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Iron(III) Versatile Catalysts for Cycloaddition of CO_2 to Epoxides and Epoxidation of Alkenes

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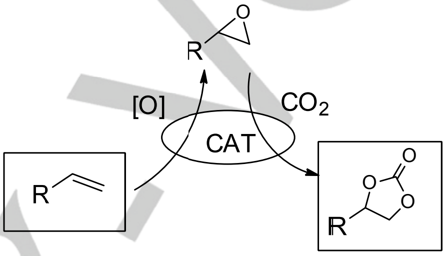
Abstract: Fe(III) complexes with tridentate pyridine-imine-phenolato ligands differing in the chain length between the imine and pyridine groups (2-methylpyridine **L1** and 2-ethylpyridine **L2**) have been synthesized. New complex [Fe(**L2**)$_2$]ClO_4 (**2**) was characterized by X-ray diffraction and spectroscopic techniques. [Fe(**L1**)$_2$]ClO_4 (**1**) and **2** form active catalysts for the cycloaddition of CO_2 to epoxides and for the epoxidation of alkenes. Catalytic systems with the more flexible skeleton (**2**) in combination with tetrabutylammonium bromide (TBAB) were more active than **1**/TBAB in the cycloaddition of CO_2 to epoxides. TOFs up to 900 h^{-1} for the selective synthesis of styrene carbonate and 3640 h^{-1} for the synthesis of glycidol carbonate were obtained using **2**/TBAB at low catalyst loadings (0.025 mol %). Additionally, **2** was also active in the epoxidation of styrene derivatives such as *trans*-stilbene (conversion 88 %) and *trans*-β-methylstyrene (conversion 100 %) using *tert*-butylhydroperoxide as oxidant at 60 ºC in acetonitrile. Epoxidation of styrene and cyclohexene proceed at low conversions.

Introduction

The synthesis of organic carbonates from epoxides and CO_2 is an atom economic process, which gives useful utility to a waste chemical such as CO_2 generated yearly at large quantity (30-32 Gt/y anthropogenic emissions).[1] However, the synthesis of the epoxide starting material; requires an additional step that sometimes involves expensive or toxic reagents and requires chemical separations.[2] Cyclic carbonates are valuable products that are widely used as excellent polar aprotic solvents in the chemical industries,[3] as electrolyte for lithium-ion secondary batteries,[4] and also as raw materials for the synthesis of small molecules[5] and polymers.[6] An interesting approach to cyclic carbonates is the direct synthesis from olefins by reaction with an oxidant and CO_2.[7] However, low selectivity towards the carbonates, formation of numerous oxidation by-products and long reaction times are often the major problems of this reaction.[8] Thus, a two step approach involving the same catalyst may be an alternative to overcome these limitations. The ideal metal complexes for both processes are on the first row transition elements, such as manganese and iron being the best options. But particularly, iron compounds posses the advantage of being relatively low toxic, widely available and cost effective. Moreover, iron complexes have variable redox chemistry. Therefore, iron-based catalytic systems may be a good option since they seem to be active both in olefin oxidation[8] and also in carbonate formation with CO_2 separately[9-12] (Scheme 1).



Scheme 1. Two step synthesis of carbonates from alkenes using the same catalyst.

Among iron-based catalysts for epoxidation[9] especially interesting are non-heme iron complexes because they are efficient and easily tunable.[9c,d] Despite they have been extensively used in epoxidation reactions, there are still few examples applied for the CO_2 and epoxide coupling.[10-12] Williams and co-workers reported a bimetallic macrocyclic iron(III) complex capable of both the formation of cyclic carbonate and polycarbonates from CO_2 and epoxides using different co-catalysts.[11] Kleij and co-workers developed iron(III) catalysts with amine triphenolate ligands,[12] which were active, with a suitable co-catalyst, to obtain cyclic carbonate products for a wide scope of substrates. Most recently, the same group reported an analogous iron(III) catalyst bearing a pyridylamine-bis(phenolate) ligand, which was also highly versatile in the conversion of a broad scope of substrates. Particularly, with terminal epoxides the cyclic carbonate was the main product, whereas with cyclohexene oxide and vinylcyclohexene oxide it was also possible to selectively obtain polycarbonates with high percentage incorporation of carbonate linkages.[13]

In this work we present an investigation into iron(III) complexes with tridentate NN’O-donor base Schiff pro-ligands, **HL1** and **HL2** (Scheme 2) as catalysts for the coupling of epoxides with CO_2 and also for the epoxidation of olefins. We previously reported the catalytic studies of analogous chromium(III) and zinc(II) complexes with these ligands.[14] Iron(III) complexes with **HL1** and **HL2** have the advantage that may lead to more stable systems than analogous zinc(II) complexes, since they stabilize higher coordination number. Moreover, base Schiff are easily prepared by condensation of a salicylaldehyde derivative with a diamine, therefore modular in nature. Pro-ligand **HL2** differs from **HL1** as it has an ethylene

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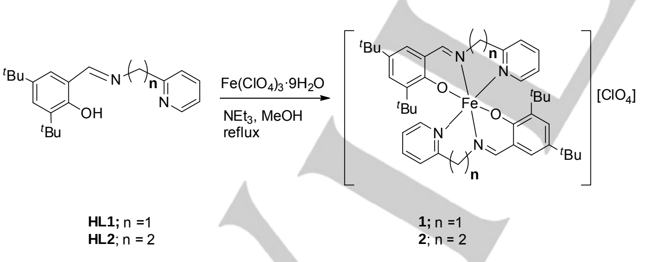
Supporting information for this article available. CCDC 1425832 for **2**.

fragment between the pyridine and the imine functionalities instead than a methylene. This may confer more flexibility to the active center. Related manganese(III) complexes with **HL1** were active catalysts in the epoxidation of alkenes,[15] but they were not active for the coupling of CO_2 and epoxides.[16]

Results and Discussion

Synthesis of ligands and complexes

The syntheses of pro-ligand **HL1**[17] and complex **1**[18] (Scheme 2) were previously reported. **HL2** was prepared following the procedure reported by Asadi *et al.*[19] by condensation of 2-(2-pyridyl)ethylamine with 3,5-di-*tert*-butylsalicylaldehyde in MeOH and was obtained spectroscopically pure (see Supplementary information). Complex **2** was obtained as an air stable dark blue solid (yield 89 %) by reaction of **HL2** with $Fe(ClO_4)_3 \cdot 9H_2O$ in refluxing methanol in the presence of triethylamine. Mass spectrometry (ESI) and elemental analysis were in accordance with the formula $[Fe(\mathbf{L2})_2][ClO_4]$. Infrared spectrum (single $\nu(ClO_4)$ band at 1085 cm^{-1})[20] and conductivity data in acetonitrile (164.9 $\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$ at $4.04 \cdot 10^{-4}$ M)[21] confirmed ClO_4^- as non-coordinating counteranion in a 1:1 electrolyte. The stretching band corresponding to the azomethine bond, ν(C=N), appeared in the infrared spectrum of **2** at 1601 cm^{-1}; at lower frequency than for the free ligand (1630 cm^{-1}). Magnetic susceptibility measurement at room temperature (μ_{eff} of 6.03 μ_B) was in good agreement with the values of high-spin d^5 iron(III) octahedral complexes with similar ligands (5.7-6.0 μ_B).[22] The electronic spectra in acetonitrile of **2** showed bands at 343 and 573 nm attributed to ligand-to-metal charge transfer (LMCT) $p\pi_{phenolate} \rightarrow d\sigma^*_{iron(III)}$ and $p\pi_{phenolate} \rightarrow d\pi^*_{iron(III)}$ transitions respectively according to literature data.[19,23] Bands at 214 and 241 nm were attributed to intraligand pyridine and phenolate $\pi \rightarrow \pi^*$ band, which were shifted respect to the free ligand **L2** (231 and 262 nm).[24]



Scheme 2. Synthesis of complexes **1** and **2**

X ray structure of 2

Single crystals of **2** suitable for a structure determination were obtained by slow evaporation of a hexane/diethylether solution at room temperature. X-ray analysis confirmed that **2** contains a monometallic cation composed of an iron(III) ion surrounded by two deprotonated ligands in a 6-coordinated pseudo-octahedral environment and a ClO_4^- acts as counterion (Figure 1). As in the structure of complex **1** reported by Verani *et al.*,[18] both tridentate ligands are meridionally coordinated. Bond distances and angles (Table 1) are in agreement with **1** and similar Fe(III) complexes.[18,22] The Fe-N(imine) (2.121(2) and 2.110(2) Å), Fe-N(pyridine) (2.255(2) and 2.249(2) Å) and Fe-O(phenolate) (1.9083(18) and 1.9044(17) Å) bond distances are in agreement with high-spin iron(III) ion.[25,26,27] The meridional coordination of each ligand leads to a *cis* orientation of the two pyridines with an N3-Fe1-N1 angle of 81.61(8)°. Similarly, the two phenolate rings are *cis* to each other with an O2-Fe1-O1 angle of 102.73(8)°. The *trans* imine nitrogen atoms have an N4-Fe1-N2 angle of 176.59(8)°.

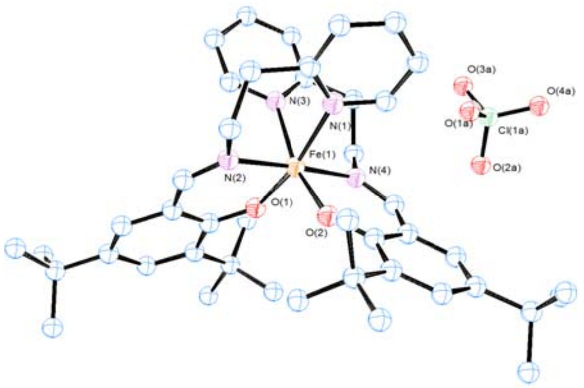


Figure 1. ORTEP drawing of complex of **2**. All hydrogen atoms and solvent molecules are omitted for clarity. Thermal ellipsoids drawn at the 50 % probability level.

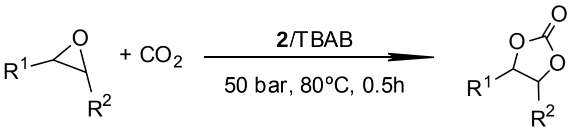
Table 1. Selected bond lengths (Å) and angles (°) for **2**.

Fe1-O2	1.9044(17)	Fe1-N2	2.121(2)	1.9044(17)
Fe1-O1	1.9083(18)	Fe1-N3	2.249(2)	1.9083(18)
Fe1-N4	2.110(2)	Fe1-N1	2.255(2)	2.110(2)
O2-Fe1-O1	102.73(8)	O2-Fe1-N4	86.37(8)	102.73(8)
O1-Fe1-N4	90.29(8)	O2-Fe1-N2	93.02(8)	90.29(8)
O1-Fe1-N2	86.57(8)	N4-Fe1-N2	176.59(8)	86.57(8)
O2-Fe1-N3	166.01(8)	O1-Fe1-N3	89.83(8)	166.01(8)
N4-Fe1-N3	87.43(8)	N2-Fe1-N3	93.89(8)	87.43(8)
O2-Fe1-N1	86.56(8)	O1-Fe1-N1	169.17(8)	86.56(8)
N4-Fe1-N1	95.90(8)	N2-Fe1-N1	87.41(8)	95.90(8)

Coupling of CO_2 to epoxides

The catalytic activity of **1** in the reaction of CO_2 with styrene oxide (**3**, Scheme 3) as a benchmark substrate was initially analyzed at conditions of 50 bar of carbon dioxide, 80 °C, 0.2 mol % catalyst during 24 h. At these conditions, complex **1** was not active (Figure 2). Addition of a co-catalyst such as tetrabutylammonium bromide (TBAB) or bis(triphenylphosphine)iminium chloride (PPNCl) (complex/co-catalyst ratio = 1/2) produced selectively the cyclic styrene carbonate according to ^1H NMR spectra with high conversion (100 and 74 % respectively, Figure 2). A control experiment using only TBAB gave lower conversion (18 %).[28, 29] The synergistic effect reported for other related systems combining a Lewis acid catalyst with TBAB onium salt co-catalyst was also observed in this case.[14]

The evolution of conversion along time was analysed running four batch catalytic reactions using always the same reactor set ups. These experiments evidenced that the conversion using **1**/TBAB was already 71 % after 3h (Figure 3). At this reaction time, increasing the loading of co-catalyst up to 5, an increase of conversion was observed (97 %, entry 1, Table 2). In order to determine the initial maximum TOF the conditions (time, catalysts loading) were optimized and the reactions were run at low conversions. Thus, at the co-catalyst/catalyst ratio of 5, further decrease of catalyst loading (up to 0.05 mol %) produced an increase of the TOF (401 h^{-1}, entries 2 and 3, Table 2).



3 R^1=Ph, R^2=H
4 R^1=Me, R^2=H
5 R^1=C_4H_9-, R^2=H
6 R^1=$C_{12}H_{25}$-, R^2=H
7 R^1=$ClCH_2$-, R^2=H
8 R^1=$HOCH_2$-, R^2=H
9 R^1=$CH_3(CH_2)_7$-, R^2= -$(CH_2)_7COOMe$
10 R^1,R^2= -$(CH_2)_4$-

Scheme 3. Cycloaddition of **3**-**10** to CO_2.

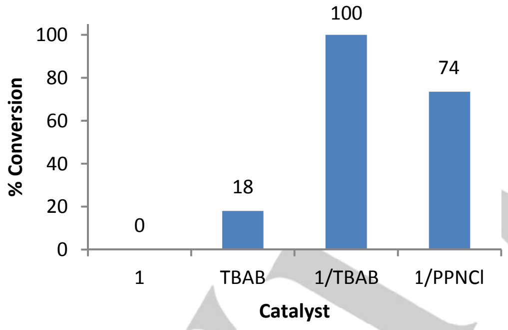


Figure 2. Co-catalyst effect on the coupling of styrene oxide and CO_2 using **1** as catalyst. Reaction conditions: catalyst 0.2 mol %, co-catalyst 0.4 mol %, temp. = 80 °C. P_{CO2} = 50 bar, time = 24 h.

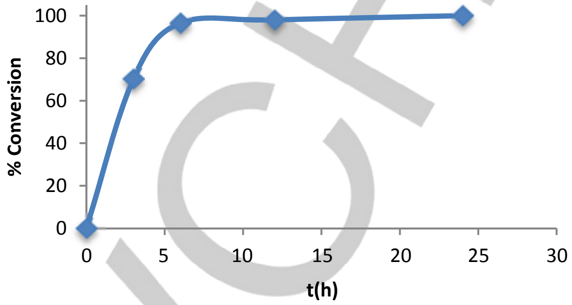


Figure 3. Coupling of styrene oxide and CO_2 along over time using **1**/TBAB catalytic system. Reaction conditions: catalyst 0.2 mol %, co-catalyst 0.4 mol %, temp. = 80 °C. P_{CO2} = 50 bar.

Complex **2** was neither active in absence of co-catalyst (entry 4, Table 2). Combination of **2** with TBAB (1/5) produced a higher conversion than **1**/TBAB (entry 5, Table 2). A decrease in pressure or temperature produced a decrease of activity (entries 6 and 7, Table 2). The optimized TOF at 50 bar and 80 °C for **2**/TBAB achieved 900 h^{-1} (entry 6, Table 2). The higher activity of **2/**TBAB may be related with its more flexible structure, which may favour the dissociation of the pyridine fragment to allow the epoxide coordination. The activity of **2**/TBAB is also higher than the one obtained with the previously reported catalytic system [Zn(**1**)$_2$].[14b] All these complexes are very selective to the cyclic carbonate *versus* the polycarbonate. This was attributed to the ability of the pyridine group to act as a pendant arm that could replace the growing polycarbonate chain and, consecutively, favour the backbiting mechanism yielding the cyclic carbonate.

Table 2. Cycloaddition of styrene oxide and CO_2 catalysed by iron(III) systems.[a]

Entry	Cat	Co-cat	t (h)	Cat/Co-cat (mol %)[b]	TOF (h^{-1})[c,d,e]
1	**1**	TBAB	3	0.2/1.0	162[f]
2	**1**	TBAB	1	0.1/0.5	270
3	**1**	TBAB	1	0.05/0.25	401
4	**2**	-	24	0.2/-	1
5	**2**	TBAB	1	0.05/0.25	580
6[g]	**2**	TBAB	1	0.05/0.25	556
7[h]	**2**	TBAB	1	0.05/0.25	82
8	**2**	TBAB	0.5	0.025/0.125	900

[a] Reaction conditions: T = 80 °C, P_{CO2} = 50 bar, styrene oxide: 43.8 mmol (5 ml). Average results of two experiments. n.d.: not determined. [b] mol % respect to the substrate. [c] measured by ^1H NMR. [d] Selectivity for the cyclic carbonate product >99 %. [e] averaged TOF (mol substrate converted·(mol catalyst)$^{-1}$·h^{-1}. [f] 97 % % Conversion. [g] 30 bar. [h] 60 °C

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Iron(III) catalyst based on amine triphenolate ligand developed by Kleij and coworkers was also found to be active for styrene carbonate formation in conjunction with TBAB co-catalyst.[12a] The authors were able to obtain high conversion (91 %) and high styrene carbonate yield (87 %) at milder conditions (room temperature and 20 bar of CO_2). Nevertheless, higher amount of TBAB (5 mol %) was added with a catalyst/co-catalyst molar ratio of 1/10.

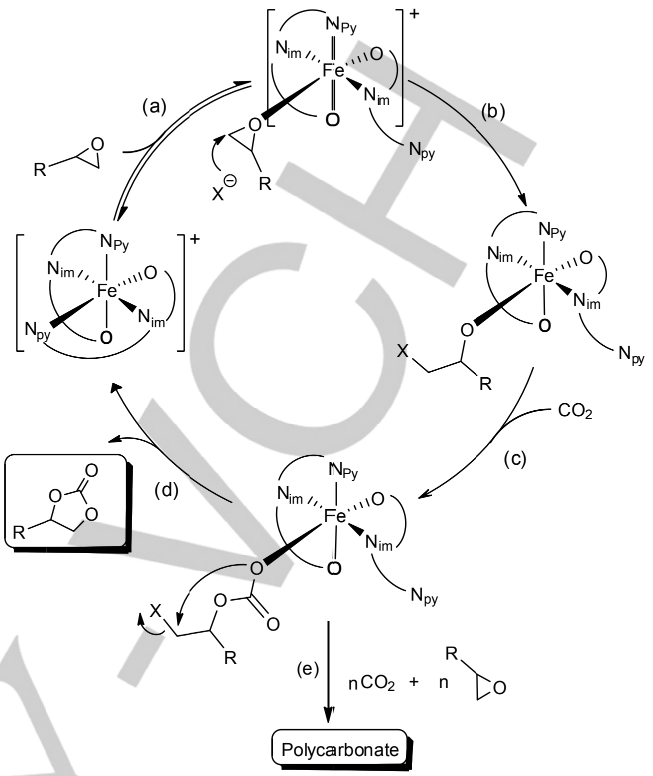
Under the optimized conditions (80 ºC, 50 bar of CO_2, catalyst/co-catalyst concentration of 0.025/0.125 mol % and during 0.5 h) the reaction of CO_2 with a series of commercial available epoxides (**4-10**, Scheme 3) was undertaken using catalyst **2**/TBAB. All these substrates were efficiently converted into the corresponding cyclic carbonates, with a selectivity of > 99 % (Table 3). The rate of the reaction decreased as the length of the chain increased (entries 1-3, Table 3). This suggests an unfavourable competition between coordination of the epoxide and decoordination of the pyridine at the iron(III) center. Functionalized epoxides such as epichlorohydrin and glycidol were also very efficiently converted to the corresponding cyclic carbonates at high rates (TOF of 1404 and 3640 h^{-1} respectively, entries 4 and 5, Table 3).

Concerning the reaction of CO_2 with cyclohexene oxide **10** using **2**/TBAB as catalyst (0.2/1.0 mol %, 80 ºC, 50 bar of CO_2, 24 h),[30] good conversion was achieved (74 %). Cyclic carbonate was formed as a single product (entry 7, Table 3). The selectivity of the reaction was strongly influenced by the use of other co-catalysts, as well as by the co-catalyts/catalyst ratio. Indeed, iron(III) complexes/PPNCl catalytic system was frequently used in the literature producing poly(cyclohexene carbonate) providing better selectivity in the polycarbonate than TBAB.[12b]

Table 3. Cycloaddition of CO_2 with epoxides (**4-10**) using catalytic system **2**/TBAB.[a]

Entry	Epoxide	TOF (h^{-1})[b,c]
1	**4**	1639
2	**5**	299
3	**6**	160
4	**7**	1404
5	**8**	3640
6[d]	**9**	2 (95[e])
7[f]	**10**	15
8[g]	**10**	2/6[h]

[a] Reaction conditions: T = 80 ºC; P_{CO2} = 50 bar; time = 0.5 h; epoxide: 3 ml; catalyst: 0.025 mol %; TBAB: 0.125 mol %. Average results of two experiments. n.d.: not determined. Selectivity for the cyclic carbonate product >99 %. [b] measured by ^{1}H NMR. [c] averaged TOF (mol substrate converted·(mol catalyst)$^{-1}$·h^{-1}. [d] cat/co-cat: 2 mol %/2 mol %; T = 100 ºC; P_{CO2} = 100 bar, 24h. [e] % Conversion, *cis*/*trans*: 33/67. [f] 24h, catalyst/co-catalyst: 0.2/1.0 mol %. [g] catalyst/co-catalyst: **2**/PPNCl 0.2/0.2 mol %. [h] ratio cyclic carbonate/polycarbonate; 58 % CO_2 content in the polycarbonate measured by ^{1}H NMR



Scheme 4. Proposed mechanism for the cycloaddition of CO_2 to epoxides catalyzed by **2**/TBAB

Using PPNCl as co-catalyst (co-catalyst/catalyst = 1) at standard conditions afforded lower conversion (37 %) to mixtures of copolymer and cyclic carbonate (entry 8, Table 3). Although not negligible, a selectivity of 21 % in the cyclic product was obtained over the copolymer. The incorporation of carbonate linkages into the polymer was only 58 %.

According to the evidences obtained from catalytic experiments together with our previous studies,[14] it could be proposed a plausible general mechanism for the coupling of CO_2 and epoxides involving the metal-NN'O Schiff complexes (Scheme 4).The initial step in the catalytic cycle involves the activation of the epoxide by coordination to the metallic center and formation of a metal-alkoxide active species. To do this, a displacement of a pyridine moiety must take place (step a, Scheme 4) since it is probably the most labile coordinating position. In fact, related Zn(II) complex has a pentacoordinate structure [Zn(**L1**-κ^3N,N',O)(**L1**-κ^2N',O)] [14b] in solid state. Once the epoxide is activated, a nucleophilic attack with the Br- or Cl- from co-catalyst (TBABr or PPNCl) takes place (step b, Scheme 4). Evidences for this substitution were obtained by ^{1}H NMR spectroscopy of the reaction of [Zn(**L1**)$_2$] with styrene oxide.[14b] The next step is the insertion of a carbon dioxide molecule into the metal-alkoxide bond leading to a carbonate linkage (step c, Scheme 4). This intermediate can either form a cyclic monomer through intramolecular rearrangement by a "back-biting" mechanism or polycarbonate through further alternating insertions of epoxide and carbon dioxide molecules. The stability of the hexacoordinate species may favor the ring closing step

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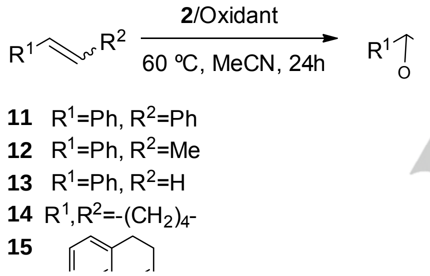
(step d, Scheme 4) against the formation of the poly(carbonate) (step e, Scheme 4).

Epoxidation of alkenes

Complex **2**, which was the best catalyst for the reaction of CO_2 with epoxides, was evaluated as catalyst (3.3 mol %) in the oxidation of alkenes **11**-**15** at 60 ºC using acetonitrile as solvent (Scheme 5). *Trans*-stilbene **11** was used as a model substrate. A screening of common oxidants (entries 1-6, Table 4) showed that *tert*-butylhydroperoxide (TBHP) provided the best conversion (88 % at 24 h, entry 1, Table 4) being the epoxide the only product detected by ^1H NMR. Using H_2O_2, addition of AcOH was required to produce low % of the epoxide (entries 2 and 3, Table 4). A modest conversion was obtained using 3-chloroperoxybenzoic acid (MPCBA) (41 %, entry 4, Table 4). Low conversions (< 15 %) were obtained with PhIO and NaClO as oxidants (entries 5 and 6, Table 4). In all the cases the *trans* epoxide was formed. The conversion of *cis*-stilbene into the corresponding epoxide using **2**/TBHP was lower than for the *trans* isomer (entries 7-9, Table 4). Lower yields were also reported in the epoxidation of *cis*-stilbene respect to the *trans* isomer using a binary system $FeCl_3·6H_2O$/imidazole.[31] From the *cis* alkene the *trans* epoxide was obtained. This suggests that a radical mechanism may be taking place.[32]



Scheme 5. Epoxidation reaction of substrates **11**-**15**.

Another substrate such as *trans*-β-methylstyrene (**12**) was transformed to the *trans*-epoxide with high selectivity and yield (entry 10, Table 4). Styrene (**13**) and cyclohexene (**14**) were epoxidized at these conditions at low conversions adding imidazole (entries 11 and 12, Table 4). A yield up to 85 % of naphthalene, identified by ^1H NMR, was obtained in the oxidation of 1,2-dihydronaphtalene (entry 15, Table 4). Formation of naphthalene sub-product that resulted from oxidative dehydrogenation of 1,2-dihydronaphtalene, was also reported using Kegin-type metal substituted polyoxotungstates catalysts with H_2O_2.[33]

Conclusions

In summary, we present stable and easy to handle iron(III) complexes bearing tridentate NN'O-donor Schiff ligands, $[Fe(NN'O)_2]ClO_4$ that proved to be efficient catalysts for the selective formation of cyclic carbonates from terminal epoxides and carbon dioxide in the presence of TBAB. The more flexible structure led to the most active system probably because it was easier to activate the epoxide by coordination to the metal center. The highly coordinative saturated species led to selective catalysts for the formation of the cyclic carbonate. The same complex is also an active catalyst for the epoxidation of substituted styrenes (stylbene and methylstyrene) using TBHP as oxidant. The stereoselectivity of the epoxidation suggests that a radical mechanism takes place. The catalytic activity for other alkenes was low.

Table 4. Catalytic oxidation of **11**-**15** using **2** as catalysts with different oxidizing agents.[a]

Entry	Subs.	Oxidant	subs/oxidant (mmol)	Conv (%)[b]	Select. (%)
1	*trans*-**11**	TBHP	0.3/0.6	88 (80)[c]	>99 (*trans*)
2	*trans*-**11**	H_2O_2	0.3/0.6	-	-
3	*trans*-**11**	H_2O_2/AcOH	0.3/0.6/0.33	16	>99 (*trans*)
4	*trans*-**11**	MCPBA	0.3/0.3	41	>99 (*trans*)
5	*trans*-**11**	PhIO	0.3/0.15	13	>99 (*trans*)
6	*trans*-**11**	NaOCl	0.3/0.3	3	>99 (*trans*)
7	*cis*-**11**	TBHP	0.3/0.6	23	>99 (*trans*)
8	*cis*-**11**	MCPBA	0.3/0.3	35	43/57 (*cis/trans*)
9	*cis*-**11**	PhIO	0.3/0.15	23	90/10 (*cis/trans*)
10	*trans*-**12**	TBHP	0.3/0.6	100	>99 *trans*
11[d]	**13**	TBHP	0.3/0.6	24[e]	n.d.
12[d]	**14**	TBHP	0.3/0.6	3[e]	n.d.
13	**15**	TBHP	0.3/0.6	85[f]	>99

[a] Reaction conditions: solvent: 5 ml; catalyst: 3.3 mol % respect to the substrate; TBHP (5.5 M in decane), H_2O_2 and H_2O_2/AcOH were added dropwise during the reaction; time = 24 h. Average results of two experiments. n.d.: not determined. [b] measured by ^1H NMR using mesitylene as an internal standard. [c] conversion (%) at 16 h. [d] 0.33 mmol of imidazole added. [e] yield in epoxide measured by GC using mesitylene as internal standard. [f] naphthalene.

Supporting Information

Detailed experimental procedures, characterization data, crystallographic date and other spectra of the compounds are given in the Supporting Information.

Acknowledgements

We gratefully acknowledge the *Ministerio de Economia y Competitividad* (CTQ2013-43438-R) and the *Departament* *d'Economia i Coneixement* (*Generalitat de Catalunya*, 2014SGR670) for financial support.

Keywords: iron • carbon dioxide • epoxidation • catalysis • carbonates

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Legends for Figures and Schemes

Scheme 6. Two step synthesis of carbonates from alkenes using the same catalyst.

Scheme 7. Synthesis of complexes **1** and **2**

Scheme 8. Cycloaddition of **3**-**10** to CO_2.

Scheme 9. Proposed mechanism for the cycloaddition of CO_2 to epoxides catalyzed by **2**/TBAB

Scheme 10. Epoxidation reaction of substrates **11**-**15**.

Figure 4. ORTEP drawing of complex of **2**. All hydrogen atoms and solvent molecules are omitted for clarity. Thermal ellipsoids drawn at the 50 % probability level.

Figure 5. Co-catalyst effect on the coupling of styrene oxide and CO_2 using **1** as catalyst. Reaction conditions: catalyst 0.2 mol %, co-catalyst 0.4 mol %, temp. = 80 ºC. P_{CO2} = 50 bar, time = 24 h.

Figure 6. Coupling of styrene oxide and CO_2 along over time using **1**/TBAB catalytic system. Reaction conditions: catalyst 0.2 mol %, co-catalyst 0.4 mol %, temp. = 80 ºC. P_{CO2} = 50 bar.

Table 5. Selected bond lengths (Å) and angles (°) for **2**.

Fe1-O2	1.9044(17)	Fe1-N2	2.121(2)	1.9044(17)
Fe1-O1	1.9083(18)	Fe1-N3	2.249(2)	1.9083(18)
Fe1-N4	2.110(2)	Fe1-N1	2.255(2)	2.110(2)
O2-Fe1-O1	102.73(8)	O2-Fe1-N4	86.37(8)	102.73(8)
O1-Fe1-N4	90.29(8)	O2-Fe1-N2	93.02(8)	90.29(8)
O1-Fe1-N2	86.57(8)	N4-Fe1-N2	176.59(8)	86.57(8)
O2-Fe1-N3	166.01(8)	O1-Fe1-N3	89.83(8)	166.01(8)
N4-Fe1-N3	87.43(8)	N2-Fe1-N3	93.89(8)	87.43(8)
O2-Fe1-N1	86.56(8)	O1-Fe1-N1	169.17(8)	86.56(8)
N4-Fe1-N1	95.90(8)	N2-Fe1-N1	87.41(8)	95.90(8)

Table 6. Cycloaddition of styrene oxide and CO2 catalysed by iron(III) systems.[a]

Entry	Cat	Co-cat	t (h)	Cat/Co-cat (mol %)[b]	TOF (h^{-1})[c,d,e]
1	**1**	TBAB	3	0.2/1.0	162[f]
2	**1**	TBAB	1	0.1/0.5	270
3	**1**	TBAB	1	0.05/0.25	401
4	**2**	-	24	0.2/-	1
5	**2**	TBAB	1	0.05/0.25	580
6[g]	**2**	TBAB	1	0.05/0.25	556
7[h]	**2**	TBAB	1	0.05/0.25	82
8	**2**	TBAB	0.5	0.025/0.125	900

[a] Reaction conditions: T = 80 ºC, P_{CO2} = 50 bar, styrene oxide: 43.8 mmol (5 ml). Average results of two experiments. n.d.: not determined. [b] mol % respect to the substrate. [c] measured by ^1H NMR. [d] Selectivity for the cyclic carbonate product >99 %. [e] averaged TOF (mol substrate converted·(mol catalyst)$^{-1}$·h^{-1}. [f] 97 % % Conversion. [g] 30 bar. [h] 60 ºC

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Table 7. Cycloaddition of CO_2 with epoxides (**4**-**10**) using catalytic system **2**/TBAB.[a]

Entry	Epoxide	TOF (h^{-1})[b,c]
1	**4**	1639
2	**5**	299
3	**6**	160
4	**7**	1404
5	**8**	3640
6[d]	**9**	2 (95[e])
7[f]	**10**	15
8[g]	**10**	2/6[h]

[a] Reaction conditions: T = 80 ºC; P_{CO2} = 50 bar; time = 0.5 h; epoxide: 3 ml; catalyst: 0.025 mol %; TBAB: 0.125 mol %. Average results of two experiments. n.d.: not determined. Selectivity for the cyclic carbonate product >99 %. [b] measured by ^{1}H NMR. [c] averaged TOF (mol substrate converted·(mol catalyst)$^{-1}$·h^{-1}. [d] cat/co-cat: 2 mol %/2 mol %; T = 100 ºC; P_{CO2} = 100 bar, 24h. [e] % Conversion, *cis*/*trans*: 33/67. [f] 24h, catalyst/co-catalyst: 0.2/1.0 mol %. [g] catalyst/co-catalyst: **2**/PPNCl 0.2/0.2 mol %. [h] ratio cyclic carbonate/polycarbonate; 58 % CO_2 content in the polycarbonate measured by ^{1}H NMR

Table 8. Catalytic oxidation of 11-15 using 2 as catalysts with different oxidizing agents.[a]

Entry	Subs.	Oxidant	subs/oxidant (mmol)	Conv (%)[b]	Select. (%)
1	*trans*-**11**	TBHP	0.3/0.6	88 (80)[c]	>99 (*trans*)
2	*trans*-**11**	H_2O_2	0.3/0.6	-	-
3	*trans*-**11**	H_2O_2/AcOH	0.3/0.6/0.33	16	>99 (*trans*)
4	*trans*-**11**	MCPBA	0.3/0.3	41	>99 (*trans*)
5	*trans*-**11**	PhIO	0.3/0.15	13	>99 (*trans*)
6	*trans*-**11**	NaOCl	0.3/0.3	3	>99 (*trans*)
7	*cis*-**11**	TBHP	0.3/0.6	23	>99 (*trans*)
8	*cis*-**11**	MCPBA	0.3/0.3	35	43/57 (*cis/trans*)
9	*cis*-**11**	PhIO	0.3/0.15	23	90/10 (*cis/trans*)
10	*trans*-**12**	TBHP	0.3/0.6	100	>99 *trans*
11[d]	**13**	TBHP	0.3/0.6	24[e]	n.d.
12[d]	**14**	TBHP	0.3/0.6	3[e]	n.d.
13	**15**	TBHP	0.3/0.6	85[f]	>99

[a] Reaction conditions: solvent: 5 ml; catalyst: 3.3 mol % respect to the substrate; TBHP (5.5 M in decane), H_2O_2 and H_2O_2/AcOH were added dropwise during the reaction; time = 24 h. Average results of two experiments. n.d.: not determined. [b] measured by ^{1}H NMR using mesitylene as an internal standard. [c] conversion (%) at 16 h. [d] 0.33 mmol of imidazole added. [e] yield in epoxide measured by GC using mesitylene as internal standard. [f] naphthalene.

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Entry for the Table of Contents

FULL PAPER

Fe(III) complexes with tridentate pyridine-imino-phenolato NN'O-donor ligands are active for the cycloaddition of CO_2 to epoxides and the epoxidation of alkenes

CO_2 activation*

Laia Cuesta-Aluja, and Anna M. Masdeu-Bultó**

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Iron(III) versatile catalysts for cycloaddition of CO_2 to epoxides and epoxidation of alkenes

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