A novel di-iron(III) catalyst for the copolymerisation of
cyclohexene oxide and CO₂ 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
CO₂ and epoxides (Scheme 1) is one of the few processes that
actually consume CO₂ 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.

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 catalysis,
including those that operate at low CO₂ pressure, thereby
improving the energy balance and net CO₂ consumption.
Recently, we reported various bimetallic Zn(II) and Co(II/III)
copolymerisation catalysts which displayed impressive activity, at only 1 atm CO₂ pressure.9-11 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 catalyst. Double metal cyanides, e.g.
[Zn₂(FeCN)₆]₄⁻, are viable heterogeneous copolymerisation
catalysts (although 50-60 atm CO₂ are required),12 however,
the homogenous 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(III)/Cr(III) salen complexes are
excellent catalysts, the Fe(III) analogues were inactive.16, 17

The macrocyclic pro-ligand, H₂L, was prepared following a
two-step procedure, in 84% overall yield.9 It was
deprotonated, using potassium hydride, and reacted with two
equivalents of [FeCl₃(DME)] (DME = dimethoxyethane) to
yield an air stable blue di-iron tetrachloride complex 1 (85%,
unoptimized) (Scheme 2).

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 CO₂ (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 CO₂ pressure.9-11
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-CHC by-product and >99% carbonate linkages in the copolymer were observed. The copolymerisation was run until solidification prevented further conversion (70%, entry 3), yielding PCHC with good productivity (TON: 694), indeed the new di-iron catalyst was as active under these conditions as the recently reported dizinc catalyst. 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 I is due to the bimetallic active site and the macroyclic ligand coordination environment. I is however not as active as the best homogenous catalytic systems reported in the literature (e.g. [salen]M(III)) catalysts (M=Co/Cr) in the presence of onium salts. 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 I is due to the bimetallic active site and the macroyclic ligand coordination environment. I is however not as active as the best homogenous catalytic systems reported in the literature (e.g. [salen]M(III)) catalysts (M=Co/Cr) in the presence of onium salts.

At lower catalyst loading (0.01%), the TON (2570) and TOF (107 h⁻¹) increased markedly as did the molecular weight (entry 4). However, GPC analysis revealed a bimodal distribution and the MALDI-ToF mass spectrum of the lower molecular weight series (Mw: 8100) revealed chains end-capped with cyclohexenyl groups and hydroxyl groups (Fig. S14). The cyclohexenyl end-group is proposed to arise by chain transfer reactions with cyclohex-1-enol, produced by elimination of HCl from the expected chloro-cyclohexanolate iron species. Indeed, traces of cyclohex-1-enol have indeed been identified in the control reaction between I (0.1%) and CHO, in absence of CO₂.

Researchers working with salen metal halide catalysts (or closely related derivatives) have observed increased productivity in the presence of ionic co-catalysts, such as ammonium salts. Under mild conditions (1 atm, 80 °C), I 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 trans-isomer). Such a mechanism is consistent with the finding that as the number of carbon atoms in the epoxide increased, the desymmetrisation decreased, with 10-membered rings giving rise to a cis/trans ratio of 1:1 in 2- and 4-membered rings. Therefore, 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 trans-isomer). 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 trans-isomer).
one of the homogeneous DMC model compounds was cis-CHC selective, however, relatively harsh conditions (52 atm CO₂) were necessary.\textsuperscript{13}

\[
\begin{array}{c}
\text{[Fe-Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{OO} \\
\text{Cl} \\
\text{[Fe-Cl}}
\end{array}
\]

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).

In order to establish the generality of the catalyses, 1 was tested with propylene (PO) and styrene oxide (SO) (Table 2).

Table 2 CO₂/PO and SO coupling catalysed by complex \(1^\text{\textsuperscript{a}}\)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Entry mol%</th>
<th>Epoxide</th>
<th>t (h)</th>
<th>T (°C)</th>
<th>% Conv.</th>
<th>TON\textsuperscript{c}</th>
<th>TOF (h\textsuperscript{-1})\textsuperscript{d}</th>
</tr>
</thead>
<tbody>
<tr>
<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>2</td>
<td>0.1 : 0.2</td>
<td>PO</td>
<td>24</td>
<td>34</td>
<td>50</td>
<td>500</td>
<td>21</td>
</tr>
<tr>
<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>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>5</td>
<td>0.1 : 0.2</td>
<td>SO</td>
<td>24</td>
<td>80</td>
<td>83</td>
<td>830</td>
<td>35</td>
</tr>
<tr>
<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>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>

\textsuperscript{a} Reaction conditions: neat epoxide, 1 atm CO₂. \textsuperscript{b} From the normalised integrals, in the \(^1\text{H}\) NMR spectra, of the methylene resonances. \textsuperscript{c} TON = mol_{prod}/mol\_cat. \textsuperscript{d} TOF = TON/h.

Catalyst 1 did not yield any copolymer, even under 10 atm CO₂ and at higher temperature (40 °C for PO, 80 °C for SO). The use of 1 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 1 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.\textsuperscript{31-34}

Catalyst 1 is slightly less active than these catalysts (c.f under related conditions to entry 6, di-AL has TON = 86 and TOF 4 h\textsuperscript{-1}).\textsuperscript{31} Interestingly, the di-AL catalysts also required two equivalents of co-catalyst and a bimetallic active site to coordinate CO₂ as a carbamate.\textsuperscript{34}

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

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\textsuperscript{‡} Electronic Supplementary Information (ESI): Experimental procedures; spectral data for 1 and PCHC. See DOI: 10.1039/b000000x

22. The chains with two hydroxyl end-groups derived from water contamination, a common phenomenon in this catalysis, e.g.ref 27.