Published as Catal. Sci. Techol. 2015, 5, 118-123. doi.org/10.1039/C4CY01187B

Catalysis Science & Technology

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Novel Iron(III) Catalyst for the Efficient and Selective Coupling of Carbon Dioxide and Epoxides to Cyclic Carbonates

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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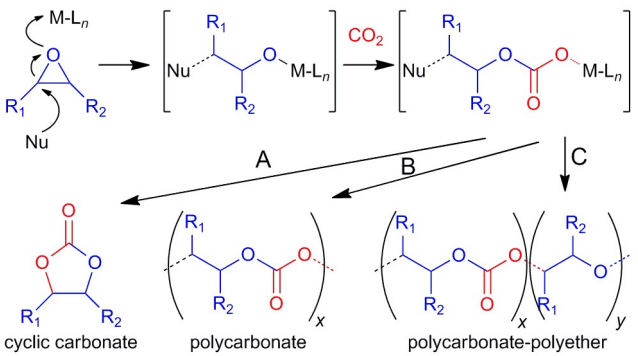
*"Re-cycling carbon dioxide with iron."*The synthesis of cyclic organic carbonatesin high yield, stereo- and chemo-selectivity was accomplished through the coupling of carbon dioxide and epoxides catalysed by a novel air-stable and easy-to-handle thioether-triphenolate iron(III) complex.

Carbon dioxide produced by the combustion of fossil fuel is (alongside methane) considered the main responsible for the so-called "*greenhouse effect*". As a matter of fact the environment is unable to buffer the huge anthropogenic release of carbon dioxide and therefore this gas is accumulated in atmosphere contributing to the climate change.[1] The efforts to reduce the CO_2 production of the most advanced countries, in the last years, should face the growing hunger of energy of the developing countries that primarily use coal as fuel in the power plants. Indeed, coal has the higher emission of CO_2 (950 g of CO_2 per kWh) compared to natural gas and oil and therefore such situation resulted even in a growing world production of CO_2. Currently, despite carbon dioxide can find application as refrigerant, fire extinguisher, supercritical solvent and extraction medium, for the recovery of oil and in the beverage industry, only 0.62 % of the atmospheric CO_2 is reutilized by humankind.[1b] The bottleneck for an intensive implementation of chemical processes based on CO_2 lies in the thermodynamic stability of this molecule that requires the coupling with energy intensive starting materials or the supplying of external energy to the involved process. Among the possible applications, the synthesis of cyclic organic carbonates via cycloaddition of CO_2 to epoxides,represents a 100% atom-economical process.[2] Cyclic organic carbonates are a class of value added products that, since their commercialization in the 1950s, have increased consistently their importance as synthetic targets.[3] Their high molecular dipole moments, dielectric constants and boiling temperatures yield them suitable as *green* highly polar aprotic solvents and as ion-carrier for lithium-based batteries. In addition, they find application for the production of additives for lubricants and paints, as alkylating agents, acyclic carbonate and, , and the synthesis of polyurethanes and polycarbonatesthorough ring opening polymerization. Industrially cyclic organic carbonates are obtained from condensation of phosgene and diols[4] or from coupling of carbon dioxide with diol,[5] oxetane or epoxides[2].



Scheme 1. Mechanism for the formation of different products in the CO_2/epoxide coupling. **A**: backbiting; **B**: alternating epoxide/CO2 insertion; **C**: formation of polyether linkages.

Typically, for the promotion of CO_2/epoxide coupling are employed binary catalytic systems including a Lewis acid and a nucleophile. The Lewis acid activates the epoxide toward the ring opening resulting from the attack of the nucleophile to the less substituted carbon atom.This reaction is followed by CO_2 insertion attack by the nucleophile, leading to an alkyl emi-carbonato unit which can undergo to the ring closure, via a backbiting mechanism producing the cyclic carbonate and regenerating the nucleophile.(path A, Scheme 1). Concurrently that intermediate can participate in an alternate insertion of further molecules of epoxide and CO_2 to afford a linear alternating polycarbonate (path B, Scheme 1).[6]Moreover the consecutive insertion of epoxide molecules leading to polyether linkages is also possible (path C,Scheme 1). The selectivity and the rate of the coupling are effected not only by the nature of

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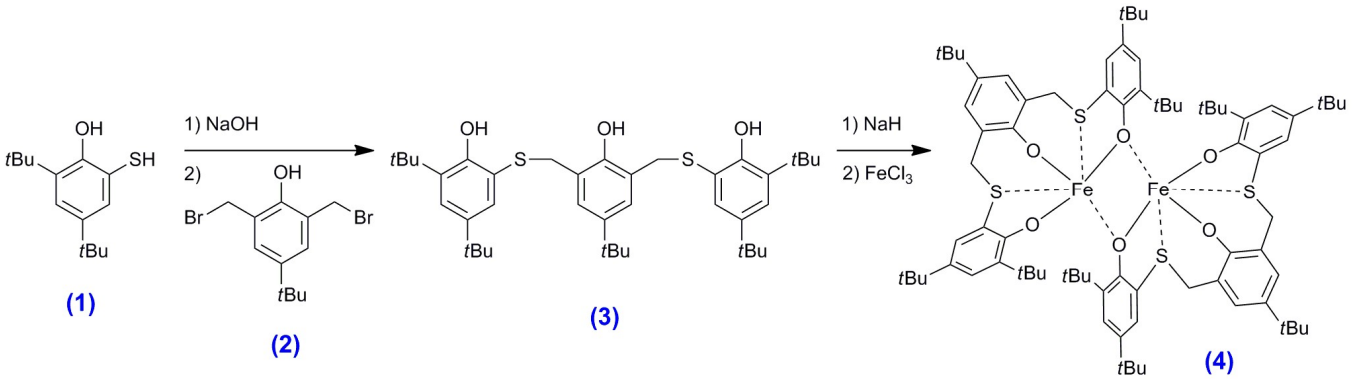
the epoxide and the catalytic system but also by the reaction conditions. Cyclic carbonates are thermodynamically favoured compared to polycarbonates, though a higher activation barrier generally should be overcome to afford their formation.[7] Quaternary ammonium or phosphonium (-onium) salts,[8] metal oxides and halides, ionic liquids[9] or organocatalysts were found active for the synthesis of cyclic carbonates, thoughsevereereaction conditions were generally required.[2] In order to obtain more active catalyst for the CO_2/epoxides coupling under milder conditions various metal complexes combined with auxiliary nucleophiles *e.g.* onium salts have been intensively studied. Complexes of magnesium,[10] aluminium,[11] chromium,[7b] cobalt,[12] copper, zinc,[13] niobium[14]and other metals[2]coupled mainly with porphyrins,[10,15] phthalocyanines, salen[2f,7b,11c], salphen[13b-d] or *N*-heterocyclic carbenes[16] ligands were found among the most effective catalystsfor this reaction. Although iron is widely available, cost effective and non-toxic, few examples of iron based catalysts for the CO_2/epoxide coupling to cyclic carbonates have been reported to date.[17] Indeed only recently a bimetallic macrocyclic-iron(III) catalyst has been shown by Williams and co-workers capable to afford both cyclic and poly-carbonates.[17a] Rieger and co-workers recently reported an iron(II)-Shiff base for the propylene carbonate synthesis.[17b] More recently Kleij and co-workers deeply investigated iron(III) chelated with aminotris(phenolate)s as effective catalysts for the coupling of CO_2 and epoxides obtaining high activity and selectivity in *sc*-CO_2.[17c-f] However in many cases these catalysts require harsh reaction conditions or high catalyst loading that limit their broad applicability. Notably, in spite of the wide coordination chemistry of iron with sulfur containing enzymes and synthetic ligands[18] such kind of complexes have been barely investigated in catalysis.[19]Indeed, the ligands used so far in the literature are based on the hard donors oxygen and nitrogen in combination with iron(III) metal centre. The use of ligands containing soft donors such sulphur can lead to a more acidic iron(III) centre resulting in an enhancement of the catalytic activity. With this target in mind we designed a new dithioether-triphenolate pro-ligand **3**.

The synthetic strategy affording the thioether-triphenolate ligand precursor 6,6'-(((5-(*tert*-butyl)-2-hydroxy-1,3-phenylene)*bis*(methylene))*bis*(sulfanediyl))*bis*(2,4-di-*tert*-butylphenol) (compound **3**, Scheme 2) involves the coupling of 3,5-di-*tert*-butyl-2-hydroxythiophenol[20] (**1**) and 2,6-*di*(bromomethyl)-4-(*tert*-butyl)phenol[21] (**2**), via nucleophilic substitution (see Scheme 2). The novel ligand precursor **3** was recrystallized in acetone and fully characterized by ^{1}H,^{13}C and two-dimensional NMR experiments, elemental analysis, MS, and FT-IR (see ESI†). The reaction of **3** with 3 equiv. of sodium hydride in THF and the subsequent addition of the corresponding sodium salt to $FeCl_3$ affords the desired thioether-triphenolate iron(III) complex (**4**, Scheme **2**).The complex **4**was recovered by recrystallization in THF as small needle-shaped crystals, unfortunately not suitable for the structural resolution by means of single crystal x-ray diffraction The formation of the adduct iron-ligand**4** was initially confirmed by elemental analysis and FT-IR spectroscopy, which revealed the disappearance of the vibrationdue to the hydroxyl of the pro-ligand as a result of the coordination of the corresponding phenolate to the iron (see ESI†, Figure S9-11).The ESI-mass spectrum of **4** shows the molecular ion peak at 1409.2 m/z which is consistent with the dinuclear structure proposed.(ESI†, Figure S8) The Evans method[22] was applied for the determination of the solution magnetic susceptibility and a value of **7**.34μB resulted at 25°C (the value is stable in the range of temperature 25-105 °C, see ESI†, Figure S6) that is higher of that predicted for a mononuclear high spin (HS) iron(III) complex andclose to the value calculated for two isolated high spin (HS)iron(III) centres (8.37 μB)[23] confirming the dimeric nature of the complex and indicating some degree of ferromagnetic coupling between the iron atoms being both in HS (s = 5/2) state.As expected for two HS iron(III) centres in octahedral environment the UV-Vis spectrum showed no d-d transitions but only a strong ligand-to-metal charge transfer absorption at 620 nm (16129 cm^{-1}; ε_{620} = 6508 $Lmol^{-1}cm^{-1}$).Furthermore,the octahedral coordination environment for the metal centresrequiresthe coordination also of the sulfur atoms, that was in effect confirmed by the shift of the vibration bands, in the infrared spectrum of the complex to respect that of the free pro-ligand, respectively in the spectral regions: 1440−1415 cm^{-1}, 1270−1220 cm^{-1} and 700−600 cm^{-1}, diagnostics for the alkyl-sulphide moiety (see Figure S12-14).[24] In particular the shift to the red,observed for the C−S stretching vibration, accounts for a weakening of the bond as a result of the coordination of the sulphur to the metal.

Notably, the addition of pyridine or epichlorohydrin(ECH), for the evaluation of the stability of complex,[17d]neither results in change of the magnetic moment (evaluated in presence of 50 equiv of ECH to respect the iron, in ordertoavoida strong perturbation of the dielectric constant of the solvent media, see Figure S6),nor in the UV-Vis spectrum (acquired in presence of 3738 equiv of ECH, see Figure S17), assessing the stability of the dimeric state.



Scheme 2. Synthesis of the iron(III) complex**4**.

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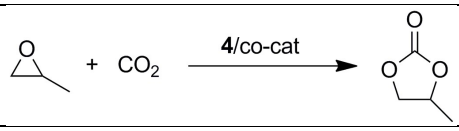
Table 1. Synthesis ofpropylene carbonate through CO_2 cycloaddition to propylene oxide catalyzed by Fe^{III} catalyst (**4**)



Entry[a]	Catalyst	Cocatalyst		Cocatalyst/Fe	T	PCO_2	t	Conv.[b,c]	TON[d]	TOF[e]
	(*mol*%)		(*mol*%)	(molar ratio)	(°C)	(MPa)	(h)	(%)		(h^{-1})
1	0.25	TBAB	0.5	1	60	2	6	>99	394	66
2	0.25	TBAB	0.5	1	60	2	3	68	270	90
3	0.025	TBAB	0.05	1	60	2	24	67	2664	111
4	0.025	TBAI	0.05	1	60	2	24	31	1240	52
5	0.025	PPNCl	0.05	1	60	2	24	50	2000	83
6	0.025	DMAP	0.05	1	60	2	24	0	-	-
7	0.025	-	-	0	60	2	24	0	-	-
8	-	TBAB	0.05	-	60	2	24	14	-	-
9	0.025	TBAB	0.025	0.5	60	2	24	23	900	38
10	0.025	TBAB	0.1	2	60	2	24	78	3112	130
11	0.025	TBAB	0.25	5	60	2	24	56	2240	93
12	0.025	TBAB	0.35	7	60	2	24	64	2560	107
13	0.025	TBAB	0.1	2	40	2	24	6.4	256	11
14	0.025	TBAB	0.1	2	70	2	24	83	3320	138
15	0.025	TBAB	0.1	2	80	2	24	96	3840	160
16	0.025	TBAB	0.1	2	100	2	6	87	3480	580
17	0.025	TBAB	0.1	2	100	1	6	73	2920	487
18	0.025	TBAB	0.1	2	100	0.5	6	61	2440	407
19	0.025	TBAB	0.1	2	100	3	6	79	3160	526

[a] Basic reaction condition: 24.6 mg of complex **4** (1.75×10^{-5} mol), solventless. [b] Determined by NMR using mesitylene as internal standard. [c] The selectivity for the formation of propylene carbonate was found>99%. [d] Overall turnover number (mol_{PC}/mol_{Cat}). [e] Overall turnover frequency (TON/reaction time).

The iron(III) complex **4** was investigated as catalyst for the coupling of the (±)-propylene oxide (PO) with the carbon dioxide in combination with several cocatalysts for the selective synthesis of the (±)-propylene carbonate (PC), under solvent free conditions. The main results are summarized in Table 1. The complete conversion of PO was observed within 6 h with a catalyst loading of 0.25 mol% and *n*-tetrabutylammonium bromide (TBAB) as cocatalyst (2 MPa; 60 °C;TBAB:Fe molar ratio = 1, entry **1**). Under the same conditions a conversion of 68 % of PO was achieved within 3 h with a high turnover frequency (TOF) value of 90 h^{-1} (entry **2**). In consequence of this encouraging initial results, the catalyst and cocatalyst concentrations were both lowered by one order of magnitude; a conversion of 67 % was reached in 24 h with a TOF value of 111 h^{-1}under this conditions (entry **3**). The use of other common cocatalysts like *n*-tetrabutylammonium iodide (TBAI), *bis*(triphenylphosphine)iminium chloride (PPNCl), 4-dimethylaminopyridine (DMAP) resulted less effective (entries **4-6**). iron(III) complex **4**in absence of cocatalyst showed no reactivity (entry 7) whereas TBAB alone (entry **8**) yields a PO conversion of only 14 % within 24 h, thus highlighting a synergic effect between the catalyst and the cocatalyst (compare entries **8** with **3**). Notably, by halving the cocatalyst loading (entry **9**) a deterioration of the catalytic performance was observed; while the doubling improves considerably the yield affording a conversion of 78 % in PC (entry **10**). Further increase of the cocatalyst amount (entries **11-12**) did not result in improved catalytic performances, and for this reason the*optimal* molar ratio of 2 was adopted for the subsequent catalytic tests (entries **13-19**; Table 1). Remarkably, the temperature strongly affected the catalytic process. At 40 °C a drop in the yield was observed (entry **13**); while rising the temperature (entries **14-16**) a strong increase of the catalytic performance was observed; at 100 °C a conversion of 87 % in 6 h with the highest found TON and TOF values of 3480 and of 580 h^{-1}, were observed respectively, confirmingadditionally the thermal stability of the catalytic system. To the best of our knowledge, these catalytic performances lie among the highest reported for iron based catalyst.[17]The reason for the observed good activity of the complex **4**can be found in the weak coordination of the soft donor atoms sulphur to the hard Lewis acid metal centre iron (III).This interaction can facilitate the

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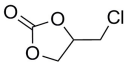
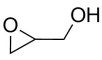
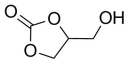
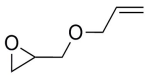
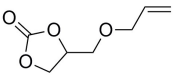
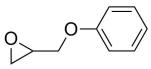
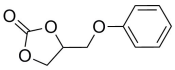
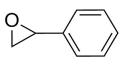
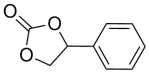
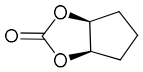
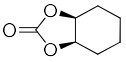
coordination of the epoxide to metal centre that is crucial for the subsequent attack of the nucleophile and the formation of the cyclic carbonate (see Scheme 1).In addition, the CO_2 pressure seems have no significant influence on the reaction course, in effect high TOF values were maintained at both low (entries **17-18**) and high pressure (entry **19**). This behaviour suggests a lesser impacton the energy barrier, during the coupling with the epoxide, of the CO_2insertionstage.

Table 2. CO_2/epoxide coupling by Fe(III) catalyst (**4**).

Entry[a]	Substrate	Product[b,c]	Conv[b,c] (%)	TON[d]	TOF[e] (h^{-1})
20			78	3120	520
21			95	9800	633
22			55	2200	367
23			43	1720	287
24[f]			39	1560	260
25[g]			27	1077	180
26[g]			13	520	87

[a] Reaction condition: substrate (7.0×10^{-2} mol), catalyst **4** (24.6 mg, 1.75×10^{-5} mol, 0.025 *mol*%), TBAB ($7.0 \cdot 10^{-5}$ mol, 0.1 *mol*%), CO_2 (2 MPa); 100 °C, 6 h. [b] Determined by NMR (mesitylene as internal standard). [c] The selectivity for the formation of the cyclic carbonate was found>99%. [d] Overall turnover number (mol_{PC}/mol_{Cat}); [e] Overall turnover frequency (TON/reaction time). [f]Gave (*R*)-styrene carbonate in 85 % yield and 72 % *ee*). [g] A selectivity >99% for the formation of the *cis* isomer carbonate was observed.

To expand the scope of the catalytic system a series of differently substituted epoxides were screened as benchmark substrates (see Table 2). Monosubstituted epoxides containing functional group such as epichlorohydrin (78 %, entry **20**) or glycidol (95 %, entry **21**) gives conversion close or even superior to that observed for CO_2/PO coupling, showing that the presence of functional groups does not affect the catalyst performance.The increase of the size, in parallel with the reduction of the electron donating propertiesof the substituents on the oxirane ring result in a slight decrease of the catalytic activity (entries **22-24**) under the same reaction conditions. Enantiomerically enriched (*R*)-styrene oxide (*ee* = 94 %) was also used in the coupling reaction with CO_2 showing a good retention of the stereochemistry (*ee* = 72 %) giving (*R*)-styrene carbonate in 6 h suggesting a good selectivity in the attack of the nucleophileFinally the cyclopentene and cyclohexene oxide, as expected for internal epoxides, were found less reactive toward the coupling with the CO_2 (entries**25-26**). As a matter of fact, the corresponding cyclic carbonates consist, respectively,of a five- or six-membered aliphatic ring interconnected with a five-membered cycle comprising the carbonatefunctionality, that result in an additional geometric strain. As a consequence for these epoxides, the formation of the polycarbonates, even with variable degree of polyether linkage, is usually prevailing over the cyclic carbonates formation resulting in many cases in a mixture of products.[7,17f,24] In our case the cyclic carbonates were produced selectively with *cis*-stereochemistry, as pointed out by FT-IR analysis, that revealed strong adsorption bands at 1800 and 1802 cm^{-1}, previously assigned to the stretching of the carbonyl, respectively for the *cis*-cyclopentene carbonate[25]and *cis*-cyclohexene carbonate[17a] (see Figure S15 and S16). This unusual stereo control for iron catalysts was already observed.[17a]

Conclusions

In summary, herein we reported on the efficient synthesis of cyclic carbonates by means of a new air stable and easy-to-handle iron(III) thioether-triphenolate complex. Experimental evidences indicate a dimeric nature for this novel complex.In presence of tetrabutylammonium bromide the title iron(III) complex **4** results very effective in the coupling of CO_2 with epoxides givingexcellent results in terms of activity,chemo- and stereo- selectivityunder solvent-free conditions. To the best of our knowledge, this catalyst showed the highest TOF for the solventless cycloaddition of CO_2 to propylene oxide under moderate reaction conditions. The catalyst resulted thermal stable and tolerant of some functional groups (*e.g.* the hydroxyl and the vinyl). The dependence of the catalytic performances towards the co-catalyst concentration, the steric and electro-donating properties of substituents of the epoxide, as well as the low dependence of the activity towards the CO_2 pressure, preliminary indicatesa greater influence of the stage of the ring-opening of the epoxide on the activation barrier for this reaction. In addition, this catalytic system showed good stereo control for the cycloaddition of CO_2 to enantiomerically enriched (*R*)-styrene oxide or cyclic epoxide yielding, respectively, the (*R*)-styrene carbonate and corresponding *cis*-cyclic carbonates isomers with good selectivity. These results clearly show that, iron(III) based catalysts are a promising alternative to more toxic and/or expensive metals for the formation of cyclic carbonates from carbon dioxide and epoxides. Further work is currently in progress in order to establish a more refined catalyst structure-reactivity relationship.

Acknowledgements

Financial support is acknowledged from the Ministero dell'Istruzione dell'Università e della Ricerca (MIUR, Roma, Italy for FARB-2013), the Regione Campania (POR FSE, project: "MAteriali e STrutture Intelligenti", MASTRI, Code 4-17-3, CUPB25B09000010007) and the Centro di Tecnologie Integrate per la Salute (Project PONa3_00138) for the 600 MHz NMR instrumental time. Alexander von Humboldt Foundation is deeply acknowledged for a renewal fellowship (C.C.) The authors are also grateful to Dr. Carmen Talotta, Dr. Patrizia Oliva and Dr. Patrizia Iannece from Università degli Studi di Salerno for technical assistance.

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† Electronic Supplementary Information (ESI) available: Experimental details and further NMR, MS, FT-IR, UV-Vis spectroscopic characterizations. See DOI: 10.1039/b000000x/

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