

From Alkenes to Cyclic Carbonates with a Stable Iron-Cross-Bridged Cyclam Catalyst

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A stable iron(III) complex with the cross-bridged cyclam 4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane catalyzes the epoxidation of aromatic alkenes and the fixation of CO₂ into

cyclic carbonates. Best results were obtained for styrene conversion to styrene carbonate.

Introduction

Cyclic carbonates are interesting compounds with many uses in industry e.g. as electrolytes for lithium-ion secondary batteries,^[1] as polar aprotic solvents in the chemical industries,^[2–5] industrial lubricants,^[6] and also as raw materials for the synthesis of small molecules^[7,8] and polymers.^[9–11] Cyclic carbonates can be obtained from the direct synthesis of olefins by reaction with an oxidant and CO₂.^[12,13] However, low selectivity towards the carbonates, formation of numerous oxidation by-products, and long reaction times are often the major problems of this reaction.^[14–19] A two-step approach involving the same catalyst may be an alternative to overcome these limitations, especially, when stable and cheap catalysts can be employed. Complexes of the first-row earth-abundant transition metals, such as iron, are excellent candidates for this purpose since, on the one side, non-heme iron complexes bearing *N*-donor ligands have been proven to be active and selective catalysts for the epoxidation of alkenes^[20,21] and, on the other side, iron complexes with *N*-donor ligands have demonstrated to be very active and selective catalysts for the formation of cyclic carbonate and/or polycarbonates.^[22–29] Regarding the one-pot catalyzed processes for the synthesis of organic carbonates from alkenes, the degree of success is still limited whether auto-tandem- orthogonal or one-pot catalysts

are employed.^[12] The main difficulty is finding a catalyst stable at the different reaction conditions, especially because the presence of the oxidant and high temperature are usually required for the cycloaddition reaction.^[12] For this reason, the one-pot option in which two catalysts operate but are introduced sequentially in the reaction vessel may be a good alternative to operate.

In a previous study, some of us used an iron catalyst for sequential epoxidation and cycloaddition reactions^[28] but the stability of the catalytic system was low. Seeking a more stable system we turned our attention to the Fe(III) complex [FeCl₂(L)][PF₆] in Figure 1, bearing the cross-bridged macrocycle 4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane ligand (L) that belongs to the family of cross-bridged cyclams.^[30] These ligands have proven highly versatile, effectively coordinating transition metal ions across different oxidation states. This capability ensures structural robustness by inhibiting both ligand exchange and hydroxide precipitation, even under elevated pH conditions.^[31] Consequently, complexes incorporating cross-bridged cyclams have found applications in diverse fields, notably in homogeneous catalysis.^[32,33] Here we extend its application to the epoxidation of alkenes and cycloaddition CO₂/epoxides.

Results and Discussion

Epoxidation of Alkenes

The catalytic activity of [Fe(L)Cl₂][PF₆] in the epoxidation of alkenes was studied with benchmark substrates **1 a–g** using *tert*-butylhydroperoxide (TBHP) as oxidant under an inert

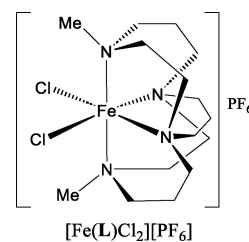


Figure 1. Complex [Fe(L)Cl₂][PF₆].

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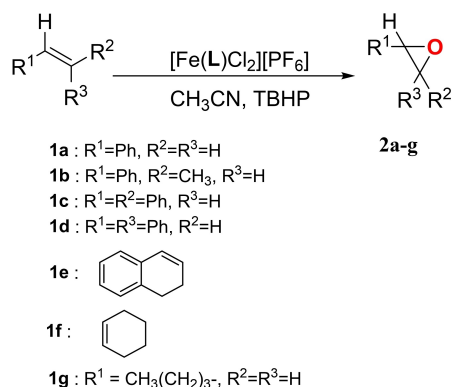
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atmosphere at different temperatures (Scheme 1). Initial optimization of the reaction conditions such as catalyst loading (1 or 2 mol%), oxidant/substrate molar ratio (2.3 and 1.1), and temperature (40 °C or 60 °C) was performed for styrene (**1a**). The results are shown in Table 1. In the blank experiment without the catalyst at 40 °C, epoxide formation was not detected (entry 1, Table 1). When the iron catalyst was added (2 mol% molar ratio with respect to the substrate) at 40 °C with a ratio TBHP/**1a** of 2.3 mol/mol, ca 40% conversion was achieved after 24 h but the main product was benzaldehyde (BA, 15% yield, entry 2, Table 1). Under the same catalyst loading and TBHP/**1a** ratio, increasing the temperature up to 60 °C, the conversion and selectivity in **2a** increased (83% and 49% respectively, entry 3, Table 1). At the same temperature, decreasing the catalyst loading to 1 mol% the selectivity increased slightly to 55% while the conversion remained high (82%, entry 4, Table 1). Using 1 mol% of catalyst, decreasing the oxidant/substrate molar ratio to 1.1 resulted in a decrease of conversion and selectivity in the epoxide (entry 5, Table 1). The addition of acids has been reported to increase the selectivity of the epoxidation.^[21,34,35] When acetic acid was added to the reaction mixture (10 eq with respect to the catalyst) a decrease in conversion and selectivity was observed (entry 6 vs entry 4, Table 1). Similarly, when the oxidant was added in small portions instead of in one fraction, the conversion after 24 h was nearly full, the yield in epoxide increased slightly but 34%



Scheme 1. Epoxidation of alkenes **1a-g** using *tert*-butyl hydroperoxide (TBHP) as oxidant and [Fe(L)Cl₂][PF₆] as the catalyst.

Entry	Catal (mol%)	Ox/alkene ^[b] (mol/mol)	T (°C)	Conv. (%) ^[c]	Yield epox. (%) ^[c]	Sel. epox.(%)	Yield BA (%) ^[c]
1	–	2.3	40	4	–	–	–
2	2	2.3	40	37	6	15	15
3	2	2.3	60	83	40	49	10
4	1	2.3	60	82	39	55	14
5	1	1.1	60	49	10	21	25
6 ^[d]	1	2.3	60	59	23	39	13
7 ^[e]	1	2.3	60	94	47	50	34

^[a] Reaction conditions: t = 24 h. ^[b] Ox=TBHP. ^[c] Conversion and yield measured by GC using mesitylene as internal standard. ^[d] Addition of 5 μL of CH₃COOH. ^[e] Slow addition of the oxidant.

Entry	Alkene	Conv. (%) ^[b]	Yield epoxide (%) ^[b]	Sel. Epoxide (%)
1	1b	99	45 (93% <i>trans</i>)	45
2	1c	85	55 (<i>trans</i>)	64
3	1d	79	40 (<i>trans</i>)	51
4	1e	93	3	4
5	1f	83	< 1	1
6	1g	82	2	2

^[a] Reaction conditions: alkene 0.8698 mmol, catalyst 1 mol% respect to alkene; TBHP/alkene molar ratio = 2.3; 60 °C, 24 h. ^[b] Conversion and yield measured by NMR using mesitylene as internal standard.

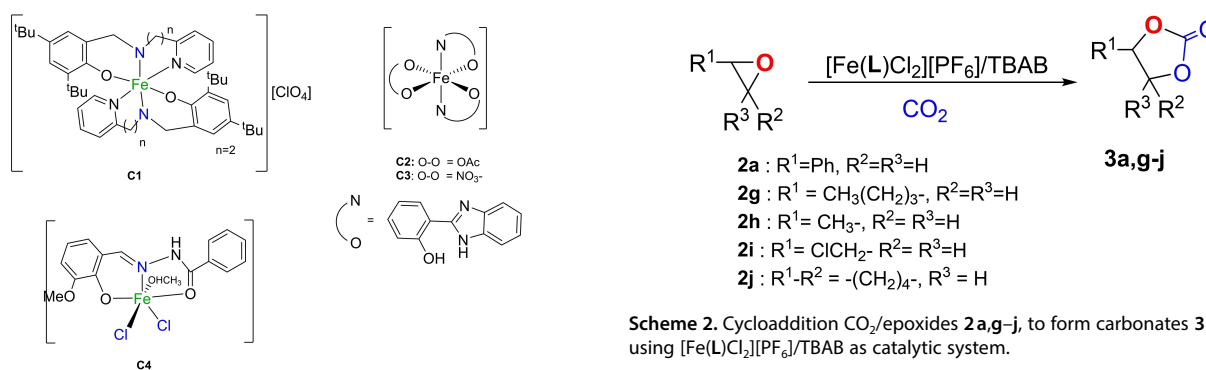
of BA was also obtained (entry 7, Table 1). Then, after the optimization of the reaction parameters, we selected a temperature of 60 °C, 1 mol% of catalyst loading at TBHP/**1a** ratio of 2.3 as optimal conditions to explore the scope of the catalyst in the epoxidation of other alkenes **1b-g** (Scheme 1).

The oxidation of alkenes **1b-g** using catalyst [Fe(L)Cl₂][PF₆] proceeded with high conversion (79–99%, Table 2) although only the phenyl derivatives were transformed in the corresponding epoxides in moderate selectivity (45–64%, entries 1–3, Table 2). The alkenes with *trans* configuration (**1b** and **1c**) and also the *cis* alkene **1d** gave place to the *trans* epoxide. This suggests that a radical mechanism takes place in which the catalyst is involved since there is no reaction in its absence.^[36] In contrast, with the related reported catalyst [Fe(cyclam)(OTf)₂] using H₂O₂ as an oxidant no change in the configuration of the product was observed that was attributed to a direct reaction of the olefin to the coordinated HOO⁻.^[37] The yields reported with the [Fe(cyclam)(OTf)₂] complex for **1c** and **1d** were 36 and 26% respectively after 20 minutes.

Concerning other reported Fe(III) catalytic systems (selected examples are listed in Table 3), in the epoxidation of styrene (**1a**) catalyst [Fe(L)Cl₂][PF₆] gave higher activity and selectivity than complex **C1**^[28] and **C2**^[38] (Figure 2) but the catalytic system bearing a benzoimidazol-phenol ligand **C3** showed better performance (entries 1–3 *versus* entry 9, Table 3).^[38] For the epoxidation of the disubstituted styrenes, (entries 4–7 *versus*

Entry	Cat/Oxidant	Alkene	Conv. (%)	Selectivity epoxide (%)	Ref
1 ^[a]	C1/TBHP	1 a	24	0	[28]
2 ^[b]	C2/H ₂ O ₂	1 a	36	81	[38]
3 ^[b]	C3/H ₂ O ₂	1 a	74	89	[38]
4 ^[a]	C1/TBHP	1 b	100	99	[28]
5 ^[a]	C1/TBHP	1 c	88	99	[28]
6 ^[a]	C1/TBHP	1 d	23	99	[28]
7 ^[c]	C4/TBHP	1 c	60	100	[40]
8 ^[c]	Fe(Cyclam)(CF ₃ SO ₂) ₂ /H ₂ O ₂	1 c	36 ^[d]	95	[39]
9 ^[e]	[Fe(L)Cl ₂][PF ₆]/TBHP	1 a	82	55	This work
10 ^[f]	[Fe(L)Cl ₂][PF ₆]/TBHP	1 b	99	45	This work
11 ^[f]	[Fe(L)Cl ₂][PF ₆]/TBHP	1 c	85	64	This work

Reaction conditions: ^[a] Substrate: 0.3 mmol, catalyst 3.3 mol % respect to alkene; TBHP/alkene molar ratio = 2; solvent: MeCN, 60 °C, 24 h. ^[b] Substrate: 1 mmol, catalyst: 0.02 mmol (2 mol %), solvent: MeCN, 60 °C, 12 h. ^[c] Substrate: 1.0 mmol, catalyst: 0.0022 mmol (0.2 mol %), TBHP/alkene molar ratio = 2, acetonitrile (5 ml), 60 °C, 24 h. ^[d] Cyclam: 1,4,8,11-tetraazacyclotetradecane, H₂O₂ (1 mmol, 30 % aqueous), alkene 1 mmol, catalyst 2 mol %, solvent: acetonitrile 5 mL, t = 20 minutes. ^[e] Yield. ^[f] See Table 1 for reaction conditions. ^[g] See Table 2 for reaction conditions.



Scheme 2. Cycloaddition CO₂/epoxides **2a,g-j**, to form carbonates **3a,g-j** using [Fe(L)Cl₂][PF₆]/TBAB as catalytic system.

Figure 2. Selected reported Fe(III) complexes used as catalysts for CO₂ cycloaddition to epoxides.

entries 10 and 11, Table 3) better results were obtained with the reported catalyst **C1** and **C4** for substrate **1b** and **1c** but the conversion was higher with [Fe(L)Cl₂][PF₆] for *cis*-stilbene **1d**. Concerning iron complexes with non-modified cyclam ligand (cyclam = 1,4,8,11-tetraazacyclotetradecane) reported by Nam et al.^[39] the epoxidation of *trans*-stilbene proceeded very efficiently to produce a 36% yield in the epoxide after 20 minutes (entry 8, Table 3) but the iron(III) complex [Fe(L)Cl₂][PF₆] used in this work has the advantage of being highly stable under air and easy to manipulate.

CO₂ Cycloaddition to Epoxides

Once examined the activity of [FeCl₂(L)][PF₆] in the epoxidation of alkenes, we proceeded to explore its catalytic activity in the insertion of CO₂ into epoxides to form cyclic carbonates (Scheme 2). We chose the benchmark substrate 1,2-epoxyhexane (**2g**) for the initial optimization of conditions. The results obtained are shown in Table 4.

Entry	Cat/TBAB (mol %) ^[b]	T (°C)	P (bar)	Conv. (%) ^[c]	Yield (%) ^[c]	TOF (h ⁻¹) ^[d]
1	0.05/-	80	20	0	–	–
2	0.05/0.1	80	20	8	6	58
3	0.05/0.25	80	20	16	13	113
4	0.05/0.25	100	20	63	53	445
5	-/0.25	100	20	36	31	48
6	0.05/0.25	100	10	38	32	264

^[a] Reaction conditions: epoxide 20 mmol, 3 h, TBAB = tetrabutylammonium bromide. ^[b] Respect to the epoxide. ^[c] Conversion and yield measured by ¹HNMR using mesitylene as internal standard. ^[d] TOF = turnover frequency, averaged mol epoxide converted per mol catalyst h⁻¹

Complex [FeCl₂(L)][PF₆] (0.05 mol % loading respect to **2g**) is not active under 20 bar of CO₂ at 80 °C after 3 h using the epoxide as solvent (entry 1, Table 4). When the commonly used nucleophile tetrabutylammonium bromide (TBAB)^[41] was added in a 1:2 molar ratio with respect to the complex, 8% conversion in the cyclic carbonate was detected by ¹HNMR (entry 2,

Table 4). Increasing the $[\text{FeCl}_2(\text{L})][\text{PF}_6]/\text{TBAB}$ ratio to 1:5 the conversion increased twofold (entry 3, Table 4) and reached 63 % (averaged TOF 445 h^{-1} , entry 4, Table 4) when the temperature was raised up to 100°C . Only the cyclic carbonate product was detected by $^1\text{H NMR}$ (Figure S5, Supplementary information). Under the same conditions, TBAB, which is known to be an active catalyst for this transformation,^[41] provided ca half this value (entry 5, Table 4). This points out that a cooperative mechanism is taking place; the catalyst activates the epoxide and the nucleophile opens the cycle to promote the insertion of CO_2 as generally accepted.^[42] A decrease in pressure to 10 bar produced a drop in conversion (entry 6, Table 4).

Once the reaction conditions for the $\text{CO}_2/2\text{g}$ coupling were set up, other epoxides **2a,2h–j** (Scheme 2) were studied. Terminal epoxides (**2a,h–i**) were transformed in the corresponding cyclic carbonates with high TOF (Figure 3) but for the disubstituted cyclohexene oxide, **2j**, the conversion was lower (Figures S2–S6, Supplementary Information).

In the case of the reaction of propylene oxide **2h**, after the reaction, the propylene carbonate obtained (95 % conversion) was separated by distillation. The residue containing the catalytic mixture was used again adding fresh propylene oxide and after a further 3 h under the same reaction conditions, a

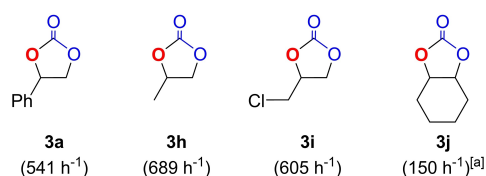


Figure 3. Carbonates obtained from the corresponding epoxides using $[\text{Fe}(\text{L})\text{Cl}_2][\text{PF}_6]$. Reaction conditions: epoxide: 20 mmol, Cat/Co-cat: 0.05/0.25 mol% respect to epoxide, $T = 100^\circ\text{C}$, $P = 20 \text{ bar CO}_2$, $t = 3 \text{ h}$. Conversion determined by $^1\text{H NMR}$.

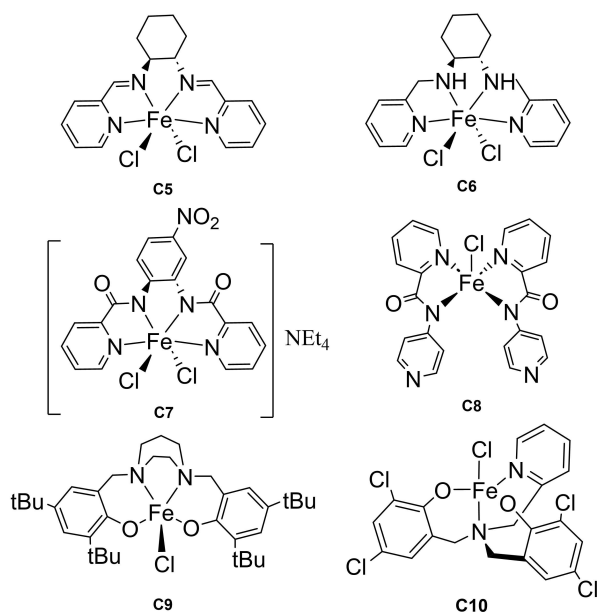


Figure 4. Selected reported iron complexes used as catalysts for epoxidation reactions.

substantial 73 % of epoxide conversion was still obtained which indicates that the catalyst is quite robust even if partial decomposition or loss of the catalyst during the product distillation could not be avoided.

Comparing the results obtained with $[\text{Fe}(\text{L})\text{Cl}_2][\text{PF}_6]$ with reported iron complexes with N4-donor ligands **C5–C10** (Figure 4, Table 5), the bis(imine)bipyridine based Fe(II) complexes **C5** and **C6** combined with TBAB showed lower averaged TOF^[43] than the iron-cyclam derivative (up to TOF 250 h^{-1} for the cycloaddition of **2h,2i/CO₂** and TOF 20 h^{-1} for the disubstituted **2j**, entries 1–4 versus entries 10 and 11, Table 5). The concentration of the iron catalyst used in these examples was higher than the one used in our report and no recycling was described for these systems. The related bis(pyridinecarboxamide) iron systems incorporating the ammonium salt such as **C7** presented also lower averaged TOF than $[\text{Fe}(\text{L})\text{Cl}_2][\text{PF}_6]$ (entry 5 versus entry 10, Table 5) but they did not require the addition of a nucleophile.^[44] Pyridine-based bidentate iron complex **C8** combined with tetrabutylammonium iodide (TBAI) provided lower TOF than $[\text{Fe}(\text{L})\text{Cl}_2][\text{PF}_6]$ (entry 6 versus entry 10, Table 5) but it could be recycled for 6 cycles with a low decrease of conversion (5 %).^[45] Tailor design of iron(III) aminophenolate catalyst provided examples with modest activity such as **C9/TBAB** (entries 7 and 8, Table 5) but introducing electron-withdrawing groups in the skeleton provided highly active catalytic systems combined with bis(triphenylphosphine)iminium chloride (PPNCl) (entry 9 versus entry 10, Table 5).^[46] Regarding analogous cyclam-derived catalytic systems, there are few examples

Table 5. Comparison of the catalytic activity of $[\text{Fe}(\text{L})\text{Cl}_2][\text{PF}_6]$ with selected reported catalysts **C5–C10** (Figure 4) for the cycloaddition of CO_2 to epoxides.

Entry	Catalytic system	Epoxide	Conv. (%)	TOF (h^{-1})	Ref
1 ^[a]	C5/TBAB	2h	100	250	[43]
2 ^[b]	C6/TBAB	2h	100	250	[43]
3 ^[a]	C6/TBAB	2i	97	243	[43]
4 ^[c]	C6/TBAB	2j	47	20	[43]
5 ^[d]	C7/-	2h	92	9	[44]
6 ^[e]	C8/TBAI	2h	96	12	[45]
7 ^[f]	C9/TBAB	2h	74	135	[46]
8 ^[f]	C9/TBAB	2a	31	57	[46]
9 ^[g]	C10/PPNCl	2h	62	1240	[50]
10 ^[h]	$[\text{Fe}(\text{L})\text{Cl}_2][\text{PF}_6]/\text{TBAB}$	2h	95	689	This work
11 ^[h]	$[\text{Fe}(\text{L})\text{Cl}_2][\text{PF}_6]/\text{TBAB}$	2j	44	150	This work

Reaction conditions: ^[a] Catalyst/Co-catalyst: 0.1/0.1 mol%; 100°C , 20 bar, 4 h. ^[b] Catalyst/Co-catalyst: 0.1/0.1 mol%; 130°C , 40 bar, 4 h. ^[c] Catalyst/Co-catalyst: 0.2/0.2 mol%; 100°C , 40 bar, 12 h. ^[d] Catalyst/Co-catalyst: 0.5/- mol%; 80°C , 35 bar, 20 h, TOF estimated from data reported. ^[e] Catalyst/Co-catalyst: 1/1 mol%; solvent: DMF (10 mL), 100°C , 15 bar, 8 h, TOF estimated from data reported. ^[f] Catalyst/Co-catalyst: 0.025/0.1 mol%; 100°C , 20 bar, 22 h. TBAI = tetrabutylammonium iodide. ^[g] Catalyst/Co-catalyst: 0.025/0.1 mol%; 100°C , 20 bar, 2 h, PPNCl = bis(triphenylphosphine)iminium chloride. ^[h] See Figure 3 for reaction conditions.

of catalysts using cyclam ligands for CO₂ fixation. Zn and Cd-cyclam complexes were not effective catalysts for the fixation of CO₂ in MeOH to form dimethyl carbonate since they formed very stable carbonato derivatives.^[47] Ni-cyclam complexes have been reported to be active in the electrochemical formation of carbonates from epoxides.^[48,49]

One-Pot Epoxidation and CO₂ Cycloaddition to Styrene

The two studies of the catalytic activity of [FeCl₂(L)][PF₆]₂ in the alkenes epoxidation and CO₂/epoxides cycloaddition allowed us to identify styrene **1a** as the best candidate for the one-pot transformation of the alkene into the cyclic carbonate.

The one-pot reaction was attempted incorporating from the beginning the oxidation catalyst [Fe(L)Cl₂][PF₆]₂ (1 mol%), the oxidant TBHP and the CO₂/epoxide catalytic system [Fe(L)Cl₂][PF₆]₂/TBAB. The conditions employed were adapted from the epoxidation reaction using 1 mol% of catalyst loading, acetonitrile as a solvent at 60 °C and under atmospheric pressure of carbon dioxide to avoid the transfer the reaction mixture into a compression vessel and work under the mildest pressure conditions. The evolution of the products formed was followed by GC using mesitylene as an internal standard and is represented in Figure 5. The reaction after 24 h presents slightly lower conversion and yield in **2a** than when epoxidation reaction was performed (82% conversion and 39% yield, entry 4, Table 1 versus 63% conversion and 25% yield under one-pot conditions). This may indicate that the presence of TBAB interferes with the epoxidation reaction catalysed by the complex as it has been reported that TBHP may react with the Br⁻ forming hypobromite, BrO⁻.^[15] After 49 h, the cyclic carbonate **3a** appeared (3% yield) achieving a 15% after 72 h.

To avoid the interference of the TBAB with the epoxidation reaction we decided to do the epoxidation and the cycloaddition in stepwise form. Thus, initially, the catalyst, the

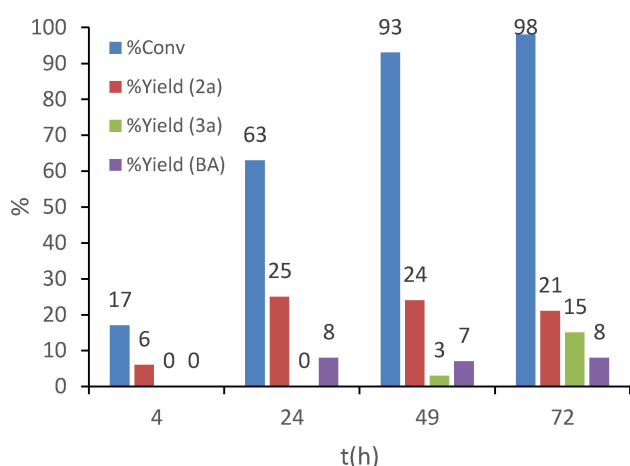


Figure 5. One-pot reaction of **1a** with TBHP and CO₂ using catalytic system [Fe(L)Cl₂][PF₆]₂/TBAB. Reaction conditions: **1a**: alkene 0.8698 mmol, catalyst 1 mol% respect to alkene; TBHP/alkene molar ratio = 2.3; 60 °C, Cat/TBAB molar ratio: 1/5, solvent = acetonitrile 2.5 mL, P = 1 bar CO₂. Conversion and yield determined by GC using mesitylene as an internal standard.

oxidant, the substrate and the internal standard were mixed in the reaction flask under an inert atmosphere. After 24 h of reaction 86% conversion of styrene to styrene epoxide (37%) and benzaldehyde (28%) was detected by GC (Figure 6). Then, TBAB was added to the reaction mixture and carbon dioxide was introduced at atmospheric pressure (balloon). In the following 24 h, ca 21% of cyclic carbonate **3a** was formed but this amount did not increase after additional 24 h.

Thus, the catalyst system based on the [FeCl₂(L)][PF₆]₂ complex showed moderate activity for the one pot conversion of styrene to styrene carbonate (15%) and improved activity (up to 21%) when the reaction was performed in stepwise form at 60 °C under 1 bar of CO₂. Compared with our previous results with iron-based catalytic systems,^[28] the stability of the Fe(III)-cyclam derived system allowed to obtain the carbonate from the alkene in one pot. In the literature, very few catalytic systems are based on earth-abundant iron metal and catalyzes the reaction under mild conditions.^[12] For example, a recyclable Fe(III) doped graphitic carbon nitride on SBA-15 catalytic material was reported by Huang et al. to provide 34.1% of styrene carbonate (93% selectivity) under 35 bar at 150 °C in 5 h.^[51] Best result in this transformation was reported by Han et al. using a Zn-based polyoxometalate-based system to obtain 92% yield of styrene carbonate at 50 °C, under 5 bar of CO₂ after 120 h reaction time.^[52]

Experimental Section

General Comments

Complex [Fe(L)Cl₂][PF₆]₂ was prepared as previously described.^[30] Reagents were purchased at Merck and used as received. Carbon dioxide (SCF Grade, 99.999%, Air Products) was used introducing an oxygen/moisture trap in the line (Agilent). NMR spectra were recorded at 400 MHz Varian using the signals of the solvent as a

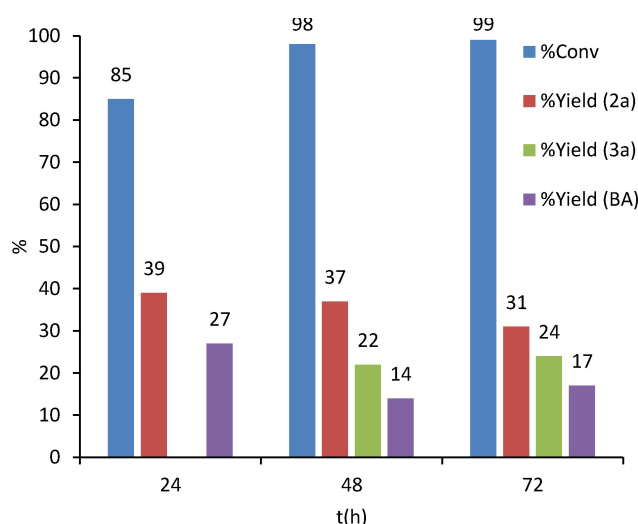


Figure 6. Stepwise reaction of **1a** with TBHP and CO₂ using catalytic system [Fe(L)Cl₂][PF₆]₂/TBAB. Reaction conditions: **1a**: 0.8698 mmol, catalyst 1 mol% respect to **1a**; TBHP/**1a** molar ratio = 2.3; Cat/TBAB molar ratio: 1/5, solvent = acetonitrile 2.5 mL, T = 60 °C, P = 1 bar CO₂. Conversion and yield determined by GC using mesitylene as an internal standard.

reference. A typical program temperature for the GC analysis started at 60 °C, then increased at a 40 °C/min rate and stopped after 2 min at 240 °C. Mesitylene was used as an internal standard.

Standard Epoxidation Reaction

Oxidation reactions were performed in a stirred Schlenk tube fitted with a water-cooled condenser. The reactions were carried out under a nitrogen atmosphere in an oil bath for heating with acetonitrile as a solvent and *tert*-butylhydroperoxide as the oxidant. In a typical experiment a mixture of the catalyst, 2.5 ml solvent, the olefin and mesitylene as internal standard were added to a Schlenk tube. After the mixture was heated to the desired temperature, the oxidant was added. At appropriate intervals, aliquots were removed and analyzed immediately by GC (styrene and cyclohexene) or dried under vacuum and analyzed by ¹HNMR. Oxidation product yields based on the initial concentration were quantified by comparison with the mesitylene internal standard.

Standard Procedure for the Synthesis of Cyclic Carbonates

The catalytic tests were carried out in a 25 mL Parr reactor heated with an oil bath. All reagents were introduced in the reactor, the autoclave was purged with CO₂ and pressurized, and then it was heated to the specific temperature to reach the desired pressure. After the reaction time, the reactor was cooled with an ice bath and slowly depressurized. With propylene oxide, a dichloromethane trap was used. The conversion was determined by ¹HNMR of the crude mixture by integral ratio between epoxide and cyclic carbonate. The yield was determined by ¹HNMR using mesitylene as an internal standard.

Recycling Experiment

The recycling experiment was carried out with the product mixture from the conversion of **2h** into **3h**. Volatile **2h** (boils at 35 °C) was easily evaporated from the crude under vacuum and then a micro-distillation column under vacuum was used to separate the carbonate **3h**. The collected **3h** from the distillation was found pure in the ¹HNMR spectrum (Figure S10 in Supplementary Information). The distillation residue, the catalyst with co-catalyst, was then reintroduced for a following run adding fresh **2h**.

One-Pot Epoxidation and CO₂ Cycloaddition to Styrene

A solution of **1a** (100 μL, 0.87 mmol), the catalyst (0.0087 mmol, 3.4 mM), TBAB (0.0435 mmol), TBHP (390 μL, 2 mmol) and mesitylene (100 μL) as the internal standard in 2.5 mL of acetonitrile were added on a Schlenk tube and the mixture was stirred under CO₂ (atmospheric pressure with a balloon) at 60 °C. At appropriate intervals, aliquots were removed and analyzed immediately by GC using mesitylene as an internal standard.

Stepwise Epoxidation and CO₂ Cycloaddition to Styrene

A solution of **1a** (100 μL, 0.87 mmol), the catalyst (0.0087 mmol, 3.4 mM), TBHP (390 μL, 2 mmol) and mesitylene (100 μL) as the internal standard in 2.5 mL of acetonitrile were added on a Schlenk tube and the mixture was stirred under nitrogen for 24 h at 60 °C. After this time, TBAB was added (0.0435 mmol) and CO₂ under atmospheric pressure was introduced with a balloon) and the reaction was stirred at 60 °C until 72 h total reaction time. At appropriate intervals, aliquots were removed and analyzed immediately by GC using mesitylene as an internal standard.

Conclusions

A Fe(III) catalyst with a cross bridged cyclam derived ligand, a stable compound, has been demonstrated to be active in the epoxidation of alkenes and in the cycloaddition of terminal epoxides separately at mild reactions conditions. The epoxidation of aromatic alkenes achieved high conversion and selectivities in the epoxides in the range of 45–64% at 60 °C. The cycloaddition of CO₂ with terminal epoxides catalyzed by the same catalyst in the presence of TBAB reached high TOF for terminal epoxides (445–689 h⁻¹) and the catalytic system could be reused maintaining a 73% conversion without the addition of fresh TBAB. The one-pot reactions provided low but significant conversion of styrene into styrene carbonate (15–24% GC yield) taking into account that the reaction was performed under atmospheric pressure of CO₂ at 60 °C. The best result was obtained when the two reactions were performed stepwise, first the epoxidation and after 24 h introducing the nucleophile TBAB and CO₂ in the system. The results obtained with this catalyst, although improvable, are new data that contribute to forming a more complete and detailed picture of the possibilities of using earth abundant metal-based catalysts, such as iron complexes, in carbon dioxide fixation.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Carbon dioxide · Iron catalysts · Cyclic carbonates · Cyclam · Epoxidation

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