

Synthesis of Cyclic Carbonates from Atmospheric Pressure Carbon Dioxide Using Exceptionally Active Aluminium(salen) Complexes as Catalysts

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Keywords: Carbon dioxide fixation / Aluminium / Schiff bases / Epoxides / Catalysis

Dimetallic aluminium(salen) complexes show exceptionally high catalytic activity for the synthesis of cyclic carbonates from terminal epoxides at ambient temperature and pressure. The process has the potential to contribute towards

decreasing atmospheric carbon dioxide emissions from the burning of fossil fuels.

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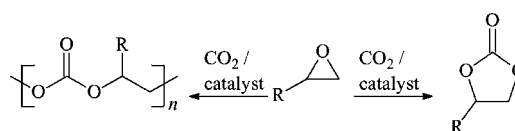
Introduction

One of the main scientific challenges facing the human race in the 21st century is controlling global warming due to increasing levels of atmospheric carbon dioxide.^[1] In the long term, it may be possible to move entirely to renewable, or non-carbon-based fuels; however, for the foreseeable future, annual consumption of fossil fuels is predicted to continue to increase markedly with a corresponding rise in atmospheric carbon dioxide levels.^[2] The only solution currently being considered to this problem 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.^[3] However, it is far from certain that long-term containment is feasible given the volatile nature of carbon dioxide.

An alternative solution to the problem would be to convert the carbon dioxide at source (taking advantage of the relatively high concentration of carbon dioxide in for example the exhaust stream of a fossil fuel power station) into a chemical for which there is a significant commercial demand.^[1,3,4] In order to be feasible, any such procedure would have to occur at atmospheric pressure and near ambient temperature; otherwise the energy required to operate the process will generate more carbon dioxide than is remediated. Unfortunately, the low chemical reactivity of carbon dioxide severely restricts the range of chemical reactions which might be feasible.

One unusually facile reaction of carbon dioxide is its insertion into epoxides to generate cyclic carbonates or a polycarbonate^[5–7] as shown in Scheme 1. Ethylene, propylene and butylene carbonates are manufactured commer-

cially and it has been estimated that cyclic carbonates and products derived from them could reduce atmospheric carbon dioxide emissions by up to 120 million tons per year if the economics of the process could be improved.^[3] The epoxide co-reactants required for the chemistry shown in Scheme 1 are readily available by the catalytic epoxidation of alkenes, a process which can be achieved using hydrogen peroxide as a green oxidant,^[8] and the alkenes can be obtained from waste plastics or biological sources. A large number of homogeneous and heterogeneous catalysts have been reported to induce the reaction between epoxides and carbon dioxide.^[7,9] However, almost all of these require elevated reaction temperatures and/or high pressures of carbon dioxide; often the reaction is conducted in supercritical carbon dioxide.



Scheme 1. Synthesis of polymeric or cyclic carbonates from CO₂ and epoxides.

Notable amongst the catalysts which have been employed to synthesise cyclic carbonates are metal(salen) complexes^[6,10] derived from aluminium,^[11] nickel,^[11a] copper,^[11a,12] zinc,^[11a,12] magnesium,^[11a] cobalt,^[11a,12–14] chromium,^[11a,15] or tin.^[16] In previous work from our group,^[17] we have demonstrated that dimetallic salen complexes display much higher catalytic activity than their monometallic counterparts in asymmetric cyanohydrin synthesis because the two metal ions can each activate one of the two components of the reaction. Polycarbonate and cyclic carbonate synthesis using chromium(salen) complexes are known to be bimolecular,^[15] therefore, we reasoned that a suitable dimetallic salen complex might display significantly improved catalytic activity in the reaction between carbon dioxide and epoxides. Here we report the successful accomplish-

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Supporting information for this article is available on the WWW under <http://www.eurjic.org> or from the author.

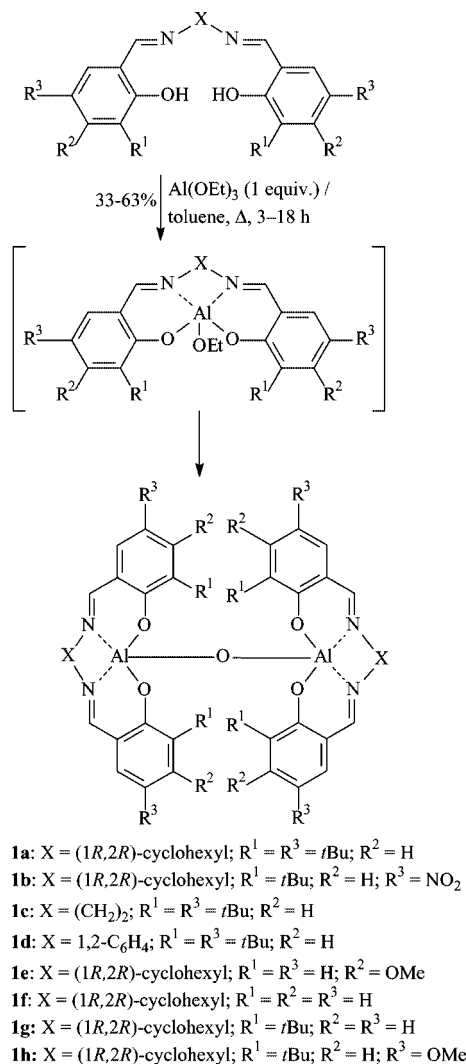
ment of this concept through the development of a dimetallic aluminium(salen) complex which will catalyse the insertion of carbon dioxide into epoxides at atmospheric pressure and ambient temperature.

Results and Discussion

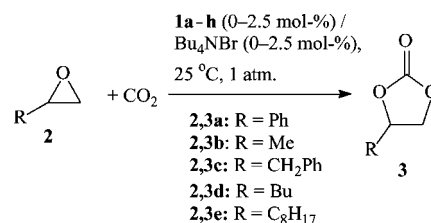
We selected aluminium as the metal of choice due to its low environmental impact and previous use in cyclic carbonate synthesis, albeit at elevated pressures of carbon dioxide (at least 6 atm).^[11] Thus, treatment of a salen ligand with aluminium triethoxide in toluene gave complexes **1a–h** as yellow or orange solids in 33–63% yields as shown in Scheme 2. The μ -O atom in complexes **1a–h** could be derived from adventitious moisture, by decomposition of ethanol formed during the reaction, and/or from the ethoxy group. Complexes **1a** and **1c** have previously been prepared by a different route^[18,19] and used to catalyse asymmetric Michael additions.^[19] The X-ray structure of complexes **1c**^[20] and **1d**^[21] have previously been reported, and the mass spectra of compounds **1a–h** confirmed their dimetallic structures (see Supporting Information).

Complexes **1a–h** were tested for their ability to catalyse the formation of carbonate **3a** from racemic styrene oxide (**2a**) and carbon dioxide under solvent-free conditions as shown in Scheme 3, and the results are summarised in Table 1. In the absence of a co-catalyst, no reaction occurred, even at 5 atm pressure and elevated temperature (Table 1, Entries 1 and 2). This is in line with previous work using aluminium(salen)-derived catalysts where reaction only occurred in the presence of a tetrabutylammonium halide,^[11a–11d] DMAP^[11e,11f] or *N*-methylimidazole^[11e] co-catalyst. The combination of complex **1a** and tetrabutylammonium bromide was found to display extremely high catalytic activity (Table 1, Entries 4–11). This combination of catalysts displayed unprecedented catalytic activity at 1 atm carbon dioxide pressure and room temperature. Tetrabutylammonium chloride and iodide were also investigated as co-catalysts, but were found to be less effective than the use of tetrabutylammonium bromide. The only previous reports of synthetic studies^[11c,13c] on the preparation of cyclic carbonates at ambient temperature required carbon dioxide pressures of 6–15 atm^[14,22] or reaction times of up to 7 d.^[23] That the observed catalysis was not due solely to the tetrabutylammonium bromide co-catalyst was demonstrated by a reaction run in the absence of an aluminium(salen) complex (Table 1, Entry 3). Although use of just 1.0 mol-% of catalyst **1a** gave a good conversion after 24 h (Table 1, Entry 10), use of 2.5 mol-% was adopted as standard in subsequent studies as this allowed good conversions (62% with 57% isolated yield) to be achieved after just 3 h (Table 1, Entry 8).

Attempts to increase the reactivity of the catalyst by varying the substituents on the aromatic rings or the diamine of the salen ligand were not successful as none of catalysts **1b–h** were significantly more active than complex **1a** (Table 1, Entries 12–18). The trend in reactivity appears



Scheme 2. Synthesis of catalysts **1a–h**.



Scheme 3. Synthesis of cyclic carbonates **3** using complexes **1a–h**.

to be related to the solubility of the catalyst in styrene oxide rather than to any steric or electronic factors, as the highest catalytic activity was observed with the most hydrophobic complexes, and complexes **1d** and **1f** which gave the lowest conversions (Table 1, Entries 14 and 16) did not fully dissolve during the reaction.

Cyclic carbonates derived from other monosubstituted epoxides could also be obtained from the combination of complex **1a** and tetrabutylammonium bromide (Scheme 3), as detailed in Table 2. Propylene oxide was a particularly reactive substrate, and only 1 mol-% of catalyst was necessary to convert it into propylene carbonate in good yield,

Table 1. Synthesis of carbonate **3a** catalysed by complexes **1a–h**.

Entry	Catalyst [mol-%]	Co-catalyst [mol-%]	CO ₂ pressure [atm]	Temp. [°C]	Time [h]	Conversion ^[a] [%]
1	1a (1.0)		1	25	3	0
2	1a (1.0)		5	50	24	0
3		Bu ₄ NBr (1.0)	1	25	3	4
4	1a (0.1)	Bu ₄ NBr (0.1)	1	25	3	5
5	1a (1.0)	Bu ₄ NBr (1.0)	1	25	3	38
6	1a (1.0)	Bu ₄ NBr (2.5)	1	25	3	56
7	1a (2.5)	Bu ₄ NBr (1.0)	1	25	3	51
8	1a (2.5)	Bu ₄ NBr (2.5)	1	25	3	62
9	1a (0.1)	Bu ₄ NBr (0.1)	1	25	24	27
10	1a (1.0)	Bu ₄ NBr (1.0)	1	25	24	86
11	1a (2.5)	Bu ₄ NBr (2.5)	1	25	24	98
12	1b (2.5)	Bu ₄ NBr (2.5)	1	25	3	50
13	1c (2.5)	Bu ₄ NBr (2.5)	1	25	3	52
14	1d (2.5)	Bu ₄ NBr (2.5)	1	25	3	33
15	1e (2.5)	Bu ₄ NBr (2.5)	1	25	3	41
16	1f (2.5)	Bu ₄ NBr (2.5)	1	25	3	28
17	1g (2.5)	Bu ₄ NBr (2.5)	1	25	3	51
18	1h (2.5)	Bu ₄ NBr (2.5)	1	25	3	64

[a] Conversions are based on ¹H NMR analysis of the reaction mixture.

even at 0 °C (Table 2; Entries 1–3). The other monosubstituted epoxides studied were converted into the corresponding carbonates in good to high yield using the standard conditions developed above (Table 2, Entries 4–7), but use of lower amounts of catalyst/co-catalyst seriously reduced the yields in these cases. Disubstituted epoxides were much less reactive with *trans*-stilbene oxide giving just 8% of the corresponding cyclic carbonate after a reaction time of 48 h, whilst cyclohexene oxide and 2-phenylpropylene oxide failed to give any cyclic carbonate under these conditions. No polycarbonate was detected in any reaction catalysed by complexes **1a–h** with any of substrates **2a–e**, indicating that these complexes display a high selectivity for cyclic carbonate rather than polycarbonate formation.

Table 2. Synthesis of carbonates **3b–e** using catalyst **1a**.

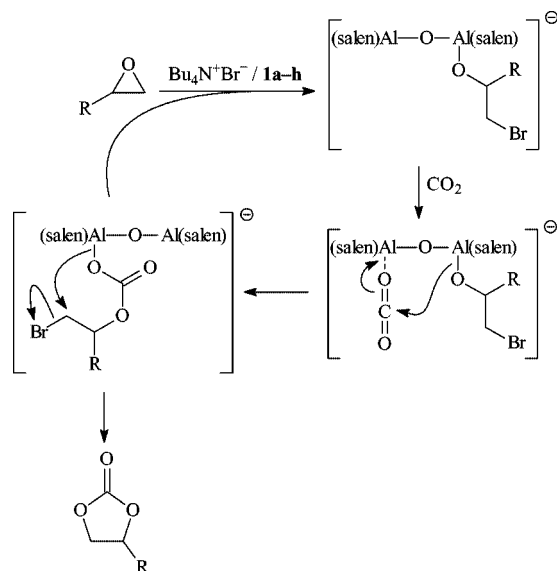
Entry ^[a]	Epoxide	1a /Bu ₄ NBr [mol-%]	Time [h]	Yield [%] ^[c]
1 ^[b]	2b (R = Me)	2.5 + 2.5	3	77
2 ^[b]	2b (R = Me)	1 + 1	3	40
3 ^[b]	2b (R = Me)	1 + 1	24	63
4	2c (R = CH ₂ Ph)	2.5 + 2.5	3	44
5	2c (R = CH ₂ Ph)	2.5 + 2.5	24	99
6	2d (R = Bu)	2.5 + 2.5	3	87
7	2e (R = C ₈ H ₁₇)	2.5 + 2.5	3	64

[a] All reactions were conducted in the absence of solvent at 1 atm pressure of carbon dioxide and at 25 °C, unless otherwise stated.

[b] Reaction at 0 °C. [c] Yield of isolated product obtained after chromatographic purification. Conversions (based on ¹H NMR analysis of the reaction mixture) are also given in the Supporting Information.

The exceptional catalytic activity of the catalysts **1a–h** is consistent with a mechanism in which both aluminium ions of the complex play a role in activating the components of the reaction as shown in Scheme 4. Thus, ring-opening of the epoxide by bromide results in an aluminium-bound alkoxide. Coordination of carbon dioxide to the second alu-

minium ion, followed by intramolecular transfer of the alkoxide onto the coordinated carbon dioxide gives an aluminium carbonate which can cyclize to form the cyclic carbonate product and regenerate both catalysts. Work is currently underway to study the kinetics of this process and to detect reaction intermediates to confirm this mechanistic hypothesis.



Scheme 4. Possible mechanism to explain the catalytic activity of complexes **1a–h**.

Conclusions

The dimetallic aluminium(salen) complexes **1a–h** display exceptionally high catalytic activity for the conversion of terminal epoxides into cyclic carbonates at room temperature and 1 atm pressure.

Experimental Section

Experimental details for the synthesis of catalysts **1a–h** and cyclic carbonates **3a–e** are given in the Supporting Information.

Supporting Information (see footnote on the first page of this article): Full experimental details and characterising data for the synthesis of catalysts **1a–h** and cyclic carbonates **3a–e**.

Acknowledgments

The authors thank Newcastle University for a studentship (to R. P.), the Engineering and Physical Sciences Research Council (EPSRC) for funding and the EPSRC national mass spectrometry service at the University of Wales, Swansea for recording mass spectra.

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Received: May 16, 2007

Published Online: June 21, 2007