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Article

An Exploration of the Coupling Reactions of Epoxides and Carbon Dioxide Catalyzed by Tetramethyltetraazaannulene Chromium(III) Derivatives: Formation of Copolymers versus Cyclic Carbonates

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The high catalytic activity of a tetramethyltetraazaannulene (tmtaa) chromium complex toward the copolymerization of cyclohexene oxide and carbon dioxide to discriminatively provide poly(cyclohexylene carbonate) has directed further studies into the capabilities of the catalyst system. Various [PPN]X ($PPN^+ =$ bis(triphenylphosphoranylidene)-ammonium) cocatalysts, where X = Cl, N_3, Br, CN, and $OBzF_5$, in the presence of (tmtaa)CrCl were examined for catalytic reactivity and selectivity for polycarbonate formation, achieving turnover frequencies of 1500 h^{-1} at 80 °C in the case of PPNCl. The catalyst system was examined under varied pressures and found to be active even at 1 bar of CO_2 pressure. In addition to cyclohexene oxide, the (tmtaa)CrCl complex was investigated for catalytic activity toward the coupling of carbon dioxide with propylene oxide, isobutylene oxide, 1,2-epoxyhexane, styrene oxide, and 4-vinyl cyclohexene oxide. Activation energies were found for the copolymerization reaction between cyclohexene oxide and carbon dioxide utilizing the tetramethyltetraazaannulene catalyst system to be 67.1 ± 4.2 $kJ \cdot mol^{-1}$ and 65.2 ± 2.5 $kJ \cdot mol^{-1}$ in neat epoxide and with methylene chloride cosolvent, respectively, upon monitoring these processes by *in situ* infrared spectroscopy. Supplementary to the studies involving (tmtaa)CrCl, electronic effects at the metal center on catalytic activity were examined through derivatization of the tmtaa ligand, resulting in increased activity as electron-donating substituents were added.

Introduction

In recent years, carbon dioxide has received much attention in both the scientific community and the general public. With atmospheric concentrations of CO_2 on the rise and the impending threat of "global climate change", many scientists are looking for ways to reduce CO_2 emissions. Others are concentrating their efforts on capture and sequestering or utilizing this greenhouse gas for industrial or health and safety benefits. Carbon dioxide has found growing application in refrigerants, water treatment, dry-cleaning, the food and agriculture industry, and chemical synthesis, either as a solvent or reagent or for chemical separation.[1]

For over a decade, our research efforts have focused on the utilization of carbon dioxide for a more environmentally benign route toward the production of polycarbonates. Currently, polycarbonates are produced industrially by the interfacial reaction between a caustic solution containing a diol, typically bisphenol A, and phosgene in a chlorinated solvent or the neat reaction between a diol and diphenyl carbonate, where the diphenyl carbonate is typically synthesized using phosgene. The resultant polycarbonate possesses excellent marks for impact strength, optical clarity, durability, and processability and has found useful applications in optics, electronics, sheeting, and the medical and automotive industries, among others.[2] This process poses several environmental concerns. Carcinogenic chlorinated solvents are used in the biphasic reaction, while phosgene gained infamy in World War I when it was employed as a chemical weapon. Coming into a more recent spotlight, bisphenol A is currently under scrutiny for leaching from poly(bisphenol A) carbonate products and causing hormone

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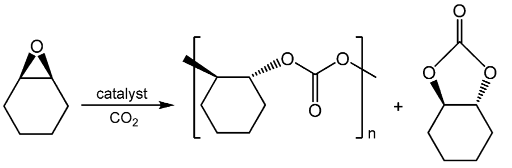
(1) (a) De Simone, J. *Greenhouse Gas Control Technologies, Proceedings of the International Conference on Greenhouse Gas Control Technologies, 6th*, Kyoto, Japan, Oct. 1−4, 2002; Elsevier Ltd.: Oxford, U.K., 2003; p 33. (b) Vansant, J. In *Recovery and Utilization of Carbon Dioxide*; Aresta, M., Ed.; Klumer Academic Publishers: The Netherlands, 2003; pp 3−50.

(2) Advances in Polycarbonates. *Proceedings of Symposium of the American Chemical Society*, March 2003, Washington, DC; Brunelle, D. J., Korn, M. R., Eds.; American Chemical Society: Washington, DC, 2005; ACS Symposium Series 898, pp281.

10.1021/ic801728e CCC: $40.75

disruption and reproductive damage to infants.[3] The aforementioned, more environmentally benign route for the production of polycarbonates under investigation in our laboratories, shown in eq 1, involves the alternative coupling of epoxides to carbon dioxide, facilitated by a metal catalyst. This subject has been reviewed comprehensively[4a,b] and includes studies involving both transition and main group metal catalysts.[4c,d]



(1)

The catalyst system presented in this correspondence utilizes a well-studied tetramethyltetraazaannulene (tmtaa) ligand architecture.[5] 5,7,12,14-Tetramethyldibenzo-[*b,i*][1,4,8,11]tetraazacyclotetradecine was first synthesized by Jaeger[6] and later modified by Goedken and co-workers,[7] involving the nickel-template condensation of acetylacetone and *o*-phenylenediamine. The resultant macrocycle contains a four-nitrogen donor core similar to that of porphyrin and, like porphyrin, can bind a plethora of transition metals, both early and late.[5] Despite their similarities, tmtaa has a pore size ~0.1 Å smaller than that of porphyrin. Steric interactions between the methyl groups and aromatic hydrogens cause the ligand to adopt a saddle shape, which, concomitantly, redirects the bonding orbitals of the donor plane slightly upward. This pair of ligand attributes results in a bound metal atom residing above the donor plane. The degree of deviation is largely dependent upon the size of the metal ion, leading to the largest deviations with early transition metals and little to no deviation with later metals. The nonplanarity of the tmtaa ligand also grants considerable solubility in common organic solvents without the need for derivation, a major drawback with porphyrin complexes. Another advantage of the tmtaa ligand is its relative low cost compared to that of porphyrins, with the tmtaa ligand being about 10-fold less expensive. The complexes of interest to our group incorporate a chromium(III) metal center, as an expansion of previous and ongoing work with the chromium(III) salen systems. The (tmtaa)CrCl complex (Figure 1), first reported by Cotton and co-workers,[8] has previously been communicated by us to be a highly active and robust catalyst for the copolymerization of cyclohexene oxide and carbon dioxide.[9] Furthermore, it is assumed to operate in the presence of cocatalysts such as PPNX (PPN$^+$ = $(Ph_3P)_2N^+$) by a similar mechanism to that of its (salen)CrX counterparts (Scheme 1).

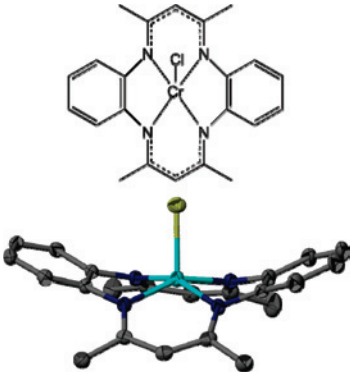
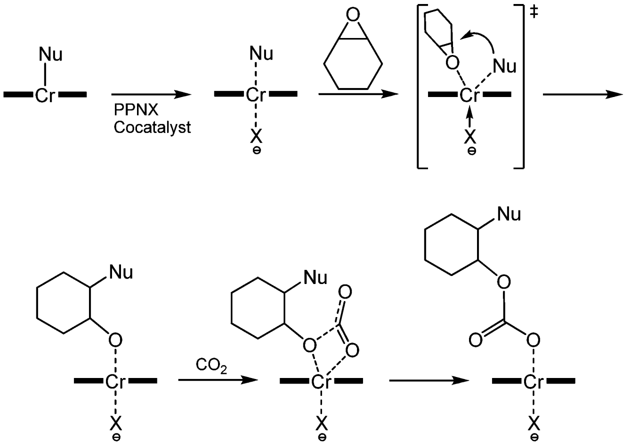


Figure 1. Skeletal representation and crystallographic structure of the (tmtaa)CrCl catalyst for the copolymerization of epoxides and carbon dioxide.

Scheme 1



The scope of this presentation is to report the further investigation and optimization of the (tmtaa)CrCl system as it pertains to ligand derivatization, the nature of the cocatalyst, and dependence on temperature and pressure, and to employ different epoxides with the hope of accessing an assortment of polycarbonates and ascertaining their inherent properties. Comprehensive kinetic studies of the copolymerization reaction performed both with a cosolvent and under solventless conditions as monitored by in situ high-pressure infrared spectroscopy are also included in this study.

Experimental Section

Reagents and Methods. All chemicals and solvents were purified using the appropriate methods immediately prior to use unless otherwise noted. 2,4-Pentanedione, *o*-phenylenediamine, 4,5-diamino-*o*-xylene, 4,5-dichloro-*o*-phenylenediamine, nickel acetate tetrahydrate, chromium(III) chloride, ammonium hexafluorophosphonate, bis(triphenylphosphoranylidene)ammonium chloride, sodium azide, potassium bromide, sodium cyanide, and sodium pentafluorobenzoate were purchased from Aldrich, TCI, Alfa Aesar, Strem, and Acros chemical companies and used without further purification. Unless otherwise specified, all manipulations were carried out on a double-manifold Schlenk vacuum line under an atmosphere of argon or in an argon-filled glovebox. ^{1}H and ^{13}C NMR spectra were acquired on a Varian Inova 300 MHz super-

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(4) (a) Darensbourg, D. J. *Chem. Rev.* **2007**, *107*, 2388–2410. (b) Coates, G. W.; Moore, D. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6618. (c) Xiao, Y.; Wang, Z.; Ding, K. *Chem.—Eur. J.* **2005**, *11*, 3668–3678. (d) Xiao, Y.; Wang, Z; Ding, K. *Macromolecules* **2006**, *39*, 128–137.

(5) (a) Cotton, F. A.; Czuchajowska, J. *Polyhedron* **1990**, *9*, 1553–2566. (b) Mountford, P. *Chem. Soc. Rev.* **1998**, *27*, 105–116.

(6) Jaeger, E. G. *Z. Anorg. Chem.* **1969**, *364*, 177–191.

(7) Goedken, V. L.; Molin-Case, J. A.; Whang, Y.-A. *J. Chem. Soc., Chem. Commun.* **1973**, 337–338.

(8) Cotton, F. A.; Czuchajowska, J.; Falvello, L. R.; Feng, X. *Inorg. Chim. Acta* **1990**, *172*, 135–136.

(9) Darensbourg, D. J.; Fitch, S. B. *Inorg. Chem.* **2007**, *46*, 5474–5476.

conducting NMR spectrometer. Infrared spectra were recorded using a Bruker Tensor 27 FTIR spectrometer.

Synthesis of 5,7,12,14-Tetramethyldibenzo[*b*,*i*][1,4,8,11]-tetraazacyclotetradecine. The ligand synthesis used was as previously reported by Goedken and Weiss[10] and is as follows. A total of 2 equiv of *o*-phenylenediamine was stirred with 1 equiv of $Ni(OAc)_2 \cdot 4H_2O$ in refluxing methanol for 5 min, resulting in a dark blue solution. An aqua-green solution was obtained upon the addition of 2 equiv of 2,4-pentanedione. The reaction was refluxed for 3 days, cooled at −4 °C, and filtered. The purple microcrystalline Ni(tmtaa) was washed with methanol, dried in vacuo, and weighed. This complex was then suspended in absolute ethanol, and anhydrous HCl was bubbled through the slurry overnight. The reaction flask was cooled and the white precipitate filtered and collected. This solid, a tetrachloronickelate salt of the ligand, was dissolved in water, and 3 equiv of ammonium hexafluorophosphonate (based on Ni(tmtaa)) was added to precipitate the ligand as a bis(hexafluorophosphonate) salt. The neutral ligand was obtained by the dropwise addition of triethylamine to a methanol solution of the PF_6^- salt until the golden yellow product no longer precipitated from solution. The neutral ligand, H_2tmtaa, was filtered, dried in the air, and weighed (36.7% overall yield).

Synthesis of 5,7,12,14-Tetramethylbis-4,5-dimethylbenzo-[*b*,*i*][1,4,8,11]tetraazacyclo-tetradecine (H_2omtaa) and 5,7,12,14-Tetramethylbis-4,5-dichlorobenzo[*b*,*i*][1,4,8,11]-tetraazacyclotetradecine (H_2tmtaaCl_4). The syntheses of H_2omtaa (octamethyltetraazaannulene) and H_2tmtaaCl_4 were adapted from literature procedures[11] and followed the procedure outlined above with the appropriate substituted *o*-phenylenediamines.

Synthesis of (tmtaa)CrCl (1), (omtaa)CrCl (2), and (tmtaaCl_4)CrCl (3). Catalysts were synthesized following the literature procedure for (tmtaa)CrCl reported by Cotton and coworkers, whereby the appropriate free ligand and anhydrous $CrCl_3$ were refluxed in benzene along with 2 equiv of triethylamine for 3 days.[8] The dark burgundy solution was filtered and the solvent removed in vacuo. The resultant material was triturated with hexanes to extract any unreacted ligand. The product is somewhat moist, air-sensitive, and typically synthesized prior to use as a catalyst. Isolated yields for the synthesis of (tmtaa)CrCl, (omtaa)CrCl, and (tmtaaCl_4)CrCl were 62%, 84%, and 77%, respectively, and are largely dependent on the quantity of benzene used to keep the product in solution. Anal. calcd for $C_{26}H_{30}N_4CrCl \cdot 2H_2O$: C, 59.82; H, 6.56; N, 10.73. Found: C, 59.88; H, 6.66; N, 10.19. Anal. calcd for $C_{22}H_{18}N_4CrCl_5 \cdot 2H_2O$: C, 43.77; H, 3.67; N, 9.28. Found: C, 44.15; H, 4.45; N, 8.78.

Synthesis of PPNX ($X = N_3$, Br, CN, or $OBzF_5$). The syntheses were slight modifications of those previously reported in the literature.[12] PPNCl was stirred overnight with a slight excess of NaX in absolute ethanol. The solution was filtered and the filtrate dried in vacuo. The salt was recrystallized from dichloromethane and ether, filtered, and dried in vacuo.

Copolymerization of Epoxides and Carbon Dioxide. High-pressure copolymerizations were carried out using a stainless steel Parr autoclave modified with a SiComp window to allow for attenuated total reflectance spectroscopy using infrared radiation on an ASI ReactIR 1000 in situ probe. For each copolymerization reaction, the desired amount of catalyst and the appropriate equivalent(s) of PPNX cocatalyst were dissolved in dichloromethane and allowed to stir for 30 min before being dried in vacuo. This activated mixture was then dissolved in 20 mL of neat epoxide and injected via the injection port into the autoclave that had been heated to the appropriate reaction temperature. A 128-scan background spectrum was collected followed by charging of the autoclave with CO_2 to the desired pressure. Concurrently with the autoclave being charged with CO_2, data collection started with a single 128-scan spectrum taken every 3 min during the course of the reaction. Profiles of the absorbance at 1750 cm^{-1} (polycarbonate) and ~1808 cm^{-1} (cyclic carbonate) versus time were recorded after baseline correction. After cooling and venting the autoclave, the polymer was extracted with dichloromethane and the solution allowed to evaporate. The unpurified mixture was then redissolved in a minimal amount of dichloromethane and precipitated with a 1 M methanol solution of hydrochloric acid. Upon settling, the supernatant solution containing the catalyst and cyclic carbonate was decanted and discarded. The purified polymer that remained was dried in vacuo at 60 °C overnight. The highest catalytic activities were obtained from the crystalline catalyst. All other activities reported herein are for comparative purposes only.

For the copolymerizations conducted for the purposes of cocatalyst comparison, the same procedure outlined above was used. The various PPNX salts used include azide, chloride, cyanide, bromide, and pentafluorobenzoate. In each run, 50 mg of catalyst with either 1 or 2 equiv of PPNX cocatalyst were used along with 20 mL of cyclohexene oxide and 500 psi of carbon dioxide, maintained at 80 °C throughout the reaction.

Investigations to determine how chloro and methyl substituents affect the electronic nature, and ultimately catalyst activity, of the ligand system were carried out at 80 °C with the catalyst, 2 equiv of $PPNN_3$, 20 mL of cyclohexene oxide, and 500 psi of carbon dioxide. The amount of catalyst was adjusted to maintain a constant monomer-to-initiator ratio ($M/I = 1700$); therefore, 57 mg and 66 mg of Cr(omtaa)Cl and Cr(tmtaaCl_4)Cl were used, respectively.

The copolymerizations done for the pressure dependence studies were conducted at 80 °C using 50 mg of (tmtaa)CrCl catalyst, 2 equiv of PPNCl, 20 mL of cyclohexene oxide, and the desired pressure of carbon dioxide. The different epoxides attempted for the copolymerization reaction were treated in the same manner as previously prescribed, involving 50 mg of (tmtaa)CrCl catalyst, 2 equiv of PPNCl as a cocatalyst, 20 mL of epoxide, and 500 psi of carbon dioxide. The reaction temperature varied depending on the epoxide used.

Cosolvent copolymerizations were conducted using the same procedure outlined above with the exception that the reaction mixture was comprised of 75 mg of catalyst, 2 equiv of $PPNN_3$ cocatalyst, 10 mL of epoxide, and 10 mL of dichloromethane in order to keep all reaction products in solution. The reactions were carried out at 500 psi of carbon dioxide and a range of temperatures. Reaction rates were monitored by the appearance of the carbonate bands in the infrared for the copolymer and cyclic carbonate.

Copolymerizations conducted for the kinetic study of (tmtaa)CrCl utilizing an anionic cocatalyst in neat epoxide were carried out at the desired temperature using 50 mg of catalyst, 2 equiv of $PPNN_3$, 20 mL of cyclohexene oxide, and 500 psi of carbon dioxide. A best fit line was applied to the first few minutes of each copolymer and cyclic carbonate profiles of each polymerization and used to determine their respective initial rates. These initial rates were used to calculate the energies of activation for polycarbonate and cyclic carbonate formation.

X-Ray Structural Studies. A Leica microscope, equipped with a polarizing filter, was used to identify suitable crystals from a sample of crystals from the same habit. The representative crystal was coated in a cryogenic protectant, such as paratone, and affixed

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(10) Goedken, V. L.; Weiss, M. C. *Inorg. Synth.* **1980**, *20*, 115.

(11) Place, D. A.; Ferrara, G. P.; Harland, J. J.; Dabrowiak, J. C. *J. Heterocycl. Chem.* **1980**, *17*, 439–443.

(12) L'Epplatenier, F. A.; Pugin, A. *Helv. Chim. Acta* **1975**, *58*, 917–929.

Table 1. Crystallographic Data for Complex **2** and H_2tmtaaCl_4

	(omtaa)CrCl (2)	H_2tmtaaCl_4
empirical formula	$C_{26}H_{30}ClCrN_4$	$C_{22}H_{20}Cl_4N_4$
fw, g/mol	485.99	482.22
temp (K)	293(2)	110(2)
wavelength	0.71073	0.71073
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a (Å)	8.974(11)	9.644(4)
b (Å)	12.227(15)	7.846(4)
c (Å)	13.150(16)	28.364(13)
α (deg)	79.57(2)	90
β (deg)	75.63(2)	98.908(4)
γ (deg)	76.14(2)	90
cell volume (Å^3)	1346(3)	2120.1(17)
Z	2	4
density (calcd)	1.199	1.511
abs coeff (mm^{-1})	0.543	0.577
obsd no. of reflns	9863	18086
no. of unique reflns ($I > 2\sigma$)	4526	3615
GoF	1.000	1.002
R,[a] % [$I > 2\sigma$]	8.00	8.79
R_w,[a] % [$I > 2\sigma$]	11.79	22.31

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$.

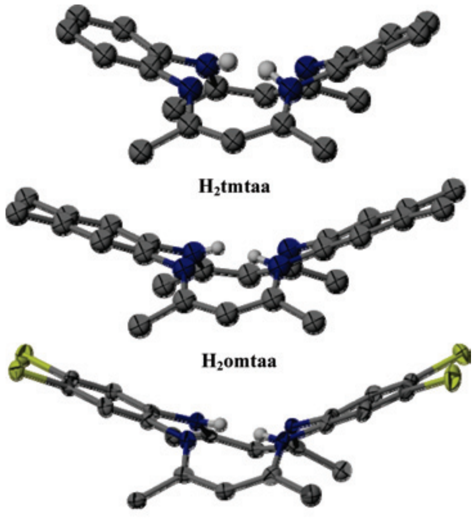

Figure 2. X-ray crystal structures of H_2tmtaa, H_2omtaa, and H_2tmtaaCl_4, respectively. Thermal ellipsoids are shown at the 50% probability level with hydrogens omitted for clarity with the exception of the amine hydrogens.

to a nylon sample loop attached to a copper mounting pin. The mounted crystals were then placed in a cold nitrogen stream (Oxford) maintained at 110 K on either a Bruker SMART 1000, GADDS, or APEX 2 three-circle goniometer.

The X-ray data were collected on either a Bruker CCD, GADDS, or APEX 2 diffractometer and covered more than a hemisphere of reciprocal space by a combination of three (or nine in the case of the GADDS) sets of exposures; each exposure set had a different φ angle for the crystal orientation, and each exposure covered 0.3° in ω. Crystal data and details on collection parameters are given in Table 1. The crystal-to-detector distance was 5.0 cm for all crystals. Crystal decay was monitored by repeating the data collection for 50 initial frames at the end of the data set and analyzing the duplicate reflections and was found to be negligible. The space group was determined on the basis of systematic absences and intensity statistics.[13] The structure was solved by direct methods and refined by full-matrix least-squares on F^2. All non-H atoms were refined with anisotropic displacement parameters. All H atoms attached to C and N atoms were placed in idealized positions and refined using a riding model with aromatic C−H = 0.93 Å, methyl C−H = 0.96 Å, and amine N−H = 0.86 Å and with fixed isotropic displacement parameters equal to 1.2 (1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of the atom to which they are attached. The methyl groups were allowed to rotate about their local 3-fold axis during refinement.

For all structures, the following were used: data reduction, SAINTPLUS (Bruker[13]); program used to solve structures, SHELXS (Sheldrick[14]); program used to refine structures, SHELXL-97 (Sheldrick[15]); molecular graphics and preparation of material for publication, SHELXTL-Plus version 5.0 (Bruker[16]) and XSEED.

Results and Discussion

The tetramethyltetraazaannulene (tmtaa) ligand was synthesized by the nickel template condensation of *o*-phenylenediamine with pentane-2,4-dione as described initially by Jaeger[6] and later modified by Goedken and co-workers.[7] The neutral H_2tmtaa ligand was isolated following removal of the dianionic tmtaa from Ni(tmtaa) in absolute ethanol by anhydrous HCl, precipitation as the PF_6^- salt affording [H_4tmtaa][PF_6]$_2$, and neutralization with triethylamine. The chromium(III) derivative was prepared following the literature procedure reported by Cotton and co-workers from H_2tmtaa and anhydrous chromium(III) chloride in refluxing benzene in the presence of 2 equiv of triethylamine.[8] Other tetraazaannulene ligands were similarly prepared from the appropriately substituted *o*-phenylenediamine and their corresponding Cr(III) derivatives synthesized in an analogous manner to that described for (tmtaa)CrCl. Although most of the studies reported at this time involved the (tmtaa)CrCl complex, other derivatives examined for catalytic activity include complexes **2** and **3**, that is, (omtaa)CrCl and (tmtaaCl_4)CrCl, where the crystal structures of H_2omtaa and H_2tmtaaCl_4 are shown in Figure 2.

The X-ray structures of H_2tmtaa and H_2omtaa have been reported elsewhere.[7,17] In the course of our studies, we have structurally characterized H_2tmtaaCl_4. These three structures of the protonated ligands exhibit only minimal differences in bond distances and bond angles, with the largest distinction being the degree of distortion inherent to the saddle shape. In order to quantify the magnitude of planar distortion, the angles between phenylenediamine moieties were measured and found to be 133.5°, 136.2°, and 140.4° for H_2tmtaa, H_2tmtaaCl_4, and H_2omtaa, respectively. No obvious trend could be seen from these deviations, which could merely be due to crystal packing. The chromium(III) complex derived from H_2omtaa, complex **2**, has been fully characterized by X-ray crystallography. A thermal ellipsoid representation of

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(13) *SAINT-Plus*, version 6.02; Bruker: Madison, WI, 1999.

(14) Sheldrick, G. *SHELXS-86*; Institut fur Anorganische Chemie der Uniseritat Gottingen: Gottingen, Germany, 1986.

(15) Sheldrick, G. *SHELXL-97*; Institut fur Anorganische Chemie der Uniseritat Gottingen: Gottingen, Germany, 1997.

(16) *SHELXTL*, version 5.0; Bruker: Madison, WI, 1999.

(17) (a) Alcock, N. W.; Cannadine, J. C.; Errington, W.; Moore, P.; Wallbridge, M. G. H. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1994**, *50*, 2037–2039. (b) Buzatu, D. A.; Nolan, S. P.; Stevens, E. D. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1995**, *51*, 1855–1857.

complex **2** is shown in Figure 3, where the chromium center resides 0.4209 above the nitrogen donor plane, along with the atom labeling scheme. Table 2 lists comparative selected bond distances and bond angles for the closely related (tmtaa)CrCl and (omtaa)CrCl derivatives. As can be seen from Table 2, there exist only minor structural differences between these two complexes.

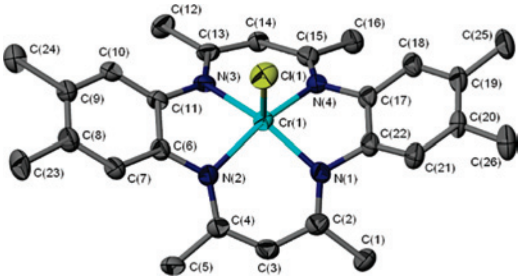


Figure 3. Thermal ellipsoid plot of **2** at 50% probability. Hydrogen atoms omitted for clarity.

Table 2. Selected Bond Distances and Angles for (tmtaa)CrCl and (omtaa)CrCl

	(tmtaa)CrCl[a]	(omtaa)CrCl
Cr−N1 (Å)	1.9881(18)	1.947(6)
Cr−N2 (Å)	1.9745(17)	2.000(6)
Cr−N3 (Å)	1.9900(18)	1.995(6)
Cr−N4 (Å)	1.9716(17)	1.957(7)
Cr−Cl (Å)	2.2607(7)	2.244(3)
N1−Cr−N2 (deg)	92.98(7)	91.8(3)
N2−Cr−N3 (deg)	81.76(7)	82.8(3)
N3−Cr−N4 (deg)	92.96(7)	91.8(3)
N1−Cr−N4 (deg)	81.78(7)	83.2(2)
Cr−N_4 (Å)	0.4235	0.4209

[a] Data taken from structure determination in ref .

In a previous publication, we have reported the kinetic parameters for the copolymerization of cyclohexene oxide and propylene oxide with carbon dioxide employing (salen)-CrCl as a catalyst.[18] In a later report, we compared the use of various cocatalysts (*N*-heterocyclic amines, phosphines, and salts containing anionic initiators) for enhancing the effectiveness of the (salen)CrCl catalyst system and clearly established that greater catalytic activity is noted when employing salts possessing nucleophilic anions.[19] Hence, for the (tmtaa)CrCl catalytic studies, only anionic initiators were utilized. Despite its sensitivity to aerobic environments, the catalyst is very robust under polymerization conditions and does not appear to degrade over time, as evidenced by the constant rate of polymer formation observed from peak profiles obtained from in situ infrared monitoring of the copolymerization process.

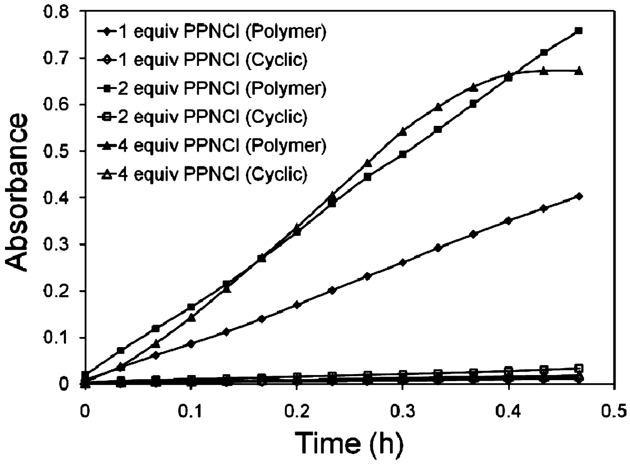
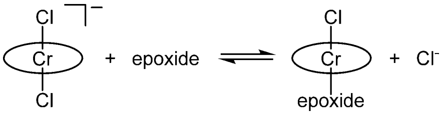


Figure 4. Reaction profiles indicating copolymer and cyclic carbonate formation with time for the copolymerization of cyclohexene oxide and CO_2 in the presence of (tmtaa)CrCl and 35 bar of carbon dioxide at 80 °C at various quantities of added PPNCl.

Copolymerization Reactivity Studies Utilizing Various PPNX Salts as Initiators. In efforts aimed at developing an optimal catalytic system, several anionic initiators were examined for their effectiveness as cocatalysts for the copolymerization of cyclohexene oxide and carbon dioxide in the presence of (tmtaa)CrCl. For this study, the PPN(bis(triphenylphosphoranylidene)ammonium) salts were chosen due to their ease of being prepared anhydrously, and the weakly interacting PPN cation provides an essentially free anion for interaction with the chromium center and ring-opening of the epoxide monomer. In our preliminary report covering the (tmtaa)CrCl catalyst utilizing $PPNN_3$ as a cocatalyst, we observed maximum catalytic activity when employing at least 2 equiv of cocatalyst.[9] The same was found to be true for PPNCl. This is illustrated in Figure 4 by the copolymer peak profiles over time for the copolymerization of cyclohexene oxide and carbon dioxide in the presence of (tmtaa)CrCl and the addition of 1, 2, and 4 equiv of PPNCl.

It should be recalled upon titrating (tmtaa)CrCl with up to 8 equiv of azide ions in methylene chloride that the infrared bands assignable to metal-bound azides reached a maximum absorbance at 2 equiv of azide ions, with a further addition of azide ions remaining free in solution, as revealed by an infrared band at 2005 cm^{-1}.[9] The $(tmtaa)Cr(N_3)_2^-$ anionic complex exhibits a strong asymmetric stretching vibration of NNN at 2043 cm^{-1}, with a shoulder at 2057 cm^{-1}. Similar (salen)chromium(III) complexes, including the $(salen)CrCl_2^-$ species, have been fully characterized by X-ray crystallography.[20] Hence, it is assumed that (tmtaa)CrCl in the presence of excess chloride ions exists as $(tmtaa)CrCl_2^-$, which in the presence of the epoxide monomer take part in the equilibrium process depicted in eq 2.



(2)

As is apparent from the reaction profiles in Figure 4, the catalytic activity for the production of poly(cyclohexylene carbonate) dramatically increased when the concentration of PPNCl was increased from 1 to 2 equiv, with only a negligible change upon further increasing it to 4 equiv. The slight initiation period observed for the copolymerization reaction employing 4 equiv of PPNCl might be attributed to

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(18) (a) Darensbourg, D. J.; Yarbrough, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 6335–6342. (b) Darensbourg, D. J.; Yarbrough, J. C.; Ortiz, C. G.; Fang, C. C. *J. Am. Chem. Soc.* **2003**, *125*, 7586–7591.

(19) Darensbourg, D. J.; Mackiewicz, R. M. *J. Am. Chem. Soc.* **2005**, *127*, 14026–14038.

(20) Darensbourg, D. J.; Moncada, A. I. *Inorg. Chem.* **2008**, in press.

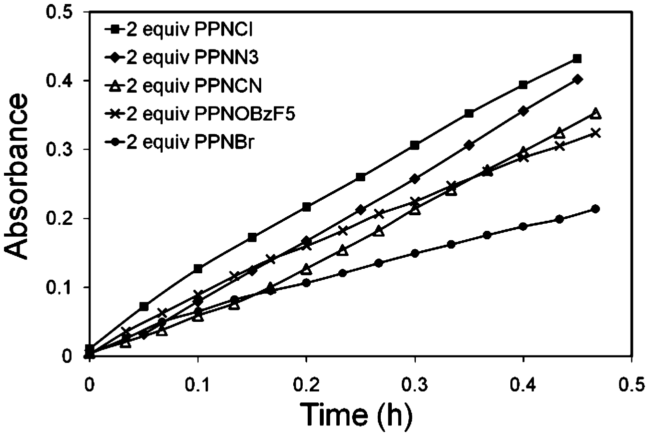

Figure 5. Reaction profiles for the copolymer formation with time for the copolymerization of cyclohexene oxide and CO_2 in the presence of (tmtaa)CrCl and 35 bar of carbon dioxide at 80 °C employing various PPNX salts as cocatalysts.

Table 3. Turnover Data for the Copolymerization of Cyclohexene Oxide and CO_2 Utilizing (tmtaa)CrCl as Catalyst and Either 1 or 2 equiv of Various PPN Salt Cocatalysts[a]

	TOF (time (h))	
PPNX	1 equiv	2 equiv
Cl	1017[b] (0.5)	1478[b] (0.5)
N_3	606 (1.55)	1482[b] (0.5)
Br	542[b] (0.67)	795 (0.67)
CN	302 (0.5)	1161[b] (0.5)
$OBzF_5$	415 (1.5)	656 (1.0)

[a] Copolymerization reactions were conducted with 50 mg of (tmtaa)CrCl as a catalyst at 80 °C and under 500 psi of CO_2 pressure for the duration indicated. [b] Runs were conducted using crystalline catalyst.

competitive metal binding between the epoxide monomer and chloride ion. The turnover frequencies (TOF; mol epoxide consumed/mol catalyst·h) when using 1 to 2 equiv of PPNCl were 1017 and 1478 h^{-1}, respectively. Consistent with our initial report utilizing $PPNN_3$ as the initiator, the production of cyclic carbonate is minimal throughout the reaction until the reaction mixture becomes highly viscous and the epoxide monomer has been sufficiently depleted. At this point, the copolymerization process becomes limited by mass transfer and backbiting of the polymer chain to provide cyclic carbonate becomes more favorable.

Figure 5 illustrates the reaction profiles for copolymer formation as a function of various PPNX salts present in 2 equiv relative to (tmtaa)CrCl. Table 3 lists the turnover frequencies for this copolymerization process in the presence of both 1 and 2 equiv of these PPNX salts. Comparatively, it is shown in Table 3 that the chloride and azide anions gave the highest catalytic activity, followed closely by cyanide, while pentafluorobenzoate and the bromide ion displayed the lowest activity of the initiators investigated herein. The pentafluorobenzoate anion has been previously reported to be a very efficient cocatalyst for cobalt(III) salen catalysts for the copolymerization of propylene oxide and carbon dioxide.[21]

In general, for runs utilizing chloride or azide initiators, 13−15 g (∼50% conversion) of *purified* copolymer was isolated from a 1.0 h reaction period. The molecular weight and polydispersity of the copolymers in THF were measured by gel permeation chromatography. Under these reaction conditions, the typical M_n value was found to be 23 000 with a polydispersity index (PDI) of 1.07. A more detailed presentation of M_n as a function of the number of equivalents of initiator may be found in our earlier report on this process.[9]

Copolymerization Optimization through Catalyst Derivatization. Unlike chromium(III) salen complexes, which require the addition of substituents on the phenolate moieties to achieve sufficient solubility, tmtaa complexes do not require such derivatization. These added ligand modifications, aside from altering solubility, also changed the electronic structure of the salen ligand, which concomitantly affected the copolymerization activity of the catalyst. For the salen ligand, it was found that the addition of electron-donating groups to the phenolate moieties and the ligand backbone increased the catalyst's activity toward the copolymerization of cyclohexene oxide and carbon dioxide.[22] In order to further optimize the chromium(III) tmtaa system, ligands were synthesized with either electron-withdrawing chloro or electron-donating methyl groups on the phenylenediamine portions of the ligand framework. The expectation was for these substituents to affect the electron density around the chromium center, thereby influencing the activity of the catalyst.

As might be anticipated on the basis of our earlier studies involving related (salen)CrCl catalysts, the TOF values for the copolymerization of cyclohexene oxide and carbon dioxide with complexes (tmtaa)CrCl (**1**), (omtaa)CrCl (**2**), and ($tmtaaCl_4$)CrCl (**3**) under comparable reaction conditions at 80 °C increase in the order **3** < **1** < **2**. That is, the catalytic activity increases as the nucleophilicity of the chromium(III) center increases, with TOFs at 80 °C being 1290 h^{-1} (**2**) > 943 h^{-1} (**1**) > 401 h^{-1} (**3**). Nevertheless, multiple runs employing various reaction conditions utilizing complexes **1** and **2** as catalysts in the presence of different anion initiators reveal only small differences in catalytic activity between these two chromium(III) derivatives. Hence, because of the greater ease of synthesizing and purifying complex **1**, we have employed this complex in our more comprehensive studies of this catalytic system.

Epoxides and Carbon Dioxide Coupling Reactions as a Function of Carbon Dioxide Pressure. We next explored the effect of carbon dioxide pressure on the rate of copolymer formation as well as the extent of CO_2 incorporation, that is, the percentage of ether linkages in thus formed polycarbonate. It was noted in previous reports that the high epoxide affinity of our early generation zinc phenoxide catalysts required high carbon dioxide pressures to counteract the propensity for polyether formation over that of polycarbonate. In contrast, the chromium(III)-based salen catalysts were shown to be very ineffective at homopolymerizing

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(21) (a) Cohen, C. T.; Chu., T.; Coates, C. W. *J. Am. Chem. Soc.* **2005**, *127*, 10869–10878. (b) Cohen, C. T.; Coates, G. W. *J. Polym. Sci., Part A* **2006**, *44*, 5182–5191. (c) Cohen, C. T.; Thomas, C. M.; Peretti, K. L.; Lobkovsky, E. B.; Coates, G. W. *Dalton Trans* **2006**, 237.

(22) Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers, J. L.; Fang, C. C.; Billodeaux, D. R.; Reibenspies, J. H. *Inorg. Chem.* **2004**, *43*, 6024–6034.

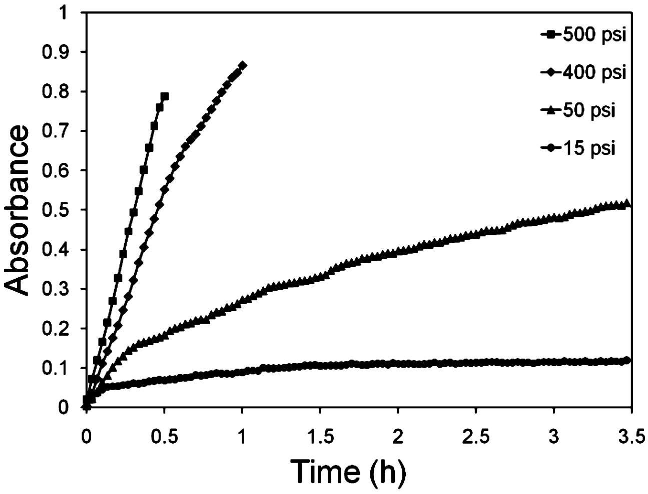

Figure 6. Effect of CO_2 pressure on the rate of polycarbonate formation from the coupling of CO_2 and cyclohexene oxide using (tmtaa)CrCl and 2 equiv of PPNCl as a cocatalyst at 80 °C.

epoxides into polyether and, hence, did not require high concentrations of carbon dioxide to produce polycarbonates with greater than 95% carbonate linkages. A similar situation was obvious when utilizing the (tmtaa)CrCl/PPNX catalyst system. That is, although the rate of copolymerization of cyclohexene oxide and CO_2 varied significantly with CO_2 pressure, at 1 atm of CO_2 pressure, the copolymer produced contained 97% carbonate linkages as evident by ^{1}H NMR.

Figure 6 displays the reaction profiles for the copolymerization of cyclohexene oxide and CO_2 at 80 °C over a range of CO_2 pressures. The concentration of CO_2 dissolved in the cyclohexene oxide medium at atmospheric CO_2 pressure was rapidly depleted, thereby inhibiting continuation of the copolymerization process. Obviously, a maintained [CO_2] under 1 atm of carbon dioxide pressure would yield an increase in copolymer production. Similar to what was noted in the case of the (salen)CrX catalysts, as the CO_2 pressure was decreased, the production of the cyclic carbonate byproduct increased.[23] The most notable instance of significant cyclohexylene carbonate formation was when the initial CO_2 pressure was 1 atm. That is, at the higher CO_2 pressures, the production of cyclic carbonate was negligible.

In Situ Kinetic Studies of the Cyclohexene Oxide/Carbon Dioxide Coupling Reaction. The coupling reaction of cyclohexene oxide and carbon dioxide as catalyzed by the (tmtaa)CrCl/PPNN$_3$ catalyst system was monitored by in situ infrared spectroscopy in order to clearly define the kinetic parameters for this process. Since the reaction mixtures for polymerization reactions conducted in neat epoxide become more viscous and governed by mass transfer as the reaction progresses, accurate kinetic data for the process over extended time periods are impossible to obtain. Hence, in order to keep all components of the reaction in solution and to thwart any viscosity changes, instead of employing neat cyclohexene oxide as a solvent, a 1:1 mixture of cyclohexene oxide and dichloromethane was employed in these studies initially. Because no appreciable rate enhancement was observed in excess of 2 equiv of cocatalyst, all polymerization runs were performed employing 75 mg of (tmtaa)CrCl (1.74×10^{-4} moles) and 2 equiv of PPNN$_3$ in 10 mL each of cyclohexene oxide and methylene chloride. These reactions were conducted over a 30° temperature range, each process resulting in an asymptotic rate profile for both copolymer and cyclic carbonate formation (Figure 7). In all cases, the introduction of the cosolvent, methylene chloride, drastically increased the time needed for the complete conversion of epoxide to products. Observed reaction rate constants at each temperature were obtained for both copolymer and cyclic carbonate formation by fitting the data in plots of $\ln[A_\infty - A_t]$ versus time, where A_∞ and A_t correspond to the infrared absorbances for the copolymer (1750 cm^{-1}) and cyclic carbonate (1808 cm^{-1}) at time = infinity and time = t, respectively (Figures 8 and 9). The respective rate constants are listed in Table 4.

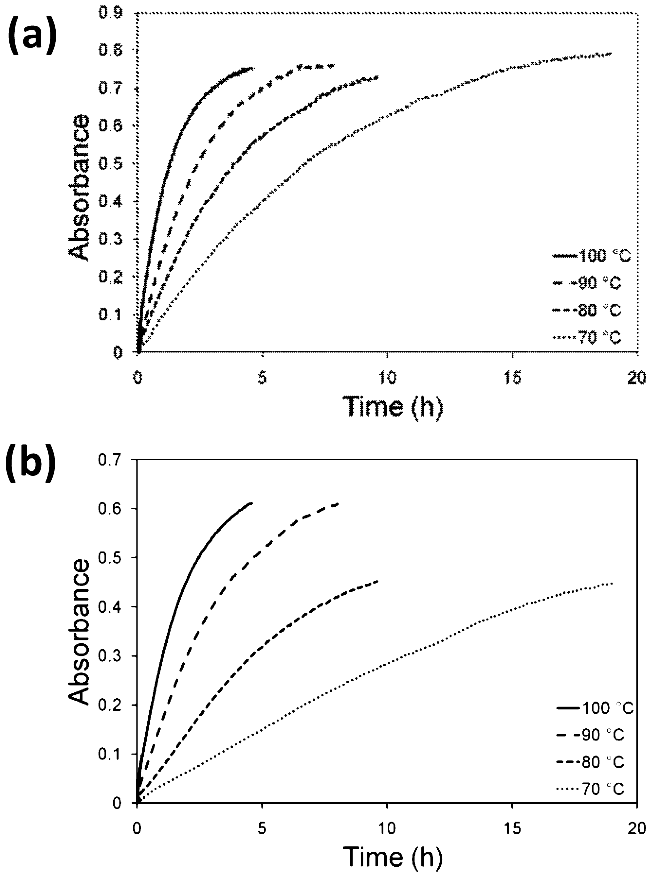

Figure 7. Kinetic traces recorded for the formation of (a) poly(cyclohexylene carbonate) and (b) cyclohexyl carbonate as a function of the temperature in methylene chloride. Reaction conditions: (tmtaa)CrCl (1.74×10^{-4} mol) and 2 equiv of PPNN$_3$ in 10 mL of cyclohexene oxide and 10 mL of methylene chloride and a CO_2 pressure of 34.5 bar.

Eyring plots of the kinetic data provided in Table 4 are shown in Figure 10, with the calculated activation parameters listed in Table 5. As anticipated from the similarities in the reaction profiles provided in Figure 7, the $\Delta G^\ddagger$ values for copolymer and cyclic carbonate formation in methylene chloride do not differ significantly at 80 °C, that is, 115.6 and 117.6 kJ·mol^{-1}, respectively. Although, the enthalpy of activation for the production of the copolymer (62.2 kJ·mol^{-1}) is less than that for cyclic carbonate production

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(23) Darensbourg, D. J.; Mackiewicz, R. M.; Billodeaux, D. R. *Organometallics* **2005**, *24*, 144–148.

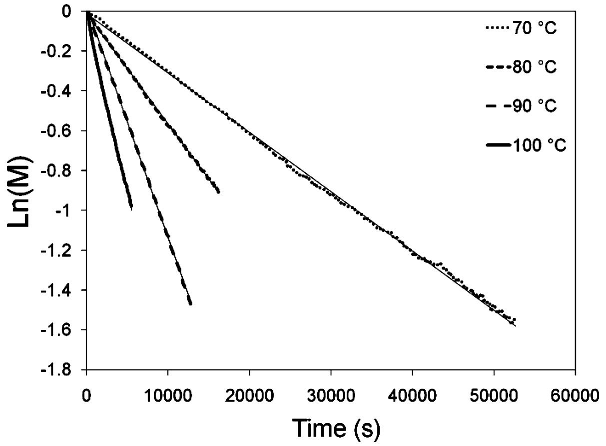

Figure 8. Plots of ln[$A_\infty - A_t$] vs time as a function of time, where A_∞ and A_t are the infrared absorbances for the polycarbonate (1750 cm^{-1}) at time = infinity and time = t, respectively. R^2 values at the various temperatures (°C) are 70 (0.9990), 80 (0.9995), 90 (0.9998), and 100 (0.9973).

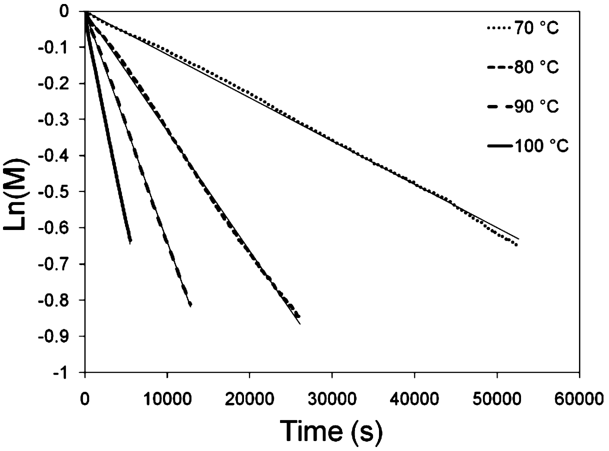

Figure 9. Plots of ln[$A_\infty - A_t$] vs time as a function of time, where A_∞ and A_t are the infrared absorbances for the cyclic carbonate (1808 cm^{-1}) at time = infinity and time = t, respectively. R^2 values at the various temperatures (°C) are 70 (0.9980), 80 (0.9988), 90 (0.9995), and 100 (0.9992).

Table 4. Temperature-Dependent Rate Constants for the Coupling of Cyclohexene Oxide and Carbon Dioxide in Methylene Chloride[a]

	k (M^{-1} sec^{-1}) × 10^3	
temp. (°C)	copolymer	cyclic carbonate
70	3.45	1.37
80	8.44[b]	4.08[b]
90	12.9	7.31
100	21.0	13.6

[a] Reaction carried out in 10 mL of methylene chloride, 1.74 × 10^{-4} mol of (tmtaa)CrCl and 2 equiv of $\mathrm{PPNN_3}$ in 10 mL of cyclohexene oxide and a $\mathrm{CO_2}$ pressure of 34.5 bar. [b] Average value of two runs.

(77.3 kJ·mol^{-1}), as has been previously reported for chromium(III) and zinc(II) catalyst systems, it is offset by a more negative $\Delta S^\ddagger$ value.[18,24]

Although the kinetic study presented above determined under homogeneous solution conditions has proven to be insightful, our focus on a more environmentally benign route for the production of polycarbonates dictates the necessity of performing a comparable, albeit limited, investigation under *solventless* conditions. As mentioned earlier, because of the increase in viscosity during copolymer production in a neat carbon dioxide swollen cyclohexene oxide medium, we are only able to quantitatively follow the reaction's progress during the early stages. Figure 11 depicts the reaction profiles for copolymer formation for processes carried out over the temperature range between 60 and 100 °C. The reactions were monitored via in situ infrared spectroscopy employing 50 mg (1.16 × 10^{-4} mol) of (tmtaa)CrCl and 2 equiv of $\mathrm{PPNN_3}$ in 20 mL of cyclohexene oxide at a $\mathrm{CO_2}$ pressure of 34.5 bar. Initial rates for copolymer and cyclic carbonate were determined over the first few minutes of the processes. These rate data are tabulated in Table 6.

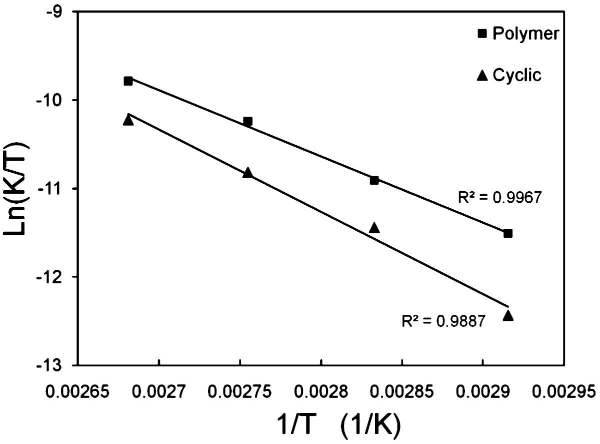

Figure 10. Eyring plot for the formation of polymer and cyclic carbonate.

Table 5. Activation Parameters for the Coupling Reactions of Cyclohexene Oxide and Carbon Dioxide in Methylene Chloride[a]

	copolymer	cyclic carbonate
$\Delta H^\ddagger$ (kJ·mol^{-1})	62.2 ± 2.5	77.3 ± 5.7
$\Delta S^\ddagger$ (J·mol^{-1}·K^{-1})	−151.3 ± 6.9	−114.2 ± 16.0
$\Delta G^\ddagger$ (kJ·mol^{-1})	115.6	117.6
E_a (kJ·mol^{-1})	65.2 ± 2.5	80.3 ± 2.5

[a] $\Delta G^\ddagger$ value calculated at the typical reaction temperature of 80 °C.

Arrhenius plots for both copolymer and cyclic carbonate formation obtained from the initial rate data listed in Table 6 are provided in Figure 12. The calculated energies of

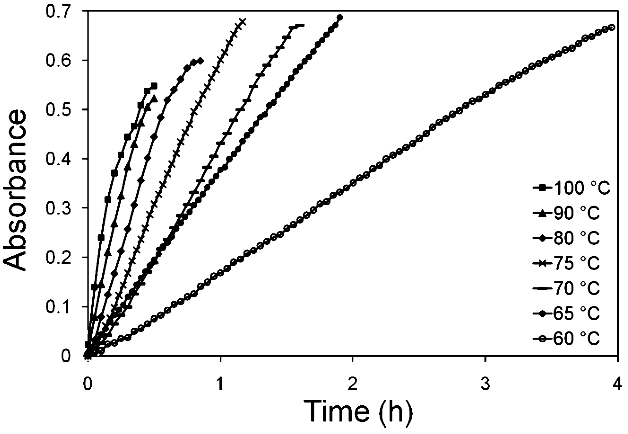

Figure 11. Effect of temperature on the rate of polycarbonate formation from the coupling of $\mathrm{CO_2}$ and cyclohexene oxide using the (tmtaa)CrCl and 2 equiv of $\mathrm{PPNN_3}$ catalyst system at a $\mathrm{CO_2}$ pressure of 34.5 bar in pure cyclohexene oxide.

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(24) Darensbourg, D. J.; Holtcamp, M. W.; Struck, G. E.; Zimmer, M. S.; Niezgoda, S. A.; Rainey, P.; Robertson, J. B.; Draper, J. D.; Reibenspies, J. H. *J. Am. Chem. Soc.* **1999**, *121*, 107–116.

Table 6. Temperature-Dependent Initial Rates for the Coupling of Cyclohexene Oxide and Carbon Dioxide in the Absence of a Cosolvent[a]

	initial rate (M/sec) × 10^5	
temp. (°C)	copolymer	cyclic carbonate
60	4.75	0.121
65	10.1	0.394
70	11.2	0.754
75	18.	0.731
80	25.6	1.50
90	36.3	1.48
100	77.9	9.21

[a] Reactions carried out in 20 mL of cyclohexene oxide, 1.16 × 10^{-4} mol of (tmtaa)CrCl and 2 equiv of $PPNN_3$ at a CO_2 pressure of 34.5 bar.

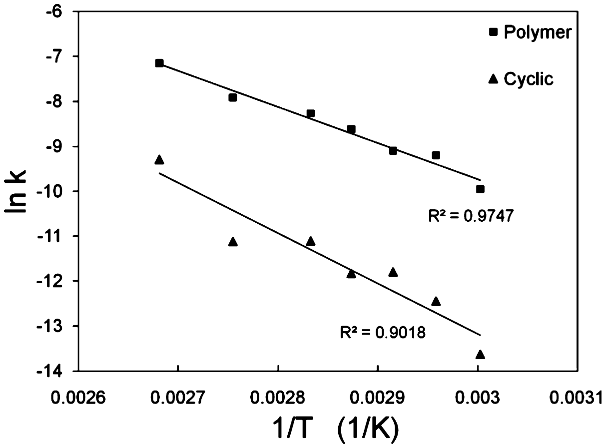

Figure 12. Arrhenius plots for polymer ($R^2 = 0.9747$) and cyclic carbonate ($R^2 = 0.9018$) formation from polymerizations carried out in neat cyclohexene oxide. Conditions: 1.16 × 10^{-4}mol of (tmtaa)CrCl and 2 equiv of $PPNN_3$ in 20 mL of cyclohexene oxide under a CO_2 pressure of 34.5 bar.

activation for the two processes are 67.1 ± 4.2 and 91.2 ± 10.5 kJ·mol^{-1}, respectively. Comparison of the E_a values for copolymer production in a cosolvent (methylene chloride), and in the early stages of the reaction performed under solventless conditions, indicate little difference for the two processes. On the other hand, the E_a for cyclic carbonate production is larger under the reaction conditions involving pure cyclohexene oxide. However, because of the low level of cyclic carbonate production in this instance, the E_a is subject to significant uncertainty, that is, an error of ±10.5 kJ·mol^{-1}. Nevertheless, a higher value for E_a is anticipated on the basis of the low rate of cyclic carbonate formation observed in the absence of a cosolvent. This is explained on the basis of the backbiting process, which leads to cyclic carbonate formation being inhibited in pure cyclohexene oxide. As previously noted, once the reaction medium becomes viscous due to copolymer formation, where chain growth is greatly retarded, the rate of cyclic carbonate production dramatically increases.[9] This is clearly illustrated in Figure 13 for a solventless copolymerization process carried out under typical reaction conditions.

Copolymerization of Other Epoxides. We have surveyed several other epoxides for their selectivity to afford the copolymer versus cyclic carbonate in the presence of the (tmtaa)CrCl/$PPNN_3$ catalyst system. These studies were conducted under typical reaction conditions, that is, 50 mg of (tmtaa)CrCl, 2 equiv of $PPNN_3$, and 34.5 bar of CO_2 in the absence of a cosolvent. Because it is well-established that higher temperatures generally lead to enhanced production of cyclic carbonates, these experiments were performed starting at temperatures close to ambient, with subsequent ramping up of the temperatures as needed to observe reaction progress. Copolymerization reactions were carried out in a stainless steel reactor and were monitored by in situ infrared spectroscopy. The epoxides examined were propylene oxide (a), styrene oxide (b), 1,2-epoxyhexane (c), isobutylene oxide (d), and 4-vinylcyclohexene oxide (e), as depicted in Figure 14.

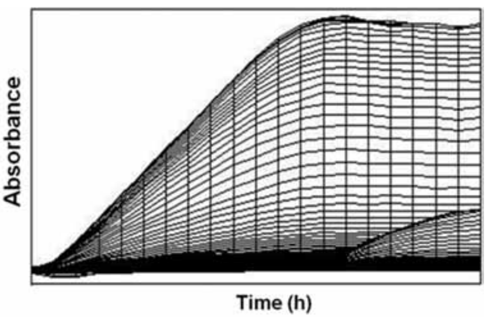

Figure 13. Time-dependent reaction profiles for the solventless copolymerization of cyclohexene oxide (20 mL) and CO_2 (34.5 bar) in the presence of 0.116 mmol of (tmtaa)CrCl and 3 equiv of $PPNN_3$ at 80 °C. Note enhancement of the cyclic carbonate production at 0.7 h after copolymer formation has reached a plateau.

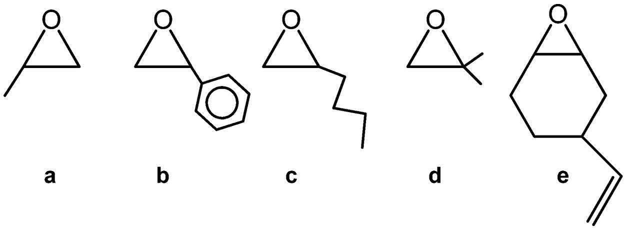

Figure 14. Epoxides surveyed for copolymer production catalyzed by (tmtaa)CrCl/$PPNN_3$.

The most widely investigated monomer for the copolymerization with carbon dioxide studied to date other than cyclohexene oxide is propylene oxide. The challenge in polymerizing aliphatic epoxides such as ethylene or propylene oxide is the ease at which these comonomers provide cyclic carbonates as opposed to polycarbonates. Nevertheless, there are several reports for the selective production of poly(propylene carbonate) from propylene oxide and CO_2 in the presence of (salen)MX complexes (M = Cr[25] or Co[26]). In particular, the (salen)CoX complexes in the association with anionic cocatalysts have been shown to provide copolymers with stereo- and regioselectivity. In this study,

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(25) (a) Darensbourg, D. J.; Phelps, A. L. *Inorg. Chem.* **2005**, *44*, 4622–4629. (b) Eberhardt, R.; Allmendinger, M.; Rieger, B. *Macromol. Rapid Commun.* **2003**, *24*, 194–196. (c) Chisholm, M. H.; Zhou, Z. *J. Am. Chem. Soc.* **2004**, *126*, 11030–11039.

(26) (a) Lu, X.-B.; Wang, Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 3574–3577. (b) Paddock, R. L.; Nguyen, S. T. *Macromolecules* **2005**, *38*, 6251–6253. (c) Qin, Z.; Thomas, C. M.; Lee, S.; Coates, G. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 5484–5487. (d) Cohen, C. T.; Chu, T.; Coates, G. W. *J. Am. Chem. Soc.* **2005**, *127*, 10869–10878. (e) Cohen, C. T.; Coates, G. W. *J. Polym. Sci., Part A* **2006**, *44*, 5182–5191. (f) Nakano, K.; Kamada, T.; Nozaki, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 7274–7277. (g) Noh, E. K.; Na, S. J.; S, S.; Kim, S.-W.; Lee, B. Y. *J. Am. Chem. Soc.* **2007**, *129*, 8082–8083. (h) Lee, B. Y.; Kwon, H. Y.; Lee, S. Y.; Na, S. J.; Han, S.-i.; Yun, H.; Lee, H.; Park, Y.-W. *J. Am. Chem. Soc.* **2005**, *127*, 3031–3037.

the copolymerization of propylene oxide and carbon dioxide using complex **1** and 2 equiv of $PPNN_3$ at 40 °C yielded a 21% conversion to the product in 1 h, with 36% of the product being the copolymer. Additionally, a 60 °C run carried out for 3 h provided 49% conversion where 15% of the product was poly(propylene carbonate). Hence, (tmtaa)CrCl in the presence of $PPNN_3$ is not a particularly effective catalyst system for this monomer, that is, less effective than the (salen)MX derivatives of chromium(III) or cobalt(III).

In an effort to examine an epoxide monomer with two substituents on an ipso-carbon center, the copolymerization of isobutylene oxide (d) with carbon dioxide was investigated. Our hope was that (tmtaa)CrCl, with its metal center being more accessible, would allow for the interaction with this sterically encumbered monomer and concomitant ring-opening. However, after some time at 40 °C, only trace quantities of cyclic carbonate were observed, which increased in its rate of formation as the temperature was raised to 60 °C and then to 80 °C. At no time was there spectral evidence for the formation of polycarbonate. Similar observations were made for reactions performed with 1,2-epoxyhexane (c) and carbon dioxide, where only cyclic carbonate was produced. It should be recalled that in the patent literature Jacobsen and co-workers have reported that (salen)CrCl in the absence of a cocatalyst was effective at copolymerizing 1,2-epoxyhexane and CO_2 to polycarbonate.[27]

Polystyrene has become a widely used commodity thermoplastic as it is colorless, transparent, rigid, economical, and easy to cast. In an effort to build upon the same aromatic functionality of polystyrene while possibly synthesizing a polymer with desirable properties, styrene oxide was subjected to copolymerization with carbon dioxide using the (tmtaa)CrCl complex as a catalyst. As mentioned vide supra pertaining to aliphatic epoxides, the ease of cyclic carbonate formation poses a challenge to affording copolymer. In earlier attempts in our laboratory, the copolymerization of styrene oxide (b) and CO_2 utilizing (salen)CrN_3 and $PPNN_3$ catalysts resulted in trace quantities of copolymer and moderate amounts of cyclic styrene carbonate.[28] In this study, the reaction was carried out starting at a temperature of 40 °C, under which conditions a small yield of cyclic carbonate was observed. Further increases in temperature to 80 °C and then to 100 °C resulted in increases in cyclic carbonate formation, but no poly(styrene carbonate) was observed via infrared spectroscopy.

Although the cyclohexene oxide monomer has been invaluable for understanding the process of epoxide/carbon dioxide coupling, the inherent properties of the resulting copolymer, poly(cyclohexylene carbonate), make it currently commercially unattractive.[29] A closely related monomer, 4-vinylcyclohexene oxide (e), offers the selective reactivity of an alicyclic epoxide similar to cyclohexene oxide with the advantage of a pendant vinyl functionality that can be post-polymerization-modified. Indeed, studies have shown it to be possible to prepare block copolymers of poly(cyclohexylene carbonate) and poly(4-vinylcyclohexylene carbonate),[30] as well as intramolecular cross-linked terpolymers of cyclohexene oxide, 4-vinylcyclohexene oxide, and carbon dioxide.[31] We have previously employed a similar strategy for intermolecularly cross-linking a copolymer prepared from [2-(3,4-epoxycyclohexyl)ethyl]trimethoxysilane and CO_2 via silsesquioxane units.[32] Figure 15 represents the reaction profiles for the formation of the copolymer and cyclic carbonate from the coupling of 4-vinylcyclohexene oxide and carbon dioxide as catalyzed by (tmtaa)CrCl and 2 equiv of PPNCl at 80 °C. The copolymerization reaction proceeded at a slower rate, that is, ~3 times slower, than the corresponding process with the cyclohexene oxide monomer. Nevertheless, the process was highly selective for copolymer formation, providing a polycarbonate with a narrow polydispersity of 1.12.

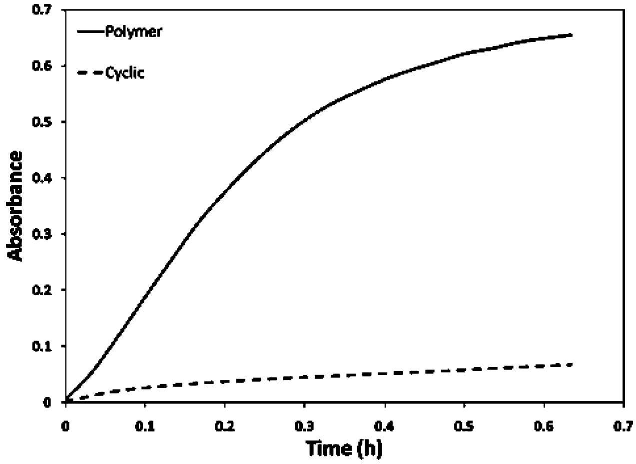

Figure 15. In situ infrared profiles of polycarbonate and cyclic carbonate formation for the copolymerization of CO_2 (34.5 bar) and 4-vinyl cyclohexene oxide (20 mL or M/I = 1300) utilizing 50 mg of (tmtaa)CrCl (0.077 mmol %) and 2 equiv of PPNCl as a cocatalyst.

Summary and Conclusions

In part, our interest in exploring *tetraazaannulene* chromium(III) derivatives as catalysts for the copolymerization of cyclohexene oxide and carbon dioxide was to compare their activity with the closely related *salicylaldimine* and *porphyrin* analogs. Although differences in reaction conditions make it difficult to quantitatively contrast the catalytic activities involving these metal complexes, it is apparent that, under optimal conditions, the (salen)CrX and (tmtaa)CrX metal complexes in the presence of anionic cocatalysts display similar activities. For example, (salen)CrX complexes exhibit a TOF of ~1150 h^{-1} at 80 °C and provide high molecular weight copolymers (50 000) with low PDIs

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(30) Hsu, T.-J.; Tan, C.-S. *Polymer* **2002**, *43*, 4535–4543.

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(1.13).[23] Under identical reaction conditions the (tmtaa)CrX complexes are somewhat more active with TOF of ∼1500 h^{-1} at 80 °C yielding a copolymer of molecular weight 30,000 with a PDI of 1.07. On the other hand, the complex containing the more expensive N_4^{-2} ligand, (porphyrin)CrX, afforded a TOF ≈ 150 h^{-1} at 110 °C, yielding a low molecular weight copolymer ($M_n \approx 3500$) with a PDI of 1.19.[33] Hence, the (tmtaa)CrX complex is slightly more active than the correspondent complex containing the ubiquitous salicylaldimine ligand and is considerably more active than analogous chromium derivatives containing the porphyrin ligand. This reactivity trend parallels the expected electron-donating ability of the ligand set about the chromium(III) center, where tmtaa > salen ≫ porphyrin. Consistent with this interpretation, the addition of electron-withdrawing chloride substituents to the tmtaa ligand retards the catalytic activity of the ($tmtaaCl_4$)CrCl derivative significantly.

An important observation resulting from this investigation is that the selectivity for formation of the copolymer versus cyclic carbonate is highly dependent on whether cosolvents are used. That is, a comparison of product selectivity under solventless and cosolvent conditions clearly shows that in the absence of a cosolvent the rate of the backbiting process for cyclic carbonate production, either at the metal center or subsequent to chain dissociation, is greatly retarded. Our current thoughts on this behavior are that enhanced cyclic carbonate formation is the result of copolymer chain dissociation from the metal center followed by facile cyclization.[26f,g,34,35]

The mechanistic aspects of the copolymerization reactions of epoxides and carbon dioxide employing (salen)CrX and those presented herein for (tmtaa)CrX correspond intimately to one another. This in turn allows for an opportunity with this tetraazaannulene chromium complex to examine one of the unresolved issues with regard to the behavior of this general class of metal complexes. That is, because the observed molecular weights of the thus formed copolymers are generally significantly less than predicted on the basis of monomer/initiator, this has been proposed to result from monomer enchainment above and below the approximately planar arrangement of $N_2O_2^{-2}$ or N_4^{-2} ligands, in other words, two polymer chains originating from a single metal center.[26d,36] Because it is relatively easy to hinder one side of the tetraazaannulene ligand with a strap (see Figure 16),[11] the resultant metal complex should allow small anions to bind to both axial sites but inhibit monomer enchainment on the strapped side. Hence, a study of the type that this baseline report describes utilizing electronically similar complexes with and without the strap should address this question in a very definitive manner. These studies are currently being pursued in our laboratories.

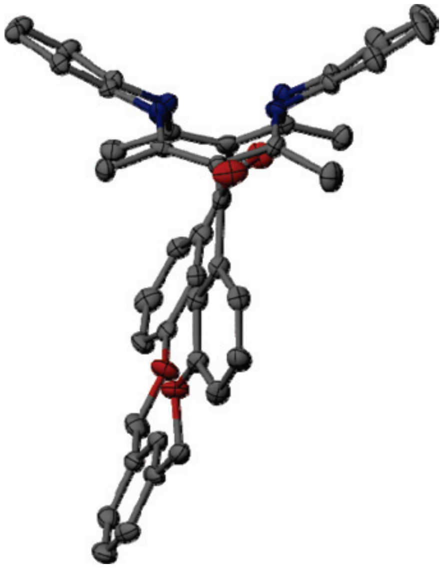

Figure 16. The H_2tmtaa ligand containing an aromatic strapping unit on the underside of the bowl-shaped ligand.[37]

Finally, these (tmtaa)chromium(III) derivatives, like other closely related complexes, are rather disappointing as catalysts for the copolymerization of aliphatic epoxides and carbon dioxide. However, they were shown to be very effective at copolymerizing other alicyclic epoxides than cyclohexene oxide, such as 4-vinylcyclohexene oxide.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structural determination of complex **2** and the $H_2tmtaaCl_4$ ligand. This material is available free of charge via the Internet at http://pubs.acs.org.

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