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PAPER

Thioether-Triphenolate Bimetallic Iron(III) Complexes as Robust and Highly Efficient Catalysts for Cycloaddition of Carbon Dioxide to Epoxides

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The selective and effective synthesis of organic carbonates under mild conditions, starting from carbon dioxide and oxiranes, catalyzed by metal complexes is currently in the focus of interest for both industrial and academic researchers. We recently developed a novel thioether-triphenolate iron(III) catalyst (C_{t-Bu}) that has proven to be highly active for the coupling of CO_2 with epoxides affording cyclic organic carbonates under solvent-free conditions. In the current work the properties of this novel class of catalysts were extensively investigated. In particular, the steric properties of ligand were modulated by, changing the substituents of the aromatic rings, in order to get a deeper knowledge of the relationship between complex structure and catalytic performance/selectivity for these iron complexes. Notably, the less steric demanding iron(III) C_H complex synthesized shows, when activated by n-tetrabutylammonium bromide, an impressive turnover frequency (TOF) of 3800 h^{-1} for the formation of propylene carbonate and glycerol carbonate which are, by far, the highest reported for an iron based catalyst and well compare with the most active catalyst based on other metals.

Introduction

The possibility to convert carbon dioxide to useful chemicals has become an important task of research in both academic and industrial environments.[1] For example, the reduction of CO_2 by reaction with hydrogen or water to produce formic acid,[2] formaldehyde and methanol[3] has been intensively studied for the intrinsic value of these molecules as chemical intermediates or fuel.[4] Similarly to other industrially relevant chemical processes, the key to overcome the chemical sluggishness of CO_2 is the development of properly designed catalytic systems able to enhance the reactivity and selectivity of such chemical transformations. In this scenario, a prominent role is played by the coupling of CO_2 with epoxides to form cyclic organic carbonates (COCs)[5] and polycarbonates[6]. In particular, COCs due their high molecular dipole moments, dielectric constants and boiling

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temperatures are employed as *green* highly polar aprotic solvents and as ion-carrier for lithium-based batteries.[7] Furthermore, they find application as valuable intermediate in organic synthesis and as monomer in the ring opening polymerization to form polycarbonates. As a result of the growing interest in using COCs in the chemical synthesis the development of efficient, selective, non-toxic and inexpensive catalytic systems able to promote the coupling between CO_2 and oxiranes or oxetanes has become a focus in the field of CO_2 chemistry.

Generally, the most active catalytic systems are based on the combination of a transition metal complex acting as Lewis acid and a suitable nucleophile (ammonium salts and phosphonium salts).[8] The widely accepted mechanism involves the Lewis acid activation of the epoxide toward the ring opening by nucleophilic attack to the less substituted carbon atom (see Scheme 1). This reaction is followed by CO_2 insertion into the formed metal-alkoxide intermediate leading to an alkyl emi-carbonato unit which can undergo the ring closure, via a backbiting mechanism producing the cyclic carbonate (**A**) or insert additional epoxide/CO_2 molecules producing polycarbonates (**B**). The fortuitous insertion of two consecutive epoxide molecules also leads to the formation of polyether segments (**C**). Consequently the choice of the metal complex, the ratio between the Lewis acid and the nucleophile and the nature of the co-catalyst, the solvent, the pressure and temperature are of pivotal importance for the selectivity of the reaction.[5a]

We have recently developed a new catalytic system[9] based on iron[10], an abundant and non-toxic metal. In particular we have reported that the dinuclear Fe(III) (**C$_{t-Bu}$**) (see Scheme 2) complex coordinated by dithioether-triphenolate-based ligands in combination with tetrabutylammonium bromide (TBAB) is an active and selective catalyst for the synthesis of various COCs. Notably the coupling of propylene oxide with CO_2, in presence of the aforementioned catalytic system, gives the corresponding carbonate with the highest TOF (580 h^{-1}), so far reported for an iron based catalyst.[11]

In order to establish a more refined catalyst structure-reactivity relationship for this new Fe(III) catalyst family here we report the synthesis of the two new iron(III) complexes **C$_H$** and **C$_{Cum}$**. Indeed we report on the influence on the catalytic performance, in term of activity and selectivity, in the CO_2/epoxide coupling reaction of the substituents on the aromatic rings in the ligands **L$_H$-L$_{Cum}$**.
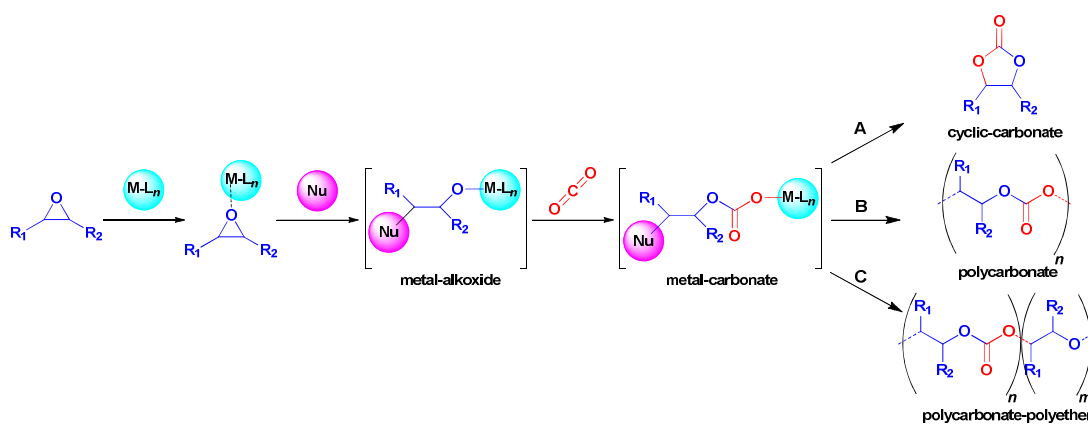
Scheme 1. Metal catalysed carbon dioxide-epoxide coupling.

Experimental

All manipulation involving air- and/or moisture-sensitive compounds were performed under nitrogen atmosphere using standard Schlenk technique and a MBraun glovebox. Toluene (99.5%; Carlo Erba) and THF (99%; Sigma-Aldrich) were used as received or refluxed for 48 h over sodium and distilled before use for moisture- and oxygen-sensitive reactions. All other reagents were used as received (Sigma-Aldrich) or distilled under reduced pressure over calcium hydride. The ligand precursor 6,6'-(((5-(*tert*-butyl)-2-hydroxy-1,3-phenylene)*bis*(methylene))*bis*(sulfanediyl))-*bis*(2,4-di-*tert*-butylphenol) (**L$_{t-Bu}$**, Scheme 2) and the corresponding iron(III) complex (**C$_{t-Bu}$**, Scheme 2) were synthesized according to the reported procedure.[9] Deuterated solvents were purchased from Euriso-Top or Sigma-Aldrich and used as received.

NMR spectra were collected on Bruker Avance spectrometers (600, 400, 300 or 250 MHz for ^{1}H): the chemical shifts were referenced to tetramethylsilane (TMS) as external reference, using the residual protio signal of the deuterated solvents. Measurements of effective magnetic moments were performed on a Bruker Avance 600 MHz spectrometer at 25 °C in CD_3CN using a 5 mm Wilmad coaxial insert NMR tube. Solutions of the complex C_H (1.7 mM) and C_{Cum} (2.1 mM) in CD_3CN with 1 % of TMS were prepared under nitrogen atmosphere. The effective magnetic moment (μ_{eff}) was calculated from $\mu_{eff} = 8\chi_g M_w T$, where χ_g (cm^3 g^{-1}) is the corrected molar susceptibility derived from $\chi_g = 3\Delta_f/4\pi f_o CM_w + \chi_o$.[12] Δ_f is the shift in frequency (Hz) of the signal of the solvent in presence of the complex from the value of the pure solvent, C is the concentration of the complex (mol cm^{-3}), M$_w$ is the molecular weight of the complex (g mol^{-1}), f_o is the operating frequency of the spectrometer (Hz), and χ_o is the mass susceptibility of the pure solvent (-0.524×10^{-6} cm^3 g^{-1} for CD_3CN). The $4\pi/3$ is the shape factor for a cylindrical sample in a superconducting magnet. Elemental analysis was performed on a CHNS Thermo Scientific Flash EA 1112 equipped with a thermal conductivity detector. ESI-MS spectra were acquired on a Quattro *micro*^{TM} API triple quadrupole mass spectrometer from Waters equipped with electrospray ion source, using acetonitrile as solvent. FT-IR measurements were carried out on a Bruker Vertex 70 spectrometer equipped with DTGS detector and a Ge/KBr beam splitter. The samples were analysed as chloroform solutions or in the form of KBr disks. UV-Vis acquisitions were collected on a PerkinElmer Lambda EZ 201.

Synthesis of the pro-ligand 2,2'-(((5-(*tert*-butyl)-2-hydroxy-1,3-phenylene)bis(methylene))bis(sulfanediyl))-bisphenol (L$_H$, Scheme 2). A 500 mL two-neck round-bottom flask equipped with condenser and magnetic stirring bar was charged, under nitrogen atmosphere, with 5.00 g of 2-mercaptophenol (35.7 mmol) dissolved in 160 mL of ethanol, 1.43 g of NaOH (35.7 mmol) and the mixture was refluxed about 1 hour until complete dissolution of the hydroxide. 6.00 g of 2,6-dibromomethyl-4-t-butylphenol (17.83 mmol) dissolved in 50 mL of ethanol were slowly added at 0 °C and the mixture heated to the reflux of the solvent that was kept overnight. The solvent was distilled off, water was added until dissolution of NaBr by-product and the aqueous phase extracted twice with methylene chloride. The combined organic phases were dried with MgSO$_4$ and, after evaporation of the solvent, the product was recovered as a white solid. Yield: 7.36 g, 96.8 %. EA for C$_{24}$H$_{26}$O$_3$S$_2$ calc.: C, 67.57; H, 6.14; S 15.03; found: C, 67.27; H, 6.07; S, 14.93. Mass spectrum: 449.3 m/z (MNa$^+$).

Synthesis of the iron(III) complex C$_H$ (Scheme 2). A 500 mL two-neck round-bottom flask, equipped with a magnetic stirring bar was charged with 0.51 g of sodium hydride (21.0 mmol) suspended in 130 mL of THF and a solution of 2.72 g of the ligand precursor L$_H$ (6.37 mmol) dissolved in 180 mL of THF was slowly added at room temperature under protective nitrogen atmosphere, thus allowed to react overnight. The resulting suspension was filtered through celite and slowly added at room temperature to 1.00 g of anhydrous iron(III) chloride (6.24 mmol) dissolved in 100 mL of THF. The rapid change of the colour to the deep purple was observed and the reaction kept overnight. The mixture was then filtered through celite and the solvent removed under reduced pressure affording a deep purple crystalline solid. Yield: 2.80 g, 94 %. EA for C$_{48}$H$_{46}$Fe$_2$O$_6$S$_4$ calc.: C, 60.13; H, 4.84; S, 13.38; found: C, 60.33 H, 4.47; S, 13.28. Mass spectrum: 981.2 m/z (MNa$^+$). UV-Vis: ε_{470} = 2804 L mol^{-1} cm^{-1}.

Synthesis of the pro-ligand 2,2'-(((5-(*tert*-butyl)-2-hydroxy-1,3-phenylene)*bis*(methylene))*bis*(sulfanediyl))-*bis*(2,4-di-(α,α'-dimethylbenzyl)phenol) (L$_{Cum}$, Scheme 2). A 50 mL two-neck round-bottom flask equipped with condenser and magnetic stirring bar was charged, under nitrogen atmosphere, with 2.02 g of 2-mercapto-4,6-bis-(α,α-dimethylbenzyl)-2-phenol (5.56 mmol) dissolved in 25 mL of ethanol, 0.30 g of NaOH (22.2 mmol) and the mixture was refluxed about 1 hour until complete dissolution of the hydroxide. 0.94 g of 2,6-dibromomethyl-4-t-butylphenol (2.8 mmol) dissolved in 10 mL of ethanol were slowly added at 0 °C and the mixture heated to the reflux of the solvent that was kept overnight. The solvent was distilled off, water was added until dissolution of NaBr by-product and the aqueous phase extracted twice with methylene chloride. The combined organic phases were dried with MgSO$_4$ and, after evaporation of the solvent, the resulting crude solid was purified by column chromatography (light petroleum/ethyl acetate = 95/5). Yield: 0.81 g, 33%. EA for C$_{60}$H$_{66}$O$_3$S$_2$ calc.: C, 80.13; H, 7.40; S 7.13; found: C, 79.94; H, 7.27; S, 7.03. Mass spectrum: 899.2 m/z (M$^+$), 922.2 m/z (MNa$^+$).

Synthesis of the iron(III) complex C$_{Cum}$ (Scheme 2). A 50 mL two-neck round-bottom flask, equipped with a magnetic stirring bar was charged with 0.073 g of sodium hydride (2.60 mmol) suspended in 20 mL of THF and a solution of 0.78 g of the ligand precursor L$_{Cum}$ (0.87 mmol) dissolved in 25 mL of THF was slowly added at room temperature under protective nitrogen atmosphere, thus allowed to react overnight. The resulting suspension was filtered through celite and slowly added at room temperature to 0.138 g of anhydrous iron(III)

chloride (0.85 mmol) dissolved in 20 mL of THF. The rapid change of the colour to the deep blue was observed and the reaction kept overnight. The mixture was then filtered through celite and the solvent removed under reduced pressure affording a deep blue crystalline solid. Yield: 0.79 g, 97.7 %. EA for $C_{120}H_{126}Fe_2O_6S_4$ calc.: C, 75.69; H, 6.67; S, 6.74; found: C, 75.42; H, 6.58; S, 6.67. Mass spectrum: 1904 m/z (M^+), 1927 m/z (MNa^+). UV-Vis: ε_{585} = 7188 L mol^{-1} cm^{-1}.

Typical procedure for CO_2/epoxide coupling to cyclic carbonates catalyzed by C_H/TBAB (referred to entry 3, Table 1). A 60 mL stainless steel pressure reactor equipped with a magnetic stirring bar was charged, under CO_2 atmosphere, with 17.1 mg of catalyst C_H ($1,79 \times 10^{-5}$ mol) and 11.5 mg of TBAB ($3,57 \times 10^{-5}$ mol) dissolved in 5.0 mL of PO (7.15×10^{-2} mol). The reaction mixture was pressurized with CO_2 at 2 MPa and stirred at 120 °C for 1 h. The reactor was cooled with ice, the CO_2 released, mesitylene was added as an internal standard and the mixture was analysed by ^{1}H-NMR spectroscopy using CD_2Cl_2 as solvent. Yield 49.2 %.

Results and Discussion

The ligands L_H-L_{Cum} were synthesized by using the same synthetic strategy reported for the synthesis of the ligand L_{t-Bu} (see Scheme 2).[9] The new ligands were purified by recrystallization or by column chromatography and fully characterized by NMR experiments, elemental analysis, MS, and FT-IR (see ESI†).

These ligands were chosen in order to study the influence of the substituents on the aromatic rings on the catalytic activity resulting by diminishing (L_H) and increasing (L_{Cum}) the steric bulk. The complexes C_H and C_{Cum} were obtained by reaction of the corresponding sodium salt obtained by reaction with 3 equivalents of NaH in THF with an equimolar amount of anhydrous $FeCl_3$ in analogy to the procedure used for the synthesis complex C_{t-Bu}.[9]
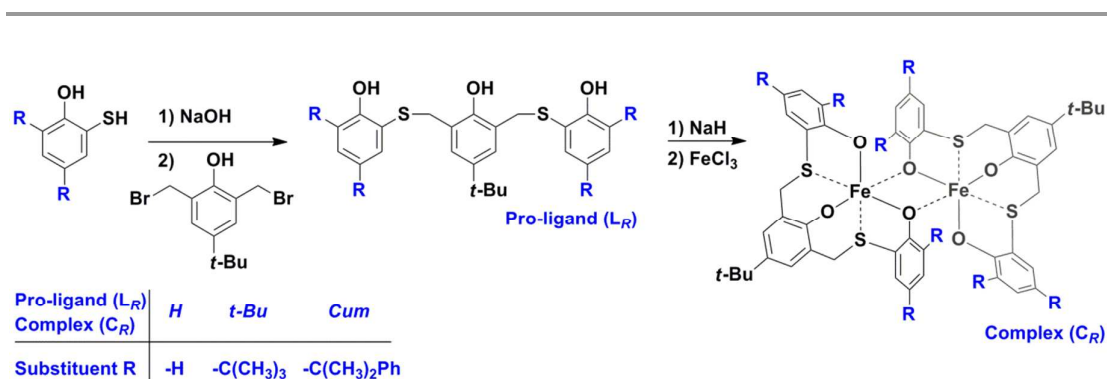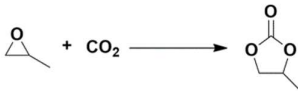

Scheme 2. Synthetic strategy for the production of the pro-ligands and of the iron(III) complexes.

The complexes C_H and C_{Cum} were recovered by crystallization in tetrahydrofuran as small needle-shaped crystals with red-purplish and deep-blue colour respectively. Unfortunately, in both cases, the crystals are not suitable for the structural resolution by means of single crystal x-ray diffraction. Indeed the formation of the adduct iron-ligand was initially confirmed by elemental analysis and FT-IR spectroscopy, which revealed the disappearance of the vibration due to the hydroxyl of the pro-ligand as a result of the coordination of the corresponding phenolate to the iron (see Figure S11 and S17). The ESI-MS spectra of C_H and C_{Cum} show the molecular ion peak at 899 and 1927 m/z respectively which are consistent with the dinuclear structure observed also in the case of the complex C_{t-Bu}. The Evans method[12] was applied for the determination of the solution magnetic susceptibility and a value of 8.1 µB for C_H and 7.2 µB for C_{Cum} resulted at 25°C that are close to the value calculated for two isolated high spin (HS) iron(III) centres (8.37 µB)[13] and to that observed previously for C_{t-Bu}[9] confirming the dimeric nature of the complexes and indicating some degree of ferromagnetic coupling between the iron atoms being both in HS (s = 5/2) state. Consequently the UV-Vis spectra, as expected for two HS iron(III) centres in octahedral environment, showed no *d-d* transitions but only a strong ligand-to-metal charge transfer absorption at 470 nm (21276 cm^{-1}; ε_{470} = 2804 L mol^{-1} cm^{-1}) for C_H and at 585 nm (21276 cm^{-1}; ε_{585} = 7188 L mol^{-1} cm^{-1}) for C_{Cum}. In addition, the coordination of sulfur atoms,

necessary to ensure the octahedral geometry for the iron centre, was confirmed by the shift of the vibration bands in the infrared spectra of the complex to respect that of the free pro-ligand, respectively in the spectral regions: 1450–1415 cm^{-1}, 1270–1220 cm^{-1} and 680–600 cm^{-1}, diagnostics for the alkyl-sulphide moiety (see Figure S12-14 and S18-20).[14] In particular the shift to the red, observed for the CH_2-S-C deformation (spectral region 1450-1415 cm^{-1}; Figure S12 and S18) and for the for the C-S stretching (spectral region 680-600 cm^{-1}; Figure S14 and S20), accounts for a weakening of the C-S bond as a result of the coordination of the sulphur to the iron, whereas the shift to the blue for the CH_2-S-C wagging (spectral region 1270-1220 cm^{-1}; Figure S13 and S19) indicates a reduced conformational mobility of the moieties after coordination to the metal.

Table 1. Synthesis of propylene carbonate through CO_2/propylene oxide coupling catalyzed by Fe(III) catalysts.

Entry[a]	Catalyst	Cocatalyst		PO/Cocat./Cat.	Solvent	T	PCO_2	Conversion[b,c]	TOF[d]
			(mol%)	(molar ratio)		(°C)	(MPa)	(%)	(h^{-1})
1	C_H	TBAB	0.05	4000/2/1	-	80	2	2.4	96
2	C_H	TBAB	0.05	4000/2/1	-	100	2	16.9	680
3	C_H	TBAB	0.05	4000/2/1	-	120	2	49.2	1970
4	C_H	TBAB	0.05	4000/2/1	-	140	2	60.5	2420
5	C_{t-Bu}	TBAB	0.05	4000/2/1	-	80	2	4.6	185
6	C_{t-Bu}	TBAB	0.05	4000/2/1	-	100	2	16.8	675
7	C_{t-Bu}	TBAB	0.05	4000/2/1	-	120	2	39.8	1595
8	C_{t-Bu}	TBAB	0.05	4000/2/1	-	140	2	57.4	2300
9	C_{Cum}	TBAB	0.05	4000/2/1	-	80	2	4.6	185
10	C_{Cum}	TBAB	0.05	4000/2/1	-	100	2	20.1	805
11	C_{Cum}	TBAB	0.05	4000/2/1	-	120	2	29.4	1175
12	C_{Cum}	TBAB	0.05	4000/2/1	-	140	2	47.5	1900
13	C_H	TBAB	0.05	4000/2/1	MEK	100	2	8.9	355
14	C_H	TBAB	0.05	4000/2/1	MEK	120	2	31.1	1245
15	C_{t-Bu}	TBAB	0.05	4000/2/1	MEK	100	2	7.8	310
16	C_{t-Bu}	TBAB	0.05	4000/2/1	MEK	120	2	20.3	810
17	C_{Cum}	TBAB	0.05	4000/2/1	MEK	100	2	8.3	330
18	C_{Cum}	TBAB	0.05	4000/2/1	MEK	120	2	21.4	855
19	C_H	TBAB	0.05	4000/2/1	-	120	0.5	35.6	1425
20	C_H	TBAB	0.05	4000/2/1	-	120	4	55.7	2230
21	C_H	TBAI	0.05	4000/2/1	-	120	2	42.3	1690
22	C_H	[PPN]Cl	0.05	4000/2/1	-	120	2	38.9	1555
23	C_H	DMAP	0.05	4000/2/1	-	120	2	0.4	16
24	C_H	TBAB	0.1	4000/4/1	-	120	2	82.4	3300
25	C_H	TBAB	0.25	4000/10/1	-	120	2	95.2	3810
26	C_{t-Bu}	TBAB	0.25	4000/10/1	-	120	2	84.6	3385
27	C_{Cum}	TBAB	0.25	4000/10/1	-	120	2	63.2	2530
28[e]	-	TBAB	0.05	4000/2/0	-	120	2	32.6	-

[a] Basic reaction conditions: propylene oxide (5 mL; 7.15×10^{-2} mol), catalyst loading = 0.025 mol% (1.79×10^{-5} mol), 1 h. [b] Determined by NMR (using mesitylene as an internal standard). [c] The selectivity for the formation of propylene carbonate was found to be >99%. [d] Turnover frequency (mol$_{PC}$ mol$_{Catalyst}^{-1}$ reaction time^{-1}). [e] Control experiment in absence of catalyst: reaction time = 24 h.

In order to check the catalytic performances of the iron(III) complexes C_H and C_{Cum} for the coupling of the (±)-propylene oxide (PO) with the carbon dioxide and directly compare the results with the previously reported catalyst C_{t-Bu} we conducted, several catalytic tests for the three complexes (C_H, C_{t-Bu}, C_{Cum}) under the same reaction conditions. The main results are summarized in Table 1. Due to the encouraging preliminarily results obtained with the catalyst C_{t-Bu} we initially decided to use a low catalyst loading (0.025% mol) and as co-catalyst the n-tetrabutylammonium bromide (TBAB) (with a co-catalyst/catalyst molar ratio of 2) under a pressure of CO_2 of 2 MPa and solvent-free conditions. The reaction time was reduced to 1 hour in order to

better evaluate the turnover frequencies (TOF) of the catalytic systems. In the temperature range 80-140 °C , an increase of the activity by increasing the temperature was observed for all the titled catalysts with a maximum for the catalyst C_H that reach a conversion of the 61% with a TOF value of 2420 h^{-1} at 140 °C (entry **4**) showing that a less encumbered metal centre is more accessible to the substrate. Notably at lower temperature (80-100 °C) the catalytic performances of the catalyst C_H are sensibly scarcer (entries **1** and **2**) compared to the more sterically demanding catalysts C_{t-Bu} and C_{Cum} (entries **5, 6** and **9, 10** respectively; see also Figure 1). This apparent contradiction is probably due to the lower solubility of the complex C_H in the reaction medium compared to the more soluble catalysts C_{t-Bu} and C_{Cum}. In order to support our hypothesis we performed therefore the reactions by using methyl ethyl ketone (MEK) as solvent with aim to suppress the negative effect on the catalytic activity due to the low solubility of the catalyst C_H. As a matter of fact the results obtained at both 100 and 120 °C clearly show that the catalytic activity of the more open catalyst C_H is comparable at 100 °C to those of the catalysts C_{t-Bu} and C_{Cum} (entries **13**, **15** and **17**) and is sensibly higher at 120 °C (entries **14**, **16** and **18**) indicating however a crucial role of the temperature in determining the catalytic activity for this class of catalysts.

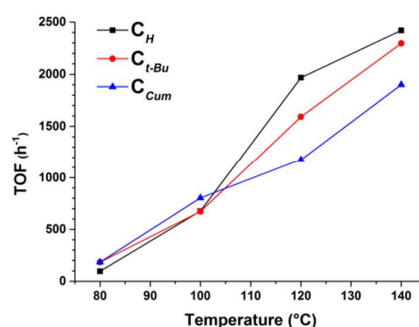

Figure 1. TOF of the iron(III) complexes as a function of the reaction temperature (entries **1-12**, Table **1**).

For the more active catalyst C_H we also explored the effect of the CO_2 pressure on the catalytic activity showing that a halving or doubling the carbon dioxide pressure has a small effect on the catalytic performances (compare entry **3** with entries **19** and **20**) .

In analogy to the results obtained in the presence of the complex C_{t-Bu} the use of other commonly employed co-catalysts such as *n*-tetrabutylammonium iodide (TBAI), *bis*(triphenylphosphine)iminium chloride (PPNCl), and 4-dimethylaminopyridine (DMAP) resulted in a lowering of the catalytic activity (entries **21-23**). In particular while the two halogen containing co-catalysts (TBAI and PPNCl) show an activity comparable to that of TBAB the use of DMAP results in a dramatic reduction of the catalytic activity. Moreover, the absence of the cocatalyst (TBAB) or of the iron(III) catalyst C_H resulted in a complete loss of the catalytic activity in the first case and in a conversion of only 33% (entry **28**) in the second case even after 24 h, highlighting a synergic effect between the catalyst and the cocatalyst for the carbonate formation.

Intriguingly, by increasing the co-catalyst/catalyst molar ratio to higher values (4 for entry **24** and 10 for entry **25**) a further increase of the catalytic activity was observed with a conversion of 95 % in 1 hour and a TOF of 3800 which is not only the highest reported so far for an iron based catalyst but well compares with the more active catalysts based on other metals.[5a] It is worth noting that also under these conditions the order of reactivity is C_H > C_{t-Bu} > C_{Cum} (entries **25**- **27**) confirming that a less sterically congested metal centre is more reactive in the CO_2/epoxide coupling.
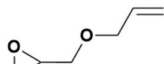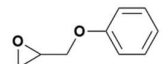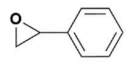
Having established that the catalyst C_H is an highly active and selective catalyst for the formation of cyclic carbonates, in order to expand the scope of this catalyst we explored the cycloaddition of CO_2 to a variety of functionalized terminal epoxides providing organic cyclic carbonates under similar catalytic conditions used in the case of propylene oxide (reaction condition of entry **3** of Table 1). The main results are reported in the Table **2**. All the substrates were conveniently converted to the corresponding cyclic carbonates with good yields even at relatively short reaction times (1 h). Notably, the glycerol carbonate[15] which is a very interesting target molecule due to its properties is straightforwardly obtained from glycidol in excellent yield (96%) with a

TOF of 3830 h^{-1} even superior to that observed for propylene oxide under the same reaction conditions (compare entry **3** of Table 1 with entry **29** of Table 2) and, also in this case, it is the higher observed TOF reported for this substrate.

Furthermore we also explored the synthesis of cyclic carbonates starting from the more challenging substrate cyclohexene oxide (CHO). Actually the formation of the cyclic carbonate from CHO is disfavored respect to the formation of the corresponding polycarbonate because the geometric strain due to the formation of two interconnected six- and five-membered cycles. In our case we obtained good conversion (63 %) within 3h with a complete selectivity toward the cyclic product in the case of the complex **C$_H$**. In this case the role of the steric bulkiness of the substituents on the aromatic rings is even more pronounced than in the case of PO with the catalytic activity decreasing with steric bulk of the substituents: **C$_H$** > **C$_{t-Bu}$** > **C$_{Cum}$** (see entries **34**-**36**).

It is worth mentioning that, as already observed for other iron based catalytic systems, the cyclic carbonates from CHO were produced selectively with *cis*-stereochemistry, as pointed out by NMR and FT-IR analysis, that revealed strong adsorption bands at 1802 cm^{-1}, previously assigned to the stretching of the carbonyl, respectively for the *cis*-cyclohexene carbonate.[11i]

Table 2. Synthesis of organic cyclic carbonate through CO$_2$/epoxide coupling catalyzed by Fe(III) catalysts.

Entry[a]	Catalyst	(mol%)	TBAB (mol%)	Epox./Cocat./Cat. (molar ratio)	Substrate	Product[b,c]	Time (h)	Conversion[b,c] (%)	TOF[d] (h^{-1})
29	C$_H$	0,025	0,05	4000/2/1			1	95,7	3830
30	C$_H$	0,025	0,05	4000/2/1			1	40,2	1610
31	C$_H$	0,025	0,05	4000/2/1			1	40	1600
32	C$_H$	0,025	0,05	4000/2/1			1	18,6	745
33	C$_H$	0,025	0,05	4000/2/1			1	16,4	655
34[e]	C$_H$	0,2	0,4	500/2/1			3	62.8	105
35[e]	C$_{t-Bu}$	0,2	0,4	500/2/1			3	23.9	40
36[f]	C$_{Cum}$	0,2	0,4	500/2/1			3	6.8	11

[a] Basic reaction conditions: epoxide = 7.15 × 10^{-2} mol, temperature = 120 °C, carbon dioxide pressure = 2 MPa. [b] Determined by NMR (using mesitylene as an internal standard). [c] The selectivity for the formation of cyclic carbonate was found to be >99%. [d] Turnover frequency (mol$_{COC}$ mol$_{Catalyst}$$^{-1}$ reaction time^{-1}). [e] A selectivity >99% for the formation of the *cis* isomer of the carbonate was observed. [f] Traces of polycarbonate were found.

Conclusions

In conclusion herein we reported on the synthesis and characterization of two new, air stable, dimeric iron(III) complexes bearing a thioether-triphenolate ligands. When activated by tetrabutylammonium bromide the title iron(III) complexes results very effective in the coupling of CO$_2$ with epoxides giving excellent results in terms of activity, chemo- and stereo- selectivity under solvent-free conditions. In particular, the less steric demanding **C$_H$** complex shows the bests catalytic performances in terms of activity and selectivity for a wide number of substrates with TOF values up to 3830 h^{-1}. These results demonstrate, for this class of catalysts, that a more accessible metal centre is crucial to increase the activity in the cycloaddition of CO$_2$ to epoxide. Finally, these outcomes clearly show that, this class of iron(III) based catalysts bearing two sulfur atoms in the ligand

skeleton are competitive in term of activity, selectivity and substrate scope respect to other catalytic systems based on more toxic and/or expensive metals for the formation of cyclic carbonates.

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