Cyclic Carbonate Synthesis Catalysed by Bimetallic Aluminium–Salen Complexes

William Clegg, Ross W. Harrington, Michael North,* and Riccardo Pasquale[a]

Abstract: The development of bimetallic aluminium–salen complexes [{Al-(salen)}₂O] as catalysts for the synthesis of cyclic carbonates (including the commercially important ethylene and propylene carbonates) from a wide range of terminal epoxides in the presence of tetrabutylammonium bromide as a cocatalyst is reported. The bimetallic structure of one complex was confirmed by X-ray crystallography. The bimetallic complexes displayed exceptionally high catalytic activity and in the presence of tetrabutylammonium bromide could catalyse cyclic carbonate synthesis at atmospheric pressure and room temperature. Catalyst-reuse experiments demonstrated that one bimetallic complex was stable for over 60 reactions, though the tetrabutylammonium bromide decomposed in situ by a retro-Menschutkin reaction to form tributylamine and had to be regularly replaced. The mild reaction conditions allowed a full analysis of the reaction kinetics to be carried out and this showed that the reaction was first order in aluminium complex concentration, first order in epoxide concentration, first order in carbon dioxide concentration (except when used in excess) and unexpectedly second order in tetrabutylammonium bromide concentration. Further kinetic experiments demonstrated that the tributylamine formed in situ was involved in the catalysis and that addition of butyl bromide to reconvert the tributylamine into tetrabutylammonium bromide resulted in inhibition of the reaction. The reaction kinetics also indicated that no kinetic resolution of racemic epoxides was possible with this class of catalysts, even when the catalyst was derived from a chiral salen ligand. However, it was shown that if enantiomerically pure styrene oxide was used as substrate, then enantiomerically pure styrene carbonate was formed. On the basis of the kinetic and other experimental data, a catalytic cycle that explains why the bimetallic complexes display such high catalytic activity has been developed.

Keywords: aluminum · carbon dioxide · cyclic carbonates · epoxides · heterogeneous catalysis

Introduction

Atmospheric carbon dioxide levels have been rising since the start of the industrial revolution due to the generation of energy by the combustion of fossil fuels.[1] As a result, two major scientific challenges facing the human race in the 21st century are reducing atmospheric carbon dioxide levels to mitigate the effects of climate change[2,3] and developing alternative and sustainable raw materials for the chemicals industry to replace the crude oil on which it is currently

based.[4] The latter problem is particularly pressing, whereas there are believed to be sufficient coal reserves to meet global energy needs for another 200 years,[5] current projections are that world-wide production of oil and gas will peak before 2020.[6]

For the foreseeable future, annual consumption of fossil fuels is predicted to continue to increase with the potential for a corresponding rise in atmospheric carbon dioxide levels.[7] The only solution to this problem currently being considered is "carbon capture and storage", which involves concentrating and compressing carbon dioxide and then storing it in disused oil/gas wells or under the ocean.[8] However, this is a highly energy intensive process that removes the carbon from the natural carbon cycle and it is far from certain that long-term containment is feasible given the volatile nature of carbon dioxide. A solution to both of these problems would be the development of commercially viable routes to basic chemicals employing carbon dioxide as the starting material.[8–10] However, if such a process should con-

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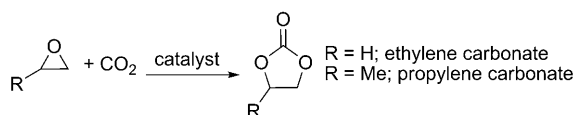
Scheme 1. Synthesis of cyclic carbonates from epoxides and CO_2.

tribute to the reduction of atmospheric carbon dioxide levels then it must be carried out at atmospheric pressure and at or near room temperature; otherwise, more carbon dioxide will be produced to generate the required energy than is consumed by the chemical reaction. Whereas chemical processes that involve the reduction of carbon dioxide to hydrogenated chemicals or fuels are inevitably endothermic, there are reactions of carbon dioxide that are exothermic.[8,9] In particular, salicylic acid has been manufactured from carbon dioxide for over a century[4,8,9] and urea is currently prepared from carbon dioxide on a 100 million tonne per annum scale.[4,10]

Another commercially important process[2,11,12] that utilises carbon dioxide is the synthesis of cyclic carbonates from epoxides[13] as shown in Scheme 1. This 100%-atom economical reaction[14] has been a commercial process for the synthesis of ethylene and propylene carbonates for over 50 years.[11] The reaction is highly exothermic ($\Delta H_r = -140$ kJ mol^{-1} for ethylene carbonate[15]), though currently used catalysts require the reaction to be carried out at high temperatures and pressures and the use of highly purified carbon dioxide.[10,11,16] Cyclic carbonates are currently manufactured on a 100–200 ktonne per annum scale and have applications including degreasing agents, electrolytes, solvents, chemical intermediates and polymerisation monomers.[11] Cyclic carbonates can also be converted into dimethyl carbonate, demand for which could exceed 30 Mtonne per annum if its cost of production could be reduced sufficiently to allow it to be used as an oxygenating additive and anti-knocking agent in petrol.[8,17] Recently, polycarbonates that are also obtained from the reaction between epoxides and carbon dioxide have also become commercially important.[18]

Ideally, cyclic carbonates would be synthesised from waste carbon dioxide produced by major fixed site producers such as fossil fuel power plants, metal production plants, chemical plants and oil refineries. However, none of the many known catalysts[11–13] could achieve the necessary level of activity at atmospheric pressure and <100 °C to allow this to be achieved in an energy efficient manner.[19] Notable amongst the catalysts that have been employed to synthesise cyclic carbonates are metal(salen) complexes[18c,20] derived from aluminium,[21] nickel,[21a] copper,[21a,22] zinc,[21a,22] magnesium,[21a] cobalt,[21a,22–24] chromium,[21a,25] tin,[26] manganese[27] or ruthenium.[28]

Previous work from our group[29] has demonstrated that bimetallic salen complexes display much higher catalytic activity in the asymmetric synthesis of cyanohydrins than their monometallic counterparts, as the two metal ions can each activate one of the two components of the reaction. Poly-

carbonate and cyclic carbonate synthesis catalysed by chromium(salen) complexes are known to be bimolecular;[25] therefore, we reasoned that a suitable bimetallic salen complex might display significantly improved catalytic activity in the reaction between carbon dioxide and epoxides. In this paper we give full details of our work in this area,[30] which was aimed at developing a catalyst, which would be sufficiently active to allow the synthesis of cyclic carbonates from waste carbon dioxide without requiring energy input.

Results and Discussion

Literature precedent suggested that metal(salen) complexes in which the metal is in the +3 oxidation state form the most active catalysts for the synthesis of cyclic carbonates.[21–25,27] Therefore, to investigate whether mononuclear complexes could catalyse the synthesis of cyclic carbonates under much milder conditions than previously reported, and to provide a benchmark against which to judge subsequent work, mononuclear metal(salen) complexes **1–5** were prepared following literature procedures.[23b,31] Although the chirality associated with the salen ligand in complexes **1–5** was superfluous for this project, the cyclohexanediamine unit and the *tert*-butyl groups on the aromatic rings were retained to enhance the solubility of the salen complexes.

The standard test reaction used throughout this project was the conversion of styrene oxide (**6a**) to styrene carbonate (**7a**) (Scheme 2). Unless stated otherwise, reactions were carried out under solvent-free conditions and carbon dioxide was obtained by evaporation of Cardice pellets without further purification or drying and was held within a balloon to maintain a carbon dioxide atmosphere at one atmosphere pressure. Results obtained with the mononuclear complexes **1–5** are presented in Table 1.

Entry 1 (Table 1) shows that under the reaction conditions shown in Scheme 2, no uncatalysed background reaction between styrene oxide and carbon dioxide takes place. En-
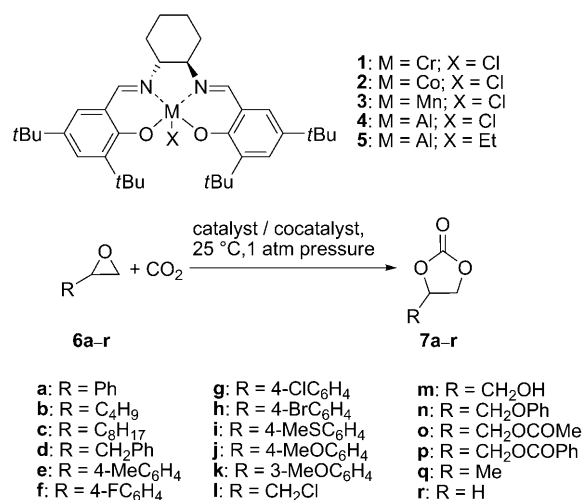

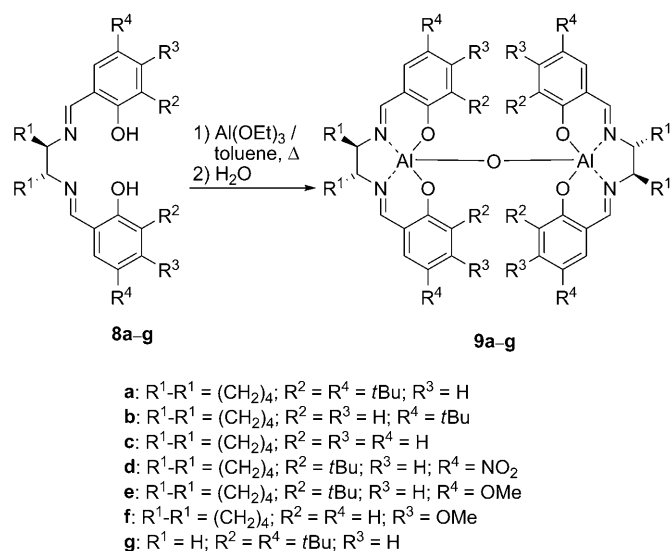Scheme 2. Synthesis of the cyclic carbonates **7a–r**.

Table 1. Attempted synthesis of styrene carbonate (**7a**) using the mono-metallic catalysts **1–5**.

Entry	Catalyst (loading [mol%])	Cocatalyst (loading [mol%])	Pressure [atm]	T [°C]	Conversion [%][a]
1			1	25	0[b]
2	**1** (1)		1	25	0
3	**2** (1)		1	25	0
4	**3** (1)		1	25	0
5	**4** (1)		1	25	0
6	**5** (1)		1	25	0
7	**1** (2.5)	Bu$_4$NBr (2.5)	1	25	20
8	**2** (1)	Bu$_4$NBr (1)	1	25	0
9	**3** (1)	Bu$_4$NBr (1)	1	25	5
10	**4** (1)	Bu$_4$NBr (1)	1	25	0
11	**5** (1)	Bu$_4$NBr (1)	1	25	0
12[c]	**3** (1)	DMAP[d] (1)	8	50	13
13[c]	**5** (1)	Bu$_4$NBr (1)	8	50	0

[a] Determined by ^{1}H NMR analysis of the unpurified reaction mixture after a reaction time of 24 h. [b] The same result was obtained from reactions carried out in the absence of solvent, or in methanol or hexane. [c] Reaction was carried out in a sealed stainless steel pressure vessel. [d] DMAP = 4-dimethylaminopyridine.

a: R^1-R^1 = (CH$_2$)$_4$; R^2 = R^4 = tBu; R^3 = H
b: R^1-R^1 = (CH$_2$)$_4$; R^2 = R^3 = H; R^4 = tBu
c: R^1-R^1 = (CH$_2$)$_4$; R^2 = R^3 = R^4 = H
d: R^1-R^1 = (CH$_2$)$_4$; R^2 = tBu; R^3 = H; R^4 = NO$_2$
e: R^1-R^1 = (CH$_2$)$_4$; R^2 = tBu; R^3 = H; R^4 = OMe
f: R^1-R^1 = (CH$_2$)$_4$; R^2 = R^4 = H; R^3 = OMe
g: R^1 = H; R^2 = R^4 = tBu; R^3 = H

Scheme 3. Synthesis of the bimetallic aluminium(salen) complexes **9**.

tries 2–6 (Table 1) further show that none of the mononuclear complexes **1–5** was able to catalyse the reaction at a catalyst loading of 1 mol%. It is well known that a cocatalyst such as tetrabutylammonium bromide[21a–c,23c,24a] or 4-di-methylaminopyridine[23b,f,25a] (DMAP) is often required in conjunction with a Lewis acid to induce cyclic carbonate synthesis from epoxides and carbon dioxide. However, as shown by entries 7–11 (Table 1), addition of tetrabutylammonium bromide as a cocatalyst to complexes **1–5** resulted in conversions of styrene oxide to styrene carbonate of only 0–20%, even when the catalyst and cocatalyst loadings were increased to 2.5 mol% (entry 7, Table 1). Finally, entries 12 and 13 (Table 1) tabulate the results obtained in the presence of a cocatalyst, along with elevated pressure and temperature. Again, at best a conversion of 13% was observed under these conditions. These results clearly illustrate that the mononuclear metal(salen) complexes **1–5** are not effective catalysts for cyclic carbonate synthesis under conditions suitable for the use of waste carbon dioxide present in exhaust gases.

A search of the Cambridge Structure Database (version 5.30 with updates to May 2009),[32] revealed that bimetallic complexes of the form [{M(salen)}$_2$O] have been structurally characterised for iron,[33] aluminium,[34] manganese,[35] chromium[36] and nickel.[37] Since the bimetallic aluminium(salen) complex **9a** had been reported to be an effective Lewis acid for Michael additions,[31c,38] cyanohydrin synthesis[39] and Passerini-type reactions,[40] it appeared reasonable that it may have activity in cyclic carbonate synthesis as well. Given the scale of the projected use, the low cost and low environmental impact of aluminium compared to transition metals was also advantageous. However, the reported synthesis of complex **9a** involved treatment of the salen ligand with expensive and pyrophoric trimethylaluminium.[31c,38a,d] Therefore, we were pleased to find that complex **9a** could also be prepared from triethoxyaluminium and salen ligand **8a** (Scheme 3). Triethoxyaluminium can be prepared in situ from aluminium metal (foil or powder) and ethanol.[41] The spectroscopic data obtained for complex **9a** matched those in the literature,[38a,d] and the structure was confirmed by a single-crystal X-ray analysis (Figure 1).

The asymmetric unit of **9a** contains two independent molecules, each with a twofold rotation axis passing through the central oxygen atom, as well as some highly disordered hexane solvent molecules. The two molecules are related to each other by a pseudo-inversion centre, but both clearly exhibit the absolute configuration (R,R), as confirmed by weak but significant anomalous dispersion effects, consistent with the synthesis strategy. They have the same general structure as previously reported [{Al(salen)}$_2$O] com-
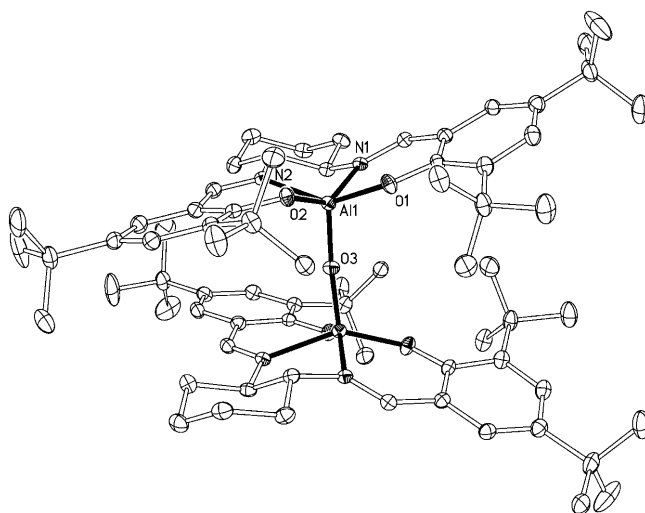

Figure 1. One of the two independent molecules of complex **9a**, with selected atom labels; H atoms and one disorder component are omitted for clarity.

plexes.[34] The Al-O-Al linkage is almost linear in both molecules (172.52(15) and 170.47(15)°); this angle varies considerably in the related structures, in the range 152.0–174.4°.[34]

Complex **9a** was then tested as a catalyst for the synthesis of styrene carbonate from styrene oxide under the standard conditions shown in Scheme 2 and the results are presented in Table 2. Complex **9a** alone was also found to be catalyti-

Table 2. Synthesis of styrene carbonate (**7a**) using the bimetallic catalyst **9a**.

Entry	Catalyst loading [mol%]	Cocatalyst (loading [mol%])	Pressure [atm]	t [h]	T [°C]	Conversion [%][a]
1[b]	1		5	24	50	0
2[b]	1	DMAP (1)	8	24	50	0
3	1	Bu$_4$NBr (1)	1	3	25	38
4	1	Bu$_4$NBr (1)	1	24	25	86
5	–	Bu$_4$NBr (1)	1	3	25	4
6	0.1	Bu$_4$NBr (1)	1	24	25	85
7	0.1	Bu$_4$NBr (0.1)	1	24	25	27
8	1	Bu$_4$NBr (2.5)	1	3	25	56
9	2.5	Bu$_4$NBr (1)	1	3	25	51
10	2.5	Bu$_4$NBr (2.5)	1	3	25	62
11	2.5	Bu$_4$NBr (2.5)	1	24	25	98

[a] Determined by ^{1}H NMR analysis of the unpurified reaction mixture. [b] Reaction was carried out in a sealed stainless steel pressure vessel.

cally inactive even at elevated pressure and temperature (entry 1, Table 2) and DMAP was not an effective cocatalyst (entry 2, Table 2). However, the combination of complex **9a** and tetrabutylammonium bromide formed a remarkably active catalyst system. Even at atmospheric pressure and 26°C, 1 mol% of each catalyst component led to a conversion of 38% of styrene oxide to styrene carbonate after just three hours (entry 3, Table 2) and a conversion of 86% after a reaction time of 24 h (entry 4, Table 2). Entry 5 (Table 2) shows that tetrabutylammonium bromide alone has negligible catalytic activity under these reaction conditions.[42] Reducing the amount of complex **9a** to 0.1 mol% had no effect on the catalytic activity (entries 4 and 6, Table 2), but simultaneous reduction of the amount of tetrabutylammonium bromide to 0.1 mol% dramatically reduced the conversion (entry 7, Table 2). As entries 8 and 9 (Table 2) show, increasing the amount of either catalyst component to 2.5 mol% led to a conversion of 51–56% in a reaction time of 3 h. The use of 2.5 mol% of both catalyst components gave a conversion of 62% after 3 h and 98% after 24 h (entries 10 and 11, Table 2). All these reactions were carried out under solvent-free conditions and attempts to use either hexane or methanol as solvent under the conditions shown in Table 2, entry 11 resulted in no reaction. For subsequent catalyst optimisation studies, the conditions of Table 2, entry 10 were adopted as standard as they gave a good conversion in a short reaction time.

A number of catalyst systems have been reported where cyclic carbonate synthesis is accelerated by the addition of water.[42d,43] However, addition of water (33 or 100 mol%) to reactions carried out under the conditions of Table 2,

entry 10 was detrimental, as the conversion was reduced to 32 and 26%, respectively. It should be noted, however, that the reactions reported in Table 2 were all carried out by using carbon dioxide obtained by evaporation of Cardice pellets without drying of the resulting gas. Hence, catalyst **9a** tolerates the presence of some water in the reaction system. Reactions carried out in dry glassware by using anhydrous carbon dioxide from a cylinder proceeded at the same rate as those using Cardice pellets (see below), so there appears to be no beneficial effect of water for the complex **9a**/tetrabutylammonium bromide catalyst system.

The influence of the halide within the tetrabutylammonium salt cocatalyst was investigated and the order of catalytic effectiveness was found to be Br > I > Cl > F as shown in Table 3. The same order of reactivity has been reported for

Table 3. Influence of the halide counterion in the cocatalyst on the catalytic activity.[a]

Cocatalyst	Conversion [%][b]	Yield of **7a** [%][c]
Bu$_4$NBr	62	57
Bu$_4$NI	35	25
Bu$_4$NCl	20	15
Bu$_4$NF	trace	0

[a] Reactions were carried out under the conditions of Table 2, entry 10. [b] Determined by ^{1}H NMR analysis of the reaction mixture without any purification. [c] Yield of isolated product obtained after chromatographic purification.

reactions catalysed by tetrabutylammonium halides and silica-supported tetrabutylammonium halides in the absence of a Lewis acid catalyst.[44] However, for chitosan-derived quaternary ammonium salts the order of reactivity was found to be I > Br > Cl[45] and for various tetraalkylammonium halides a reactivity order of Cl > Br > I was reported.[46] It is well established[27,28,42a,47] that the role of the halide is to open the epoxide ring by forming a halo–alkoxide intermediate, which depending on the catalyst system may be coordinated to a Lewis acid. The alkoxide subsequently reacts with carbon dioxide to form a (coordinated) carbonate; then the halide acts as a leaving group during formation of the five-membered ring (Scheme 4). Thus, the catalytic effect of the halide is determined by a balance of its nucleophilicity and leaving-group ability, as well as by the stability of the tetraalkylammonium salt under the reaction conditions. For these reasons, the relative activity of the halide counterion will vary from one catalyst system to another depending on the nature of the Lewis acid catalyst, if used, and the reaction conditions. This also explains why catalyst **9a** was inactive in the absence of a tetraalkylammonium halide cocatalyst (Table 2, entry 1).

To optimise the structure of the bimetallic aluminium-(salen) complex, the variation of the substituents on the aromatic rings was investigated by the preparation of complexes **9b–i**[34b,48] from the known[49] salen ligands following the method shown in Scheme 3. Complexes **9b–i** were tested as catalysts for the addition of carbon dioxide to styrene oxide under the conditions of Table 2, entry 10, and the
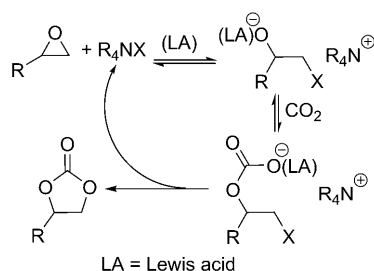
Scheme 4. Role of the halide in the cyclic carbonate synthesis.

results are presented in Table 4. When the *tert*-butyl groups were gradually removed from the aromatic rings, the catalytic efficiency decreased (entries 1–3, Table 3). This trend appeared to be related to the decreasing solubility of the catalyst (**9c** did not fully dissolve in the reaction mixture) as it was made more hydrophilic rather than to any steric effect. Complexes **9d–f** were designed to probe the electronic influence of the substituents on the aromatic rings, but no trend was apparent (entries 4–6, Table 3).

Table 4. Influence of the ligand structure on the catalyst activity.[a]

Entry	Catalyst	Conversion [%][b]	Entry	Catalyst	Conversion [%][b]
1	**9a**	62	6	**9f**	41
2	**9b**	51	7	**9g**	52
3	**9c**	28	8	**9h**	14
4	**9d**	50	9	**9i**	33
5	**9e**	64			

[a] Reactions were carried out under the conditions of Table 2, entry 10. [b] Determined by ^{1}H NMR analysis of the reaction mixture without any purification.

The cyclohexanediamine unit at the heart of complexes **9a–f** could be replaced by less expensive achiral diamines to give complexes **9g–i**. However, whereas the ethylenediamine-derived catalyst **9g** retained a good level of activity (entry 7, Table 3), the 1,3-propylenediamine and 1,2-diaminobenzene-derived complexes **9h,i** were very poor catalysts, which again appears to be related to their low solubility in the reaction mixture. Whereas complex **9e** appeared to have marginally better catalytic activity than complex **9a**, the ease of synthesis of the ligand required for complex **9a** meant that it was retained as the preferred catalyst arising from this study.

Having optimised the catalyst structure and reaction conditions, the applicability of the complex **9a**/tetrabutylammonium bromide system to the synthesis of cyclic carbonates other than styrene carbonate was investigated. Thus, monosubstituted epoxides[50] **6a–p** were reacted with 2.5 mol% of **9a** and 2.5 mol% of tetrabutylammonium bromide at 25°C under solvent-free conditions. The results of this study are shown in Table 5. Entries 1–4 show that epoxides **6a–d**[51] containing alkyl chains or unsubstituted aromatic rings are good substrates for the reaction. Entries 5–11 (Table 5) show that a wide range of substituents can be accommodat-
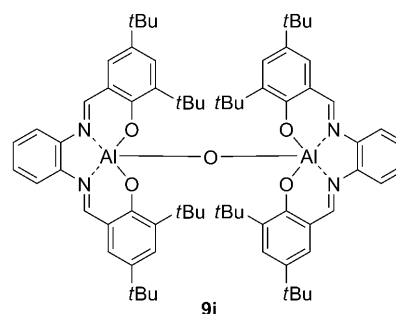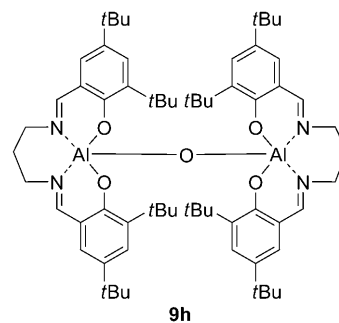
Table 5. Synthesis of the cyclic carbonates **7a–r**.[a]

Entry	Epoxide	t [h]	Yield [%][b]	Entry	Epoxide	t [h]	Yield [%][b]
1	**6a**	3	62	10	**6j**	24	79 (30)[c]
2	**6b**	3	87	11	**6k**	24	72 (48)[c]
3	**6c**	3	64	12	**6l**	3	60
4	**6d**	3	44	13	**6m**	3	36
5	**6e**	3	77	14	**6n**	3	55
6	**6f**	24	81 (36)[c]	15	**6o**	3	34
7	**6g**	3	42	16	**6p**	3	58
8	**6h**	3	31	17	**6q**[d]	3	77
9	**6i**	24	78 (24)[c]	18	**6r**[e]	24	76

[a] All reactions were carried out by using 2.5 mol% of **9a** and 2.5 mol% of tetrabutylammonium bromide at atmospheric pressure and 25°C unless stated otherwise. [b] Yield of isolated product obtained after chromatographic purification. [c] Determined by GCMS analysis of the reaction mixture after 3 h. [d] Reaction carried out at 0°C. [e] Reaction carried out in a stainless steel reactor vessel at room temperature and 6 atm.

ed on the aromatic ring of aryl epoxides **6e-k**,[52] although in some cases it is necessary to extend the reaction time to 24 h to obtain high yields of the cyclic carbonates. Functional groups are also tolerated on the alkyl chain of an aliphatic epoxide as shown by entries 12–16 (Table 5). Thus, both glycidyl chloride (**6l**) and glycidol (**6m**) were converted into the corresponding cyclic carbonates as were glycidyl phenyl ether (**6n**)[53] and glycidyl esters (**6o,p**).[54] The low yield obtained with glycidol was due to the poor solubility of complex **9a** in this polar substrate.

For the commercially important[11] cyclic carbonates propylene carbonate (**7q**) and ethylene carbonate (**7r**), the reaction conditions had to be modified due to the volatile nature of propylene oxide and ethylene oxide. For the synthesis of propylene carbonate, the reaction was conducted at 0°C and gave a good yield after a reaction time of 3 h (Table 5, entry 17). To enable gaseous ethylene oxide (**6r**) to

be converted into ethylene carbonate, the reaction was carried out at six atmospheres pressure in a sealed stainless steel reactor at room temperature. A good yield was obtained after a reaction time of 24 h (Table 5, entry 18).

However, only monosubstituted epoxides were found to be effective substrates for the complex **9a**/tetrabutylammonium bromide catalyst system. Of the five 1,1- and 1,2-disubstituted epoxides **10a–e**[51,52,55] studied, only *trans*-stilbene oxide (**10a**) gave any conversion to the corresponding cyclic carbonate, and then only 8% conversion was observed after a reaction time of 48 h by using the same conditions as for the reactions shown in Table 5. In all cyclic carbonate syntheses throughout this work, the cyclic carbonates **7** were the only products formed. In particular, no polycarbonate was formed even though aluminium(salen) complexes are known to catalyse polycarbonate formation from epoxides and carbon dioxide,[31d] and no epoxide hydrolysis or rearrangement products were detected. The latter are common byproducts of cyclic carbonate syntheses carried out under harsher reaction conditions.[56]

The need to use 2.5 mol% of catalyst **9a** to obtain a rapid rate of cyclic carbonate formation was a potential problem to the large-scale adoption of this chemistry, unless the catalyst could be recovered unchanged at the end of the reaction and reused. To investigate this, the synthesis of propylene carbonate (**7q**) from propylene oxide (**6q**) was carried out by using 2.5 mol% of both complex **9a** and tetrabutylammonium bromide. The reaction was carried out at 0°C for three hours, and after this time the product and any unreacted starting material were distilled directly from the reaction flask, leaving the solid catalysts behind. Additional propylene oxide and carbon dioxide were then added to the flask and the reaction was repeated.

Figure 2 shows the results of sixty reuses of complex **9a**. The data in Figure 2 clearly indicate that complex **9a** is not decomposed during the cyclic carbonate synthesis. There is some scatter in the data due to the distillation after each reaction cycle, nevertheless it is clear that the catalytic activity of the complex **9a**/tetrabutylammonium bromide system degrades over a period of about seventeen reactions. However, addition of a new batch of tetrabutylammonium bromide completely restores the catalytic activity, leading to the conclusion that the tetrabutylammonium bromide, but not complex **9a**, decomposes during the reaction. This conclusion was supported by GC–MS analysis of the product of each reaction cycle. In some cases, a second species was detected in the GC trace, which was identified as tributylamine by mass spectrometry (Figure 2).[57] The batch of catalyst **9a** used in the 60 experiments shown in Figure 2 achieved a total turnover number of 1027 with no apparent loss of catalytic activity.
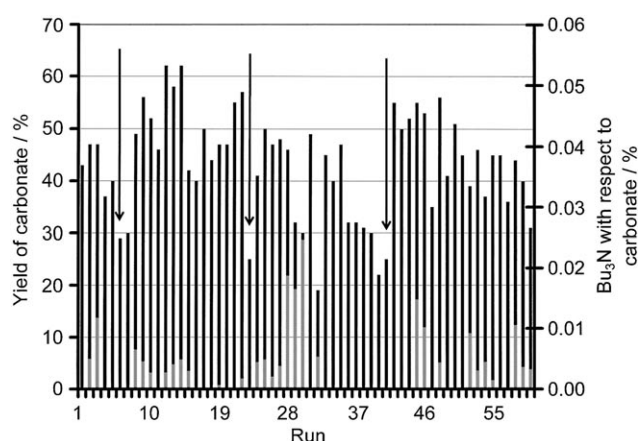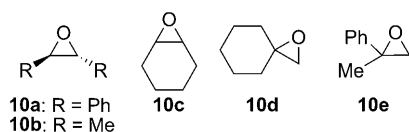

Figure 2. Reuse of complex **9a** within 60 reactions. The black bars indicate the amount of propylene carbonate formed whilst the grey bars indicate the amount of detected tributylamine. The three arrows indicate where additional tetrabutylammonium bromide was added.

The detection of tributylamine in reactions catalysed by complex **9a**/tetrabutylammonium bromide provided important mechanistic information regarding the mode of action of the catalyst system (vide infra). A control experiment involving the distillation of propylene carbonate from a mixture of propylene carbonate and tetrabutylammonium bromide proved that the formation of tributylamine did not occur during the distillation process,[57] and it was also shown that the tributylamine was not formed by decomposition of tetrabutylammonium bromide within the GC–MS system.[57] It is known that tetraalkylammonium halides can decompose to tertiary amines by an S_N2 reaction[58] (the reverse Menschutkin reaction) or by an E2 reaction[59] (Hofmann elimination) to give alkyl halides and alkenes as the byproducts, respectively. Neither butyl bromide nor butene was detected by GC–MS. To distinguish between these two mechanisms, the conversion of styrene oxide (**6a**) into styrene carbonate (**7a**) catalysed by complex **9a** and trimethylanilinium bromide (2.5 mol% of each component) was studied. Trimethylanilinium bromide is a much less effective cocatalyst than tetrabutylammonium bromide (6% conversion of styrene oxide to styrene carbonate after 24 h), which could be due to the poor solubility of the anilinium bromide in the reaction mixture. Nevertheless, dimethylaniline was detected in the reaction mixture by GC–MS.[57] As trimethylanilinium bromide cannot undergo a Hofmann elimination, this observation indicates that the decomposition of the quaternary ammonium salt occurs by a reverse Menschutkin reaction. The failure to detect butyl bromide (or methyl bromide) by GC–MS is probably due to their reaction with one of the reaction components to give a non-volatile byproduct.

To understand why the bimetallic aluminium(salen) complexes **9** were such active catalysts for the synthesis cyclic carbonates, and to investigate what role (if any) the tertiary amine formed in situ plays in the catalytic cycle, a study of the reaction kinetics for the synthesis of styrene carbonate

10a: R = Ph **10b:** R = Me   **10c**   **10d**   **10e**

catalysed by complex **9a** was undertaken.[60] The first challenge in this study was finding a suitable solvent because the standard conditions used for catalyst screening (see Scheme 2) involved solvent-free conditions and preliminary studies showed that catalyst **9a** was inactive when conventional solvents (e.g., hexane, methanol) were used. However, propylene carbonate is a liquid at room temperature and is being increasingly used as a polar aprotic solvent.[61] As propylene carbonate (**7q**) could be formed from propylene oxide in up to 77% yield catalysed by complex **9a** (Table 5, entry 17), it clearly did not inhibit the activity of the catalysts. Therefore, the catalytic activity of complex **9a** and tetrabutylammonium bromide in propylene carbonate and ethylene carbonate as solvents was investigated. The latter reaction was carried out at 40°C to keep the reaction within the liquid range of ethylene carbonate (m.p. 34–35°C). Both cyclic carbonates were found to be effective solvents.[57] The reactions were slightly faster in ethylene carbonate; this may be related to the higher reaction temperature, but the use of propylene carbonate was adopted for the kinetics work due to the experimental convenience of being able to carry out reactions at 26°C. The success of reactions carried out in propylene carbonate is probably related to the known solubility of carbon dioxide in this solvent.[62]

The progress of reactions could be monitored by sampling and subsequent GC–MS analysis (see Table 5), but this method was limited in the number of available data points and the timescale over which reactions could be monitored. Therefore, the use of in situ FTIR spectroscopy to monitor the reactions was investigated. Figure 3 shows a stack plot of the FTIR spectra recorded for the synthesis of styrene carbonate from styrene oxide catalysed by complex **9a**/tetrabutylammonium bromide. For reactions carried out under solvent-free conditions, the increase in intensity of the peak due to the carbonyl stretch vibration of the styrene carbonate at $\tilde{v} = 1800$ cm^{-1} provided a convenient way to monitor

the progress of the reactions. However, when the reaction was carried out in propylene carbonate, the carbonyl absorption of the propylene carbonate masked that of the styrene carbonate and no change in absorption intensity at 1800 cm^{-1} was apparent. The styrene carbonate absorptions at $\tilde{v} = 1100$ and 1000 cm^{-1} (Figure 3) were also masked by the solvent.

Reactions carried out in propylene carbonate could, however, be followed by monitoring the absorption at $\tilde{v} = 876$ cm^{-1}, as this area of the spectrum was not obscured by propylene carbonate absorptions. The peak at 876 cm^{-1} corresponds to the epoxide C–O stretch mode[27a] and diminishes in intensity during the conversion of styrene oxide into styrene carbonate (Figure 3). That the rate of disappearance of styrene oxide corresponded to the rate of formation of styrene carbonate (i.e., that there were no side reactions or build up of an intermediate) was confirmed by monitoring a reaction in propylene carbonate by both in situ FTIR (at $\tilde{v} = 876$ cm^{-1}) and by sampling followed by analysis of the amounts of styrene oxide and styrene carbonate present by GC–MS. The GC–MS data points were found to fit to the FTIR intensity data.[57]

Prior to starting a full kinetics analysis, the relative catalytic activity of dinuclear complex **9a** and mononuclear complex **5** was studied. Figure 4 shows the reaction profiles obtained by using in situ FTIR for reactions catalysed by tetrabutylammonium bromide (2.5 mol%) alone, complex **5** and tetrabutylammonium bromide (2.5 mol% each), and complex **9a** and tetrabutylammonium bromide (2.5 mol% each). It is apparent that the combination of mononuclear complex **5** and tetrabutylammonium bromide is only marginally more active than tetrabutylammonium bromide alone, whereas the combination of dinuclear complex **9a** and tetrabutylammonium bromide shows significantly enhanced catalytic activity.

The reaction kinetics shown in Figure 4 are pseudo-zero order as the reactions were carried out under solvent-free
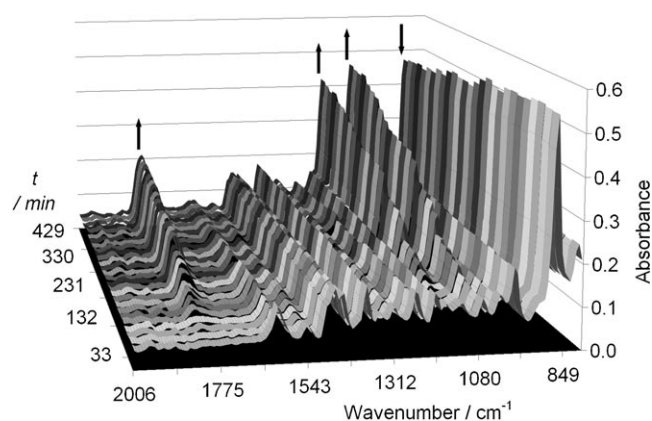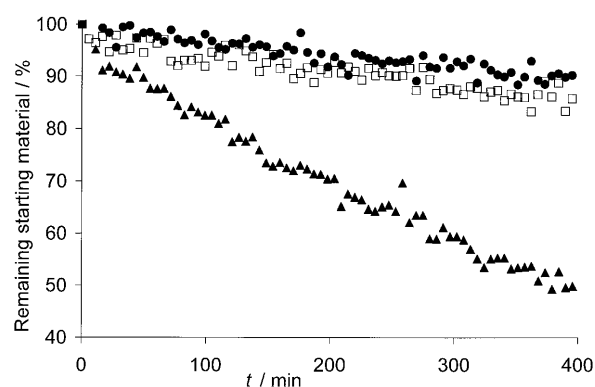

Figure 3. FTIR spectra of the synthesis of styrene carbonate from styrene oxide under solvent-free conditions by using complex **9a** (2.5 mol%) and tetrabutylammonium bromide (2.5 mol%) as catalyst. The up arrows indicate peaks resulting from styrene carbonate at $\tilde{v} = 1800$, 1100 and 1000 cm^{-1}, whereas the down arrow indicates the peak referring to styrene oxide at $\tilde{v} = 876$ cm^{-1}.

Figure 4. Comparison of the kinetics of styrene carbonate synthesis catalysed by tetrabutylammonium bromide alone (●), complex **5** and tetrabutylammonium bromide (□), and complex **9a** and tetrabutylammonium bromide (▲). All reactions were carried out under solvent-free conditions at 26°C with one atmosphere pressure of CO$_2$ and monitored by in situ FTIR spectroscopy at $\tilde{v} = 1800$ cm^{-1}.
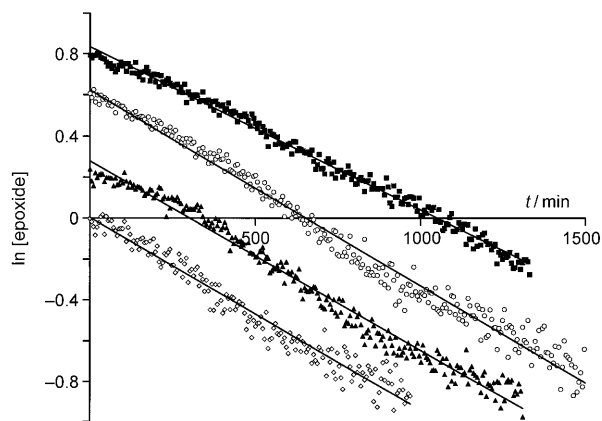
Figure 5. First-order kinetics plots for the conversion of styrene oxide into styrene carbonate at 26 °C in propylene carbonate with one atmosphere pressure of CO_2 catalysed by complex **9a** (46 mM) and tetrabutylammonium bromide (48 mM) and monitored by in situ FTIR spectroscopy at $\tilde{\nu} = 876$ cm^{-1}. (■: [styrene oxide]$_0$ = 2.2 M, $y = -0.0008x + 0.8339$, $R^2 = 0.9912$; ○: [styrene oxide]$_0$ = 1.8 M, $y = -0.0010x + 0.6226$, $R^2 = 0.9845$; ▲: [styrene oxide]$_0$ = 1.3 M, $y = -0.0009x + 0.2797$, $R^2 = 0.9817$; ◇: [styrene oxide]$_0$ = 1.0 M, $y = -0.0009x + 0.0039$, $R^2 = 0.9606$).

conditions. However, when reactions catalysed by complex **9a** were carried out in propylene carbonate, first-order kinetics were observed. Figure 5 shows the first-order kinetics plots obtained with four different initial concentrations of styrene oxide and clearly illustrates that first-order kinetics are observed over a wide range of styrene oxide concentrations. The full rate equation for the synthesis of styrene carbonate by using catalyst **9a** and tetrabutylammonium bromide will have the form shown in Equation (1). Since complex **9a** and tetrabutylammonium bromide both act both as catalysts (and assuming their concentration does not change significantly during the reaction), Equation (1) can be re-written as Equation (2). For any reaction in which the concentration of carbon dioxide remains constant (including the reactions shown in Figure 5 where a large excess of carbon dioxide was used), the rate equation can be further simplified to Equation (3), from which it can be deduced that the reactions shown in Figure 5 are first order in styrene oxide concentration ($a = 1$). Taking the logarithm of Equation (3) leads to Equation (4), which can be used to obtain the orders with respect to carbon dioxide, complex **9a** and tetrabutylammonium bromide.

$$\text{Rate} = k[\text{epoxide}]^a[\text{CO}_2]^b[\mathbf{9a}]^c[\text{Bu}_4\text{NBr}]^d \tag{1}$$

$$\text{Rate} = k_{\text{obs}}[\text{epoxide}]^a[\text{CO}_2]^b \quad \text{where } k_{\text{obs}} = k[\mathbf{9a}]^c[\text{Bu}_4\text{NBr}]^d \tag{2}$$

$$\text{Rate} = k_{\text{obs}'}[\text{epoxide}]^a \quad \text{where } k_{\text{obs}'} = k[\text{CO}_2]^b[\mathbf{9a}]^c[\text{Bu}_4\text{NBr}]^d \tag{3}$$

$$\log(k_{\text{obs}'}) = b\log[\text{CO}_2] + c\log[\mathbf{9a}] + d\log[\text{Bu}_4\text{NBr}] \tag{4}$$

The order with respect to the carbon dioxide concentration [b in Eqs. (1)–(4)], could not be determined from ex-

periments carried out under a pure carbon dioxide atmosphere. Therefore, the apparatus was redesigned to allow reactions to be carried out at one atmosphere pressure, but with carbon dioxide and nitrogen both being fed continuously during the reaction from gas cylinders through mass flow controllers (12.5 mL min^{-1} total flow).[57] This allowed the concentration of carbon dioxide in the atmosphere above the reaction to be varied, whilst being held at a constant value during a particular reaction. The rate at which carbon dioxide dissolves in propylene carbonate is known,[63] and is far faster than the rate of cyclic carbonate formation. Therefore, a rapid equilibrium will be established between the mole fraction of carbon dioxide in the gas phase above the reaction and the concentration of carbon dioxide dissolved in the reaction mixture. Thus, the concentration of dissolved carbon dioxide will be proportional to the mole fraction of carbon dioxide in the gas flow over the reaction. A control experiment showed that when the gas flow was 100 % carbon dioxide, formation of styrene carbonate occurred at the same rate as when a static atmosphere of 100 % carbon dioxide was used.[57] The results of experiments carried out at five different carbon dioxide mole fractions in the range 3.7–23.1 % gas flow are shown in Figure 6. A plot of log-($k_{\text{obs}'}$) against log[CO_2] had a slope of 0.93 suggesting that $b = 1$ [Eq. (4)].[57] This was confirmed by Figure 7, which shows a plot of $k_{\text{obs}'}$ against the carbon dioxide mole fraction, resulting in a linear correlation passing through the origin [as required by Eq. (3)]. However, at mole fractions of carbon dioxide greater than 23 %, the correlation between $k_{\text{obs}'}$ and the carbon dioxide mole fraction was not linear, corresponding to saturation of the propylene carbonate solution with carbon dioxide.[57]

To determine the order with respect to the concentration of complex **9a** [c in Eqs. (1)–(4)], reactions were carried out
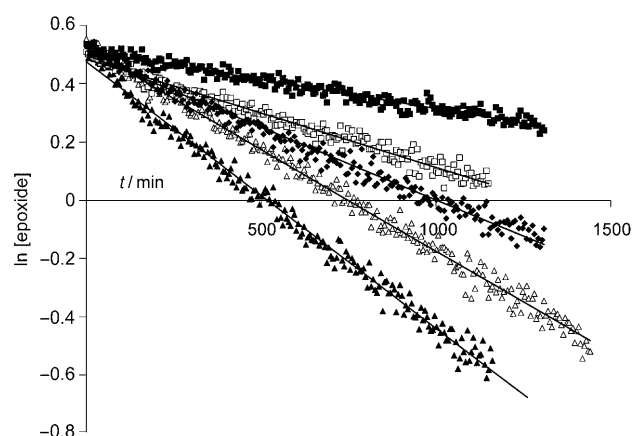

Figure 6. First-order kinetics plot at five different gas-phase mole fractions of CO_2. The reactions were carried out in propylene carbonate at 26 °C with [**9a**] = 47 mM, [Bu$_4$NBr] = 48 mM and [styrene oxide]$_0$ = 1.7 M and monitored by in situ FTIR spectroscopy at $\tilde{\nu} = 876$ cm^{-1}. (■: [CO_2] = 3.7 %, $y = -0.0002x + 0.5118$, $R^2 = 0.9545$; □: [CO_2] = 7.1 %, $y = -0.0004x + 0.4834$, $R^2 = 0.9692$; ◆: [CO_2] = 11.0 %, $y = -0.0005x + 0.4981$, $R^2 = 0.983$; △: [CO_2] = 14.3 %, $y = -0.0007x + 0.5221$, $R^2 = 0.9922$; ▲: [CO_2] = 23.1 %, $y = -0.0009x + 0.4738$, $R^2 = 0.9907$).

under a carbon dioxide atmosphere at four different concentrations of complex **9a** (Figure 8). The data were analysed according to Equations (3) and (4) as discussed above for
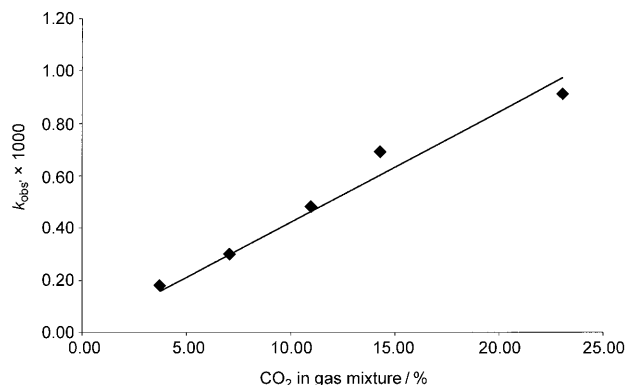

Figure 7. Plot of $k_{obs'}$ against CO_2 mole fraction in the gas phase ($y = 0.0422x$, $R^2 = 0.9642$).

determining the order with respect to carbon dioxide. The double logarithmic plot[57] had a slope of 1.1, again suggesting that the reaction was first order in the concentration of complex **9a**. This was again confirmed by a plot of $k_{obs'}$ against [**9a**] (Figure 9), which gave a linear correlation passing through the origin.

Reactions at four different concentrations of tetrabutylammonium bromide were used to determine the order with respect to the concentration of ammonium bromide [d in Eqs. (1)–(4)]. Figure 10 shows the FTIR data recorded at the different tetrabutylammonium bromide concentrations. Notably, at the lowest concentration (23 mM), the reaction has a significant induction period, which, in view of the detection of tributylamine in the reaction mixture, was suspected to be a result of the in situ formation of tributyl-

Figure 9. Plot of $k_{obs'}$ against [**9a**] ($y = 322.24x$, $R^2 = 0.9767$).

Figure 10. Styrene carbonate synthesis at four different concentrations of Bu_4NBr. The reactions were carried out in propylene carbonate under a CO_2 atmosphere at 26°C with [styrene oxide]$_0 = 1.6$ M and [**9a**] $= 48$ mM and monitored by in situ FTIR spectroscopy at 876 cm^{-1}. (▲: [Bu_4NBr] $= 23$ mM; □: [Bu_4NBr] $= 27$ mM; ■: [Bu_4NBr] $= 37$ mM; △ [Bu_4NBr] $= 48$ mM).

amine being necessary for the synthesis of cyclic carbonates. It was not possible to increase the concentration of tetrabutylammonium bromide above 50 mM as this represented the solubility limit of the ammonium salt in propylene carbonate. Transformation of the data presented in Figure 10 into first-order kinetics plots[57] still gave a linear correlation between ln[epoxide] and time, though with a less good fit for the reaction carried out at the lowest concentration of tetrabutylammonium bromide (23 mM) as a result of the induction period. Surprisingly, the double logarithmic plot of log-($k_{obs'}$) against log[Bu_4NBr] had a slope of two, indicating that the reaction was second order in tetrabutylammonium bromide concentration.[57] This was confirmed by a plot of $k_{obs'}/[Bu_4NBr]$ against [Bu_4NBr] (Figure 11), which gave a linear correlation passing through the origin.

The results of this kinetic study show that the synthesis of styrene carbonate catalysed by complex **9a** and tetrabutylammonium bromide obeys the following rate equation:
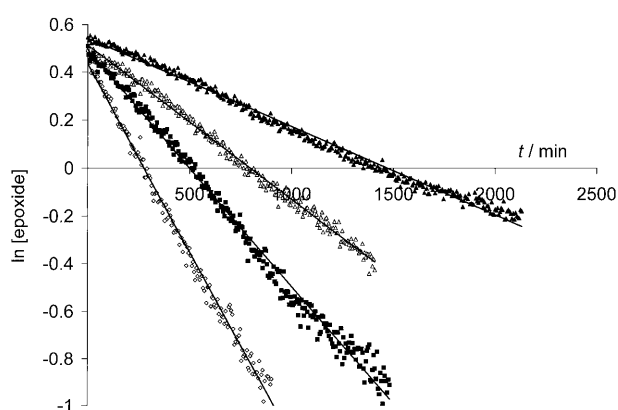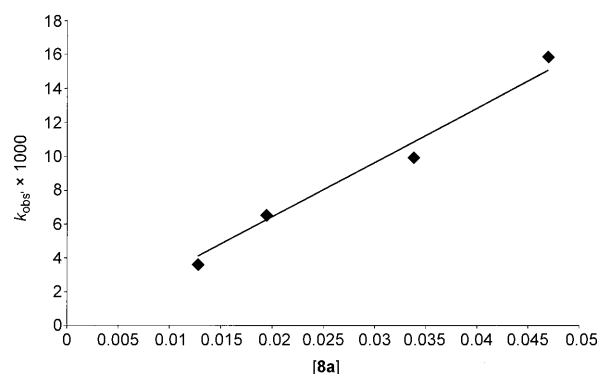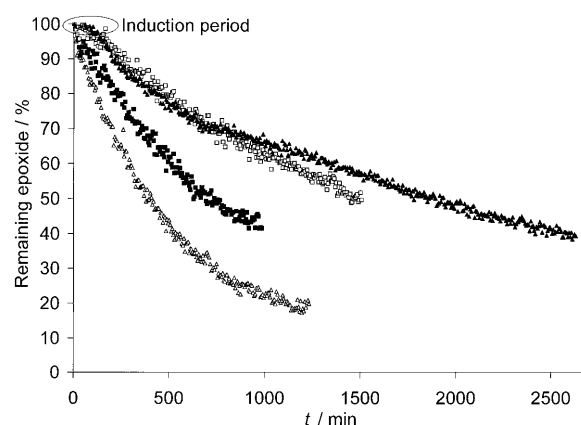

Figure 8. First-order kinetics plot at four different concentrations of complex **9a**. The reactions were carried out in propylene carbonate under a CO_2 atmosphere at 26°C with [Bu_4NBr] $= 48$ mM and [styrene oxide]$_0 = 1.6$ M and monitored by in situ FTIR spectroscopy at $\tilde{\nu} = 876$ cm^{-1}. (▲: [**9a**] $= 13$ mM, $y = -0.0004x + 0.5429$, $R^2 = 0.9916$; △: [**9a**] $= 19$ mM, $y = -0.0006x + 0.51330$, $R^2 = 0.9934$; ■: [**9a**] $= 34$ mM, $y = -0.0010x + 0.49405$, $R^2 = 0.9914$; ◇: [**9a**] $= 47$ mM, $y = -0.0016x + 0.4347$, $R^2 = 0.9927$).

$$\text{Rate} = k[\text{epoxide}][CO_2][\textbf{9a}][Bu_4NBr]^2$$

The unexpected feature of this rate equation was the second-order dependence on the concentration of tetrabutylammonium bromide. As discussed above (Scheme 4), one well established role of the tetraalkylammonium bromide in the synthesis of cyclic carbonates is to provide the bromide, which is needed to ring open the epoxide.[27,28,42a,47] However, the kinetic data suggest that the tetrabutylammonium bromide has another function before the
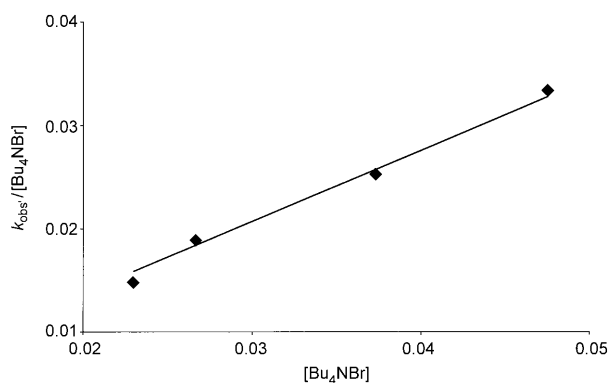

Figure 11. Plot of $k_{obs'}/[Bu_4NBr]$ against $[Bu_4NBr]$, which shows that the synthesis of styrene carbonate is second order in $[Bu_4NBr]$ ($y = 0.6908x$, $R^2 = 0.9913$).

rate-determining step of the catalytic cycle. The kinetic data (Figure 10) also showed that the reaction had an induction period when the concentration of tetrabutylammonium bromide was low. As tributylamine is known to be formed in situ (Figure 2), this suggested that the tributylamine was involved in the catalytic cycle. To investigate this assumption, a further series of kinetic experiments was carried out in which tributylamine as well as tetrabutylammonium bromide and complex **9a** were added to the reactions. A control experiment using tributylamine and complex **9a** (2.5 mol% each) but no tetrabutylammonium bromide as the catalyst system gave just 1% conversion of styrene oxide to styrene carbonate after a reaction time of 24 h as determined by GC–MS.

To account for the possible involvement of tributylamine in the catalytic cycle, Equations (1)–(4) were modified to give Equations (5)–(7). Two additional series of kinetics experiments were then carried out to determine the order with respect to tetrabutylammonium bromide and tributylamine under these reaction conditions.

$$\text{Rate} = k[\text{epoxide}]^a[\text{CO}_2]^b[\mathbf{9a}]^c[\text{Bu}_4\text{NBr}]^d[\text{Bu}_3\text{N}]^e \qquad (5)$$

$$\text{Rate} = k_{obs'}[\text{epoxide}]^a$$
$$k_{obs'} = k[\text{CO}_2]^b[\mathbf{9a}]^c[\text{Bu}_4\text{NBr}]^d[\text{Bu}_3\text{N}]^e \qquad (6)$$

$$\log(k_{obs'}) = b\log[\text{CO}_2] + c\log[\mathbf{9a}] + d\log[\text{Bu}_4\text{NBr}] + e\log[\text{Bu}_3\text{N}] \qquad (7)$$

The first series of kinetics experiments was carried out by

using four different concentrations of tetrabutylammonium bromide in conjunction with complex **9a** (2.5 mol%) and tributylamine (1.25 mol%) to determine the order with respect to the tetrabutylammonium bromide concentration in the presence of tributylamine. These reactions again obeyed first-order kinetics (Figure 12) and a plot of $\log(k_{obs'})$ against $\log[\text{Bu}_4\text{NBr}]$ was linear with a slope of 0.66 (Figure 13). Thus, addition of tributylamine to the reaction significantly reduces the order with respect to tetrabutylammonium bromide [d in Eqs. (1)–(7)] from 2 to 0.66. It is also significant that none of the reactions included in Figure 12 showed an induction period (see Figure 10) even though the lowest concentration of tetrabutylammonium bromide used to generate the data in Figure 12 was the same as the lowest concentration used in Figure 10.
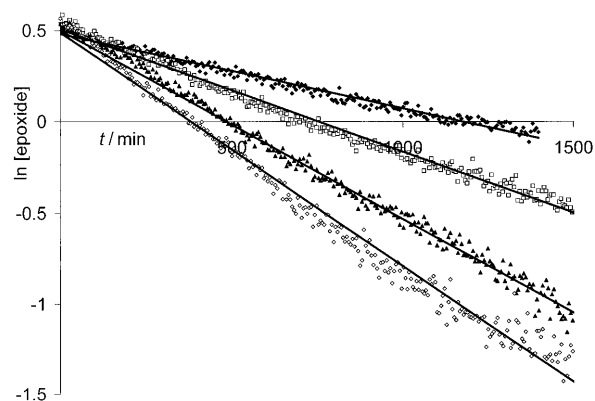

Figure 12. Synthesis of styrene carbonate at four different concentrations of Bu_4NBr in the presence of Bu_3N. The reactions were carried out in propylene carbonate under a CO_2 atmosphere at 26 °C with [styrene oxide]$_0 = 1.6$ M, [**9a**] = 46 mM, [Bu_3N] = 23 mM and monitored by in situ FTIR spectroscopy at $\tilde{\nu} = 876$ cm^{-1}. (◆: [Bu_4NBr] = 22 mM, $y = -0.0004x + 0.4811$, $R^2 = 0.9804$; □: [Bu_4NBr] = 46 mM, $y = -0.0007x + 0.5063$, $R^2 = 0.9883$; ▲: [Bu_4NBr] = 92 mM, $y = -0.0010x + 0.5002$, $R^2 = 0.9827$; ◇: [Bu_4NBr] = 140 mM, $y = -0.0013x + 0.4882$, $R^2 = 0.9851$).

In an attempt to determine the order with respect to tributylamine [e in Eqs. (5)–(7)], a series of three experiments was carried out in which the concentration of tetrabutylammonium bromide was fixed at 1.25 mol% whereas the concentration of tributylamine was varied in the range 12–45 mM. The kinetic data for these experiments were very similar to one another, and a plot of $\log(k_{obs'})$ against $\log[\text{Bu}_3\text{N}]$ indicated that the order with respect to tributylamine was very low (ca. 0.13).[57] The concentration of tributylamine generated in situ by decomposition of tetrabutylammonium bromide was extremely low as shown in Figure 2 and by the fact that the concentration of tetrabutylammonium bromide can be treated as constant throughout a reaction. Therefore, a possible explanation of these results was that the amount of added tributylamine was sufficient to result in saturation kinetics so that little or no variation in the reaction rate with an increasing concentration of tributylamine was observed. Support for this hypothesis came
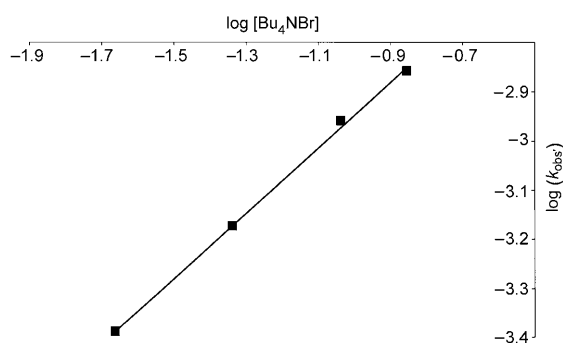
Figure 13. Double logarithmic plot $\log(k_{obs})$ against $\log[Bu_4NBr]$ to determine the order with respect to $[Bu_4NBr]$ in the presence of $[Bu_3N]$ ($y = 0.6642x - 2.2835$, $R^2 = 0.9994$).

from a series of kinetic experiments in which butyl bromide rather than tributylamine was added to the reaction along with tetrabutylammonium bromide and complex **9a**. The results (Figure 14) indicate that butyl bromide is an inhibitor of the reaction and are consistent with it requaternising tributylamine formed in situ. Once again, the reaction rate was independent of the amount of added butyl bromide, which is consistent with even the smallest amount added being a large excess relative to the amount of tributylamine present in the reaction mixture.

To show that the kinetics results were generally applicable and not relevant only to styrene oxide, the rates of reactions of seven substituted styrene oxides with carbon dioxide were monitored under the conditions shown in Figure 5 with an initial concentration of the epoxide of 1.8 M. In each case overall first-order kinetics was observed,[57] and the first-order rate constants are given in Table 6. The fact that all of the epoxides obeyed the same rate equation suggests that the results are generally applicable. Hammett plots[57] constructed by using Hammett substituent constants (either σ or σ^+) failed to provide any correlation between $\log(k_H/k_X)$ and the substituent constant, which suggests that the elec-

tronic nature of the aromatic substituents does not determine the reaction rate.

Table 6. First-order rate constants for the reactions of substituted styrene oxides.[a]

Epoxide	Aryl substituent	k_{obs} [min^{-1}][b]	σ	σ^+	ν_{max}[c] [cm^{-1}]
6f	4-F	0.00175	0.06	−0.07	876
6j	4-MeO	0.00531	−0.27	−0.78	876
6e	4-Me	0.00170	−0.14	−0.31	875
6a	H	0.00148	0	0	876
6k	3-MeO	0.00095	0.11	0.11	[d]
6i	4-MeS	0.00092	0	−0.60	885
6g	4-Cl	0.00071	0.23	0.11	876
6h	4-Br	0.00052	0.23	0.15	876

[a] Reactions were carried out at 26°C in propylene carbonate with [epoxide]$_0$ = 1.8 M, under one atmosphere pressure of CO_2 catalysed by complex **9a** (46 mM) and tetrabutylammonium bromide (48 mM) and monitored by in situ FTIR spectroscopy. [b] Average value obtained from two experiments. [c] Frequency used to monitor the reactions by in situ FTIR. [d] Reaction monitored by GC–MS instead of in situ FTIR due to the epoxide C–O stretch vibration at approximately $\tilde{\nu} = 875$ cm^{-1} being obscured by other vibrations.

As complex **9a** is derived from enantiomerically pure (*R,R*)-diaminocyclohexane, there was potential to carry out a kinetic resolution of a racemic epoxide by the formation of a cyclic carbonate. This has previously been achieved by using Co^{III}(salen) complexes.[23b,c,24] However, the kinetic data presented in Figure 5–14 show no change in rate at 50% conversion, which suggests that the aluminium complex **9a** would not be able to carry out a kinetic resolution. This was confirmed by carrying out a reaction with racemic styrene oxide under the standard conditions (Scheme 2), but stopping the reaction at 50% conversion. Both the unreacted styrene oxide and the styrene carbonate were isolated and found to be racemic by chiral HPLC analysis.[57]

Although a kinetic resolution was not possible, the effect of using enantiomerically pure styrene oxide was investigated to see if the stereochemistry of the epoxide was retained during the styrene carbonate synthesis. Thus, enantiomerically pure (*R*)-styrene oxide (*ee* > 98%) was treated with catalyst **9a** and tetrabutylammonium bromide under the standard reaction conditions (Scheme 2). Styrene carbonate was isolated in 76% yield after a reaction time of 20 h and was determined to be enantiomerically pure by chiral HPLC analysis.[57] Hence, the conversion of epoxides into cyclic carbonates by using complex **9a** and tetrabutylammonium bromide as the catalyst system preserves the stereochemistry of the epoxide.

Based on the mechanistic results presented above, it was possible to develop a catalytic cycle for the synthesis of cyclic carbonates, which explains the uniquely high catalytic activity of the complex **9a**/tetrabutylammonium bromide catalyst system (Scheme 5). The catalytic cycle starts with the coordination of the epoxide to a Lewis acidic aluminium of complex **9a**, followed by ring-opening of the epoxide by bromide to form the metal-coordinated bromo alkoxide **11**.
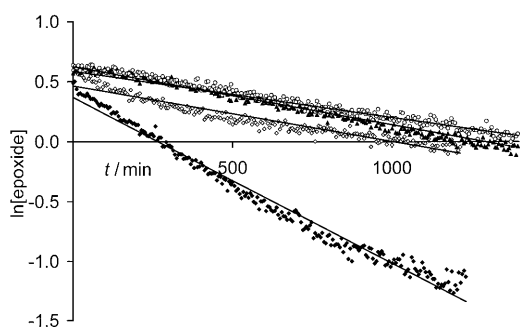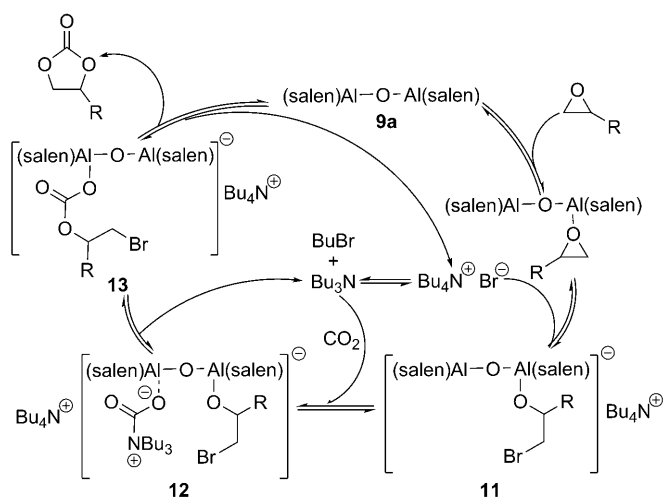

Figure 14. Influence of butyl bromide on the rate of the formation of styrene carbonate. The reactions were carried out at 26°C with [styrene oxide]$_0$ = 1.6 M, [**9a**] = 48 mM, [Bu$_4$NBr] = 45 mM and in the presence of excess CO_2. Reactions were monitored by in situ FTIR spectroscopy at $\tilde{\nu} = 876$ cm^{-1}. (◆: [BuBr] = 0 mM, $y = -0.0014x + 0.3691$, $R^2 = 0.9804$; ○: [BuBr] = 5 mM, $y = -0.0004x + 0.5861$, $R^2 = 0.9666$; ▲: [BuBr] = 26 mM, $y = -0.0005x + 0.6249$, $R^2 = 0.978$; ◇: [BuBr] = 45 mM, $y = -0.0005x + 0.4652$, $R^2 = 0.9213$).

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Scheme 5. Catalytic cycle for the cyclic carbonate synthesis by using complex **9a** and Bu$_4$NBr.

The fact that only terminal epoxides were used as substrates for the catalyst system, combined with the absence of any Hammett correlation for substituted aryl epoxides (Table 6)[57] indicates that ring-opening occurs at the terminal end of the epoxide. This is also consistent with the complete retention of stereochemistry observed when enantiomerically pure styrene carbonate was used.

GC analysis of the reaction mixtures showed that tributylamine is generated in situ and the kinetic data obtained from reactions carried out with added tributylamine or butyl bromide clearly indicate that the tributylamine is involved in the catalytic cycle. As amines and other nitrogenous bases are known to react with carbon dioxide to form carbamic acids or carbamates,[64,65] the role of the tributylamine can be explained by its reaction with carbon dioxide and complex **11** to form complex **12**. Complex **12** contains both a coordinated alkoxide and a coordinated carbon dioxide derived species that bears a good leaving group. Thus, the key carbonate-forming reaction can now occur intramolecularly to form the aluminium-bounded carbonate **13** and regenerate tributylamine. It is the ability of complex **12** to activate and preorganise both components of the reaction that accounts for the unique catalytic activity of bimetallic aluminium complexes such as **9a**. Cyclisation of the aluminium-bound carbonate in complex **13** eliminates the cyclic carbonate product and regenerates tetrabutylammonium bromide and complex **9a**.

The catalytic cycle shown in Scheme 5 is consistent with the observed reaction kinetics provided certain conditions are met, and in particular accounts for the second-order dependence on the tetrabutylammonium bromide concentration as two tetrabutylammonium bromide molecules are involved in the catalytic cycle. The first-order dependence on the carbon dioxide concentration implies that the rate-limiting step of the catalytic cycle occurs after carbon dioxide is involved in the mechanism. Thus, the first step which could be rate limiting is the formation of complex **12**. As both sub-

sequent steps in the catalytic cycle are intramolecular, it is probable that the formation of complex **12** is actually the rate-limiting step. The first-order dependence on the concentration of complex **9a** implies that the coordination of the epoxide to complex **9a** does not proceed to completion. If it did, then saturation kinetics (and hence a zero-order dependence with respect to the concentration of complex **9a**) would be observed. This is also consistent with attempts to monitor cyclic carbonate synthesis by in situ NMR spectroscopy, or by electrospray mass spectrometry. In both cases, complex **9a** was the only aluminium-containing species that could be detected, which implies that species **11**–**13** are only formed with undetectable low concentrations. Similarly, the interaction between carbon dioxide and tributylamine must be a non-saturated equilibrium process.

Conclusion

Bimetallic aluminium salen complexes ([{Al(salen)}$_2$O]) have been developed as exceptionally active catalysts for the synthesis of cyclic carbonates from terminal epoxides in the presence of tetrabutylammonium bromide as a cocatalyst. The system displays catalytic activity at room temperature and atmospheric pressure under solvent-free conditions and the complexes are stable for over 60 reuses of the catalyst system. Thus, the system has the potential to be used to manufacture cyclic carbonates from waste carbon dioxide produced by major fixed-site producers, such as power stations, chemical plants, oil refineries, aluminium smelters or foundries. The most active catalysts were the most hydrophobic ones, consistent with the need for the catalyst to dissolve in the epoxide.

The mild reaction conditions allowed a detailed study of the reaction kinetics by using in situ FTIR spectroscopy.[27] The reaction was found to follow first-order kinetics in each reaction component, except for tetrabutylammonium bromide, for which an unexpected second-order dependence was observed. This was shown to be a result of the formation of tributylamine, which was generated in situ from tetrabutylammonium bromide and also showed catalytic activity. The kinetics indicated that no kinetic resolution occurred during the synthesis of cyclic carbonates.[23b,c,24] However, it was demonstrated that enantiomerically pure styrene oxide could be converted into styrene carbonate without racemisation.

On the basis of the experimental evidence, a catalytic cycle for the synthesis of cyclic carbonates has been proposed. The key feature of the mechanism is the preorganisation and activation of both components of the reaction by the bimetallic aluminium complex, which explains the exceptionally high levels of catalytic activity observed with the bimetallic complexes. The mechanism also fully explains the role of the tetrabutylammonium bromide by providing a role for the in situ generated tributylamine in activating the carbon dioxide. It is notable that many other catalyst systems for cyclic carbonate synthesis require the presence of a

tetraalkylammonium salt[21a–c,23c,24a] or a nucleophilic amine, such as 4-dimethylaminopyridine (DMAP),[23b,f,25a] as a cocatalyst, and the mechanism shown in Scheme 5 unifies these two catalyst classes. Presumably, if no halide is present, then the amine ring-opens the epoxide. Some metal-based catalysts are unstable in the presence of high concentrations of amines, which may explain why a particular metal-based catalyst tends to be active with either a tetraalkylammonium salt or a nucleophilic amine as cocatalyst, but not both.

Our work on cyclic carbonate synthesis is continuing and is directed towards the development of one-component catalyst systems[66] and immobilised catalysts[67] that are suitable for use in a flow reactor, as well as for the integration of energy and chemicals production.[68]

Experimental Section

Details of chemicals and instrumentation are given in the Supporting Information.

Synthesis of complex 9a by using aluminium metal: Salen ligand **8a** (1.0 g, 2.0 mmol) was added to EtOH (50 mL). Powdered aluminium or pieces of aluminium foil (0.1 g, 4.0 mmol) and a crystal of iodine (ca. 100 mg) were added and the reaction was heated to reflux with stirring for 24 h. The aluminium was seen to dissolve during the reaction with the formation of a grey suspension. After cooling, the solvent was evaporated in vacuo and the residue was taken up in CH_2Cl_2 and filtered through a pad of celite (ca. 5 cm) to remove aluminium residues. The filtrate was then washed with H_2O (3×30 mL), brine (30 mL) and then dried (Na_2SO_4). The CH_2Cl_2 was then evaporated and the residue rinsed with Et_2O leaving complex **9a** as a light yellow powder (1.04 g, 98%). $[\alpha]_D^{20} = -640$ ($c = 0.09$ in toluene) [lit.[31c]: $+715$ ($c = 1.0$ in toluene), for (S,S) enantiomer]. Spectroscopic data were consistent with the literature.[31c,38a,d]

Synthesis of complexes 9a–i by using aluminium(triethoxide): The corresponding salen ligand[49] **8a–i** (2.75 mmol) in toluene (40 mL) was heated to reflux under nitrogen, then Al(OEt)$_3$ (0.89 g, 5.5 mmol) was added, along with additional toluene (40 mL). The reaction mixture was stirred under reflux for 3–5 h before being allowed to cool to room temperature. The solvents were evaporated in vacuo, and the residue was dissolved in CH_2Cl_2 (200 mL) and extracted with H_2O (2×100 mL) and brine (2× 100 mL). The organic layer was dried (Na_2SO_4) and solvents were evaporated in vacuo to give a solid, which was purified as specified for each complex. Details for known complexes **9a,g,i** are given in the Supporting Information.

Complex 9b: The reaction was heated at reflux overnight and gave a yellow powder (1.11 g, 45%) after washing with cold Et_2O followed by chromatography on Sephadex LH50 by using toluene/ethanol (1:1) as eluent. $[\alpha]_D^{20} = -372$ ($c = 0.1$ in CHCl$_3$); ^{1}H NMR (500 MHz, CDCl$_3$, TMS): $\delta = 8.28$ (s, 4H), 7.29 (dd, $^3J(H,H) = 8.1$ Hz, $^4J(H,H) = 2.1$ Hz, 4H), 7.14 (d, $^4J(H,H) = 2.7$ Hz, 4H), 6.84 (d, $^3J(H,H) = 8.7$ Hz, 4H), 3.4–3.2 (m, 4H), 2.0–1.4 (m, 16H), 1.45 ppm (s, 36H); IR (ATR): $\tilde{v} = 2951$, 1633, 1538 cm^{-1}; MS (MALDI): m/z: 935.5 [M+H]$^+$, 893.6, 847.5, 775.4, 573.4, 459.3; HRMS (ESI): m/z: calcd for C$_{56}$H$_{73}$N$_4$O$_5$Al$_2$: 935.5212 [M+H]$^+$; found: 935.5223.

Complex 9c: The reaction was heated at reflux overnight and gave a yellow powder (0.74 g, 33%) after washing with cold Et_2O. $[\alpha]_D^{20} = -381$ ($c = 0.1$ in CHCl$_3$); ^{1}H NMR (500 MHz, CDCl$_3$, TMS): $\delta = 8.27$ (s, 4H), 7.5–7.4 (m, 4H), 7.2–7.1 (m, 4H), 7.0–6.9 (m, 4H), 6.9–6.8 (m, 4H), 3.4–3.3 (m, 4H), 2.0–1.5 ppm (m, 16H); IR (ATR): $\tilde{v} = 2863$, 1628, 1601, 1537 cm^{-1}; MS (MALDI): m/z: 711.3 [M+H]$^+$, 669.3, 364.1, 347.1; HRMS (ESI): m/z: calcd for C$_{40}$H$_{41}$N$_4$O$_5$Al$_2$: 711.2708 [M+H]$^+$; found: 711.2708.

Complex 9d: Obtained as an orange solid (1.31 g, 63%) after washing with Et_2O. $[\alpha]_D^{20} = -575$ ($c = 0.1$ in toluene); ^{1}H NMR (500 MHz, CDCl$_3$, TMS): $\delta = 8.64$ (s, 4H), 8.36 (s, 4H), 8.02 (s, 4H), 3.7–3.8 (br, 4H), 3.7–2.0 (m, 16H), 1.55 ppm (s, 36H); IR (ATR): $\tilde{v} = 2925$, 1638, 1599, 1573 cm^{-1}; MS (ESI): m/z: 1115.4 [M+H]$^+$; HRMS (ESI): m/z: calcd for C$_{56}$H$_{69}$N$_8$O$_{13}$Al$_2$: 1115.4615 [M+H]$^+$; found: 1115.4536.

Complex 9e: The reaction was heated at reflux overnight and gave a yellow powder (0.38 g, 30%) after washing with cold Et_2O followed by chromatography on Sephadex LH50 by using toluene/EtOH (1:1) as eluent. $[\alpha]_D^{20} = -612$ ($c = 0.1$ in CHCl$_3$); ^{1}H NMR (500 MHz, CDCl$_3$, TMS): $\delta = 8.26$ (s, 4H), 6.91 (d, $^4J(H,H) = 3.0$ Hz, 4H), 6.49 (d, $^4J(H,H) = 3.0$ Hz, 4H), 3.70 (s, 12H), 3.4–3.2 (m, 4H), 2.0–1.4 (m, 16H), 1.41 ppm (s, 36H); IR (ATR): $\tilde{v} = 2949$, 1627, 1552 cm^{-1}; MS (MALDI): m/z: 1055.6 [M+H]$^+$, 876.6, 848.5, 519.3, 494.3; HRMS (ESI): m/z: calcd for C$_{60}$H$_{81}$N$_4$O$_9$Al$_2$: 1055.5634 [M+H]$^+$; found: 1055.5641.

Complex 9f: The reaction was heated at reflux overnight and gave a yellow powder (0.79 g, 35%) after washing with cold Et_2O. $[\alpha]_D^{20} = -753$ ($c = 0.1$ in CHCl$_3$); ^{1}H NMR (500 MHz, CDCl$_3$, TMS): $\delta = 9.87$ (s, 4H), 7.18 (dd, $^3J(H,H) = 8.9$ Hz, $^4J(H,H) = 3.0$ Hz, 4H), 7.03 (d, $^4J(H,H) = 3.1$ Hz, 4H), 6.97 (d, $^3J(H,H) = 9.0$ Hz, 4H), 3.82 (s, 12H), 3.8–3.5 (m, 4H), 1.5–1.2 ppm (m, 16H); IR (ATR): $\tilde{v} = 2937$, 2838, 1606, 1537 cm^{-1}; MS (MALDI): m/z: 831.3 [M+H]$^+$, 789.3, 662.4, 407.1; HRMS (ESI): m/z: calcd for C$_{44}$H$_{49}$N$_4$O$_9$Al$_2$: 831.3130 [M+H]$^+$; found: 831.3139.

Complex 9h: Obtained as a yellow powder (1.60 g, 54%) after washing with cold Et_2O. ^{1}H NMR (500 MHz, CDCl$_3$, TMS): $\delta = 8.32$ (s, 4H), 7.48 (d, $^4J(H,H) = 2.4$ Hz, 4H), 7.01 (d, $^4J(H,H) = 2.7$ Hz, 4H), 4.1–3.9 (br m, 8H), 3.2–3.0 (br m, 4H), 1.46 (s, 36H), 1.29 ppm (s, 36H); IR (ATR): $\tilde{v} = 2959$, 2159, 1621, 1258 cm^{-1}; MS (ESI): m/z: 1079.7 [M+H]$^+$, 868.7, 531.3, 360.3, 264.2; HRMS (ESI): m/z: calcd for C$_{66}$H$_{97}$N$_4$O$_5$Al$_2$: 1079.7090 [M+H]$^+$; found: 1079.7168.

General procedure for the synthesis of cyclic carbonates at atmospheric pressure: A mixture of one of the epoxides **6a–q** (2 mmol), Bu$_4$NBr (0–2.5 mol%) and one of the bimetallic aluminium(salen) complex **9a–i** (0–2.5 mol%) was vigorously stirred until complete dissolution occurred, then CO_2 was passed through the flask at atmospheric pressure. After being stirred at 25°C for 3–24 h, a sample of the reaction was analysed by ^{1}H NMR spectroscopy to determine the conversion, and the reaction mixture was purified as specified for each cyclic carbonate. Details for known cyclic carbonates are given in the Supporting Information.

4-(4-Fluorophenyl)-l,3-dioxolan-2-one (7 f): Conversion of 36% after 3 h. **7 f** was obtained as a white solid (0.29 g, 81%) after a reaction time of 24 h and purification by flash chromatography by using hexane/EtOAc (1:1) as eluent. m.p. 88–93°C; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): $\delta = 7.5$–7.4 (m, 2H), 7.2–7.0 (m, 2H), 5.66 (t, $^3J(H,H) = 7.8$ Hz, 1H), 4.79 (t, $^3J(H,H) = ^2J(H,H) = 8.4$ Hz, 1H), 4.32 ppm (t, $^3J(H,H) = ^2J(H,H) = 8.4$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): $\delta = 163.6$ (d, $^1J(C,F) = 993$ Hz), 154.3 (d, $^7J(C,F) = 6.0$ Hz), 131.9 (d, $^4J(C,F) = 12.0$ Hz), 127.9 (d, $^3J(C,F) = 33.0$ Hz), 116.4 (d $^2J(C,F) = 87.0$ Hz), 77.3, 70.9 ppm; IR (neat): $\tilde{v} = 3066$, 1755, 1606, 1509 cm^{-1}; MS (EI): m/z (%): 182 (50) [M^+], 137 (30), 123 (55), 108 (100), 96 (50), 83 (25); HRMS (ESI): m/z: calcd for C$_9$H$_7$O$_3$FNa: 205.0277 [M+Na]$^+$; found: 205.0263.

4-(4-Thiomethylphenyl)-l,3-dioxolan-2-one (7i): Conversion 24% after 3 h. **7i** was obtained as a white solid (0.33 g, 78%) after a reaction time of 24 h and purification by flash chromatography (gradient from hexane to ethyl acetate as eluent). m.p. 66–68°C; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): $\delta = 7.28$ (s, 4H), 5.63 (t, $^3J(H,H) = 8.1$ Hz, 1H), 4.77 (t, $^3J(H,H) = ^2J(H,H) = 8.7$ Hz, 1H), 4.32 (t, $^3J(H,H) = ^2J(H,H) = 9.0$ Hz, 1H), 2.49 ppm (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): $\delta = 154.7$, 141.6, 127.6, 126.9, 100.0, 78.0, 71.1, 15.9 ppm; IR (ATR): $\tilde{v} = 1787$, 1155, 1045 cm^{-1}; MS (EI): m/z (%): 210 (100) [M^+], 166 (40), 137 (40), 91 (25); HRMS (ESI): m/z: calcd for C$_{10}$H$_{10}$O$_3$NaS: 233.0248 [M+Na]$^+$; found: 233.0228.

4-(3-Methoxyphenyl)-l,3-dioxolan-2-one (7k): Conversion 48% after 3 h. **7k** was obtained as a transparent oil (0.28 g, 72%) after a reaction time of 24 h and purification by flash chromatography (gradient from hexane to EtOAc as eluent). ^{1}H NMR (300 MHz, CDCl$_3$, TMS): $\delta = 7.37$ (t, $^3J(H,H) = 9.6$ Hz, 1H), 6.9–6.7 (m, 3H), 5.24 (t, $^3J(H,H) = 10.0$ Hz, 1H), 4.18 (t, $^3J(H,H) = ^2J(H,H) = 10.8$ Hz, 1H), 3.60 (t, $^3J(H,H) = ^2J(H,H) = 9.6$ Hz, 1H), 2.98 ppm (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$, TMS): $\delta =$

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181.0, 174.1, 152.4, 143.7, 127.9, 124.6, 119.7, 77.9, 69.6, 50.0 ppm; IR (neat): $\tilde{\nu}=2922$, 1785, 1603 cm^{-1}; MS (EI): m/z (%): 194 (100) [M^+], 150 (25), 91 (20); HRMS (ESI): m/z: calcd for $C_{10}H_{11}O_4$: 195.0657 [$M+$H]$^+$; found: 195.0677.

Ethylene carbonate (7r):[21d,69,70] A sample vial was charged with Bu$_4$NBr (0.09 g, 2.5 mol%) and complex **9a** (0.33 g, 2.5 mol%) and then cooled in an ice bath for 15 min, after which time ethylene oxide (0.48 g, 10.95 mmol) was added through a syringe. The reaction vial was then placed into a stainless steel reactor vessel, previously saturated with dry-ice pellets (approximately 5 g). The vessel was sealed and the reaction mixture was vigorously stirred for 24 h at room temperature, after which time the system had reached an internal pressure of approximately 6 atm. Then, excess CO$_2$ and unreacted ethylene oxide were vented, and the product was obtained as a white solid (0.73 g, 76%) after Kugelrohr distillation. m.p. 33–34°C (lit.:[69] 34–35°C). Spectroscopic data were consistent with the literature.[21d,69,70]

General procedure for the synthesis of styrene carbonate at greater than one atmosphere pressure: A sample vial was charged with DMAP or Bu$_4$NBr (0.02 mmol, 1.0 mol%), a metal(salen) complex (**3**, **5** or **9a**) (0.02 mmol, 1.0 mol%), styrene oxide (**6a**) (0.20 g, 1.67 mmol) and a magnetic stirrer bar. The reaction vial was then placed into a stainless steel reactor vessel, previously saturated with dry-ice pellets (approximately 5 g). The vessel was quickly sealed and placed into a thermostatted bath at 50°C. The reaction mixture was vigorously stirred for 24 h at 50°C, during which time the system maintained an internal pressure of approximately 8 atm. Then, the excess carbon dioxide was vented, and a sample of the reaction mixture was analysed by ¹H NMR spectroscopy to determine the conversion of styrene oxide to styrene carbonate.

Reuse of catalyst 9a in the synthesis of propylene carbonate: Complex **9a** (0.36 mmol, 2.5 mol%) and Bu$_4$NBr (0.36 mmol, 2.5 mol%) were placed in a 25 mL round bottomed flask equipped with a magnetic stirrer bar and a SubaSeal. The mixture was placed in an ice-bath and left for 10 min with CO$_2$ passing through the flask from a balloon inflated with several dry-ice pellets, until the system equilibrated to 0°C. Propylene oxide (**6q**) (0.83 g, 14.00 mmol) was then injected to the reaction mixture, which was stirred vigorously at 0°C for 3 h. The flask was then opened to air and allowed to warm to room temperature. During this time any unreacted propylene oxide evaporated. Propylene carbonate was isolated directly from the reaction flask by micro-distillation under reduced pressure (10 Torr) by using a Büchi Kugelrohr system at 140°C and was obtained as a transparent liquid. The product was analysed by ¹H NMR spectroscopy and GC–MS. The catalyst left in the reaction flask was reused in the next cycle following the procedure reported above.

General procedure for kinetics experiments by using CO$_2$ pellets: An epoxide (0.8–5.5 mmol), an aluminium salen complex **5**,**9a** (0–0.09 mmol), Bu$_4$NBr (0–0.4 mmol), tributylamine (0–0.04 mmol) and butyl bromide (0–45 mmol) were added to propylene carbonate (0.0–1.4 mL) and stirred vigorously until complete dissolution occurred. The solution was then added to a 200 mL Schlenk flask, which had been dried in an oven overnight and was equipped with a magnetic stirrer bar. The flask was fitted with the FT-IR probe and placed in a thermostatted bath at 26°C. A FT-IR spectrum was recorded to calibrate the initial concentration of the epoxide. CO$_2$ was then flushed into the reaction flask from a balloon containing several dry-ice pellets connected to the side tap of the Schlenk flask. A FT-IR spectrum was recorded every 5.5 min. The reaction could also be monitored by GC–MS by withdrawing samples from the reaction every 30 min. After completion of the reaction, the FT-IR peak areas (or GC areas) were converted into concentrations of epoxide by using a predetermined calibration table[57] and plotted against time to obtain the reaction profile.

Determination of the reaction order with respect to CO$_2$: Styrene oxide (**6a**) (3.33 mmol), complex **9a** (0.08 mmol) and Bu$_4$NBr (0.08 mmol) were added to propylene carbonate (1.43 mL) and the mixture was vigorously stirred until complete dissolution occurred. The solution was then added to a 200 mL Schlenk flask with two glass taps that had been dried in an oven overnight and was equipped with a magnetic stirrer bar. The flask was fitted with the FT-IR probe and placed in a thermostatted bath at 26°C. A FT-IR spectrum was recorded to calibrate the initial concen-

tration of styrene oxide. CO$_2$ mixtures (4–100% v/v) were prepared from cylinders of CO$_2$ and N$_2$, which were connected to mass flow controllers (20–200 mL min^{-1}) through PTFE tubing. The gas streams were adjusted in order to obtain a constant flow rate of 12.5 mL min^{-1}, and passed through the reaction vessel. The flow rate was regularly checked with a digital Varian Intelliflow flow-meter. A FT-IR spectrum was recorded every 5.5 min. After completion of the reaction, the FT-IR peak areas were converted into concentrations of epoxide by using a predetermined calibration table[57] and plotted against time to obtain the reaction profile.

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