

(Tetramethyltetraazaannulene)chromium Chloride: A Highly Active Catalyst for the Alternating Copolymerization of Epoxides and Carbon Dioxide

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A tetramethyltetraazaannulene complex incorporating a chromium(III) metal center has been shown to be highly active toward the copolymerization of cyclohexene oxide and carbon dioxide to afford poly(cyclohexene carbonate) in the presence of [PPN]₃ [PPN⁺ = bis(triphenylphosphoranylidene)ammonium] as a cocatalyst. An asymptotical rate increase was observed, leveling at 2 equiv of cocatalyst with a maximum turnover frequency of 1300 h⁻¹ at 80 °C. A benefit of this new catalyst system over that of the previously studied less-active (salen)CrX system is that the (tmtaa)-CrCl catalyst has a much lower propensity toward the formation of a cyclic carbonate byproduct throughout the copolymerization reaction.

Chromium(III) Schiff base complexes have been shown to be highly active and robust catalysts for the copolymerization of carbon dioxide and epoxide to afford polycarbonates in a process that is essentially atom-economic.¹ Cobalt(III) analogues have similarly been shown to be quite active for this alternating copolymerization process.² Porphyrin ligands, including those exhibiting supercritical carbon dioxide solubility, incorporating a chromium(III) metal center have similarly been found to facilitate this copolymerization reaction but with significantly lower activities and affording copolymers of much lower molecular weights than their Schiff base analogues.^{3,4} In an effort to develop better catalysts for this copolymerization process, as well as a deeper understanding of the mechanistic aspects of these catalytic systems, the tetramethyltetraazaannulene (tmtaa) complex of chromium(III), **1**, has been investigated. The tmtaa ligand, which is a conjugated macrocycle containing

a four-nitrogen donor core, is more electron-donating than the porphyrin ligand and similarly has the ability to bind the metal atom above the donor plane.⁵ For example, (tmtaa)-CrCl exhibits a molecular structure as depicted in Figure 1, where the square-pyramidal chromium center contains an apically bound chloride.⁶ The chromium center was found to reside 0.435(1) Å above the nitrogen donor plane, resulting in a partially constrained cavity on the underside of the complex. Nevertheless, a hexacoordinated chromium(II) complex has been structurally characterized, Cr(tmtaa)(py)₂, which displays trans-bound pyridine ligands with similar Cr–N distances [2.138(18) and 2.059(19) Å].⁷

We synthesized the tmtaa ligand according to the nickel-template condensation of *o*-phenyldiamine with pentane-2,4-dione procedure as described initially by Jaeger⁹ and modified by Goedken and co-workers.¹⁰ The (tmtaa)CrCl catalyst employed herein was prepared as reported by Cotton and co-workers.^{6,8} Copolymerization reactions of cyclohexene oxide and carbon dioxide utilizing **1** as the catalyst were

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(3) (a) Kruper, W. J.; Dellar, D. V. *J. Org. Chem.* **1995**, *60*, 725–727. (b) Mang, S.; Cooper, A. I.; Colclough, M. E.; Chauhan, N.; Holmes, A. B. *Macromolecules* **2000**, *33*, 303–308. (c) Although it is difficult to quantitatively compare catalytic activities because of differences in the reaction conditions, it is apparent that (salen)CrX catalysts are considerably more effective than their (porphyrin)CrX analogues. For example, at 80 °C and 35 bar for a 0.043 mol % catalyst loading, (salen)CrN₃/1 equiv of PPN₃ provided a TOF ≈ 1150 h⁻¹ with *M*_n = 50000 and PDI = 1.13,⁴ whereas at 110 °C and 227 bar for a 0.26 mol % catalyst loading (tfpp)CrCl/1 equiv of DMAP afforded a TOF ≈ 150 h⁻¹ with *M*_n ≈ 3500 and PDI = 1.19.^{2b}

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(8) Crystals suitable for X-ray analysis were obtained from a benzene solution of the complex layered with hexane. Because no crystal data files of the original structure were deposited, we redetermined the structure of complex **1** at 110 K. The metric parameters were similar to those reported from ambient temperature data but were of greater accuracy with *R*₁ = 0.0419 and *R*_w = 0.0623 and a goodness-of-fit of 1.011. A structure report and CIF files may be found in the Supporting Information.

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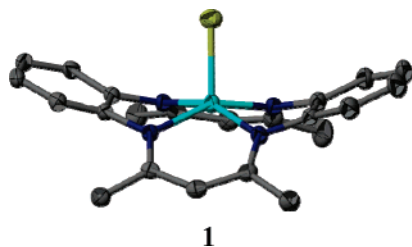


Figure 1. Ball-and-stick representation showing the saddle shape of the ligand and the out-of-plane distortion of the chromium center in (tmtaa)-CrCl.⁸

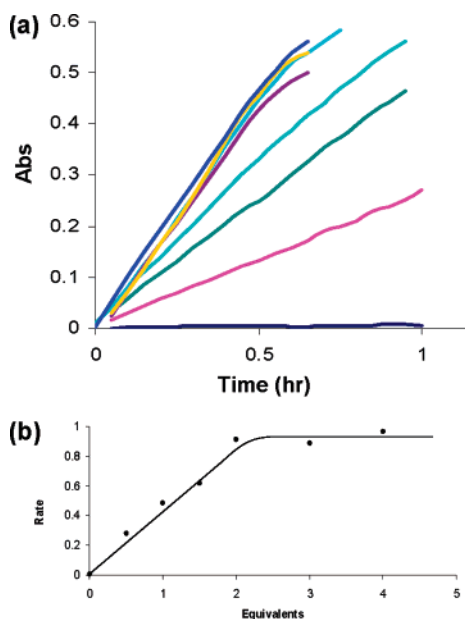
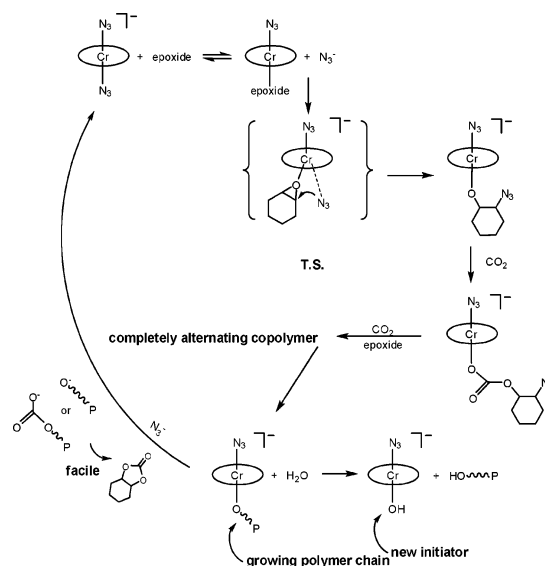


Figure 2. Copolymerization conditions: 50 mg of complex **1** (0.059 mol %), M/I = 1700, 20 mL of cyclohexene oxide, 35 bar of carbon dioxide, 80 °C, 1–2 h reaction time. (a) Polymer peak (~1750 cm⁻¹) trace of copolymerizations conducted with various cocatalyst ([PPN]N₃) loadings: (black line) 0.0 equiv; (pink line) 0.5 equiv; (dark teal line) 1.0 equiv; (medium teal line) 1.5 equiv; (light teal line) 2.0 equiv; (burgundy line) 3.0 equiv; (yellow line) 4.0 equiv; (purple line) 6.0 equiv. (b) Profile of the rate versus cocatalyst equivalents.

carried out in a 300 mL stainless steel Parr reactor modified to accommodate an ASI ReactIR SiCOMP probe.¹¹ The reactions were monitored by observance of the growing polymer chain by its IR absorption at 1750 cm⁻¹ due to the carbonate function (Figure 2a). The relative rates of copolymerization of cyclohexene oxide and carbon dioxide as a function of [cocatalyst] while maintaining a constant [complex **1**] were obtained from the linear portions of the absorbance of the 1750 cm⁻¹ vibrational mode of the carbonate function versus time traces. As the copolymeri-

Scheme 1



zation reaction proceeds to high levels of conversion (>60%), its rate is greatly diminished because of the viscous nature of the more dense polymer phase.¹² Recall that the ATR crystal is located at the bottom of the reactor, eventually becoming heavily coated with copolymer and impervious to detection of further polymer formation.

As illustrated in Figure 2a, the rate of poly(cyclohexylene carbonate) formation was dependent on the cocatalyst loading, maximizing at 2 equiv. This is readily apparent in Figure 2b, which illustrates the rate of copolymer formation as a function of the equivalents of cocatalysts, reaching a plateau above 2 equiv of [PPN]N₃. The maximum rate provided a turnover frequency (TOF) of 1300 mol of epoxide consumed/mol of catalyst per h, with only trace quantities of cyclic carbonate production. This nonoptimized activity represents a significant increase over optimized (salen)CrCl derivatives under similar reaction conditions.¹³ In the absence of [PPN]N₃, (tmtaa)CrCl under the same reaction conditions produced essentially pure polyether (2% carbonate linkages) in rather low yield. This latter observation is consistent with a hexacoordinate, electron-rich metal complex being necessary for the facile insertion of carbon dioxide into the metal–alkoxide bond.^{1e,f}

In a series of separate experiments, titration of complex **1** with [PPN]N₃ revealed that the stepwise reaction defined in eq 1 proceeds quantitatively to the right. That is, the apical chloride ligand is easily displaced by azide in a CH₂Cl₂

(11) In a typical experiment, 50 mg of (tmtaa)CrCl was activated by dissolution in methylene chloride with varying equivalents of bis-(triphenylphosphoranylidene)ammonium azide ([PPN]N₃). Upon drying in vacuo, the activated catalyst was dissolved in 20 mL of cyclohexene oxide (0.059 mol % catalyst loading or M/I = 1700) and added to the predried reactor via its injection port. The reactor was then pressurized with bone-dry carbon dioxide to 35 bar and maintained at 80 °C. The polycarbonate copolymer was extracted with methylene chloride, precipitated with acidified methanol, dried, and weighed. The copolymer was analyzed by ¹H NMR to determine the percentage of carbonate linkage in the isolated polycarbonate. In general, 13–15 g of purified copolymer was isolated from a 1 h reaction period. The molecular weight and polydispersity of the copolymers in THF were measured by gel permeation chromatography.

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(14) Although we have not isolated the azide complexes depicted in eq 1, the analogous derivatives involving (salen)CrCl as the reactant have been isolated and crystallographically characterized.¹⁵ In this instance, the ν_{N₃} IR region in solution are nearly identical. It should be noted that metal-bound azide and free azide are easily distinguished by IR spectroscopy. In this and the closely related (salen)CrN₃ catalytic systems, MALDI time-of-flight mass spectral measurements on low molecular weight copolymers reveal azide end groups in the polycarbonates formed.¹³

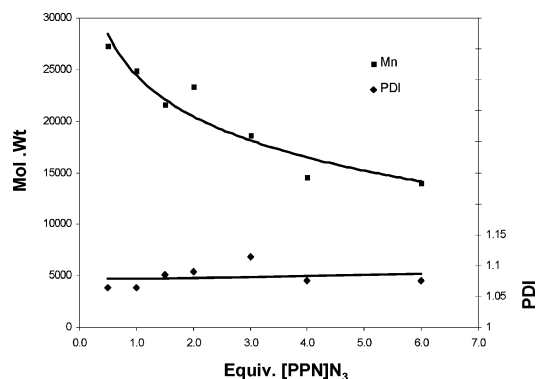


Figure 3. Plot showing molecular weights and polydispersities of the polymer formed at various cocatalyst loadings, e.g., at 0.5 equiv of [PPN] N_3 , $M_n = 27300$ with a PDI of 1.07, and at 6.0 equiv of [PPN] N_3 , $M_n = 13900$ with a PDI of 1.08. All reactions were carried out to approximately the same level of conversion.

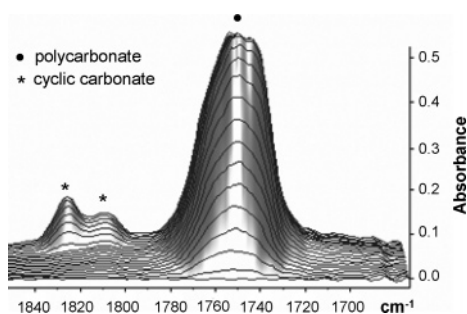
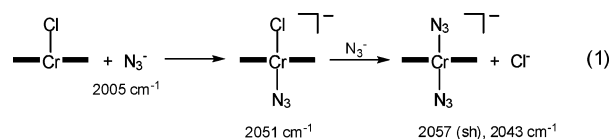


Figure 4. IR spectral traces of copolymer and cyclic carbonate formation with respect to time.

solution as revealed by IR spectroscopy in the ν_{N_3} region (see the Supporting Information).^{14,15} Hence, the most active catalytic species is the $(\text{tmtaa})\text{Cr}(\text{N}_3)_2^-$ complex, where one or both of the azide ions are interacting with the chromium center during the initiation process (see Scheme 1). That is, as depicted in the skeletal transition state in Scheme 1, the azide anionic initiator is shown to maintain some interaction with the metal center during the epoxide ring-opening process. Although this need not be the case in this instance, an analogous transition state would be anticipated for epoxide enchainment to avoid polymer chain dissociation and concomitant facile formation of cyclic carbonate. That is, it is thought that the free polymer chain undergoes the backbiting process to afford the thermodynamically stable cyclic carbonate easier than when it is bound to the metal center.^{16,17}

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 (19) An alternative explanation involves chain-transfer reactions between the anionic cocatalyst and the growing polymer chain. However, the lack of concomitant cyclic carbonate production during copolymer formation suggests that this is not the case (vide supra).
 (20) For example, under the same reaction conditions, $(\text{salen})\text{CrCl}$ in the presence of 2 equiv of [PPN] N_3 afforded cyclic carbonate at a continuous rate during the copolymerization process, increasing with an increase in the cocatalyst concentration. Andreatta, J. R.; Darensbourg, D. J. Unpublished results.
 (21) Our initial investigations reveal that complex **1** in the presence of 1 equiv of [PPN] N_3 is highly selective for the production of poly(propylene carbonate) at 45 °C.

Although the lower molecular weight of the copolymer observed as compared to its theoretical value might indicate monomer enchainment on both sides of the $(\text{tmtaa})\text{Cr}$ moiety, we have no definitive evidence to suggest this is the case. Indeed, steric hindrance provided by the saddle-shaped ligand system should prohibit that from occurring.



All isolated copolymers exhibited high molecular weights as determined by gel permeation chromatography in tetrahydrofuran (THF), with a narrow polydispersity, along with a high carbon dioxide incorporation (greater than 95%). A decrease in the molecular weight was noted with an increase in the cocatalyst loading (Figure 3), which is consistent with a chain-transfer mechanism from an increase in accompanying water.^{18,19} This was supported by carrying out a reaction in the presence of 1 equiv of [PPN] N_3 with 5 equiv of water. Although the catalytic activity was not diminished, the molecular weight was greatly reduced in the presence of excess water from 25000 (PDI = 1.07) to 9000 (PDI = 1.16). Importantly, contrary to the previously reported chromium salen catalyst systems where cyclic carbonate production was enhanced in the presence of excess cocatalyst (> 1 equiv),²⁰ this behavior was not observed in this instance. Because this increase in cyclic carbonate production in the presence of excessive concentrations of anions is attributed to competitive anion binding with the metal versus the growing polymer chain, this observation suggests that the *tmtaa* catalyst binds the polymer chain with a greater affinity than its salen analogue. Figure 4 illustrates this clearly, where cyclic formation is suppressed during copolymer formation and only becomes significant after the monomer concentration is lowered.

In conclusion, the chromium tetramethyltetraazaannulene complex has proved to be highly active for the copolymerization of cyclohexene oxide and carbon dioxide for the production of high molecular weight poly(cyclohexylene carbonate) with narrow polydispersities, affording TOFs an order of magnitude greater than their metal porphyrin analogues under milder reaction conditions. Current efforts are underway to explore a wide range of electronic variations of the *tmtaa* ligand and the epoxide monomer, as well as experiments designed to better elucidate the mechanistic details of this process.²¹

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Supporting Information Available: X-ray crystallographic files in CIF format for the structural determination of complex **1** and details of $(\text{tmtaa})\text{CrCl}$ reactions with [PPN] N_3 in a methylene chloride solution. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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