Catalysis Science & Technology

PAPER

Synthesis of cyclic carbonates catalysed by aluminium heteroscorpionate complexes†‡

Cite this: DOI: 10.1039/c3cy00810j

José A. Castro-Osma,[ab] Carlos Alonso-Moreno,[b] Agustín Lara-Sánchez,[b] Javier Martínez,[b] Michael North*[a] and Antonio Otero*[b]

Received 15th October 2013,
Accepted 19th November 2013

DOI: 10.1039/c3cy00810j

www.rsc.org/catalysis

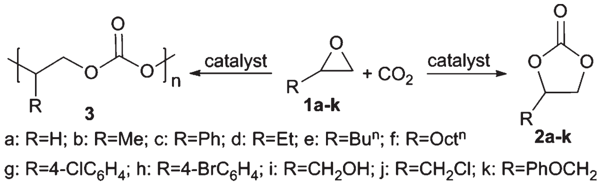
Parallel catalyst screening was used to develop new aluminium scorpionate based catalysts for the synthesis of cyclic carbonates from epoxides and carbon dioxide. Nineteen complexes were included in the catalyst screening, which resulted in the development of trimetallic complex **27** which had the same catalytic activity at one bar carbon dioxide pressure that the initial lead complex (**8**) had at ten bar carbon dioxide pressure. The combination of complex **27** and tetrabutylammonium bromide could be used to form cyclic carbonates from a range of terminal epoxides and kinetic studies showed that the reactions were first order in epoxide, complex **27** and tetrabutylammonium bromide concentrations. Based on this data a catalytic cycle has been proposed which accounts for all of features of the catalyst system.

Introduction

Carbon dioxide is a stable molecule with very low standard heat of formation (ΔH_f^o = −394 kJ mol^{-1}) and standard Gibbs energy of formation (ΔG_f^o = −395 kJ mol^{-1}).[1] However, there are many reactions of carbon dioxide which are exothermic and/or exergonic. In general, such reactions require the reaction of carbon dioxide with one or more molecules with a significantly higher ΔH_f^o and ΔG_f^o to produce a product which also has a low ΔH_f^o and ΔG_f^o. Well known commercially important reactions include the reaction of carbon dioxide with ammonia to form urea (ΔH_r = −101 kJ mol^{-1})[2] and the reaction of carbon dioxide with sodium phenolate to form the sodium salt of salicylic acid (ΔH_r = −31 kJ mol^{-1}).[3] Thus, carbon dioxide is increasingly being seen as a sustainable carbon source for a future chemicals industry which would not be dependent on crude oil supplies. This has resulted in a significant increase in interest in carbon dioxide chemistry in recent years[4] and the challenge is not so much overcoming the thermodynamics of the reactions, but rather finding suitable catalysts to lower the often rather high activation energies and allow reactions to be carried out at closer to ambient temperature and pressure.[5]

Another exothermic reaction of carbon dioxide is its reaction with epoxides **1** and this can be controlled to form either cyclic carbonates[7] **2** or aliphatic-polycarbonates[7,8] **3** (Scheme 1). These reactions are both highly exothermic (ΔH_r = −144 kJ mol^{-1} for the synthesis of ethylene carbonate[1] **2a**) being driven largely by the release of the strain energy in the three-membered epoxide ring. However, neither reaction occurs spontaneously, rather a suitable catalyst is required.

Aliphatic-polycarbonates **3** have the potential to provide greener alternatives to both aromatic-polycarbonates[9] (derived from bisphenol-A and phosgene) and to the polyether-polyols used within polyurethane foams.[10] A number of companies are working to commercialize the production of aliphatic-polycarbonates, and particularly effective catalysts for this reaction have been developed by the groups of Coates,[11] Darensbourg,[9,12] Lee[13] and Williams.[14] In contrast, the synthesis of cyclic carbonates **2** has been a commercial process since the 1950's[15] and cyclic carbonates already have a number of important applications[16] including as electrolytes for lithium-ion batteries[16,17] and as polar aprotic solvents.[16,18] Commercially, the two most important cyclic



Scheme 1 Synthesis of cyclic- and polycarbonates.

---

[a] Green Chemistry Centre of Excellence, Department of Chemistry, The University of York, Heslington, York, YO10 5DD, UK. E-mail: michael.north@york.ac.uk; Fax: +44 (0)1904 322 705; Tel: +44 (0)1904 324 545

[b] Departamento de Química Inorgánica, Orgánica y Bioquímica, Universidad de Castilla-La Mancha, 13071 Ciudad Real, Spain. E-mail: Antonio.Otero@uclm.es; Fax: +34 926 295 318; Tel: +34 926 295 300

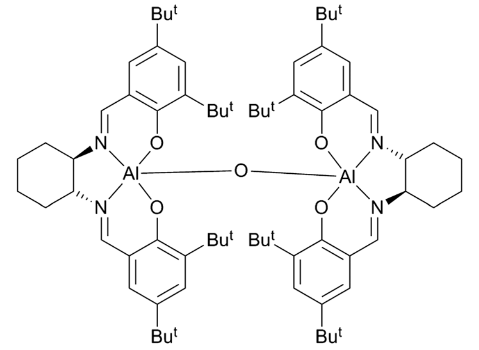
† This Article is Published in Celebration of the 50th Aniversary of the Opening of the Chemistry Department at the University of York.

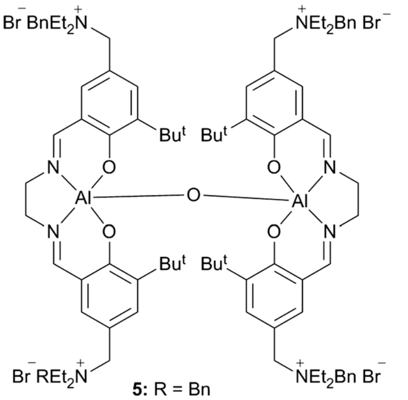
‡ Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra and mass spectra for cyclic carbonates **2a–k** and all kinetic plots. See DOI: 10.1039/c3cy00810j

This journal is © The Royal Society of Chemistry 2013

carbonates are ethylene carbonate **2a** and propylene carbonate **2b**. Current commercial processes for the production of cyclic carbonates rely on the use of relatively inefficient quaternary ammonium or phosphonium salts as catalysts[19] and this necessitates the reactions being carried out at high temperatures and pressures. However, in recent years, metal(salen) or metal(salophen) complexes have been developed by the groups of North[20,21] and Kleij[22] respectively which have a synergistic catalytic effect when used with quaternary ammonium cocatalysts and allow the synthesis of cyclic carbonates to occur at or close to room temperature and pressure.

Our previous work[23] started with the synthesis of bimetallic aluminium(salen) complex **4** (Fig. 1) and the demonstration that, in the presence of a tetrabutylammonium bromide cocatalyst, it would catalyse the synthesis of cyclic carbonates from terminal epoxides and carbon dioxide at ambient temperature and pressure.[20] Subsequent mechanistic studies highlighted the importance of the bimetallic nature of complex **4** as this allows the epoxide and carbon dioxide to both be activated and to be pre-organised for an intramolecular reaction.[24] Subsequently, one-component and immobilized catalysts **5** and **6** (Fig. 1) were prepared and shown to be active in both batch reactions and a gas-phase flow reactor. Complexes **4** and **6** were shown to be compatible with waste carbon dioxide present in power station flue gas[25] and complex **4** could also utilize the carbon dioxide present in compressed air and catalyse the synthesis of cyclic carbonates from internal epoxides at elevated temperatures and pressures.[26]


4


5: R = Bn
6: R = $(CH_2)_3$silica

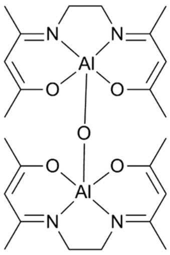

7

Fig. 1 Aluminium complexes which catalyse the synthesis of cyclic carbonates from terminal epoxides and carbon dioxide.

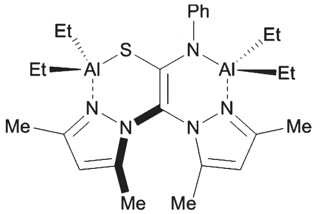

8

Fig. 2 Heteroscorpionate aluminium complex which catalyse the synthesis of cyclic carbonates from terminal epoxides and carbon dioxide.

Based on the importance of a bimetallic catalyst, we also prepared aluminium complex **7** (Fig. 1) based on the simpler acen ligand and showed that it was also an effective catalyst for the synthesis of cyclic carbonates from terminal epoxides and carbon dioxide at room temperature and 1 bar pressure.[27] Recently, other workers have also reported active catalysts for cyclic carbonate synthesis based on μ-oxo bridged bimetallic aluminium[28] or iron^{III} complexes.[29]

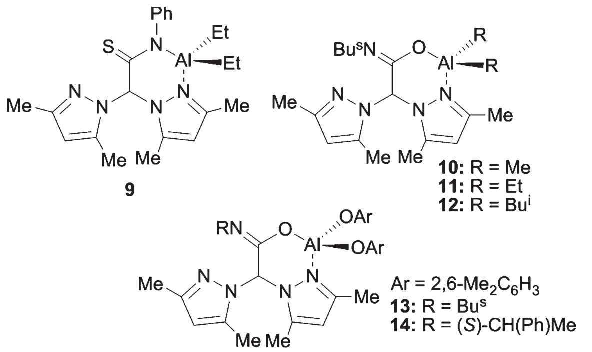
In recent years, the use of heteroscorpionate ligands has been widely explored due to their coordination abilities and the catalytic applications of their complexes.[30] In this context, Otero and coworkers have reported the synthesis of acetamidate and thioacetamidate heteroscorpionate aluminium complexes based on a bis(pyrazol-1-yl)methane moiety.[31] In these complexes, the heteroscorpionate ligand exhibits high versatility in its coordination mode due to the presence of three possible tautomers in solution.[32] These complexes act as efficient and versatile single-site initiators in the ring-opening polymerization and copolymerization of cyclic esters and in the ring-expansion polymerization of ε-caprolactone.[31] In a previous paper,[33] we also reported a different class of bimetallic aluminium complex **8** (Fig. 2), as a catalyst for the synthesis of cyclic carbonates from terminal epoxides. Complex **8** was active at room temperature, but did require an elevated pressure (10 bar) of carbon dioxide to display good levels of catalytic activity. In this paper we report the results of an extended study on the use of nineteen complexes related to complex **8** as catalysts for cyclic carbonate synthesis under mild reaction conditions.

Results and discussion

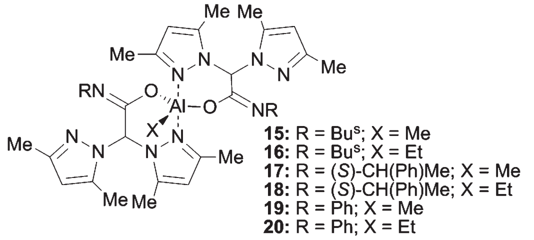
The structures of the aluminium complexes used in this study are shown in Fig. 3. These complexes have all been previously reported and characterized[31] and fall into five classes:

Complexes **9–12** are mononuclear alkylaluminium complexes in which the metal ion is coordinated to a single bis-pyrazole ligand.

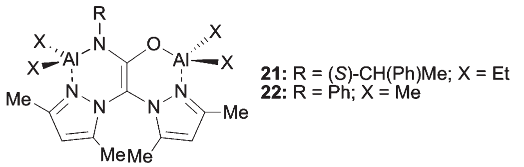
Complexes **13–14** are mononuclear aluminium phenoxide complexes in which the metal ion is coordinated to a single bis-pyrazole ligand.



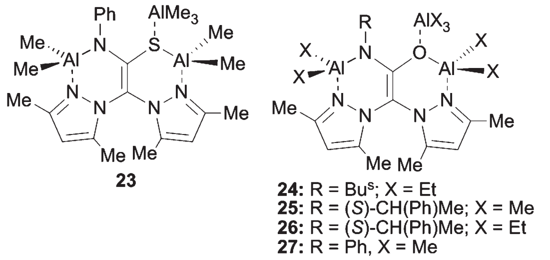
Mononuclear complexes with a single bis-pyrazole ligand



Mononuclear complexes with two bis-pyrazole ligands



Binuclear Complexes



Trinuclear Complexes

Fig. 3 Aluminium scorpionate complexes.

Complexes **15–20** are mononuclear alkylaluminium complexes in which the metal ion is coordinated to two bis-pyrazole ligands.

Complexes **21–22** are binuclear alkylaluminium complexes in which the metal ions are coordinated to a single bis-pyrazole ligand.

Complexes **23–27** are trinuclear alkylaluminium complexes in which the metal ions are coordinated to a single bis-pyrazole ligand.

Complex **9** was included in our previous study of aluminium scorpionate complexes[33] and was included here as a moderately active mononuclear catalyst with which complexes **10–27** could be compared.

Each of complexes **9–27** was initially screened for the conversion of styrene oxide **1c** into styrene carbonate **2c** at room temperature and 10 bar carbon dioxide pressure. Reactions were carried out in the absence of any solvent for 24 hours using 5 mol% of both complex **9–27** and tetrabutylammonium bromide, these conditions having previously been found to be optimal for reactions catalysed by complex **8**.[33] The catalyst screening was facilitated by carrying out reactions in parallel in magnetically stirred glass tubes within a two litre stainless steel pressure reactor. In this way, nine catalysts could be screened at once and the low volatility of styrene oxide and styrene carbonate combined with the raised pressure ensured that there was no cross-contamination of the reactions. Each reaction was then analysed by ^{1}H NMR spectroscopy without any purification to determine the conversion of epoxide **1c** into cyclic carbonate **2c** and the results are shown in Table 1. In all cases, the only species detected by ^{1}H NMR spectroscopy were unreacted epoxide and styrene carbonate. In particular, no formation of polycarbonate was observed in any of these reactions.

Mononuclear imidate complexes **10–12** all displayed good levels of catalytic activity under these reaction conditions (Table 1, entries 2–4, compared to the previously reported mononuclear thioamidate complex **9** (Table 1, entry 1). This suggests that the more electron-withdrawing oxygen–nitrogen ligand of complexes **10–12** generates a more Lewis acidic and hence more active aluminium ion than the nitrogen–nitrogen ligand of complex **9**. Changing the alkyl groups attached to the aluminium ion in complexes **10–12** to aryloxy groups in complexes **13–14** however had a very detrimental effect on the catalytic activity of the complexes (Table 1, entries 5–6). Based on previous work with complex **8**, this is likely to be due to the rapid hydrolysis of the alkyl groups of complexes **10–12**, leading to catalytically active μ-oxo bridged dimers or oligomers, a process which will be much slower for aryloxy complexes **13–14**. This is consistent with the fact that

Table 1 Conversion of epoxide **1c** into styrene carbonate **2c** using catalysts **9–27**[a]

Entry	Catalyst	10 bar[b] (%)	TOF[c] (h^{-1})	1 bar[b] (%)	TOF[c] (h^{-1})
1	**9**	44	0.37		
2	**10**	78	0.65		
3	**11**	77	0.64		
4	**12**	79	0.66		
5	**13**	28	0.23		
6	**14**	38	0.32		
7	**15**	46	0.38		
8	**16**	51	0.43		
9	**17**	39	0.33		
10		23	0.19		
11	**19**	26	0.22		
12	**20**	31	0.26		
13	**21**	100	0.83	77	0.64
14	**22**	60	0.50		
15	**23**	92	0.77	73	0.61
16	**24**	100	0.83	77	0.64
17	**25**	92	0.77	52	0.43
18	**26**	100	0.83	77	0.64
19	**27**	100	0.83	100	0.83

[a] Reactions carried out at room temperature and 1 or 10 bar CO_2 pressure for 24 hours using 5 mol% of catalyst and 5 mol% of Bu_4NBr cocatalyst. [b] Conversion determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [c] TOF = moles of product/(moles of catalyst · time).

complexes **10–12** all had essentially identical catalytic activity, suggesting that the alkyl groups attached to the aluminium may be displaced during the conversion of complexes **10–12** into catalytically active species.

Complexes **15–20** in which the aluminium ion is attached to two bidentate bis-pyrazole ligands, as well as an alkyl group, all displayed low to moderate catalytic activity (Table 1, entries 7–12). In these cases, the aluminium ion is sterically hindered by the two large ligands, so even if the alkyl group is displaced, the resulting μ-oxo bridged aluminium complexes will not be a good Lewis acid and will not be able to effectively coordinate too and hence activate epoxide **1c** towards ring-opening.

Bimetallic complex **21** was found to be a highly active catalyst, giving complete conversion of epoxide **1c** into styrene carbonate **2c** under the reaction conditions (Table 1, entry 13). Comparison of the results obtained for complexes **10–12** and **21** (Table 1, entries 2–4, 13) shows the added benefit of using a bimetallic complex. However, in this case the nature of the group attached to the enamine nitrogen atom was critical as changing this from a large alkyl group to a flat aryl group (complex **22**) resulted in a significant decrease in catalytic activity of the resulting complex (Table 1, entry 14), to a level below that seen for monometallic complexes **10–12**.

Finally coordination of an additional trialkylaluminium to the oxygen or sulphur atoms of bimetallic complexes gave trimetallic complexes **23–27**. These complexes all formed very active catalysts (Table 1, entries 15–19) with complexes **24**, **26** and **27** giving complete conversion of styrene oxide to styrene carbonate.

It is notable that all of the highly active catalysts were binuclear or trinuclear complexes. Four complexes (**21**, **24**, **26**, **27**) had given complete conversion of styrene oxide to styrene carbonate at 10 bar pressure and two other complexes (**23** and **25**) had given 92% conversion. Therefore, these six complexes were selected for a second round of catalyst screening in which the pressure was reduced from 10 bar to 1 bar, the results again being given in Table 1. All six complexes were still catalytically active under these conditions, and trimetallic complexes **23** and **25** which had given less than 100% conversion at 10 bar pressure again gave the lowest conversions at 1 bar carbon dioxide pressure. Bimetallic complex **21** and trimetallic complexes **24** and **26** all gave the same conversion (77%) at 1 bar pressure, a significant decrease compared to the 100% conversion observed at 10 bar pressure. In contrast, trimetallic complex **27** was now clearly seen to be the most active catalyst as it still gave complete conversion even at 1 bar carbon dioxide pressure.

Complex **27** was therefore selected for further reaction optimization and the effect of reducing the catalyst and cocatalyst loading (whilst maintaining a 1 : 1 catalyst to cocatalyst ratio) was investigated (Table 2). However, at room temperature and 1 bar carbon dioxide pressure, reducing the complex **27** and tetrabutylammonium bromide loadings to 2.5 mol% each reduced the conversion of epoxide **1c** to cyclic carbonate **2c** from 100 to 40% (Table 2, entries 1 and 2). Further reduction of the catalyst loadings to 1 mol% further reduced the conversion to 31% (Table 2, entry 3), though interestingly even at a 0.5 mol% loading of complex **27** and tetrabutylammonium bromide, a 16% conversion was obtained (Table 2, entry 4). Control experiments showed that under these reaction conditions, complex **27** alone had no catalytic activity (Table 2, entry 5), and tetrabutylammonium bromide alone gave only 5% conversion (Table 2, entry 6). The influence of the halide counterion in the tetraalkylammonium salt was also investigated and it was found that Br > I > Cl > F (Table 2, entries 1, 7–9). This is the same order of reactivity found in previous work[23] on cyclic carbonate synthesis using complex **4** and suggests that the optimal results are obtained when the halide is a good nucleophile (to ring-open the epoxide) and a good leaving group (to allow the cyclic carbonate to form). However, if the halide is too good a leaving group (iodide), then reformation of the epoxide can compete with reaction with carbon dioxide resulting in a slower rate of reaction. These results indicate, as far as we are aware, that complex **27** is the third most active aluminium based catalyst for styrene carbonate synthesis known (behind complexes **4** and **7**).

Table 2 Optimization of the synthesis of styrene carbonate **2c** using catalyst **27** and Bu_4NBr[a]

Entry	**27** (mol%)	Bu_4NX (mol%)	Conversion[b] (%)	TOF[c] (h^{-1})
1	5	Br (5)	100	0.83
2	2.5	Br (2.5)	40	0.33
3	1	Br (1)	31	0.26
4	0.5	Br (0.5)	16	0.13
5	5	0	0	0.00
6	0	Br (5)	5	0.04
7	5	F (5)	0	0.00
8	5	Cl (5)	34	0.28
9	5	I (5)	69	0.58

[a] Reactions carried out at room temperature and 1 bar CO_2 pressure for 24 hours. [b] Determined by ^1H NMR spectroscopy of the crude reaction mixture. [c] TOF = moles of product/(moles of catalyst · time).

Since complex **27** contains seven aluminium bound methyl groups in three different environments and the results discussed above had suggested that hydrolysis of these methyl groups by adventitious moisture might be important for the catalysis, the influence of added water on the catalytic activity of complex **27** was investigated. As shown in Fig. 4, the addition of up to 0.75 mol% of water had no detectable detrimental effect on the catalytic activity when 5 mol% of complex **27** and tetrabutylammonium bromide were used as catalysts. However, addition of just 1 mol% of water (enough to hydrolyse just 1 in every 17.5 aluminium bound methyl groups in complex **27**) reduced the conversion from 100 to 73%. Further addition of water resulted in a rapid drop in catalytic activity, giving a conversion of just 14% when 2.5 mol% of water was added. Thereafter, addition of up to 20 mol% of water (sufficient to hydrolyse all of the aluminium bound methyl groups) had no further detrimental effect on the catalytic activity of complex **27**.

This journal is © The Royal Society of Chemistry 2013

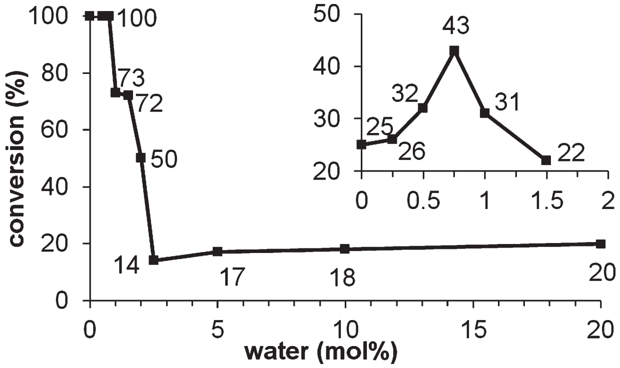


Fig. 4 Influence of added water on the conversion of styrene oxide **1c** into styrene carbonate **2c** after 24 hours at room temperature catalysed by complex **27** and Bu_4NBr (5 mol% each) with 1 bar CO_2. The inset is the results obtained using 2.5 mol% of complex **27** and Bu_4NBr.

The above experiments resulted in complete conversion of styrene oxide into styrene carbonate when up to 0.75 mol% of water was added. To more fully investigate the effect of small amounts of water (0–1.5 mol%), the study was repeated using just 2.5 mol% of both complex 27 and tetrabutylammonium bromide so that the reactions would not go to completion. The results are shown in the inset to Fig. 4 and indicate that there is an optimal amount of water (0.75 mol% when using 2.5 mol% of catalysts) and that use of more or less than this amount of water results in a lower conversion.

These results suggest that the catalytically active species derived from complex 27 still contains most of the aluminium bound methyl groups, but that approximately 9% of the aluminium methyl groups will have been hydrolysed to aluminium oxides. The same trend was previously seen for catalysis using complex 8 where the optimal amount of water was 0.75 mol% when using 5 mol% of complex 8 as catalyst.[33] The results can be explained on the basis of the catalytically active species being a dimer or higher oligomer with oxygen bridges between aluminium units replacing some of the methyl groups. However, addition of too much water will result in over hydrolysis to either a cross-linked catalytically inactive polymer or to aluminium oxides.

Having optimized the reaction conditions, the synthesis of eleven cyclic carbonates **2a–2k** derived from terminal epoxides **1a–1k** was investigated using 5 mol% of complex **27** and tetrabutylammonium bromide at room temperature (except for propylene oxide **1b** which was used at 0 °C due to its volatility) and 1 bar carbon dioxide pressure (except for gaseous ethylene oxide **1a** which was used in a sealed reactor at 2.5 bar) with no added water. In each case the reaction was left for 24 hours, then analysed to give a conversion and the cyclic carbonate separated and purified to give an isolated yield. The results of this study are shown in Table 3.

In general, all of the terminal epoxides studied gave good to excellent conversions to the corresponding cyclic carbonates under these conditions. Notably, this includes the functionalized epoxides **1i**, **1j** (Table 3, entries 11 and 12). The two exceptions were the aryl substituted epoxides **1g**, **1h** which under the standard conditions gave only moderate conversions to the corresponding cyclic carbonates **2g**, **2h** (Table 3, entries 7 and 9). However, these reaction mixtures were observed to solidify during the reaction, and by simply carrying out the reactions at 50 °C this could be avoided and the reactions then went to completion (Table 3, entries 8 and 10).

As an alternative way of avoiding problems due to reaction mixtures solidifying, the use of a solvent was also investigated. Table 4 summarises the results obtained when six different aprotic solvents were used. In all cases, the conversion was lower than when the reaction was carried out under solvent free conditions, but the combination of complex **27** and tetrabutylammonium bromide was more solvent tolerant than other catalyst systems for cyclic carbonate synthesis.[6,19] Butan-2-one was included in this study due to the excellent

Table 3 Conversion of epoxides **1a–1k** into cyclic carbonates **2a–2k** using catalyst **27** and Bu_4NBr[a]

Entry	Epoxide	Temperature (°C)	Conversion[b]	Yield[c]	TOF[d] (h^{-1})
1	**1a**	18	[e]	67	0.56
2	**1b**	0	[e]	85	0.71
3	**1c**	18	100	89	0.77
4	**1d**	18	100	85	0.74
5	**1e**	18	84	72	0.71
6	**1f**	18	100	92	0.60
7	**1g**	18	63	54	0.45
8	**1g**	50	100	84	0.70
9	**1h**	18	43	39	0.33
10	**1h**	50	100	86	0.72
11	**1i**	18	71	66	0.55
12	**1j**	18	94	82	0.68
13	**1k**	18	90	78	0.65
14[f]		18	11	7	0.06

[a] Reactions carried out at room temperature and 1 bar CO_2 pressure for 24 hours using 5 mol% of complex **27** and 5 mol% of Bu_4NBr cocatalyst. [b] Determined by ^1H NMR spectroscopy of the crude reaction mixture. [c] Yield of pure isolated cyclic carbonate. [d] TOF = moles of product/(moles of catalyst · time). [e] The volatile nature of epoxides **1a**, **1b** meant that conversions could not be determined. [f] Reaction carried out at 10 bar CO_2 pressure for 72 hours.

Table 4 Influence of solvent on the synthesis of styrene carbonate **2c** using catalyst **27** and Bu_4NBr[a]

Entry	Solvent	Conversion[b]	TOF[c] (h^{-1})
1	Toluene	83	0.69
2	Propylene carbonate **2b**	81	0.68
3	Acetonitrile	87	0.72
4	Butan-2-one	41	0.34
5	Dichloromethane	72	0.60
6	Tetrahydrofuran	58	0.48

[a] Reactions carried out at room temperature and 1 bar CO_2 pressure for 24 hours using 5 mol% of complex **27** and 5 mol% of Bu_4NBr cocatalyst at an epoxide concentration of 1.7 M. [b] Determined by ^1H NMR spectroscopy of the crude reaction mixture. [c] TOF = moles of product/(moles of catalyst · time).

results that Kleij *et al.* have previously reported in this solvent.[34] The results in Table 4 show that >80% conversions could be obtained in both toluene (Table 4, entry 1) and the polar aprotic solvents propylene carbonate[16,18] and acetonitrile (Table 4, entries 2 and 3) whilst other functionalized solvents gave lower conversions (Table 4, entries 4–6).

In view of the high catalytic activity shown by the complex **27**–tetrabutylammonium bromide catalyst system, an attempt was made to extend the chemistry to internal epoxides. These are well known to be much more challenging substrates for cyclic carbonate synthesis, but recently some significant successes have been made in this area.[26,35] Therefore, the conversion of cyclohexene oxide **28** into its cyclic carbonate **29** was investigated (Scheme 2). However, only an 11% conversion was obtained, even when the carbon dioxide pressure was increased to 10 bar and the reaction time extended to 72 hours (Table 2, entry 14). It was however possible to isolate a pure sample of compound **29**, and comparison of its NMR spectra with those reported in the literature[26,36] confirmed that the cyclic carbonate was formed as the *cis*-isomer, thus indicating that cyclic carbonate synthesis catalysed by complex **27**–tetrabutylammonium bromide proceeds with retention of the epoxide stereochemistry through a double inversion process.

To investigate the mechanism of cyclic carbonate synthesis catalysed by complex **27** and tetrabutylammonium bromide, a study of the reaction kinetics was carried out. This work required that the reaction was carried out in a solvent, and based on the results shown in Table 4, the use of acetonitrile was first investigated. However, it was desirable that kinetically monitored reactions went to high conversion in less than eight hours, and to achieve this, the reactions were carried out at 60 °C. Unfortunately, under these conditions, evaporation of the acetonitrile was a problem, so propylene carbonate was used as the solvent. Reactions were then carried out with styrene carbonate **1c** as substrate with an excess of carbon dioxide. Samples were removed from the reaction every hour and analysed by ^1H NMR spectroscopy to determine the conversion of epoxide **1c** into cyclic carbonate **2c** and hence to allow the concentrations of **1c** and **2c** to be calculated.

All the kinetic experiments showed a good fit to first order kinetics,‡ which, since carbon dioxide is present in excess, implies that the reactions are first order in styrene oxide: rate = k_{obs}[**1c**]. This was confirmed by reactions carried out at four different initial concentrations of styrene oxide **1c** which showed that the rate of formation of styrene carbonate **2c** increased as the initial concentration of styrene oxide **1c** increased (Fig. 5).

The concentrations of complex **27** and tetrabutylammonium bromide do not change during the reaction, so their contribution to the rate equation is incorporated within k_{obs}: $k_{obs} = k[\mathbf{27}]^x[Bu_4NBr]^y$. Thus, $\log(k_{obs}) = \log(k) + x\cdot\log[\mathbf{27}] + y\cdot\log[Bu_4NBr]$, so by carrying out reactions at various concentrations of complex **27** or tetrabutylammonium bromide whilst keeping all other conditions constant, a plot of $\log(k_{obs})$ against [**27**] or [Bu_4NBr] allows the order with respect to these two reaction components to be determined.‡ Control experiments showed that even at 60 °C in propylene carbonate, complex **27** (5 mol%) or tetrabutylammonium bromide (5 mol%) alone had minimal catalytic activity (after 7 hours; less than 1% reaction with complex **27** and 12% reaction with tetrabutylammonium bromide).‡ Reactions were thus carried out (in duplicate) at four concentrations of complex **27** and the resulting log/log plot had a slope of 0.93 suggesting that the reaction was first order in complex **27** concentration (*i.e.* that $x = 1$). This was confirmed by a plot of k_{obs} *versus* [**27**] which was also found to fit to a straight line (Fig. 6).

Similarly, reactions were carried out in duplicate at four concentrations of tetrabutylammonium bromide and the resulting log/log plot had a slope of 1.09 suggesting that the reaction was first order in tetrabutylammonium bromide concentration (*i.e.* that $y = 1$). This was confirmed by a plot of k_{obs} *versus* [Bu_4NBr] which was also found to fit to a straight line (Fig. 7). Thus, the synthesis of styrene carbonate **2c** from

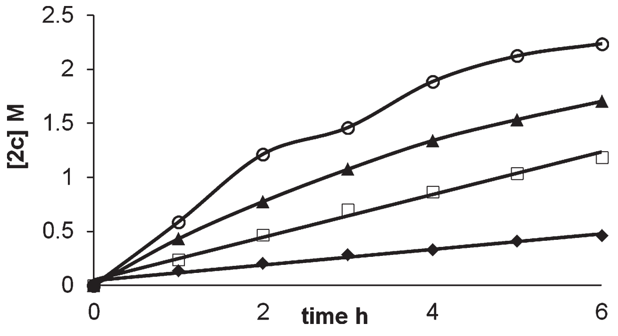
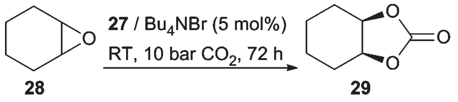


Fig. 5 Dependence of the rate of formation of **2c** on the concentration of epoxide **1c**. Reactions were carried out at 60 °C in propylene carbonate with [Bu_4NBr] = [**27**] = 70 mM. Filled diamonds, [**1c**]$_0$ = 0.81 M; empty squares, [**1c**]$_0$ = 1.58 M; filled triangles, [**1c**]$_0$ = 2.03 M; empty circles, [**1c**]$_0$ = 2.51 M.



Scheme 2 Synthesis of *cis*-cyclohexyl carbonate.

This journal is © The Royal Society of Chemistry 2013

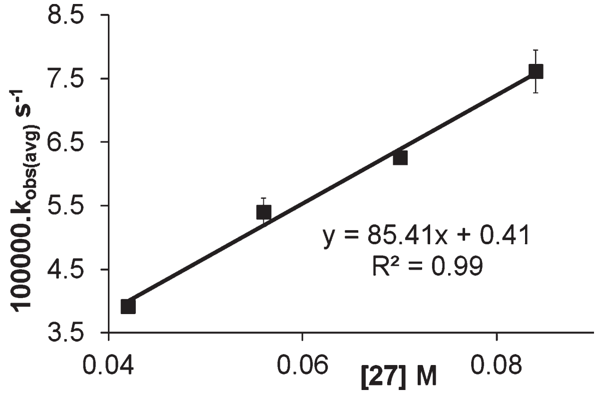


Fig. 6 Plot of the observed first order rate constant *versus* [**27**]. $k_{obs(avg)}$ is the average of two separate kinetic experiments at each concentration. The error bars are based on the results of the two separate kinetic experiments. Reactions were carried out at 60 °C in propylene carbonate with [**1c**]$_0$ = 1.6 M, [Bu_4NBr] = 70 mM and [**27**] = 42–84 mM.

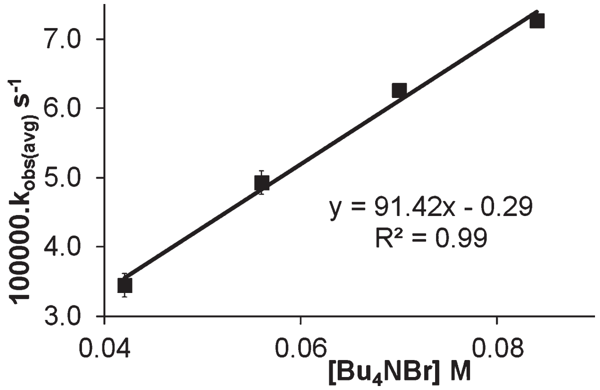
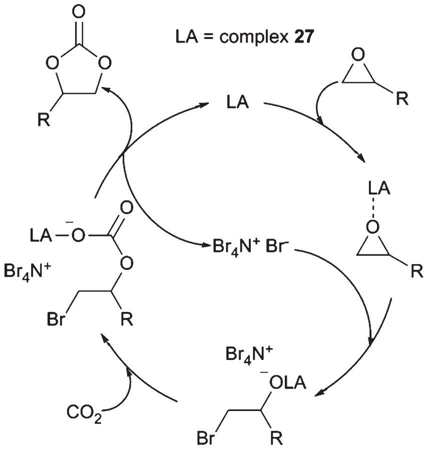


Fig. 7 Plot of the observed first order rate constant *versus* [Bu_4NBr]. $k_{obs(avg)}$ is the average of two separate kinetic experiments at each concentration. The error bars are based on the results of the two separate kinetic experiments. Reactions were carried out at 60 °C in propylene carbonate with [**1c**]$_0$ = 1.6 M, [**27**] = 70 mM and [Bu_4NBr] = 42–84 mM.

styrene oxide **1c** catalysed by complex **27** and tetrabutylammonium bromide can be represented by the rate equation: rate = k[Bu_4NBr][**27**][**1c**]. This rate equation has the same dependence on catalyst, tetrabutylammonium bromide and epoxide concentrations as that previously determined for reactions catalysed by complex **8** and in both cases, the reactions showed a good fit to overall first order kinetics.[33] This suggests that cyclic carbonate synthesis catalysed by complexes **8** and **27** occurs through the same mechanism and a possible catalytic cycle is shown in Scheme 3. It is well known[6] that the tetrabutylammonium bromide cocatalyst ring-opens the Lewis-acid coordinated epoxide to form a halo-alkoxide. In the case of catalysis by complex **27** (or more precisely by an *in situ* formed μ-oxo bridged oligomer of complex **27**), one of the three aluminium ions can act as the Lewis acid. Carbon dioxide can then insert into the metal alkoxide bond to give a metal carbonate which can ring-close to form the cyclic carbonate and regenerate the tetrabutylammonium bromide as shown in Scheme 3. The first order dependence of the kinetics on the concentration of complex **27** indicates that each monomer unit within the oligomer is independently catalytically active and thus that there is no cooperative catalysis between aluminium ions. Such cooperative catalysis was previously seen for reactions catalysed by complexes **4–7**,[23,24] but not for reactions catalysed by complex **8**.[33]



Scheme 3 Catalytic cycle for cyclic carbonate synthesis catalysed by complex **27** and Bu_4NBr.

Conclusions

Parallel catalyst screening has been used to enhance the activity of an initial aluminium scorpionate complex **8**, resulting in the development of trimetallic complex **27**. A combination of complex **27** and tetrabutylammonium bromide forms an active catalyst system for the synthesis of cyclic carbonates from carbon dioxide and terminal epoxides at ambient temperature and pressure. The turn over frequency (0.8 h^{-1}) observed with complex **27** at one bar carbon dioxide pressure is the same as that previously found for complex **8** at ten bar carbon dioxide pressure.

Whilst a large number of catalysts have been reported for the synthesis of cyclic carbonates from terminal epoxides and carbon dioxide, the vast majority of these require pressures above 15 bar and temperatures above 90 °C.[6] Only a small number of catalyst systems have been reported to be active at (or below) room temperature and at one bar carbon dioxide pressure. Of the aluminium based systems which are active under such mild conditions, complex **27** with a TOF of up to 0.8 h^{-1} is the third most active, outperformed only by complexes **4** and **7** (TOF 13–64 h^{-1}).[23,37] Other aluminium based catalysts have TOFs of <0.02 to 0.5 h^{-1} under similar reaction conditions.[38]

Experimental

Commercially available chemicals (Alfa, Aldrich, Fluka) were used as received. Complexes **9–27** were prepared as reported previously.[31] GC–MS were recorded on a Varian CP-800-SATURN 2200 GC–MS ion-trap mass spectrometer using a FactorFour (VF-5 ms) capillary column (30 m × 0.25 mm) with helium as the carrier gas. The conditions used were: initial temperature 60 °C, hold at initial temperature for 3 min then ramp rate 15 °C min^{-1} to 270 °C; hold at final temperature for 5 min. For the first 3.50 min, the eluent was routed away from the mass detector. Subsequently, the detector was operated in full EI scan mode. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300 MHz for ^{1}H and 75 MHz for ^{13}C. All spectra were recorded at ambient temperature and were referenced to the residual solvent peak.

General procedure for catalyst screening at 10 bar pressure

Styrene oxide **1c** (1.7 mmol), catalyst (83.0 μmol) and Bu_4NBr (26.7 mg, 83.0 μmol) were placed in a sample vial fitted with a magnetic stirrer bar and placed in a two litre stainless steel pressure reactor. Sufficient cardice pellets were added to the reactor to generate a pressure of 10 bar once they evaporated. The reaction mixture was stirred at room temperature for 24 h, then the conversion of styrene oxide **1c** to styrene carbonate **2c** was determined by analysis of a sample by ^{1}H-NMR spectroscopy.

General procedure for catalyst screening at 1 bar pressure

Styrene oxide **1c** (1.7 mmol), catalyst (83.0 μmol) and Bu_4NBr (26.7 mg, 83.0 μmol) were placed in a sample vial fitted with a magnetic stirrer bar and placed in a large conical flask. Cardice pellets were added to the conical flask which was fitted with a rubber stopper pierced by a deflated balloon. The reaction mixture was stirred at room temperature for 24 h, then the conversion of styrene oxide **1c** to styrene carbonate **2c** was determined by analysis of a sample by ^{1}H-NMR spectroscopy.

General procedure for synthesis of cyclic carbonates 2b–2k at 1 bar pressure

An epoxide **1b–1k** (1.7 mmol), catalyst **27** (42.1 mg, 83.0 μmol) and Bu_4NBr (26.7 mg, 83.0 μmol) were placed in a sample vial fitted with a magnetic stirrer bar and placed in a large conical flask. Cardice pellets were added to the conical flask which was fitted with a rubber stopper pierced by a deflated balloon. The reaction mixture was stirred for 24 h at 0 °C for epoxide **1b**, 50 °C for epoxides **1g**, **h** or 18 °C for all other substrates. For epoxides **1c–1k**, the conversion of epoxide to cyclic carbonate was then determined by analysis of a sample by ^{1}H-NMR spectroscopy. The remaining sample was filtered through a plug of silica, eluting with CH_2Cl_2 to remove the catalyst. The eluent was evaporated *in vacuo* to give either the pure cyclic carbonate or a mixture of cyclic carbonate and unreacted epoxide. In the latter case, the mixture was purified by flash chromatography using a solvent system of first hexane, then hexane–EtOAc (9 : 1), then hexane–EtOAc (3 : 1), then EtOAc to give the pure cyclic carbonate. Cyclic carbonates **2a–2k** are all known compounds and the spectroscopic data for samples prepared using catalyst **27** were consistent with those reported in the literature.[24,33]‡

Propylene carbonate (2b). Obtained as a colourless liquid (143.9 mg, 85%). δ_H ($CDCl_3$) 1.50 (3H, d *J* 6.3 Hz, CH_3), 4.04 (1H, dd *J* 8.3, 7.4 Hz, OCH_2), 4.57 (1H, t *J* 8.3 Hz, OCH_2), 4.8–4.9 (1H, m, OCH); δ_C ($CDCl_3$) 19.2, 70.5, 73.2, 154.7.

Styrene carbonate (2c). Obtained as a white solid (242.3 mg, 89%). Mp 49–51 °C (lit.[24,33] 50–51 °C). δ_H ($CDCl_3$) 4.36 (1H, t *J* 8.6 Hz, OCH_2), 4.82 (1H, t *J* 8.4 Hz, OCH_2), 5.70 (1H, t *J* 8.0 Hz, PhCHO), 7.3–7.5 (5H, m, ArH); δ_C ($CDCl_3$) 71.0, 77.8, 125.7, 129.2, 129.6, 136.0, 154.5.

1,2-Butylene carbonate (2d). Obtained as a colourless liquid (163.7 mg, 85%). δ_H ($CDCl_3$) 1.00 (3H, t *J* 7.1 Hz, CH_3), 1.6–1.9 (2H, m, CH_2), 4.05 (1H, dd *J* 6.3, 5.3 Hz, OCH_2), 4.49 (1H, t *J* 8.1 Hz, OCH_2), 4.5–4.7 (1H, m, OCH); δ_C ($CDCl_3$) 8.6, 27.0, 69.1, 78.1, 155.2.

1,2-Hexylene carbonate (2e). Obtained as a colourless liquid (172.1 mg, 72%). δ_H ($CDCl_3$) 0.91 (3H, t *J* 7.1 Hz, CH_3), 1.2–1.6 (4H, m, 2 × CH_2), 1.6–1.9 (2H, m, CH_2), 4.06 (1H, dd *J* 8.4, 7.2 Hz, OCH_2), 4.52 (1H, t *J* 8.1 Hz, OCH_2), 4.68 (1H, qd *J* 7.5, 5.4 Hz, OCH); δ_C ($CDCl_3$) 13.5, 22.1, 26.3, 33.4, 69.2, 77.0, 154.8.

1,2-Decylene carbonate (2f). Obtained as a colourless liquid (305.4 mg, 92%). δ_H ($CDCl_3$) 0.86 (3H, t *J* 6.8 Hz, CH_3), 1.1–1.6 (12H, m, 6 × CH_2), 1.6–1.9 (2H, m, CH_2), 4.04 (1H, dd *J* 8.4, 7.2 Hz, OCH_2), 4.50 (1H, dd *J* 8.4, 7.8 Hz, OCH_2), 4.8–4.6 (1H, m, OCH); δ_C ($CDCl_3$) 14.2, 22.7, 24.5, 29.2, 29.2, 29.4, 31.9, 34.0, 69.5, 77.1, 155.2.

4-Chlorostyrene carbonate (2g). Obtained as a white solid (276.8 mg, 84%). Mp 66–69 °C (lit.[24,33] 68–69 °C). δ_H ($CDCl_3$) 4.31 (1H, t *J* 7.8 Hz, OCH_2), 4.82 (1H, t *J* 8.4 Hz, OCH_2), 5.68 (1H, t *J* 7.9 Hz, OCH), 7.32 (2H, d *J* 8.5 Hz, ArH), 7.42 (2H, d *J* 8.5 Hz, ArH); δ_C ($CDCl_3$) 70.7, 77.0, 127.1, 129.4, 134.5, 135.8, 154.1.

4-Bromostyrene carbonate (2h). Obtained as a white solid (346.9 mg, 86%). Mp 72–75 °C (lit.[24,33] 68–69 °C). δ_H ($CDCl_3$) 4.31 (1H, t *J* 8.2 Hz, OCH_2), 4.81 (1H, t *J* 8.4 Hz, OCH_2), 5.66 (1H, t *J* 8.0 Hz, OCH), 7.25 (2H, dd *J* 8.4, 1.8 Hz, ArH), 7.58 (2H, dd *J* 8.1 Hz, 2.0 Hz, ArH); δ_C ($CDCl_3$) 70.7, 77.1, 123.8, 127.3, 132.4, 135.0, 154.2.

Glycerol carbonate (2i). Obtained as a colourless liquid (129.3 mg, 66%). δ_H (DMSO-d$_6$) 3.50 (1H, dd *J* 12.6, 3.2 Hz, CH_2OH), 3.66 (1H, dd *J* 12.6, 2.6 Hz, CH_2OH), 4.28 (1H, dd *J* 8.1, 5.8 Hz, CH_2O), 4.48 (1H, t *J* 8.3 Hz, CH_2O), 4.7–4.8 (1H, m, OCH), 5.26 (1H, br, OH); δ_C (DMSO-d$_6$) 60.6, 65.8, 76.9, 155.0.

3-Chloropropylene carbonate (2j). Obtained as a colourless liquid (185.8 mg, 82%). δ_H ($CDCl_3$) 3.6–3.9 (2H, m, CH_2Cl), 4.41 (1H, dd *J* 9.0, 8.7 Hz, OCH_2), 4.60 (1H, t *J* 8.5 Hz, OCH_2), 4.9–5.0 (1H, m, OCH); δ_C ($CDCl_3$) 43.9, 67.1, 74.4, 154.4.

3-Phenoxypropylene carbonate (2k). Obtained as a white solid (270.5 mg, 84%). Mp 94–97 °C (lit.[24,33] 94–95 °C). δ_H ($CDCl_3$) 4.16 (1H, dd *J* 10.6, 3.6 Hz, CH_2OPh), 4.26 (1H, dd *J* 10.6, 4.2 Hz, CH_2OPh), 4.5–4.7 (2H, m, OCH_2), 5.0–5.1 (1H, m, OCH), 6.9–7.0 (2H, m, 2×ArH), 7.04 (1H, t *J* 7.5 Hz, ArH),

This journal is © The Royal Society of Chemistry 2013

7.2–7.5 (2H, m, 2×ArH); δ_C ($CDCl_3$) 66.2, 67.3, 74.0, 114.9, 122.1, 129.6, 154.3, 158.0.

Synthesis of ethylene carbonate 2a

A sample vial was charged with Bu_4NBr (26.7 mg, 83.0 μmol) and catalyst **27** (42.1 mg, 83.0 μmol) and then cooled in an ice bath for 15 min, after which time ethylene oxide (75.0 mg, 1.7 mmol) was added through a syringe. The reaction vial was then placed into a stainless steel reactor vessel, previously saturated with cardice pellets (approximately 2 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 2.5 bar. Then, excess CO_2 and unreacted ethylene oxide were vented. The remaining sample was filtered through a plug of silica, eluting with CH_2Cl_2 to remove the catalyst. The eluent was evaporated *in vacuo* and the product was obtained as a colourless liquid (100 mg, 67%). δ_H ($CDCl_3$) 4.54 (CH_2); δ_C ($CDCl_3$) 64.3, 155.0.

Synthesis of cyclic carbonate 29 at 10 bar pressure

Cyclohexene oxide **28** (156.8 mg, 1.6 mmol), catalyst **27** (42.1 mg, 83.0 μmol) and Bu_4NBr (26.7 mg, 83.0 μmol) were placed in a sample vial fitted with a magnetic stirrer bar and placed in a stainless steel pressure reactor. Sufficient cardice pellets were added to the reactor to generate a pressure of 10 bar once they evaporated. The reaction mixture was stirred at room temperature for 72 h, then the conversion of epoxide **28** to cyclic carbonate **29** was determined by analysis of a sample by ^{1}H-NMR spectroscopy. The remaining sample was filtered through a plug of silica, eluting with CH_2Cl_2 to remove the catalyst. The eluent was evaporated *in vacuo* to give a mixture of cyclic carbonate and unreacted epoxide. The mixture was purified by flash chromatography using a solvent system of first hexane, then hexane–EtOAc (9 : 1), then hexane–EtOAc (3 : 1), then EtOAc to give compound **29** (15.9 mg, 7%) as a white solid with spectroscopic data consistent with those reported in the literature.[26] Mp 34–36 °C (lit.[26] 34–35 °C). δ_H ($CDCl_3$) 1.3–1.4 (2H, m, CH_2), 1.5–1.7 (2H, m, CH_2), 1.8–2.0 (4H, m, 2×CH_2), 4.6–4.7 (2H, m); δ_C ($CDCl_3$) 19.2, 26.8, 75.9, 155.5.

Determination of the reaction kinetics

Styrene oxide **1c** (0.10 g, 0.83 mmol), catalyst **27** (2.5, 5.0, 7.5 or 10 mol%) and Bu_4NBr (2.5, 5.0, 7.5 or 10 mol%) were dissolved in propylene carbonate (0.50 mL) in a sample vial fitted with a magnetic stirrer bar and placed in a large conical flask. Cardice pellets were added to the conical flask which was fitted with a rubber stopper pierced by a deflated balloon. The reaction was stirred at 60 °C. Samples were taken at convenient intervals (approximately every hour) and analysed by ^{1}H NMR spectroscopy to determine the relative concentrations of styrene oxide **1c** and styrene carbonate **2c**.

Notes and references

1 Data obtained and derived from the NIST database: http://webbook.nist.gov/chemistry/name-ser.html accessed on 28th July 2013.

2 A. Behr, *Chem. Eng. Technol.*, 1987, **10**, 16–27.

3 M. Aresta and A. Dibenedetto, *Catal. Today*, 2004, **98**, 455–462.

4 M. Aresta and A. Dibenedetto, *Dalton Trans.*, 2007, 2975–2992; K. M. K. Yu, I. Curcic, J. Gabriel and S. C. E. Tsang, *ChemSusChem*, 2008, **1**, 893–899; *Carbon Dioxide as Chemical Feedstock*, ed. M. Aresta, Wiley-VCH, Weinheim, 2010, pp. 1–375; P. Styring and K. Armstrong, *Chem. Today*, 2011, **29**, 28–31.

5 M. North, *Chem. Today*, 2012, **30**, number 3 May/June: Monographic supplement: Catalysis applications 3–5. Q3

6 M. Yoshida and M. Ihara, *Chem.–Eur. J.*, 2004, **10**, 2886–2893; J. Sun, S.-I. Fujita and M. Arai, *J. Organomet. Chem.*, 2005, **690**, 3490–3497; W.-L. Dai, S.-L. Luo, S.-F. Yin and C.-T. Au, *Appl. Catal., A*, 2009, **366**, 2–12; T. Sakakura and K. Kohno, *Chem. Commun.*, 2009, 1312–1330; M. North, R. Pasquale and C. Young, *Green Chem.*, 2010, **12**, 1514–1539; A. Decortes, A. M. Castilla and A. W. Kleij, *Angew. Chem., Int. Ed.*, 2010, **49**, 9822–9837.

7 R. Zevenhoven, S. Eloneva and S. Teir, *Catal. Today*, 2006, **115**, 73–79; P. P. Pescarmona and M. Taherimehr, *Catal. Sci. Technol.*, 2012, **2**, 2169–2187; X.-B. Lu and D. J. Darensbourg, *Chem. Soc. Rev.*, 2012, **41**, 1462–1484; N. Kielland, C. J. Whiteoak and A. W. Kleij, *Adv. Synth. Catal.*, 2013, **355**, 2115–2138.

8 H. Sugimoto and S. Inoue, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 5561–5573; D. J. Darensbourg, R. M. Mackiewicz, A. L. Phelps and D. R. Billodeaux, *Acc. Chem. Res.*, 2004, **37**, 836–844; G. W. Coates and D. R. Moore, *Angew. Chem., Int. Ed.*, 2004, **43**, 6618–6639; D. J. Darensbourg, *Inorg. Chem.*, 2010, **49**, 10765–10780; M. R. Kember, A. Buchard and C. K. Williams, *Chem. Commun.*, 2011, **47**, 141–163; S. Klaus, M. W. Lehenmeier, C. E. Anderson and B. Rieger, *Coord. Chem. Rev.*, 2011, **255**, 1460–1479; X.-B. Lu, W.-M. Ren and G.-P. Wu, *Acc. Chem. Res.*, 2012, **45**, 1721–1735; D. J. Darensbourg and S. J. Wilson, *Green Chem.*, 2012, **14**, 2665–2671; N. Ikpo, J. C. Flogeras and F. M. Kerton, *Dalton Trans.*, 2013, **42**, 8998–9006.

9 D. J. Darensbourg and S. J. Wilson, *J. Am. Chem. Soc.*, 2011, **133**, 18610–18613.

10 S. H. Lee, A. Cyriac, J. Y. Jeon and B. Y. Lee, *Polym. Chem.*, 2012, **3**, 1215–1220.

11 M. Cheng, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 1998, **120**, 11018–11019; M. Cheng, N. A. Darling, E. B. Lobkovsky and G. W. Coates, *Chem. Commun.*, 2000, 2007–2008; M. Cheng, D. R. Moore, J. J. Reczek, B. M. Chamberlain, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2001, **123**, 8738–8749; S. D. Allen, D. R. Moore, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2002, **124**, 14284–14285; D. R. Moore, M. Cheng,

This journal is © The Royal Society of Chemistry 2013

E. B. Lobkovsky and G. W. Coates, *Angew. Chem., Int. Ed.*, 2002, **41**, 2599–2602; Z. Qin, C. M. Thomas, S. Lee and G. W. Coates, *Angew. Chem., Int. Ed.*, 2003, **42**, 5484–5487; D. R. Moore, M. Cheng, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2003, **125**, 11911–11924; C. M. Byrne, S. D. Allen, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2004, **126**, 11404–11405; C. T. Cohen and G. W. Coates, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 5182–5191; C. T. Cohen, C. M. Thomas, K. L. Peretti, E. B. Lobkovsky and G. W. Coates, *Dalton Trans.*, 2006, 237–249.

12 For leading references see: G.-P. Wu, S.-H. Wei, X.-B. Lu, W.-M. Ren and D. J. Darensbourg, *Macromolecules*, 2010, **43**, 9202–9204; G.-P. Wu, S.-H. Wei, W.-M. Ren, X.-B. Lu, B. Li, Y.-P. Zu and D. J. Darensbourg, *Energy Environ. Sci.*, 2011, **4**, 5084–5092; G.-P. Wu, S.-H. Wei, W.-M. Ren, X.-B. Lu, T.-Q. Xu and D. J. Darensbourg, *J. Am. Chem. Soc.*, 2011, **133**, 15191–15199; G.-P. Wu, D. J. Darensbourg and X.-B. Lu, *J. Am. Chem. Soc.*, 2012, **134**, 17739–17745; D. J. Darensbourg, R. R. Poland and A. L. Strickland, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 127–133; G.-P. Wu, P.-X. Xu, X.-B. Lu, Y.-P. Zu, S.-H. Wei, W.-M. Ren and D. J. Darensbourg, *Macromolecules*, 2013, **46**, 2128–2133.

13 For leading references see: B. Y. Lee and A. Cyriac, *Nat. Chem.*, 2011, **3**, 505–507; A. Cyriac, S. H. Lee and B. Y. Lee, *Polym. Chem.*, 2011, **2**, 950–956; A. Cyriac, S. H. Lee, J. K. Varghese, J. H. Park, J. Y. Jeon, S. J. Kim and B. Y. Lee, *Green Chem.*, 2011, **13**, 3469–3475; J. K. Varghese, A. Cyriac and B. Y. Lee, *Polyhedron*, 2012, **32**, 90–95; S. H. Lee, A. Cyriac, J. Y. Jeon and B. Y. Lee, *Polym. Chem.*, 2012, **3**, 1215–1220; J. Y. Jeon, J. J. Lee, J. K. Varghese, S. J. Na, S. Sujith, M. J. Go, J. Lee, M.-A. Ok and B. Y. Lee, *Dalton Trans.*, 2013, **42**, 9245–9254.

14 M. R. Kember, A. J. P. White and C. K. Williams, *Inorg. Chem.*, 2009, **48**, 9535–9542; M. R. Kember, P. D. Knight, P. T. R. Reung and C. K. Williams, *Angew. Chem., Int. Ed.*, 2009, **48**, 931–933; M. R. Kember, A. J. P. White and C. K. Williams, *Macromolecules*, 2010, **43**, 2291–2298; K. L. Orchard, J. E. Harris, A. J. P. White, M. S. P. Shaffer and C. K. Williams, *Organometallics*, 2011, **30**, 2223–2229; F. Jutz, A. Buchard, M. R. Kember, S. B. Fredriksen and C. K. Williams, *J. Am. Chem. Soc.*, 2011, **133**, 17395–17405; A. Buchard, F. Jutz, M. R. Kember, A. J. P. White, H. S. Rzepa and C. K. Williams, *Macromolecules*, 2012, **45**, 6781–6795; M. R. Kember, F. Jutz, A. Buchard, A. J. P. White and C. K. Williams, *Chem. Sci.*, 2012, **3**, 1245–1255; M. R. Kember, J. Copley, A. Buchard and C. K. Williams, *Polym. Chem.*, 2012, **3**, 1196–1201; M. R. Kember and C. K. Williams, *J. Am. Chem. Soc.*, 2012, **134**, 15676–15679.

15 W. J. Peppel, *Ind. Eng. Chem.*, 1958, **50**, 767–770.

16 J. H. Clements, *Ind. Eng. Chem. Res.*, 2003, **42**, 663–674; B. Schäffner, F. Schäffner, S. P. Verevkin and A. Börner, *Chem. Rev.*, 2010, **110**, 4554–4581.

17 K. Xu, *Chem. Rev.*, 2004, **104**, 4303–4417; V. Etacheri, R. Marom, R. Elazari, G. Salitra and D. Aurbach, *Energy Environ. Sci.*, 2011, **4**, 3243–3262.

18 M. North, F. Pizzato and P. Villuendas, *ChemSusChem*, 2009, **2**, 862–865; M. North and M. Omedes-Pujol, *Tetrahedron Lett.*, 2009, **50**, 4452–4454; W. Clegg, R. W. Harrington, M. North, F. Pizzato and P. Villuendas, *Tetrahedron: Asymmetry*, 2010, **21**, 1262–1271; M. North and P. Villuendas, *Org. Lett.*, 2010, **12**, 2378–2381; M. North and M. Omedes-Pujol, *Beilstein J. Org. Chem.*, 2010, **6**, 1043–1055; C. Beattie, M. North and P. Villuendas, *Molecules*, 2011, **16**, 3420–3432; M. Morcillo, M. North and P. Villuendas, *Synthesis*, 2011, 1918–1925; P. Lenden, P. M. Ylioja, C. González-Rodríguez, D. A. Entwistle and M. C. Willis, *Green Chem.*, 2011, **13**, 1980–1982.

19 M. North, Synthesis of cyclic carbonates from carbon dioxide and epoxides, in *New and Future Developments in Catalysis: Activation of* CO_2, ed. S. L. Suib, Elsevier, London, 2013, ch. 13.

20 J. Meléndez, M. North and R. Pasquale, *Eur. J. Inorg. Chem.*, 2007, 3323–3326; M. North and C. Young, *ChemSusChem*, 2011, **4**, 1685–1693; M. North, P. Villuendas and C. Young, *Tetrahedron Lett.*, 2012, **53**, 2736–2740.

21 J. Meléndez, M. North and P. Villuendas, *Chem. Commun.*, 2009, 2577–2579; M. North, P. Villuendas and C. Young, *Chem.–Eur. J.*, 2009, **15**, 11454–11457; M. North and P. Villuendas, *ChemCatChem*, 2012, **4**, 789–794.

22 For leading references see: M. Taherimehr, A. Decortes, S. M. Al-Amsyar, W. Lueangchaichaweng, C. J. Whiteoak, E. C. Escudero-Adán, A. W. Kleij and P. P. Pescarmona, *Catal. Sci. Technol.*, 2012, **2**, 2231–2237; A. Coletti, C. J. Whiteoak, V. Conte and A. W. Kleij, *ChemCatChem*, 2012, **4**, 1190–1196; M. V. Escárcega-Bobadilla, M. M. Belmonte, E. Martin, E. C. Escudero-Adán and A. W. Kleij, *Chem.–Eur. J.*, 2013, **19**, 2641–2648; F. Castro-Gómez, G. Salassa, A. W. Kleij and C. Bo, *Chem.–Eur. J.*, 2013, **19**, 6289–6298; N. Kielland, E. C. Escudero-Adán, M. M. Belmonte and A. W. Kleij, *Dalton Trans.*, 2013, **42**, 1427–1436; D. Anselmo, G. Salassa, E. C. Escudero-Adán, E. Martin and A. W. Kleij, *Dalton Trans.*, 2013, **42**, 7962–7970.

23 M. North, *ARKIVOC*, 2012, 610–628, part (i).

24 M. North and R. Pasquale, *Angew. Chem., Int. Ed.*, 2009, **48**, 2946–2948; W. Clegg, R. W. Harrington, M. North and R. Pasquale, *Chem.–Eur. J.*, 2010, **16**, 6828–6843.

25 I. S. Metcalfe, M. North, R. Pasquale and A. Thursfield, *Energy Environ. Sci.*, 2010, **3**, 212–215; J. Meléndez, M. North, P. Villuendas and C. Young, *Dalton Trans.*, 2011, **40**, 3885–3902; M. North, B. Wang and C. Young, *Energy Environ. Sci.*, 2011, **4**, 4163–4170.

26 C. Beattie, M. North, P. Villuendas and C. Young, *J. Org. Chem.*, 2013, **78**, 419–426.

27 M. North and C. Young, *Catal. Sci. Technol.*, 2011, **1**, 93–99.

28 C.-Y. Li, D.-C. Liu and B.-T. Ko, *Dalton Trans.*, 2013, **42**, 11488–11496.

29 A. Buchard, M. R. Kember, K. G. Sandeman and C. K. Williams, *Chem. Commun.*, 2011, **47**, 212–214; C. J. Whiteoak, E. Martin, M. M. Belmonte, J. Benet-Buchholz and A. W. Kleij, *Adv. Synth. Catal.*, 2012, **354**, 469–476.

This journal is © The Royal Society of Chemistry 2013

30 See for example: A. Otero, J. Fernández-Baeza, A. Antiñolo, J. Tejeda and A. Lara-Sanchez, *Dalton Trans.*, 2004, 1499–1510; C. Pettinari and R. Pettinari, *Coord. Chem. Rev.*, 2005, **249**, 663–691; H. R. Bigmore, S. C. Lawrence, P. Mountford and C. S. Tredget, *Dalton Trans.*, 2005, 635–651; R. G. Howe, C. S. Tredget, S. C. Lawrence, S. Subongkoj, A. R. Cowley and P. Mountford, *Chem. Commun.*, 2006, 223–225; H. Kopf, B. Holzberger, C. Pietraszuk, E. Hübner and N. Burzlaff, *Organometallics*, 2008, **27**, 5894–5905; G. A. Santillan and C. J. Carrano, *Dalton Trans.*, 2009, 6599–6605; A. Otero, J. Fernández-Baeza, A. Lara-Sánchez and L. F. Sánchez-Barba, *Coord. Chem. Rev.*, 2013, **257**, 1806–1868.

31 A. Otero, A. Lara-Sánchez, J. Fernández-Baeza, C. Alonso-Moreno, J. Tejeda, J. A. Castro-Osma, I. Márquez-Segovia, L. F. Sánchez-Barba, A. M. Rodríguez and M. V. Gómez, *Chem.–Eur. J.*, 2010, **16**, 8615–8619; A. Otero, A. Lara-Sánchez, J. Fernández-Baeza, C. Alonso-Moreno, J. A. Castro-Osma, I. Márquez-Segovia, L. F. Sánchez-Barba, A. M. Rodríguez and J. C. García-Martínez, *Organometallics*, 2011, **30**, 1507–1522; J. A. Castro-Osma, C. Alonso-Moreno, I. Márquez-Segovia, A. Otero, A. Lara-Sánchez, J. Fernández-Baeza, A. M. Rodríguez, L. F. Sánchez-Barba and J. C. García-Martínez, *Dalton Trans.*, 2013, **42**, 9325–9337; J. A. Castro-Osma, C. Alonso-Moreno, M. V. Gómez, I. Márquez-Segovia, A. Otero, A. Lara-Sánchez, J. Fernández-Baeza, L. F. Sánchez-Barba and A. M. Rodríguez, *Dalton Trans.*, 2013, **42**, 14240–14252; J. A. Castro-Osma, C. Alonso-Moreno, J. C. García-Martinez, J. Fernández-Baeza, L. F. Sánchez-Barba, A. Lara-Sánchez and A. Otero, *Macromolecules*, 2013, **46**, 6388.

32 A. Otero, J. Fernández-Baeza, A. Lara-Sanchez, C. Alonso-Moreno, I. Márquez-Segovia, L. F. Sánchez-Barba and A. M. Rodríguez, *Angew. Chem., Int. Ed.*, 2009, **48**, 2176–2179; A. Otero, A. Lara-Sanchez, J. Fernández-Baeza, E. Martínez-Caballero, I. Márquez-Segovia, C. Alonso-Moreno, L. F. Sánchez-Barba, A. M. Rodríguez and I. López-Solera, *Dalton Trans.*, 2010, **39**, 930–940.

33 J. A. Castro-Osma, A. Lara-Sánchez, M. North, A. Otero and P. Villuendas, *Catal. Sci. Technol.*, 2012, **2**, 1021–1026.

34 A. Decortes and A. W. Kleij, *ChemCatChem*, 2011, **3**, 831–834; R. M. Haak, A. Decortes, E. C. Escudero-Adán, M. M. Belmonte, E. Martin, J. Benet-Buchholz and A. W. Kleij, *Inorg. Chem.*, 2011, **50**, 7934–7936; C. J. Whiteoak, A. Nova, F. Maseras and A. W. Kleij, *ChemSusChem*, 2012, **5**, 2032–2038; C. J. Whiteoak, B. Gjoka, E. Martin, M. M. Belmonte, E. C. Escudero-Adán, C. Zonta, G. Licini and A. W. Kleij, *Inorg. Chem.*, 2012, **51**, 10639–10649; D. Anselmo, V. Bocokić, A. Decortes, E. C. Escudero-Adán, J. Benet-Buchholz, J. N. H. Reek and A. W. Kleij, *Polyhedron*, 2012, **32**, 49–53.

35 C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adán, E. Martin and A. W. Kleij, *J. Am. Chem. Soc.*, 2013, **135**, 1228–1231; C. J. Whiteoak, E. Martin, E. Escudero-Adán and A. W. Kleij, *Adv. Synth. Catal.*, 2013, **355**, 581–589.

36 D. J. Darensbourg, S. J. Lewis, J. L. Rodgers and J. C. Yarbrough, *Inorg. Chem.*, 2003, **42**, 10639–10649.

37 X.-B. Lu, Y.-J. Zhang, K. Jin, L.-M. Luo and H. Wang, *J. Catal.*, 2004, **227**, 537–541.

38 N. Takeda and S. Inoue, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 3564–3567; K. Kasuga, S. Nagao, T. Fukumoto and M. Handa, *Polyhedron*, 1996, **15**, 69–72.