Iron(III) *N,N*-Dialkylcarbamates Catalyze the Formation of Cyclic Carbonates from Carbon Dioxide and Epoxides at Ambient Conditions via Dynamic CO$_2$ Trapping as Carbamato Ligand

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Abstract. Easily available and inexpensive Fe(III) carbamates was employed in the solventless synthesis of a series of cyclic carbonates from epoxides, by reaction with CO$_2$ at room temperature and atmospheric pressure, in the presence of a co-catalyst. Different experimental conditions (type and concentration of catalyst and co-catalyst, as well as reaction time) were investigated: Fe(O$_2$CNEt$_2$)$_3$ and NBu$_4$Br acted as the best catalyst/co-catalyst combination, allowing the formation of propylene carbonate and 1,2-butylene carbonate with quantitative yield and selectivity during 24 h of reaction time. According to NMR and DFT studies, the reaction proceeds with the dynamic trapping of carbon dioxide as a carbamato ligand.

Introduction

The development of sustainable synthetic routes exploiting carbon dioxide as a largely available, cost effective and non toxic C1 synthon represents one of the most intriguing challenges for contemporary chemistry research.[1] Processes converting CO_2 into a range of useful chemicals have witnessed significant progress in the last decade,[2] and in particular the synthesis of cyclic carbonates from CO_2 and epoxides has been established even on industrial scale, overcoming the formerly critical use of toxic phosgene (Scheme 1).[3]
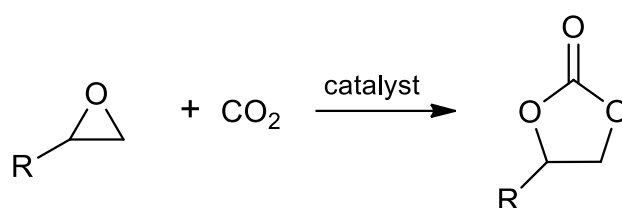
Scheme 1. CO_2/epoxide coupling reaction affording cyclic carbonates.

Cyclic carbonates are valuable compounds finding applications in several fields, e.g. as non-protic high boiling polar solvents,[4] monomers for polymer synthesis,[5] fine chemicals [6] and electrolytes for lithium-ion batteries.[7]

A wide variety of catalytic systems successfully perform the CO_2/epoxide coupling to access cyclic carbonates,[8] including metal complexes,[9] metal free organocatalysts,[10] ionic liquids [11] and various heterogeneous systems.[12] Concerning the metal complexes, Schiff bases,[13] porphyrins[14] and polyphenolates[15] are amongst the most commonly employed ligands.

In the light of environmental issues, the development of simple and efficient catalytic systems based on non toxic and earth abundant metals is of ultimate importance to modern synthetic chemistry,[16] and iron certainly plays a central role in this scenario.[17]

Various iron compounds have been proposed to catalyze the coupling of CO_2 with propylene oxide or more complex epoxides, working either in the presence or in the absence of a co-catalyst;[18] in most of the cases, the use of high CO_2 pressure (5-90 bar) and/or high temperature (>80 °C) are generally required in order to achieve satisfactory performances.[13c,19] Remarkably, only few

examples of iron complexes, all containing macrocyclic amino-phenolato ligands, are effective in the CO_2/epoxide conversion to cyclic carbonates under mild conditions (RT, p_{CO_2} = 1-2 bar), even when the simplest epoxide (i.e., propylene oxide) is concerned.[20]

Homoleptic metal carbamates, $M(O_2CNR_2)_n$, are inexpensive and versatile materials that have found application as catalytic precursors for some homogeneous reactions, including the alkene hydrogenation [21] and the polymerization of cyclic esters [22] and alkenes.[23] $M(O_2CNR_2)_n$ are an intrinsic form of CO_2 activation, being easily accessible from the parent metal chlorides by reaction with dialkylamines under atmospheric CO_2 pressure (Eq. 1).[24]

$$MCl_n + n\ CO_2 + 2n\ NHR_2 \rightarrow M(O_2CNR_2)_n + n\ (NH_2R_2)Cl \qquad (1)$$
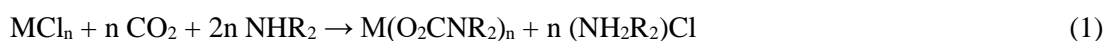
The carbamato ligand has proven to be generally labile towards exchange with free CO_2,[25] and this feature suggested some potential in CO_2 catalysis. Herein, we propose for the first time metal carbamates as CO_2 activation catalysts: Fe(III) compounds effectively, in combination with a co-catalyst converted a series of epoxides into the respective cyclic carbonates by reaction with carbon dioxide at room temperature and atmospheric pressure.

Results and discussion

We selected the easily available iron carbamates $Fe^{II}(O_2CNEt_2)_2$[26] and $Fe^{III}(O_2CNEt_2)_3$[27] to evaluate their catalytic potential in the formation of propylene carbonate (PC) from propylene oxide (PO) and CO_2. The solvent-free reactions were carried out during 24 h at 25°C and 1 atm, in the presence of $[NBu_4]Br$ (TBAB) as a co-catalyst (Table 1).

Table 1. Conversion and selectivity values of PO/CO_2 to PC conversion by Fe catalysts.

H₃C—(epoxide) + CO₂ → (Fe catalyst, TBAB) → 4-methyl-1,3-dioxolan-2-one (propylene carbonate, H₃C substituted)
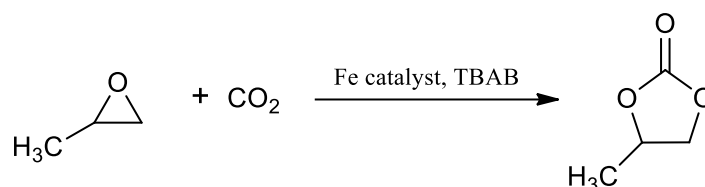
Entry	Catalyst	Conversion [%][a]	Selectivity [%][b]
1	$Fe(O_2CNEt_2)_2$	47	>99
2	$Fe(O_2CNEt_2)_3$	66	>99
3	$FeCl_3$	47	38
4	----	1%	>99
Reaction conditions: propylene oxide (PO) (1 mL, 14.3 mmol), catalyst 1mol%, TBAB 1mol%, T = 25°C, $p(CO_2)$ = 1 bar, t = 24 h. [a]Determined by ^1H NMR [28]using mesitylene as standard. [b]Calculated with respect to PC.			

Both iron compounds afforded PC with almost quantitative selectivity and moderate conversion. For the sake of comparison, $FeCl_3$ was investigated under the same experimental conditions, as an alternative, simple iron-based catalyst.[29] In this case, the reaction stood out with a low selectivity value (38%): ^1H NMR analysis on the final mixture showed the presence of by-products which could not be identified. A blank experiment (Table 1, entry 4) demonstrated that a catalyst is needed to achieve an appreciable conversion.

As a result of the preliminary outcomes, we focused on $Fe(O_2CNEt_2)_3$ as a promising catalyst, concentrating on optimization procedures and further epoxide/CO_2 coupling reactions. First, we investigated the effect of the catalyst concentration (Table 2).

Table 2.PO/CO_2 to PC conversion using different amounts of $Fe(O_2CNEt_2)_3$ as catalyst.

Entry	$Fe(O_2CNEt_2)_3$[mol %]	Conversion [%] [a]	Selectivity [%] [b]
1	0	0	
2	0.1	33	>99
3	1	64	>99
4	2	79	>99
Reaction conditions: propylene oxide (PO) (1 mL, 14.3 mmol), TBAB 1 mol%, T = 25 °C, $p(CO_2)$ = 1 bar, t = 24 h. [a]Determined by ^1H NMR [28]using mesitylene as standard. [b]Calculated with respect to PC.			

The results shown in Table 2 outline a beneficial effect of the increase of catalyst concentration, the conversion reaching a maximum value (79%) when the iron complex was used approximately at its solubility limit in PO (2 mol%), without affecting selectivity.

Then, on account of previous studies evidencing the crucial role exerted by the co-catalyst in CO_2/epoxide coupling reactions,[16c,e,18,30] we studied the synthesis of PC by using a selection of possible co-catalysts (Table 3). The concentration of the iron compound was fixed at 0.1 mol% throughout all these tests, to better evaluate the effect of the co-catalyst.

Table 3. PO/CO_2 to PC conversion catalyzed by $Fe(O_2CNEt_2)_3$ in association with different co-catalysts.

Entry	Cocatalyst (%)	Conversion [%] [a]	Selectivity [%] [b]
1	NONE	38	0
2	[NBu$_4$]Cl (0.1%)	12	83
3	[NBu$_4$]Cl (1%)	29	72
4	[NBu$_4$]Br (0.1%)	31	95
5	[NBu$_4$]Br (1%)	33	>99
6	[NBu$_4$]Br (2%)	57	>99
7[c]	[NBu$_4$]Br (2%)	>99	>99
8	[NBu$_4$]I (0.1%)	46	17
9	[NBu$_4$]I (1%)	54	72
10	DMAP (0.1%)	16	19
11	DMAP (1%)	43	3
12	[PPN]Cl (0.1%)	33	27
13	[PPN]Cl (1%)	40	50
Reaction conditions: propylene oxide (PO) (1 mL, 14.3 mmol), catalyst 0.1 mol%, T = 25 °C, p(CO_2) = 1 bar, t = 24 h. [a]Determined by ^{1}H NMR [28] using mesitylene as standard. [b]Calculated with respect to PC. [c]Catalyst concentration = 1%.			

The results shown in Table 3 indicate that the process is inefficient in the absence of co-catalyst, and that [NBu$_4$]Br (TBAB) performed as the best co-catalyst. The identity of by-products generated from those reactions occurring with low selectivity could not be clearly established, these species being featured by very broad NMR signals. We suppose the possible formation of poly/oligoethers [31] and of cyclic carbamates, the latter resulting from amine released from fragmentation of carbamato ligands. Otherwise, the formation of polycarbonates could be ruled out. Remarkably, the

combination of $Fe(O_2CNEt_2)_3$ with TBAB, respectively in 1 mol% and 2 mol% concentration, yielded quantitative conversion and selectivity during an optimal time of 24 h (Table 4).
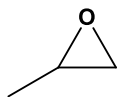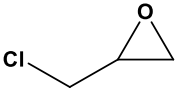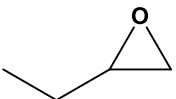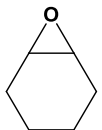
Table 4. Effect of reaction time on PO/CO_2 to PC conversion.

Entry	Time (h)	Conversion [%] [a]	Selectivity [%] [b]
1	1	21	>99
2	16	36	>99
3	20	64	>99
4	24	>99	>99
Reaction conditions: propylene oxide (PO) (1 mL, 14.3 mmol), catalyst 1 mol%, co-catalyst (TBAB) 2%, T = 25 °C, $p(CO_2)$ = 1 bar. [a]Determined by ^1H NMR [28]using mesitylene as standard. [b]Calculated with respect to PC.			

Having found that the $Fe(O_2CNEt_2)_3$/TBAB system is effective in the conversion of propylene oxide to propylene carbonate at room temperature and atmospheric pressure, we shifted our attention to the analogous reactions involving different epoxides, and the catalysts $Fe(O_2CN^iPr_2)_3$ and $Fe(O_2CNBz_2)_3$ ($^iPr = CHMe_2$; $Bz = CH_2Ph$)[27] were also used in these experiments, see Table 5.

Table 5. Synthesis of cyclic carbonates from CO_2 and various epoxides using $Fe(O_2CNR_2)_3$ as catalytic precursors.

Epoxide	Entry	Catalytic precursor [a]	Conversion [%] [b]	Yield (%) [c]	Selectivity [%] [d]
	1	$Fe(O_2CNEt_2)_3$	>99	90	>99
	2	$Fe(O_2CN^iPr_2)_3$	85	80	>99
	3	$Fe(O_2CNBz_2)_3$	82	69	>99
	4	$Fe(O_2CNEt_2)_3$	60	n.d. [e]	>99
	5[f]	$Fe(O_2CNEt_2)_3$	76	n.d.	>99
	6	$Fe(O_2CN^iPr_2)_3$	61	n.d.	>99
	7	$Fe(O_2CNBz_2)_3$	60	n.d.	>99
	8[g]	$Fe(O_2CNEt_2)_3$	>99	88	>99
	9[g]	$Fe(O_2CN^iPr_2)_3$	75	73	>99
	10[f]	$Fe(O_2CNBz_2)_3$	80	67	>99
	11	$Fe(O_2CNEt_2)_3$	7	n.d.	>99
	12	$Fe(O_2CN^iPr_2)_3$	6	n.d.	>99
	13	$Fe(O_2CNBz_2)_3$	4	n.d.	>99

	Entry	Catalyst			
(styrene oxide structure)	14	Fe(O$_2$CNEt$_2$)$_3$	60	n.d.	>99
	15[f]	Fe(O$_2$CNEt$_2$)$_3$	90	87	>99
	16	Fe(O$_2$CN^{i}Pr$_2$)$_3$	31	n.d.	>99
	17	Fe(O$_2$CNBz$_2$)$_3$	44	n.d.	>99

Reaction conditions: see Experimental. [a] Et = C$_2$H$_5$; ^{i}Pr = CH(CH$_3$)$_2$; Bz = CH$_2$Ph. [b] Determined by ^{1}H NMR [28] using mesitylene as standard. [c] Determined on the isolated product. [d] Calculated with respect to PC. [e] n.d.: not determined. [f] t = 48 h. [g] Determined by ^{1}H NMR using CH$_2$Cl$_2$ as standard.

All the epoxides were carbonated into the respective cyclic carbonates with nearly quantitative selectivity. The effective conversion of propylene oxide and 1,2-butylene oxide (Table 5, entries 1 and 8) at room temperature using CO$_2$ at atmospheric pressure represents a rare feature in the field of iron-catalyzed CO$_2$/epoxide coupling processes. Interestingly, the cyclic carbonate produced from cyclohexene oxide was exclusively of cis-stereochemistry according with the comparison of ^{1}H and ^{13}C NMR spectra registered and previously reported.[32] Cyclic carbonates were isolated in high yields by addition of water to the reaction system, followed by dichloromethane extractions (Table 5, Entries 1, 2, 3, 8, 9, 10 and 15). When Fe(O$_2$CNBz$_2$)$_3$ was used as catalyst, the hydrolytic treatment required a small amount of sulphuric acid, affecting the final yields. As a matter of fact, the performance exhibited by Fe(O$_2$CNEt$_2$)$_3$ is superior even when compared to the best iron catalysts reported to date operating under mild conditions, with reference to the same organic substrates.[20] In general, Fe(O$_2$CNEt$_2$)$_3$ was slightly more effective than the analogous diisopropyl and dibenzyl species. On the other hand, the substantial inertness of cyclohexene oxide is consistent with literature reports, the transformation into the corresponding cyclic carbonate usually being unsuccessful at atmospheric pressure and room temperature.[19b,20a,33]

To shed light on the mechanism of the iron carbamate catalysis, we performed NMR [34] and DFT studies. First, the stoichiometric reaction between Fe(O$_2$CNEt$_2$)$_3$, PO and TBAB (molar ratio = 1:4:1) was studied by NMR spectroscopy in the absence of external CO$_2$, using CDCl$_3$ as solvent. A sluggish conversion of PO to PC was recognized, reaching 10% after 72 h (see Figure S1 in the Supporting Information). This result suggested that the epoxide/CO$_2$ coupling could proceed with

pre-activation of reacting CO_2, via a dynamic incorporation in the iron complex as a carbamato ligand.

DFT calculations were therefore carried out to substantiate this hypothesis. Preliminary calculations on iron(III) dimethyl- and diethylcarbamato species support the idea of D1 polymers with bridging ligands and octahedral geometry around the Fe centres. Accordingly, the IR spectrum of $Fe(O_2CNEt_2)_3$ shows an intense band at 1488 cm^{-1}, ascribable to the asymmetric stretching vibration of bidentate (terminal or bridging) $[(O_2CNEt_2)]^-$ groups. On the other hand, the more sterically hindered isopropyl derivative is characterized by a strong absorption above 1500 cm^{-1} (1579 cm^{-1}), indicating the presence of at least one monodentate ligand.[27]

The model tri-iron chains $[Fe_3(\mu\text{-}O_2CNR_2)_6(\kappa^2\text{-}O_2CNR_2)_2]^+$ (R = Me, Et) are very stable with respect to fragmentation into monomers (Eq. 2), despite the favourable entropy variations (ca. 120 cal mol^{-1} K^{-1}):

$$[Fe_3(\mu\text{-}O_2CNR_2)_6(\kappa^2\text{-}O_2CNR_2)_2]^+ \rightarrow [Fe(\kappa^2\text{-}O_2CNR_2)_2]^+ + 2\,[Fe(\kappa^2\text{-}O_2CNR_2)_3] \qquad (2)$$

$\Delta G = + 66.7$ kcal mol^{-1} (R = Me); $+ 60.0$ kcal mol^{-1} (R = Et).

The DFT-optimized structure of $[Fe_3(\mu\text{-}O_2CNMe_2)_6(\kappa^2\text{-}O_2CNMe_2)_2]^+$ is representatively shown in Figure 1, while a view of the homologous structure $[Fe_3(\mu\text{-}O_2CNEt_2)_6(\kappa^2\text{-}O_2CNEt_2)_2]^+$ is given in Figure S2.
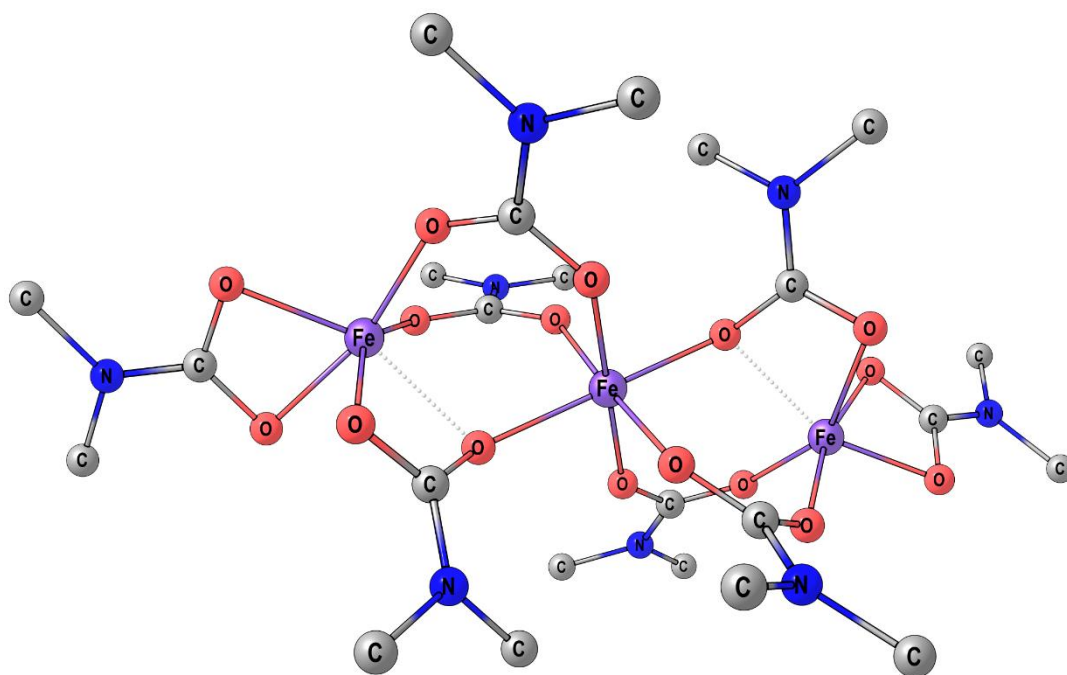
Figure 1. DFT-optimized structure of $[Fe_3(\mu\text{-}O_2CNMe_2)_6(\kappa^2\text{-}O_2CNMe_2)_2]^+$. Hydrogen atoms omitted for clarity. Selected averaged computed bond lengths and angles referred to the central iron atom: Fe-O 2.008 Å, O-Fe-O (trans) 175.4°.

To reduce the computational effort, the former was selected as the starting point for further calculations. In addition, the model was further simplified by replacing the terminal κ^2-carbamates with chlorides, and bromide ion was introduced as a counteranion simulating the role of the co-catalyst. In conclusion, we identified $[Fe_3(\mu\text{-}O_2CNMe_2)_6Cl_2]Br$ (**A**, Figure 2) as the most simple, reliable model of the catalytic system, and we proceeded to investigate the possible reactivity around the central iron.
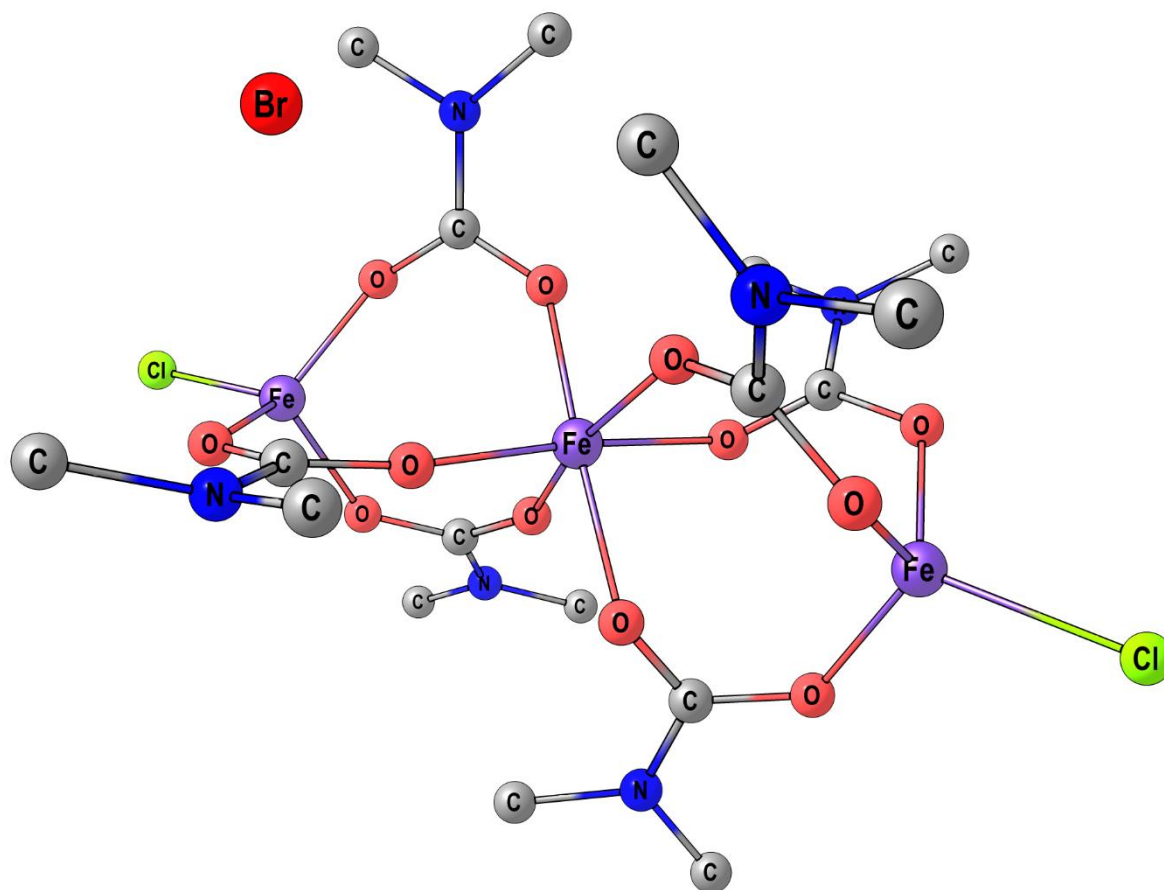
Figure 2. DFT-optimized structure of [Fe$_3$(μ-O$_2$CNMe$_2$)$_6$Cl$_2$]Br (**A**). Hydrogen atoms omitted for clarity. Selected averaged computed bond lengths and angles referred to the central iron atom: Fe-O 1.999 Å, O-Fe-O (trans) 173.3°.

The addition of propylene oxide (PO) to [Fe$_3$(μ-O$_2$CNMe$_2$)$_6$Cl$_2$]Br giving **B** is slightly endergonic (see Scheme 2 for an overall view of reaction intermediates, and Figure S4). Notwithstanding, subsequent Br-ring opening to **C**(Figure S5) strongly lowers the Gibbs free energy of the system. On the other hand, the alternative Fe-coordination of CO$_2$ and interaction of the latter with bromide affords the less probable intermediate **C′** in Scheme 2 (see also Figure S6). It is therefore reasonable to assume that the first substrate interacting with the iron catalyst is PO rather than CO$_2$. Noticeably, no stable intermediate was obtained on considering the reaction between **C** and external CO$_2$. Conversely, the intramolecular nucleophilic attack on the C−Br bond by a carbamato ligand leads to the formation of **D** (Figure S7), that is only about 3 kcal mol^{-1} less stable than **C**. In **D**, the alkoxido-carbamato anion [OCH(Me)CH$_2$OC(NMe$_2$)O]$^-$ behaves as a bridging ligand towards two iron centres. The Alkoxide termination can attack the adjacent carbonylic function, generating one

coordinated molecule of propylene carbonate (PC) and a Fe−NMe$_2$unit. This amido-complex, **E** (Figure S8), is the highest-energy intermediate of the process, being 15.3 kcal mol^{-1} less stable than the reactants. The release of PC by incoming CO$_2$affords **F** (Figure S9),and the successive transformation of the [Fe-NMe$_2$] fragment into [Fe(O$_2$CNEt$_2$)] allows the recovery of the catalytic precursor, making the overall reaction thermodynamically favourable (ΔG = −7.7 kcal mol^{-1}).

Despite the fact that the simplified molecular model can only supply qualitative information about the catalytic reaction, the DFT calculations agree with the experimental evidence (NMR) that carbamato ligands in the catalyst play a non-innocent role in the activation of CO$_2$along the formation of cyclic carbonates.
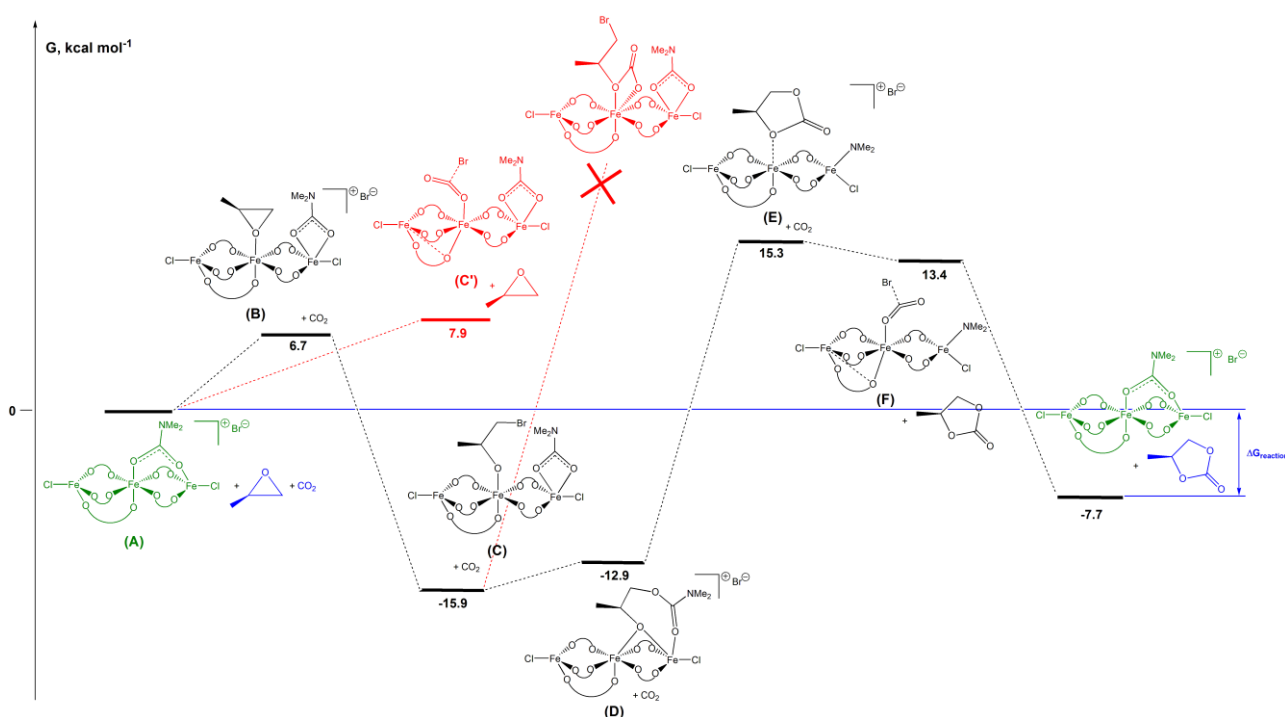
Scheme 2. Proposed DFT-optimized intermediates and relative Gibbs free energy values for the formation of PC from PO and CO$_2$, catalyzed by a Fe(III)-carbamate.

Conclusions

The use of carbon dioxide as a convenient C1 building block has been established as one of the most intriguing challenges of modern synthetic chemistry, and in this setting a variety of efficient

catalytic systems have been reported for the CO_2/epoxide coupling reaction to obtain cyclic carbonates. In the light of the key importance of mild reaction conditions 3[a] and the central role played by iron in the development of environmentally benign processes, we have described herein the use of Fe(III) carbamates as simple, easily available and cost effective catalysts working in the solventless conversion of a series of epoxides into the respective cyclic carbonates, at room temperature and atmospheric CO_2 pressure. Under optimized reaction conditions, including the use of tetrabutylammonium bromide as co-catalyst, quantitative conversion and quantitative selectivity were achieved starting from propylene oxide and 1,2-butylene oxide. In view of the easy availability of large amounts of the catalytic precursor, $Fe(O_2CNEt_2)_3$ impresses as one of the most attractive and efficient iron catalysts reported to date for the CO_2/propylene oxide coupling. According to preliminary DFT and NMR investigations, the performance exhibited by iron carbamates may be related to the previously documented lability of the metal-carbamato moiety towards CO_2 exchange, thus determining an unusual pathway for CO_2 activation. In general, although still rather unexplored for their catalytic applications, iron carbamates appear to be promising systems for the next advance in sustainable CO_2 organic chemistry.

Experimental section

General details. Unless otherwise stated, all the operations were carried out under a nitrogen atmosphere using standard Schlenk techniques. The reaction vessels were oven dried at 140 °C prior to use, evacuated (10^{-2} mmHg) and then filled with nitrogen. CO_2 (99.99%) was purchased from Rivoira. The chemicals, of the highest purity available, were purchased from Sigma Aldrich or TCI Europe, and stored under nitrogen atmosphere as received. $FeCl_3$,[35] $Fe(O_2CNEt_2)_2$[26] and $Fe(O_2CNR_2)_3$ (R = Et, ^{i}Pr, CH_2Ph)[27] were prepared according to literature procedures. Solvents (Sigma Aldrich)and mesitylene were distilled before use over appropriate drying agents. Infrared spectra were recorded at 298 K on a FTIR-Perkin Elmer Spectrometer, equipped with an UATR sampling accessory. NMR spectra were recorded at 298 K on a Bruker Avance II DRX400

instrument equipped with a BBFO broadband probe. Values of selectivity and conversion were evaluatedon[1]H NMR spectra using mesitylene as internal standard.
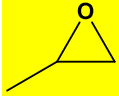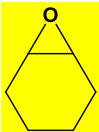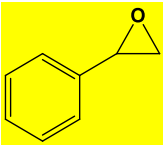
Iron catalysts, $Fe(O_2CNR_2)_3$.

The iron(III) carbamates $Fe(O_2CNR_2)_3$, R = ...) were prepared according to the literature procedure (REF) from $FeCl_3$ and...........................The analytical and spectroscopic data are as reported in the literature (REF). In the following, the solid state IR characterization of the compounds, not reported in the literature, is reported: R = $-CH_2CH_3$, ν/cm^{-1} = 2973w, 2931w, 2869w, 1488vs ($\tilde{\nu}_{C=O}$ asym), 1456m-s, 1428s, 1374m, 1309s ($\tilde{\nu}_{C=O}$ sym), 1222m, 1089m, 1073w, 972w, 939w, 804m, 785m. R = $-CH(CH_3)_2$, ν/cm^{-1} = 2961w, 2931w, 2873vw, 1579m-s ($\tilde{\nu}_{C=O}$ asym), 1564m, 1527m-s, 1487s, 1465s, 1445s, 1382m, 1347vs ($\tilde{\nu}_{C=O}$ sym), 1211w-m, 1159m-s, 1134w-m, 1059m, 1034w, 900vw, 869vw, 811m, 795m-s, 729vw. R = $-CH_2Ph$, ν/cm^{-1} = 3087vw, 3063vw, 3028w, 1478vs ($\tilde{\nu}_{C=O}$ asym), 1453m-s, 1428s, 1319m-s ($\tilde{\nu}_{C=O}$ sym), 1270m-s, 1206w, 1074w, 1029w, 966w, 858w, 796m, 753w-m, 695vs.

Catalytic reactions.

The iron compound and TBAB (Table 6) were introduced into a Schlenk tube, which was evacuated by a vacuum pump and then filled with CO_2 at atmospheric pressure. The vacuum/CO_2 sequence was repeated twice. Epoxide (1 mL) was added, and the resulting mixture was stirred for 24 hours at 25 °C with periodical addition of CO_2. Afterwards, mesitylene as internal standard (0.30 mL) was added, and ca. 0.1 mL of the mixture was mixed with $CDCl_3$ (0.5 mL) in a NMR tube. Subsequent NMR analysis allowed the determination of selectivity and conversion values.

Table 6. Experimental details of the synthesis of cyclic carbonates from CO_2 and epoxides using $Fe(O_2CNR_2)_3$ as catalytic precursors.
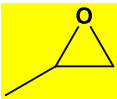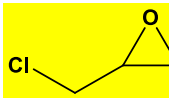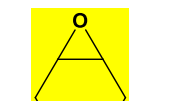
Epoxide	Entry	Catalytic precursor,[a] (g, mmol)	TBAB, (g, mmol)
(propylene oxide)	1	$Fe(O_2CNEt_2)_3$ (....., ...)	(....., ...)
	2	$Fe(O_2CN^iPr_2)_3$ (....., ...)	(....., ...)
	3	$Fe(O_2CNBz_2)_3$ (....., ...)	(....., ...)
(epichlorohydrin)	4	$Fe(O_2CNEt_2)_3$ (....., ...)	(....., ...)
	5[b]	$Fe(O_2CNEt_2)_3$ (....., ...)	(....., ...)
	6	$Fe(O_2CN^iPr_2)_3$ (....., ...)	(....., ...)
	7	$Fe(O_2CNBz_2)_3$ (....., ...)	(....., ...)
(butylene oxide)	8	$Fe(O_2CNEt_2)_3$ (....., ...)	(....., ...)
	9	$Fe(O_2CN^iPr_2)_3$ (....., ...)	(....., ...)
	10[b]	$Fe(O_2CNBz_2)_3$ (....., ...)	(....., ...)
(cyclohexene oxide)	11	$Fe(O_2CNEt_2)_3$ (....., ...)	(....., ...)
	12	$Fe(O_2CN^iPr_2)_3$ (....., ...)	(....., ...)
	13	$Fe(O_2CNBz_2)_3$ (....., ...)	(....., ...)
(styrene oxide)	14	$Fe(O_2CNEt_2)_3$ (....., ...)	(....., ...)
	15[b]	$Fe(O_2CN^iPr_2)_3$ (....., ...)	(....., ...)
	16	$Fe(O_2CNBz_2)_3$ (....., ...)	(....., ...)
	17	$Fe(O_2CNEt_2)_3$ (....., ...)	(....., ...)

[a] Et = C_2H_5; ^{i}Pr = $CH(CH_3)_2$; Bz = CH_2Ph. [b] t = 48 h.

Isolation of cyclic carbonates.
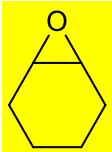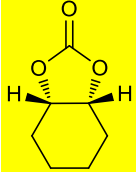
A Schlenk tube containing the iron catalyst and TBAB (Table 7) was added of the epoxide (3 mL) under CO_2 atmosphere. The resulting mixture was stirred for 24 hours at 25 °C with periodical addition of CO_2. The solution obtained at the end of the experiment was treated with H_2O (5 mL). In the case of $Fe(O_2CNBz_2)_3$ (Entry.....), H_2O (10 mL) and H_2SO_4 95-97% (2 mL) were added. The resulting mixture was stirred for 4 hours, and then the cyclic carbonate was extracted with dichlorometane (5 x 5 mL). The organic phases were collected, and the volatiles were evaporated under vacuum. The residue was dried over $MgSO_4$ and its purity was checked by GC and NMR spectroscopy (Table 8).

Table 7. Experimental details of the synthesis and isolation of cyclic carbonates from CO_2 and epoxides using $Fe(O_2CNR_2)_3$ as catalytic precursors.

Epoxide	Entry	Catalytic precursor,[a] (g, mmol)	TBAB, (g, mmol)	Yield (%)
	1	Fe(O₂CNEt₂)₃ (....., ...)	(....., ...)	
	2	Fe(O₂CNⁱPr₂)₃ (....., ...)	(....., ...)	
	3	Fe(O₂CNBz₂)₃ (....., ...)	(....., ...)	
	4	Fe(O₂CNEt₂)₃ (....., ...)	(....., ...)	
	5[b]	Fe(O₂CNEt₂)₃ (....., ...)	(....., ...)	
	6	Fe(O₂CNⁱPr₂)₃ (....., ...)	(....., ...)	
	7	Fe(O₂CNBz₂)₃ (....., ...)	(....., ...)	
	8	Fe(O₂CNEt₂)₃ (....., ...)	(....., ...)	
	9	Fe(O₂CNⁱPr₂)₃ (....., ...)	(....., ...)	
	10[b]	Fe(O₂CNBz₂)₃ (....., ...)	(....., ...)	
	11	Fe(O₂CNEt₂)₃ (....., ...)	(....., ...)	
	12	Fe(O₂CNⁱPr₂)₃ (....., ...)	(....., ...)	
	13	Fe(O₂CNBz₂)₃ (....., ...)	(....., ...)	
	14	Fe(O₂CNEt₂)₃ (....., ...)	(....., ...)	
	15[b]	Fe(O₂CNⁱPr₂)₃ (....., ...)	(....., ...)	
	16	Fe(O₂CNBz₂)₃ (....., ...)	(....., ...)	
	17	Fe(O₂CNEt₂)₃ (....., ...)	(....., ...)	

[a] Et = C_2H_5; ⁱPr = $CH(CH_3)_2$; Bz = CH_2Ph. [b] t = 48 h.

Table 8. ^{1}H NMR data (δ/ppm, $CDCl_3$ solutions) of epoxides and cyclic carbonates.

R = Me	2.92 (m, 1H); 2.68 (t, 1H); 2.37 (t, 1H); 1.25 (d, 3H)	4.80 (m, 1H); 4.50 (t, 1H); 3.96 (t, 1H); 1.42 (d, 3H)
R = CH₂Cl	4.34, 3.49 (dd, 2H); 3.05 (m, 1H); 2.69 (t, 1H); 2.50 (m, 1H)	4.88 (m, 1H); 4.44 (t, 1H); 4.22 (m, 1H); 3.68, 3.60 (dd, 2H)
R = CH₂CH₃	2.87 (m, 1H); 2.71 (t, 1H); 2.45 (t, 1H); 1.55 (m, 2H); 1.05 (t, 3H)	4.69 (m, 1H); 4.55 (t, 1H); 4.09 (t, 1H); 1.78 (m, 2H); 1.01 (t, 3H)
R = Ph	7.43–7.34 (m, 5H); 3.88 (t, 1H); 3.15 (t, 1H); 2.82 (q, 1H)	7.47–7.39 (m, 5H); 5.66 (t, 1H); 4.77 (t, 1H); 4.31 (t, 1H)

2.80 (br, 2H); 1.63 (m, 2H); 1.55 (m, 2H); 1.13 (m, 2H); 0.96 (m, 2H)	4.63 (br, 2H); 1.88 (m, 2H); 1.78 (m, 2H); 1.37 (m, 2H); 1.19 (m, 2H)

Computational details

The computational geometry optimizations of the complexes were carried out without symmetry constrains, using the hybrid-GGA EDF2 functional [36] in combination with the 6-31G(d,p) basis set and the ECP-based LANL2DZ basis set for bromine.[37] The ''unrestricted'' formalism was always applied, and the initial multiplicity was introduced considering five unpaired electrons for each metal ion. The stationary points were characterised by IR simulations (harmonic approximation), from which zero-point vibrational energies and thermal corrections (T = 298.15 K) were obtained.[38] Calculations were performed with Spartan '16 (Wavefunction Inc.), build 2.0.3,[39] running on Intel Xeon-bases x84-64 workstations.

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Supporting Information

^{1}H NMR study of CO_2 transfer (Figure S1); optimized DFT geometries (Figures S2-S9). Cartesian coordinates of the DFT structures are collected in a separated .xyz file.

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