Cr(salophen) Complex Catalyzed Cyclic Carbonate Synthesis At Ambient Temperature And Pressure

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ABSTRACT: The combination of a chromium(III)(salophen) bromide complex and tetrabutylammonium bromide is shown to catalyze the reaction between terminal epoxides and carbon dioxide at ambient temperature and one bar carbon dioxide pressure and between internal epoxides and carbon dioxide at 80 oC and 10 bar carbon dioxide pressure to form cyclic carbonates. The optimal conditions involve the use of 1.5–2.5 mol% of both the chromium(III)(salophen) bromide complex and tetrabutylammonium bromide and result in the formation of cyclic carbonates in 57–92% isolated yield after a reaction time of 24 hours. Under these conditions, no polycarbonate formation is observed except when cyclohexene oxide is used as substrate. The reactions were found to proceed with retention of epoxide stereochemistry. A study of the reaction kinetics revealed that the chromium(III) complex and tetrabutylammonium bromide react together to form a six-coordinate anionic chromium complex which is the actual catalyst and a catalytic cycle is proposed which explains the experimentally observed results.

KEYWORDS: Chromium; salophen; cyclic carbonate; epoxide; carbon dioxide.

Introduction

The chemical utilization of carbon dioxide is currently undergoing a significant resurgence of interest due to the realization that carbon capture and utilization can provide a cost effective complement to carbon capture and storage and that carbon dioxide is an inexpensive and sustainable alternative carbon source for the chemicals industry.[[1]](#endnote-1),[[2]](#endnote-2) There are two main challenges in carbon dioxide chemistry. The first of these is that carbon dioxide has a very negative heat of formation (Hfo = 394 kJ mol-1)[[3]](#endnote-3) so there are rather few reactions of carbon dioxide that have negative enthalpies or Gibbs energies of reaction. The second challenge is that very few reactions of carbon dioxide occur spontaneously, so effective catalysts have to be developed even for reactions which do have negative enthalpies and Gibbs energies of reaction.



**Scheme 1.** Reaction between carbon dioxide and epoxides.

These challenges are highlighted in the reaction between carbon dioxide and epoxides (Scheme 1). This reaction is exothermic (Hr = 144 kJ mol1 for the reaction between carbon dioxide and ethylene oxide to form ethylene carbonate[[4]](#endnote-4)), largely due to the release of the ring–strain associated with the three membered ring within the epoxide. However, carbon dioxide does not react spontaneously with epoxides, a suitable catalyst is required and depending upon the choice of catalyst (and reaction conditions), the reaction can be controlled to form either a cyclic carbonate[[5]](#endnote-5),[[6]](#endnote-6) (the thermodynamic product of the reaction), or an aliphatic polycarbonate6,[[7]](#endnote-7) (the kinetic product of the reaction). These are both important reactions, with cyclic carbonate production having been commercialized over 50 years ago[[8]](#endnote-8) and cyclic carbonates now having a range of applications including as polar aprotic solvents[[9]](#endnote-9),[[10]](#endnote-10) electrolytes for lithium ion batteries[[11]](#endnote-11) monomers for polymer synthesis[[12]](#endnote-12) and intermediates for the synthesis of other chemicals.[[13]](#endnote-13) Aliphatic polycarbonate production is just in the process of being commercialized7d,[[14]](#endnote-14) as aliphatic polycarbonates have the potential to replace aromatic polycarbonates[[15]](#endnote-15) and can also be used in the production of polyurethanes.[[16]](#endnote-16)

Even though the synthesis of cyclic carbonates from epoxides and carbon dioxide is a highly exothermic reaction, commercial processes still operate at high temperatures and pressures and use highly purified carbon dioxide.[[17]](#endnote-17) This is because the catalysts used commercially are quaternary ammonium[[18]](#endnote-18) or phosphonium[[19]](#endnote-19) salts which are inexpensive but not very effective catalysts. As a result, the commercial synthesis of cyclic carbonates is currently a net carbon dioxide emitter rather than consumer. Over the last nine years we have developed bimetallic aluminum(salen) complexes such as **1** (Chart 1) as much more effective catalysts for cyclic carbonate synthesis.[[20]](#endnote-20) The combination of complex **1** and a quaternary ammonium or phosphonium halide cocatalyst (2.5 mol% of each catalyst component) is capable of converting a wide range of terminal epoxides into the corresponding cyclic carbonates at room temperature (or below) and one bar carbon dioxide pressure[[21]](#endnote-21) and in some cases with kinetic resolution of the epoxide.[[22]](#endnote-22) Recently, we have shown that complex **1** with no halide cocatalyst can catalyze the synthesis of cyclic carbonates from terminal epoxides and carbon dioxide under optimal reaction conditions.[[23]](#endnote-23) Reactions catalyzed by complex **1** were also shown to be compatible with the unpurified carbon dioxide produced by methane combustion in a membrane–based oxyfuel combustion system.[[24]](#endnote-24) By raising the temperature to 50 oC and the carbon dioxide pressure to 25 bar, even compressed air could be used as the carbon dioxide source and at 60 oC and 10 bar carbon dioxide pressure, internal epoxides could be converted into the corresponding cyclic carbonates.[[25]](#endnote-25) Subsequently, one–component[[26]](#endnote-26) **2** and immobilized[[27]](#endnote-27) **3** catalysts were prepared and used in both batch and gas–phase flow reactors. Immobilized catalysts **3** were shown to be compatible with waste carbon dioxide present in power station flue gas.[[28]](#endnote-28)



**Chart 1.** Aluminum based catalysts for cyclic carbonate synthesis.

Recently, we have been seeking to extend our studies of cyclic carbonate synthesis away from aluminum(salen) complexes and have demonstrated that bimetallic aluminum(acen) complexes[[29]](#endnote-29) such as **4** and aluminum heteroscorpionate complexes[[30]](#endnote-30) such as **5** also give highly active catalysts for cyclic carbonate synthesis at room temperature and one bar carbon dioxide pressure. However, we[[31]](#endnote-31) and others[[32]](#endnote-32) were also interested in exploring the use of metals other than aluminum. Previous work has reported the use of salen complexes of chromium,[[33]](#endnote-33),[[34]](#endnote-34) cobalt,33,[[35]](#endnote-35),[[36]](#endnote-36) copper,35,[[37]](#endnote-37) magnesium,33a manganese,[[38]](#endnote-38) nickel,[[39]](#endnote-39) ruthenium,[[40]](#endnote-40) tin,[[41]](#endnote-41) titanium[[42]](#endnote-42) and zinc35,37,[[43]](#endnote-43) as catalysts for cyclic carbonate synthesis under appropriate reaction conditions. However, in our previous work21b we found that mononuclear salen complexes of aluminum, chromium, cobalt and manganese were not effective catalysts under mild reaction conditions (1 bar CO2 pressure and room temperature). In view of the excellent results reported using zinc(salophen) complexes such as **6** (Chart 2),[[44]](#endnote-44) we therefore decided to investigate the use of the salophen ligand with a metal in the +3 oxidation state and herein report the results of a study using chromium(salophen) complexes as catalysts.



**Chart 2.** Metal(salophen) complexes for cyclic carbonate synthesis.

Results and Discussion

The condensation reaction of substituted salicylaldehydes and various *o*-phenylenediamines gave several salophen ligands with different steric and electronic properties. Subsequent reaction with chromium(II) chloride under an argon atmosphere and oxidation by air afforded the respective chromium(III) salophen complexes in excellent yield as shown in Scheme 2. Complexes **7a** and **7e** have previously been reported and used as catalysts for the copolymerization of oxetanes and carbon dioxide.[[45]](#endnote-45) The X-ray structure of complex **7a** has previously been reported[[46]](#endnote-46) and the infrared and mass spectra of compounds **7a**–**k** confirmed their structures (see Experimental section and Supporting Information).



**Scheme 2.** Synthesis of chromium(salophen) complexes **7a-k**.

Complex **7a** was first tested as a catalyst for the formation of styrene carbonate **9a** from styrene oxide **8a** and carbon dioxide under solvent-free conditions as shown in Scheme 3, and the results are shown in Table 1. Control experiments (Table 1, entries 1–2) showed that neither tetrabutylammonium bromide nor chromium(salophen) complex **7a** displayed significant catalytic activity in the absence of the other catalyst component. This is in line with previous work using chromium(salen) derived catalysts where the reaction only occurred in the presence of a cocatalyst.33,34 The combination of complex **7a** and tetrabutylammonium bromide, tetrabutylammonium iodide or bis(triphenylphosphoranylidene)ammonium bromide as cocatalyst was found to be a highly efficient catalyst system (Table 1, Entries 5, 7 and 9). Tetrabutylammonium fluoride, tetrabutylammonium chloride, 4-dimethylaminopyridine and bis(triphenylphosphoranylidene)ammonium chloride were also investigated as cocatalysts, but were found to be less effective (Table 1, Entries 3, 4, 8 and 10). The trend found for the influence of the halide counterion in the cocatalyst on the catalyst activity was Br ≈ I > Cl > F (Table 1, Entries 3–9). This suggests that the optimal results are obtained when the halide is a good nucleophile and also a good leaving group, so that the anion can effectively ring-open the epoxide and be displaced to allow the formation of the cyclic carbonate. Doubling the concentration of tetrabutylammonium bromide (Table 1, entry 6) did not significantly increase the conversions.



**Scheme 3.** Synthesis of cyclic carbonates **9a**–**j** using complexes **7a**–**k**.

**Table 1.**Synthesis of carbonate**9a**catalyzed by complex**7a**.a

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Entry** | **Cocatalyst** | **Conv. 3h (%)b** | **TOFc (h-1)** | **Conv. 6h (%)d** | **TOFc (h-1)** | **Conv. 24h (%)e** | **TOFc (h-1)** |
| 1 | - | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |
| 2 | Bu4NBr | 0 | 0.00 | 0 | 0.00 | 1 | 0.02 |
| 3 | Bu4NF | 3 | 0.40 | 9 | 0.60 | 34 | 0.57 |
| 4 | Bu4NCl | 10 | 1.33 | 20 | 1.33 | 62 | 1.03 |
| 5 | Bu4NBr | 37 | 4.93 | 60 | 4.00 | 100 | 1.67 |
| 6 | Bu4NBr (5 mol%) | 41 | 5.46 | 65 | 4.33 | 100 | 1.67 |
| 7 | Bu4NI | 34 | 4.53 | 53 | 3.53 | 93 | 1.55 |
| 8 | PPNCld | 18 | 2.40 | 29 | 1.93 | 62 | 1.03 |
| 9 | PPNBre | 31 | 4.13 | 47 | 3.13 | 91 | 1.52 |
| 10 | DMAPf | 0 | 0.00 | 0 | 0.00 | 2 | 0.03 |

*a* Reactions carried out at room temperature and 1 bar CO2 pressure for 24 hours using 2.5 mol% of catalyst and 2.5 mol% of cocatalyst. *b* Conversion determined by 1H NMR spectroscopy of the crude reaction mixture. *c*TOF = moles of product/(moles of catalyst · time). *d* Bis(triphenylphosphoranylidene)ammonium chloride. *e* Bis(triphenylphosphoranylidene)ammonium bromide. *f* 4-Dimethylaminopyridine.

The synthesis of ten cyclic carbonates **9a–j** derived from terminal epoxides **8a–j** was investigated using 2.5 mol% of complex **7a** and tetrabutylammonium bromide at room temperature and 1 bar carbon dioxide pressure (except for propylene oxide **8b** which was used at 0 oC due to its volatility) to investigate whether complex **7a** provided a good catalyst system before further optimization (Table 2, Scheme 3). To our delight, catalyst **7a** was able to convert a wide range of terminal epoxides into their corresponding cyclic carbonates in good to excellent yields at ambient temperature and pressure.

**Table 2.**Conversion of epoxides **8a–j** into cyclic carbonates **9a–j** using catalyst **7a** and Bu4NBra

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Entry** | **Epoxide** | **Temperature (oC)** | **Conversion (%)*b*** | **Yield (%)*c*** |
| 1 | **8a** (R = Ph) | 25 | 100 | 93 |
| 2 | **8b** (R = Me) | 0 | d | 71 |
| 3 | **8c** (R = Et) | 25 | 100 | 84 |
| 4 | **8d** (R = Bu) | 25 | 100 | 88 |
| 5 | **8e** (R = Oct) | 25 | 100 | 79 |
| 6 | **8f** (R = CH2Cl) | 25 | 100 | 91 |
| 7 | **8g** (R = CH2OH) | 25 | 67 | 64 |
| 8 | **8h** (R = CH2OPh) | 25 | 77 | 72 |
| 9 | **8i** (R = 4-ClC6H4) | 25 | 80 | 73 |
| 10 | **8j** (R = 4-BrC6H4) | 25 | 60 | 50 |
| 11 | **8i** (R = 4-ClC6H4) | 50 | 100 | 85 |
| 12 | **8j** (R = 4-BrC6H4) | 50 | 100 | 89 |

*a* Reactions carried out at 1 bar CO2 pressure for 24 hours using 2.5 mol% of complex **7a** and 2.5 mol% of Bu4NBr cocatalyst. *b* Determined by 1H NMR spectroscopy of the crude reaction mixture. *c* Yield of pure isolated cyclic carbonate. *d*The volatile nature of epoxide **8b** meant that conversion could not be determined.

After testing epoxides **8a–j** using complex **7a** as catalyst and in view of the potential of this chromium(III)salophen chloride based system, a catalyst optimization study was carried out using tetrabutylammonium bromide as cocatalyst and styrene oxide as substrate at room temperature and one bar pressure of carbon dioxide. In order to increase the activity of the catalyst the substituents on the aromatic rings of the salophen ligand were varied. Catalysts with *t*Bu groups on the salicylaldehyde moieties **7a**, **7c** and **7d** and the unsubstituted salicylaldehyde catalyst **7b** gave excellent conversions after 24 hours and very similar conversions after 3 and 6 hours (Table 3, entries 1–4). This trend can be related to the absence of any steric effect. Complexes **7e**–**f** were synthesized to study the electronic influence of the substituents on the aromatic rings. It is apparent that electronic effects have a significant impact on the activity of the catalyst (Table 3, entries 5–6). If an electron-donating methoxy group is introduced to the catalyst, the catalytic activity increases. However strong electron-withdrawing substituents such as NO2 (**7f**) on the aromatic ring decrease the activity. This trend can be explained by considering the interaction between the Lewis-acidic chromium complex and the bromo-alkoxide intermediate formed by reaction of the epoxide with tetrabutylammonium bromide. Electron-donating substituents of the salophen ligand will weaken the chromium to alkoxide bond and thus facilitate the carbon dioxide insertion step. In contrast, electron-withdrawing substituents will strength the chromium to alkoxide bond and make its reaction with carbon dioxide more difficult.

The introduction of substituents at R1 had a less marked effect (Table 3, entries 7–9). Complex **7g** with 2,3-diaminonapthalene as the diamine backbone showed slightly lower activity than complex **7b** derived from 1,2-diaminobenzene. The introduction of an electron-donating methyl group to the R1 position (**7h**) gave lower activity than **7b**, but a substitution by Cl (**7i**) gave a catalyst with slightly higher productivity for the synthesis of styrene carbonate than **7b** after 24 hours.

As complexes (**7c** and **7e**) had given complete conversion of styrene oxide to styrene carbonate in 24 hours at room temperature and 1 bar of carbon dioxide pressure (Table 3, Entries 3 and 5) the synthesis of catalysts **7j**–**k** was undertaken, combining the optimal aldehydes and the optimal diamine. However, these catalysts were found to be less active than catalysts **7c** and **7e** after 24 hours (Table 1, entries 10–11). Therefore, catalyst **7e** was chosen as the best catalyst as it gave higher conversions after 3 and 6 hours than catalyst **7c**.

**Table 3.**Synthesis of carbonate**9a**catalyzed by complexes**7a–k.**a



|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Entry** | **Catalyst** | **Conv. (%)b** | **TOFc (h-1)** | **Conv. (%)d** | **TOFc (h-1)** | **Conv. (%)e** | **TOFc (h-1)** |
| 1 | **7a** | 31 | 4.13 | 51 | 3.40 | 93 | 1.55 |
| 2 | **7b** | 31 | 4.13 | 49 | 3.27 | 92 | 1.53 |
| 3 | **7c** | 30 | 4.00 | 53 | 3.53 | 100 | 1.67 |
| 4 | **7d** | 21 | 2.80 | 41 | 2.73 | 92 | 1.53 |
| 5 | **7e** | 45 | 6.00 | 69 | 4.60 | 100 | 1.67 |
| 6 | **7f** | 7 | 0.93 | 13 | 0.87 | 41 | 0.68 |
| 7 | **7g** | 12 | 1.60 | 26 | 1.73 | 85 | 1.42 |
| 8 | **7h** | 12 | 1.60 | 27 | 1.80 | 72 | 1.20 |
| 9 | **7i** | 21 | 2.80 | 43 | 2.87 | 95 | 1.58 |
| 10 | **7j** | 27 | 3.60 | 47 | 3.13 | 100 | 1.67 |
| 11 | **7k** | 30 | 4.00 | 52 | 3.47 | 97 | 1.62 |

*a* Reactions carried out at room temperature and 1 bar CO2 pressure for 24 hours using 2.5 mol% of catalyst and 2.5 mol% of Bu4NBr cocatalyst. *b* Conversion determined by 1H NMR spectroscopy of the crude reaction mixture after 3h. *c*TOF = moles of product/(moles of catalyst · time). *d* Conversion determined by 1H NMR spectroscopy of the crude reaction mixture after 6h. *e* Conversion determined by 1H NMR spectroscopy of the crude reaction mixture after 24h.



**Chart 3.** Counterion optimization for chromium(salophen) complexes

To further optimize the composition of the catalyst, the effect of altering the counterion present in the most active catalyst (complex **7e**) was investigated (Chart 3). The catalytic activity of complexes **7e**, **l**–**o** was found to vary depending upon the counterion with the order of reactivity bromide > chloride > acetate > iodide > tosylate (entries 1-5, Table 4). In general, the more nucleophilic the counterion, the more active the catalyst system is for cyclic carbonate formation. A similar trend was seen in chromium(III)salen complexes by Darensbourg,46 where a higher catalytic activity was obtained when using a more nucleophilic azide counterion instead of a chloride counterion of the catalysts. The trend is however broken by the iodide counterion (entry 3, Table 4) probably be due to the large size of the iodide counterion hindering the reaction.

**Table 4.**Synthesis of carbonate**9a**catalyzed by complexes**7e**, **l**–**o.**a



|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Entry** | **Catalyst** | **Conv. (%)b** | **TOFc (h-1)** | **Conv. (%)d** | **TOFc (h-1)** | **Conv. (%)e** | **TOFc (h-1)** |
| 1 | **7e** | 45 | 6.00 | 69 | 4.60 | 100 | 1.67 |
| 2 | **7l** | 44 | 5.87 | 71 | 4.73 | 100 | 1.67 |
| 3 | **7m** | 28 | 3.73 | 46 | 3.07 | 100 | 1.67 |
| 4 | **7n** | 34 | 4.53 | 57 | 3.80 | 100 | 1.67 |
| 5 | **7o** | 4 | 0.53 | 7 | 0.47 | 42 | 0.70 |

*a* Reactions carried out at room temperature and 1 bar CO2 pressure for 24 hours using 2.5 mol% of catalyst and 2.5 mol% of Bu4NBr cocatalyst. *b* Conversion determined by 1H NMR spectroscopy of the crude reaction mixture after 3h. *c*TOF = moles of product/(moles of catalyst · time). *d* Conversion determined by 1H NMR spectroscopy of the crude reaction mixture after 6h. *e* Conversion determined by 1H NMR spectroscopy of the crude reaction mixture after 24h.

Having optimized the composition of the catalyst, the synthesis of cyclic carbonates **9a–j** from terminal epoxides **8a–j** was studied using 2.5 mol% of both complex **7l** and tetrabutylammonium bromide at room temperature and 1 bar carbon dioxide pressure for 24 hours. This study allowed the catalytic efficiency of complexes **7a** and **7l** to be compared for a range of epoxides as there may be a dependence of the catalytic activity on the solubility of the catalyst in the epoxide. The results of this study are shown in Table 5. In general, catalysts **7a** and **7l** gave very similar conversions (compare Tables 1 and 5), but complex **7l** gave better results with epoxides **8g** and **8j** which gave the lowest conversions in reactions catalyzed by complex **7a**. Therefore, complex **7l** was felt to be the more generally applicable catalyst and was used for further studies. Notably, the catalysts were compatible with aliphatic, aromatic and functionalized substrates containing halogen and hydroxyl groups. There was also no apparent influence of epoxide size on catalyst activity. This may be connected to the stability of the salophen ligand in complexes **7a,l** and the ease of epoxide coordination to mononuclear complexes bearing a planar salophen ligand.

**Table 5.**Conversion of epoxides **8a–j** into cyclic carbonates **9a–j** using catalyst **7l** and Bu4NBra

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Entry** | **Epoxide** | **temperature (oC)** | **conversion*b*** | **Yield*c*** |
| 1 | **8a** (R = Ph) | 25 | 100 | 92 |
| 2 | **8b** (R = Me) | 0 | d | 57 |
| 3 | **8c** (R = Et) | 25 | 100 | 86 |
| 4 | **8d** (R = Bu) | 25 | 95 | 81 |
| 5 | **8e** (R = Oct) | 25 | 89 | 82 |
| 6 | **8f** (R = CH2Cl) | 25 | 100 | 78 |
| 7 | **8g** (R = CH2OH) | 25 | 86 | 72 |
| 8 | **8h** (R = CH2OPh) | 25 | 71 | 71 |
| 9 | **8i** (R = 4-ClC6H4) | 25 | 100 | 78 |
| 10 | **8j** (R = 4-BrC6H4) | 25 | 71 | 49 |
| 11 | **8i** (R = 4-ClC6H4) | 50 | 100 | 91 |
| 12 | **8j** (R = 4-BrC6H4) | 50 | 100 | 89 |

*a* Reactions carried out at 1 bar CO2 pressure for 24 hours using 2.5 mol% of complex **7l** and 2.5 mol% of Bu4NBr cocatalyst. *b* Determined by 1H NMR spectroscopy of the crude reaction mixture. *c* Yield of pure isolated cyclic carbonate. *d*The volatile nature of epoxide **8b** meant that conversion could not be determined.

In order to expand the substrate scope, the synthesis of cyclic carbonates from internal epoxides and carbon dioxide was investigated using the catalyst system comprised of complex **7l** and tetrabutylammonium bromide. Even though internal epoxides are less reactive than terminal epoxides, successful catalysts for these substrates have been recently developed.30c,32,[[47]](#endnote-47) In view of this lower reactivity, reactions with internal epoxides were carried out at 50 oC and 10 bar carbon dioxide pressure for 24 hours (Scheme 4) and initial experiments with cyclohexene oxide **10a** showed that under these conditions the complex **7l** and tetrabutylammonium bromide loadings could be reduced from 2.5 to 1.5 mol% without having a major effect on the conversion (82 and 78% respectively). However, further reduction of the loading of complex **7l** and tetrabutylammonium bromide to 0.5 mol% resulted in the conversion decreasing to just 20%.

 **Scheme 4.** Synthesis of polycyclohexene carbonate **11a** or cyclic carbonates **11b**-**f** using complex **7l** and tetrabutylammonium bromide as catalyst system.

Disubstituted cyclic carbonates **11b**-**f** were synthesized in moderate to good yield from their corresponding internal epoxides **10b**-**f** and carbon dioxide using 1.5 mol% of both complex **7l** and tetrabutylammonium bromide at 50 oC and 10 bar carbon dioxide pressure under solvent free conditions for 24 hours (Table 6). It is worth noting that when cyclohexene oxide **10a** was used, poly(cyclohexene carbonate) was obtained in 72% yield (Table 6, entry 1) as previously reported by Darensbourg and coworkers.34 However, no polycarbonate formation was observed when other epoxides were used, rather the cyclic carbonate product was obtained with a selectivity higher than 99%. Under these reaction conditions, cyclopentene oxide **10b** was a good substrate, giving cyclic carbonate **11b** in 66% yield (Table 6, entry 2). The *cis-* and *trans*– cyclic carbonates **11c** and **11d** were isolated in low yield (Table 6, entry 3 and 4), with almost complete retention of stereochemistry. Stilbene oxide **10e** gave no conversion at 50 oC as it is a solid under these reaction conditions. Sterically hindered epoxide **10f** was converted into the cyclic carbonate product **11f** in 52% yield.

**Table 6.** Conversion of epoxides **10a**-**f** into poly(cyclohexene carbonate) **11a** or cyclic carbonates **11b**-**f** using catalyst **7l** and Bu4NBr*a*



|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Entry** | **Substrate** | **Conversion 50 ºC (%)b** | **Yield 50 ºC (%)c** | **Conversion 80 ºC (%)b** | **Yield 80 ºC (%)c** |
| 1 | **10a** | 78d | 72d | 80d | 76d |
| 2 | **10b** | 72 | 66 | 93 | 85 |
| 3 | **10c** | e | 20 | e | 21, 63f |
| 4 | **10d** | e | 19 | e | 25, 60f |
| 5 | **10e** | 0 | 0 | 98 | 89 |
| 6 | **10f** | 58 | 52 | 100 | 87 |

*a* Reactions carried out at 10 bar CO2 pressure for 24 hours using 1.5 mol% of catalyst **7l** and 1.5 mol% of Bu4NBr cocatalyst. *b* Conversion determined by 1H NMR spectroscopy of the crude reaction mixture after 24h. *c* Yield of pure isolated cyclic carbonate. *d*Poly(cyclohexene) carbonate was obtained. *e*The volatile nature of epoxide meant that conversion could not be determined. *f* Using3.0 mol% of Bu4NBr.

By increasing the reaction temperature to 80 ºC and keeping the catalyst concentration at 1.5 mol%, epoxides **10b**-**f** were successfully converted into cyclic carbonates **11b**-**f** in 60−89% yield (Table 6). Once again, poly(cyclohexene carbonate) was obtained in 76% yield with a high content of carbonate linkages (>99%) and PCHC/CHC ratio (>99%) when cyclohexene oxide **10a** was used as substrate (Table 6, entry 1). Poly(cyclohexene carbonate) was characterized by 1H-NMR and 13C-NMR and Gel Permeation Chromatography (GPC) (See Supporting Information). 13C-NMR confirmed that poly(cyclohexene carbonate) **11a** obtained is atactic as both isotactic (153.7 ppm) and syndiotactic (153.0153.3 ppm) diads were observed. GPC showed that the polycarbonate prepared using chromium complex **7l** as catalyst at 80 °C and 10 bar CO2 had Mn = 20,518 and Mw = 23,202 (Mw/Mn = 1.13) relative to polystyrene standards (See Supporting Information).

On the other hand, the cyclic carbonate product was obtained when epoxides **10b**-**f** were used. As expected, at 80 oC the catalyst system displays higher activity resulting in an increase in the yield of the corresponding cyclic carbonate (Table 6, entries 26). Under these reaction conditions, cyclopentene carbonate **11b** was isolated in 85% yield (Table 6, entry 2). When the same reaction conditions were applied to epoxides **10c** and **10d**, the *cis–* and *trans*– cyclic carbonates **11c** and **11d** were isolated in poor yield. However, by increasing the tetrabutylammonium bromide loading to 3 mol%, the yields of cyclic carbonates **11c­–d** increased to 60–63% (Table 6, entries 3 and 4). A 97:3 ratio of *cis–* and *trans*– isomers of cyclic carbonate **11c** was observed from *cis*–epoxide **10c,** whilst complete retention of stereochemistry of *trans*isomer of cyclic carbonate **11d** from *trans*epoxide **10d** was observed. *Trans*–stilbene oxide **10e** was successfully converted into *trans*–1,2–diphenylethylene carbonate **11e** in 89% isolated yield at 80 ºC (Table 6, entry 5). Finally, epoxide **10f** was converted into its corresponding cyclic carbonate product **11f** in 87% yield under these reaction conditions.

The use of internal epoxides **10a**-**f** as substrates gave us the opportunity to gain insight into the reaction mechanism and study the stereochemistry of the synthesis of cyclic carbonates catalyzed by complex **7l** and tetrabutylammonium bromide. Analysis of the NMR spectra of cyclic carbonates **11a–g** revealed that cyclic carbonate formation catalyzed by complex **7l** and tetrabutylammonium bromide occurs with retention of the epoxide stereochemistry.30,32,47,[[48]](#endnote-48) These results are in good agreement with the general mechanism proposed for the synthesis of cyclic carbonates catalyzed by a combination of a Lewis acid (including chromium metal complexes) and a nucleophile as catalyst system5,33,34 in which the epoxide undergoes two substitution reactions at the less hindered carbon atom.47,48

To further study the reaction mechanism, a kinetic study of the synthesis of styrene carbonate **9a** catalyzed by catalyst **7l** and tetrabutylammonium bromide was carried out at 50 oC and 1 bar carbon dioxide pressure under solvent free conditions. Samples were taken from the reaction every 30 minutes and analyzed by high-performance liquid chromatography (HPLC) to determine the conversion of styrene oxide **8a** into styrene carbonate **9a**. We have previously shown that under these conditions, the reaction follows zero order kinetics in the early stages of the reaction since the epoxide acts as substrate and reaction solvent, but as the reaction proceeds the reaction follows first order kinetics as the cyclic carbonate becomes the main species in the reaction mixture.23,30c

The general rate equation for this reaction is shown in Equation (1). Since the concentration of carbon dioxide, complex **7l** and tetrabutylammonium bromide do not change during the reaction, Equation (1) may be written as Equation (2). As aforementioned, in the early stages of the reaction, the concentration of styrene oxide **8a** does not change, so the kinetics can be fitted to zero order kinetics and the rate equation can be written as Equation (3). However, as the reaction proceeds, the reaction becomes first order in epoxide **8a** concentration and the rate equation may be expressed as Equation (4).

Rate = k[**8a**]a[CO2]b[**7l**]c[Bu4NBr]d (1)

Rate = kobs[**8a**]a where kobs = k[CO2]b[**7l**]c[Bu4NBr]d (2)

Rate = k0obs, where k0obs = k0[**8a**]a[CO2]b[**7l**]c[Bu4NBr]d (3)

Rate = k1obs[**8a**], where k1obs = k1[CO2]b[**7l**]c[Bu4NBr]d (4)

The order with respect to the concentration of complex **7l** and tetrabutylammonium bromide were studied by carrying out two sets of reactions at four different concentrations of complex **7l** or tetrabutylammonium bromide, keeping the concentration of the other catalyst component constant.[[49]](#endnote-49) Firstly, the order with respect to the [Bu4NBr] was studied using [**7l**] = 175 mM and [Bu4NBr] = 175–437 mM. The log [Bu4NBr] / log k0obs and log [Bu4NBr] / log k1obs plots had slopes of 0.96 and 1.05 respectively, indicating that the reaction is first order with respect to the concentration of tetrabutylammonium bromide (d = 1).49  This was also confirmed by plotting k0obs or k1obs versus [Bu4NBr] which also showed a good fit to a straight line which passed through the origin (Figure 1).



**Figure 1.** Plot of the observed first order rate constant versus [Bu4NBr]. Reactions were carried out at 50 oC under solvent free conditions with [**7l**] = 175 mM and [Bu4NBr] = 175–437 mM. Data shown are the average of two experiments with the individual experiments being used to indicate the error bars.

The order with respect to the [**7l**] was firstly studied with [Bu4NBr] = 175 mM and [**7l**] = 175–437 mM. The slope obtained when plotting log [**7l**] / log k1obs was 0.09 (Figure 2), indicated that the reaction is zero order with respect to the concentration of catalyst **7l** under conditions where [Bu4NBr] < [**7l**] (c = 0).49 However, when the kinetic study was repeated with [Bu4NBr] = 437 mM and [**7l**] = 87–350 mM ([Bu4NBr] > [**7l**]), the slopes obtained when plotting log [**7l**] / log k0obs and log [**7l**] / log k1obs were 0.81 and 1.07 respectively, indicating that the reaction is first order with respect to the concentration of catalyst **7l** (c = 1).49 This was confirmed by plotting k0obs and k1obs versus [**7l**] which also showed a good fit to a straight line which passed through the origin (Figure 3).



**Figure 2.** Plot of the log(k1obs avg) against log[**7l**]. Reactions were carried out at 25 oC under solvent free conditions with [Bu4NBr] = 175 mM and [**7l**] = 175–437 mM. Data shown are the average of two experiments with the individual experiments being used to indicate the error bars.



**Figure 3.** Plot of the observed first order rate constant versus [**7l**]. Reactions were carried out at 25 oC under solvent free conditions with [Bu4NBr] = 437 mM and [**7l**] = 87–350 mM. Data shown are the average of two experiments with the individual experiments being used to indicate the error bars.

Consequently, the rate equation for the synthesis of styrene carbonate **9a** from styrene oxide **8a** catalyzed by complex **7l** and tetrabutylammonium bromide with [Bu4NBr] > [**7l**] at 25 oC and one bar pressure of carbon dioxide may be expressed as shown in Equation (5) during the early stages of the reaction or as shown in Equation (6) during the latter stages of the reaction.

Rate = k0obs, where k0obs = k0[**8a**][CO2][**7l**][Bu4NBr] (5)

Rate = k1obs[**8a**], where k1obs = k1[CO2][**7l**][Bu4NBr] (6)

From the kinetic experiments it is apparent that the chromium(salophen) complex and tetrabutylammonium bromide interact to form a new 1:1 species, the concentration of which depends upon the concentration of the limiting catalyst component. Darensbourg and co-workers have shown by X-ray crystallography that chromium(salen) chloride compounds form six-coordinate complexes in the presence of two equivalents of anions such as Cl-, CN-, N3-, and NCO-.[[50]](#endnote-50) By extending this reasoning to our chromium(salophen) system, Bu4NBr could act as an anion source to form a six-coordinate [chromium(salophen)Br2]- complex **12** (Scheme 5). This would explain the need for an excess of Bu4NBr to study the order with respect to the concentration of complex **7l** in our chromium(salophen)/Bu4NBr catalyst system.

 **Scheme 5.** Formation of [chromium(salophen)Br2]- complex in the presence of bromide anions.

Experiments were conducted in which tetrabutylammonium bromide was added to a solution of catalyst **7l**, to determine if the observation of a Br-Cr-Br system was possible. Tetrabutylammonium bromide was added to a solution of the catalyst in dichloromethane in 0.5 molar equivalent aliquots up to 5 molar equivalents, and the solution was analysed via UV-VIS and FT-IR spectroscopy.

UV-Vis analysis showed an increase in absorbance at approximately 418 and 506 nm on addition of tetrabutylammonium bromide, with the increase in absorbance plateauing after adding 3.5 molar equivalents of tetrabutylammonium bromide. A slight shift in peak position also occurred for both peaks, from 506 to 512 nm and 423 to 413 nm respectively. This suggests that a change in the structure of the catalyst is occurring during the addition of from 0.5 to 3.5 molar equivalents of tetrabutylammonium bromide (Figure 4).



**Figure 4.** UV-Vis spectra on addition of tetrabutylammonium bromide to a solution of **7l** in dichloromethane.

In the FT-IR spectra, a new peak is present at 697 cm-1 which is not visible in the spectra of tetrabutylammonium bromide or catalyst **7l** alone (Figure 5). The peak appears after 1.5 equivalents of tetrabutylammonium bromide is added, and shows no major changes after adding 3-3.5 equivalents. A peak at 730 cm-1 also grows in intensity during to the addition of tetrabutylammonium bromide and appears at a slightly different shift than is seen in pure tetrabutylammonium bromide (738 cm-1).



**Figure 5.** IR spectra obtained on addition of tetrabutylammonium bromide to a solution of **7l** in dichloromethane.

Taking into account that cyclic carbonate formation occurs with retention of the epoxide stereochemistry and that the reaction kinetics indicate a first order dependence on the concentration of the catalyst and Bu4NBr, the mechanism shown in Scheme 6 is proposed. On addition of one equivalent of Bu4NBr to a Cr(salophen) bromide complex, the six–coordinate bis–bromide complex [Cr(salophen)Br2]- is formed. Upon addition of the epoxide to the catalyst system an equilibrium is established between the bis–bromide complex **12** and the epoxide adduct Cr(salophen)Br·epoxide. It has been reported that this equilibrium is shifted towards the neutral epoxide adduct in pure epoxide solution.50 The non–coordinated bromide attacks the less hindered carbon of the epoxide with the first inversion of the stereochemistry. Then, carbon dioxide is inserted into the chromium–oxygen bond to form a metal carbonate which ring–closes with a second inversion to afford the cyclic carbonate with overall retention of the epoxide stereochemistry.



**Scheme 6.** Proposed mechanism for the synthesis of cyclic carbonates from epoxides and carbon dioxide catalyzed by complex **7l** and tetrabutylammonium bromide as catalyst system.

Conclusions

Chromium salophen complexes **7a****o** have been developed as highly active catalysts for the synthesis of cyclic carbonates from terminal epoxides and carbon dioxide in the presence of tetrabutylammonium bromide as a cocatalyst. The catalyst system formed by the combination of complex **7l** and tetrabutylammonium bromide displays excellent catalytic activity at room temperature and one bar pressure of carbon dioxide under solvent-free conditions. The substrate scope was evaluated and the catalyst system displayed a broad substrate scope catalyzing cyclic carbonate formation from alkyl, aryl and functionalized terminal epoxides as well as internal epoxides in good to excellent yields. Cyclic carbonates were synthesized with a selectivity higher than 99% except when cyclohexene oxide **10a** was used as substrate. In this case, poly(cyclohexene carbonate) was obtained in good yield.

The reaction kinetics of the catalytic process were studied and the reaction was found to be first-order with respect to the concentration of complex **7l** and tetrabutylammonium bromide. From the kinetic study, we can conclude that both catalyst components interact to form a six-coordinate [Cr(salophen)Br2]- complex **12**, which is the catalytically active species. Based on the experimental results and the kinetic study, a possible mechanism for the synthesis of cyclic carbonates catalyzed by complex **7l** and tetrabutylammonium bromide has been proposed.

Even though there are many catalyst systems that have been reported in the literature for cyclic carbonate synthesis, most of them require the use of high temperature and pressure, which emits more carbon dioxide than is used. We have shown that chromium(salophen) complex **7l** is an efficient catalyst for the synthesis of cyclic carbonates even from challenging epoxides under mild reaction conditions.

**Experimental Part**

All chemicals were provided by Alfa Aesar, Acros Organics, Sigma-Aldrich or Fischer Scientific. Carbon dioxide was purchased from BOC and used without further purification. All reaction solvents were obtained from Fischer-Scientific unless otherwise stated and were HPLC grade wherever possible. For reactions which required anhydrous conditions, all glassware was pre-dried in a heated oven (≈ 120 °C), flame dried whilst *in vacuo* and then kept under a nitrogen or argon atmosphere. Dry solvents were pre-dried and purified using a Pure Solv MD-7 solvent purification system.

1H and 13C NMR spectra were obtained from a Jeol ECS-400 or Jeol ECX-400 NMR spectrometer (400 MHz) at room temperature. 1H NMR spectra were referenced using the CHCl3 peak of CDCl3 at 7.26 ppm or TMS at 0.00 ppm, and 13C NMR spectra were referenced using the middle peak of the triplet CDCl3 peak at 77.00 ppm. MS analysis was run using a Bruker microTOF MS, twinned with an Agilent series 1200 LC for ESI spectrometry, or a Water GCT Premier MS, twinned with an Agilent (HP) 7890A GC for EI and LIDFI mass spectrometry. IR spectra of samples were obtained neat using a PerkinElmer UATR Two FT-IT spectrometer. Spectra were analyzed using the PerkinElmer software “Spectrum”. UV-Vis spectra of samples were obtained in solution using a Shimadzu UV-1800 Spectrometer and Quartz UV-Vis cells (1 cm). Melting points of samples were measured using a Stuart SMP3 melting point apparatus (25 °C – 350 °C). High-performance liquid chromatographywas performed on an Agilent 1220 instrument fitted with a diode-array detector using a Chiralcel OD column (25 cm by 4.6 mm), using hexane/isopropanol (80:20 %v/v) as eluent and a flow rate of 1.00 mL/min. XRF analysis was performed using a Horiba XGT-7000 XRF Spectrometer with a Rh X-Ray generator. Analysis of samples and standards were performed with no X-Ray filter, a preset time of 60 seconds, and an X-Ray voltage of 30 keV with a beam size of 1.2 mm. The calibration curves were created by mixing together standards of known Cr and halide concentrations, made into pellets after mixing together with a pestle and mortar, and comparing the intensity readings obtained to the known concentrations. All samples and standards were analyzed 8 times. The average value of the 8 runs was used in consequent calculations. Quantification of chromium in catalyst samples was performed via ICP-MS. Samples were prepared by first dissolving the desired sample in 5 mL of TraceSELECT® solvent grade of nitric acid (Sigma-Aldrich) in a sample vial. The sample was then heated to 110 °C for three hours with a glass cover on top of the vial to avoid sample evaporation. The samples were then left to cool to room temperature and then further diluted to 100 mL with ultrapure water in a 100 mL volumetric flask. Any further dilutions were performed using ultrapure water if required. The samples were analyzed with an Agilent 7700x ICP-MS, using nickel sample and skinner cones, and the analysis was run under helium. In terms of sampling, the sample was taken up for 60 seconds, stabilized for 40 seconds, and washed for 60 seconds (5% HCl for 30 seconds, and 2% HNO3 washes for 30 seconds). Each sample was run three times and the overall mean value of chromium in ppm or ppb was obtained.

**General synthesis of chromium(salophen) complexes 7a-k**

Salophen ligand (1.0 eq.) was dissolved in dry THF (50 mL) under argon. Then, anhydrous CrCl2 (1.0 eq.) was added and the mixture was stirred for 24 hours under argon. Air was bubbled through the flask for another 24 hours. Then, Et2O was added and the organic layer was washed with a saturated solution of ammonium chloride (2×25 mL) and brine (2×50 mL). The organic layer was dried (Na2SO4) and the solvent was removed under reduced pressure to give chromium(salophen) complexes **7a**-**k** as a red–brown solids (Yield: 69-95%).

 **Chromium complex 7a**:Yield: 0.3785 g, 97%. Mass Spec ESI: Calc: [C36H46CrN2O2]+: 590.2959. Found: 590.2972, Mass Spec LIFDI: Calc: [C36H26CrClN2O2]+: 625.27. Found: 625.27. IR neat (selected absorbances): 2652, 2904, 2867 (C-H alkyl) 1602 (C=N), 1524 (C=C aromatic), 1198 (C-O), 1171 (C-N), 748 (C-H) cm-1. Melting point: > 350 °C. ICP-MS: expected Cr = 8.3%, found Cr = 8.4%.

**Chromium complex 7b**:Yield: 0.9282 g, 91%. Mass Spec ESI: Calc: [C20H14CrN2O2]+: 336.0455. Found: 366.0463, Mass Spec LIFDI: Calc: [C20H14CrN2O2]+: 336.05. Found: 336.05. IR neat (selected absorbances): 1606 (C=N), 1537 (C=C aromatic), 1189 (C-O), 1150 (C-N), 749 (C-H) cm-1.Melting point: > 350 °C. ICP-MS: expected Cr = 12.9%, found Cr = 12.6%.

**Chromium complex 7c**: Yield: 0.180 g, 76%. Mass Spec ESI: Calc: [C28H30CrN2O2]+: 478.1707. Found: 478.1715. Mass Spec LIDFI: Calc: [C28H30CrClN2O2]+: 513.14. Found: 513.15. IR neat (selected absorbances): 2953 (C-H alkyl), 1601 (C=N), 1385 (C=C aromatic), 1185(C-O), 1026 (C-N), 748 (C-H) cm-1. Melting point: > 350 °C. ICP-MS: expected Cr = 10.1%, found Cr = 9.8%.

**Chromium complex 7d**: Yield: 0.5738 g, 95%. Mass Spec ESI: Calc: [C28H30CrN2O2]+: 478.1707. Found: 478.1698. Mass Spec LIDFI: Calc: [C28H30CrClN2O2]+: 513.17 Found: 513.18. IR neat (selected absorbances): 2956, 2918, 2649 (C-H alkyl), 1614 (C=N), 1579 (C=C aromatic), 1260 (C-O), 1180 (C-N), 746 (C-H) cm-1. Melting point: > 350 °C. XRF: expected ratio Cr/Cl = 1/1, found ratio Cr/Cl = 1/0.97. ICP-MS: expected Cr = 10.1%, found Cr = 10.2%.

**Chromium complex 7e**: Yield: 0.0501 g, 90%. Mass Spec ESI: Calc: [C30H34CrN2O4]+: 538.1928. Found: 538.1918. Mass Spec LIDFI: Calc: [C30H34CrClN2O4]+: 573.16. Found: 573.18. IR neat (selected absorbances): 2917 (C-H alkyl), 1601 (C=N), 1532 (C=C aromatic), 1361 (C-O from C-O-Me), 1211 (C-O), 1050 (C-N), 744 (C-H) cm-1. Melting point: > 350 °C. XRF: expected ratio Cr/Cl = 1/1, found ratio Cr/Cl = 1/0.96.

**Chromium complex 7f**: Yield: 0.1055 g, 90 %. Mass Spec ESI: Calc: [C28H28CrClN4O6]+: 603.1098. Found: 603.1205. IR neat (selected absorbances): 2958, 2921, 2854 (C-H alkyl), 1607 (C=N), 1587 (N-O) 1523 (C=C aromatic), 1323 (C-O), 1285 (N-O) 1199 (C-N), 744 (C-H) cm-1. Melting point: > 350 °C. ICP-MS: expected Cr = 12.9%, found Cr = 12.6%.

**Chromium complex 7g**: Yield: 0.3118 g, 85%. Mass Spec ESI: Calc: [C24H16CrN2O2]+: 416.0622. Found: 416.0634. Mass Spec LIDFI: Calc: [C24H16CrClN2O2]+: 451.03. Found: 451.04. IR neat (selected absorbances): 2917, 2849 (C-H alkyl), 1604 (C=N), 1530 (C=C aromatic), 1197 (C-O), 1150 (C-N), 747 (C-H) cm-1. Melting point: > 350 °C.

**Chromium complex 7h**: Yield: 0.1632 g, 69%. Mass Spec ESI: Calc: [C22H18CrN2O2]+: 394.0768. Found: 394.0756. Mass Spec LIDFI: Calc: [C22H18CrClN2O2]+: 429.05. Found: 429.08. IR neat (selected absorbances): 2917, 2846 (C-H alkyl), 1592 (C=N), 1461 (C=C aromatic), 1259 (C-O), 1027 (C-N), 751 (C-H) cm-1. Melting point: > 350 °C.

 **Chromium complex 7i**: Yield: 0.268 g, 75%. Mass Spec ESI: Calc: [C20H12Cl2CrN2O2]+: 433.9676. Found: 433.9653. Mass Spec LIDFI: Calc: [C20H12Cl2CrN2O2]+: 433.97. Found: 433.98. IR neat (selected absorbances): 2918, 2849 (C-H alkyl), 1607 (C=N), 1530 (C=C aromatic), 1148 (C-O), 1029 (C-N), 752 (C-Cl) cm-1. Melting point: > 350 °C. XRF: expected ratio Cr/Cl = 1/3, found ratio Cr/Cl = 1/3.3.

**Chromium complex 7j**: Yield: 0.0332 g, 82%. Mass Spec ESI: Calc: [C28H28Cl2CrN2O2]+: 546.0928. Found: 546.0913. Mass Spec LIDFI: Calc: [C28H28Cl3CrN2O2]+: 581.06. Found: 581.08. IR neat (selected absorbances): 2917 (C-H alkyl), 1596 (C=N), 1530 (C=C aromatic), 1187 (C-O), 1147 (C-N), 870 (C-Cl), 749 (C-H) cm-1. Melting point: > 350 °C. XRF: expected ratio Cr/Cl = 1/3, found ratio Cr/Cl = 1/2.9.

**Chromium complex 7k**: Yield: 0.0156, 83%. Mass Spec ESI: Calc: [C30H32Cl2CrN2O4]+: 606.1140. Found: 606.1134. Mass Spec LIDFI: Calc: [C30H32Cl3CrN2O4]+: 643.11. Found: 643.08. IR neat (selected absorbances): 2919, 2850 (C-H alkyl), 1597 (C=N), 1530 (C=C aromatic), 1357 (C-O from C-O-Me), 1159 (C-O), 1057 (C-N), 822 (C-Cl), 778 (C-H) cm-1. Melting point: > 350 °C. XRF data: expected ratio Cr/Cl = 1/3, found ratio Cr/Cl = 1/2.8. ICP-MS: expected Cr = 8.1%, found Cr = 8.2%.

**Synthesis of chromium(salophen) complex 7l**: complex **7e** (0.0756 g, 0.132 mmol) was dissolved in CH2Cl2 (15 mL), to form a dark red solution, and was stirred with sat. aq. sodium bromide solution (55 mL) in a round bottom flask. The solvents were left stirring vigorously for three hours. The red organic layer was then extracted from the clear aqueous layer, dried (Na2SO4), filtered and concentrated *in vacuo* to afford the product as a dark red solid (0.0345 g, 42%). Mass Spec LIDFI: Calc: [C30H34BrCrN2O4]+ = 617.11. Found: 617.09. Mass Spec LIDFI: Calc: [C30H34CrN2O4]+ = 538.19. Found: 538.21. IR neat (selected absorbances): 2953 (C-H alkyl), 1601 (C=N), 1533 (C=C aromatic), 1359 (C-O from C-O-Me), 1208 (C-O), 1055 (C-N), 751 (C-H) cm-1. Melting point: > 350 °C. XRF showed no chlorine present.

**Synthesis of chromium(salophen) complex 7m**: The synthesis of **7m** was carried out in an identical manner to **7l**, using complex **7e** (0.0816 g, 0.1421 mmol) and a sat. aq. sodium iodide solution (55 mL) to give compound **7m** as a dark red solid (0.0489 g, 52 %). Mass Spec LIDFI: Calc: [C30H34ICrN2O4]+ = 665.10. Found: 665.09. Mass Spec LIDFI: Calc: [C30H34CrN2O4]+ = 538.19. Found: 538.19. IR neat (selected absorbances): 2923 (C-H alkyl), 1602 (C=N), 1533 (C=C aromatic), 1359 (C-O from C-O-Me), 1207 (C-O), 1057 (C-N), 751 (C-H) cm-1. Melting point: > 350 °C. XRF showed no chlorine present.

**Synthesis of chromium(salophen) complex 7n**: The synthesis of **7n** was carried out in an identical manner to **7l**, using complex **7e** (0.1007 g, 0.1754 mmol) and a sat. aq. sodium acetate solution (55 mL) to give compound **7n** as a dark red solid (0.0872 g, 83 %). Mass Spec LIDFI: Calc: [C32H37CrN2O6]+ = 597.21. Found: 597.20. Mass Spec LIDFI: Calc: [C30H34CrN2O4]+ = 538.19. Found: 538.19. IR neat (selected absorbances: 2930 (C-H alkyl), 1602 (C=N), 1531 (C=C aromatic), 1360 (C-O from C-O-Me), 1207 (C-O), 1058 (C-N), 748 (C-H) cm-1. Melting point: > 350 °C. XRF showed no chlorine present.

**Synthesis of chromium(salophen) complex 7o**: Complex **7e** (0.0790 g, 0.138 mmol) was dissolved in dry acetonitrile (2 mL) to form a dark red solution. Toluene-*p*-sulfonate (0.0520 g, 0.175 mmol) was dissolved in acetonitrile (4 mL) to form a white clear solution. The toluene-*p*-sulfonate solution was added slowly to the complex **7e** solution, and was left stirring under argon with the round-bottom flask covered with foil for 18 hours. The reaction mixture was filtered through Celite and washed through with acetonitrile (15 mL). The solution was concentrated *in vacuo* to afford complex **7o** as a dark red solid (0.0752 g, 77%). Mass Spec LIDFI: Calc:[C30H34CrN2O4]+ = 538.19. Found: 538.24. Mass Spec LIDFI: Calc:[C37H41CrN2O7S]+ = 709.20. Found: 709.17. IR neat (selected absorbances): 2951 (C-H alkyl), 1601 (C=N), 1534 (C=C aromatic), 1358 (C-O from C-O-Me), 1150 (C-O), 1057 (C-N), 794 (C-H) cm-1. Melting point: > 350 °C. XRF showed no chlorine present.

**General procedure for catalyst synthesis of cyclic carbonates at 1 bar pressure**

An epoxide (1.66 mmol), catalyst **7a** or **7l** (0.025 mmol) and Bu4NBr (8 mg, 0.025 mmol) were placed in a sample vial fitted with a magnetic stirrer bar and placed in a large conical flask. Cardice pellets were added to the conical flask which was then fitted with a rubber stopper pierced by a deflated balloon. The reaction mixture was stirred at 25 ºC for 24 hours. The conversion of epoxide to cyclic carbonate was determined by analysis of a sample by 1H NMR spectroscopy. Cyclic carbonates **9a–j** are all known compounds and the spectroscopic data of samples prepared using catalysts **7a** and **7l** were consistent with those reported in the literature.21,23,30,44,47,48

**Styrene carbonate** (**9a**): Purification by flash column chromatography with hexane/EtOAc (6:4) gave a white solid (251 mg, 92%). m.p. 53–55 ºC (lit.21,23,30 50–51 ºC); 1H NMR (400 MHz, CDCl3) **7.30–7.19 (m, 5H, Ph), 5.52 (t, *J* = 8.0 Hz, 1H, OCH), 4.64 (t, *J* = 8.0 Hz, 1H, CH2), 4.16 (t, *J* = 8.0 Hz, 1H, CH2);13C NMR (100 MHz, CDCl3) **154.7 (C=O), 135.6 (ArC), 129.4 (ArCH), 128.9 (ArCH), 125.7 (ArCH), 77.8 (OCH), 70.9 (OCH2); IR (neat, cm–1): ν 3068, 3039, 2981, 2925, 1773, 1553; HRMS (ESI+): calcd. for C9H8O3 [M+Na]+ 187.0366, found 187.0363.

**Propylene carbonate** (**9b**): Purification by flash column chromatography with hexane/EtOAc (8:2) gave a colorless liquid (114 mg, 57%). 1H NMR (400 MHz, CDCl3) **4.87–4.79 (m, 1H, OCH), 4.52 (t, *J* = 8.0 Hz, 1H, CH2), 3.99 (t, *J* = 8.0 Hz, 1H, CH2), 1.46 (d, *J* = 6.4 Hz, 1H, CH3); 13C NMR (100 MHz, CDCl3) **155.0 (C=O), 73.5 (OCH), 70.6 (OCH2), 19.2 (CH3); IR (neat, cm–1): ν 2987, 2924, 1782; HRMS (ESI+): calcd for C4H6O3 [M+Na]+ 125.0209 found 125.0213.

**1,2–Butylene carbonate** (**9c**): Purification by flash column chromatography with hexane/EtOAc (8:2) gave a colorless liquid (237 mg, 86%). 1H NMR (400 MHz, CDCl3) **4.69–4.62 (m, 1H, OCH), 4.52 (t, *J* = 8.0 Hz, 1H, CH2), 4.08 (t, *J* = 8.0 Hz, 1H, CH2), 1.86–1.71 (m, 2H, CH2), 1.02 (t, *J* = 8.0 Hz, CH3); 13C NMR (100 MHz, CDCl3) **155.1 (C=O), 78.0 (OCH), 69.0 (OCH2), 26.9 (CH2), 8.5 (CH3); IR (neat, cm–1): ν 2938, 2942, 2885, 1781; HRMS (ESI+): calcd for C5H8O3 [M+Na]+ 139.0366, found 139.0363.

**1,2–Hexylene carbonate** (**9d**): Purification by flash column chromatography with hexane/EtOAc (6:4) gave a colorless liquid (194 mg, 81%). 1H NMR (400 MHz, CDCl3) **4.71–4.65 (m, 1H, OCH), 4.51 (t, *J* = 8.0 Hz, 1H, CH2), 4.06 (t, *J* = 8.0 Hz, 1H, CH2), 1.83–1.63 (m, 2H, CH2), 1.47–1.29 (m, 4H, 2×CH2), 0.91 (t, *J* = 8.0 Hz, 3H, CH3); 13C NMR (100 MHz, CDCl3) **155.1 (C=O), 77.0 (OCH), 69.3 (OCH2), 33.5 (CH2), 26.3 (CH2), 22.2 (CH2), 13.7 (CH3); IR (neat, cm–1): ν 2959, 2933, 2873, 1786; HRMS (ESI+): calcd for C7H12O3 [M+Na]+ 167.0679, found 167.0678.

**1,2–Decylene carbonate** (**9e**): Purification by flash column chromatography with hexane/EtOAc (8:2) gave a colorless liquid (272 mg, 82%). 1H NMR (400 MHz, CDCl3) **4.72–4.65 (m, 1H, OCH), 4.51 (t, *J* = 8.0 Hz, 1H, CH2), 4.06 (t, *J* = 8.0 Hz, 1H, CH2), 1.84–1.62 (m, 2H, CH2), 1.48–1.26 (m, 12H, 6×CH2), 0.87 (t, *J* = 8.0 Hz, CH3); 13C NMR (100 MHz, CDCl3) **155.0 (C=O), 77.0 (OCH), 69.4 (OCH2), 33.8 (CH2), 31.7 (CH2), 29.2 (CH2), 29.1 (CH2), 29.0 (CH2), 24.3 (CH2), 22.6 (CH2), 14.0 (CH3); HRMS (ESI+): calcd for C11H20O3.  IR (neat, cm–1): ν 2924, 2855, 1794, 1551, HRMS (ESI+): calcd for C11H21O3 [M+H]+ 201.1485, found 201.1487. calcd for C11H21O3 [M+Na]+ 223.1305, found 223.1308.

**3–Chloropropylene carbonate** (**9f**): Purification by flash column chromatography with hexane/EtOAc (6:4) gave a white solid (176 mg, 78%). m.p. 67–69 ºC (lit.21,23,30 68–69ºC);1H NMR (400 MHz, CDCl3) **4.98–4.92 (m, 1H, OCH), 4.59 (t, *J* = 8.0 Hz, 1H, OCH2), 4.41 (t, *J* = 8.0 Hz, 1H, OCH2), 3.79–3.71 (m, 2H, CH2Cl); 13C NMR (100 MHz, CDCl3) **154.0 (C=O), 74.2 (OCH), 67.0 (OCH2), 43.7 (CH2Cl); IR (neat, cm–1): ν 2966, 2925, 1780, 663; HRMS (ESI+): calcd for C4H5ClO3 [M+Na]+ 158.9819, found 158.9815.

**Glycerol carbonate** (**9g**): Purification by flash column chromatography with hexane/EtOAc (6:4) gave a colorless liquid (141 mg, 72%). 1H NMR (400 MHz, CDCl3) **4.85–4.77 (m, 1H, CH), 4.53 (t, *J* = 8.3 Hz, 1H, OCH2), 4.45 (dd *J* = 9.3, 5.8 Hz, 1H, OCH2), 4.00 (ddd *J* = 12.7, 5.7, 3.1 Hz, 1H, C*H*OH), 3.68 (ddd *J* = 9.3, 7.6, 4.1 Hz, 1H, C*H*OH); 2.01 (dd *J* = 7.0, 5.7 Hz, 1H, CHO*H*); 13C NMR (100 MHz, CDCl3) **155.1 (C=O), 76.4 (OCH), 65.7 (OCH2), 61.7 (CH2OH); IR (neat, cm–1): ν 3385, 2899, 1795; HRMS (ESI+): calcd for C8H15O6 [M+EtOAc]+ 207.0863, found 207.0865.

**3–Phenoxypropylene carbonate** (**9h**): Purification by flash column chromatography with hexane/EtOAc (8:2) gave a white solid (229 mg, 71%). m.p. 9798 ºC (lit.21,23,30 94–95 ºC); 1H NMR (400 MHz, CDCl3) **7.31 (t, *J* = 8.0 Hz, 2H, *m*–Ph), 7.02 (t, *J* = 8.0 Hz, 1H, *p*–Ph), 6.91 (d, *J* = 8.0 Hz, 2H, *o*–Ph), 5.06–5.00 (m, 1H, OCH), 4.64–4.52 (m, 2H, OCH2), 4.24 (dd, *J* = 11.0, 4.0 Hz, 1H, CH2), 4.15 (dd, *J* = 11.0, 4.0 Hz, 1H, CH2); 13C NMR (100 MHz, CDCl3) **157.7 (C=O), 154.6 (ArC), 129.7 (ArCH), 122.0 (ArCH), 114.6 (ArCH), 74.1 (OCH), 66.8 (OCH2), 66.2 (CH2); IR (neat, cm–1): ν 2924, 1788, 1598; HRMS (ESI+): calcd for C10H10O4 [M+Na]+ 217.0471, found 217.0474.

**4–Chlorostyrene carbonate** (**9i**): Purification by flash column chromatography with hexane/EtOAc (6:4) gave a white solid (299 mg, 91%). m.p. 66–68 ºC (lit.21,23,30 68–69ºC);  1H NMR (400 MHz, CDCl3) **7.35 (d, *J* = 8.0 Hz, 2H, ArH), 7.24 (d, *J =* 8.0 Hz2H, ArH), 5.59 (t, *J =* 8.0 Hz, 1H, CH), 4.73 (t, *J* = 8.0 Hz, 1H, CH2), 4.23 (t, *J* = 8.0 Hz, 1H, CH2); 13C NMR (100 MHz, CDCl3) **154.5 (C=O), 135.8 (ArC), 134.2 (ArC), 129.5 (ArCH), 127.2 (ArCH), 77.2 (OCH), 71.0 (OCH2); IR (neat, cm–1): ν 2964, 2912, 2342, 1960, 1866, 1789; HRMS (ESI+): calcd for C9H7ClO3 [M+H]+ 220.9976, found 220.9975.

**4–Bromostyrene carbonate** (**9j**): Purification by flash column chromatography with hexane/EtOAc (8:2) gave a white solid (357 mg, 89%). m.p. 72–73 ºC (lit.21,23,30 68–69 ºC); 1H NMR (400 MHz, CDCl3) **7.59 (d, *J* = 8.0 Hz, 2H, ArH), 7.24 (d, *J =* 8.0 Hz, 2H, ArH), 5.64 (t, *J =* 8.0 Hz, 1H, CH), 4.80 (t, *J* = 8.0 Hz, 1H, CH2), 4.30 (t, *J* = 8.0 Hz, 1H, CH2); 13C NMR (100 MHz, CDCl3) **154.5 (C=O), 134.8 (ArC), 132.5 (ArCH), 127.4 (ArCH), 123.9 (ArC), 77.2 (CH), 70.9 (CH2); IR (neat, cm–1): ν 2963, 2910, , 1786; HRMS (ESI+): calcd for C9H7BrO3 [M+Na]+ 264.9471, found 264.9470.

**General procedure for synthesis of cyclic carbonates at 10 bar pressure**

An epoxide **10a–f** (1.7 mmol), catalyst **7l** (0.025 mmol) and Bu4NBr (8 mg, 0.025 mmol) were placed in a multipoint reactor with a magnetic stirrer bar and autoclave was pressurized at 10 bar pressure of carbon dioxide. The reaction mixture was stirred at 50ºC or 80 ºC for 24 h. Conversion of epoxide to cyclic carbonate was then determined by analysis of a sample by 1H NMR spectroscopy. The remaining sample was filtered through a plug of silica, eluting with CH2Cl2 to remove the catalyst. The eluent was evaporated in *vacuo* to give either the pure cyclic carbonate or a mixture of cyclic carbonate and unreacted epoxide. In the latter case, the mixture was purified by flash chromatography using a solvent system of first hexane, then hexane:EtOAc (9:1), then hexane:EtOAc (3:1), then EtOAc to give the pure cyclic carbonate. Cyclic carbonates **11a–f** are all known compounds and the spectroscopic data for samples prepared using catalyst **7l** were consistent with those reported in the literature.25,30,47,48

**Poly(cyclohexene carbonate) 11a**. Obtained as a light orange solid. (207 mg, 76%); 1H NMR (400 MHz,CDCl3, 298 K): **4.95–4.50 (bs, 2H, CHO), 2.20–1.80 (bs, 2H, CH2), 1.80–1.20 (bs, 6H, CH2); 13C{1H} NMR (100 MHz, CDCl3, 298 K) **153.8, 77.1, 29.7, 23.1.

***cis*-1,2-Cyclopentene carbonate** (**11b**). Obtained as a white solid. (181 mg, 85%); m.p. 31−33 °C (lit.25,30,47,48 29−30 °C); 1H NMR (400 MHz,CDCl3, 298 K): **5.15–5.02 (m, 2H, CHO), 2.23–2.08 (m, 2H, CH2), 1.90–1.57 (m, 4H, CH2); 13C{1H} NMR (100 MHz,CDCl3, 298 K) **155.4, 81.8, 33.1, 21.5; IR (neat, cm-1): 2971, 2874, 1786; HRMS (ESI+): calcd. m/z 151.0366 [M+Na]+; found: 151.0368.

***cis*-2,3-Butene carbonate** (**11c**).25,30,47,48 Obtained colourless liquid in a 97:3 mixture of *cis*- and *trans*- isomers (121 mg, 63%); 1H NMR (400 MHz,CDCl3, 298 K): **4.81 (m, 2H, CH), 1.31 (6H, d *J* 6.1 Hz, CH3); 13C{1H} NMR (100 MHz,CDCl3, 298 K) **154.3, 75.9, 14.1; IR (neat, cm-1): 2958, 2897, 1789; HRMS (ESI+): calcd. m/z 139.0366 [M+Na]+; found: 139.0366.

***trans*-2,3-Butene carbonate** (**11d**). Obtained as a white solid (116 mg, 60%); m.p. 29−31 °C (lit.25,30,47,48 29−30 °C); 1H NMR (400 MHz,CDCl3, 298 K): **4.36–4.26 (m, 2H, CH), 1.44 (d, *J* 6.1 Hz, 3H, CH3); 13C{1H} NMR (100 MHz, CDCl3, 298 K) **154.4, 79.8, 18.2; IR (neat, cm-1): 2951, 2873, 1781; HRMS (ESI+): calcd. m/z 139.0366 [M+Na]+; found: 139.0371.

***trans*-1,2-Diphenylethylene carbonate** (**11e**). Obtained as a white solid. (355 mg, 89%); m.p. 111–112 °C (lit.25,30,47,48 110–111 °C); 1H NMR (400 MHz,CDCl3, 298 K): **7.35–7.45 (m, 6H, ArH), 7.25–7.35 (m, 4H, ArH), 5.43 (s, 2H, CH); 13C{1H} NMR (100 MHz,CDCl3, 298 K) **154.1, 134.8, 129.8, 129.2, 126.1, 85.3; IR (neat, cm-1): 3048, 2974, 1810, 1459; HRMS (ESI+): calcd. m/z 263.0679 [M+Na]+; found: 263.0687.

***trans*-1-Phenyl-2-methylethylene carbonate**(**11f**). Obtained as a white solid. (257 mg, 87%); m.p. 110–113 °C (lit.25,30,47,48 110–111 °C); 1H NMR (400 MHz,CDCl3, 298 K): **7.50–7.29 (m, 5H, ArH), 5.13 (d, *J* 8.0 Hz, 1H, CH), 4.60 (m, 1H, CH), 1.56 (d, *J* 6.2 Hz, 3H, CH3); 13C{1H} NMR (100 MHz, CDCl3, 298 K) **154.4, 135.1, 129.8, 129.3, 126.1, 85.0, 80.8, 18.4; IR (neat, cm-1): 3010, 2950, 1800, 1459; HRMS (ESI+): calcd. m/z 201.0522 [M+Na]+; found: 201.0527.

**Determination of the reaction kinetics**

Styrene oxide **8a** (0.2 g, 1.66 mmol), catalyst **7l** (1.0, 2.0, 3.0, 4.0 or 5.0 mol %) and Bu4NBr (1.0, 2.0, 3.0, 4.0 or 5.0 mol%) were placed in a sample vial fitted with a magnetic stirrer bar and placed in a large conical flask. Cardice pellets were added to the conical flask which was fitted with a rubber stopper pierced by a deflated balloon. The reaction was stirred at 50 ºC. Samples were taken at convenient intervals (approximately every 30 minutes) and analyzed by HPLC.

**Supporting Information**. Copies of the 1H and 13C NMR spectra and mass spectra for cyclic carbonates **9a**–**j** and **11a**–**f**. Kinetic plots for the study of the synthesis of styrene carbonate **9a** catalyzed by catalyst **7l** and tetrabutylammonium bromide. This material is available free of charge via the Internet at http://pubs.acs.org.

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TOC entry:

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