

# Catalysis Science & Technology

Cite this: *Catal. Sci. Technol.*, 2011, **1**, 93–99

www.rsc.org/catalysis

PAPER

## Bimetallic aluminium(acen) complexes as catalysts for the synthesis of cyclic carbonates from carbon dioxide and epoxides

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Received 21st October 2010, Accepted 14th November 2010

DOI: 10.1039/c0cy00023j

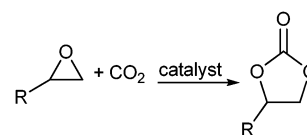
The development of bimetallic  $\mu$ -oxoaluminium(acen) complexes as highly active catalysts for the synthesis of cyclic carbonates from terminal epoxides and carbon dioxide is described. The resulting homogeneous catalysts are used in batch reactions for the synthesis of cyclic carbonates at room temperature and one atmosphere pressure.

### Introduction

Over 90% of all commercially manufactured organic chemicals are sourced from crude oil, a non-renewable resource, production of which has been predicted to peak by 2020<sup>1</sup> with known reserves being exhausted by 2056 at current rate of consumption.<sup>2</sup> Therefore, over the next fifty years the global chemicals industry needs to develop alternative and sustainable starting materials.

One solution to this problem would be to use carbon dioxide as the starting material for the industrial synthesis of chemicals<sup>3,4</sup> or fuels.<sup>5</sup> However, it is essential that such processes require little or no energy input (unless they can be achieved photochemically<sup>6</sup>); otherwise, the dependence on fossil fuels will be restored. This leads to a requirement for reactions which can be carried out at atmospheric pressure and at or near room temperature. Carbon dioxide is relatively unreactive due to its high oxidation state. However, it does undergo a number of exothermic reactions.<sup>3b</sup> Thus, salicylic acid has been manufactured from carbon dioxide for over a century<sup>3b,e,f</sup> by the Kolbe–Schmitt reaction ( $\Delta H_r = -31.4 \text{ kJ mol}^{-1}$ )<sup>3b</sup> and urea is currently prepared from carbon dioxide on a 100 million tonne per annum scale<sup>3d,e</sup> ( $\Delta H_r = -137 \text{ kJ mol}^{-1}$ ).<sup>7</sup>

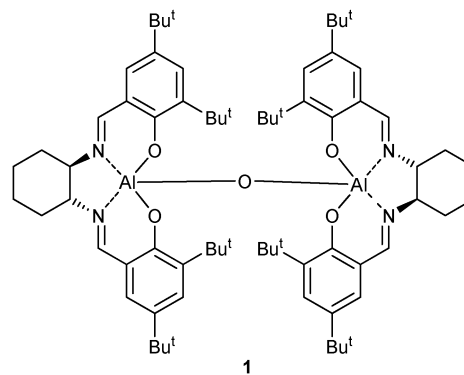
Another reaction which utilizes carbon dioxide is the synthesis of cyclic carbonates<sup>4,8,9</sup> by its 100% atom economical reaction with epoxides as shown in Scheme 1. This is a highly exothermic reaction ( $\Delta H_r = -140 \text{ kJ mol}^{-1}$  for ethylene carbonate<sup>10</sup>) and has been a commercial process since the 1950's.<sup>8</sup> Although this reaction is highly exothermic, currently used catalysts require the reaction to be carried out at high temperatures and pressures using highly purified carbon dioxide.<sup>3d,9,11</sup> the current market for cyclic carbonates is only about 100–200 kTonne per annum,<sup>9</sup> but they are



**Scheme 1** Synthesis of cyclic carbonates from epoxides and  $\text{CO}_2$ .

manufactured on a larger scale as intermediates in the production of ethylene glycol and dimethyl carbonate.<sup>4</sup> Cyclic carbonates are used as degreasing agents, electrolytes for lithium-ion batteries and polar aprotic solvents.<sup>12,13</sup> They can also be converted into dimethyl carbonate<sup>4</sup> which has been shown to be an excellent oxygenating additive for both petrol<sup>14</sup> and aviation fuel.<sup>15</sup> The reaction between epoxides and carbon dioxide can also produce polycarbonates<sup>16</sup> which are also commercially important.<sup>17</sup>

In previous work,<sup>18</sup> we have shown that the combination of bimetallic aluminium(salen) complex **1**<sup>19,20</sup> and tetrabutylammonium bromide formed an exceptionally active catalyst system for the synthesis of cyclic carbonates from terminal epoxides at room temperature and atmospheric pressure under solvent free conditions. Complex **1** was subsequently shown to be compatible with carbon dioxide produced by combustion of methane in an oxy-fuel combustion system, thus providing a model for a future highly integrated energy and chemical production facility in which the only waste is water.<sup>21</sup>



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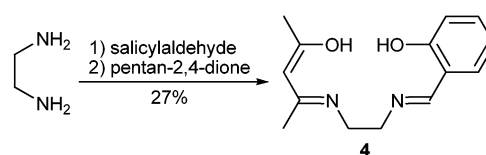
Immobilized versions of catalyst **1** were prepared,<sup>22</sup> which allowed cyclic carbonate synthesis to be achieved in a gas phase flow reactor for the first time.<sup>23</sup> The immobilized versions of catalyst **1** were also shown to be compatible with the NO<sub>x</sub> and SO<sub>x</sub> present in power station flue gas.<sup>24</sup>

One important factor affecting the viability of catalysts for cyclic carbonate synthesis is the cost of production of the catalyst, especially since about 50 tonnes of catalyst would be required to remove 92 000 tonnes of carbon dioxide per annum from the flue gases of a fossil-fuel power station<sup>24</sup> and produce sufficient ethylene carbonate to satisfy the current market demand.<sup>9</sup> The synthesis of complex **1** as initially reported,<sup>18</sup> costs £766 mol<sup>-1</sup>.† This cost can be reduced by replacing the (*R,R*)-cyclohexanediamine used for the synthesis of catalyst **1** with ethylenediamine. However, whilst this is effective for the production of immobilized versions of complex **1**,<sup>21,22</sup> it reduces the solubility and hence catalytic activity of the homogeneous version of the catalyst.<sup>18</sup> In this manuscript, we report an alternative approach for reducing the cost of bimetallic aluminium complexes, namely the replacement of salicylaldehyde (cost £5 mol<sup>-1</sup>) or its more expensive substituted derivatives with pentan-2,4-dione (cost £2.2 mol<sup>-1</sup>) resulting in the formation of bimetallic  $\mu$ -oxoaluminium(acen) complexes.<sup>25</sup>

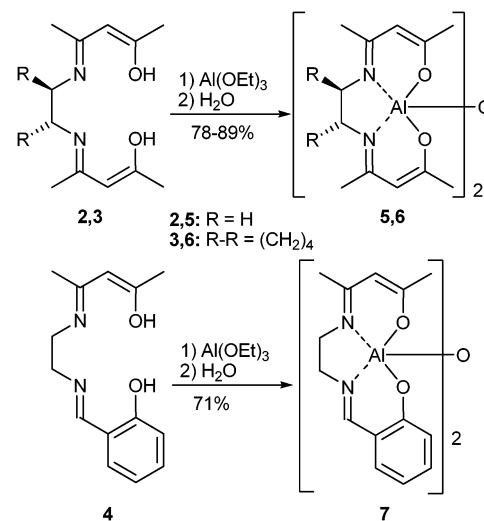
## Results and discussion

Ligands **2–4** were initially chosen for study in this project. Acen ligands<sup>26,27</sup> **2,3** are derived from the condensation of pentan-2,4-dione with ethylenediamine and (*R,R*)-cyclohexanediamine respectively and offer the simplest and most cost effective synthesis, whilst unsymmetrical salen ligand **4** was included as it has a structure which combines aspects of both salen and acen ligands. Ligand **4** was prepared from ethylenediamine, salicylaldehyde and acetylacetone (Scheme 2) by adapting a procedure previously used for the synthesis of related salen ligands.<sup>28</sup> Complexation of ligands **2–4** to aluminium(triethoxide) followed by an aqueous work-up gave bimetallic  $\mu$ -oxoaluminium complexes **5–7** as shown in Scheme 3. Whilst mononuclear aluminium(acen) complexes have been prepared before,<sup>25,29</sup> complexes **5** and **6** are the first examples of binuclear aluminium(acen) complexes.

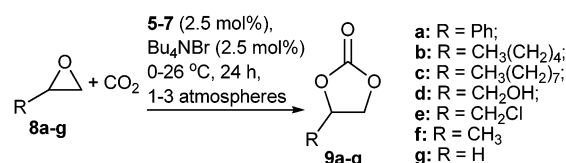
The catalytic activity of complexes **5–7** was investigated using terminal epoxides **8a–g** (Scheme 4). In each case, the reaction was carried out using 2.5 mol% of catalyst and 2.5 mol% of tetrabutylammonium bromide under a carbon dioxide atmosphere and in the absence of any solvent. Reactions involving epoxides **8a–e** were carried out at one atmosphere pressure and at 26 °C, whilst reactions involving epoxide **8f** were carried out at 0 °C due to the low boiling point of propylene oxide. Since ethylene oxide **8g** is a gas, reactions involving this substrate were carried out at 26 °C in a sealed stainless steel reactor with a carbon dioxide pressure of less than three atmospheres. In the case of reactions involving liquid epoxides **8a–f**, samples were withdrawn and analysed by <sup>1</sup>H NMR spectroscopy to determine the conversions after



Scheme 2 Synthesis of ligand **4**.



Scheme 3 Synthesis of complexes **5–7**.



Scheme 4 Synthesis of cyclic carbonates **9a–g** using catalysts **5–7**.

three and six hours as well as after 24 h. Reactions involving ethylene oxide **8g** were simply left for 24 h before being analysed. The results of this study are shown in Table 1.

It is apparent from Table 1 that all three catalysts **5–7** were catalytically active and could convert each of epoxides **8a–g** into the corresponding cyclic carbonate **9a–g**. Whilst there was some variation in catalytic activity between substrates **8a–g**, generally salen complex **7** displayed the highest catalytic activity followed by achiral acen complex **5**, with chiral acen complex **6** being the least active. The good catalytic activity associated with catalyst **5** is notable as it is the most easily prepared of complexes **5–7** and also less expensive (£595 mol<sup>-1</sup>) than catalysts **1**, **6** or **7**.

Having shown that bimetallic aluminium(acen) complexes **5** and **6** were catalytically active, the use of functionalized acen ligands was investigated with the aim of producing a one-component acen catalyst analogous to the one-component and immobilized bimetallic aluminium(salen) complexes we have previously reported.<sup>22–24</sup> Initially, the introduction of substituents in the central position of the acen ligand was investigated, as this is the closest analogy to the positioning of substituents *para*- to the phenol of the corresponding salen complex **1**.<sup>22–24</sup> To test the effect of introducing substituents at

† All costings are based on the prices of the largest quantities quoted in 2010 laboratory chemical catalogues.

**Table 1** Synthesis of cyclic carbonates **9a–g** using catalysts **5–7**

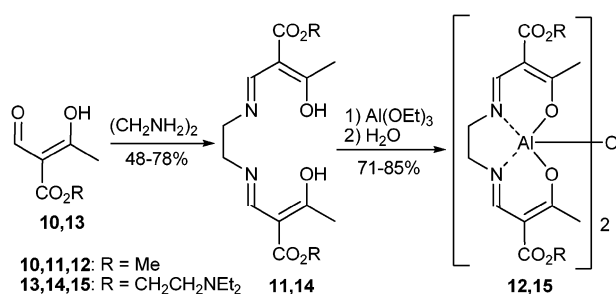
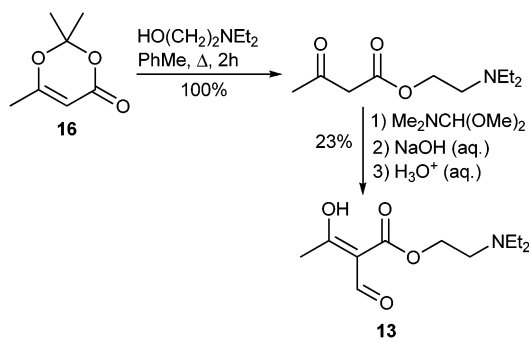
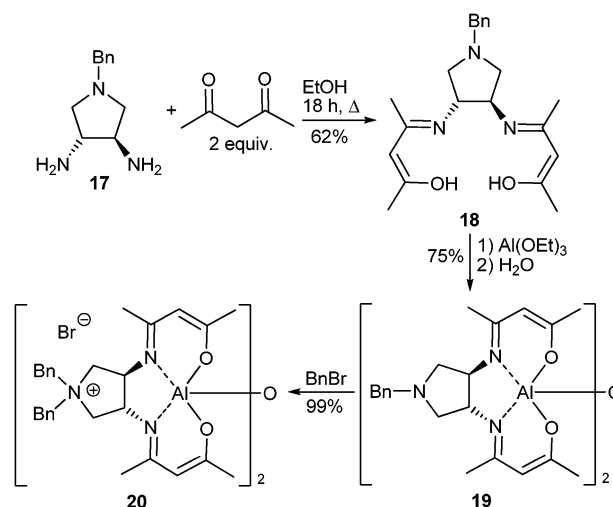
Epoxide	Conversion % (after 3, 6 and 24 h)		
	Catalyst <b>5</b>	Catalyst <b>6</b>	Catalyst <b>7</b>
<b>8a</b>	33, 52, 85	39, 59, 91	60, 72, 93
<b>8b</b>	97, 97, 100	76, 89, 94	95, 99, 100
<b>8c</b>	31, 48, 92	59, 68, 87	43, 59, 100
<b>8d</b>	33, 67, 98	29, 54, 80	48, 63, 100
<b>8e</b>	89, 100, 100	41, 65, 89	76, 98, 100
<b>8fa</b>	42, 52, 73	50, 58, 75	39, 42, 70
<b>8g<sup>b</sup></b>	58 (24 h)	53 (24 h)	100 (24 h)

<sup>a</sup> Reaction carried out at 0 °C. <sup>b</sup> Reaction carried out in a sealed reactor at <3 atmospheres pressure of CO<sub>2</sub>.

this position, methyl ester containing ligand **11** and aluminium complex **12** were first prepared from methyl 2-carboxy-3-oxobutanoate<sup>30</sup> **10** as shown in Scheme 5. Subsequently, the corresponding 2-(diethylamino)ethyl ester derivatives **14** and **15** were also prepared, with the required aldehyde precursor **13** being prepared by adaptation of a literature route<sup>31</sup> for the synthesis of related compounds starting from the diketene–acetone adduct **16** as shown in Scheme 6.

However, when tested under the conditions of Scheme 4 with styrene oxide **8a** as the substrate, complexes **12** and **15** were found to show significantly lower levels of catalytic activity than unsubstituted complex **5**. Thus, complex **12** gave conversions to styrene carbonate of 7, 15 and 36% after reaction times of 3, 6 and 24 h and complex **15** gave a conversion of just 17% after a reaction time of 24 h.

Since the introduction of substituents on the acen ligand resulted in severe loss of catalytic activity, an alternative approach was adopted, namely the incorporation of amino or ammonium substituents on the diamine. Thus, known<sup>32</sup>

**Scheme 5** Synthesis of substituted acen complexes **12** and **15**.**Scheme 6** Synthesis aldehyde **13**.**Scheme 7** Synthesis of acen complexes **19** and **20**.

pyrrolidine derivative **17** was converted into acen ligand **18** and then into complexes **19** and **20** as shown in Scheme 7. However, when complex **19** was used as a catalyst for the synthesis of styrene carbonate **9a** from styrene oxide **8a** in the presence of tetrabutylammonium bromide under the conditions of Scheme 4, only a 6% conversion was obtained after 24 h. One-component catalyst **20** was similarly unreactive, giving a conversion of just 5% from a reaction carried out in the absence of tetrabutylammonium bromide. The extremely low catalytic activity of complex **20** is probably related to its very low solubility and may also be related to an inappropriate positioning of the ammonium salt to allow activation of carbon dioxide and epoxide within the same catalyst molecule,<sup>18b</sup> though in the latter case, the combination of complex **19** and tetrabutylammonium bromide would have been expected to form a more active catalyst system.

## Conclusions

In conclusion, we have demonstrated for the first time that bimetallic aluminium(acen) complexes can form highly active catalysts for cyclic carbonate synthesis. Reactions require the presence of tetrabutylammonium bromide as a catalyst, but can be carried out at room temperature and atmospheric pressure with a range of terminal epoxides. The cost of production per mole of the most active acen catalyst (**5**) is 22% lower than the cost of production of salen complex **1** which is significant given the potential large scale application of these catalysts. Attempts to introduce substituents onto the acen ligands resulted in the formation of complexes with severely retarded catalytic activity.

## Experimental

### General experimental details

Commercially available chemicals (Alfa, Aldrich, Fluka) were used as received. Toluene was distilled over sodium before use.

GCMS 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  $\times$  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<sup>-1</sup> to 270 °C; hold at final temperature for 5 min;  $T_R$  7.33 min (styrene oxide),  $T_R$  12.09 min (styrene carbonate). For the first 3.5 min, the eluent was routed away from the mass detector. Subsequently, the detector was operated in full EI scan mode.

Low- and high-resolution electrospray mass spectra (ES) were recorded on a Waters LCT Premier MS time of flight spectrometer using positive ion mode. Samples were injected directly into the spectrometer from a syringe pump.

Infrared spectra were recorded using a Varian 800 FT-IR Scimitar series spectrometer fitted with an ATR attachment. Optical rotations were recorded on a Perkin-Elmer 343 polarimeter in a thermostatted cell of length 0.25 dm using the sodium D-line, and a suitable solvent that is reported along with the concentration (in g per 100 mL). Melting points were obtained using a Barnstead electrothermal 9100 system.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300 MHz for <sup>1</sup>H and 75 MHz for <sup>13</sup>C. All spectra were recorded at ambient temperature and were referenced to the residual solvent peak. For <sup>1</sup>H NMR spectra, multiplicities are reported as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad) or a combination of these.

#### Ligand 4

Ethylene diamine (2.7 g, 45.0 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and salicylaldehyde (5.0 g, 41.0 mmol) was added in a slow stream to the stirring solution. The resulting yellow solution was stirred at ambient temperature for 30 min. Pentan-2,4-dione (4.5 g, 45.0 mmol) was then added and the mixture heated to reflux with stirring for one hour. The reaction was then allowed to cool to room temperature and the resulting yellow solid was dissolved in hot methanol (10 mL) and then cooled to room temperature. A yellow crystalline precipitate formed which was filtered and identified as the unwanted, symmetric salen ligand. The mother liquor was evaporated *in vacuo* to give ligand **4** as a yellow/amber powder (2.7 g, 27%). Mp 121–122 °C.  $\nu_{\max}$ (ATR) 1605, 1547, 1523 and 1453 cm<sup>-1</sup>.  $\delta_H$ (300 MHz, CDCl<sub>3</sub>) 1.96 (3 H, s, CH<sub>3</sub>), 1.99 (3 H, s, CH<sub>3</sub>), 3.41 (2 H, m, CH<sub>2</sub>), 3.75 (2 H, m, CH<sub>2</sub>), 6.9–7.0 (2 H, m, ArH), 7.2–7.3 (2 H, m, ArH), 8.35 (1 H, s, N=CH).  $\delta_C$ (75 MHz, CDCl<sub>3</sub>) 18.8, 28.7, 43.2, 49.9, 95.7, 117.1, 118.2, 118.8, 131.4, 132.6, 161.0, 162.9, 173.0, 195.3.  $m/z$ (ES) 247.1 (MH<sup>+</sup>, 100); HRMS (ES): calculated for MH<sup>+</sup> (C<sub>14</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub>) 247.1447, found 247.1460.

#### Complex 5

Acen ligand **2**<sup>24</sup> (1.0 g, 4.5 mmol) was dissolved in toluene (25 mL) and aluminium triethoxide (1.5 g, 8.9 mmol) was added. The resulting mixture was refluxed for 6 h, then cooled and the solvent was removed *in vacuo*. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL), washed with water (3  $\times$  10 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and the solvent evaporated. The residue was

washed with Et<sub>2</sub>O (100 mL) to give complex **5** (0.9 g, 78%) as a light yellow powder.  $\nu_{\max}$ (ATR) 1605, 1522 and 1419 cm<sup>-1</sup>.  $\delta_H$ (300 MHz, CDCl<sub>3</sub>) 1.99 (12 H, s, 4  $\times$  CH<sub>3</sub>), 2.03 (12 H, s, 4  $\times$  CH<sub>3</sub>), 3.4–3.7 (8 H, m, 4  $\times$  CH<sub>2</sub>), 5.11 (4 H, s, 4  $\times$  =CH).  $\delta_C$ (75 MHz, CDCl<sub>3</sub>) 21.7, 25.6, 46.2, 99.8, 177.4, 199.4.  $m/z$ (ES) 515.2 (MH<sup>+</sup>, 100); HRMS (ES): calculated for MH<sup>+</sup> (C<sub>24</sub>H<sub>37</sub>N<sub>4</sub>O<sub>5</sub>Al<sub>2</sub>) 515.2395, found 515.2358.

#### Complex 6

Chiral acen ligand **3**<sup>25</sup> (4.0 g, 14.4 mmol) was dissolved in dry toluene (100 mL) and the solution heated to reflux. Aluminium triethoxide (4.8 g, 28.5 mmol) was then added and the reaction heated to reflux for four hours then cooled to room temperature. The solvent was evaporated *in vacuo*, then the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL), washed with water (3  $\times$  20 mL) and dried (Na<sub>2</sub>SO<sub>4</sub>). Solvent was evaporated *in vacuo* and the residue washed with Et<sub>2</sub>O (25 mL) to give complex **6** (4.0 g, 89%) as a pale yellow solid. Mp > 185 °C (decomp.).  $[z]_D^{25}$  –340 (CHCl<sub>3</sub>,  $c$  = 0.1).  $\nu_{\max}$ (ATR) 1607, 1572 and 1463 cm<sup>-1</sup>.  $\delta_H$ (300 MHz, CDCl<sub>3</sub>) 1.43 (8 H, m, 4  $\times$  CH<sub>2</sub>), 1.76 (4 H, m, 2  $\times$  CH<sub>2</sub>), 1.91 (12 H, s, 4  $\times$  CH<sub>3</sub>), 1.99 (2 H, m, CH<sub>2</sub>), 2.01 (12 H, s, 4  $\times$  CH<sub>3</sub>), 2.17 (2 H, m, CH<sub>2</sub>), 2.42 (2 H, m, 2  $\times$  NCH), 3.11 (2 H, m, 2  $\times$  NCH), 4.82 (2 H, s, 2  $\times$  =CH), 5.05 (2 H, s, 2  $\times$  =CH).  $\delta_C$ (75 MHz, CDCl<sub>3</sub>) 24.3, 24.6, 25.4, 25.7, 27.0, 28.8, 31.3, 33.4, 57.8, 61.1, 100.2, 102.1, 163.3, 167.7, 176.3, 179.2;  $m/z$ (ES) 623.3 (MH<sup>+</sup>, 100). HRMS (ES): calculated for MH<sup>+</sup> (C<sub>32</sub>H<sub>49</sub>N<sub>4</sub>O<sub>5</sub>Al<sub>2</sub>) 622.3256, found 622.3273.

#### Complex 7

Salacen ligand **4** (1.0 g, 4.1 mmol) was dissolved in toluene (40 mL) and heated to reflux. Aluminium triethoxide (1.3 g, 8.3 mmol) was then added and the reaction heated to reflux for four hours under a nitrogen atmosphere then cooled to room temperature. The solvent evaporated *in vacuo*, then the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL), washed with water (3  $\times$  20 mL) and dried (Na<sub>2</sub>SO<sub>4</sub>). Solvent was evaporated *in vacuo* and Et<sub>2</sub>O (25 mL) was added to the residue. The solution was cooled to 0 °C and a yellow precipitate formed which was collected by filtration to give complex **7** (0.8 g, 71%) as a pale yellow solid. Mp. > 230 °C (decomp.).  $\nu_{\max}$ (ATR) 1637, 1603, 1526, 1478, 1455 and 1408 cm<sup>-1</sup>.  $\delta_H$ (300 MHz, CDCl<sub>3</sub>) 2.07 (6 H, s, CH<sub>3</sub>), 2.10 (6 H, s, CH<sub>3</sub>), 4.06 (4 H, br, 2  $\times$  CH<sub>2</sub>), 4.27 (4 H, br, 2  $\times$  CH<sub>2</sub>), 4.97 (2 H, s, 2  $\times$  =CH), 6.63 (2 H, t  $J$  = 7.4 Hz, 2  $\times$  ArH), 7.04 (2 H, d  $J$  = 7.5 Hz, 2  $\times$  ArH), 7.15 (2 H, t  $J$  = 7.3 Hz, 2  $\times$  ArH), 7.44 (2 H, d  $J$  = 7.4 Hz, 2  $\times$  ArH), 8.26 (2 H, s, 2  $\times$  N=CH).  $\delta_C$ (75 MHz, CDCl<sub>3</sub>) 19.2, 26.3, 50.8, 59.6, 98.3, 118.7, 120.4, 128.4, 131.0, 134.7, 157.6, 163.1, 166.6, 173.1.  $m/z$ (ES) 559.2 (MH<sup>+</sup>, 100); HRMS (ES): calculated for MH<sup>+</sup> (C<sub>28</sub>H<sub>33</sub>N<sub>4</sub>O<sub>5</sub>Al<sub>2</sub>) 559.2082, found 559.2083.

#### General method for the synthesis of cyclic carbonates **9a–f** using catalysts **5–7**

An epoxide **8a–f** (1.66 mmol), catalyst **5–7** (0.0415 mmol) and Bu<sub>4</sub>NBr (0.0415 mmol) were placed in a sample vial fitted with a magnetic stirrer bar and placed in a large conical flask. The conical flask was placed in an oil bath thermostated at 26 °C



(or an ice/water bath at 0 °C when propylene oxide **8f** was the substrate). Cardice pellets were added to the conical flask which was fitted with a rubber stopper pierced by a needle attached to a deflated balloon. The reaction was stirred for 24 h with samples being removed after 3, 6 and 24 h for analysis by  $^1\text{H}$  NMR spectroscopy to determine the conversion of epoxide to cyclic carbonate. Cyclic carbonates **9a–f** had spectroscopic data consistent with those previously reported.<sup>23</sup>

#### General method for the synthesis of ethylene carbonate **9g** using catalysts **5–7**

Catalyst **5–7** (0.0415 mmol) and  $\text{Bu}_4\text{NBr}$  (0.0415 mmol) were added to a reaction vial to which pre-cooled ethylene oxide **9g** (0.18 g, 2.01 mmol) was added. The reaction vial was fitted with a magnetic stirrer and placed inside a stainless steel reaction vessel along with sufficient cardice pellets to pressurize the system to approximately 3 atmospheres. The stainless steel reactor was sealed and the reaction left to stir at 26 °C for 24 h after which the remaining ethylene oxide was allowed to evaporate, then  $\text{Et}_2\text{O}$  (ca. 20 mL) was added to the residue. The resulting mixture was filtered to remove catalyst and  $\text{Bu}_4\text{NBr}$  and the solution evaporated *in vacuo* to give ethylene carbonate **9g**.

#### Ligand **11**

Methyl 2-carboxy-3-oxobutanoate<sup>28</sup> **10** (4.0 g, 27.8 mmol) was dissolved in ethanol (50 mL) and 1,2-diaminoethane (0.93 mL, 13.9 mmol) was added dropwise, after which the reaction was stirred at room temperature for 4 h. The solvent and excess diamine were removed *in vacuo*, leaving compound **11** (3.4 g, 78%) as a yellow/orange oil.  $\nu_{\text{max}}(\text{ATR})$  1702 (s), 1622 (s) and 1570  $\text{cm}^{-1}$  (s).  $\delta_{\text{H}}(300 \text{ MHz}, \text{CDCl}_3)$  1.93 (6 H, s,  $2 \times \text{CH}_3$ ), 3.72 (6 H, s,  $2 \times \text{OCH}_3$ ), 3.84 (4 H, br,  $2 \times \text{CH}_2$ ), 7.09 (2 H, s,  $2 \times \text{N}=\text{CH}$ ).  $\delta_{\text{C}}(75 \text{ MHz}, \text{CDCl}_3)$  22.7, 53.9, 54.7, 107.4, 156.3, 163.0, 191.7.

#### Complex **12**

Ligand **11** (2.0 g, 6.4 mmol) was dissolved in toluene (50 mL) and heated to reflux. Aluminium triethoxide (2.1 g, 12.8 mmol) was added in portions and the reaction heated at reflux for 4 h. After cooling to room temperature, the toluene was evaporated *in vacuo* and the residue taken up in  $\text{CH}_2\text{Cl}_2$  (50 mL). The solution was washed with water ( $3 \times 20 \text{ mL}$ ) and brine (20 mL), then dried ( $\text{Na}_2\text{SO}_4$ ) and the solvent evaporated *in vacuo* to leave complex **12** (1.6 g, 71%) as a yellow powder. Mp > 175 °C (decomp.).  $\nu_{\text{max}}(\text{ATR})$  1695 (m) and 1616  $\text{cm}^{-1}$  (s).  $\delta_{\text{H}}(300 \text{ MHz}, \text{CDCl}_3)$  2.18 (12 H, s,  $4 \times \text{CH}_3$ ), 3.70 (12 H, s,  $4 \times \text{OCH}_3$ ), 4.23 (8 H, br,  $4 \times \text{CH}_2$ ), 8.20 (4 H, s,  $4 \times \text{N}=\text{CH}$ ).  $\delta_{\text{C}}(75 \text{ MHz}, \text{CDCl}_3)$  20.3, 51.3, 54.8, 110.3, 140.7, 160.9, 175.4.  $m/z(\text{ES})$  705.2 ( $\text{M} + \text{CH}_3^+$ , 100), 691.2 ( $\text{MH}^+$ , 15); HRMS (ES): calculated for  $[\text{M} + \text{CH}_3]^+$  ( $\text{C}_{29}\text{H}_{39}\text{N}_4\text{O}_{13}\text{Al}_2^+$ ) 705.2144, found 705.2193.

#### 2-Diethylaminoethyl 3-oxobutanoate<sup>33</sup>

2,2,6-Trimethyl-1,3-dioxin-4-one **16** (6.0 mL, 45.0 mmol) was dissolved in toluene (30 mL) and 2-diethylaminoethanol (5.0 mL, 37.7 mmol) was added. The reaction was then stirred at reflux for 2 h. The solvent was evaporated leaving

2-diethylaminoethyl 3-oxobutanoate (7.6 g, 100%) as a pale yellow oil.  $\delta_{\text{H}}(300 \text{ MHz}, \text{CDCl}_3)$  0.94 (6 H, t,  $J = 7.2 \text{ Hz}$ ,  $2 \times \text{NCH}_2\text{CH}_3$ ), 2.19 (3 H, s,  $\text{COCH}_3$ ), 2.48 (4 H, t,  $J = 7.2 \text{ Hz}$ ,  $2 \times \text{NCH}_2\text{CH}_3$ ), 2.62 (2 H, t,  $J = 6.3 \text{ Hz}$ ,  $\text{NCH}_2$ ), 3.39 (2 H, s,  $\text{CH}_2$ ), 4.12 (2 H, t,  $J = 6.3 \text{ Hz}$ ,  $\text{OCH}_2$ ).  $\delta_{\text{C}}(75 \text{ MHz}, \text{CDCl}_3)$  11.6, 29.9, 47.3, 49.8, 50.8, 63.3, 166.9, 200.4.

#### Aldehyde **13**

2-Diethylamino-3-oxobutanoate (7.6 g, 37.7 mmol) was mixed with *N,N*-dimethylformamide dimethylacetal (5.1 mL, 37.7 mmol) and stirred at room temperature for 2 h. Then, 1 M aqueous NaOH solution (40 mL) was added and the reaction allowed to stir for another 2 h during which time a bright yellow colour developed. The reaction was neutralised using aqueous HCl and the product extracted into  $\text{CH}_2\text{Cl}_2$  ( $5 \times 30 \text{ mL}$ ). The organic phase was dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated *in vacuo* leaving aldehyde **13** (2.0 g, 23%) as a viscous yellow oil.  $\delta_{\text{H}}(300 \text{ MHz}, \text{CDCl}_3)$  0.92 (6 H, t,  $J = 7.2 \text{ Hz}$ ,  $2 \times \text{NCH}_2\text{CH}_3$ ), 2.05 (3 H, s,  $\text{CH}_3$ ), 2.54 (4 H, q,  $J = 7.2 \text{ Hz}$ ,  $2 \times \text{NCH}_2\text{CH}_3$ ), 2.60 (2 H, t,  $J = 5.5 \text{ Hz}$ ,  $\text{NCH}_2$ ), 4.14 (2 H, t,  $J = 5.5 \text{ Hz}$ ,  $\text{OCH}_2$ ), 9.28 (1 H, s,  $\text{CHO}$ ).  $\delta_{\text{C}}(75 \text{ MHz}, \text{CDCl}_3)$  7.3, 23.3, 49.5, 55.4, 60.1, 108.9, 159.5, 171.3, 180.8.

#### Ligand **14**

Aldehyde **13** (2.0 g, 8.7 mmol) was dissolved in ethanol (50 mL) and 1,2-diaminoethane (0.3 mL, 4.4 mmol) added slowly. The mixture was stirred at room temperature for four hours, then the ethanol and excess amine were evaporated *in vacuo* and the residue taken up in  $\text{CH}_2\text{Cl}_2$  (50 mL). The organic phase was washed with water ( $5 \times 20 \text{ mL}$ ) and dried ( $\text{Na}_2\text{SO}_4$ ). Evaporation of the solvent *in vacuo* gave ligand **14** (1.0 g, 48%) as a dark orange oil.  $\delta_{\text{H}}(300 \text{ MHz}, \text{CDCl}_3)$  0.96 (12 H, t,  $J = 7.1 \text{ Hz}$ ,  $4 \times \text{NCH}_2\text{CH}_3$ ), 2.22 (6 H, s,  $2 \times \text{CH}_3$ ), 2.56 (8 H, q,  $J = 7.1 \text{ Hz}$ ,  $4 \times \text{NCH}_2\text{CH}_3$ ), 2.64 (4 H, t,  $J = 5.5 \text{ Hz}$ ,  $2 \times \text{NCH}_2$ ), 3.86 (4 H, br,  $\text{NCH}_2\text{CH}_2\text{N}$ ), 4.21 (4 H, t,  $J = 5.5 \text{ Hz}$ ,  $2 \times \text{OCH}_2$ ), 8.28 (2 H, s,  $2 \times \text{CHO}$ ).  $\delta_{\text{C}}(75 \text{ MHz}, \text{CDCl}_3)$  7.7, 20.1, 49.5, 56.4, 56.9, 59.3, 107.5, 154.1, 159.5, 188.8.

#### Complex **15**

Ligand **14** (0.75 g, 1.6 mmol) was dissolved in toluene (20 mL) and heated to reflux. Aluminium triethoxide (0.53 g, 3.2 mmol) was added in portions, then the reaction was stirred at reflux for a further 5 h. After cooling to room temperature, the toluene was evaporated *in vacuo* and the residue taken up in  $\text{CH}_2\text{Cl}_2$  (50 mL). The solution was washed with water ( $3 \times 20 \text{ mL}$ ) and brine (20 mL), then dried ( $\text{Na}_2\text{SO}_4$ ) and the solvent evaporated *in vacuo* to leave complex **15** (0.7 g, 85%) as an amber powder. Mp > 215 °C (decomp.).  $\nu_{\text{max}}(\text{ATR})$  1703 and 1622  $\text{cm}^{-1}$ .  $\delta_{\text{H}}(300 \text{ MHz}, \text{CDCl}_3)$  0.95 (24 H, t,  $J = 7.3 \text{ Hz}$ ,  $8 \times \text{NCH}_2\text{CH}_3$ ), 2.18 (12 H, s,  $4 \times \text{CH}_3$ ), 2.56 (16 H, t,  $J = 7.3 \text{ Hz}$ ,  $\text{NCH}_2\text{CH}_3$ ), 2.66 (8 H, t,  $J = 5.6 \text{ Hz}$ ,  $4 \times \text{NCH}_2$ ), 4.21 (8 H, t,  $J = 5.6 \text{ Hz}$ ,  $4 \times \text{OCH}_2$ ), 4.24 (8 H, br,  $4 \times \text{CH}_2$ ), 8.14 (4 H, s,  $4 \times \text{N}=\text{CH}$ ).  $\delta_{\text{C}}(75 \text{ MHz}, \text{CDCl}_3)$  8.0, 20.3, 47.5, 56.6, 57.1, 60.2, 108.6, 139.7, 159.5, 178.2.  $m/z(\text{ES})$  1031.6 ( $\text{MH}^+$ , 100); HRMS (ES): Calculated for  $\text{MH}^+$  ( $\text{C}_{48}\text{H}_{81}\text{N}_8\text{O}_{12}\text{Al}_2\text{O}^+$ ) 1031.5550, found 1031.5523.

## Ligand 18

To a solution of diamine **17**<sup>30</sup> (0.2 g, 1.0 mmol) dissolved in ethanol (50 mL) was added 2,4-pentanedione (1.6 mL, 0.3 mmol) and the reaction was heated at reflux for 18 h. The reaction was cooled to room temperature, then the solvent was evaporated and the residue taken up in CH<sub>2</sub>Cl<sub>2</sub> (50 mL). The solution was washed with water (3 × 20 mL) and brine (20 mL), then dried (Na<sub>2</sub>SO<sub>4</sub>). Evaporation of the CH<sub>2</sub>Cl<sub>2</sub> gave ligand **18** (0.3 g, 62%) as a beige yellow solid. Mp 154–159 °C.  $\delta_{\text{H}}$ (300 MHz, CDCl<sub>3</sub>) 1.8–1.9 (2 H, m, CH<sub>2</sub>), 1.91 (6 H, s, 2 × CH<sub>3</sub>), 2.10 (6 H, s, 2 × CH<sub>3</sub>), 2.7–2.8 (2 H, m, CH<sub>2</sub>), 3.56 (2 H, s, CH<sub>2</sub>Ph), 3.7–3.8 (2 H, m, 2 × CHN), 4.8–4.9 (2 H, m, 2 × =CH), 7.15–7.27 (5 H, m, ArH).  $\delta_{\text{C}}$ (75 MHz, CDCl<sub>3</sub>) 18.6, 25.3, 62.1, 65.8, 68.0, 101.3, 127.1, 128.5, 129.0, 142.0, 157.3, 180.9.

## Complex 19

Ligand **18** (0.30 g, 0.84 mmol) was dissolved in dry toluene (60 mL) and heated to reflux. Aluminium triethoxide (0.27 g, 1.68 mmol) was added and the reaction heated for 24 h. The resulting solution was cooled to room temperature, washed with water (3 × 15 mL) and brine (15 mL), then dried (Na<sub>2</sub>SO<sub>4</sub>). Evaporation of the solvent gave complex **19** (0.24 g, 75%) as a yellow powder. Mp decomp > 210 °C.  $[\alpha]_{\text{D}}^{22} - 660$  (CHCl<sub>3</sub>,  $c = 0.1$ ).  $\nu_{\text{max}}$ (ATR) 1690, 1620, 1517 and 1454 cm<sup>-1</sup>.  $\delta_{\text{H}}$ (300 MHz, CDCl<sub>3</sub>) 1.8–1.9 (4 H, m, 2 × CH<sub>2</sub>), 2.08 (12 H, s, 4 × CH<sub>3</sub>), 2.11 (12 H, s, 4 × CH<sub>3</sub>), 2.7–2.8 (4 H, m, 2 × CH<sub>2</sub>), 3.58 (4 H, s, 2 × CH<sub>2</sub>Ph), 3.7–3.8 (4 H, m, 4 × CHN), 4.51 (4 H, m, 4 × CH=), 7.1–7.3 (10 H, m, ArH).  $\delta_{\text{C}}$ (75 MHz, CDCl<sub>3</sub>) 19.6, 25.7, 62.1, 65.7, 67.6, 109.0, 127.1, 128.5, 129.0, 142.0, 155.8, 164.6.  $m/z$ (ES) 381.2 (MH<sup>+</sup>, 100); HRMS (ES): calculated for MH<sup>+</sup> (C<sub>21</sub>H<sub>28</sub>N<sub>3</sub>O<sub>2</sub>Al<sup>+</sup>) 381.1997, found 381.2011.

## Complex 20

Complex **19** (0.1 g, 0.1 mmol) was dissolved in MeCN (5 mL) and BnBr (0.1 mL, 0.8 mmol) was added. The resulting mixture was heated to reflux and stirred for 24 h during which time a dark orange precipitate formed. After cooling, the solvent was evaporated and the resulting material taken up in ether (ca. 20 mL) and filtered to give complex **20** (0.11 g, 99%) as a yellow/orange solid which was insoluble in most solvents. Mp > 285 °C (decomp.).  $\nu_{\text{max}}$ (ATR) 1697, 1617, 1509 and 1432 cm<sup>-1</sup>.

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