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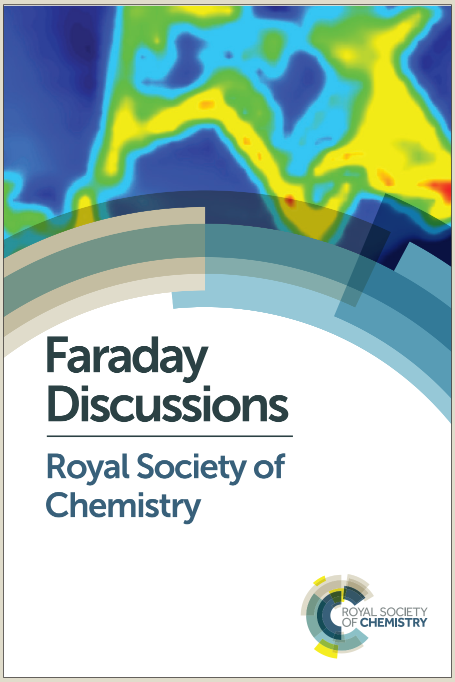

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A MALDI-TOF MS analysis study of the binding of 4-(*N,N*-dimethylamino)pyridine to amine-bis(phenolate) chromium(III) chloride complexes: Mechanistic insight into differences in catalytic activity for CO_2/epoxide copolymerization

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Abstract

Tetradentate amine-bis(phenolato)chromium(III) chloride complexes, [**L**CrCl], are capable of catalyzing the copolymerization of cyclohexene oxide with carbon dioxide to give poly(cyclohexane) carbonate. When combined with 4-(*N*,*N*-dimethylamino)pyridine (DMAP) these catalyst systems yield low molecular weight polymers with moderately narrow polydispersities. The coordination chemistry of DMAP with five amine-bis(phenolato)chromium(III) chloride complexes was studied by matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS). The amine-bis(phenolato) ligands were varied in the nature of their neutral pendant donor-group and include oxygen-containing tetrahydrofurfuryl and methoxyethyl moieties, or nitrogen-containing *N*,*N*-dimethylaminoethyl or 2-pyridyl moieties. The relative abundance of mono and bis(DMAP) adducts, as well as DMAP-free ions is compared under various DMAP:Cr complex ratios. The [**L**Cr]$^+$ cations show the ability to bind two DMAP molecules to form six-coordinate complex ions in all cases, except when the pendant group is *N*,*N*-dimethylaminoethyl (compound **3**). Even in the presence of a 4:1 ratio of DMAP to Cr, no ions corresponding to [$\mathbf{L}^3$Cr(DMAP)$_2$]$^+$ were observed for the complex containing the tertiary sp^3-hybridized amino donor in the pendant arm. The difference in DMAP-binding ability of these compounds results in differences in catalytic activity for alternating copolymerization of CO_2 and cyclohexene oxide. Kinetic investigations by infrared spectroscopy of compounds **2** and **3** show polycarbonate formation by **3** is twice as fast as that of compound **2** and that no initiation time is observed.

Introduction

The copolymerization of carbon dioxide with epoxides to yield polycarbonates has become one of the most extensively studied process that generates potentially valuable materials from CO_2.[1-6] Carbon dioxide is an appealing C1 feedstock because it is widely available, inexpensive, and nontoxic.[7] The variety of metal complexes shown to perform this reaction is impressive and complexes 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) and propylene oxide (PO).

Homogeneous catalysts for epoxide/CO_2 copolymerization have involved various ligand classes including, for example, porphyrin Cr[24,60-61] and Al[13] compounds. 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] Tetravalent group 4 (Ti and Zr) and 14 (Ge and Sn) metals supported by planar trianionic bis(phenolato) ligands reported by Nozaki and co-workers 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 (Fig. 1)[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 *N*-methylimidazole (*N*-MeIm) or dimethylaminopyridine (DMAP).

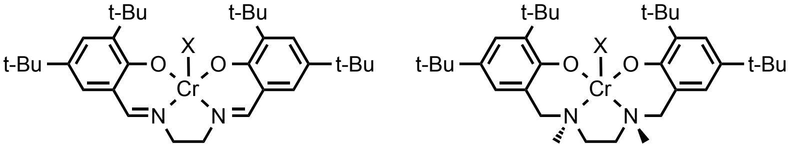
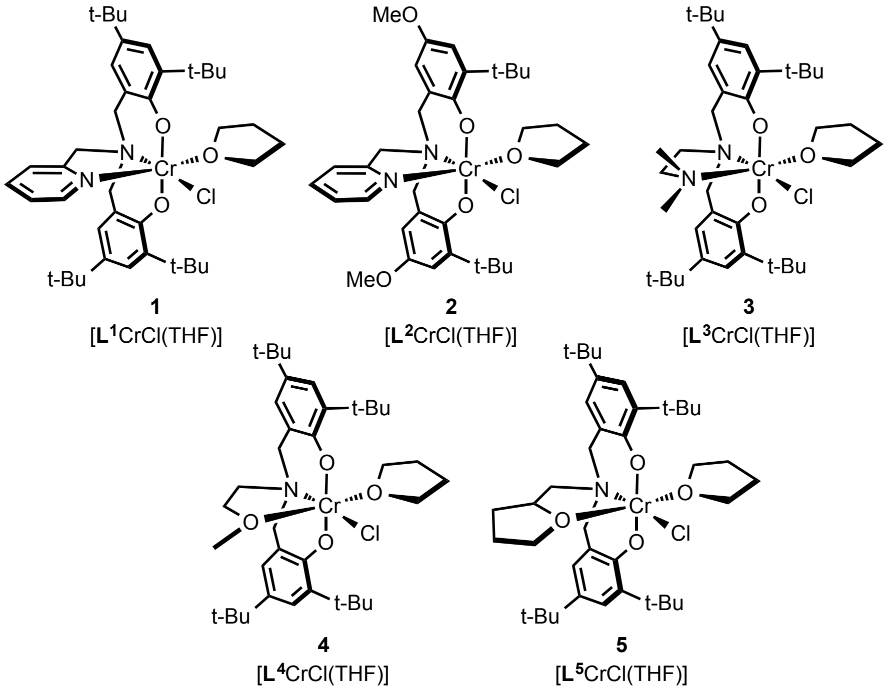


Fig. 1 Salen and Salan chromium(III) complexes used in CO_2/epoxide copolymerization

Whereas compounds of the Salen and Salan ligands represent the most investigated homogeneous systems for CO_2/epoxide copolymerization, we have been interested in the use of the related tetradentate amine-bis(phenolato) ligand class.[68-71] This ligand offers possibilities 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. Mechanistic information is, of course, beneficial for the design of highly efficient catalyst systems for CO_2/epoxide copolymerization.[17,29,66,72-75] and mass spectrometry has been particularly useful in this regard. Electrospray ionization (ESI) mass spectrometry and collision-induced dissociation (CID) have been employed to study the interactions of DMAP co-catalyst with Salen- and Salan chromium chloride complexes and how these interactions influence catalyst activity.[66] ESI-MS has also been used to confirm intermediates in CO_2/PO copolymerization by single-site cobalt Salen catalysts.[54] Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) MS has been used by Duchateau and co-workers to investigate zinc catalyzed copolymerization of cyclohexene oxide and CO_2.[76-77]

Darensbourg and co-workers have conducted elegant kinetics studies on epoxide/CO_2 copolymerization catalyzed by binary SalenCrX (where X = Cl^- or N_3^-) with Lewis basic (neutral or ionic) cocatalysts wherein initiation was proposed to occur via a bimetallic process and propagation via a monometallic enchainment of epoxides.[25-26,78-79] These reports suggest that the binding of co-catalyst to the metal centre labilizes the *trans*-orientated growing polymer chain. A released “free” alkoxide or carboxylate-terminated polymer fragment promotes insertion of CO_2 into the metal-alkoxide bond. These Salen-based complexes also exhibit long induction periods that are not observed in related Salan-based systems employing DMAP as the added Lewis base. In this report, we use MALDI-TOF MS to examine the DMAP binding affinity for five amine-bis(phenolato)chromium chloride complexes (Fig. 2) The observed resistance to dimer and bis(DMAP) adduct formation in complex **3** is believed to corroborate with the absence of an induction period and a faster rate of polycarbonate formation catalyzed by this complex vs. the other derivatives. These studies provide a comparative assessment of the mechanistic behaviour of amine-bis(phenolate)chromium-based catalysts for CO_2/epoxide copolymerization against the benchmark Salen and Salan chromium(III) systems.



1 [$\mathbf{L}^1$CrCl(THF)]

2 [$\mathbf{L}^2$CrCl(THF)]

3 [$\mathbf{L}^3$CrCl(THF)]

4 [$\mathbf{L}^4$CrCl(THF)]

5 [$\mathbf{L}^5$CrCl(THF)]

Fig. 2 Chromium(III) complexes used in this study.

Experimental

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. Anhydrous dichloromethane was obtained by purification using an MBraun Manual Solvent Purification System. Reagents were purchased either from Aldrich or Alfa Aesar and used without further purification. Complexes **1** – **5** were prepared via the previously reported methods.[68,80]

MALDI-TOF MS was performed using 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). Samples were prepared in the glove box and sealed under nitrogen in a Ziploc© bag for transport to the instrument. Anthracene was used as the matrix. The matrix, complex and DMAP were dissolved in dichloromethane at a concentration of approximately 1 mg/0.1 mL. The complex and DMAP were mixed together in ratios of 1:0.5, 1:1, 1:2 and 1:4, and once combined with the matrix, 0.5 μL of this mixture was spotted on a MALDI plate and left to dry under nitrogen in a glove box. Images of mass spectra were prepared using mMass^{TM} software (www.mmass.org).

Infrared spectra of reaction progress were obtained using a Mettler-Toledo ReactIR™ 15 spectrometer equipped with silver halide fibre conduit attached to a SiComp Sentinel™ high-pressure window fitted to a 100 mL stainless steel Parr autoclave reactor.

A representative preparation of samples for analysis by MALDI-TOF MS is provided. 0.2094 g of complex **1** (3.3225×10^{-4} mol) and 0.0397 g of DMAP (3.249×10^{-4} mol) were placed in a sample vial and just enough dichloromethane was added to dissolve the solids. This solution was filtered through a glass fibre plug into another sample vial and the vial was capped, sealed with Parafilm and stored at – 35 °C in the glove box freezer until required.

A stock solution of 8.7 mg of anthracene in 800 μL of dichloromethane was prepared. Samples of complex **1** with their required DMAP loading were dried under vacuum. A measured quantity of each sample was dissolved in 200 μL of CH_2Cl_2 and 80 μL of this solution was transferred to another vial along with 80 μL of the stock anthracene solution. These solutions were spotted onto a MALDI plate and the spectra obtained.

For MALDI-TOF MS analysis on samples exposed to air, all prepared samples, once analyzed under air-free preparation described above, were removed from the glove box and exposed to air. The solvents were allowed to evaporate and after two or three days the samples where redissolved in CH_2Cl_2 and analyzed once again.

Results and Discussion

The binding of DMAP to five chromium complexes (Fig. 2) was investigated by preparing dichloromethane solutions of each complex with varying ratios of DMAP. The resulting solutions were evaporated to dryness and then re-dissolved with the matrix (anthracene). These solutions of analyte and matrix were spotted on the MALDI plate in air and under air-free conditions. The MALDI-TOF mass spectra of complexes **1**, **2**, **4** and **5** in the absence of DMAP exhibited numerous ions, including ions resulting from dimers and their fragments. The exception was complex **3**, which gave a relatively clean spectrum showing two main ions corresponding to $[\mathbf{L^3}CrCl]^{+\cdot}$ and $[\mathbf{L^3}Cr]^{+}$. Ions containing the weakly coordinating THF present in **1** – **5** are, as anticipated, consistently absent from the mass spectra of these complexes. The MALDI-TOF MS of mixtures of complexes **1** – **5** and varying amounts of DMAP showed the presence of complicated mixtures of ions. The ions observed or predicted for complex **2** in the presence of DMAP are given in Fig. 3. The labels **F1** – **F12** also apply to ions arising from complexes **1** and **3** – **5**, except of course for the nature of the amine-bis(phenolato) ligand present ($\mathbf{L}^1$ to $\mathbf{L}^5$, present in complexes **1** – **5**, respectively). The MALDI-TOF mass spectra for **2**/DMAP and **3**/DMAP mixtures in different molar ratios are shown in Fig. 4. When the molar ratio of **2** to DMAP is 1:0.5, a complicated mass spectrum results and many ions could not be readily identified. It is clear, however, that dichromium-containing ions are present along with DMAP-containing fragments, including $[\mathbf{L}^2\mathrm{CrCl(DMAP)}]^{+\cdot}$, **F6**. Also, a significant abundance of ions attributed to unmetallated ligand, $\mathrm{H_2}\mathbf{L}^2$ (**F1**) are observed. With an increase in DMAP to Cr ratio of 1:1, the mass spectrum simplifies considerably and readily identifiable ions are observed. Under these conditions, the base peak occurs at *m/z* 577.1, corresponding to $[\mathbf{L}^2\mathrm{CrCl}]^{+\cdot}$ (**F3**) with the next most abundant peak at *m/z* 699.2, representing $[\mathbf{L}^2\mathrm{CrCl(DMAP)}]^{+\cdot}$. Ions at higher *m/z* corresponding to dichromium-containing fragments **F9**, **F10**, **F11** and **F12** were also observed. Increasing the loading of DMAP further (**2**:DMAP of 1:2 and 1:4) resulted in the formation of [**2** – THF – Cl + 2DMAP]$^+$ ions, **F7**. The **3**/DMAP system demonstrates much less complex mass spectra. Addition of 0.5 equiv. of DMAP per Cr centre causes the appearance of $[\mathbf{L}^3\mathrm{Cr(DMAP)}]^+$ (**F5**) and $[\mathbf{L}^3\mathrm{CrCl(DMAP)}]^{+\cdot}$ (**F6**) and increasing the DMAP to Cr ratio (2 and 4 equiv. DMAP to Cr) has little influence on the number of ions observed and there was no evidence for $[\mathbf{L}^3\mathrm{Cr(DMAP)_2}]^+$ (**F7**) or dichromium-containing ions. The other significant species observed in the **3**/DMAP system is **F4** (*m/z* 574.3), which results from chloride loss to give $[\mathbf{L}^3\mathrm{Cr}]^+$. It is interesting that even with 4 equiv. of DMAP the base peaks for both **2** and **3** correspond to the DMAP-free ion, **F3**, with *m/z* of 577.1 for **2** and 609.2 for **3**, which suggests that this ion exhibits surprisingly high stability even to loss of chloride. Six-coordinate species of **3** appear to be unfavoured as shown by the much higher abundance of the four- and five-coordinate ions, **F2**, **F4** and **F5**.

A comparison of the relative abundance of the various fragment ions in compounds **1** – **5** with different amounts of DMAP added is shown in Fig. 5. For all five complexes, the abundance of the DMAP-coordinated cation, $[\mathbf{L}\mathrm{Cr(DMAP)}]^+$ **F5**, increases expectedly with increasing the amount of DMAP added. Changing the pendant donor group, however, appears to influence the coordination chemistry of DMAP with these complexes, as well as the stability of the complexes themselves in the gas phase. The nitrogen donor pendant arms, i.e. pyridyl in **1** and **2** (abbreviated as BuBuPyr and BuMethPyr in Fig. 5), and dimethylaminoethyl in **3** (abbreviated as $BuBuNMe_2$ in Fig. 5) generate very stable molecular ions **F3**, which comprise the base peaks in their respective mass spectra. Oxygen donor pendant arms, i.e. methoxyethyl in **4** (abbreviated as BuBuMe in Fig. 5) and, in particular, tetrahydrofurfuryl in **5** (abbreviated as BuBuTHF in Fig. 5) show lower stability of the molecular ions as judged by the lower relative abundance. As the amount of DMAP is increased compared to **4**, the DMAP adduct accompanied by chloride loss ($[\mathbf{L}^4\mathrm{Cr(DMAP)}]^+$, **F5**) becomes more abundant as well as the DMAP coordinated radical cation, $[\mathbf{L}^4\mathrm{CrCl(DMAP)}]^{+\cdot}$ **F6**. Complex **5** stands out as being most readily fragmented under MALDI conditions. The base peak was consistently identified as the unmetallated ligand, $H_2\mathbf{L}^5$ at *m/z* 537.4 (the isotopic pattern of this ion is actually a combination of the radical cation of $[H_2\mathbf{L}^5]^{+\cdot}$ as well as $[H\mathbf{L}^5]^{+\cdot}$ and $[\mathbf{L}^5]^{+\cdot}$ resulting from losses of $H^\cdot$ and/or single electrons during laser desorption). This suggests $\mathbf{L}^5$ is (relatively) poor at stabilizing Cr(III) complexes. Our previous reports of the CO_2/cyclohexene oxide copolymerization catalyzed by **5** with DMAP co-catalyst showed moderate activities (conversions of 64%, average TONs of 300, $M_n \sim 6{,}000$ g/mol, $Đ = 1.5 – 1.7$).[70] By comparison, we observed the catalyst system comprised of **1**/DMAP under these conditions provided conversions of 80% (TON of 400, $M_n \sim 10{,}000$ g/mol, $Đ = 1.1$ to 1.7).[68]

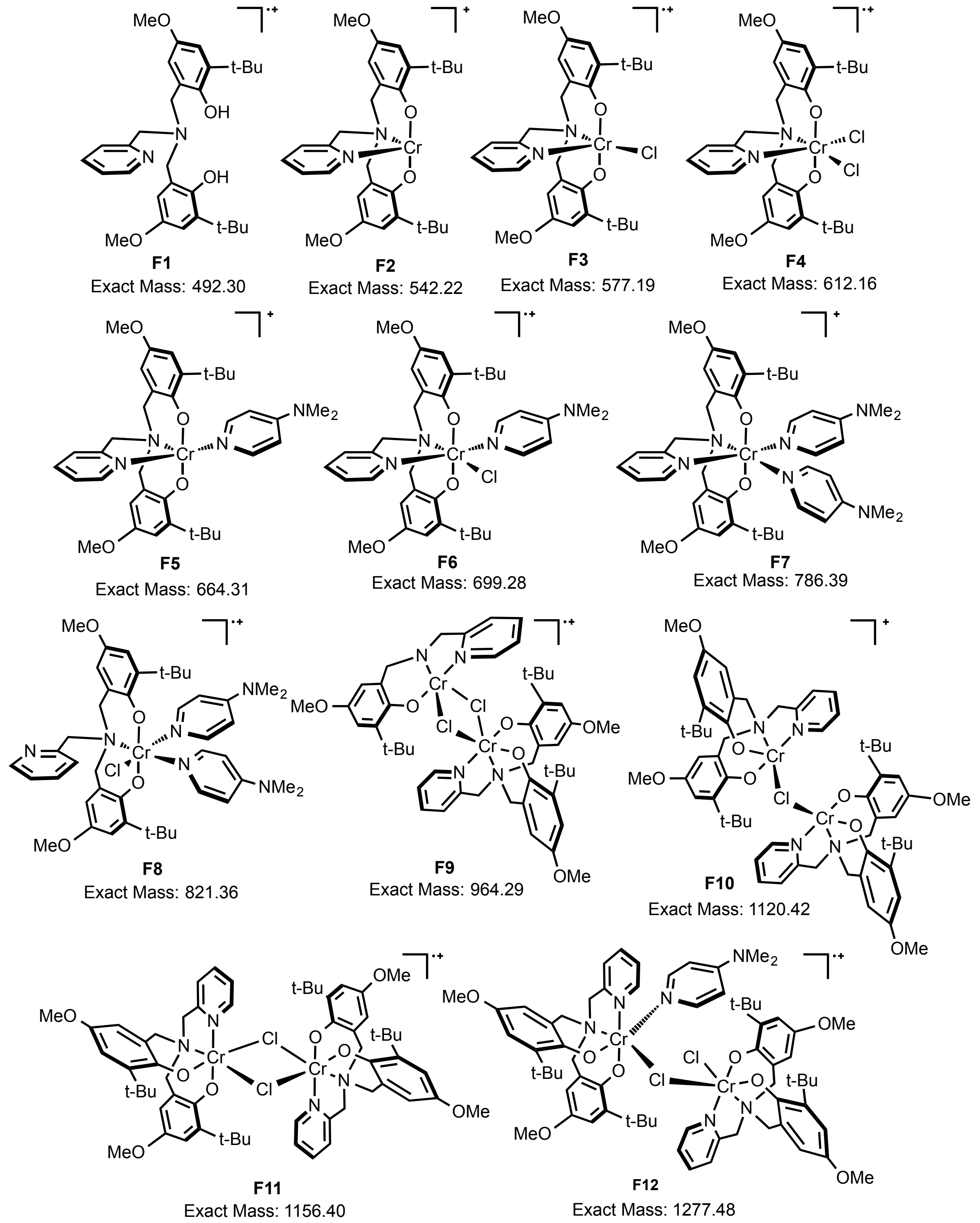
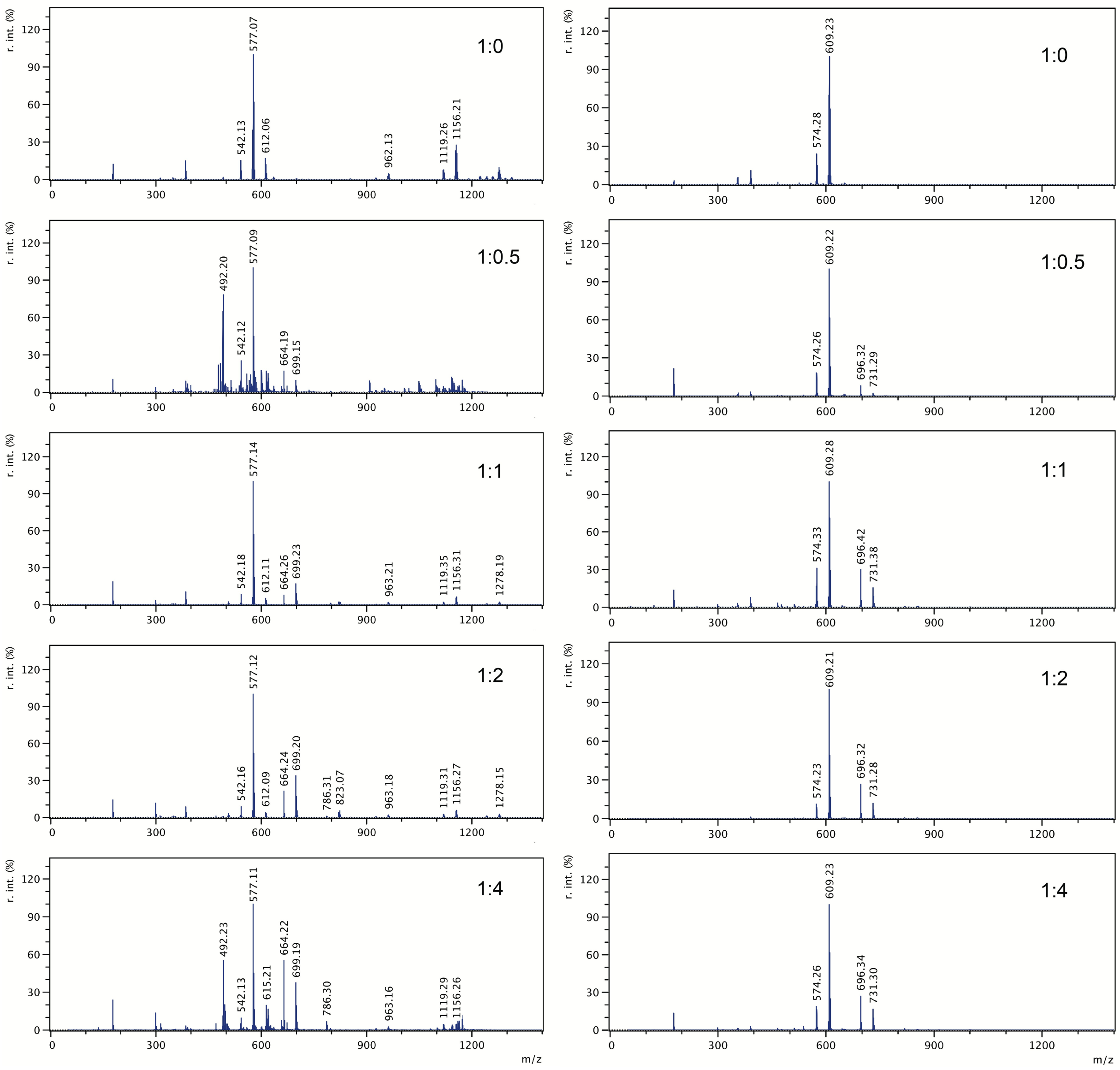


Fig. 3 Anticipated and observed fragments for complex **2**. Fragments of complexes **1** and **3** – **5** are represented by the analogous structures shown for **F1** – **F12**.



2/DMAP **3**/DMAP

Fig. 4 MALDI-TOF mass spectra of the mixtures resulting from combinations of complex **2** (left) and complex **3** (right) with different molar ratios of DMAP as shown: 1:0, 1:0.5, 1:1, 1:2 and 1:4.

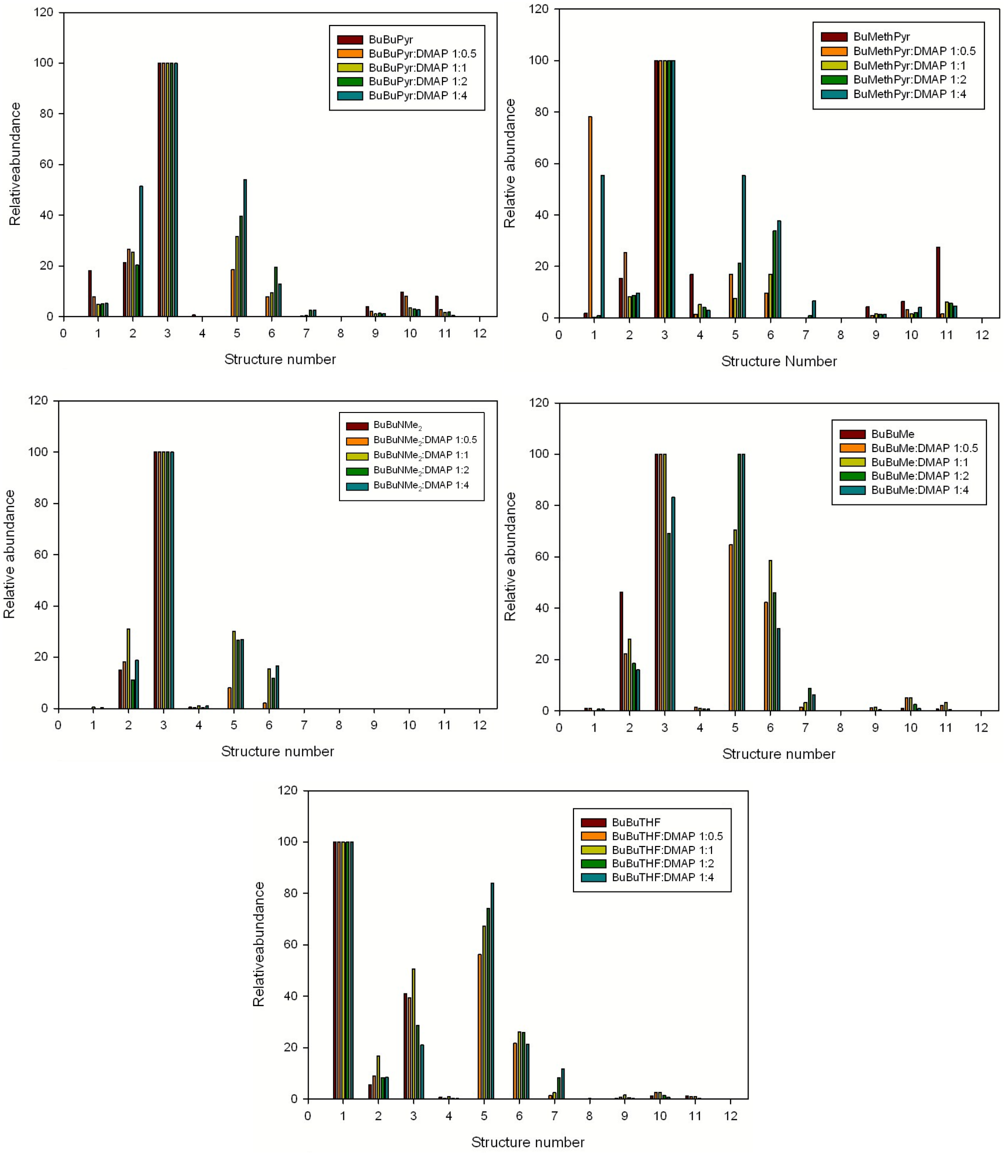
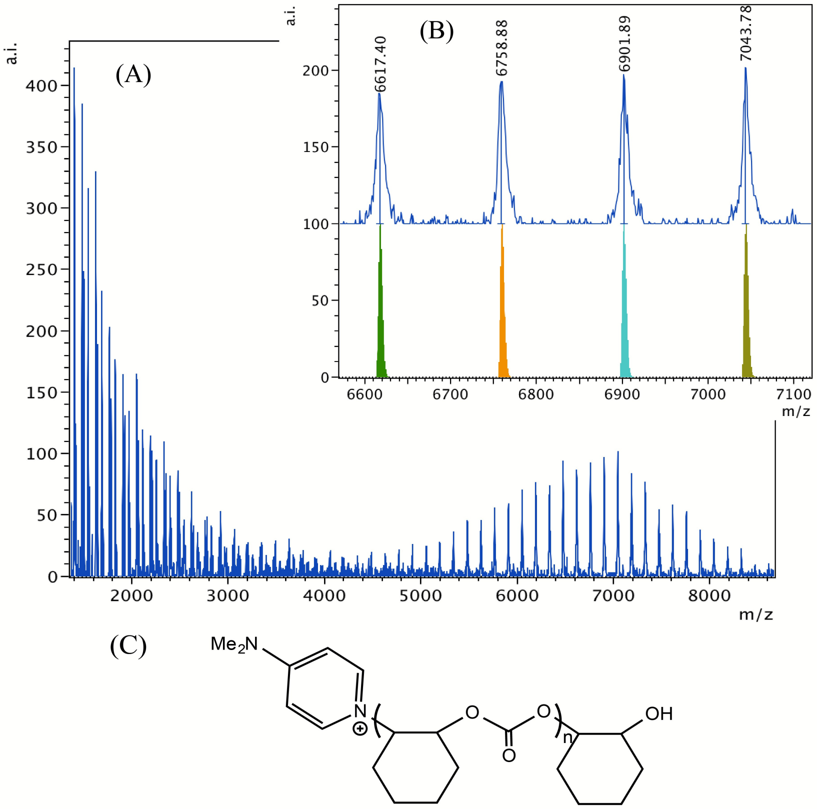


Fig. 5 Comparison of relative abundance of fragment ions in compounds **1** – **5** with varying amounts of DMAP as indicated. Relative abundance is given in % and structure numbers 1 – 12 correspond to fragments/ions shown in Fig. 3.

The difference in ion stability observed between compound **3** and the other four complexes can perhaps be attributed to the steric hindrance created by the dimethylaminoethyl group found in $\mathbf{L}^3$/complex **3**. Furthermore, the presence of two sp^3-hybridized amino donors in **3** reduces the Lewis acidity of the metal centre. Hence, sterically the Cr centre is more encumbered preventing the formation of chloride-bridged dimers, as previously[68] crystallographically authenticated for $[\mathbf{L}^1\mathrm{Cr}]_2(\mu\text{-Cl})_2$ and as postulated based on the presence of *m/z* 1260.6 (corresponding to **F11**) observed in the MALDI-TOF mass spectrum of **1**. Electronically, the more electron-rich Cr centre in **3** compared to **1**, for example, results in a lower affinity for the neutral DMAP than the anionic chloride ligand. A similar trend has been observed in comparing the affinity of SalenCrX and SalanCrX complexes (Fig. 1) for DMAP.[66] These trends in binding affinity for DMAP are believed to influence the CO_2/epoxide copolymerization activity of the binary catalyst systems of SalenCrCl and SalanCrCl with DMAP. Rieger and co-workers reported the selectivity for copolymerization of CO_2 with propylene oxide (PO) catalyzed by SalenCrCl and DMAP improved considerably with a SalenCrCl:DMAP ratio of 1:0.5.[27] Therefore, the formation of species containing one DMAP rather than two is likely preferred for initiation of copolymerization.[66]

The mechanism of copolymerization of CO_2 and cyclohexene oxide by binary catalyst systems of SalenCrX and N-heterocyclic bases such as DMAP has been investigated in detail by Darensbourg.[29] The proposed mechanism involves the formation of carbamate intermediates resulting from reaction of DMAP with CO_2 to generate a zwitterion, which was identified by ν_{CO2} bands at 2097 and 2017 cm^{-1}. Furthermore, Darensbourg reports a correlation between the disappearance of “free DMAP” as observed by *in-situ* FTIR with the initiation time observed for the formation of polycarbonate. Lu and co-workers studied the initiator role of DMAP in CO_2/propylene oxide copolymerization by ESI-MS and observed species corresponding to [$^-OCH(CH_3)CH_2$-$DMAP^+ + H^+$] and, with time, the growth of peaks corresponding to addition of units of PO + CO_2, that is, *m/z* [181.1 + n(102)]. This was interpreted as evidence that formation of carbamate zwitterions is not required for initiation of copolymerization. We have conducted detailed end group analysis of poly(cyclohexane)-carbonate[68,70] and poly(propylene)carbonate[69] formed by catalyst systems composed of **1**, **2** and **5** with DMAP. Use of complex **1** or **2** with 0.5 or 1 molar equiv. of DMAP in 500 molar equiv. of neat CHO shows only –Cl and –OH end groups with no initiation by DMAP observed. When a mixture of co-catalysts is used, the end group properties become more complicated. The polymer obtained using a 1:1:1 mixture of complex **2**, DMAP and PPNCl (bis(triphenylphosphine)iminium chloride) under the same conditions shows MALDI-TOF mass spectra where –Cl, –DMAP and –OH end groups were observed (Fig. 6). It is likely that the presence of the additional equiv. of nucleophile competes with the binding of DMAP to the chromium centre, hence generating more “free DMAP”, which can undergo intermolecular nucleophilic attack at a chromium-bound epoxide. We also previously reported the MALDI-TOF MS characterization of polymer obtained using the tetrahydrofurfuryl-functionalized complex **5** and DMAP.[70] Interestingly, the **5**/DMAP catalyst system *also* showed complicated mass spectra with –Cl, DMAP and –OH end groups despite using equimolar amounts of **5** and DMAP and the apparent stronger bonding affinity of DMAP to the Cr centre in **5** (i.e. the appearance of [$\mathbf{L}^5$Cr(DMAP)$_2$]$^+$ ions for 1:1 rations of **5**:DMAP). However, whereas the base peak for compounds **1** – **4** correspond to [**L**CrCl]$^{+\cdot}$ (**F3**) the base peak for **5** is the unmetallated ligand, [H$_2$$\mathbf{L}^5$]$^{+\cdot}$ (**F1**), regardless of DMAP concentration. This suggests the $\mathbf{L}^5$ ligand coordinates more weakly to the metal than $\mathbf{L}^1$ – $\mathbf{L}^4$, and this results in the poorly controlled polymerization previously observed.



[122 ($C_7H_{10}N_2$) + 142*n* (repeating unit) + 82 (C_6H_{10}) + 17 (OH)]

Fig. 6. (A) MALDI-TOF mass spectrum of polycarbonate produced by equimolar **2**/DMAP/PPNCl at 60 °C and 40 bar CO_2. (B) Higher mass region (*m/z* 6600 – 7100, n = 45 - 48) of the spectrum with calculated masses of fragments shown beneath the observed spectrum. (C) Proposed structure of the high mass range polymer.

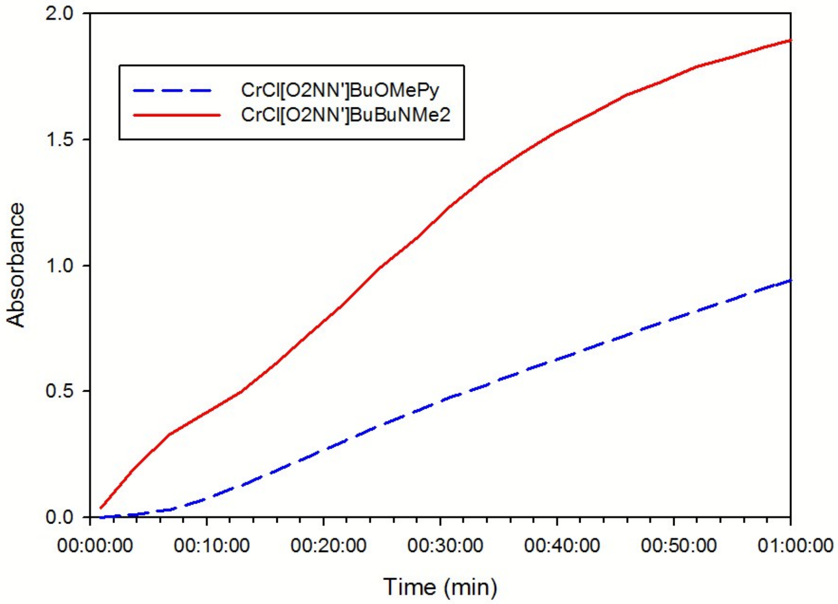


Fig. 7 Time profiles (for the first h) of the absorbance at 1750 cm^{-1} (corresponding to polycarbonate) using **2** (dashed blue line) and **3** (solid red line) as catalyst. Reaction conditions: [Cr]:[CHO]:[DMAP] = 1:500:1, 24 h total experiment time, 60 °C, 40 bar CO_2.

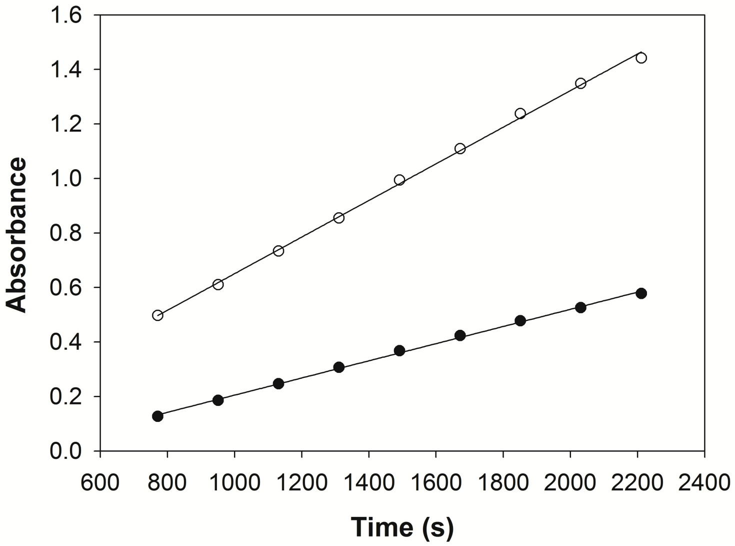
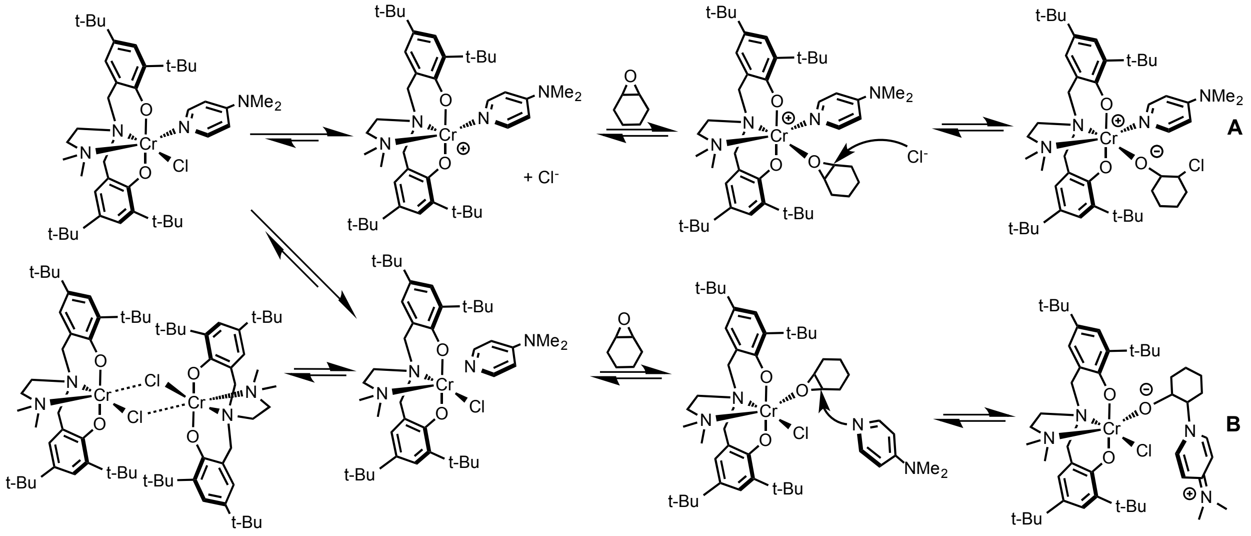


Fig. 8 Representative plots of absorbance vs. time for the linear portion of polycarbonate formation for the data presented in Fig. 7. Straight lines represent best fits of the data for compound **2** (●), $y = 3.15 \times 10^{-4}x - 1.10 \times 10^{-1}$, $R^2 = 9.99 \times 10^{-1}$; and compound **3** (○) $y = 6.72 \times 10^{-4}x - 2.09 \times 10^{-2}$, $R^2 = 9.99 \times 10^{-1}$.

It has been observed that the SalenCrX/DMAP system differs considerably from the SalanCrX/DMAP system in that it exhibits a lengthy induction period of up to 2 h for the copolymerization of CO_2/PO. The SalanCrX/DMAP system, on the other hand, shows propagation of polymer after a period of 10 min.[66] Also, the SalanCrX system displays higher TOFs, selectivity for polymer over cyclic carbonate formation, and gives higher polymer molecular weights with narrow dispersities. The differences in activity were attributed to the differing affinity for DMAP binding to the Salan- and Salen chromium compounds. Furthermore, as DMAP loading is increased, a decrease in polymer molecular weight is observed for both the SalanCrX and SalenCrX catalyst systems.[25,27,66,79] The relationship between induction period, reaction rate and DMAP-binding affinity for amine-bis(phenolate)chromium chloride complexes was investigated in order to assess whether a similar trend is observed to that of the Salan and Salen-based systems. The copolymerization of CHO with CO_2 by complexes **2** and **3** using 1:1 DMAP:Cr in 500 molar equiv. of neat epoxide was conducted at 60 °C and 40 bar CO_2. The reaction rates were monitored by infrared spectroscopy and following the carbonate region (absorbance at 1750 cm^{-1}) over time (Fig. 7). The time profile for the first hour shows virtually no induction period for **3**/DMAP, and only a short one (approx. 10 min.) for **2**/DMAP. The polymerization rate of **3**/DMAP was also observed to be much faster than that of complex **2** (Fig. 8). These results are in agreement with the MALDI-TOF MS analysis above, namely the propensity for **2** to form stable, six-coordinate adducts and dimers results in a lower activity towards epoxide/CO_2 copolymerization than complex **3**, which shows no evidence of dimer formation and relatively low abundance of six-coordinate [$\mathbf{L^3}$CrCl(DMAP)]$^{+\cdot}$.

Comparisons of the possible mechanisms of action of SalenCrX and SalanCrX complexes have identified the nature of the binding of the tetradentate ligand as being influential in catalyst activity,[29,35,37,66,81] The crystallographically authenticated SalenCrX and SalenCrXL complexes (where X is a monodentate anionic ligand, e.g. Cl^- or N_3^-, and L is a neutral monodentate ligand, e.g. DMAP or O=PCy_3) show the Salen ligand exhibits a planar orientation. SalanCrXL complexes, however, with the presence of sp^3-hybridized tertiary amino donors give distorted octahedral structures where the tetradentate Salan ligand occupies *cis*-α or *cis*-β orientiations where the two monodentate ligands are found in *cis*-postions rather than the *trans* coordination mode often found in SalenCrXL complexes. The amine-bis(phenolate) complexes **1** – **5** exhibit bonding orientations related to the Salan systems. Based on the above comparisons and on the observed end-groups in the polycarbonates obtained under equimolar ratios of DMAP/PPNCl to the Cr compounds, and comparisons of the influence of the ligand on the ability for stable six-coordinate ions to be observed by MALDI-TOF MS, a mechanism can be proposed for CO_2/epoxide copolymerization by **1** – **5** with DMAP as co-catalyst. The initiation steps available for complex **3**/DMAP catalyst system are shown in Scheme 1. The relative abundance of **F3** and **F5** compared to **F6** suggests the first equilibrium lies to the right, leading to a very short induction period. Also, whereas dimer formation is observed in the MALDI-TOF mass spectrum of **1**, **2**, **4** and **5**, no evidence of dimeric **3** was observed. Dimer formation, therefore, may be a reason for the presence of the induction period observed for **2** but not for complex **3**. As previously proposed by Lu and co-workers, progress along either Path A or B may be inhibited by excess DMAP, leading to the formation of $[\mathbf{L}Cr(DMAP)_2]^+$ in the case of path A, or increase the reversibility of the first equilibrium step in path B by hindering DMAP dissociation. Competitive binding of epoxide allows activation of the first monomer fragment, which undergoes nucleophilic attack by either Cl^- or DMAP. For conditions where DMAP end groups are absent (as for 1:0.5 or 1:1 combinations of complex **1** or **2** with DMAP as discussed above), path A is preferred resulting from the high affinity of DMAP bonding to the metal centre. For complex **3**, which is more electron rich at the Cr centre, DMAP dissociation at lower concentrations of that base is more prevalent, hence "free DMAP" is available to induce ring opening of the epoxide, generating –DMAP terminated polycarbonate (path B). DFT studies have been reported on the mechanism of epoxide/CO_2 copolymerization by metal Salen complexes.[82] Rieger and co-workers proposed the growing polymer chains undergo dissociation from the metal centre during polymerization, with chain-transfer resulting from high co-catalyst loading leading to low molecular weight polymers.[73] Baik and Nguyen studied the role of DMAP in SalenCr-catalyzed PO/CO_2 copolymerization.[72] Their findings support the role of the SalenCrCl complex as a Lewis acid the activates the epoxide ring, promoting its opening by an external nucleophile, such as DMAP. No evidence for a bimetallic pathway or simultaneous activation of both the epoxide and CO_2 was obtained. Unlike Rieger's proposal, attempts at creating an unsaturated Cr(III) centre through chloride loss or alkoxide dissociation resulted in significant energy penalties. Baik and Nguyen concluded that such steps were not possible in this case, therefore a ring-opening step similar to that shown in Scheme 1B is favoured. If the same case holds for compounds **1** – **5**, the presence of epoxide ring opening by chloride (leading to the observed –Cl end groups by MALDI-TOF MS) implies this step must happen by an intramolecular mechanism akin to a migratory insertion between cisoid ligands on the metal centre. Computational studies to investigate this possibility are currently underway.



Scheme 1. Two initiation paths via intermolecular nucleophilic attack available for **3**/DMAP. Path **A** leads to initiation by Cl; Path **B** leads to initiation by DMAP.

Conclusions

The MALDI-TOF mass spectra of amine-bis(phenolato)chromium(III) chloride complexes in the presence of DMAP in various amounts demonstrated that the ability for DMAP to bind to the chromium centre was influenced by the nature of the pendant neutral donor group on the tetradentate ligand. Where the donor was an ether (methoxyethyl or tetrahydrofurfuryl) or pyridyl group (complexes **1**, **2**, **4** and **5**), two DMAP molecules could be observed to bind. These complexes also demonstrated a propensity to form dimeric species, likely via chloride-bridges that we have previously structurally authenticated. For dimethylaminoethyl-functionalized ligands, no evidence for the binding of two DMAP molecules was observed, even at four equiv. of DMAP per Cr. Furthermore, no dimeric species were observed in their mass spectra. This difference in coordination chemistry was found to influence the catalytic activity of these compounds toward the copolymerizaton of CO_2 with cyclohexene oxide. In the presence of 1 equiv. of DMAP, the activity of the diamino-bis(phenolato)chromium chloride complex **3** was found the be faster than that of complex **2**. End group analysis of the polymers by MALDI-TOF

MS suggests the DMAP-containing end groups occur when the concentration of unbound DMAP is high, suggesting an intermolecular nucleophilic attack. Chloride-containing end-groups were most commonly observed at molar equiv. levels of DMAP loading, suggesting DMAP is not competitive with chloride in terms of epoxide ring-opening and binding to the metal centre is more favourable. Increasing chloride concentration, interestingly, leads to DMAP-containing polycarbonate, which may be explained by the formation of dichloride chromium species and release of free DMAP into the reaction.

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