponding symmetric *trans*- $(\text{salen})\text{CrX}_2^-$  anions as revealed by X-ray crystallography and ESI-MS. For all anions examined the displacement of X in *trans*- $(\text{salen})\text{CrX}_2^-$  with the cyclic ethers (propylene oxide, cyclohexene oxide, or oxetane) to provide *trans*- $(\text{salen})\text{CrX}\cdot$ cyclic ether adducts in TCE solution greatly favored the anionic complexes. The ring-opening of bound epoxides by  $X^-$  readily occurred at ambient temperature, with propylene oxide being ring-opened by azide at a significantly

faster rate than the corresponding process involving cyclohexene oxide. On the contrary, the ring-opening of bound oxetane occurred readily at temperatures near 100 °C and greater, with this process being retarded in the presence of excess X anions such as  $\text{N}_3^-$ ,  $\text{CN}^-$ , or  $\text{NCO}^-$  which strongly bind to the chromium(III) center. It was further shown that both inorganic azides are involved in epoxide or oxetane ring-opening leading to formation of the similar organic azides.

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**Supporting Information Available:** X-ray crystallographic files in CIF format for the structure determination of complexes **3**, **4**, **5**, **6**, and **7**. Resolved four structures of the anions found in complex **7** with accompanying selected bond distances and angles. IR spectra of TCE of  $(\text{salen})\text{CrN}_3/n\text{-Bu}_4\text{NCl}$  after cyclohexene oxide at ambient temperature. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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