Metal and halide free catalyst for the synthesis of cyclic carbonates from epoxides and carbon dioxide

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ABSTRACT *N,N'*-Phenylenebis(5-*tert*-butylsalicylideneimine) is shown to be an effective single-component catalyst for the metal and halide free synthesis of cyclic carbonates from epoxides and carbon dioxide. Using this bis-phenolic catalyst, a series of eight epoxides has been converted into the corresponding cyclic carbonates. Many closely related catalyst structures were found to be catalytically inactive and the structural features necessary for catalytic activity have been delineated. Unusually, reactions could be carried out under solvent free conditions, or in the green solvents 2-MeTHF and propylene carbonate. Stereochemical studies showed that carbon dioxide insertion occurs exclusively at the terminal end of the epoxide and does so with loss of stereochemical purity if a 1-deutero-2-alkyl epoxide is used as substrate. On the basis of this evidence, a dual activation mechanism is proposed in which one phenol acts as a Brønsted acid to activate the epoxide, whilst the other reacts with carbon dioxide to form a carbonic half-ester intermediate which then ring-opens the activated epoxide. Two pathways are subsequently available for cyclization to a cyclic carbonate which have opposite stereochemical consequences. The experimental results suggest that ring-opening of the epoxide by the carbonic half-ester is the rate determining step of the catalytic cycle.

KEYWORDS Cyclic carbonate; Epoxide; Salophen; Organocatalyzed; Carbon dioxide.

**Introduction**

Carbon dioxide is widely recognized as the primary greenhouse gas that leads to global warming. Emissions of carbon dioxide have increased by more than 40% since the start of the industrial revolution, from a pre-industrial level of 280 ppm to 410 ppm in 2018. The International Panel on Climate Change (IPCC) predicts that the atmosphere may contain up to 570 ppm carbon dioxide by 2100.1 On the other hand, carbon dioxide can be regarded as a readily and globally available, inexpensive and non-toxic carbon source in the synthetic chemists’ toolbox. As a result, a number of pioneering studies on the catalytic transformations of carbon dioxide have been undertaken in recent years.2-9 In particular, the formation of both five- and six-membered cyclic carbonates from epoxides (or oxetanes) and carbon dioxide has received growing interest (Scheme 1) and this area of research has been extensively developed and reviewed.10-12 Due to their unique properties such as high dipole moment, high dielectric constant and high boiling point, cyclic carbonates are used as polar aprotic solvents and as a component of the electrolyte of lithium-ion batteries.13-15 Moreover, cyclic carbonates can also be used as monomers for the synthesis of polyurethanes,16 polycarbonates17 and polyglycerol.18



**Scheme 1.** Synthesis of cyclic carbonates.

Most effort in cyclic carbonate synthesis from epoxides and carbon dioxide has been focused on metal-based homogeneous catalysts, including those based on aluminum,19-21 iron,22-25 zinc26-28 and cobalt,29 all of which are capable of exhibiting high catalytic activity and selectivity. Organocatalysts have also started to attract interest for the synthesis of cyclic carbonates as they are often more cost-effective, more sustainable and less toxic than metal-containing complexes. A number of organocatalysts have been studied for this reaction,12 including ammonium salts,30-32 phosphonium salts,32-35 imidazolium salts36,37 and imidazolium-based ionic liquids.38-40 A number of two-component systems consisting of polyols and a quaternary ammonium salt have also been developed.41-43 However, these systems all include a bromide or iodide as part of the catalyst system and the corrosive nature of these halides towards standard stainless steel reactors is a distinct disadvantage in the commercial use of such catalysts.10c

In 2004, Shi and coworkers reported the use of 4-dimethylamino-pyridine (DMAP) together with salen ligands as a binary catalytic system for the transformation of epoxides into cyclic carbonates at 120 °C and 35 bar carbon dioxide pressure.44 Other metal- and halide-free catalytic systems for the conversion of epoxides and carbon dioxide into cyclic carbonates have also been developed. These include DBU/cellulose, 45 amino acids,46 amino acid/ionic liquids47 and alkanolamines.48 More recently, Kim and coworkers reported the use of tertiary amines as organocatalysts for the synthesis of cyclic carbonates from epoxides and carbon dioxide.49 Amongst the amines studied, *N*,*N*,*N’*,*N’*-tetraethylethylenediamine **1** exhibited moderate to excellent efficiency. For example, the coupling reaction between epichlorohydrin **2a** and carbon dioxide using 0.1 mol% of tertiary diamine catalyst **1**, at 120 °C and 10 bar carbon dioxide pressure for 12 hours, afforded cyclic carbonate **3a** in 83% conversion (Scheme 2).



**Scheme 2.** Synthesis of cyclic carbonate **3a** using catalyst **1**.

In previous work we have reported the use of aluminum and chromium complexes of salophen ligand **4** (Figure 1) as catalysts for the conversion of both terminal and internal epoxides into cyclic carbonates.50 Since ligand **4** contains two tertiary amines as part of its structure, as well as two phenols which are known to be capable of cocatalysing cyclic carbonate synthesis,41-43 we decided to investigate the use of salophen **4** and related species as organocatalysts for cyclic carbonate synthesis and in this paper we report the results of this study.



**Figure 1.** Salophen ligand **4**.

**Results and Discussion**

Salophen **4** and its aldehyde precursor **5** (Figure 2), both of which contain tertiary amine groups, were initially screened as catalysts for the conversion of epichlorohydrin **2a** into cyclic carbonate **3a** under the same conditions used by Kim for catalyst **1** (Scheme 3). When used at a loading of 0.1 mol% at 120 °C and 10 bar carbon dioxide pressure for 3.5 hours, salophen **4** induced 70% conversion of epichlorohydrin **2a** to cyclic carbonate **3a** (Table 1, entry 1). This is higher than the 59% conversion reported by Kim using tertiary diamine **1** under the same reaction conditions. Encouraged by this result, 3-phenoxypropylene oxide **2b** was investigated as a substrate under the same reaction conditions, but no conversion was observed (Table 1, entry 2). When the catalyst loading was increased to 1 mol%, 34% conversion of epoxide **2b** into cyclic carbonate **3b** was achieved after 3.5 hours (Table 1, entry 3) and with a prolonged reaction time of 24 hours, 100% conversion was achieved (Table 1, entry 4). When aldehyde **5** was used as a catalyst with epoxides **2a,b** no conversions to cyclic carbonates **3a,b** were observed with a 1 mol% catalyst loading (Table 1, entries 5 and 6). However, by increasing the catalyst loading to 10 mol% and the reaction time to 24 hours, aldehyde **5** did show some catalytic activity with epoxide **2b** (Table 1, entry 7).



**Figure 2.** Phenols **5-7**.



**Scheme 3.** Synthesis of cyclic carbonates **3a**,**b** using organocatalysts **4-13**.

**Table 1.** Comparison of the catalytic activities of phenols **4-7**.a

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Entry | Catalyst (mol%) | Epoxide | Time (h) | Conversionb (%) |
| 1 | **4** (0.1) | **2a** | 3.5 | 70 |
| 2 | **4** (0.1) | **2b** | 3.5 | 0 |
| 3 | **4** (1.0) | **2b** | 3.5 | 34 |
| 4 | **4** (1.0) | **2b** | 24 | 100 |
| 5 | **5** (1.0) | **2a** | 3.5 | 0 |
| 6 | **5** (1.0) | **2b** | 3.5 | 0 |
| 7 | **5** (10.0) | **2b** | 24 | 55 |
| 8 | **6** (1.0) | **2b** | 3.5 | 0 |
| 9 | **7** (1.0) | **2b** | 3.5 | 0 |
| 10 | **6** (10.0) | **2b** | 24 | 0 |
| 11 | **7** (10.0) | **2b** | 24 | 0 |

a) All reactions were carried out at 120 oC and 10 bar CO2 pressure under solvent free conditions. b) Conversions have a standard deviation of 7%.

These results suggested that there was more to the catalytic activity observed for salophen **4** than just the presence of tertiary amines. Since phenols are also known catalysts for cyclic carbonate synthesis,41 simple phenols **6** and **7** which lack an amino group were tested as catalysts. However, both compounds displayed no activity with epoxide **2b** under the standard reaction conditions or even when used at 10 mol% catalyst loading with a reaction time of 24 hours (Table 1, entries 8­–11). This suggested that the salophen framework and the juxtaposition of the functionalities on each of its salicylimine units was important for the catalytic activity of compound **4**. Therefore, salens and salophens **8-14** and half-salophen **15** (Figure 3) were prepared and studied as catalysts.



**Figure 3.** Compounds **8-15**.

The catalytic activity of salophen **8** and salens **9**-**10** were tested using epoxide **2b** as substrate, at 120 °C and 10 bar carbon dioxide pressure under solvent-free conditions with 1 mol% of catalyst and the results are summarized in Table 2. Unsubstituted salophen **8** exhibited much higher reactivity than salophen **4** for the formation of cyclic carbonate **3b** under the same reaction conditions, giving 70% conversion after 3.5 hours (Table 2, entry 1). After 24 hours, the conversion increased to 100% (Table 2, entry 2). This confirmed that the tertiary amines in salophen **4** were not responsible for its catalytic activity. The analogous salens, **9** and **10**, were found to show no catalytic activity under these conditions (Table 2, entries 3 and 4) which suggests that the 1,2-diaminobenzene unit in salphen **8** is essential for the catalytic activity. Even when used at a 10 mol% catalyst loading with a reaction time of 24 hours, salen **9** exhibited no catalytic activity (Table 2, entry 5), though salen **10** did give 20% conversion under these conditions (Table 2, entry 6). Salophen and salen have different 3D-structures due to the difference in hybridization of the carbon atoms linking the two nitrogen atoms51 and this will place the phenol units in the two salicylimine units in different relative orientations in salophen and salen derivatives as discussed in more detail later in this manuscript. Kleij has previously shown experimentally and theoretically that the relative position of phenol groups is important for catalysis in polyphenols, albeit in a catalyst system that included tetrabutylammonium iodide.41

To further increase the activity of salophen **8**, *tert*-butyl substituents were introduced onto the aromatic rings of the salicylimines, giving organocatalysts **11-13**. Compounds **11**-**13** were tested under the standard screening conditions for 3.5 hours using epoxide **2b** and the results are summarized in Table 2. Salophens **11** and **12**, which have *tert*-butyl groups adjacent to the phenols, did not show any catalytic activity (Table 2, entries 7 and 8). Even when used at a 10 mol% catalyst loading with a reaction time of 24 hours, these salophens only gave conversions of 20-27% (Table 2, entries 9 and 10). However, salophen **13**, with *tert*-butyl groups in the *para*-position relative to the phenol, showed the highest conversion (93%) for the formation of cyclic carbonate **3b** from epoxide **2b** (Table 2, entry 11). The excellent catalytic activity of **13** is ascribed to the absence of substituents adjacent to the phenols, which could inhibit their catalytic function. The *para-tert*-butyl group does however increase the solubility of the catalyst which explains its high catalytic activity.

**Table 2.** Comparison of the catalytic activities of catalysts **8**-**15**.a

|  |  |  |  |
| --- | --- | --- | --- |
| Entry | Catalyst (mol%) | Time (h) | Conversionb (%) |
| 1 | **8** (1 mol%) | 3.5 | 70 |
| 2 | **8** (1 mol%) | 24 | 100 |
| 3 | **9** (1 mol%) | 3.5 | 0 |
| 4 | **10** (1 mol%) | 3.5 | 0 |
| 5 | **9** (10 mol%) | 24 | 0 |
| 6 | **10** (10 mol%) | 24 | 20 |
| 7 | **11** (1 mol%) | 3.5 | 0 |
| 8 | **12** (1 mol%) | 3.5 | 0 |
| 9 | **11** (10 mol%) | 24 | 20 |
| 10 | **12** (10 mol%) | 24 | 27 |
| 11 | **13** (1 mol%) | 3.5 | 93 |
| 12 | **14** (1 mol%) | 3.5 | 0 |
| 13 | **15** (1 mol%) | 3.5 | 0 |
| 14 | **15** (10 mol%) | 24 | 0 |

a) All reactions were carried out at 120 oC and 10 bar CO2 pressure under solvent free conditions using epoxide **2b** as substrate. b) Conversions have a standard deviation of 7%.

To test the importance of unhindered phenols, salophen **14** with methyl groups adjacent to the phenol groups was prepared and was again found to be catalytically inactive (Table 2, entry 12). To ascertain whether a single phenolic fragment combined with an imine would also be catalytically active, compound **15** was synthesized and tested as a catalyst under the same reaction conditions. However, compound **15** was devoid of catalytic activity, even when used at a catalyst loading of 10 mol% for 24 hours (Table 2, entries 13 and 14), indicating that two phenol groups, located opposite one another within a salophen framework is an essential feature of the catalysts.

Having optimized the structure of the organocatalyst to salophen **13**, the reaction conditions were further optimized. Epoxide **2b** was again used as substrate, whilst the catalyst loading, reaction temperature and carbon dioxide pressure were varied. When the catalyst loading was decreased to 0.1 mol%, or the temperature lowered to 100 °C, no conversion of epoxide **2b** into cyclic carbonate **3b** occurred (Table 3, entry 1 and 2). When the pressure was decreased to 5 bar, catalyst **13** was still efficient and 94% conversion of epoxide **2b** to cyclic carbonate **3b** was achieved after 3.5 hours (Table 3, entry 3). Even at 1 bar carbon dioxide pressure, a moderate conversion of 68% was achieved after a reaction time of 24 hours (Table 3, entry 4).

**Table 3.** Influence of reaction parameters on the catalytic activity of salphen **13**.a

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Entry | **13** (mol%) | Temperature (oC) | Pressure (bar) | Time (h) | Conversionb (%) |
| 1 | 0.1 | 120 | 10 | 3.5 | 0 |
| 2 | 1.0 | 100 | 10 | 3.5 | 0 |
| 3 | 1.0 | 120 | 5 | 3.5 | 94 |
| 4 | 1.0 | 120 | 1 | 24 | 68 |

a) All reactions were carried out under solvent free conditions using epoxide **2b** as substrate. b) Conversions have a standard deviation of 7%.

To investigate the general applicability of organocatalyst **13**, terminal epoxides **2a-g** were used as substrates with 1 mol% of catalyst **13** at 120 °C and 10 bar carbon dioxide pressure for 3.5 hours (Scheme 4) and the results of this study are shown in Table 4. For epoxide **2a**, the standard reaction conditions were sufficient to achieve 84% conversion to cyclic carbonate **3a** which could be isolated in 76% yield (Table 4, entry 1). In a preparative experiment, cyclic carbonate **3b** was isolated in 88% yield (Table 4, entry 2). However, for epoxides **2c**-**g**, the reactions were slower so the catalyst concentration was increased to 5 mol%, and the reaction time lengthened to 24 hours. Under these conditions, epoxides **2c,d** were excellent substrates (Table 4, entries 3,4) and epoxide **2e** was a moderate substrate (Table 4, entry 5). However, epoxides **2f,g** still gave moderate to no conversion (Table 4, entries 6,7). Further increasing the catalyst concentration to 10 mol% gave complete conversion of epoxide **2f** to styrene carbonate **3f** (Table 4, entry 8), but still gave only 20% conversion of epoxide **2g** to cyclic carbonate **3g** (Table 4, entry 9).



**Scheme 4.** Synthesis of cyclic carbonates **3a-g** using organocatalyst **13**.

The decreasing conversions observed with epoxides **2c,e-g** seemed to correlate with a decrease in the hydrophobicity of the epoxide which suggested that the lower conversions might be due to a lack of solubility of the catalyst in these epoxides. Therefore, the use of solvents was investigated. Ethyl acetate, 2-butanone and *iso*-propyl acetate all showed no improvement for the coupling reaction between epoxide **2f** and carbon dioxide carried out at 120 °C and 10 bar pressure for 3.5 hours. However, the use of 2-methyl tetrahydrofuran (2-MeTHF) as solvent increased the conversion of styrene oxide **2f** to styrene carbonate **3f** from 50 to 90% and the product could be isolated in 84% yield (Table 4, entry 10). Similarly, the conversion of hex-1-ene oxide **2g** into cyclic carbonate **3g** increased from zero to 62% under the same conditions but with a 24 hour reaction time (Table 4, entry 11). 2-MeTHF is a biomass derived green solvent,52 so its use does not negatively impact on the sustainability of the catalytic process. Internal epoxides are known to be challenging substrates50 for cyclic carbonates synthesis, and neither cyclohexene oxide nor stilbene oxide underwent any reaction when treated with catalyst **13**, even after 72 hours in 2-MeTHF.

**Table 4.** Synthesis of cyclic carbonates **3a-g**.a

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Entry | Product | **13** (mol%) | Time (h) | Conversionb (%) | Yieldb (%) |
| 1 | **3a** | 1.0 | 3.5 | 84 | 76 |
| 2 | **3b** | 1.0 | 3.5 | 93 | 88 |
| 3 | **3c** | 5.0 | 24 | 100 | 89 |
| 4 | **3d** | 5.0 | 24 | 96 | 86 |
| 5 | **3e** | 5.0 | 24 | 71 | 51 |
| 6 | **3f** | 5.0 | 24 | 50 |  |
| 7 | **3g** | 5.0 | 24 | 0 |  |
| 8 | **3f** | 10.0 | 24 | 100 |  |
| 9 | **3g** | 10.0 | 24 | 20 |  |
| 10b | **3f** | 5.0 | 24 | 90 | 84 |
| 11b | **3g** | 5.0 | 24 | 62 | 57 |

a) All reactions were carried out at 120 oC and 10 bar CO2 pressure. b) 2-MeTHF was used as solvent. b) Conversions and yields have a standard deviation of 7%.

There is a well-established mechanism (Scheme 5) for cyclic carbonate synthesis from epoxides and carbon dioxide which has been shown to be applicable to a wide range of metallic and non-metallic catalyst systems.19e,21b,i,29c,43,53 The epoxide is first activated by a Lewis or Brønsted acid, then a nucleophile ring-opens the activated epoxide to form an alkoxide which reacts with carbon dioxide to form a carbonate and eliminates the nucleophile/leaving group to form the cyclic carbonate. This mechanism is clearly applicable to catalyst systems that contain a halide capable of acting as the nucleophile/leaving group and would also be compatible with catalysis by amines such as DMAP or *N*,*N*,*N’*,*N’*-tetraethylethylenediamine **1** which could act as nucleophiles. However, catalyst **13** contains no suitable nucleophile/leaving group. Whilst the phenols within compound **13** could potentially act as nucleophiles and ring-open the epoxide, the resulting ether would not be expected to be a good leaving group and so cyclisation to form the cyclic carbonate would not occur. Hence, a study was undertaken to investigate how salophen **13** acts as a catalyst.



**Scheme 5**. Standard mechanism for cyclic carbonate synthesis.

Analysis of the Cambridge crystal structure database revealed that there were 42 crystal structures of salophen ligands and over 100 structures of salen ligands derived from a 1,2-diamine and two aldehydes. In every one of these salen and salophen structures, the phenols are intramolecularly hydrogen bonded to the imines as shown in Figure 4. The salophen crystal structures can then be grouped into three classes as shown in Figure 5. In all but five structures, the crystal structure is *C1*-symmetrical with one phenol ring virtually coplanar with the 1,2-diaminobenzene unit and the other phenol ring twisted out of this plane (Figure 5a).54 There are four examples (all with a *tert*-butyl group adjacent to the phenols) of a *C2*-symmetrical structure which has one phenol rings bent slightly above and the other below the plane of the 1,2-diamiinobenzene.55 (Figure 5b). There is a single example of another *C2*-symmetric structure in which both phenol rings are out of the plane and on the same side of the 1,2-diaminobenzene (Figure 5c).56 In contrast, salen ligands adopt one of the two *C2*-symmetrical structures represented by Figure 5b,c.57 In both cases, however, the sp3-hybridized carbon atoms in the diamine units enable the phenol rings to be twisted much further out of the diamine plane than is the case for salophen derivatives.



**Figure 4**. Intramolecular hydrogen bonding in salen and salophen crystal structures.



**Figure 5**. Schematic representations of the solid state structures of salophens and salens. The 1,2-diamino unit is represented by the red line and the phenol by blue lines.

Since compound **13** was not amongst the previously reported salophen crystal structures, its single crystal X-ray structure was determined. As shown in Figure 6, its solid state structure is *C1*-symmetric and of the form represented by Figure 5a, the most common structure for salophens. Analysis of the X-ray structure showed that the angles between the 1,2-diaminobenzene plane and the planes of the two phenol rings were 9.5 and 58.6o. Whilst it is attractive to explain the catalytic differences between salen and salophens on the basis of their differing solid-state structures, 1H NMR spectroscopy shows that all these compounds are *C2*-symmetrical in solution, so the solid-state structures may not reflect the catalytically active form of the catalysts.



**Figure 6**. Ortep diagram of the X-ray structure of compound **13**. Intramolecular hydrogen bonds are shown by the pale blue lines.

It is apparent from Scheme 5 that the standard mechanism involves two steps (highlighted in red) which invert the stereochemistry of a 1,2-disubstituted epoxide and hence the reaction proceeds with overall retention of stereochemistry. Since 1,2-disubstituted epoxides are not substrates for catalyst **13**, mechanistic studies were carried out using monodeuterated *trans*-decylene oxide21b **2h** as the substrate at 120 °C and at carbon dioxide pressures of 1-60 bar (Scheme 6). The results shown in Table 5 indicate that the reaction proceeds with nearly or complete loss of the epoxide stereochemistry at all pressures studied, a result that is not consistent with the mechanism shown in Scheme 5. A control experiment using enantiomerically pure (*R*)-glycidyl phenyl ether **2b** with salophen catalyst **13** at 120 °C and 10 bar carbon dioxide pressure was also carried out. This reaction gave enantiomerically pure (*R*)-cyclic carbonate **3b** as determined by chiral HPLC. Thus, unlike deuterated substrate **2h**, epoxide (*R*)-**2b** reacted with complete retention of the epoxide stereochemistry. This indicated that the loss of stereochemistry seen in reactions involving *trans*-**2h** was exclusively due to epimerization at the terminal carbon of the epoxide and no loss of stereochemistry occurred at the internal carbon.



**Scheme 6**. Synthesis of *trans*- and *cis*-**3h**.

**Table 5**. Ratios of *trans*- and *cis*-**3g** under a range of carbon dioxide pressures.

|  |  |  |  |
| --- | --- | --- | --- |
| Entry | Pressure (bar) | Conversiona (%) | *trans*-**3h**:*cis*-**3h** |
| 1 | 1 | 89 | 60:40 |
| 2 | 5 | 97 | 50:50 |
| 3 | 10 | 93 | 50:50 |
| 4 | 20 | 97 | 55:45 |
| 5 | 50 | 95 | 55:45 |
| 6 | 60 | 98 | 60:40 |

a) Conversions have a standard deviation of 7%.

The formation of both *cis-* and *trans-***3h** from exclusively *trans*-epoxide **2h** suggests that two different catalytic cycles are operating with catalyst **13** and a reaction mechanism consistent with all of the observed catalytic features is shown in Scheme 7. Thus, one of the phenol groups of catalyst **13** acts as a Brønsted acid to activate the epoxide, whilst the other activates the carbon dioxide by formation of a carbonic half-ester to give intermediate **16**. Simple phenols are not particularly good nucleophiles, but the intramolecular hydrogen bonding observed for salophen derivatives54-56 will increase the nucleophilicity of the phenol oxygen atom. Attempts to detect intermediates arising from the interaction of salophen **13** with either an epoxide (by 1H NMR) or carbon dioxide (by IR) were however unsuccessful, so we cannot state which interaction occurs first. The carbonic ester can then intramolecularly ring-open the activated epoxide exclusively at the terminal carbon with inversion of configuration to give intermediate alcohol **17**. From intermediate **17** there are two pathways for cyclic carbonate synthesis. Direct intramolecular cyclisation of the alcohol onto the carbonyl of the carbonate within structure **17** gives the cyclic carbonate with overall inversion of stereochemistry (pathway 1, Scheme 7). Alternatively, the alcohol of intermediate **17** can react with a second molecule of carbon dioxide to form bis-carbonate **18** which can then cyclise with elimination of the aromatic carbonate (pathway 2, Scheme 7). This will involve a second inversion of configuration and result in the formation of cyclic carbonate with overall retention of configuration.



**Scheme 7**. Mechanism of cyclic carbonate synthesis catalyzed by bis-phenol **13**.

The rate of conversion of carbonate **17** into bis-carbonate **18** would be expected to be dependent on the concentration of carbon dioxide in the reaction mixture which will be dependent on the carbon dioxide pressure. Therefore, the approximately constant 1:1 ratio of *trans:cis*-**3h** observed over a range of 60 bars of carbon dioxide pressure (Table 5) suggests that the rate determining step for both pathways is the conversion of intermediate **16** into **17**. To rule out the possibility that the results in Table 5 might be due to a very low solubility of carbon dioxide in epoxide **2h**, the use of propylene carbonate **3i** (Figure 7) was investigated since carbon dioxide is known to be highly soluble in this cyclic carbonate.58 When epoxide **2h** was reacted in propylene carbonate under 10 bar carbon dioxide pressure at 120 °C in the presence of 5 mol% of catalyst **13**, a 50:50 mixture of *cis*- and *trans*-**3g** was again obtained.DFT calculations have previously been carried out on cyclic carbonate synthesis catalyzed by a wide range of metal-containing and metal-free catalysts.59,60 In most cases, ring-opening of the epoxide by a nucleophile (step a in Scheme 5) was found to be the rate determining step of the catalytic cycle60 which is consistent with the conversion of **16** into **17** being rate determining for catalysis by salophen **13**.



**Figure 7.** Cyclic carbonate **3i**.

**Experimental**

Phenols **5-7** are commercially available. Epoxide **2h**21band imines **8–15** were prepared by literature methods.61 Crystals of salophen **13** suitable for X-ray analysis were obtained by recrystallization from EtOH.

Synthesis of cyclic carbonates catalyzed by salophen **13**

Epoxide **2a-h** (1.66 mmol) and catalyst **13** (1 mol% or 5 mol%) were placed in a glass sample vial fitted with a magnetic stirrer bar, which was then placed in a 300 mL stainless steel autoclave and heated to 120 ºC before being pressurized to the required carbon dioxide pressure. The reaction mixture was stirred for 24 hours, then cooled with liquid N2 before the pressure was released and the pressure vessel opened. For reactions carried out at 1 bar CO2 pressure, the sample vial was fitted with a balloon filled with CO2 instead of being placed in the autoclave. The conversion of epoxide to cyclic carbonate was determined by analysis of a sample by 1H NMR spectroscopy. Then the products were purified by flash chromatography. Cyclic carbonates **3a**-**h** are all known compounds and the spectroscopic data of samples prepared using catalyst **13** were consistent with those reported previously.43

**3–Chloropropylene carbonate (3a):** Purification by flash chromatography with hexane/EtOAc (6:4) gave compound **3a** (171 mg, 76%) as a white solid. m.p. 67–69 °C (lit.43 68–69 °C); 1H NMR (400 MHz, CDCl3) 4.98–4.92 (1H, m, OCH), 4.57 (1H, t *J* 8.0 Hz, OCH2), 4.41 (1H, t *J* 8.0 Hz, OCH2), 3.78–3.70 (2H, m, CH2Cl); 13C NMR (100 MHz, CDCl3) 154.2 (C=O), 74.2 (OCH), 66.9 (OCH2), 43.7 (CH2Cl); IR (neat, cm–1): ν 2973, 2698, 2121, 2017, 1971 and 1793; HRMS (ESI+): calculated for C4H5ClO3Na [M+Na]+ 158.9819, found 158.9815.

**3–Phenoxypropylene carbonate (3b):** Purification by flash chromatography with hexane/EtOAc (8:2) gave compound **3b** (283 mg, 88%) as a white solid. m.p. 94–96 °C (lit.43 94–95 °C); 1H NMR (400 MHz, CDCl3) 7.30 (2H, t *J* 8.0 Hz, ArH), 7.02 (1H, t *J* 8.0 Hz, ArH), 6.91 (2H, d *J* 8.0 Hz, ArH), 5.06–5.01 (1H, m, OCH), 4.65–4.53 (2H, m, OCH2), 4.24 (1H, dd *J* 11.0, 4.0 Hz, CH2OPh), 4.16 (1H, dd *J* 11.0, 4.0 Hz, CH2OPh); 13C NMR (100 MHz, CDCl3) 157.7 (C=O), 154.6 (ArC), 129.7 (ArCH), 122.0 (ArCH), 114.6 (ArCH), 74.0 (OCH), 66.8 (OCH2), 66.2 (OCH2); HRMS (ESI+): calculated for C10H10O4Na [M+Na]+ 217.0471, found 217.0473.

**1,2–Dodecylene carbonate (3c):** Purification by flash chromatography with hexane/EtOAc (8:2) gave compound **3c** (337 mg, 89%) as a colourless liquid. 1H NMR (400 MHz, CDCl3) 4.73–4.66(1H, m, OCH), 4.52 (1H, t *J* 8.0 Hz, OCH2), 4.06 (1H, t *J* 8.0 Hz, OCH2), 1.84–1.70 (2H, m, CH2), 1.63–1.26 (16H, m, 8×CH2), 0.88 (3H, t *J* 8.0 Hz, CH3); 13C NMR (100 MHz, CDCl3) 155.1 (C=O), 77.1 (OCH), 69.4 (OCH2), 33.9 (CH2), 31.8 (CH2), 29.5 (CH2), 29.4 (CH2), 29.3 (CH2), 29.2 (CH2), 29.1 (CH2), 24.3 (CH2), 22.6 (CH2), 14.1 (CH3); IR (neat, cm–1): ν 2931, 2832 and 1798; HRMS (ESI+): calculated for C13H24O3Na [M+Na]+ 251.1618, found 251.1621.

**4–Chlorostyrene carbonate (3d):** Purification by flash chromatography with hexane/EtOAc (6:4) gave compound **3d** (283 mg, 86%) as a white solid. m.p. 67–69 °C (lit.43 68–69 °C);  1H NMR (400 MHz, CDCl3) 7.43 (2H, d *J* 8.0 Hz, ArH), 7.30 2Hd *J* 8.0 HzArH), 5.66 (1H, t *J* 8.0 Hz, OCH), 4.80 (1H, t *J* 8.0 Hz, OCH2), 4.31 (1H, t *J* 8.0 Hz, OCH2); 13C NMR (100 MHz, CDCl3) 154.6 (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 2973, 2698, 2121, 2017, 1971 and 1793; HRMS (ESI+): calculated for C9H8ClO3 [MH]+ 220.9984, found 220.9976.

**1,2–Decylene carbonate (3e):** Purification by flash chromatography with hexane/EtOAc (8:2) gave compound **3e** (169 mg, 51%) as a colourless liquid. 1H NMR (400 MHz, CDCl3) 4.71–4.68(1H, m, OCH), 4.52 (1H, t *J* 8.0 Hz, OCH2), 4.06 (1H, t *J* 8.0 Hz, OCH2), 1.83–1.63 (2H, m, CH2), 1.47–1.26 (12H, m, 6×CH2), 0.87 (3H, t *J* 8.0 Hz, CH3); 13C NMR (100 MHz, CDCl3) 155.1 (C=O), 77.0 (OCH), 69.4 (OCH2), 33.9 (CH2), 31.8 (CH2), 29.3 (CH2), 29.1 (CH2), 29.0 (CH2), 24.3 (CH2), 22.6 (CH2), 14.1 (CH3); HRMS (ESI+): calculated for C11H20O3Na [M+Na]+ 223.1305, found 223.1315.

**Styrene carbonate (3f):** Purification by flash chromatography with hexane/EtOAc (6:4) as eluent gave compound **3f** (228 mg, 84%) as a white solid. m.p. 49–51 °C (lit.43 50–51 °C); 1H NMR (400 MHz, CDCl3) 7.41–7.31 (5H, m, Ph), 5.68 (1H, t *J* 8.0 Hz, OCH), 4.80 (1H, t *J* 8.0 Hz, OCH2), 4.35 (1H, t *J* 8.0 Hz, OCH2); 13C NMR (100 MHz, CDCl3) 154.7 (C=O), 135.6 (ArC), 129.7 (ArCH), 129.2 (ArCH), 125.8 (ArCH), 78.0 (OCH), 71.1 (OCH2); IR (neat, cm–1): ν 3060, 3029, 2961, 2903, 1791 and 1599; HRMS (ESI+): calculated for C9H8O3Na [M+Na]+ 187.0366, found 187.0361.

**1,2–Hexylene carbonate (3g):** Purification by flash chromatography with hexane/EtOAc (6:4) gave compound **3g** (136 mg, 57%) as a colourless liquid. 1H NMR (400 MHz, CDCl3) 4.73–4.66(1H, m, OCH), 4.52 (1H, t *J* 8.0 Hz, OCH2), 4.05 (1H, t *J* 8.0 Hz, OCH2), 1.86–1.65 (2H, m, CH2), 1.48–1.35 (4H, m, 2×CH2), 0.91 (3H, t *J* 8.0 Hz, CH3); 13C NMR (100 MHz, CDCl3) 155.1 (C=O), 76.8 (OCH), 69.4 (OCH2), 33.5 (CH2), 26.4 (CH2), 22.2 (CH2), 13.8 (CH3); IR (neat, cm–1): ν 2941, 2922, 2899 and 1796; HRMS (ESI+): calculated for C7H12O3Na [M+Na]+ 167.0679, found 167.0682.

**Conclusions**

Salophens have often has been used as ligands to form Lewis acidic metal complexes which catalyze the synthesis of cyclic carbonates from epoxides and carbon dioxide.11 In this work we have shown that uncomplexed salophen ligands such as **4, 8** and **13** are themselves capable of acting as Brønsted acid catalysts under reaction conditions comparable to those often used for metal(salophen) complexes. Hence, whilst it is common practice to carry out a blank experiment in which no catalyst is added to reactions, it would also be prudent to carry out control experiments in which the ligand is screened for catalytic activity in the absence of a metal. The same precautions should be applied to any reaction capable of being catalyzed by both Lewis and Brønsted acids. Salophens constitute a new family of bifunctional organocatalysts for cyclic carbonate synthesis which require no corrosive halide cocatalysts and which appear to function by a novel reaction mechanism.

**Supporting Information**. The following files are available free of charge. Details of instrumentation used, 1H and 13C NMR spectra of cyclic carbonates **3a–h**, chiral HPLC traces of racemic and enantiomerically pure cyclic carbonate **3b** and 1H and 13C NMR spectra of phenols **8–14**.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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SYNOPSIS (Graphical Abstract).

