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[OSSO]-Type Fe(III) Metallate as Single-Component Catalyst for the CO_2 Cycloaddition to Epoxides

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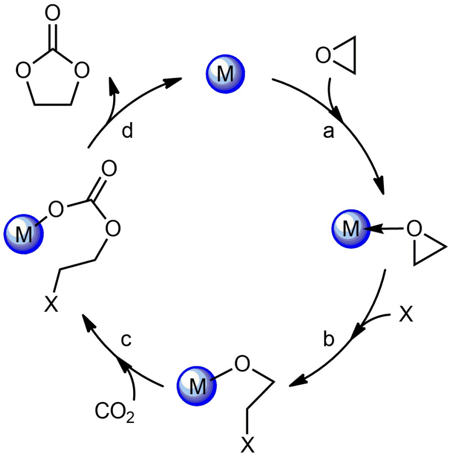
Abstract. A new [OSSO]-Fe(III) metallate complex was prepared and characterized. We demonstrated that such metallate is the real catalytic active species for the cycloaddition of CO_2 to the epoxides, formed from the in situ reaction of the related [OSSO-]Fe(III) neutral complexes and tetrabutylammonium bromide. The metallate complex was used as a single component catalyst for the formation of cyclic organic carbonates from ten epoxides and CO_2 at 1 bar pressure.

Keywords: carbon dioxide fixation; iron; cycloaddition; homogeneous catalysis

The use of carbon dioxide (CO_2) as chemical feedstock is a growing area of interest for chemists and chemical engineers, not only because CO_2 reutilization can contribute to the reduction of the carbon footprint in many chemical processes, but also because it is a cheap, non-toxic molecule that can be advantageously employed in many chemical processes replacing more toxic C1 sources such as carbon monoxide and phosgene.[1] In this field, the cycloaddition of CO_2 to the epoxides is one of the most studied reaction,[2] due to the favourable thermodynamic of the overall process, and to the usefulness of the target molecules that can be used as high-boiling polar solvents,[3] in batteries as ion carriers,[4] and as chemical intermediates.[5]

The catalysts that have shown the best performances are those based on binary systems, constituted by a Lewis acid and a nucleophile.[2] In the widely accepted mechanistic scenario (Scheme 1) the role of the metal centre is to activate the epoxide (a) for the nuchleophilic attack of the anion (b), giving the formation of the meta-alkoxo intermediate that undergoes the CO_2 insertion (c) followed by the back-biting (d) with formation of the cyclic carbonate. Usually, the most common nuchleophiles used in the binary systems are those based on quaternary ammonium or phosphonium salts, or ionic liquids bearing nucleophilic counter anions.[2]



Scheme 1. General Mechanism for the Cycloaddition of CO_2 to the epoxides.

It should be noted that while it is common to denote the Lewis-acidic metal as the “catalyst” and the nucleophile as the “cocatalyst”, the latter promotes the cycloaddition reaction even in the absence of the metal complex, albeit with lower activity.[6] On the contrary, only few metal complexes give good conversion of the epoxides to the cyclic carbonates without the addition of an excess of the suited nucleophile.[7] These cases are usually based on dinuclear metal complexes, or a bimetallic reaction mechanism is invoked in which one metal center furnish the nuchleophile and another one activate the epoxide. However, a clear picture defining the real role of the nucleophile and the metal complex and how they interact is still missing.

Lately, we reported the use of a new class of [OSSO]-type Fe(III) complexes, activated by tetrabutyl ammonium bromide (TBAB), for the synthesis of COCs under very mild reaction conditions.[8] We demonstrated that, despite the

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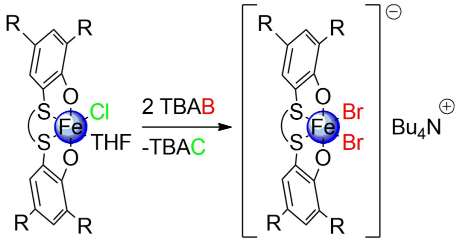
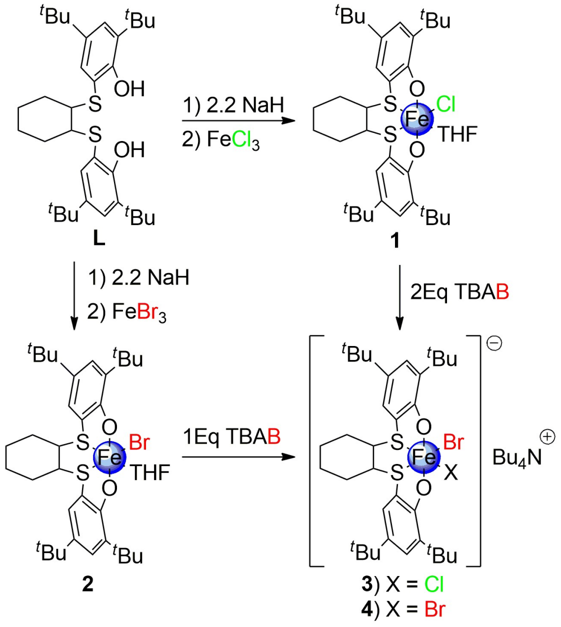
mononuclear nature of these complexes, the reaction mechanism proceeds through a bimetallic pathway and, supported by UV-vis measurements and DFT calculations, we proposed that the Fe-complexes react with the cocatalyst, leading to the formation of a metallate species which is the real catalytic active species (Scheme 2).



Scheme 2. Proposed in situ formation of [OSSO]-Fe(III) metallate complexs.

Here we report on the synthesis, isolation and characterization of this metallate species, and its use as single component catalyst for the synthesis of COCs from CO_2 and epoxides. The putative real catalyst was prepared independently from the previously studied chloride complex **1** and the new bromide complex **2** (Scheme 2). The complex **2** was prepared with the same procedure used for the complex **1**,[8] and fully characterized (see supporting information). At first, the reaction of **1** with 2 equivalents of TBAB was performed in dichloromethane (DCM). In these conditions, the release of tetrabutylammonium chloride (TBAC) occurs, so the complex **3** was recovered by extraction with a toluene/hexane mixture to obtain the pure complex.



Scheme 3. Synthesis of [OSSO]-Fe(III) complexes **1**-**4**.

Since the presence of an equilibrium between chloride and bromide cannot be excluded a priori, the complex **4** was prepared starting from the bromide complex **2**, in order to avoid the presence of chloride anion in the reaction medium. The complex **4** was fully characterized by elemental analysis, NMR Evans method, high resolution MS, UV-vis and FT-IR spectroscopy and all the analysis confirmed the formation of the desired di-bromide substituted metallate species (see Supporting Information). The same analysis conducted on the complex **3** support the formation of a similar species, but some differences can be detected. For example, the FT-IR spectra of **3** and **4** are almost superimposable, except for some bands around 800 and 1050 cm^{-1} (Figure 1).

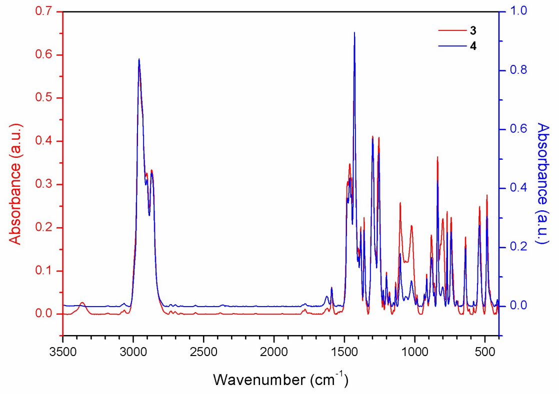


Figure 1. Comparison of the FT-IR spectra of the complex **3** (red line) and the complex **4** (blue line).

Such differences can be ascribed to the incomplete substitution of chlorine with bromine in the complex **3**, with the formation of a mixed chloride/bromide species. The ESI FT-ICR MS analysis revealed the different composition of the complexes **3** and **4** (Figures S14 and S15). For comparison, the in situ formation of the metallate species was confirmed by the mass spectra of the complexes **1** and **2**, respectively in the presence of 2 and 1 equivalents of TBAB (Figure S12 and S13).

To elucidate the role of the halide anion in the cycloaddition reaction, the complexes **1**-**2** were tested under the same reaction conditions, varying the TBAB/Fe molar ratio from 0/1 to 5/1. The reaction of CO_2 with hexene oxide (**4a**) was selected as benchmark, and the results are listed in table 1. Both the complexes **1** and **2** were found to be inactive in the absence of TBAB (entries 1 and 6, Table1). The presence of 0.5 equivalents of TBAB activates the catalysts, obtaining a conversion around 10 % in both cases (entries 2 and 7, Table1). Increasing the TBAB loading to 1 or 2 equivalents with respect to the Fe(III) concentration, the complex **2** showed higher activity (entries 3-4 and 8-9, Table1), reaching a conversion of 84 % with a TOF of 35 h^{-1}. Using an excess of TBAB, both the systems reached a conversion around 90 % (entries 5 and 10, Table1).

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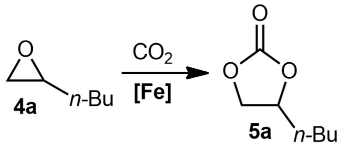
Table 1. **4a**/CO_2 Coupling Promoted by **1**–**4**.



4a

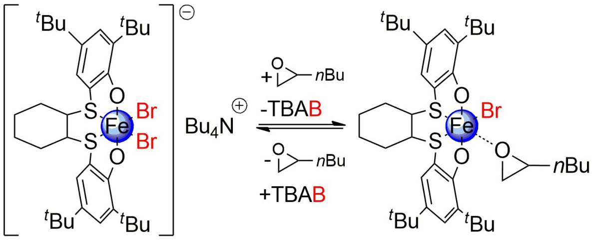
5a

Entry	Complex$^{a)}$ mol%	TBAB mol%	TBAB/Fe mol/mol	Conv$^{b)}$ mol%	TOF$^{c)}$ h^{-1}
1	**1** (0.1)	-	0/1	0	-
2	**1** (0.1)	0.05	0.5/1	11	4.6
3	**1** (0.1)	0.1	1/1	32.3	13.5
4	**1** (0.1)	0.2	2/1	57.7	24.0
5	**1** (0.1)	0.5	5/1	88.9	37.0
6	**2** (0.1)	-	0/1	0	0.0
7	**2** (0.1)	0.05	0.5/1	9.7	4.0
8	**2** (0.1)	0.1	1/1	53	22.1
9	**2** (0.1)	0.2	2/1	84	35.0
10	**2** (0.1)	0.5	5/1	92	38.3
11$^{d)}$	**1** (0.05) + **3** (0.05)	-	-	15.7	6.5
12$^{d)}$	**3** (0.1)	-	-	59.8	24.9
13$^{d)}$	**3** (0.1)	0.3	3/1	86	35.8
14$^{e)}$	**2** (0.05) + **4** (0.05)	-	-	23.7	9.9
15$^{e)}$	**4** (0.1)	-	-	60	25.0
16$^{e)}$	**4** (0.1)	0.3	3/1	92	38.3

$^{a)}$Reaction conditions: HO = 4.15×10^{-2} mol; T = 35 °C; $P(CO_2)$ = 1 bar; reaction time = 24 h, neat. $^{b)}$Determined by ^1H NMR using mesitylene as internal standard. The selectivity toward the formation of HC was always found to be >99%. $^{c)}$Turnover frequency ($mol_{HO} \cdot mol_{Catalyst}^{-1} \cdot$ reaction $time^{-1}$). $^{d)}$Complex **3** obtained from complex **1**. $^{e)}$Complex **3** obtained from complex **2**.

Since the ring opening of the epoxide was identified as the rate determining step of the reaction promoted by the system **1**/TBAB,[9] the higher activity of the system **2**/TBAB can be ascribed to the higher nucleophilicity of the bromide with respect to the chloride. Indeed, since TBAC is formed by the reaction of **1** with TBAB, and the free chloride anion participate in the equilibrium between the neutral and anionic form of the complex, and excess of 5 equivalents of TBAB is required to obtain catalytic activity similar to that of complex **2** with only 2 equivalents of TBAB (compare entries 5 and 9, Table1).

In order to confirm that the metallate complex is the real catalytic active species, the complexes **3** and **4** were then used in the same reaction (entries 11-16, Table1). At first, two 1/1 mixtures of **3** or **4** with **1** or **2** respectively, were tested leaving the Fe total loading to 0.1 mol% (entries 11 and 14, Table1). With our delight both the mixtures were active, leading to the selevtive formation of the hexene carbonate **5a**. The mixture of **2** and **4** was the most active, confirming that the presence of chloride slows the proceeding of the reaction. When used alone, the two complexes gave almost the same conversion, with a TOF of 25 h^{-1} (entries 12 and 15, Table1). To compare the activity of **3** and **4** with that of **1** and **2**, the reaction was repeated in the presence of 3 equivalents of TBAB with respect to the metallate (entries 13 and 16, Table1). The presence of TBAB has a beneficial role on the reaction, reaching a TOF of 38 h^{-1} in the case of **4**, that is the same TOF obtained with the complex **2** in the presence of an excess of TBAB (entry 10, Table 1). The benign effect of TBAB on the catalytic activity can be explained taking into account that, after the dissolution of the catalyst in the neat epoxide, an equilibrium between the free metallate and the complex binding the substrate take place (Scheme 4). Since the ring opening of the Fe-coordinated epoxide involves the Fe-mediated attack of a bromide anion, the presence of an excess of TBAB moves the equilibrium to the left, granting the proper amount of the metallate in the reaction medium.



Scheme 4. Equilibrium involving the coordination of **4a** to the Fe centre of the metallate **4**.

The complex **4** was then tested as single component catalyst for the conversion of a group of variously substituted epoxides in the corresponding COCs, using a catalyst loading of 0.2 mol% in order to shorten the reaction time to 6 hours (Scheme 5). The reaction of the benchmark substrate **4a** proceeds well, with a TOF of 40 h^{-1}. The less encumbered epoxide **4b** reacts faster, with an initial TOF of 54 h^{-1}. Increasing the bulkiness of the substrate in the case of epoxy-dodecane **4c**, results in an attenuation of the catalytic activity. The same effect on the catalytic activity was observed in the case of the formation of styrene carbonate **5d**. Compared to **4a**, the reaction of the glycidyl epoxides **4e-g** proceeds faster, with a TOF as high as 57 h^{-1} in the case of methyl glycidyl ether. In the case of epichlorohydrin **4h** and disubstituted substrates **4i-j** a catalyst loading of 0.4 mol% was used, since the reaction of these epoxides was found to proceed slower under the mild reaction conditions used for the study,[8] and the formation of the corresponding carbonates **5h-j** was accomplished with good activities. In particular, **5i** and **5j** were obtained with a high degree of stereoretention with respect to the starting epoxide.

In conclusion, we isolated and characterized the catalytic active species for the formation of COCs promoted by the [OSSO]-Fe(III) complexes. These species was used as single component catalyst for the reaction of several epoxides under very mild reaction conditions (Fe = 0.2 mol%; 1 bar of CO_2 pressure,

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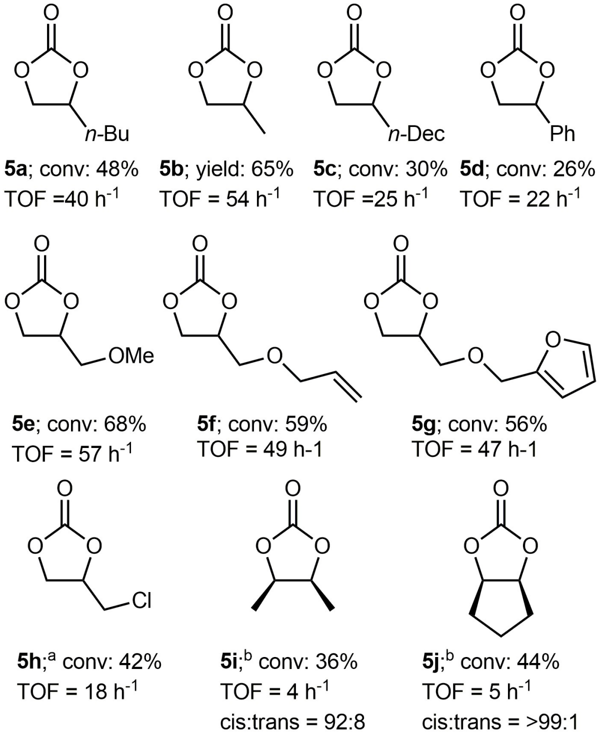
35 °C). Apart to the good catalytic activity and selectivity of this system, the results described in these study furnish an explanation of the role of the cocatalyst in the metal mediated cycloaddition of CO_2 to the epoxides, that was still missing and is crucial for the development of new high active catalysts.



5a; conv: 48% TOF =40 h^{-1}

5b; yield: 65% TOF = 54 h^{-1}

5c; conv: 30% TOF =25 h^{-1}

5d; conv: 26% TOF = 22 h^{-1}

5e; conv: 68% TOF = 57 h^{-1}

5f; conv: 59% TOF = 49 h-1

5g; conv: 56% TOF = 47 h-1

5h;[a] conv: 42% TOF = 18 h^{-1}

5i;[b] conv: 36% TOF = 4 h^{-1} cis:trans = 92:8

5j;[b] conv: 44% TOF = 5 h^{-1} cis:trans = >99:1

Scheme 5. Scope in epoxides. Reaction conditions: Epoxide = $4.15 \cdot 10^{-2}$ mol; **4** = 0.2 mol% T = 35 °C; $P(CO_2)$ = 1 bar; reaction time = 6 h, neat. Conversion determined by ^1H NMR using mesitylene as internal standard. The selectivity toward the formation of cyclic carbonate was always found to be >99%. Turnover frequency = $mol_{epoxide} \cdot mol_4^{-1} \cdot$ reaction $time^{-1}$). a) **4** = 0.4 mol%. b) **4** = 0.4 mol%; T = 50 °C; $P(CO_2)$ = 10 bar; reaction time = 24 h

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COMMUNICATION

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