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Chromium(III) amine-bis(phenolate) complexes as catalysts for copolymerization of cyclohexene oxide and CO_2†

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†Electronic supplementary information (ESI) available. MALDI-TOF MS and UV-Vis spectra of **1** and **2**, representative ^{1}H and ^{13}C NMR and MALDI-TOF mass spectra of PCHC, and crystallographic information file (CIF) for $(\mathbf{1})_2\cdot LiCl\cdot THF$ (CCDC reference: 974612). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/xxxxxxxxxx.

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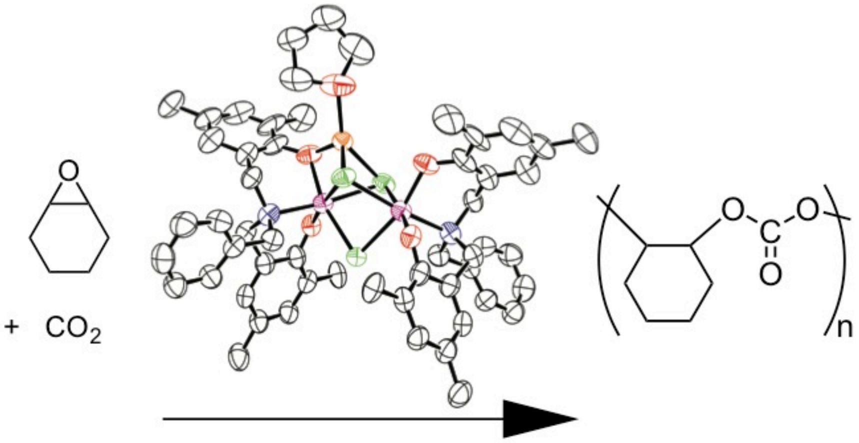


Chromium complexes of a tri- and tetradentate amine-bis(phenolate) ligands in combination with chloride, azide or DMAP nucleophiles are effective catalysts for the copolymerization of CO_2 with cyclohexene oxide to give polycarbonates.

Abstract

Amine-bis(phenolate) chromium(III) complexes catalyze the copolymerization of cyclohexene oxide with carbon dioxide. These catalysts incorporate tetra- or tridentate amine-bis(phenolate) ligands and when combined with dimethylaminopyridine (DMAP) or bis(triphenylphosphoranylidene)ammonium chloride or azide, (PPNCl or $PPNN_3$), yield low molecular weight polymers with moderately narrow polydispersities. The tetradentate ligand containing catalysts show higher conversions and yields of polycyclohexene carbonate, but with a wide variety of polymer end groups as shown my MALDI-TOF mass spectrometry.

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] Carbon dioxide is an appealing C1 feedstock because it is widely available, inexpensive, and nontoxic.[7] Many homogeneous catalysts containing metals such as Mg,[8] Al,[9-13] Zn,[14-22] Cr,[23-38] Co[6,39-58] and Fe[59] have been examined for use in the copolymerization of carbon dioxide (CO_2) and epoxides, particularly cyclohexene oxide (CHO).

Homogeneous catalysts applied to CHO and CO_2 copolymerization have involved a variety of ligand classes including Cr[24,60-61] and Al[13] porphyrins. Darensbourg and Holtcamp introduced the use of Zn phenoxides for epoxide/CO_2 copolymerization,[62-64] whereas Coates and co-workers explored the use of β-diketiminate (BDI) ligand systems with Zn at lower pressures and temperatures than had previously been reported.[14] 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 towards epoxide and CO_2 copolymerization.[65] By far 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[23,25-30,33,36,38,66] and Co.[39,44-45,52-53,67] These catalysts typically require nucleophilic co-catalysts such as chlorides, bromides 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).

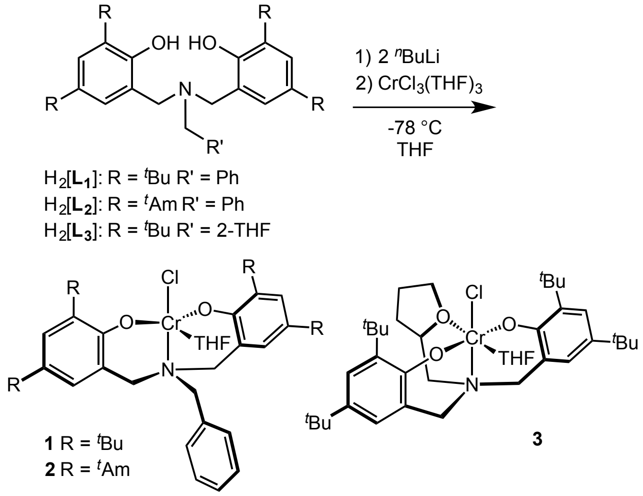
Whereas compounds of the salen (and the related salan) ligands represent the most investigated homogeneous systems for CO_2/epoxide copolymerization, we recently reported the use of the related tetradentate amine-bis(phenolato) ligand class.[68-69] Synthesis of these ligands occurs by a modified Mannich condensation reaction, and changing the substituents on the phenolate groups or pendant arms alters the steric and electronic properties.[70-71] Work in our group has involved investigating the catalytic properties of various mid-to-late transition metal complexes of these ligands. Metals such as Cr,[72] Co[73-74] and Fe,[75-78] have shown diverse structural, spectroscopic and electronic properties, whereas Co(II) and Co(III) complexes of these ligands were shown to couple CO_2 with propylene oxide under neat conditions to give propylene carbonate.[79]

Because Cr(III) catalysts have shown excellent activity towards CO_2/epoxide copolymerization, we began a program to study the potential of our Cr(III) amine-bis(phenolato) complexes to catalyze this reaction. In previous studies, bulky *t*-butyl substituents on the phenolate groups 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. In this study, the influence of the pendant donor is evaluated, first by replacing the pyridyl-containing arm with a non-coordinating benzyl group. Two of these tridentate ligands were assessed with one possessing *t*-butyl groups in the 2 and 4 position relative to the phenolic OH group. The other tridentate ligand employs the mildly larger *t*-amyl (*t*-pentyl) groups in these positions. Also, a tetradentate ligand having a tetrahydrofuranyl group in place of the pyridyl donor was examined for its copolymerization activity. Herein, we report the use of these three Cr(III) amine-bis(phenolate) complexes in the presence of ionic and neutral initiators as catalysts for the co-polymerization of cyclohexene oxide with CO_2.

Results and discussion

Synthesis and characterization of Cr complexes.

The amine-bis(phenol) compounds benzylamino-*N*,*N*-bis(2-methylene-4,6-di-*tert*-butylphenol) ($H_2[\mathbf{L_1}]$), benzylamino-*N*,*N*-bis(2-methylene-4,6-di-*tert*-amylphenol) ($H_2[\mathbf{L_2}]$) and 2-tetrahydrofurfurylamino-*N*,*N*-bis(2-methylene-4,6-*tert*-butylphenol) ($H_2[\mathbf{L_3}]$), were prepared according to previously reported procedures.[71,80-81] Cr(III) complexes **1** and **2** were synthesized via reaction of the protonated ligands $H_2[\mathbf{L_1}]$ and $H_2[\mathbf{L_2}]$, respectively, at –78 °C in THF with *n*-butyllithium followed by reaction of the resulting dilithium salt with $CrCl_3(THF)_3$ in THF at –78 °C to produce green solids in 80% yield (Scheme 1). The complexes were characterized using MALDI-TOF mass spectrometry and UV-vis spectroscopy (see ESI†). Elemental analysis was unable to unequivocally identify whether **1** and **2** contained 1 or fewer THF molecules per CrCl[**L**] formula unit. Given the preference of Cr(III) complexes of these ligands to adopt six-coordinate geometries, some degree of THF coordination is expected. The synthesis and characterization (including single crystal diffraction) of complex **3** was previously reported.[72]



Scheme 1. Synthesis of **1 – 3**.

MALDI-TOF mass spectrometry is useful for the characterization of coordination and organometallic complexes, particularly for paramagnetic compounds where NMR spectroscopy is of limited use.[82-83] The MALDI-TOF mass spectrum of complex **1** shows peaks at *m/z* 628.28 corresponding to the $[CrCl[\mathbf{L_1}]]^{+\cdot}$ ion (see Figures S1–S3†). Ligand fragment ion peaks are shown at *m/z* 538.15 and the fragment ion corresponding to the loss of the chloride, $[Cr[\mathbf{L_1}]]^{+}$ occurs at *m/z* 593.33. The isotopic distribution pattern of the experimental $[CrCl[\mathbf{L_1}]]^{+\cdot}$ is in agreement with the theory for **1**. In addition to peaks corresponding to monomeric complexes, higher masses were observed at *m/z* 1221.6 suggesting the presence of bimetallic fragments corresponding to $[\{[Cr[\mathbf{L_1}]\}_2Cl]^{+\cdot}$ and others. Crystallographic evidence supporting the existence of bimetallic species will be discussed below. Similarly, compound **2** shows the loss of the chloride complex from the parent ion at *m/z* 649.31 in the mass spectrum and an intense peak at *m/z* 684.27 corresponding to $[CrCl[\mathbf{L_2}]]^{+\cdot}$ (Figures S4 – S6).

Electronic absorption spectra of complexes **1** and **2** in dichloromethane show multiple bands in the UV and visible regions. The absorption maxima observed in the UV region (below 300 nm) are caused by π→π* transitions involving the phenolate units. Bands are also observed in the region between 300 and 400 nm, which are assigned to charge transfer transitions from the p_π orbital (HOMO) of the phenolate oxygen to the empty d_{x2-y2}/d_{z2} and the half-filled d_π, orbitals of Cr(III). Weaker bands arising from d-d transitions were observed in the visible region at 560 and 720 nm.

Dark green single crystals of **1** suitable for X-ray diffraction analysis were isolated by slow evaporation of a toluene solution under a N_2 atmosphere in a glove box. The resulting structure is shown in Figure 1 and selected bond distances and angles are listed in Table 1. In the solid state, **1** is an unsymmetric, dichromium complex with both transition metal atoms exhibiting distorted face-sharing octahedral coordination. Each chromium atom is coordinated by an amine-bis(phenolate) ligand and three bridging chlorides, thus leading to seven anionic ligands surrounding two Cr(III) ions. The surplus negative charge is offset by a THF-bound lithium ion. This Li(THF) fragment is disordered in the asymmetric unit such that it exists in two sites of 50% occupancy bound to two of the bridging chlorides and one phenolate oxygen of each amine-bis(phenolate) ligand. The Cr–Cl distances in $(\mathbf{1})_2\cdot$LiCl·THF are 2.425(3) and 2.386(2) Å and fall within the range of other complexes of chromium(III) bearing three bridging chlorides.[84-87] Of the three Cl atoms, two are related by symmetry. The longer of the two Cr–Cl bonds, Cr(1)–Cl(1), is likely due to the coordination of the Li ion rather than due to any *trans* influence. Metal-metal bonds between Cr(III) centres are not expected and the observed Cr···Cr interatomic distance of 3.1615(13) Å supports the absence of any such interaction. Therefore, the formation of what can be described as a LiCl adduct of a dimer of compound **1** must be the result of the thermodynamic stability of an octahedral ligand field for Cr(III). As mentioned above, the elemental analysis of the bulk material for **1** and **2** are consistent with formulations possessing between 0 and 1 molecules of THF per CrCl[**L**] formula unit, but does not support the presence of significant amounts of LiCl. The structurally authenticated complex **3** was also shown to contain a six-coordinate CrCl(THF)[$\mathbf{L_3}$] formulation, bearing the tetradentate ligand [$\mathbf{L_3}$].[72]

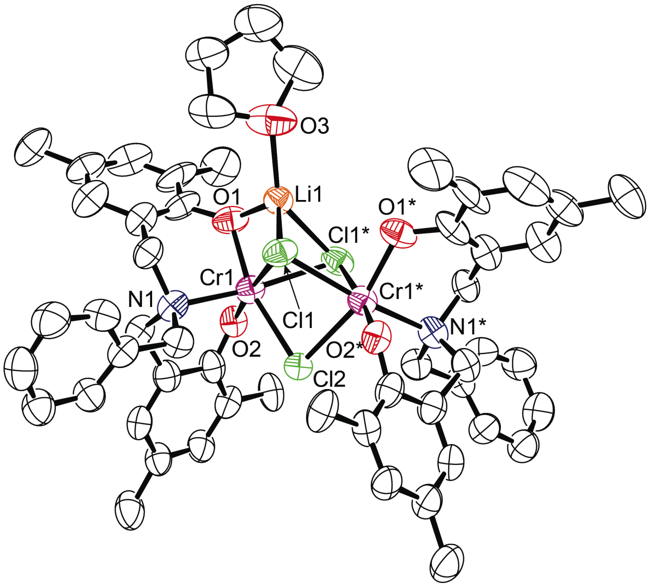


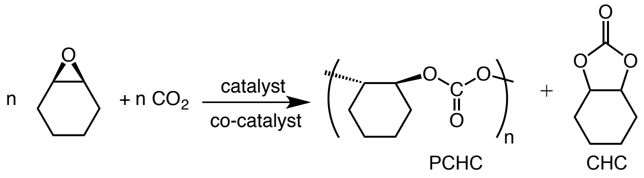
Figure 1. Molecular structure (ORTEP) and partially labelled numbering scheme of (**1**)$_2$·LiCl·THF. Ellipsoids are shown at 50% probability. Hydrogen atoms and methyl groups on phenolate *t*-butyl groups are omitted for clarity. Symmetry operations used to generate equivalent atoms (*): -x+2, -x+y+1, -z+1/3.

Table 1. Interatomic distances (Å) and angles (°) for $(\mathbf{1})_2\cdot LiCl\cdot THF$.

Bond Length (Å)			
Cr(1)-O(2)	1.870(5)	Cr(1)-Cl(1)	2.425(3)
Cr(1)-O(1)	1.921(6)	Cr(1)-Cl(2)	2.386(2)
Cr(1)-N(1)	2.108(7)	Cr(1)···Cr(1)*	3.1615(13)
Li(1)-Cl(1)	2.06(7)	Li(1)-O(1)	1.70(5)
Li(1)-O(3)	1.44(7)	Cr(1)···Li(1)	2.40(8)
Bond angles (°)			
O(2)-Cr(1)-N(1)	91.3(3)	Cl(2)-Cr(1)-Cl(1)	82.25(7)
O(1)-Cr(1)-N(1)	92.6(3)	O(2)-Cr(1)-Cl(1)	174.19(19)
O(1)-Cr(1)-Cl(2)	164.4(2)	O(1)-Cr(1)-Cl(1)	89.5(2)
N(1)-Cr(1)-Cl(2)	100.5(2)	N(1)-Cr(1)-Cl(1)	91.2(2)
O(2)-Cr(1)-Cl(1)	96.59(19)	Cl(2)-Cr(1)-Cl(1)	81.98(7)
O(2)-Cr(1)-O(1)	95.7(3)	Cl(1)-Cr(1)-Cl(1)	81.26(11)
O(1)-Cr(1)-Cl(1)	83.6(2)	Cr(1)-Cl(1)-Cr(1)	81.08(8)
N(1)-Cr(1)-Cl(1)	171.5(2)	Cr(1)-Cl(2)-Cr(1)*	82.98(10)
		O(1)-Cr(1)-Cl(1)	89.5(2)

Copolymerization of CO_2 and cyclohexene oxide

The copolymerization of CHO and CO_2 was investigated using complexes **1** – **3**. Neutral or ionic co-catalysts such as (4-dimethylamino)pyridine (DMAP), bis(triphenylphosphoranylidene)ammonium chloride or azide, (PPNX where X = Cl^- or N_3^-) were employed in this study and were shown to be important for the formation of the desired polymer. For each of **1**, **2** or **3**, strictly poly(cyclohexene carbonate) (PCHC) was produced with no evidence of cyclohexene carbonate (CHC) formation (Scheme 2).



Scheme 2. The copolymerization of CHO and CO_2 producing PCHC.

Initial reactions were performed by combining the tridentate ligand-containing compounds **1** and **2** with DMAP, PPNCl or $PPNN_3$ co-catalysts in neat epoxide and placing the mixture under elevated pressures of CO_2 and heating to 60 °C (Table 2). The combination of **1** and DMAP at 45 bar CO_2 and 60 °C showed only 33.8% conversion to PCHC by NMR (entry 1). The yield of polymer obtained by precipitation from acidified methanol was only 12.7%, which suggests that the oligomers obtained are of low molecular weight and highly soluble in methanol. Only the precipitated products obtained were characterized by MALDI-TOF MS and gel permeation chromatography (GPC). Conducting the reaction at room temperature shows no conversion of CHO (entry 2). The alternating copolymerization of CHO with CO_2 to form PCHC typically requires higher temperatures,[1,3,5,68] and such is the case for catalyst **1** (and **3**, see below). Using PPNCl or $PPNN_3$ as cocatalyst shows improved conversion and yield of PCHC (entries 3 and 4). Complex **2** combined with DMAP proved inferior to complex **1** (entry 5), likely because of the increased steric hindrance caused by the *t*-amyl (*t*-pentyl) groups. For both catalysts **1** and **2**, only low molecular weight polymers were obtained ranging between 1.1 to 3.8 kg mol^{-1} and possessing moderate molecular weight distributions (PDIs of 1.5 to 2.1).

Catalyst **3** (possessing a tetradentate ligand) proved superior to both **1** and **2**. When combined with DMAP at 60 °C and 40 bar CO_2, good conversions and yields of polycarbonate were obtained (Table 3, entries 1 and 2). The activity was very sensitive to catalyst loading as lowering it to 0.1% Cr vs. CHO showed a decrease in CHO conversion (entry 3). The polymer obtained was also shown by GPC to have lower molecular weight than that obtained under the higher catalyst loading conditions. Using PPNCl or $PPNN_3$ co-catalysts gave the best results (76.3% conversion of PCHC) (entries 4 and 5, respectively). The poor solubility of these co-catalysts in CHO required dissolving the catalyst and co-catalyst in dichloromethane, whereupon removal of solvent gives a material now soluble in CHO. This procedure has also been used when these ionic co-catalysts are used with salen- or salan-based Cr(III) catalysts[35,37] and with related diamine-bis(phenolate) Cr(III) catalysts.[68] Similar levels of conversion and polymer yield were reported by our group using an analogue of **3** with PPNCl. In that study, the neutral pendent donor was a pyridyl group rather than a tetrahydrofuranyl donor.[68] Although fairly high yielding in polymer of moderate weights (approximately 6 kg mol^{-1}), the catalysts exhibit slow TOFs. Shortening reaction times to 6 and 3 h (entries 6 and 7, respectively) showed a decrease in conversions and commensurate decreases in isolated polymer yield. An inspection of the molecular weights shows a trend towards increasing polymer chain lengths over time, which is consistent with the lower isolated yield of polymer due to increased solubility of the lower molecular weight material. Lastly, the use of a cocatalyst and elevated temperatures appear crucial for copolymerization of CO_2 with CHO by **3**, since no polymer was obtained in the absence of co-catalyst (entry 8) or at room temperature (entry 9).

Table 2. Results of the Copolymerization of CHO and CO_2 by Catalysts **1** and **2** with DMAP or PPNX salts.[a]

Entry	Catalyst	Co-Catalyst	Temp (°C)	Pressure (bar)	% Conversion [b]	%Yield [c]	TON [d]	TOF [e] (/h)	M_n [f] (kg/mol)	PDI[f] (M_w/M_n)
1	1	DMAP	60	45	33.8	12.7	169	7.1	2.3	1.58
2	1	DMAP	25	45	0	0	0	0	-	-
3[g]	1	PPNCl	60	45	51.5	44.3	258	11	2.8	1.56
4 [g]	1	$PPNN_3$	60	42	44.8	27.0	224	9.3	3.8	1.48
5	2	DMAP	60	40	18.7	6.63	93.5	3.9	1.1	2.10
6[h]	2	DMAP	60	42	13.7	5.41	68.5	2.9	ND	ND

[a] Polymerization reactions were carried out in neat CHO (5 mL) for 24 h using catalyst and co-catalyst of loading of 0.2%. [b] Calculated by ^1H NMR. [c] Isolated yield. [d] Calculated by conversion. [e] Turnover frequency is moles of PCHC produced per mol of Cr per hour. [f] Determined by gel permeation chromatography in $CHCl_3$, calibrated with polystyrene standards. [g] Dissolved in 4 mL dichloromethane prior to adding CHO. [h] Duplicate run of previous entry. ND = not determined.

Table 3. Results of the Copolymerization of CHO and CO_2 for Catalyst **3** with DMAP or PPNX salts.[a]

Entry	Co-Catalyst	Time (h)	Temp (°C)	Pressure (bar)	% Conversion [b]	%Yield [c]	TON [d]	TOF[e] (/h)	M_n[f] (kg/mol)	PDI[f] (M_w/M_n)
1	DMAP	24	60	40	68.0	58.9	340	14	5.7	1.48
2[g]	DMAP	24	60	43	59.9	60.8	300	12	ND	ND
3[h]	DMAP	24	60	43	28.6	16.4	286	12	2.8	1.67
4[i]	PPNCl	24	60	42	76.3	73.7	382	16	5.7	1.46
5[i]	$PPNN_3$	24	60	41	76.3	64.1	382	16	6.4	1.42
6[i]	PPNCl	6	60	41	49.5	37.3	248	41	4.5	1.39
7[i]	PPNCl	3	60	43	33.0	22.8	165	55	3.0	1.63
8	None	6	60	42	0	0	0	0	-	-
9	DMAP	24	25	40	0	0	0	0	-	-

[a] Polymerization reactions were carried out in neat CHO (5 mL), using catalyst and co-catalyst of loading of 0.2%. [b] Calculated by ^1H NMR. [c] Isolated yield. [d] Calculated from % conversion. [e] Turnover frequency is moles of PCHC produced per mol of Cr per hour. [f] Determined by gel permeation chromatography in $CHCl_3$, calibrated with polystyrene standards. [g] Duplicate run of previous entry. [h] Catalyst and co-catalyst of loading of 0.1%. [i] Dissolved in 4 mL dichloromethane prior to adding CHO. ND = not determined.

Structural analysis of the copolymers.

As shown by ^{1}H NMR of the resulting polymer, carbonate linkages dominate and the existence of ether linkages is in very low abundance (see Figure S8†). The stereochemistry of the isolated poly(cyclohexene carbonate) was determined by ^{13}C NMR. Examining the carbonyl region shows the polymer is atactic, consisting of isotactic and syndiotactic PCHC (Figure S9†).[88-89] 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.[57] Similarly, although **3** possesses chirality in the 2-position of the tetrahydrofuranyl group, no stereo control is observed and again atactic polymer is obtained.

MALDI-TOF MS studies were performed in order to gain insight into experimental values of the number average molecular weights of the copolymers and analysis of possible end-groups providing mechanistic details for this system. In the MALDI-TOF mass spectra of these copolymers, multi-modal molecular weight distributions were observed showing multiple end-group series, all separated with a repeating unit of m/z 142. The different end-groups can be attributed to the mechanism, in particular the initiation step involved in the copolymerization process, and the catalyst systems used. In addition to the use of an appropriate acidic matrix, sodium trifluorocetate was added as cationizing agent, however, models of the spectra obtained suggest polymer cations could also be obtained by protonation and NaTFA was not always required to obtain a useful MALDI-TOF spectrum.

For catalyst **1**, several polymer chains possessing different end-groups were observed when PPNCl or PPNN$_3$ was used as co-catalyst according to the conditions shown in Table 2, entries 3 and 4, respectively. The MALDI-TOF spectrum obtained using PPNCl is shown in Figure 2 and shows a multimodal molecular weight distribution. In the 2000 to 4000 *m/z* region of the mass spectrum, four series of polymer chains are detected. Series (a) consists of an ether linkage located within the polymer (not necessarily at a chain end as illustrated) and two chloride end-groups [35 (Cl) + 142*n* (repeating unit) + 180 ($C_{12}H_{20}O$) + 35 (Cl)], which may be a result of chain transfer.[90] Series (b) consists of two hydroxyl end-groups [17 (OH) + 142*n* (repeating unit) + 82 (C_6H_{10}) + 17 (OH)] suggesting evidence of chain-transfer as a result of hydrolysis.[36,91] Series (c) consists of one chloride and hydroxyl-end-group [35 (Cl) + 142*n* (repeating unit) + 82 (C_6H_{10}) + 17 (OH)]. This series occurs over a wide mass range from 2000 to 7000 *m/z* in the spectrum and is the expected polymer if epoxide ring-opening is initiated by nucleophilic attack by a chloride and the copolymerization is terminated by protonolysis of the metal-alkoxide. Series (d) contains Cl groups at both termini of the polymer [35 (Cl) + 142*n* (repeating unit) + 82 (C_6H_{10}) + 35 (Cl)], which could arise from intermolecular chain transfer of two chloride-initiated polymer chains.

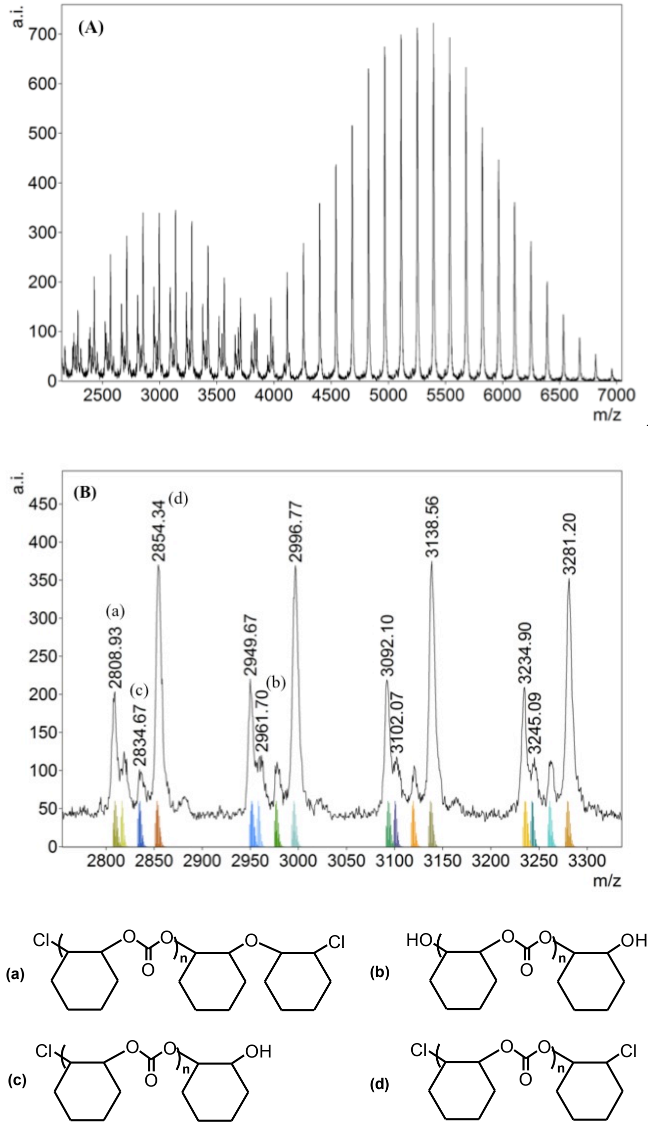


Figure 2. (A) MALDI-TOF MS of PCHC produced according to Table 2, entry 3. (B) Lower mass region (2750 – 3350 m/z, n = 18 – 21) of the spectrum with modeled polymer chains, a – d.

For the polymer obtained in the presence of PPNN$_3$, the spectrum obtained (Figure S10†) shows two end-group types in the lower molecular weight series. Series (a) consists of an ether linkage and two chloride end-groups as shown above, which may be a result of chain transfer. Series (b) consists of two chloride chain ends but lacking an ether linkage as in series (d) above. The higher molecular weight series (c) is the expected chloride-initiated and hydroxyl-terminated polymer as described previously. Perhaps surprisingly, no azide-containing end-groups were observed in the mass spectrum despite the use of $PPNN_3$ as co-catalyst.

The polymer obtained using complex **2** with DMAP as described in Table 2, entry 5 showed three end-group types in its MALDI-TOF mass spectrum (Figure S11†). Series (a) consists of a chloride-initiated and hydroxyl-terminated polymer. Series (b) and (c) suggest DMAP-initiated, hydroxy-terminated polymers with series (b) containing an ether linkage. Therefore series (b) consists of [122 ($C_7H_{10}N_2$) + 142*n* (repeating unit) + 180 ($C_{12}H_{20}O$) + 17 (OH)] chains and series (c) of [122 ($C_7H_{10}N_2$) + 142*n* (repeating unit) + 82 (C_6H_{10}) + 17 (OH)] chains.

The mass spectra of polymers formed by **3** were more complicated than those obtained using catalyst **1** or **2** and some peaks could not be satisfactorily identified. The mass spectrum of the polymer obtained using catalyst **3** and DMAP as described in Table 3, entry 1 is shown in Figure 3 and six different end-groups could be identified (Figure S12†). The lower molecular weight series (a) contains an ether linkage and two hydroxyl end groups [17 (OH) + 142*n* (repeating unit) + 180 ($C_{12}H_{20}O$) + 17 (OH)], likely resulting from intermolecular chain transfer. Series (b) contains DMAP-initiated, hydroxyl-terminated polymer [122 ($C_7H_{10}N_2$) + 142*n* (repeating unit) + 180 ($C_{12}H_{20}O$) + 17 (OH)]. Series (c) consists of the commonly observed chloride-initated, hydroxyl-terminated chain [35 (Cl) + 142*n* (repeating unit) + 82 (C_6H_{10}) + 17 (OH)]. Series (d) contains Cl groups at both termini of the polymer, again likely resulting from intermolecular chain transfer [35 (Cl) + 142*n* (repeating unit) + 82 (C_6H_{10}) + 35 (Cl)] and is observed at higher mass as well. In the higher molecular weight region, series (e) consists of chloride and hydroxyl chain-ends and an ether linkage [35 (Cl) + 142*n* (repeating unit) + 180 ($C_{12}H_{20}O$) + 17 (OH)]. Series (f) ends possesses two hydroxyl groups, [17 (OH) + 142*n* (repeating unit) + 82 (C_6H_{10}) + 17 (OH) + 7 (Li)], suggesting evidence of chain-transfer as a result of protonolysis. The presence of Li^+ likely arises from adventitious LiCl remaining from the synthesis of **3**. The highest molecular weight polymer (between 7500 and 12000 m/z) consists of chloride and hydroxyl end groups and an ether linkage [35 (Cl) + 142*n* (repeating unit) + 180 ($C_{12}H_{20}O$) + 17 (OH)].

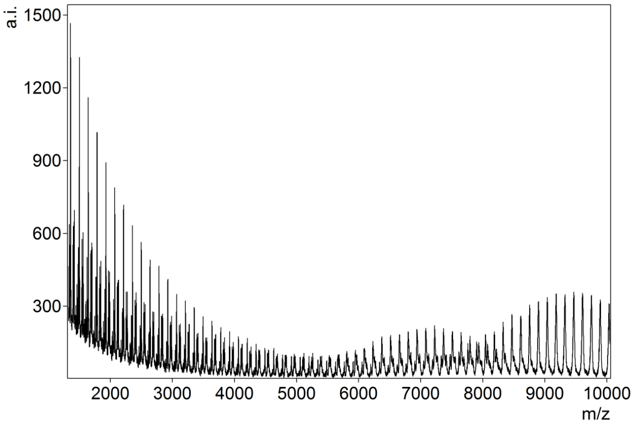


Figure 3. MALDI-TOF spectrum of PCHC produced by **3** and DMAP (Table 3, entry 1).

Using $PPNN_3$ as co-catalyst also leads to polymers containing various end-groups (Figure 4). The differing end groups result from seven polymer chains attributed to various molecular weights (Figure S13†). In the lower molecular weight region, series (a) is modeled to have an ether linkage and two hydroxyl end groups [17 (OH) + 142*n* (repeating unit) + 180 ($C_{12}H_{20}O$) + 17 (OH)]. Series (b) suggests initiation by the azide nucleophile and termination by protonolysis [42 (N_3) + 142*n* (repeating unit) + 180 ($C_{12}H_{20}O$) + 17 (OH)]. Series (c) contains two hydroxyl groups and is cationized by adventitious Li^+ [17 (OH) + 142*n* (repeating unit) + 82 (C_6H_{10}) + 17 (OH) + 7 (Li)]. Series (d) also appears to be initiated by an azide anion and terminated by the expected hydroxyl group [42 (N_3) + 142*n* (repeating unit) + 82 (C_6H_{10}) + 17 (OH)]. In the higher molecular weight region, assignment of the end groups becomes less straightforward and the presence of azide (from the $PPNN_3$), chloride (from **3**) and hydroxyl end groups can be found. Chain transfer leads to complicated scrambling of chain ends as well as the incorporation of ether linkages as described above. As was observed in the polymer obtained using DMAP (Figure 3, Table 3, entry 1), the highest molecular weight polymer (between 6000 and 9000 m/z) consists of chloride and hydroxyl end groups and an ether linkage [35 (Cl) + 142*n* (repeating unit) + 180 ($C_{12}H_{20}O$) + 17 (OH)].

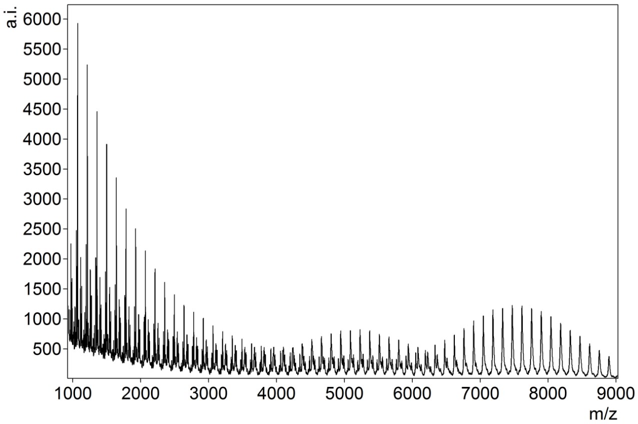


Figure 4. MALDI-TOF spectrum of PCHC produced by **3** and $PPNN_3$ (Table 3, entry 5).

Conclusions

Chromium amine-bis(phenolate) complexes **1** – **3** showed promising activity for the copolymerization of CHO and CO_2 in the presence of three co-catalysts (DMAP, PPNCl, and $PPNN_3$) to give PCHC with no evidence of cyclic carbonate being formed and with a high degree of carbonate linkages. The steric effect of substituents on the phenolate fragments of the tridentate amine-bis(phenolate) ligand appeared to influence the catalyst activity. Complex **2**, containing *t*-amyl substituents on the phenolate, showed lower activity than **1**, possessing *t*-butyl groups. However, both these tridentate ligand-containing complexes showed lower activity than **3**, which contained a tetradentate ligand. The activity of **3** was found to be similar to that of a related chromium(III) diamine-bis(phenolate) complex previously reported by us, but the polymers obtained generally possessed lower molecular weights and broader polydispersities. It is believed that the coordination sphere around the metal must be stabilized by the presence of strongly electron donating ligands. Tridentate variants of amine-bis(phenolates) are less electron donating than tetradentate ligands, and the tetrahydrofuranyl donor is more weakly coordinating than our previously reported pyridyl-containing analogue. Further investigations into the influence of the pendant donor and substituents are being conducted.

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 glove box. $CrCl_3(THF)_3$,[92] the proligands $H_2[\mathbf{L_1}]$, $H_2[\mathbf{L_2}]$, $H_2[\mathbf{L_3}]$[71,80-81] and complex **3**[72] were prepared according to previously reported procedures. CHO was purchased from Aldrich and distilled from CaH_2. THF was purified by distillation from sodium/benzophenone ketyl under nitrogen. All other solvents were purified by an MBraun Manual Solvent Purification System. $PPNN_3$ was prepared according to the literature procedure.[93] 99.998% (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.

Instrumentation

^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III 300 MHz spectrometer. All copolymerization reactions were carried out in a 100 mL stainless steel Parr® 5500 autoclave reactor with a Parr® 4836 controller. N.B. Caution should be taken when operating high-pressure equipment. UV-vis spectroscopy was conducted on an Ocean Optics USB4000+ fiber optic spectrophotometer. Elemental analysis was performed at Guelph Chemical Laboratories, Guelph, ON, Canada. Gel permeation chromatography (GPC) analysis was performed on a Viscotek VE 2001 GPCMax at 35 °C equipped with a Viscotek VE 3580 RI Detector, Phenogel narrow-bore 5 μm 100 Å, 5 μm Linear(2) columns (300 x 4.60 mm) and a 5 μm guard column. Samples were prepared at a concentration of 2 mg/mL and left to equilibrate for ~ 2 h. The samples were filtered through 0.2 μm syringe filters before analysis. The GPC columns were eluted with chloroform (HPLC grade) at a flow rate of 0.30 mL/min with a 100 μL injection volume. Eight 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 was performed by using an Applied Biosystems 4800 MALDI TOF/TOF Analyzer equipped with a reflectron, delayed ion extraction and high performance nitrogen laser. Anthracene was used as the matrix for analysis of **1** and **2**. The matrix and chromium complex were dissolved in toluene at a concentration of 20 mg/mL separately. The matrix and chromium complex solutions were mixed together at a ratio of 1:1, and the mixture was spotted on the MALDI plate and left to dry. Samples were prepared in the glove box and sealed under nitrogen in a Ziploc™ bag for transport to the spectrometer. For polymer analysis, either 2,5-dihydroxybenzoic acid (DHBA) or 1,8,9-trihydroxyanthrancene[94] was used as the matrix with sodium trifluoroacetate (NaTFA) as cationizing agent. The matrix and NaTFA were dissolved in THF at a concentration of 2 mg/mL. The polymer was dissolved at approximately 2 mg/mL. The matrix and polymer solutions were mixed together in a ratio of 1 to 1.1 μL and this mixture was spotted on the MALDI plate and left to dry.

Synthesis of Cr(III) complexes

1: H_2[**L_1**] (4.89 g, 9.00 mmol) was dissolved in THF (50 mL) and cooled to –78 °C. *n*-Butyllithium (1.6 M in hexanes, 12.37 mL, 19.79 mmol) was slowly added to give a clear red solution, which was warmed to room temperature and further stirred for 2 h. This mixture was transferred via cannula to a suspension of $CrCl_3(THF)_3$ (3.37 g, 9.00 mmol) in THF (50 mL) cooled to –78 °C to give a dark green mixture. Upon warming to room temperature and stirring for 18 h the solids dissolved giving a dark green solution. The solvent was removed *in vacuo* and the solid 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 6.01 g (95% for CrCl(THF)[**L_1**]) of dark green powder. Elemental analysis is unable to unequivocally differentiate between the THF-free or the solvent-containing complex. Anal. Calcd for $C_{37}H_{51}ClCrNO_2$: C, 70.62; H, 8.17; N, 2.23. Anal. Cald for $C_{37}H_{51}ClCrNO_2\cdot(C_4H_8O)$: C, 70.21; H, 8.48; N, 2.00. Found: C, 70.57; H, 8.33; N, 1.96. MS (MALDI-TOF) *m/z* (%, ion): 628.4 (100, $[CrCl[L]^+]$), 593.4 (95, $[Cr[L]^+]$).

2: H_2[**L_2**] (4.06 g, 6.77 mmol) was dissolved in THF (50 mL) and cooled to –78 °C. *n*-Butyllithium (1.6 M in hexanes, 9.31 mL, 14.90 mmol) was slowly added to give a bright red solution, which was warmed to room temperature and further stirred for 2 h. This mixture was transferred via cannula to a suspension of $CrCl_3(THF)_3$ (2.54 g, 6.77 mmol) in THF (50 mL) cooled to –78 °C to give a dark green mixture. Upon warming to room temperature and stirring for 18 h the solids dissolved giving a dark green 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 4.57 g (98.6% for CrCl(THF)[**L$_2$**]) of dark green powder. Elemental analysis is unable to unequivocally differentiate between the THF-free or the solvent-containing complex. Anal. Calcd for $C_{41}H_{59}ClCrNO_2$: C, 71.85; H, 8.68; N, 2.04. Anal. Cald for $C_{41}H_{59}ClCrNO_2{\cdot}(C_4H_8O)$: C, 71.35; H, 8.92; N, 1.85. Found: C, 71.61; H, 8.45; N, 1.90. MS (MALDI-TOF) *m/z* (%, ion): 628.4 (83, $[CrCl[L]^+]$), 593.4 (100, $[Cr[L]^+]$).

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 ESI†. The data were processed using CrystalClear[95] software and corrected for Lorentz and polarization effects and absorption.[96] Neutral atom scattering factors for all non-hydrogen atoms were taken from the *International Tables for X-ray Crystallography*.[97] The structure was solved by direct methods using SIR92[98] and expanded using Fourier techniques (DIRDIF99).[99] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. Anomalous dispersion effects were included in F_{calc};[100] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[101] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[102] All calculations were performed using the CrystalStructure[103] crystallographic software package except for refinement, which was performed using SHELXL-97.[104] Disordered lattice solvent for **1** was removed through applying Platon’s Squeeze[105] procedure. Structural illustrations were created using ORTEP-III (v. 2.02) for Windows.[106]

Copolymerization procedure

The appropriate amount of monomer was added to the catalyst and co-catalyst in a glove box. The reactant solution was then added via a long-needled syringe to a 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 until the temperature reached below 4 °C and then vented in the fume hood. An aliquot was taken immediately after opening the reactor for the determination of conversion by NMR. The contents of the reactor were extracted with CH_2Cl_2 and the polymer precipitated using cold acidic methanol. For reactions done in the presence of PPNCl or $PPNN_3$, the catalyst and co-catalyst were first combined in 4 mL of CH_2Cl_2 in the glove box, stirred for 30 minutes then dried *in vacuo*. This generated a material that was soluble in cyclohexene oxide. The remaining procedure was followed as described above.

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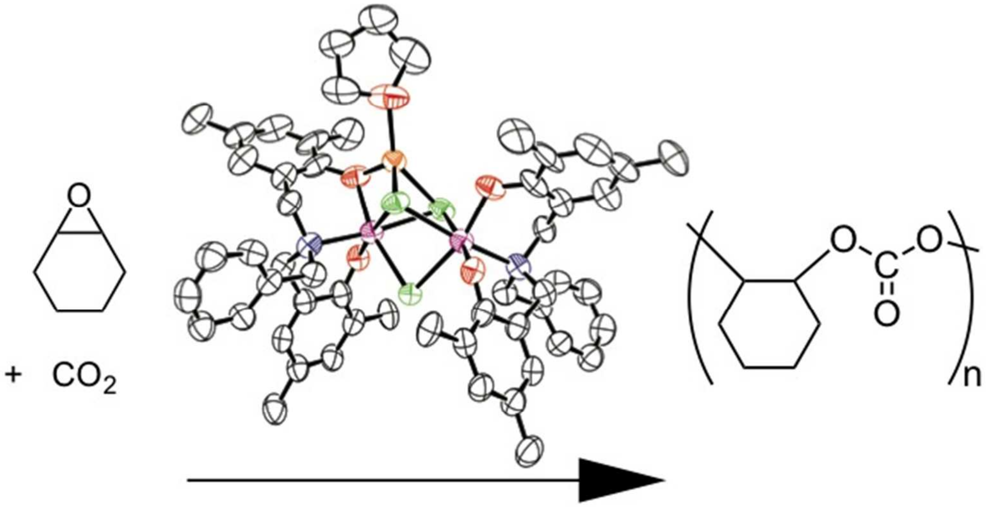

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