## One-component catalysts for cyclic carbonate synthesis†

Jaisiel Meléndez, Michael North\* and Pedro Villuendas

Received (in Cambridge, UK) 6th January 2009, Accepted 6th March 2009 First published as an Advance Article on the web 18th March 2009 DOI: 10.1039/b900180h

Homogeneous and immobilized one-component catalysts for the conversion of epoxides and carbon dioxide into cyclic carbonates at atmospheric pressure and room temperature have been developed.

Two major challenges facing the global chemical community over the next two decades are: stabilizing and reducing atmospheric carbon dioxide levels to mitigate the effects of climate change;<sup>1</sup> and developing sustainable raw materials for the chemicals industry to replace crude oil.<sup>2</sup> One approach to both of these problems is the development of commercially viable routes to basic chemicals that employ carbon dioxide as the starting material.<sup>3,4</sup> However, if such a process is to contribute to reducing 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 generating the required energy than is consumed by the chemical reaction.

Salicylic acid has been commercially prepared from carbon dioxide for over a century,<sup>2,3</sup> urea is currently prepared from carbon dioxide on a 100 million ton per annum scale<sup>2,4</sup> and a number of other reactions of carbon dioxide are known to be exothermic.<sup>3</sup> There has also been considerable interest in the hydrogenation of carbon dioxide<sup>5</sup> to formic acid, formalde-hyde, or methanol, though these processes will only be viable if hydrogen becomes available on a large scale from non-fossil-fuel sources.<sup>6</sup>

Another commercially important process<sup>2,7,8</sup> that utilises carbon dioxide is the 100% atom economical synthesis of cyclic carbonates from epoxides<sup>9</sup> shown in Scheme 1. This is already a commercial process for the synthesis of both ethylene and propylene carbonates, though currently used catalysts require the reaction to be carried out at high temperature and high pressure using highly purified carbon dioxide.<sup>4,7</sup> Under these conditions, the reaction generates more carbon dioxide than it consumes. Metal(salen) complexes have been widely studied as catalysts for cyclic carbonate synthesis with aluminium,<sup>10</sup> chromium,<sup>11</sup> cobalt,<sup>12</sup> ruthenium,<sup>13</sup> tin<sup>14</sup> and manganese<sup>15</sup> complexes being reported to be active in the presence of elevated pressures of carbon dioxide. Cobalt and chromium(salen) complexes have also been used for the enantioselective synthesis of cyclic

*E-mail: Michael.north@ncl.ac.uk; Fax: +44 870 131 3783; Tel: +44 191 222 7128* 



Scheme 1 Synthesis of cyclic carbonates from epoxides.

carbonates by a kinetic resolution of epoxides<sup>12,16</sup> and aluminium, chromium, cobalt and tin(salen) complexes have been used to prepare polycarbonates.<sup>17</sup> In 2007, however, we reported the development of bimetallic aluminium(salen) complex 1 as a uniquely active catalyst for the synthesis of cyclic carbonates from terminal epoxides at atmospheric pressure and room temperature.<sup>18</sup> These reactions required the presence of tetrabutylammonium bromide as a cocatalyst. Recently, we reported detailed mechanistic studies on this catalytic system<sup>19</sup> and showed that the tetrabutylammonium bromide plays two key roles in the catalytic cycle: providing bromide to ring-open the epoxide and generating tributylamine in situ, which reacts with the carbon dioxide to form a carbamate salt. The bimetallic aluminium complex then brings these two species together and allows them to combine intramolecularly to complete the catalytic cycle.

Whilst the complex 1-tetrabutylammonium bromide catalyst system had exceptionally high catalytic activity, the need for two separate catalysts was a disadvantage, especially given the desirability of immobilising the catalyst and employing it in a flow reactor. Herein, we report the synthesis and catalytic activity of single-component catalysts which build on the mechanistic understanding of the reaction and combine the key features of complex 1 and tetrabutylammonium bromide within a single entity. The first design for a single-component catalyst is represented by structure 7a-d. This incorporates four tetraalkylammonium bromide units in each bimetallic complex unit since reaction kinetics using complex 1 had shown the reaction to be second order in tetrabutylammonium bromide.<sup>19</sup> Catalysts 7 were prepared as shown in Scheme 2. Thus, treatment of known<sup>20</sup> salicylaldehyde derivatives 2a,b with diethylamine gave tertiary amines 3a,b, which could be condensed with 1,2-diamines 4a,b to give salen ligands 5a-d. Reaction of diamines 5a-d with benzyl bromide in acetonitrile gave bis-ammonium salts 6a-d. Treatment of ligands **6a,b** with triethoxyaluminium gave the desired

School of Chemistry and University Research Centre in Catalysis and Intensified Processing, Bedson Building, University of Newcastle, Newcastle upon Tyne, UK NE1 7RU.

<sup>†</sup> Electronic supplementary information (ESI) available: Experimental details for the synthesis of catalysts and cyclic carbonates and characterization data for all new compounds. See DOI: 10.1039/b900180h



Scheme 2 Synthesis of one-component catalysts 7a-d, 9a,b and 10a,b.

catalysts **7a–b**.<sup>†</sup> For the synthesis of catalysts **7c,d**, it was necessary to reverse the last two steps. Thus, treatment of ligands **5c,d** with triethoxyaluminium gave bimetallic complexes **8c,d**, which when treated with benzyl bromide gave catalysts **7c,d**.

Complex **7a** was a highly effective catalyst for the conversion of terminal epoxides into cyclic carbonates at room temperature and atmospheric pressure. Representative results are given in Table 1.<sup>1</sup> Thus, ten racemic terminal epoxides were converted into the corresponding cyclic carbonates with good to excellent conversions and isolated yields after reaction times of 3–6 hours using 2.5 mol% of catalyst **7a** under solvent-free conditions. When enantiomerically pure styrene oxide was used as substrate, chiral HPLC analysis of samples withdrawn after 3 and 6 hours indicated that the styrene carbonate was also enantiomerically pure.

In addition to epoxides bearing simple alkyl or aryl substituents, catalyst 7a was also compatible with functionalized

 Table 1
 Synthesis of cyclic carbonates using catalysts 7a-d<sup>a</sup>

Catalyst	Epoxide $R =$	Conversion (hours) <sup>b</sup>	% Yield (hours)
7a	Ph	71 (3), 97 (6)	89 (6)
7a	$CH_3(CH_2)_3$	30 (3)	63 (6)
7a	$CH_3(CH_2)_7$	44 (3), 81 (6)	68 (6)
7a	CH <sub>2</sub> OH	55 (3), 79 (6)	65 (6)
7a	$CH_2Cl$	84 (3), 100 (6)	81 (6)
7a	Me <sup>c</sup>	50 (3)	62 (6)
7a	4-MeC <sub>6</sub> H <sub>4</sub>	59 (3), 85 (6), 95 (24)	89 (24)
7a	$4-BrC_6H_4$	37 (3), 50 (6), 93 (24)	85 (24)
7a	$4-ClC_6H_4$	30 (3), 44 (6), 98 (24)	83 (24)
7a	4-MeSC <sub>6</sub> H <sub>4</sub>	37 (3), 49 (6), 66 (24)	51 (24)
7b	Ph	69 (3), 88 (6), 99 (24)	90 (24)
7c	Ph	48 (3), 60 (6), 73 (24)	55 (24)
7d	Ph	54 (3), 69 (6), 89 (24)	74 (24)

<sup>*a*</sup> Reactions carried out under solvent-free conditions using 2.5 mol% of catalyst **7a–d**. For full experimental details see ESI<sup>†</sup>. <sup>*b*</sup> Determined by <sup>1</sup>H NMR spectroscopy. <sup>*c*</sup> Reaction carried out at 0 °C.

epoxides such as glycidol and glycidyl chloride. The conversion of propylene oxide into propylene carbonate is also significant in view of the commercial importance of this reaction. Another feature of these reactions is the complete absence of polycarbonate formation.<sup>2,17</sup>

Catalysts **7b–d** in which the structure of the salen ligand has been simplified by removal of the *tert*-butyl groups and/or cyclohexyl ring were also effective catalysts. Compared to complex **7a** however, complexes **7b–d** were all slightly less effective in the conversion of styrene oxide into styrene carbonate in a given period of time, which in the case of catalysts **7c,d** is related to the poor solubility of these complexes in styrene oxide.

To further demonstrate the utility of a one-component catalyst system, immobilized versions of catalysts 7 were prepared from ligands **5a,b**. Thus, treatment of ligands **5a,b** with triethoxyaluminium gave bimetallic complexes **8a,b**<sup>‡</sup> which reacted with bromomethylpolystyrene to give immobilized catalysts **9a,b** containing a single tetraalkylammonium salt. Subsequent reaction of complexes **9a,b** with benzyl bromide gave tetralkylammonium salt containing catalysts **10a,b**.

Cyclic carbonate synthesis using catalysts 9 and 10 required a solvent to swell the resin beads and propylene carbonate was found to be a suitable solvent.<sup>19</sup> Reactions were then carried out with styrene oxide as substrate at 26 °C under an atmosphere of carbon dioxide using 2.5 mol% of catalyst.† Under these conditions, complex 9a was found to be a recyclable catalyst and in three consecutive reactions produced styrene carbonate in yields of 100, 94 and 70% after reaction times of 20 hours. Although catalyst 9a contains only a single tetraalkylammonium bromide, its high level of catalytic activity is consistent with the important role played by amino groups in activating the carbon dioxide for cyclic carbonate synthesis.<sup>19</sup> Under the same conditions, catalyst 10a gave styrene carbonate yields of 79, 73, 66 and 60% over four consecutive reactions. In contrast however, supported catalyst 9b displayed very low reactivity, giving just 8% conversion of styrene oxide to styrene carbonate. The activity of this system was however markedly improved by converting it to the tetraammonium salt 10b, which gave styrene carbonate yields of 79, 71, 67 and 64% in four consecutive reactions.

Thus, eight one-component catalysts for cyclic carbonate synthesis have been prepared and shown to exhibit high activity in reactions carried out at atmospheric pressure and room temperature. Polymer-supported catalysts **9** and **10** are the first heterogeneous catalysts to display catalytic activity under such mild reaction conditions and open the possibility of using these and related systems in continuous flow reactors.

The authors thank the EPSRC and CarbonConnections for financial support.

## Notes and references

<sup>‡</sup> Complexes **8a,b** were also active catalysts for the conversion of styrene oxide to styrene carbonate, but only in the presence of tetrabutylammonium bromide.

1 H. Arakawa, M. Aresta, J. N. Armor, M. A. Barteau, E. J. Beckman, A. T. Bell, J. E. Bercaw, C. Creutz, E. Dinjus,

- D. A. Dixon, K. Domen, D. L. DuBois, J. Eckert, E. Fujita, D. H. Gibson, W. A. Goddard, D. W. Goodman, J. Keller, G. J. Kubas, H. H. Kung, J. E. Lyons, L. E. Manzer, T. J. Marks, K. Morokuma, K. M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielson, W. M. H. Sachtler, L. D. Schmidt, A. Sen, G. A. Somorjai, P. C. Stair, B. R. Stults and W. Tumas, *Chem. Rev.*, 2001, **101**, 953–996.
- 2 T. Sakakura, J.-C. Choi and H. Yasuda, Chem. Rev., 2007, 107, 2365–2387.
- 3 M. Aresta and A. Dibenedetto, *Catal. Today*, 2004, **98**, 455–462; M. Aresta and A. Dibenedetto, *Dalton Trans.*, 2007, 2975–2992.
- 4 I. Omae, Catal. Today, 2006, 115, 33-52.
- 5 P. G. Jessop, F. Joó and C.-C. Tai, *Coord. Chem. Rev.*, 2004, **248**, 2425–2442.
- 6 A. Baiker, Appl. Organomet. Chem., 2000, 14, 751-762.
- 7 J. H. Clements, *Ind. Eng. Chem. Res.*, 2003, 42, 663–674;
   M. Yoshida and M. Ihara, *Chem.-Eur. J.*, 2004, 10, 2886–2893.
- 8 R. Zevenhoven, S. Eloneva and S. Teir, *Catal. Today*, 2006, **115**, 73–79.
- 9 J. Sun, S.-I. Fujita and M. Arai, J. Organomet. Chem., 2005, 690, 3490–3497.
- X.-B. Lu, X.-J. Feng and R. He, *Appl. Catal.*, *A*, 2002, **234**, 25–32;
   X.-B. Lu, R. He and C.-X. Bai, *J. Mol. Catal. A: Chem.*, 2002, **186**, 1–11;
   X.-B. Lu, Y.-J. Zhang, K. Jin, L.-M. Luo and H. Wang, *J. Catal.*, 2004, **227**, 537–541;
   X.-B. Lu, Y.-J. Zhang, B. Liang, X. Li and H. Wang, *J. Mol. Catal. A: Chem.*, 2004, **210**, 31–34;
   M. Alvaro, C. Baleizao, E. Carbonell, M. El Ghoul, H. García and B. Gigante, *Tetrahedron*, 2005, **61**, 12131–12139;
   H. Zhou, W.-Z. Zhang, C.-H. Liu, J.-P. Qu and X.-B. Lu, *J. Org. Chem.*, 2008, **73**, 8039–8044.
- R. L. Paddock and S. T. Nguyen, J. Am. Chem. Soc., 2001, 123, 11498–11499; M. Alvaro, C. Baleizao, D. Das, E. Carbonell and H. García, J. Catal., 2004, 228, 254–258; D. J. Darensbourg, C. C. Fang and J. L. Rodgers, Organometallics, 2004, 23, 924–927; M. Ramin, F. Jutz, J.-D. Grunwaldt and A. Baiker, J. Mol. Catal. A: Chem., 2005, 242, 32–39; D. J. Darensbourg, P. Bottarelli and J. R. Andreatta, Macromolecules, 2007, 40, 7727–7729; X. Zhang, Y.-B. Jia, X.-B. Lu, B. Li, H. Wang and L.-C. Sun, Tetrahedron Lett., 2008, 49, 6589–6592.
- 12 R. L. Paddock and S. T. Nguyen, *Chem. Commun.*, 2004, 1622–1623; X.-B. Lu, J.-H. Xiu, R. He, K. Jin, L.-M. Luo and X.-J. Feng, *Appl. Catal.*, A, 2004, **275**, 73–78; X.-B. Lu, B. Liang, Y.-J. Zhang, Y.-Z. Tian, Y.-M. Wang, C.-X. Bai, H. Wang and R. Zhang, *J. Am. Chem. Soc.*, 2004, **126**, 3732–3733; S.-W. Chen, R. B. Kawthekar and G.-J. Kim, *Tetrahedron Lett.*, 2007, **48**, 297–300; T. Chang, H. Jing, L. Jin and W. Qiu, *J. Mol. Catal. A: Chem.*, 2007, **264**, 241–247; C.-X. Miao, J.-Q. Wang, Y. Wu, Y. Du and L.-N. He, *ChemSusChem*, 2008, **1**, 236–241; L. Jin, Y. Huang, H. Jing, T. Chang and P. Yan, *Tetrahedron: Asymmetry*, 2008, **19**, 1947–1953. cobalt.
- 13 H. Jing, T. Chang, L. Jin, M. Wu and W. Qiu, *Catal. Commun.*, 2007, **8**, 1630–1634.
- 14 H. Jing, S. K. Edulji, J. M. Gibbs, C. L. Stern, H. Zhou and S. T. Nguyen, *Inorg. Chem.*, 2004, 43, 4315–4327.
- 15 F. Jutz, J.-D. Grunwaldt and A. Baiker, J. Mol. Catal. A: Chem., 2008, **279**, 94–103.
- A. Berkessel and M. Brandenburg, Org. Lett., 2006, 8, 4401–4404.
   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; H. Sugimoto and S. Inoue, J. Polym. Sci., Part A: Polym. Chem., 2004, 42, 5561–5573; D. J. Darensbourg, Chem. Rev., 2007, 107, 2388–2410; S. S. J. K. Min, J. E. Seong, S. J. Na and B. Y. Lee, Angew. Chem., Int. Ed., 2008, 47, 7306–7309.
- 18 J. Meléndez, M. North and R. Pasquale, *Eur. J. Inorg. Chem.*, 2007, 3323–3326.
- 19 M. North and R. Pasquale, *Angew. Chem., Int. Ed.*, 2009, DOI: 10.1002/anie.200805451.
- 20 S. J. Angyal, P. J. Morris, J. R. Tetaz and J. G. Wilson, J. Chem. Soc., 1950, 2141–2145; F. Minutolo, D. Pini, A. Petri and P. Salvadori, Tetrahedron: Asymmetry, 1996, 7, 2293.