

A Bimetallic Iron(III) Catalyst For CO₂/Epoxide Coupling[‡]

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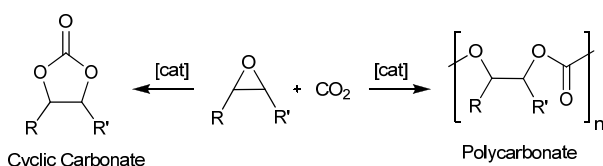
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A novel di-iron(III) catalyst for the copolymerisation of cyclohexene oxide and CO₂ to yield poly(cyclohexene)carbonate, under mild conditions, is reported. The catalyst selectivity was completely changed on addition of an ammonium co-catalyst to yield 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.

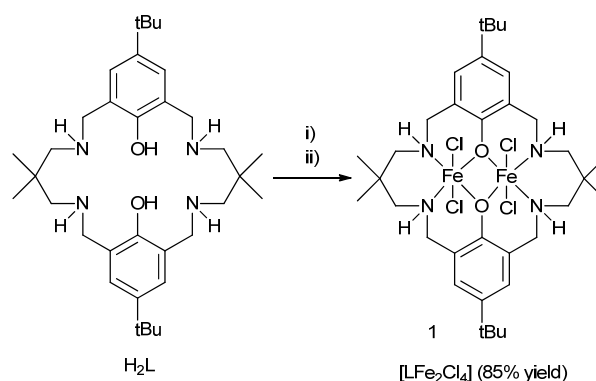


Scheme 1. Coupling of CO₂/epoxides.

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 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 catalysis. Double metal cyanides, e.g. [Zn₃[Fe(CN)₆]₂], are viable heterogeneous copolymerisation catalysts (although 50-60 atm CO₂ 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(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).



Scheme 2. Synthesis of **1**. Reagents and conditions: (i) 2 KH, THF, -25 °C, 2 h; (ii) 2 [FeCl₃(DME)], THF, 25 °C, 20 h.

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

Table 1 CO₂/CHO reaction catalysed by complex **1**^a

Entry	Catalyst mole%	<i>p</i> (CO ₂) (atm)	Time (h)	% CHO Conversion ^b	TON ^c	TOF (h ⁻¹) ^d	% CHC	% PCHC [% Carbonate] ^{b,e}	<i>M</i> _n [<i>M</i> _w / <i>M</i> _n] ^f
1	0.1% 1	1	48	29	290	6	7 (<i>trans</i>)	93 [66]	2000 [1.55]
2	0.1% 1	10	5	24	235	47	1 (<i>trans</i>)	99 [99]	3,100 [1.18]
3	0.1% 1	10	24	70	694	29	1 (<i>trans</i>)	99 [99]	11,700 [1.13]
4	0.01% 1	10	24	25	2570	107	1 (<i>trans</i>)	99 [99]	17,200 [1.03] 8,100 [1.06]
5	0.1% 1 + 0.4% [PPN]Cl	1	48	41	410	9	100 (99% <i>cis</i>)	-	-
6	0.1% 1 + 0.2% [PPN]Cl	1	120	33	330	3	100 (97% <i>cis</i>)	-	-
7	0.1% 1 + 0.1% [PPN]Cl	1	24	20	200	8	89 (96% <i>cis</i>)	11 [27]	-
8	1% 1 + 2% [PPN]Cl	1	24	90	90	4	100 (99% <i>cis</i>)	-	-
9	0.1% 1 + 0.2% [PPN]Cl	10	24	70	700	29	76 (96% <i>cis</i>)	24 [99]	2300 [1.26]

^a Reaction conditions: neat CHO, 80 °C. ^b 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*)). ^c TON = mol_{CHO used}/mol₁. ^d TOF = TON/h. ^e % Carbonate = (copolymer carbonate linkages)/(copolymer carbonate + ether linkages) ^f Determined by GPC, in THF, using narrow *M*_w polystyrene standards as calibrants.

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.⁹ ¹³C{¹H}NMR spectroscopy showed that the PCHC was atactic (Fig. S6).²¹ 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 macrocyclic ligand coordination environment.

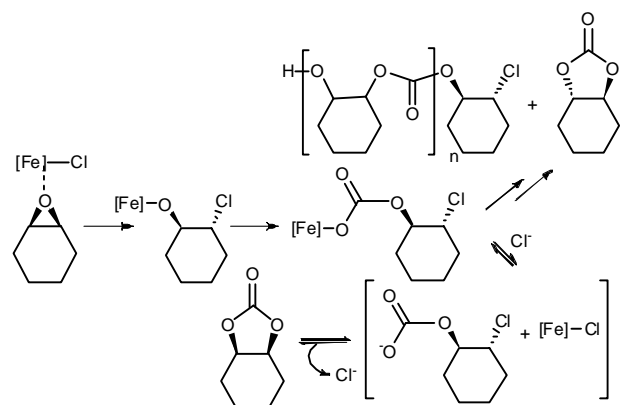
At lower catalyst loading (0.01%), the TON (2570) and TOF (107 h⁻¹) increased markedly as did the molecular weight (entry 4). However, GPC analysis revealed a bimodal distribution and the MALDI-ToF mass spectrum of the lower molecular weight series (*M*_n: 8100) revealed chains end-capped with cyclohexenyl groups and hydroxyl groups (Fig. S14).¹⁰ 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 **1** (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.^{7, 22, 23} Indeed, catalyst **1** is less active than

the best [(salen)M(III)] catalysts (M=Co/Cr) in the presence of -onium salts.⁸ However, 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 *trans*-isomer) in the ¹H NMR spectrum (Figs. S3,4).²⁴

To our knowledge, this is the first example of an Fe active site for either the copolymerisation or cyclisation of epoxides/CO₂.⁵⁻⁷ Furthermore, the formation of *cis*-CHC is unusual: the *trans*-isomer is more commonly formed, usually by back-biting reactions under thermodynamic control (Scheme 3).^{7, 25} However, the low pressure and moderate 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,^{13, 26-28} indeed, many common cyclic

carbonate catalysts are inactive for CHO.^{5, 29, 30} Interestingly, 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).

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**^a

Entry	Catalyst mol% 1 : mol% [PPN]Cl	Epoxide	t (h)	T (°C)	% Conv. ^b	TON ^c	TOF (h ⁻¹) ^d
1	0.1 : 0.2	PO	24	25	18	180	8
2	0.1 : 0.2	PO	24	34	50	500	21
3	0.5 : 1	PO	48	25	91	182	4
4	0.1 : 0.2	SO	24	25	3	30	1
5	0.1 : 0.2	SO	24	80	83	830	35
6	0.5 : 1	SO	24	25	17	34	1
7	0.5 : 1	SO	20	80	98	196	10

^a Reaction conditions: neat epoxide, 1 atm CO₂. ^b From the normalised integrals, in the ¹H NMR spectra, of the methylene resonances ^c TON = mol_{CHO}/mol_I. ^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.³⁰⁻³³ 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⁻¹).³⁰ Interestingly, the di-Al catalysts also required two equivalents of co-catalyst; a mechanism was proposed whereby one Al centre binds and ring-opens the epoxide and the other delivers the CO₂, which was pre-coordinated as a carbamate salt.³³

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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