A bimetallic iron(III) catalyst for CO$_2$/epoxide coupling

Antoine Buchard,™ Michael R. Kember,* Karl Sandeman‡ and Charlotte K. Williams*‡

Received (in XXX, XXX) Xth XXXXXXXXXX 200X, Accepted Xth XXXXXXXXXX 200X
First published on the web Xth XXXXXXXXXX 200X
DOI: 10.1039/b000000x

A novel di-iron(III) catalyst for the copolymerisation of cyclohexene oxide and CO$_2$ to yield poly(cyclohexene)carbonate, under mild conditions, is reported. The catalyst selectivity was completely changed on addition of an ammonium co-catalyst to yield only the cis-isomer of the cyclic carbonate, also under mild conditions. Additionally, the catalyst was active for propylene carbonate and styrene carbonate production at 1 atm pressure.

Carbon dioxide is an attractive, renewable C-1 source: it is non-toxic, highly abundant, relatively inexpensive and a waste product of many processes.1–4 The metal catalysed coupling of CO$_2$ and epoxides (Scheme 1) is one of the few processes that actually consume CO$_2$ and it provides a sustainable alternative synthesis of carbonates. The catalyst, and reaction conditions, control formation of either a cyclic carbonate5 or polycarbonate;6,8 the trans-cyclic carbonate is the thermodynamic product. Aliphatic polycarbonates are applied as binders, adhesives and coatings, whilst cyclic carbonates are used as high boiling solvents, electrolytes, fuel additives and as sustainable reagents.

![Scheme 1. Coupling of CO$_2$/epoxides.](image)

Various metal complexes are successful copolymerisation catalysts, usually having Zn(II), Co(II/III), Cr(III) or Al(III) active sites.6, 7 There is much scope for new metal catalysts, including those that operate at low CO$_2$ pressure, thereby improving the energy balance and net CO$_2$ consumption. Recently, we reported various bimetallic Zn(II) and Co(II/III) copolymerisation catalysts which displayed impressive activity, at only 1 atm CO$_2$ pressure.5–11 Here, we report a novel di-iron(III) catalyst which is selective for the production of either poly(cyclohexene) carbonate (PCHC) or cyclohexene carbonate (CHC). Iron is a particularly attractive metal due to its ready availability and low-cost, yet it has received scant attention in either catalysis. Double metal cyanides, e.g. [Zn$_2$Fe(CN)$_6$]$_2^-$, are viable heterogeneous copolymerisation catalysts (although 50-60 atm CO$_2$ are required),12 however, the homogeneous analogues were less active, under the same conditions.13, 14 Some heterobimetallic tert-butoxides iron complexes were also reported.15 Importantly, these species all rely on Zn(II) or La(III) centres as the active site. Furthermore, although Co(II)/Cr(III) salen complexes are excellent catalysts, the Fe(III) analogues were inactive.16, 17

The macrocyclic pro-ligand, H$_2$L, was prepared following a two-step procedure, in 84% overall yield.9 It was deprotonated, using potassium hydride, and reacted with two equivalents of [FeCl$_3$](DME) (DME = dimethoxyethane) to yield an air stable blue di-iron tetrachloride complex 1 (85%, unoptimized) (Scheme 2).

![Scheme 2. Synthesis of 1. Reagents and conditions: (i) 2 KH, THF, -30-25 °C, 2 h; (ii) 2 [FeCl$_3$(DME)], THF, 25 °C, 20 h.](image)

The complex’s paramagnetism rendered NMR spectroscopy ineffective, but the stoichiometry was confirmed by elemental analysis and mass spectrometry. The UV-Vis spectrum (Fig. S1) showed a strong ligand-to-metal charge transfer absorption at 590 nm.18 No other d–d transitions were detected, in agreement with the complex having two high-spin (HS) iron(III) centres in octahedral coordination environments. The effective magnetic moment, determined by Evans’ NMR method,19 at 293 K was 8.2 μB (8.37 μB is calculated for two isolated HS Fe(III)). Further investigation, using a Oxford Instruments Vibrating Sample Magnetometer in a field of 8 Tesla, shows the saturation moment (at 4.2 K) is approximately 9 μB (Fig. S2). These findings are consistent with a bimetallic complex in which both Fe(III) centres are in the HS (S=5/2) state,20 possibly with some ferromagnetic coupling.

Complex 1 was evaluated as a cyclohexene oxide (CHO) copolymerisation catalyst, reactions were conducted in neat CHO, at 80 °C and under 1-10 atm of carbon dioxide (Table 1). It was active at just 1 atm of CO$_2$ (entry 1), producing a copolymer in 93% yield, with 7% trans-cyclohexene carbonate (CHC). However, the quality of the copolymer was sub-optimal, with only 66 % carbonate linkages. The TON and TOF values were slightly lower than those of analogous Zn(II)/Co(II/III) species, but still showed good values at such low CO$_2$ pressure.5–11
On increasing the pressure to 10 atm (entry 2), the rate of copolymerisation was significantly increased with the activity being ~8 times greater than at 1 atm. Also, the quality of PCHC was excellent: only trace quantities of the trans-CHO by-product and >99% carbonate linkages in the copolymer were observed. The copolymerisation was run until solidification prevented further conversion (70%, entry 3), with the MALDI-ToF mass spectrum of the lower molecular weight species reported in the literature (e.g. [(salen)M(III)]Cl). Gel permeation chromatography (GPC) indicated a molecular weight of 11,700 and narrow polydispersity index (1.13) (Fig. S7). At low conversion (entry 2, 24%), the MALDI-ToF mass spectrum showed a major series of peaks corresponding to PCHC with chloride end-groups (Fig. S10-S12).

A copolymerisation mechanism is proposed (Scheme 3) where the Fe-Cl bond(s) initiate the ring-opening of CHO to generate an Fe-OR species, which undergo CO₂ insertion to produce an iron-carbonate intermediate. Propagation and copolymerisation occurs by sequential repetition of the ring-opening and insertion reactions. It is likely that the unprecedented activity of 1 is due to the bimetallic active site and the macroyclic ligand coordination environment. 1 is however not as active as the best homogenote catalytic systems reported in the literature (e.g. [(salen)M(III)] catalysts (M=Co/Cr) in the presence of onium salts). Under mild conditions (1 atm, 80 °C), 1 produced exclusively cis-cyclohexene carbonate on activation with bis(trisphenylphosphino)iminium chloride ([PPN]Cl) (entries 5-7). It is notable that [PPN]Cl was completely inactive when used on its own. On increasing the loading (entry 8), 90% conversion to cis-CHC was achieved, in 24 h. The cis-CHC product was characterised by a carbonyl stretching frequency in the FTIR spectrum at 1804 cm⁻¹ (vs. 1825 cm⁻¹ for the trans-isomer) and by the chemical shift of the methyne protons, at 4.63 ppm (vs. 3.90 ppm for the cis-isomer) in the H NMR spectra, of the methylene resonances, including PCHC carbonate isomer requires a mechanism involving a double-insertion to temperature used here are insufficient to yield significant quantities of trans-CHC (c.f. entries 1-4). The formation of the cis-isomer requires a mechanism involving a double-inversion of CHO stereochemistry (Scheme 3). It is proposed that [PPN]Cl facilitates exchange reactions between the initiating iron carbonate species and chloride ions. The putative anionic carbonate species would be significantly more nucleophilic than the metal bound carbonate and so undergo intramolecular nucleophilic substitution, chloride elimination and formation of the cis-CHC. Such a mechanism is consistent with the finding that as the number of equivalents of [PPN]Cl is reduced so the percentage of cis-isomer reduces (entries 5-7). If a single equivalent of [PPN]Cl is used, some copolymerisation also occurs, highlighting the importance of excess chloride (vs. 1) to prevent competitive binding of epoxide at the initiating Fe-carbonate species and competing copolymerisation. Increasing the pressure of CO₂ to 10 atm, keeping all other conditions the same, led to an increase in production of PCHC (with 99% carbonate linkages), with low amounts of the trans-CHC also being observed (entry 9). There are only a few reports of cis-CHC production from CO₂, and indeed, many common cyclic carbonate catalysts are inactive for CHO.

### Table 1: CO₂/CHO reaction catalysed by complex 1

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst mole%</th>
<th>p(CO₂) (atm)</th>
<th>Time (h)</th>
<th>% CHO Conversion</th>
<th>TON*</th>
<th>TOF (h⁻¹)</th>
<th>% CHC</th>
<th>% PCHC [Carbonate]%</th>
<th>Mₘ/Mₘ⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1% 1</td>
<td>1</td>
<td>48</td>
<td>29</td>
<td>290</td>
<td>6</td>
<td>7 (trans)</td>
<td>93 [66]</td>
<td>2000 [1.55]</td>
</tr>
<tr>
<td>2</td>
<td>0.1% 1</td>
<td>10</td>
<td>5</td>
<td>24</td>
<td>235</td>
<td>47</td>
<td>1 (trans)</td>
<td>99 [99]</td>
<td>3,100 [1.18]</td>
</tr>
<tr>
<td>3</td>
<td>0.1% 1</td>
<td>10</td>
<td>24</td>
<td>70</td>
<td>694</td>
<td>29</td>
<td>1 (trans)</td>
<td>99 [99]</td>
<td>11,700 [1.13]</td>
</tr>
<tr>
<td>4</td>
<td>0.01% 1</td>
<td>10</td>
<td>24</td>
<td>25</td>
<td>2570</td>
<td>107</td>
<td>1 (trans)</td>
<td>99 [99]</td>
<td>17,200 [1.03]</td>
</tr>
<tr>
<td>5</td>
<td>0.1% 1 + 0.4%</td>
<td>1</td>
<td>48</td>
<td>41</td>
<td>410</td>
<td>9</td>
<td>100 (99% cis)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>0.1% 1 + 0.2%</td>
<td>1</td>
<td>120</td>
<td>33</td>
<td>330</td>
<td>3</td>
<td>100 (97% cis)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>0.1% 1 + 0.1%</td>
<td>1</td>
<td>24</td>
<td>20</td>
<td>200</td>
<td>8</td>
<td>89 (96% cis)</td>
<td>11 [27]</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>0.1% 1 + 2%</td>
<td>1</td>
<td>24</td>
<td>90</td>
<td>90</td>
<td>4</td>
<td>100 (99% cis)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>0.1% 1 + 0.2%</td>
<td>1</td>
<td>10</td>
<td>24</td>
<td>700</td>
<td>29</td>
<td>76 (96% cis)</td>
<td>24 [99]</td>
<td>2300 [1.26]</td>
</tr>
</tbody>
</table>

* Reaction conditions: neat CHO, 80 °C. From the normalised integrals, in the ¹H NMR spectra, of the methylene resonances, including PCHC carbonate (δ: 4.65 ppm), PCHC ether (δ: 3.45 ppm), and CHC (δ: 3.9 (trans) or 4.63 ppm (cis)). TON = molCHO/mol inhibitor. TOF = TON/h. % Carbonate = (carbonate carbonyl linkages)/(copolymer carbonate + ether linkages). Determined by GPC, in THF, using narrow Mₘ polystyrene standards as calibrants.
one of the homogeneous DMC model compounds was cis-CHC selective, however, relatively harsh conditions (52 atm CO₂) were necessary.¹³

![Scheme 3. Proposed mechanism for CO₂/CHO coupling (for clarity, only (R,S)-CHO is represented here although the same reactions occur for the enantiomer, yielding a racemic mixture of cis-CHC and atactic PCHC).](image)

In order to establish the generality of the catalyses, I was tested with propylene (PO) and styrene oxide (SO) (Table 2).

**Table 2 CO₂/PO and SO coupling catalysed by complex I**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Entry</th>
<th>mol% 1: mol%</th>
<th>Epoxide</th>
<th>t (h)</th>
<th>T (°C)</th>
<th>% Conv.</th>
<th>TON</th>
<th>TOF (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>0.1 : 0.2</td>
<td>PO</td>
<td>24</td>
<td>25</td>
<td>18</td>
<td>180</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.1 : 0.2</td>
<td>PO</td>
<td>24</td>
<td>34</td>
<td>50</td>
<td>50</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.5 : 1</td>
<td>PO</td>
<td>48</td>
<td>25</td>
<td>91</td>
<td>182</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.1 : 0.2</td>
<td>SO</td>
<td>24</td>
<td>25</td>
<td>3</td>
<td>30</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.1 : 0.2</td>
<td>SO</td>
<td>24</td>
<td>80</td>
<td>83</td>
<td>83</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.5 : 1</td>
<td>SO</td>
<td>24</td>
<td>25</td>
<td>17</td>
<td>34</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>0.5 : 1</td>
<td>SO</td>
<td>20</td>
<td>80</td>
<td>98</td>
<td>196</td>
<td>10</td>
</tr>
</tbody>
</table>

* Reaction conditions: neat epoxide, 1 atm CO₂. From the normalised integrals, in the ¹H NMR spectra, of the methylene resonances * TON = molₑₐₛₜ/molₑₓ₂, * TOF = TON/h.

The use of I and two equivalents of [PPN]Cl gave a good catalyst for production of propylene carbonate (PC) and styrene carbonate (SC). It was even active under mild conditions: 25 °C and 1 atm CO₂ (entries 1, 4). Although, the activity was much improved by increasing the temperature (entries 2, 5, 7) and/or the catalyst loading (entries 3, 6, 7).

Thus, using 0.5% of I and 1% of [PPN]Cl, 91% conversion of PO into cyclic propylene carbonate was achieved within 48 h at 25 °C (entry 3). At 80 °C, the conversion of SO was >80% after 24 h (entry 5), or within 6 h at higher catalyst loadings. There are only a few cyclic carbonate catalysts active under such mild conditions, the best of which are di-aluminium salen complexes.¹³⁻⁻¹⁴ Catalyst I is slightly less active than these catalysts (*c.f.* related conditions to entry 6, di-AI has TON = 86 and TOF 4 h⁻¹).¹¹ Interestingly, the di-AI catalysts also required two equivalents of co-catalyst and a bimetallic active site to coordinate CO₂ as a carbamate.¹⁴

In conclusion, a novel di-iron catalyst for CO₂/epoxide coupling is reported. The catalyst shows good productivity and activity for the sequential copolymerisation of CHO and CO₂, under mild conditions. The combination of the new catalyst and more than two equivalents of [PPN]Cl leads to the selective formation of cis-cyclohexene carbonate. The catalyst can be generally applied, yielding propylene carbonate and styrene carbonate, under only 1 atm pressure CO₂. This is the first example of an iron catalyst for either the production of cyclohexene cyclic carbonate or polycarbonate. Furthermore it is a rare example of catalysis at 1 atm for these processes and is a cis-selective carbonate catalyst.

**Notes and references**

a) Department of Chemistry, Imperial College London, London, SW7 2AZ, United Kingdom Tel: +44(0)20 7594 5790; E-mail: c.k.williams@imperial.ac.uk; b) Department of Physics, Imperial College London, London, SW7 2AZ, United Kingdom

† Electronic Supplementary Information (ESI): Experimental procedures; spectral data for I and PCHC. See DOI: 10.1039/b000000x

22. The chains with two hydroxyl end-groups derived from water procedures; spectral data for all materials.