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Copolymerization of Cyclohexene Oxide and CO_2 with a Chromium Diamine-bis(phenolate) Catalyst

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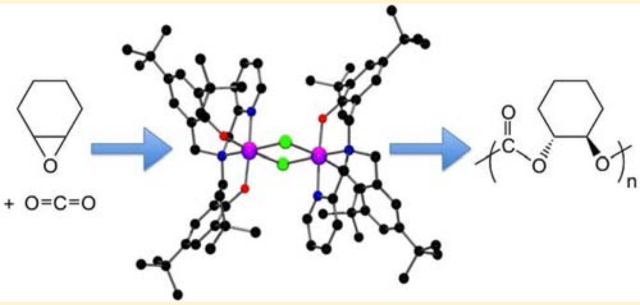
Supporting Information

ABSTRACT: A diamine-bis(phenolate) chromium(III) complex, $\{CrCl[O_2NN']^{BuBu}\}_2$ catalyzes the copolymerization of cyclohexene oxide with carbon dioxide. The synthesis of this metal complex is straightforward, and it can be obtained in high yields. This catalyst incorporates a tripodal amine-bis(phenolate) ligand, which differs from the salen or salan ligands typically used with Cr and Co complexes that have been employed as catalysts for the synthesis of such polycarbonates. The catalyst reported herein yields low molecular weight polymers with narrow polydispersities. Structural and spectroscopic details of this complex along with its copolymerization activity for cyclohexene oxide and carbon dioxide are presented.



INTRODUCTION

The copolymerization of epoxides and carbon dioxide to yield polycarbonates has become an important process that generates potentially valuable materials from renewable starting materials.[1−6] The use of carbon dioxide as a C1 feedstock is appealing due to its widespread availability, low cost, and nontoxicity.[7] A wide variety of homogeneous catalysts containing metals such as Al,[8−12] Zn,[13−21] Cr,[22−37] Co,[6,38−56] and most recently Fe[57] have been examined for use in the copolymerization of carbon dioxide (CO_2) and epoxides, including cyclohexene oxide (CHO).

Previous reports of homogeneous catalysis toward CHO and CO_2 copolymerization include such ligand classes as the porphyrins, where Cr[23,58,59] and Al[12] complexes have been used. Another established ligand system introduced by Darensbourg and Holtcamp used for epoxide/CO_2 copolymerization includes the phenoxides, where Zn is commonly the metal used.[60−62] Although these Zn complexes did not produce high turnover frequencies (TOFs), they did provide a leap from the original heterogeneous Zn catalysts to homogeneous systems. The search for a more active catalyst led Coates and co-workers to explore the use of β-diiminate (BDI) ligand systems with Zn at lower pressures and temperatures than had previously been reported.[13] The most widely studied ligands for epoxide/CO_2 copolymerization have been the salen[3−5] and, more recently, the salan ligands, which have been primarily used with Cr[22,24−29,32,35,37,63] and Co.[38,42,43,50,51,64] Nucleophilic cocatalysts are typically required with the most commonly used being chlorides or azides paired with bulky cations such as PPN (PPN = bis(triphenylphosphoranylidene)-ammonium) or tetrabutylammonium, or neutral bases such as dimethylaminopyridine (DMAP) or *N*-methylimidazole (*N*-MeIm). Because of their easily modifiable steric and electronic properties, these catalyst systems exhibit some of the highest activities reported to date, such as Darensbourg's report of a Cr(salen) catalyst, which exhibits a TOF of 1153 h^{-1} for the copolymerization of CHO and CO_2.[29] Cr-salan complexes also show high TOFs and under certain conditions rival the activities of the well-defined Cr-salen analogues.[32] Darensbourg recently reported the use of a CrCl(salan) complex which copolymerized propylene oxide and CO_2 with a TOF of 405 h^{-1} using 1 equiv of $[PPN]N_3$ as the cocatalyst at 60 °C and 34 bar CO_2 for 4 h.[34]

Detailed mechanistic studies of the copolymerization of CO_2 and epoxides at salen and salan complexes have recently been carried out.[18,21,38,63,65] Several pathways have been proposed based on identification of key intermediates using X-ray crystallography, infrared spectroscopy, or mass spectrometry. Some possible pathways for a model salen complex are described in Figure 1. Monometallic initiation pathways can occur via intermolecular nucleophilic attack (for example, by an

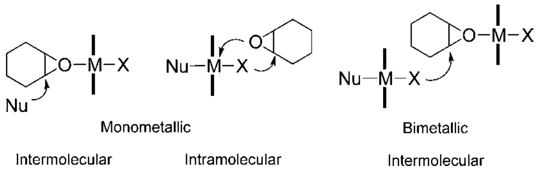


Figure 1. Initiation pathways for a model complex containing a planar salen ligand, a nucleophilic cocatalyst, Nu, and an anionic leaving group, X, which is typically a halide, azide or acetate.

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added neutral or anionic nucleophilic cocatalyst, Nu) on a precoordinated epoxide. This results in the cocatalyst nucleophile, Nu (such as chloride, azide or DMAP), being incorporated into the chain end-group of the growing polymer. Alternatively, intramolecular ring-opening of the coordinated epoxide monomer by a nucleophile may occur. The incoming nucleophile (Nu) binds to the metal site increasing the leaving group ability of ligand X, which would then become incorporated in the polymer chain end group. As both Nu and X can serve as initiator groups, either one may be observed in the chain end. However, if the loss of the X group occurs rapidly (either during a catalyst preactivation step or as an equilibrium with epoxide coordination), it would be possible for the X group to perform an intermolecular ring-opening of the coordinated epoxide. Lastly, two metal complexes may follow an intermolecular interaction, where an activated nucleophile (either X or Nu) on one metal site may ring open an epoxide that is coordinated to the metal site of a different complex.

Other metals and ligands are also being studied for epoxide/CO_2 copolymerization. For example, Nozaki and co-workers reported tetravalent group 4 (Ti and Zr) and 14 (Ge and Sn) metals supported by planar trianionic bis(phenolato) ligands have shown activity toward epoxide and CO_2 copolymerization, although the activities are typically lower than for previously reported catalysts.[66]

Whereas compounds of the salen (and the related salan) ligands represent the most investigated homogeneous systems for CO_2/epoxide copolymerization, the related tetradentate, tripodal amine-bis(phenolato) ligand class has yet to be investigated for this reaction. These ligands can be easily synthesized via a modified Mannich condensation reaction, and their desired steric and electronic properties may be obtained through changing the substituents on the phenolate groups or pendant arms.[67,68] We have studied these ligands in combination with various mid-to-late transition metals, including Cr,[69] Co,[70] and Fe,[71−74] and they have shown a diverse range of structural, spectroscopic, and electronic properties. We have also recently reported that Co(II) and Co(III) complexes of these ligands are capable of coupling CO_2 with propylene oxide under neat conditions (no added solvent) to give cyclic propylene carbonate.[75] Unfortunately, these Co complexes failed to produce any polypropylene carbonate under these conditions.

Because Cr(III) catalysts have shown excellent activity toward CO_2/epoxide copolymerization, we began a program to study the potential of our Cr(III) amine-bis(phenolato) complexes to catalyze this reaction. For this study, bulky *t*-butyl substituents on the phenolate groups were employed, and a pyridyl pendant arm comprised the second neutral donor site (Figure 2). This metal−ligand combination offers new avenues for development of potentially highly active catalysts because of the modifiable nature of the donor sites, their steric and electronic properties, and their geometry, which differs from that exhibited by the salen and salan-based systems. For example, the planar salen-based systems cause the nucleophilic cocatalyst, Nu, or epoxide monomer to preferentially bind trans to the X ligand. Trivalent metal complexes of tetradentate, tripodal amine-bis(phenolate) ligands, however, direct the incoming nucleophile or monomer to bind cis to the X group and trans to either an anionic phenolate donor or a neutral pendant donor (Figure 3). In this study, the pyridyl-containing ligand is used because of the favorable activity shown by cobalt complexes of this ligand for the coupling of CO_2 and propylene oxide to give propylene carbonate in good to excellent yields. Herein, we report the use of a Cr(III) amine-bis(phenolate) complex in the presence of ionic and neutral initiators as a catalyst for the copolymerization of cyclohexene oxide with CO_2.

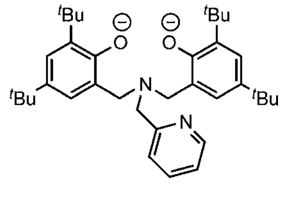


Figure 2. Tetradentate diamine-bis(phenolato) ligand [L] used in this study.

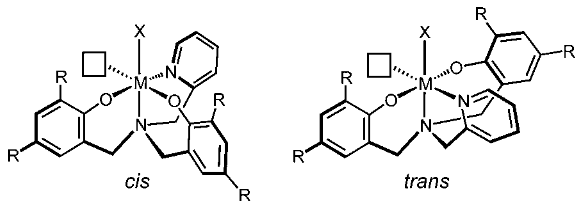
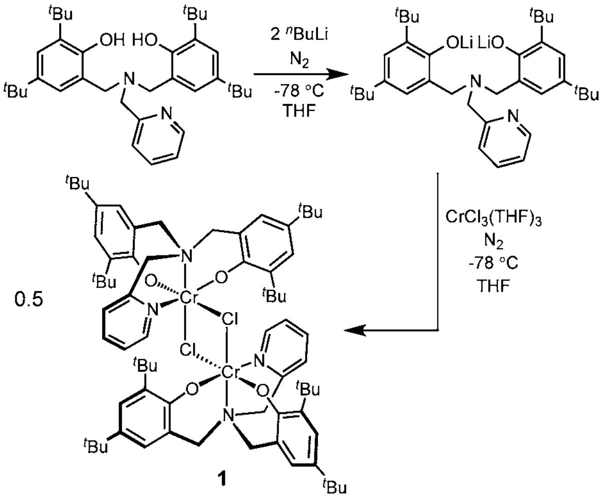


Figure 3. Position of vacant site available for coordination of incoming nucleophilic cocatalyst, Nu, or epoxide relative to nucleophilic ligand X. Phenolate donors may exhibit either cis or trans orientations.

RESULTS AND DISCUSSION

Synthesis and Characterization of Cr Complex 1. The Cr(III) diamine-bis(phenloate) complex (**1**) was synthesized via reaction of the protonated ligand at −78 °C in tetrahydrofuran (THF) with *n*-butyllithium followed by reaction of the resulting dilithium salt with $CrCl_3(THF)_3$ in THF at −78 °C to produce a brown solid in 80% yield (Scheme 1). The complex was characterized using MALDI-TOF mass spectrometry and UV−vis spectroscopy (see Supporting Information) and its composition as CrCl[L] confirmed by elemental analysis.

Scheme 1. Synthetic Route to $\{CrCl[L]\}_2$, Complex 1



Single crystals suitable for X-ray diffraction were grown from a benzene solution under N_2. In the solid-state, the structure of **1** was found to be a chloride-bridged dimer (Figure 4). The complex lies on an inversion center located within the Cr_2Cl_2 rhomboid and the Cr(III) centers exhibit distorted octahedral geometries. Although six coordinate chromium(III) complexes are common, non-Cp compounds bearing two bridging chlorides (Cr(μ-Cl)$_2$Cr) are not. These complexes often possess phosphines,[76,77] bis(phosphino)amines[78−80] or phosphinimines,[81] sulfanylamines,[82,83] or κ^2-nacnac ligands.[84] The structurally characterized Cr(μ-Cl)$_2$Cr motifs containing five-coordinate Cr(III) metal centers possess κ^2-nacnac[84−86] or diamidosilylether ligands.[87] Related dimeric Cr(III) complexes possessing salen and acacen (*N*,*N*′-bis(*t*-butylacetylacetone)-1,2-ethylenediamine) ligands have been used for copolymerization of cyclohexene oxide and CO_2; however, these compounds possessed bis-hydroxo bridging groups.[88] The Cr(1)−Cl(1)−Cr(1)* angle in **1** was 95.66(3)°, and the chlorides are orientated cis to the nitrogen on the pendant pyridyl group. This angle is typical of what is reported for other Cl-bridged Cr(III) dimers. The Cr−Cl bond distances are asymmetric at 2.4050(8) and 2.4431(8) Å. These distances are within the range observed for five or six-coordinate chromium(III) chloride-bridged species.

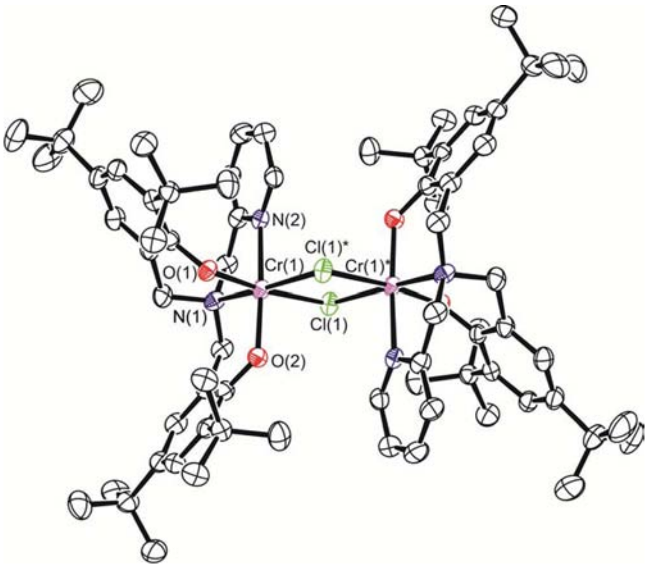
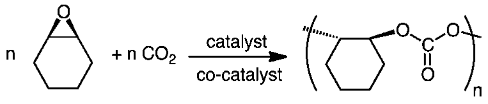


Figure 4. Molecular structure (ORTEP) and partial numbering scheme of $\{CrCl[O_2NN']^{BuBu}\}_2$ **1**. Ellipsoids are drawn at 50% probability. Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Cr(1)−O(2) = 1.9050(18), Cr(1)−O(1) = 1.9110(18), Cr(1)−N(2) = 2.103(2), Cr(1)−N(1) = 2.080(2), Cr(1)−Cl(1) = 2.4050(8), Cr(1)−Cl(1) = 2.4431(8), Cr(1)···Cr(1)* = 3.5935(2); O(2)−Cr(1)−O(1) = 93.33(8), O(2)−Cr(1)−N(1) = 91.15(8), O(2)−Cr(1)−N(2) = 171.78(8), N(1)−Cr(1)−N(2) = 80.96(8), N(1)−Cr(1)−Cl(1) = 173.80(7), N(2)−Cr(1)−Cl(1) = 94.74(6), O(1)−Cr(1)−Cl(1) = 173.93(6), O(2)−Cr(1)−Cl(1) = 91.89(6), Cl(1)−Cr(1)−Cl(1)* = 84.34(3), Cr(1)−Cl(1)−Cr(1)* = 95.66(3). Symmetry operation used to generate equivalent atoms: 1 − *x*, −*y*, 1 − *z*.

The room temperature effective magnetic moment of **1** in the solid state was observed to be 3.4 μ_B per mol of Cr(III), which is slightly lower than expected for a magnetically dilute $S = 3/2$ Cr(III) center.[89] Variable temperature magnetic measurements show the magnetic moment is virtually constant over the temperature range studied (2 to 300 K), and no evidence of exchange between the Cr(III) centers is observed (see Supporting Information).

Copolymerization of CO_2 and Cyclohexene Oxide. The copolymerization of CHO and CO_2 was investigated using complex **1**. Neutral or ionic cocatalysts such as (4-dimethylamino)pyridine (DMAP), bis(triphenylphosphoranylidene)ammonium chloride or azide, ([PPN]X where X = Cl^- or N_3^-) were employed in this study and were shown to be important for the formation of the desired product. When CHO, CO_2, complex **1**, and a cocatalyst are combined, strictly poly(cyclohexene carbonate) (PCHC) is produced with no evidence of cyclohexene carbonate (CHC) formation (Scheme 2).

Scheme 2. Copolymerization of CHO and CO_2 Producing PCHC



Initial reactions were performed by combining **1** with the ionic cocatalysts in neat epoxide and placing the mixture under elevated pressures of CO_2 (Table 1). Reactions were first explored at room temperature over 24 h in the presence of [PPN]Cl and [PPN]N_3 (entries 1 and 7). In both cases the activities were found to be low. Therefore, reaction temperatures were elevated to 60 °C (entry 2 for [PPN]Cl and entry 9 for [PPN]N_3) while still maintaining pressures of 40 bar, which gave increased TOFs. The PPN salts are poorly soluble in CHO, therefore subsequent reactions had the catalyst and cocatalyst mixture first dissolved in dichloromethane, which is the customary protocol employed when using this ionic cocatalyst with salen- or salan-based Cr^{III} catalysts.[34,36] Upon removal of the dichloromethane, the resulting catalyst mixture becomes soluble in CHO. This suggests that the [PPN]N_3 or [PPN]Cl cocatalysts react with **1** to possibly generate monometallic six-coordinate Cr(III) anions, $(CrX_2[O_2NN']^{BuBu})^-$, where X = Cl^- or N_3^- ligands, or a combination of the two. Similar anionic hexacoordinate Cr(III) anions of salen ligands have been previously reported.[90] Although we were unable to obtain structural authentication of such a species from complex **1**, we have previously reported that monometallic, six-coordinate Cr(III) solvento complexes of related ligands containing tetrahydrofurfuryl pendant arms can be obtained from THF solutions.[69] It is therefore suspected that the dimeric structure of **1** in the solid state may dissociate to give monometallic species when dissolved in cyclohexene oxide. Upon removal of the dichloromethane, the resulting catalyst mixture becomes soluble in CHO, and this improved solubility results in increased yield and TOF (entry 9 versus entry 10 for [PPN]N_3). The chloride salt gave lower yields of polycarbonate and moderately slower TOFs than the azide initiator, (entries 4 and 10, respectively). Reactions performed at 80 °C and 24 bar for 3 h (entries 5 and 11) gave the highest activities for these cocatalysts, but lower polymer molecular weights and broader polydispersity compared to reactions performed at 60 °C. A duplicate run shows this observation is reproducible and not due to premature termination or chain transfer caused by adventitious moisture (entry 6). Interestingly, increasing the amount of [PPN]N_3 cocatalyst from 0.5 equiv per Cr site (entry 11) to 1 equiv (entry 12) was not

Table 1. Results of the Copolymerization of CHO and CO_2 for Catalyst 1 with [PPN]X Salts[a]

entry	[Cr]:[CHO]:[Co-Cat.]	time (h)	temp. (°C)	pressure (bar)	% yield[b]	TON	TOF[c]	M_n[d] (kg/mol)	PDI[d] (M_w/M_n)
1	1:500:0.5 ([PPN]Cl)	24	22	39	13	65	3	ND[f]	ND
2	1:500:0.5 ([PPN]Cl)	24	60	45	72	360	15	11.7	2.3
3	1:500:0.5 ([PPN]Cl)	6	60	23	53	265	44	10.6	1.2
4[e]	1:500:0.5 ([PPN]Cl)	4	60	44	60	300	75	6.6	1.3
5[e]	1:500:0.5 ([PPN]Cl)	3	80	24	45	225	75	3.9	1.4
6[e]	1:500:0.5 ([PPN]Cl)	3	80	24	45	225	75	3.6	1.4
7	1:500:0.5 ([PPN]N_3)	24	25	38	59	295	12	9.5	1.4
8	1:500:0.5 ([PPN]N_3)	4	25	38	11	55	14	ND	ND
9	1:500:0.5 ([PPN]N_3)	4	60	43	52	260	65	7.2	1.4
10[e]	1:500:0.5 ([PPN]N_3)	4	60	40	71	355	89	7.1	1.2
11[e]	1:500:0.5 ([PPN]N_3)	3	80	24	58	290	97	3.8	1.3
12[e]	1:500:1 ([PPN]N_3)	3	80	23	55	275	92	2.7	1.4

[a] All polymerization reactions were carried out in neat CHO (4 mL). [b] Calculated by ^1H NMR. [c] Turnover frequency (TOF) is moles of repeating units produced per mol of Cr per hour. [d] Determined by gel permeation chromatography in $CHCl_3$, calibrated with polystyrene standards. [e] Activated in 4 mL of dichloromethane prior to adding CHO. [f] ND = not determined because of low yield of polymer produced.

Table 2. Results of the Copolymerization of CHO and CO_2 for Catalyst 1 with DMAP[a]

entry	[Cr]:[CHO]:[Co-Cat.]	time (h)	temp. (°C)	pressure (bar)	% yield[b]	TON	TOF[c]	M_n[d] (kg/mol)	PDI[d] (M_w/M_n)
1[e]	1:500:0.5 ([PPN]Cl)	3	80	24	45	233	78	3.9	1.4
2[e]	1:500:0.5 ([PPN]N_3)	3	80	24	58	296	99	3.8	1.3
3	1:500:0.5	3	80	24	58	288	96	9.2	1.2
4	1:500:0.5	24	21	39	25	123	5	5.8	1.3
5	1:500:0.5	24	60	44	81	400	17	13.1	1.4
6	1:500:0.5	19	60	42	83	417	22	10.3	1.1
7	1:500:0.5	12	60	40	77	382	32	9.4	1.1
8	1:500:0.5	6	60	44	63	318	53	11.5	1.7
9	1:500:0.5	2	60	44	29	150	75	ND[f]	ND
10	1:500:0.5	3	80	47	59	266	89	10.4	1.4
11	1:500:0.5	3	80	12	43	200	67	3.9	1.5
12	1:1000:0.5	6	60	43	12	122	20	ND	ND
13	1:500:1	3	80	22	69	349	116	8.0	1.1
14	1:500:1	1	80	24	47	219	219	4.8	1.3
15	1:1000:1	3	80	26	22	198	66	2.0	1.3
16	1:500:0	24	25	38	0	0	0	NA[f]	NA
17	1:500:0	24	60	43	7	33	1	ND	ND
18	0:500:0.5	24	60	45	0	0	0	NA	NA
19[g]	1:500:0.5	3	80	47	30	148	49	3.3	1.5
20	1:500:2	1	80	24	0	0	0	NA	NA

[a] All polymerization reactions were carried out in neat CHO (4 mL) using DMAP as the cocatalyst except where noted otherwise. [b] Calculated by ^1H NMR. [c] Turnover frequency (TOF) is moles of repeating units produced per mol of Cr per hour. [d] Determined by gel permeation chromatography in $CHCl_3$, calibrated with polystyrene standards. [e] Entries 5 and 11 from Table 1 have been reproduced here for comparative purposes. Activated in 4 mL of dichloromethane prior to adding CHO. [f] ND = not determined because of low yield of polymer obtained or difficulty in purification. NA = not applicable (no polymer obtained). [g] Reaction performed in 4:1 Toluene/CHO mixture.

found to improve the yield or activity of the system, but instead led to a modest broadening of polymer polydispersity.

Molecular weights were found to range between 2.7 and 11.7 kg/mol, when employing ionic cocatalysts. The highest molecular weights were observed after longer reaction times (entries 2 and 7). However, at higher temperatures (80 °C) a decrease in M_n was observed (entries 5, 6, 11, and 12). The polydispersity (M_w/M_n) values generally fell within the range of 1.2 to 1.4, with the exception of entry 2 where a very broad PDI was observed.

The effect of changing the cocatalyst to DMAP, a neutral base, was also explored for the copolymerization of CHO and CO_2 (Table 2). The azide initiator gave moderately higher yields of polycarbonate than the chloride salt (entries 1 and 2, reproduced from entries 5 and 11 in Table 1), whereas [PPN]N_3 and DMAP were very similar in inducing activity (entries 2 and 3, respectively). DMAP, however, is soluble in neat CHO thus simplifying the procedure compared to using the onium salts. The effect of temperature on the rate of copolymerization was also evident. Comparing the reactions carried out at 21 and 60 °C reveals a significant influence on the catalytic activities (entries 4 and 5, respectively). When performed at 60 °C, shorter reaction time was required to still maintain good yields and activities compared to reactions carried out for 24 h (entries 6 to 8), although after 2 h only moderate yields of oligomers of low molecular weight are obtained as shown by NMR, therefore the product could not be suitably purified for GPC or MALDI-TOF MS analysis. (entry 9). However, a significant increase in activity was observed upon raising the reaction temperature from 21 °C for 24 h (entry 3) to 80 °C for 3 h (entry 10). Decreasing the pressure to 12 bar while maintaining a temperature of 80 °C for 3 h showed a reduction in yield and TOF (entry 11). Decreasing the catalyst loading to 0.1 mol % from 0.2 mol % had a detrimental effect on the activity as shown in entry 12 and NMR spectroscopy showed only oligomers of polycarbonate were obtained, therefore no GPC data are given.

The amount of cocatalyst used is significant for the activity of this system. Increasing the ratio of DMAP to one equivalent per Cr center produced higher TOFs of 116 and 219 h^{-1} (entries 13 and 14, respectively), but again, lower catalyst loading caused a decreased yield of polycarbonate (entry 15). Clearly, the chloride-bridged dimer observed in the solid state is unlikely to persist in solution where potentially coordinating solvents (such as CHO) or Lewis basic cocatalysts are present. Therefore, the catalytically active species is most likely monomeric, similar to the salen analogues. Interestingly, PCHC could be produced without the need of a cocatalyst, albeit only in very low yields and TOF. Temperature was shown to be an important factor, because performing the reaction at 25 °C showed no conversion of CHO (entry 16), whereas at 60 °C 7% yield of polycarbonate was obtained (entry 17). In the absence of **1**, DMAP alone showed no conversion to PCHC or CHC (entry 18). To address the problem of mass transfer limitations on the overall yield of polymer, the reaction was performed in a 4:1 mixture of toluene and cyclohexene oxide (entry 19). However, the dilution of the reactants resulted in a polymer yield half of that obtained in neat CHO at the same temperature, pressure, and reaction time (entry 10). Lastly, using 2 equiv of DMAP per Cr center shuts down polymerization entirely (entry 20).[22] A recent report described an ESI-MS study of the coordination chemistry of DMAP with salen and salan chromium complexes. It showed that for salen complexes preferential binding of two DMAP molecules was observed, whereas the salan chromium complexes usually bind one molecule of DMAP. This was proposed to explain the lower activity shown by chromium salen complexes for copolymerization of propylene oxide and CO_2 compared to their salan analogues.[63]

Structural Analysis of the Copolymers. Preliminary results show that the percentage of carbonate linkages is dependent on the temperature at which the copolymerization was performed. At ambient temperature (Table 2, entry 4) ~13% of the copolymer consists of polyether linkages, while at higher temperatures only ~2% of the polymer consists of polyether fragments. It should also be noted that polyethers were not obtained when CHO solutions of **1** and DMAP were heated to 80 °C in the absence of CO_2. This observation suggests homopolymerization is not competitive to copolymer formation, unlike what is observed in related Cr^{III} catalytic systems for propylene oxide copolymerization.[3,5] The alternating copolymerization of CHO with CO_2 to form PCHC typically requires higher temperatures, and such is the case for catalyst **1**.[1,3,5]

The stereochemistry of the isolated poly(cyclohexene carbonate) was determined by examining the carbonyl region of its ^{13}C NMR spectrum, which showed the dominant configuration is atactic, consisting of mainly isotactic copolymer along with a significant percentage of syndiotactic PCHC (Figure 5).[91,92] The relative stereochemistry of the polymer obtained using achiral **1** is similar to that obtained using racemic tetradentate salen cobalt complexes with chiral diamine backbones.[55]

The number average molecular weights (M_n), determined by gel permeation chromatography (GPC) were found to only modestly increase with increased reaction time (Table 2, entries 5 to 8). Also, the polymer molecular weights observed are considerably smaller than the theoretical values. This suggests a chain-transfer process may be occurring because of a small amount of moisture in the reaction. A representative GPC trace of the polymer obtained from Table 2, entry 13 is given in the Supporting Information. The highest molecular weight of 13.1 kg/mol was observed after 24 h (Table 2, entry 5) whereas lower CO_2 pressures gave lower M_n. For all entries in Table 2 the polydispersity indices (PDIs) were found to be narrow ranging from 1.11 to 1.66.

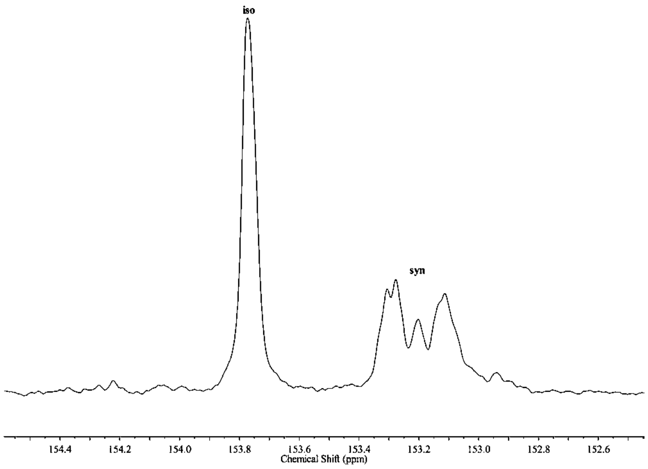


Figure 5. Carbonyl region of the ^{13}C NMR spectrum of CHO/CO_2 copolymer prepared at 60 °C and 44 bar for 6 h with DMAP as cocatalyst (Table 2, entry 8).

Matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) studies were performed to gain insight into the differences observed for theoretical and experimentally determined (GPC) values of the number average molecular weights of the copolymers. 2,5-Dihydroxybenzoic acid was used as the matrix without addition of a cationizing agent. The fragments in the spectrum were therefore treated as $[M+H]^+$ ions. In the MALDI-TOF mass spectra of these copolymers, multimodal molecular weight distributions were observed showing multiple series of signals all separated with a repeating unit of 142 *m/z* (Figure 6). A closer inspection of these repeating fragments shows the existence of four polymer chains whose molecular weights differ

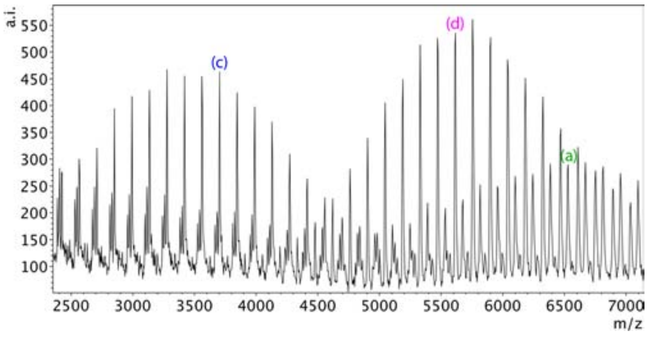


Figure 6. MALDI-TOF spectrum of poly(cyclohexene carbonate) obtained using **1** with DMAP as cocatalyst (Table 2, entry 13) showing distribution of three major components, (a), (c), and (d), of polymer mixture. Component (b) is observed primarily in the lower *m/z* range (see Supporting Information).

because of differing end groups (Figures 7 and 8). Molecular weight series marked (a) corresponds to the presence of two hydroxyl-terminated end groups [17 (OH) + 142*n* (repeating cyclohexene carbonate unit) + 99 ($C_6H_{11}O$)], which would result from water contamination causing chain transfer.[35,93] Series (b) is the expected series if polymerization is initiated by ring-opening of an epoxide monomer by a Cl and terminated by hydrolysis [35.5 (Cl) + 142*n* (repeating unit) + 82.0 (C_6H_{10}) + 17.0 (OH)]. Series (c) [35.5 (Cl) + 142*n* (repeating unit) + 82.0 (C_6H_{10}) + 35.5 (Cl)] contains Cl groups at both termini of the polymer and suggests that the chlorides from complex **1** (or from [PPN]Cl when it is used as the cocatalyst) are initiating the production of PCHC but are also somehow involved in the termination of the process. Series (c) could result from chain transfer between two growing polymer chains resulting in a single polymer containing two initiation sites as end groups. Series (d) is modeled to have an ether linkage-containing end group, which may be caused by double epoxide insertion as observed in the work of Williams et al.[94] Although a chain-transfer reaction appears to be occurring, indication of any broadening of the molecular weights is not evident. A similar observation was made by Nozaki et al.,[35] who suggest the copolymerization is arising in an immortal fashion, and this could likewise be occurring here. Regardless of the cocatalyst used, the chain ends are still limited to those shown in Figure 8. Specifically, no DMAP-containing polymers are observed by MALDI-TOF, unlike other examples where DMAP-containing end groups have been observed.[48,63]

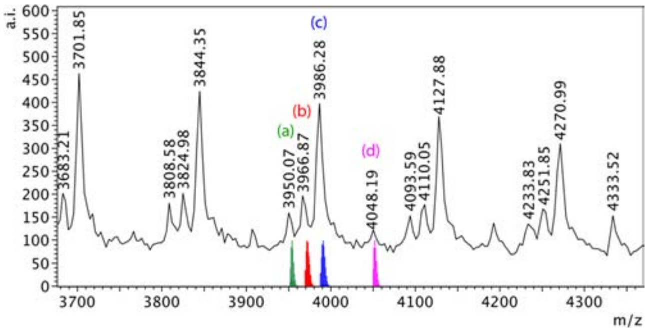


Figure 7. Magnified section of MALDI-TOF mass spectrum for poly(cyclohexenecarbonate) (*n* = 26−29) obtained using **1** with DMAP as cocatalyst. Modeled isotopic masses are shown for polymers (a−d) where *n* = 27 and containing chain ends shown in Figure 8.

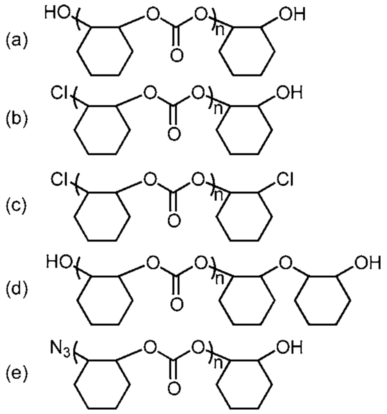


Figure 8. Series of chain end-groups observed in MALDI-TOF MS of copolymer produced by **1** and catalyst.

When [PPN]Cl was used (Table 1, entry 5), the MALDI showed series (a), (b), and (c), but no (d) was observed. When $[PPN]N_3$ was used (Table 1, entry 11), (a−c) were visible, and also no (d) was observed, but instead peaks assignable as $[N_3(C_7H_{10}O_3)_nC_6H_{10}OH]$ (e) were observed (see Supporting Information). However, as the combined mass of the end groups is 142.1 g/mol, which is identical to the mass of the repeating cyclohexene carbonate fragment, attributing this series to a cyclic polymer (resulting from polymer backbiting) cannot be discounted.

Thermal properties of the copolymers were also investigated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements. Representative traces of polymer obtained in Table 1, entry 8, are given in the Supporting Information. The onset of weight loss for PCHC was observed to range between 214 and 235 °C. The glass transition temperature (T_g) at the midpoint was found to range between 90 and 108 °C. Similar weight loss and T_g values for PCHC have been reported by others.[34,53] Two independently prepared polymer samples were analyzed by ICP-MS and were shown to contain Cr concentrations of 149 and 170 ppm. These concentrations are encouragingly low, given that the polymers obtained were purified from dichloromethane solutions by precipitation using methanol.

■ CONCLUSIONS

Chromium diamine-bis(phenolate), $\{CrCl[O_2NN']^{BuBu}\}_2$ (**1**), was shown to copolymerize CHO and CO_2 in the presence of three cocatalysts (DMAP, [PPN]Cl, $[PPN]N_3$) to give PCHC with no evidence of cyclic carbonate being formed and with a high degree of carbonate linkages. The number average molecular weights were shown to be lower than expected, but the polydispersities observed are generally narrow. The amount of Cr contaminants in the resulting polymer was also found to be relatively low given the simple method of purification. The influence of the pendant donor and substituents on the phenolate fragments of the amine-bis(phenolate) ligand are currently under investigation.

■ EXPERIMENTAL SECTION

General Experimental Conditions. Unless otherwise stated, all manipulations were performed under an atmosphere of dry oxygen-free nitrogen by means of standard Schlenk techniques or using an MBraun Labmaster glovebox. $CrCl_3(THF)_3$ was prepared by the standard method,[95] whereas $H_2[O_2NN']^{BuBu}$, was prepared by a modified literature procedure by using water instead of methanol as the reaction medium.[68,69] UV−vis spectroscopy was conducted on an Ocean Optics USB4000+ fiber optic spectrophotometer. Variable-temperature magnetic moments were measured on crystalline samples at 1000 G using a Quantum Design MPMS-5S SQUID magnetometer. The data were corrected for background and for the diamagnetism of all atoms. Elemental analysis was performed at Canadian Microanalytical Service, Ltd. Delta, BC, Canada. CHO was purchased from Aldrich and freshly distilled from CaH_2. THF and benzene were purified by distillation from sodium/benzophenone ketyl under nitrogen. All other solvents were purified by an MBraun Manual Solvent Purification System. $[PPN]N_3$ was prepared according to the literature procedure.[96] 4.8 Supercritical fluid chromatography grade CO_2 was supplied from Praxair in a high-pressure cylinder equipped with a liquid dip tube. All ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ purchased from Cambridge Isotope Laboratories, Inc. ^1H NMR spectra were recorded on either a Bruker AVANCE 500 MHz or Bruker AVANCE III 300 MHz spectrometer. All ^{13}C NMR spectra were recorded on a Bruker AVANCE III spectrometer at 75.487 MHz. Chemical shifts are given in ppm relative to TMS. All copolymerization reactions were carried out in a 300 mL stainless steel Parr 5500 autoclave reactor with a Parr 4836 controller. N.B. Caution should be taken when operating high-pressure equipment.

$\{CrCl[O_2NN']^{BuBu}\}_2$ (1). $H_2[O_2NN']^{BuBu}$ (4.00 g, 7.42 mmol) was dissolved in THF (50 mL) and cooled to −78 °C. *n*-Butyllithium (1.6 M in hexanes, 9.3 mL, 14.84 mmol) was slowly added to give a dark orange solution of $Li_2[O_2NN']^{BuBu}$, which was warmed to room temperature and further stirred for 2 h. This mixture was transferred via cannula to a suspension of $CrCl_3(THF)_3$ (2.75 g, 7.40 mmol) in THF (50 mL) cooled to −78 °C to give a dark brown mixture. Upon warming to room temperature and stirring for 16 h the solids dissolved giving a dark brown solution. The solvent was removed in vacuo, and the residue was extracted into toluene. The mixture was filtered through Celite, and the solvent was removed under vacuum. The product was washed with pentane and dried to yield 4.62 g of dark brown powder. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution of **1** in benzene at room temperature in a glovebox under nitrogen. Anal. Calcd for $C_{36}H_{50}ClCrN_2O_2$: C, 67.47; H, 7.86; N, 4.37. Found: C, 67.12; H, 8.36; N, 4.38. MS (MALDI-TOF) *m*/*z* (%, ion): 1259.6 (10, $[Cr_2Cl_2[L]_2^+]$), 629.3 (80, $[CrCl[L]^+]$), 593.3 (20, $[Cr[L]^+]$). UV−vis (CH_2Cl_2) λ_{max}, nm (ε): 235 (46 500), 280 sh (23 000), 380 sh (3100), 600 (450).

X-ray Crystallography. Diffraction data for compound **1** were collected on a Rigaku Saturn CCD area detector with a SHINE optic and Mo−Kα radiation and solved on an AFC8-Saturn 70 single crystal X-ray diffractometer from Rigaku, equipped with an X-stream 2000 low temperature system. Crystallographic and structure refinement data are given in Table 3. The data were processed using CrystalClear[97] software and corrected for Lorentz and polarization effects and absorption.[98] Neutral atom scattering factors for all non-hydrogen atoms were taken from the *International* Tables *for X-ray Crystallography*.[99] The structure was solved by direct methods using SIR92[100] and expanded using Fourier techniques (DIRDIF99).[101] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. Anomalous dispersion effects were included in F_{calc};[102] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[103] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[104] All calculations were performed using the CrystalStructure[105] crystallographic software package except for refinement, which was performed using SHELXL-97.[106] Disordered lattice solvent for **1** was removed through applying Platon's Squeeze[107] procedure. Structural illustrations were created using ORTEP-III (v. 2.02) for Windows.[108]

Table 3. Crystallographic and Structure Refinement Data for 1

chemical formula	$[(C_{36}H_{50}N_2O_2)ClCr]_2(C_6H_6)_{2.5}$
formula weight	1455.79
T/K	153
color, habit	blue, prism
crystal dimensions/mm	0.21 × 0.14 × 0.08
crystal system	monoclinic
space group	$P2_1/c$ (#14)
a/Å	15.3979(12)
b/Å	13.4522(10)
c/Å	21.3183(17)
α/deg	90
β/deg	109.020(2)
γ/deg	90
V/Å^3	4174.7(6)
Z	2
D_c/ g cm^{-3}	1.158
μ(MoKα)/cm^{-1}	3.73
F(000)	1558
reflections collected	53 858
independent reflections	8 649
R(int)	0.064
R, wR^2 (all)[a]	0.0847, 0.1668
R, wR^2 $[I > 2\sigma(I)]$[a]	0.0640, 0.1548
GOF on F^2	1.077
CCDC reference	864455

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Copolymerization Procedure. Reactions were carried out neat with the appropriate amount of monomer added to the catalyst (0.5 g) and cocatalyst in a glovebox. The reactant solution was added via syringe to a 300 mL Parr autoclave, which was predried under vacuum overnight at 80 °C. The autoclave was then charged with the appropriate pressure of CO_2 and left to stir at the desired temperature and time period. After the desired time the autoclave was cooled in an ice bath and vented in the fume hood. An aliquot for NMR was taken immediately after opening for the determination of yield and conversion. The copolymer was extracted with CH_2Cl_2 and reprecipitated in cold, acidic methanol. For reactions done in the presence of [PPN]X salts, complex **1** and the cocatalyst were first combined in 4 mL of CH_2Cl_2 and allowed to stir for 30 min before removal of solvent in vacuo. The remaining procedure was followed in the same manner as described above.

Inductively Coupled Plasma Mass Spectrometry. Analysis of 100 mg of purified and dried PCHC sample was dissolved in distilled concentrated nitric acid. The sample was heated on a hot plate overnight. This was followed by dilution of the sample to 60 g with Nanopure water. The solution was centrifuged, diluted to 10%, and analysis was carried out on an Elan DRCII ICP-MS.

Thermal Gravimetric Analysis. Thermal gravimetric analysis (TGA) was performed with a TA Instruments Q500. Samples (8 mg) were loaded onto a platinum pan and subjected to a dynamic high-resolution scan, with an initial heating rate of 20 °C/min. Each sample was heated from room temperature to 400 °C.

Differential Scanning Calorimetry Measurements. Glass transition (Tg) temperatures were measured using a Mettler Toledo DSC 1 STAR System equipped with a Julabo FT 100 immersion cooling system, using a R1150 refrigerant in an EtOH bath with a working range of −100 to +20 °C. Samples (∼4 mg) were weighed into 40 μL aluminum pans and subjected to two heating cycles. The first heating cycle consisted of heating from 0 to 100 °C at a rate of 10 °C/min, held for 2 min at 100 °C and then cooled back to 0 at 10 °C/min. The sample was held at this temperature for 2 min and subjected to a second heating cycle from 0 to 180 °C at a rate of 10 °C/min.

Gel Permeation Chromatography. Gel permeation chromatography (GPC) analysis was performed on a Viscotek VE 2001 GPCMax at 35 °C equipped with a Viscotek VE 3580 RI Detector, and two phenogel 5 μ Linear Mixed Bed columns purchased from Phenomenex (300 × 4.60 mm column in series with a 100 Å, 300 × 4.60 mm column). Samples were prepared at a concentration of 2 mg/mL and left to equilibrate for ∼2 h. The samples were filtered through syringe filters before analysis. The GPC columns were eluted with chloroform (HPLC grade) at a flow rate of 0.35 mL/min with a 100 μL injection volume. Six polystyrene standards were used in making the calibration curve, bracketing molecular ranges from 1050 to 3 800 000 Da. No further corrections were performed on the molecular weights obtained.

MALDI-TOF Mass Spectrometry. MALDI mass spectrometry for complex **1** were carried out on a QSTAR XL hybrid quadrupole/time-of-flight MS equipped with an o-MALDI ion source. Anthracene was used as the matrix. An Applied Biosystems 4800 MALDI TOF/TOF Analyzer equipped with a reflectron, delayed ion extraction, and high performance nitrogen laser (200 Hz operating at 355 nm) was used for polymer analysis. 2,5-Dihydroxybenzoic acid (DHBA) was used as the matrix. The matrix was dissolved in THF at a concentration of 10 mg/mL. Polymer was dissolved in THF at approximately 1 mg/mL. The matrix and polymer solutions were mixed together at a ratio of 5 to 1, respectively; 1 μL of this was spotted on the MALDI plate and left to dry.

ASSOCIATED CONTENT

Supporting Information

UV−vis spectrum and variable-temperature magnetic moment plot of **1**, representative ^{1}H NMR spectra of PCHC, MALDI-TOF MS of **1** and PCHC, TGA, DSC traces for PCHC, and crystallographic information file (CIF) for complex **1** (CCDC reference: 864455). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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