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Introduction

The copolymerization of epoxides and carbon dioxide to yield polycarbonates has garnered growing interest as a process for generating potentially valuable materials from renewable starting materials.¹⁻⁶ Due to its widespread availability, low cost, and nontoxicity carbon dioxide is appealing as a C1 feedstock⁷ and many homogeneous catalysts have been examined for use in the copolymerization of CO_2 and epoxides. These catalysts can employ a variety of metal sites, such as Al,⁸⁻¹² Zn,¹³⁻²¹ Cr,²²⁻³⁷ Co^{6,38-56} and most recently Fe.⁵⁷ Most studies focus on cyclohexene oxide (CHO) as the epoxide reagent with propylene oxide (PO) being much less studied. While PO has been a problematic reagent because of the propensity to form cyclic propylene carbonate (PC), its use is still warranted given polypropylene carbonate possesses desirable physical properties.⁵⁸

Previous reports of epoxide and CO_2 copolymerization include such ligand classes as the porphyrins, where $Cr^{23,59,60}$ and Al^{12} complexes have been used. Another established ligand system introduced by Darensbourg and Holtcamp used

Reaction of CO₂ with propylene oxide and styrene oxide catalyzed by a chromium(III) amine-bis-(phenolate) complex†

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A diamine-bis(phenolate) chromium(iii) complex, $\{CrCl[O_2NN']^{BuBu}\}_2$ catalyzes the copolymerization of propylene 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 when the reaction is performed at room temperature. Performing the reaction at elevated temperatures causes the selective synthesis of propylene carbonate. The copolymerization activity for propylene oxide and carbon dioxide, as well as the coupling of carbon dioxide and styrene oxide to give styrene carbonate are presented.

for epoxide/CO2 copolymerization includes the phenoxides, where Zn is commonly the metal used.⁶¹⁻⁶³ Coates and coworkers subsequently explored 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/CO2 copolymerization have been the salen³⁻⁵ and, more recently, the salan ligands, which have Cr^{22,24-29,32,35,37,64} with been primarily used and Co.^{38,42,43,50,51,65} Nucleophilic co-catalysts 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). Due to 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 CO2.29 Cr-salan complexes also show high TOFs and under certain conditions rival the activities of the well-defined Cr-salen analogs.³² Darensbourg recently reported the use of a CrCl(salan) complex which copolymerized propylene oxide and CO2 with a TOF of 405 h⁻¹ using 1 equivalent of [PPN]N3 as the co-catalyst at 60 °C and 34 bar CO₂ 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^{18,21,38,64,66} and some possible initiation pathways for a model salen complex are described in Fig. 1. Monometallic initiation pathways can occur *via* intermolecular

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

nucleophilic attack (for example, by an added neutral or anionic nucleophilic co-catalyst, Nu) on a pre-coordinated epoxide. This results in the co-catalyst nucleophile, Nu (such as chloride, azide or DMAP) being incorporated into the chain end-group of the growing polymer. Intramolecular ring opening of the coordinated epoxide monomer by a nucleophile may alternatively 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 pre-activation 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.

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^{70–72} and Fe,^{73–76} and they have shown a diverse range of structural, spectroscopic and electronic properties.

We have recently reported the use of Cr(m) catalyst **1a** (Fig. 2) for the copolymerization of CO_2 with cyclohexene oxide to give polycyclohexene carbonate.⁷⁷ We then sought to investigate whether other epoxides could be used. For this study, bulky *t*-butyl substituents *ortho* to the C–O groups on the phenolates were employed, and a pyridyl pendant arm comprised the second neutral donor site. 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 co-catalyst, Nu, or epoxide monomer to preferentially bind *trans* to the X ligand. Trivalent



Fig. 2 Diamino-bis(phenolato) chromium chloride complexes used in this study. R = t-Bu (**1a**), R = Me (**1b**) (left). Position of vacant site available for coordination of incoming nucleophilic co-catalyst, Nu, or epoxide relative to nucleophilic ligand X. Phenolate donors may exhibit either *cis* or *trans* orientations (right).



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 (Fig. 2). In this study, we report the use of Cr(m) amine-bis(phenolate) complexes in the presence of ionic and neutral initiators as catalysts for the coupling or copolymerization of propylene oxide or styrene oxide with CO_2 .

Results and discussion

The synthesis and structure of **1a** has been previously reported⁷⁷ and **1b** can be obtained a similar route, which is reported here. Although the solid-state structure of **1b** has not been obtained at this time, its spectroscopic properties are similar to those of **1a** and it is therefore highly likely that it also exists as a dichloro-bridged species. Furthermore, a dihydroxide-bridged product derived from **1b** has been obtained during the course of this study and structurally authenticated. Further details of this product are given below.

Initial studies were conducted on propylene oxide (PO) with CO_2 catalyzed by complex **1a**. As outlined in Scheme 1, either the cyclic product, propylene carbonate (PC), and/or the polymer, poly(propylene carbonate) (PPC), were obtained for this process depending on the conditions used. The copolymerization reactions investigated utilized common co-catalysts previously reported in the literature to give high yields of copolymer.^{28,78} Neutral or ionic co-catalysts such as

(4-dimethylamino)pyridine (DMAP), bis(triphenylphosphoranylidene)iminium chloride or azide (PPNCl or PPNN₃), and tetrabutylammonium bromide (TBABr) have been shown to play an important role in the outcome of the desired product.

When only 1a with no co-catalyst was used, 100% conversion of PO to PC was observed regardless of reaction temperature as shown in Table 1, entries 1 and 2. However, complex 1a combined with PPNN₃ co-catalyst gives high selectivity for polycarbonate at room temperature and moderate pressure of CO_2 . The polymer obtained is of low molecular weight but also narrow polydispersity (entry 3). Without 1a, no PPC was produced, observing an 85% conversion to PC after 24 hours (entry 4). It has previously been shown that PPN salts with strong nucleophilic anions, e.g. PPNCl, are good catalysts in their own right for the coupling of CO_2 with neat epoxides.⁷⁹ Changing the amount of co-catalyst from 1 equivalent (entry 3) to 0.5 equivalents (entry 5), did not prove to have a significant effect on the activity, however, a lower number average molecular weight (M_n) was observed when using a higher loading of PPNN₃. Generally, comparable results were obtained using PPNN₃ (entries 5 and 6) or PPNCl (entries 8 and 12) as the cocatalyst under otherwise similar conditions. The catalyst loading also proved to be an important parameter. Using a 0.1% catalyst loading vs. epoxide monomer (entry 7) gave good selectivity for polycarbonate, but low yield. The polymer obtained was found to have a similar molecular weight to that obtained when employing a 0.2% catalyst loading with PPNN₃ (entry 5), but was more polydisperse. These molecular weight values were reproducible over three runs. Increasing the

catalyst loading to 0.2% (entry 8) gave a much higher yield of polycarbonate and maintained selectivity. Generally, using PPNCl as the co-catalyst (entries 8–12) gave good-to-excellent selectivity for polycarbonate, but required long reaction times. After 12 or 6 h (entries 10 and 11, respectively) modest yields of polymer were obtained. Since the PPNX salts were found to be sparingly soluble in epoxides at room temperature, a reaction was carried out where the autoclave was brought into the glove box in order to add complex **1a** and the desired equivalents of co-catalyst and epoxide accurately. This procedure showed an improvement in the yield, while still maintaining good M_n and PDI (entry 12).

Mass transfer limitations inhibited the ability to increase yields due to the solidification of the polymer. Therefore, the use of a non-coordinating solvent, toluene, was explored to prevent precipitation of the polymer in the autoclave during the reaction. Unfortunately, no copolymer or cyclic carbonate was produced in the presence of a co-solvent (entry 13). Heating the reaction to 80 °C for 4 h (entry 14) did not improve the yield of polymer. Under these conditions, quantitative conversion of propylene oxide to cyclic propylene carbonate was observed instead. This result was not surprising as Darensbourg and co-workers have shown that cyclic propylene carbonate preferentially forms at higher reaction temperatures.25

DMAP (entries 15 and 16) and TBABr (entries 17 and 18) were screened as Lewis basic co-catalysts. However, they were found to be inferior to PPNCl under the conditions investigated in entry 8. Using DMAP as co-catalyst at room

Table T	copolymenzation of coupling of PO and CO ₂										
Entry	[Cr]:[PO]:[Co-Cat.] (per Cr centre)	Time (h)	Temp. (°C)	Pressure (bar)	Yield ^b PPC (%)	Selectivity ^c (%)	Conversion ^b (%)	TON ^d	$\begin{array}{c} {\rm TOF}^d \\ {\rm (h}^{-1} {\rm)} \end{array}$	M_n^e (kg mol ⁻¹)	$M_{ m w}/M_{ m n}^{\ e}$
1^f	1:270:0	24	60	47	0	0	100	0	0	NA^{g}	NA
2^{f}	1:270:0	48	25	40	0	0	100	0	0	NA^{g}	NA
3	1:500:1 (PPNN ₃)	24	23	38	83	88	94	414	17	5.5	1.14
4^{f}	0:500:1 (PPNN ₃)	24	23	45	0	0	85	0	0	NA	NA
5	1:500:0.5 (PPNN ₃)	24	25	45	83	93	89	422	18	21.1	1.15
6^h	1:500:0.5 (PPNN ₃)	6	25	40	59	96	61	280	47	12.4	1.19
7	1:1000:0.5 (PPNCl)	24	25	42	33	82	40	315	13	18.7	1.40
8	1:500:0.5 (PPNCl)	24	23	37	85	93	100	418	17	13.3	1.40
9	1:500:0.5 (PPNCI)	16	22	39	69	95	91	334	21	10.9	1.27
10	1:500:0.5 (PPNCI)	12	23	40	42	51	81	223	19	8.7	1.21
11	1:500:0.5 (PPNCI)	6	25	40	41	93	44	200	33	12.4	1.19
12^h	1:500:0.5 (PPNCI)	6	25	40	59	92	64	287	48	11.5	1.17
13 ⁱ	1:500:0.5 (PPNCI)	4	25	37	0	0	0	0	0	NA	NA
14^{f}	1:500:0.5 (PPNCl)	4	80	47	0	0	100	0	0	NA	NA
15	1:500:0.5 (DMAP)	24	24	39	73	73	100	386	16	12.7	1.32
16 ^f	1:500:0.5 (DMAP)	24	60	47	0	0	99	0	0	NA	NA
17	1:500:0.5 (TBABr)	24	25	40	42	46	65	212	9	ND^{g}	ND
18 ^f	1:500:0.5 (TBABr)	24	60	48	0	0	100	0	0	NA	NA
19^{f_j}	1:500:1 (TBABr)	24	22	37	0	0	100	0	0	NA	NA
20^{j}	1:500:1 (PPNCI)	24	22	39	66	83	80	330	14	6.4	1.19

 Table 1
 Copolymerization or coupling of PO and CO2⁴

^{*a*} Polymerization reactions were carried out in neat PO (2.8 mL) using **1a**, except where noted. ^{*b*} Yield calculated for PPC formation, conversion is % PO consumed as determined by ¹H NMR. ^{*c*} Selectivity of polycarbonate over cyclic carbonate in units of % as determined by ¹H NMR of the crude product. ^{*d*} Turnover number (TON) is moles of repeating units of PPC produced per mol of Cr, turnover frequency (TOF) is moles of PPC produced per mol of Cr, turnover frequency (TOF) is moles of PPC formed only PC. ^{*g*} NA = not applicable (no polymer obtained), ND = not determined due to lack of polymer and/or work-up related issues. ^{*h*} Loaded reagents into autoclave in glove box. ^{*i*} Reaction performed in toluene (16 mL). ^{*j*} **1b** used as initiator.

temperature and a CO₂ pressure of 39 bar gave 73% yield of polycarbonate in good selectivity after 24 h (entry 15). However, raising the temperature of the reaction to 60 °C led to nearly quantitative yield of propylene carbonate instead (entry 16). A similar trend was observed when TBABr was employed as the co-catalyst. Modest yield of polymer was obtained at room temperature (entry 17) but raising the temperature, again, gives quantitative yield of propylene carbonate and no polymer (entry 18). This temperature dependence is an intriguing feature of the reaction mechanism. The selectivity of a combination of catalyst and co-catalyst can be switched very easily by varying the temperature of the reaction. In short, performing the reaction at room temperature produces polycarbonate whereas raising the temperature produces propylene carbonate in high yield. When complex 1b was used as initiator using TBABr as co-catalyst at room temperature, excellent yields of PC were obtained but no PPC was observed (entry 19). Using PPNCl was more successful in producing polycarbonate (entry 20).

Comparing to recent results in the literature, Darensbourg and co-workers³⁴ reported an effective catalyst system using 1 equivalent of PPNN₃ in *rac*-PO with a CrCl(salan) derivative. Poly(propylene carbonate) was obtained at room temperature and under relatively low pressure yielding a polymer with a molecular weight of 8.0 kg mol⁻¹ and a turnover frequency of 21 h⁻¹. By comparison, entries 5 and 11 in Table 1 (using 0.5 equivalents of PPNN₃ and PPNCl, respectively) achieved TOFs of 47 and 48 h⁻¹. Lu, Zhang and co-workers have observed the use of a Cr(salan) complex in the presence of 1 equivalent of DMAP gave TOFs of 86 h⁻¹ at room temperature and lowpressure.⁶⁴

Although this new catalyst system shows similar catalytic activity to Cr salen and salan systems for PO/CO_2 copolymerization, Co(salen) catalysts are observed to have the highest activities, best stereochemical control and highest molecular weights reported in the literature.^{45,51,56}

NMR spectroscopy

¹H NMR was used in the initial analysis of the product formed, whereby an aliquot of the crude reaction mixture was analyzed immediately after the reaction was terminated, in order to determine the conversion/yield and selectivity of the products produced. Integration of the methine protons in the ¹H NMR spectra allowed quantitative determination of the amount of cyclic carbonate produced relative to polycarbonate formation (Fig. 3). Interestingly it was also noticed that if the catalyst was not totally removed from the polymer in CDCl₃ (aliquot samples for NMR analysis), depolymerization occurred causing propylene carbonate formation to increase over the period of 1 week at room temperature (Fig. 4).

In addition, ¹H NMR allowed for the identification of etherlinkages, which were just discernable in the spectra. The copolymerization of PO and CO₂ by complex **1a**, therefore, afforded approximately 99% carbonate linkages. MALDI-TOF MS studies have also provided evidence towards a highly alternating copolymer. Quantitative ¹³C NMR of the carbonyl region

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Fig. 3 $\,^{1}\text{H}$ NMR of the copolymerization of PO and CO_2 (Table 1, entry 3, 300 MHz, CDCl_3).



Fig. 4 1 H NMR of the depolymerization of PPC to PC with time (300 MHz, CDCl₃).

allowed for the determination of regiochemistry in PPC (Fig. 5). Similar to related catalysts^{34,80} complex **1a** is highly selective for head-to-tail (HT) linkages (Fig. 6) showing 80–100% regioselectivity, whereas the polymer obtained using **1b** (entry 20) showed nearly exclusively HT regioregularity (Fig. 5 inset).

Mass spectrometry

The MALDI-TOF spectrum of poly(propylene carbonate) produced in Table 1, entry 8 (using 1a and PPNCl as the catalytic system), along with end group assignments is shown in Fig. 7. The MALDI-TOF spectrum of polymer produced using 1a and PPNN₃ (Table 1, entry 5) is given in ESI.[†] The observed mass spectra show the presence of three polymer chains. The lowest molecular weight corresponds to series (a), [Cl (35) + 102*n* (repeating unit) + C₃H₇O (59)] where PPC is found to have end groups with a chloride as the initiator and a hydroxyl at the terminating end. Series (b) is found to have both ends terminated by Cl, [Cl (35) + 102*n* (repeating unit) + C₃H₆Cl (77)]. The highest molecular weight series (c), [Cl (35) + 102*n* (repeating

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154.8 154.7 154.6 154.5 154.4 154.3 154.2 154.1 154.0 153.9 153.8 153.7 153.6 153.5 153.4 153.3 Chemical Shift (nom)

Fig. 5 Carbonyl region of the ¹³C NMR spectrum in $CDCl_3$ of PO/CO_2 copolymer prepared with **1a** and PPNCI (Table 1, entry 7). Inset: Carbonyl region of ¹³C NMR spectrum of copolymer prepared with **1b** and PPNCI (Table 1, entry 20).



unit) + $C_6H_{12}O(100)$ + Cl (35)] is modeled to have an ether-containing group within the polymer, likely resulting from double insertion of an epoxide unit during the reaction. Isotopic masses modeled for series a-c are found to agree well with the experimental peaks. In addition, all co-catalysts were observed to give the same three polymer chains in their MALDI-TOF spectra. This suggests ring opening of the epoxide is induced by the Cl group of the metal complex rather than by the cocatalyst because no DMAP, bromide or azide-containing endgroups were identified in the MALDI-TOF spectra when those nucleophiles were used as co-catalysts.

Gel permeation chromatography

Gel permeation chromatography (GPC) was utilized in the determination of polymer molecular weights and polydispersity indices (PDIs). Resulting molecular weights listed in Table 1 were found to be dependent on reaction time. Higher molecular weights were generally obtained over longer reaction times. PDIs were usually observed to be narrow, with most ranging between 1.1 and 1.4. Similar to the MALDI-TOF MS



Fig. 7 (A) MALDI-TOF MS of PPC produced by **1a** (Table 1, entry 8). (B) Magnified region of the spectrum (n = 44-48). Modeled isotopic masses (when n = 47) and images for polymer chains with end groups (a–c).

results, bimodal distributions were also observed in some GPC traces making accurate analysis of M_n values difficult.

Thermal analysis (DSC and TGA)

Thermal analysis was also performed on the polymers obtained. Differential scanning calorimetry (DSC) measurements of the PPC afforded glass transitions (T_g) ranging from 35 °C to 40 °C. The DSC trace and observable T_g for PPC produced by complex **1a**, Table 1, entry 8 is given in ESI.[†] The T_g values obtained are found to be within the ranges reported in the literature.^{53,81} Thermal gravimetric analysis (TGA) indicated 50% decomposition (T_{50}) at 146–187 °C. A representative TGA trace and derivative plot is shown in ESI.[†] Darensbourg and coworkers have shown a similar TGA value where the onset of weight loss at 175 °C was determined for PPC.³⁴

Coupling of styrene oxide and CO₂

Preliminary studies were also conducted on the reaction of styrene oxide (SO) and carbon dioxide (Scheme 2). All reactions were performed in neat SO and initiated by complex **1a**. In all cases, only the cyclic product, styrene carbonate (SC) was obtained. The ¹H NMR spectra of the products were found to



Scheme 2 Coupling of SO and CO₂ to give styrene carbonate.

be consistent with previously characterized SC (see ESI[†]).⁸² An aliquot was taken from the reaction mixture in order to calculate the % yield.

Complex 1a does exhibit some activity for the cyclic carbonate product, styrene carbonate at high temperatures and pressures (Table 2). Reactions performed at room temperature using DMAP as co-catalyst and approximately 40 bar CO₂ pressure did not yield any carbonate-containing product (entry 1). Increasing reaction temperature to 80 °C yielded 16% SC after 3 hours under 50 bar CO_2 (entry 2). Increasing the temperature further to 100 °C (entry 3), gave an improved yield and TOF by almost double that of entry 2. Since the reactions were observed to proceed slowly even at high temperatures, longer reaction times were investigated. Using DMAP as co-catalyst at 80 °C and 50 bar over 18 h gave 38% yield of styrene carbonate (entry 4). Changing the co-catalyst to PPNCl yielded 65% SC over 18 h (entry 5). Unfortunately, no copolymer was produced with this Cr initiator and these co-catalysts. This result was not surprising as the copolymerization of SO/CO₂ to form poly (styrene carbonate) is known to be very difficult to achieve due to the occurrence of the ring-opening at the methine Ca-O bond. The electron-withdrawing nature of styrene oxide causes backbiting to occur through intramolecular cyclic elimination.⁸² Recent advances with Co(salen) catalysts⁸²⁻⁸⁴ in conjunction with PPNX [X = acetate or 2,4-dinitrophenoxy] cocatalysts, has produced alternating poly(styrene carbonate) with an increase in thermal stability.⁸²

Mechanistic considerations

Epoxide/ CO_2 copolymerization has been proposed to proceed by a coordination-insertion mechanism *via* a monometallic single site or through a bimetallic dual site fashion. Darensbourg and co-workers for example, have performed detailed mechanistic studies for Cr(salen)X and Cr(salan)X complexes towards epoxide/ CO_2 copolymerization.⁴

The proposed mechanism for this system is shown in Scheme 3. Based on the results obtained, preliminary mechanistic insights can be proposed. For instance, experimental findings from MALDI-TOF MS have suggested that a chloride (originating from the Cr complex) can initiate the ring-opening of the epoxide whether a neutral or ionic co-catalyst is utilized. In the copolymerization of PO/CO₂ only chloride end groups were observed as possible initiators in the MALDI-TOF MS. However, in our previous study involving CHO, hydroxyl and chloride initiators were observed.⁷⁷ The presence of the OH end groups along with lower than expected $M_{\rm n}$ values suggests chain transfer reactions are occurring, likely due to trace water.^{33,85,86} Therefore, the initiation step in the mechanism likely involves the co-catalyst (Nu) binding to Cr, displacing the Cl⁻ from the metal. This Cl⁻ can now ring-open the bound epoxide at the methine carbon (R') and start the polymerization process. Through this newly formed chromium alkoxide (Cr-OR) bond, CO₂ can insert at R producing a polycarbonate chain with HT regiochemistry. Sequential additions of epoxide and CO₂ allow propagation of the growing polymer chain. The copolymerization can then be terminated by addition of alcohol or water (pathway A, Scheme 3). From the MALDI-TOF MS analysis, the expected OH end groups were observed in the polypropylene carbonate, however, chloride-terminated groups were also found on these polymers. These may be a result of chain transfer occurring between two growing polymer fragments, producing a polymer with two Cl-groups as the chain ends as shown in pathway B. This pathway would also result in a HH or TT linkage where the chain combination occurs. Although an intermolecular process is shown for pathway B in Scheme 3, an intramolecular chain transfer could also occur for two polymer chains growing on a single metal site as has been proposed for salen complexes that catalyze the copolymerization of PO with CO2.38 The formation of ether linkages is produced through double epoxide insertion (pathway C). Pathway D illustrates a possible route to the formation of polymer series (c), which contains chloro-terminated groups as well as an ether linkage.

Isolation of Cr hydroxide complex

Single crystals from the reaction of CO_2 and PO in the presence of **1b** were obtained upon venting the system and allowing some of the unreacted PO to evaporate (Table 1, entry 20). Analysis of these crystals by X-ray diffraction showed them to

Table 2	Coupling reaction of SO and CO ₂ catalyzed by 1a ⁻									
Entry	[Cr]:[SO]:[Co-Cat.]	Time (h)	Temp. (°C)	Pressure (bar)	Yield (%)	TON^b	TOF ^c			
1	1:500:0.5 (DMAP)	24	21	40	0	NA^d	NA^d			
2	1:500:0.5 (DMAP)	3	80	50	16	79	26			
3	1:500:0.5 (DMAP)	3	100	50	28	140	47			
4	1:500:0.5 (DMAP)	18	80	50	38	190	11			
5	1 : 500 : 0.5 (PPNCl)	18	80	45	65	313	17			

^{*a*} All reactions were carried out in neat SO (4 mL). ^{*b*} Calculated by ¹H NMR. ^{*c*} Turnover frequency is moles of SC produced per mol of Cr per hour. ^{*d*} NA = not applicable (no carbonate-containing product obtained).

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Scheme 3 Proposed mechanism for the copolymerization of CO₂ with epoxides by Cr amine-bis(phenolate) complexes.

be the hydroxide-bridged dimer **2** (Fig. 8). This compound likely results from the hydrolysis of complex **1b** by adventitious moisture.

The complex lies on an inversion centre located within the Cr_2O_2 rhomboid and the Cr(III) centres exhibit distorted octahedral geometries. Related dimeric Cr(III) complexes



Fig. 8 Molecular structure (ORTEP) and partial numbering scheme of {Cr(μ -OH)-[O₂NN']^{BuMe}]₂ **2**. Ellipsoids are drawn at 50% probability. Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): Cr1–O1 = 1.912(2), Cr1–O2 = 1.939(2), Cr1–O3 = 1.989(2), Cr1–O3* = 2.014(2), Cr1–N1 = 2.081(3), Cr1–N2 = 2.081(3), Cr1-··Cr1* = 3.0673(13); O1–Cr1–O2 = 92.01(10), O1–Cr1–O3 = 91.16(10), O2–Cr1–N1 = 92.02(10), O2–Cr1–N2 = 86.80(10), N1–Cr1–N2 = 80.83(12), N1–Cr1–O3 = 173.64(10), N2–Cr1–O3 = 96.71(11), O2–Cr1–O3 = 93.70(9), O3–Cr1–O3* = 79.97(3), Cr1–O3–Cr1* = 100.03(10). Symmetry operation used to generate equivalent atoms: -x + 1, -y, -z + 2.

possessing salen and acacen (*N*,*N*'-bis(*t*-butylacetylacetone)-1,2-ethylenediamine) ligands and dibridging-hydroxo groups have been used for copolymerization of cyclohexene oxide and CO_2 .⁸⁷ The Cr(1)–O(3)–Cr(1)* angle in **2** is 100.04(10)° and the hydroxides are orientated *cis* to the nitrogen on the pendant pyridyl group. This angle is typical of what is reported for other HO-bridged Cr(m) dimers. The Cr–OH bond distances are asymmetric at 1.989(2) and 2.014(2) Å and are within the range observed for five or six-coordinate chromium(m) hydroxide-bridged species.

Conclusions

The chromium chlorido diamine-bis(phenolate) complex, $\{CrCl[O_2NN']^{BuBu}\}_2$ (1a), was shown to effectively couple PO with CO2 in the presence of co-catalysts (DMAP, PPNCl, PPNN₃). Good activities were observed for the formation of PPC at low temperatures but at elevated temperatures the reaction was selective for PC formation. The number average molecular weights of the polycarbonate were found to be lower than expected, but the polydispersities observed were generally narrow. Preliminary results suggest the chloride on the Cr complex plays an important role in the initiation of the epoxides in order to generate polycarbonate. Further investigation into the influence of the pendant donor and substituents on the phenolate fragments of the amine-bis(phenolate) ligand are currently underway.

Experimental

General

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 DP glove box. PO and SO were purchased from Aldrich and freshly distilled from CaH2 and vacuum transferred into a sealed ampule prior to use. All solvents were purified by an MBraun Manual Solvent Purification System. 1a and H₂[O₂NN']^{BuMe} were prepared according to the previously reported procedures.^{74,77} PPNN₃ was prepared according to the literature procedure.⁸⁸ Supercritical Fluid Chromatography (4.8 Grade) CO₂ was supplied from Praxair in a high-pressure cylinder equipped with a liquid dip tube. All ¹H and ¹³C NMR were performed in CDCl₃ purchased from Cambridge Isotope Laboratories, Inc. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AVANCE III 300 MHz spectrometer at 300 and 75.5 MHz, respectively. 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 such high-pressure equipment.

Synthesis

1b: A 1.6 M hexanes solution of n-butyllithium (11.7 mL, 18.7 mmol) was added via syringe to a stirring solution of $H_2[O_2NN']^{BuMe}$ (3.92 g, 8.50 mmol) in THF (50 mL) at -78 °C. The reaction mixture was warmed to room temperature and stirred for 2 h to give a clear orange solution. This mixture was transferred via cannula to a solution of CrCl₃(THF)₃ (3.29 g, 8.86 mmol) in THF (50 mL) at -78 °C to give a purple suspension. Upon warming to room temperature under nitrogen a dark purple mixture remained. 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 2.37 g of green powder (49% yield). Anal. Calcd for C₃₀H₃₈ClCrN₂O₂: C, 65.98; H, 7.01; N, 5.13. Found: C, 65.83; H, 7.10; N, 5.24. MS (MALDI-TOF) m/z (%, ion): 1090.4 (12, [(CrCl- $[L]_{2}^{+}$, 545.2 (96, $[CrCl[L]]^{+}$), 510.2 (25, $[Cr[L]]^{+}$). Single crystals of 2 were obtained from a solution of 1b in propylene oxide after performing the polymerization procedure described below.

X-ray crystallography

Diffraction data for compound 2 were collected on a Rigaku Saturn CCD area detector with a SHINE optic and Mo-K α 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 CrystalClear⁸⁹ software and corrected for Lorentz and polarization effects and absorption.⁹⁰ Neutral atom scattering factors for all non-hydrogen atoms were taken from the *International Tables for X-ray Crystallography*.⁹¹ The structure was solved by

Table 3 Crystallographic and structure refinement data for 2

Chemical formula	$[(C_{31}H_{39}N_2O_6)Cr]_2 \cdot 2CH_2Cl_2$
Formula weight	1225.16
T/K	163
Color, habit	Black-red, prism
Crystal dimensions/mm	$0.40 \times 0.32 \times 0.12$
Crystal system	Monoclinic
Space group	$P2_1/c$ (#14)
a/Å	14.239(7)
b/Å	13.204(7)
c/Å	18.420(9)
$\alpha/^{\circ}$	90
$\beta/^{\circ}$	95.586(6)
$\gamma/^{\circ}$	90
$V/\text{\AA}^3$	3447(3)
Ζ	2
$D_{\rm c}/{\rm g}~{\rm cm}^{-3}$	1.180
$\mu(MoK\alpha)/cm^{-1}$	5.17
F(000)	1292
Reflections collected	32 578
Independent reflections	7115
<i>R</i> (int)	0.0707
$R, wR_2 (all)^a$	0.0903, 0.2384
$R, WR_2 [I > 2\sigma(I)]^a$	0.0791, 0.2262
GOF on F^2	1.064
CCDC reference	897967
${}^{a}R_{1} = \Sigma(F_{1} - F_{1})/\Sigma F_{1})$; w $R_{2} = [$	$\sum (w(F_{-}^{2} - F_{-}^{2})^{2}) / \sum w(F_{-}^{2})^{2}]^{1/2}$

direct methods using SIR9292 and expanded using Fourier techniques (DIRDIF99).93 All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model, except H3A. H3A was located in its difference map position and was refined with a fixed displacement ellipsoid 1.5 times that of O3, and was refined positionally with a distance restraint. All atoms were introduced prior to the application of Squeeze. Anomalous dispersion effects were included in F_{calc} ⁹⁴ the values for Δf and $\Delta f'$ were those of Creagh and McAuley.⁹⁵ The values for the mass attenuation coefficients are those of Creagh and Hubbell.96 All calculations were performed using the CrystalStructure⁹⁷ crystallographic software package except for refinement, which was performed using SHELXL-97.98 The Platon Squeeze99 procedure was applied to recover 173 electrons per unit cell in one void (total volume 1009 $Å^3$); that is 86.5 electrons per formula unit. Disordered solvent lattice dichloromethane molecules (42 electrons per CH₂Cl₂; 2 molecules per formula unit) were present prior to the application of Squeeze; however, a satisfactory point atom model could not be achieved. The application of Squeeze gave a good improvement in the data statistics and allowed for a full anisotropic refinement of the structure. Structural illustrations were created using ORTEP-III (v. 2.02) for Windows.¹⁰⁰ CCDC reference number 897967 (2) contains the supplementary crystallographic data for this paper.

Polymerization procedure

For all reactions carried out in neat epoxide, the appropriate amount of monomer was added to the catalyst (0.05 g) and cocatalyst in a glove box. The reactant solution was added *via* a long-needled syringe to a 300 mL Parr® autoclave, which was pre-dried 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 onium salts, complex **1a** and the co-catalyst were first activated in 4 mL of CH_2Cl_2 and allowed to stir for 30 minutes and then dried *in vacuo*. The remaining procedure was followed in the same manner as the neat reactions.

Mass spectrometry

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⁻¹. Polymer was dissolved in THF at approximately 1 mg mL⁻¹. The matrix and polymer solutions were mixed together at a ratio of 5 to 1, respectively; 1 μ L of this was spotted on the MALDI plate and left to dry. Images of mass spectra were prepared using mMassTM software (http:// www.mmass.org).

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 5µ 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⁻¹ 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⁻¹ 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.

Differential scanning calorimetry

Glass transition (T_g) temperatures were measured using a Mettler Toledo DSC 1 STARe 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⁻¹, held for 2 min at 100 °C and then cooled back to 0 °C at 10 °C min⁻¹. 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⁻¹.

Thermal gravimetric analysis

TGA was performed with a TA Instrument 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⁻¹. Each sample was heated from room temperature to 400 °C.

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