

Unexpected “Ferrate” Species as Single-Component Catalyst for the Cycloaddition of CO₂ to Epoxides

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ABSTRACT: A soluble ferrate salt was synthesized by treating a novel protonated pyridine-containing macrocyclic ligand with iron(III) bromide. Its good activity as a stand-alone catalyst in CO₂ cycloaddition reactions to epoxides was assessed. Good yields of cyclic organic carbonates were obtained, especially with terminal epoxides, under solvent-free reaction conditions (T = 100 °C, P (CO₂) = 0.8 MPa), without the need of any Lewis base as the co-catalyst. This system proved to be active and selective towards the cyclic carbonates formation, with a broad reaction scope. A scale-up reaction on 2.5 mL of propylene oxide was performed and the robustness of the catalyst was proved up to three recycles (TON = 1020).

1. Introduction

The exponential increase of carbon dioxide (CO₂) emission in the atmosphere is becoming an alarming problem which threatens the whole environment [1,2]. For this reason, many researchers are focused on developing catalytic systems for the reutilization of carbon dioxide as a feedstock for chemical production [3]. Its cheapness and non-toxicity represents an interesting possibility to replace other C1 sources. One of the most studied transformation involving CO₂ is the reaction with epoxides to give cyclic organic carbonates [4,5], which finds application in many fields as high-boiling non-toxic solvents,

electrolytes for batteries and as intermediates for further chemical transformations [6]. The mechanism of such reaction has been deeply investigated, and the combination of a nucleophilic species and a Lewis acid (usually a transition metal complex) is often required [7–9]. First, the epoxide is activated by the metal for the nucleophilic attack of a halide anion to form a “metal-alkoxo” species that undergoes CO₂ insertion and subsequent “backbiting” to yield the cyclic carbonate. The nucleophilic species for the ring-opening of the epoxide are very often quaternary ammonium salts, which are active in such transformations even in absence of any metal complex, albeit with a low activity [10].

The binomial “onium” salt and metal complex seems to be crucial to obtain good conversions of the starting epoxide and high yields of carbonates, with only poor examples of metal complexes (mainly dinuclear) active in the absence of any additive [11,12].

We have recently disclosed that a well-defined Zn(II) complex of a pyridine-containing macrocyclic ligand (Pc-L) is a competent catalyst for the CO₂ cycloaddition to terminal epoxides under mild reaction conditions and without the need of any nucleophilic co-catalyst [13]. In the perspective of using greener solutions for chemical synthesis, iron represents one of the best choices of metal source. It is considered one of the most promising metals for homogeneous catalysis given to its natural abundance and non-toxicity concurrently with its high chemical reactivity [14]. In recent years, quite a few iron complexes active as catalysts in the chemical fixation of CO₂ with epoxides have been reported (Figure 1) [15–20].

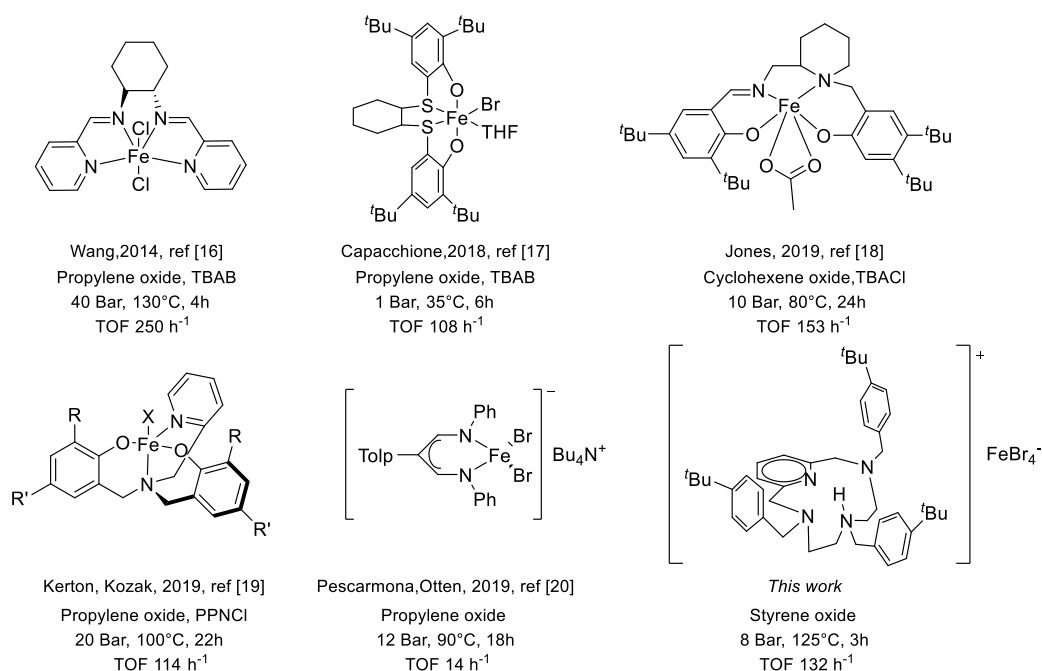


Figure 1. Recently reported iron-based homogeneous catalytic systems for the cycloaddition of CO₂ to epoxides.

In our ongoing studies of ferric complexes of Pc-L as homogeneous catalysts for selective oxidation reactions [21–23], we become interested in exploring their reactivity as bifunctional catalysts for the CO₂ activation and functionalization. Here we report the synthesis and characterization of a new “ferrate” species obtained by reaction of a protonated Pc-L ligand with FeBr₃ and its use as a stand-alone catalyst for the cyclic carbonates production from CO₂ and epoxides without the addition of any external nucleophile.

2. Experimental section

2.1. General considerations

All the reactions that involved the use of reagents sensitive to oxygen or to hydrolysis were carried out under an inert atmosphere. The glassware was previously dried in an oven at 110 °C and was set with cycles of vacuum and nitrogen. All chemicals and solvents were commercially available and used as received except where specified. ¹H NMR analyses were performed with 400 MHz spectrometers at room temperature. The coupling constants (*J*) are expressed in hertz (Hz), and the chemical shifts (δ) in ppm. Catalytic tests were analysed by ¹H NMR spectroscopy. Low resolution MS spectra were recorded with instruments equipped with ESI/ion trap sources. The values are expressed as mass–charge ratio and the relative intensities of the most significant peaks are shown in brackets. Elemental analyses were recorded in the analytical laboratories of Università degli Studi di Milano. The ligand and the complex were synthesized as detailed in the Supporting information.

2.2 Synthesis of complex 3

To an acetonitrile solution of ligand **2** (0.17 mmol in 5.0 mL) an acetonitrile solution of iron(III) bromide (0.17 mmol in 3.0 mL) was slowly added. The solution was left stirring for 1 hour. The solvent was evaporated to dryness in vacuum and the residue was washed several times with hexane to yield a red powder. The product was fully characterized by ESI-MS and elemental analysis. MS-ESI(+): calculated for C₄₄H₆₁N₄ 645.48, found 645.51 (100%, M⁺). MS-ESI(-): calculated for FeBr₄ 375.60, found 375.80 (100%, FeBr₄⁻). Elemental analysis calculated for C₄₄H₆₁Br₄FeN₄ C, 51.74; H, 6.02; N, 5.49; found C, 51.41; H, 6.01; N, 5.42.

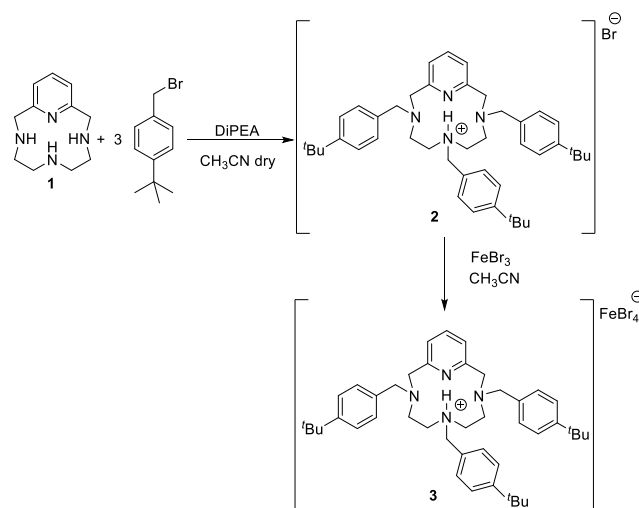
2.3. General procedure for CO₂/epoxide cycloaddition

A 250 mL stainless steel autoclave reactor was equipped with three 2.5 mL glass vials, containing the catalyst/epoxide mixture (0.25 mol% in 250 μL of substrate) and, when required, 125 μL of PC

(propylene carbonate) as a co-solvent. The vials were equipped with magnetic stirring bars and sealed with specific caps. The autoclave was then charged with 0.5 MPa CO₂ and vented-off. This operation was performed twice and then the autoclave was charged with 0.8 MPa CO₂ and placed in the heating bath (see tables captions) for 3-6 hours. The reactor was then cooled and the CO₂ pressure released. To each vial, the appropriate amount of internal standard (mesitylene) and 1.0 mL of chloroform were added. An aliquot of the resulting solution (300 μL) was taken and diluted with 350 μL of CDCl₃ to perform quantitative ¹H NMR analysis. Products were isolated by silica-gel chromatography (**5b** and **5k**) (hexane/AcOet 5:1) or directly collected by filtration as a pure solid from the reaction mixture (**5g**) (see Supplementary material).

3. Results and Discussion

Ligand **2** was prepared, albeit in modest yield (<50%) by *N*-alkylation of ligand **1** in the presence of DiPEA (*N,N*-diisopropylethylamine, Scheme 1). Instead of the expected neutral ligand, by cooling down an acetone solution, we obtained the macrocycle as the bromohydrated salt, which was fully characterized, including structure determination by single crystal X-Ray Diffraction (Figure 2). The ligand adopts a *cis* (+++) conformation [24]. The protonated nitrogen is the one opposite to the pyridinic ring and the hydrogen points towards the macrocyclic cavity [25], which is hindered by the *N*-substituents. Given the fact that isolation and handling of ligand **2** was easier in the protonated form (see Supplementary material), we decided treating an acetonitrile solution of cationic macrocycle **2** with iron(III) bromide and the novel ferrate species **3** was isolated in good yields (81%) and purity.



Scheme 1. Synthesis of the ferrate complex **3**.

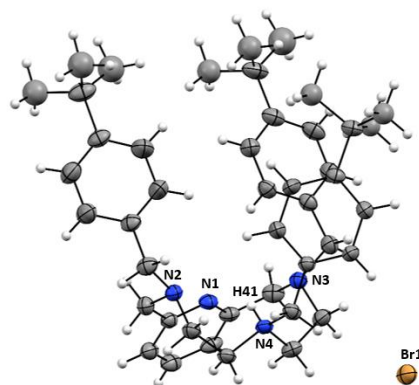
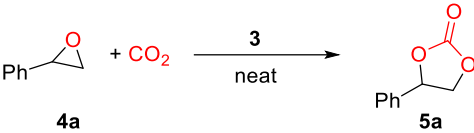


Figure 2. Molecular structure of the bromohydrated ligand, **2** (50% probability thermal ellipsoids). Selected bond lengths (Å): N1...H41 2.26, N2...H41 2.53, N3...H41 2.59. The 'butyl groups are disordered and were refined with two isotropic models; only the sites with the highest *sof* are displayed. The water molecule was omitted for clarity.[‡]

A similar formation of a singly protonated macrocycle with the iron incorporated into the anion has been also reported in the case of sterically encumbered 1,4,7-triazacyclononane complexes [26]. The presence of the FeBr_4^- counter-anion was confirmed by ESI(-)-MS spectroscopy and the elemental analysis was in agreement with the proposed structure. Unfortunately, all the crystallization tests for complex **3** failed. Block colourless crystals of compound **2** suitable for X-ray analysis were grown precisely in an attempt to crystallize compound **3** from an ethanolic solution by slow diffusion of water. A sort of equilibrium between “ate” and free iron bromide species should be considered, as already predicted by Capacchione and co-workers [27] and as recently disclosed by Hein *et al.* in the case of indium bromide [28] and this equilibrium might be the reason of the failure in obtaining pure crystals of complex **3**. The formation of tetrahalogeno-ferrate anions is well described [29] and we have already reported its formation in the case of a related $[\text{Fe}^{\text{III}}(\text{Cl})_2(^{3\text{Bn}}\text{Pc-L})](\text{FeCl}_4)$ complex [22]. These species form upon the reaction of an iron salt with an ammonium halide or by disproportionation of the iron salt. The intermediacy of anionic iron(III) bromide complexes as catalyst from the reaction between a ferric complex and TBAB has been proposed on the basis of kinetic and DFT calculations [17]. Recently, it was shown that indeed ferrate salts may act as single-component catalyst, without the need of any additional nucleophile [20]. Our assumption was that the ferrate complex **3** could act as nucleophile and at the same time would guarantee the Lewis acid behaviour and thus it was a good candidate as catalyst for the cycloaddition of CO_2 to epoxides. The macrocyclic ligand, on the other hand, thanks to the presence of bulky 'butyl groups, provides good solubility. Finally, bromide acts as a better nucleophile for the reaction, in comparison with chloride or

iodide anions, weighting its ability to ring-open the epoxide and acts as a leaving group [20]. The catalytic activity of **3** was tested using styrene oxide (SO) as the benchmark substrate.

Table 1: Optimization of the reaction conditions.^[a]



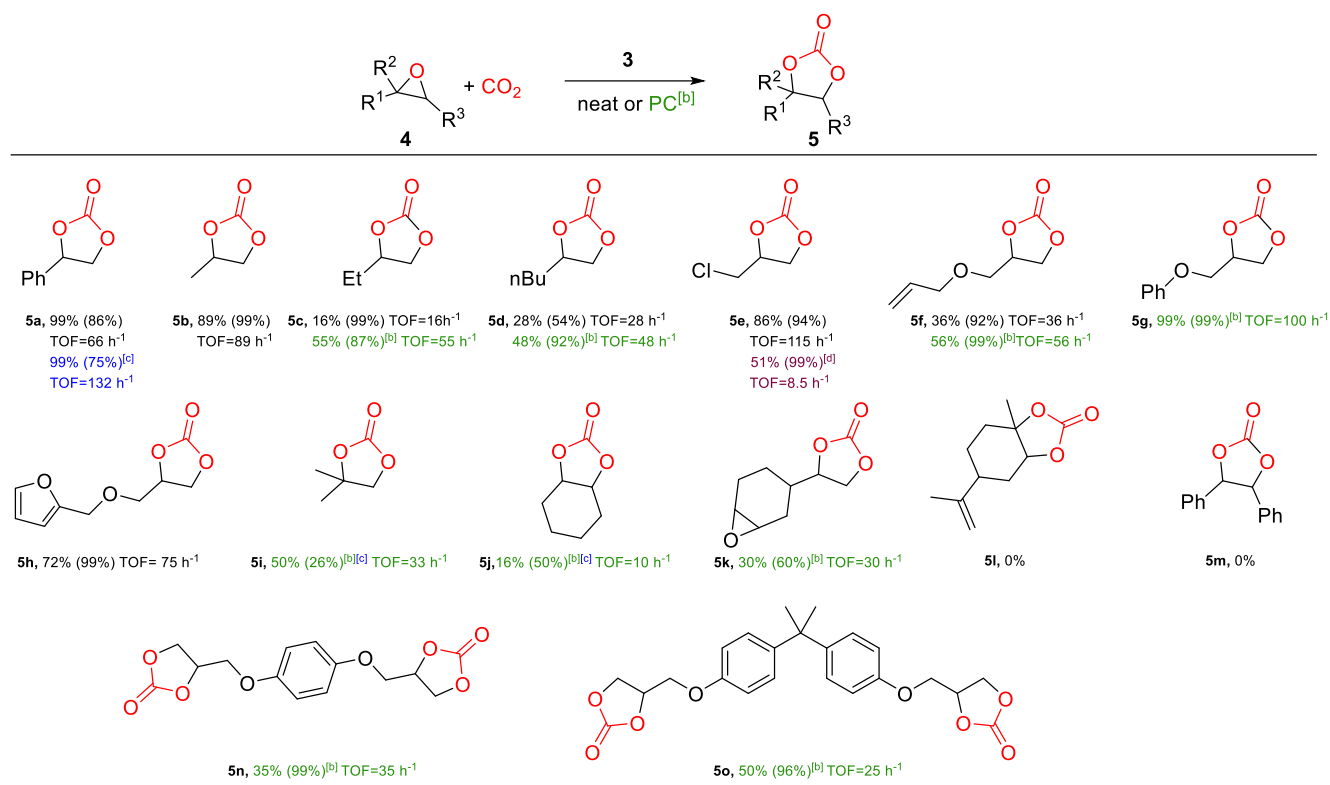
Entry	Cat. mol%	t (h)	Con. 4a %	Sel. 5a %	TOF ^[b] (h ⁻¹)
1	3 0.5%	3	99	62	66
2	3 0.25%	3	99	75	132
3	TBAB 0.25%	3	25	92	33
4	3 0.25%, TBAB 0.25%	3	99	99	132
5 ^[c]	3 0.5%	4	99	80	50
6 ^[c]	3 0.25%	4	85	83	85
7 ^[c]	3 0.1%	4	23	61	57
8 ^[c]	FeBr₃ 0.5%	4	39	0	20
9 ^[c]	2 0.5%	4	<1	<1	-
10 ^[c]	3 0.25%	6	99	86	66
11 ^[d]	3 0.25%	24	66	42	11
12 ^[e]	3 0.25%	60	38	66	2.5

^[a] Reaction conditions: styrene oxide (SO) 2.19 mmol; P (CO₂) = 0.8 MPa; T = 125 °C. Conversion and selectivity determined by ¹H NMR using mesitylene as the internal standard. ^[b] Turnover frequency (mol_{4a}(converted)·mol_{cat}⁻¹·reaction time⁻¹). ^[c] T = 100 °C. ^[d] T = 100 °C, P (CO₂) = 0.1 MPa. ^[e] T = 25 °C, P (CO₂) = 0.1 MPa.

Optimization of the reaction conditions, such as the catalyst loading, temperature, pressure and reaction time (Tables S1-S4), gave promising results: 0.25 mol% of catalyst were able to convert quantitatively SO in 3 hours at 125 °C and 0.8 MPa of CO₂ pressure (entry 2, Table 1, TON = 396, TOF = 132 h⁻¹). It is known, but not always highlighted in recent literature, that simple tetrabutylammonium bromide (TBAB) [30] alone is active in this transformation (entry 3, Table 1), but when compared to our catalytic system, a 4-fold difference in the TOF could be observed. However, when TBAB (0.25 mol%) is added to **3** (0.25 mol%), full conversion with total selectivity in SC (>99%) is observed (entry 4, Table 1). The optimal pressure of CO₂ was found to be 0.8 MPa with a loss of activity and selectivity when decreasing the pressure (Table S2). Slightly better selectivities for styrene carbonate (SC) were obtained at 100 °C (entries 5 and 6, Table 1). It should be pointed out that iron(III) bromide completely failed to yield SC under the optimised conditions (Entry 8, Table 1) and that ligand **2** alone in the absence of ferrate is not a competent catalyst (Entry 9, Table 1). Finally, a complete SO conversion with good selectivity for SC was achieved in 6 hours reaction time, with just a 0.25 mol% catalyst loading (entry 10, Table 1), and the system showed to be active also under mild reaction conditions (room temperature and atmospheric pressure), albeit upon prolonged reaction times (entries 11 and 12, Table 1).

Once having found the optimised experimental conditions, several others epoxides were screened. If the reaction proceeded smoothly in SO due to the good solubility of **3**, alkyl-substituted substrates were by far worse solvents for the complex and this resulted in a loss of activity, especially when increasing the alkyl chain length. To solve this problem, in selected cases, we decided to use propylene carbonate (PC) as a co-solvent. PC is a high-boiling, strong polar aprotic green solvent [31] that considerably enhanced the solubility of our complex and boosted the activity (Table 2).

Table 2. Scope of the cycloaddition of CO₂ to epoxides catalysed by the ferrate complex **3**. Results expressed as conversion (selectivity in brackets).^[a]



^[a] Reaction conditions: epoxide 250 μ L; **3** = 0.25 mol% T = 100 $^{\circ}$ C; P (CO₂) = 0.8 MPa; reaction time = 3 – 6h (see Supporting information); neat. Results expressed as conversion (selectivity) determined by ¹H NMR using mesitylene as the internal standard. TOF = mol_{4(converted)}·mol₃⁻¹·reaction time⁻¹. ^[b] Propylene carbonate (PC) as solvent. ^[c] T = 125 $^{\circ}$ C. ^[d] P (CO₂) = 0.1 MPa, reaction time 24 h.

In general, our complex was performing well in this transformation for the majority of the epoxides, with a remarkable higher activity in the case of terminal ones. For instance, linear alkyl epoxides **4b-4d** could be converted in high selectivities. Epichlorohydrin carbonate **5e** was obtained in a high yield and selectivity with a remarkable TOF value of 115 h⁻¹. A remarkable selectivity in **5e** (99%) was obtained at atmospheric CO₂ pressure, albeit upon prolonged reaction times (24 h). On the other hand, substrates such as cyclohexene oxide **4j** and 2-methyl-1,2-epoxypropane **4i** were found to be converted in a very poor yield (and only at T = 125 $^{\circ}$ C), while even more sterically hindered epoxides such as limonene

oxide **4l** and stilbene oxide **4m** did not react at all. It is interesting to note that, in the case of 4-vinylcyclohexene dioxide **4k**, the only product obtained was the terminal carbonate **5k**, in 18% isolated yield. Glycidyl ethers were generally reactive (**4f**, **4g**, **4h**) and, for that reason, we tested some di-glycidyl ethers derivatives, which find place as monomers in polymer chemistry for epoxides thermosets and NIPUs (non-isocyanate polyurethanes) [32]. Bisphenol-A diglycidyl ether **4o** was converted to the dicarbonate compound **5o** in a good yield (48%) and very high selectivity (96%) in PC at 100 °C in just 4 hours. Diglycidylether of hydroquinone **4n** was converted into the corresponding di-carbonate **5q** in a moderate yield (35%).

A ten-fold scale-up reaction (2.5 mL of epoxide) was performed to evaluate the activity of our catalytic system in such conditions, using propylene oxide (PO) **4b** as the substrate. The results obtained at 100 °C and 4 h reaction time were highly satisfying with a TON of 396 (TOF = 99 h⁻¹) and PC was isolated pure, after filtration over a silica plug, in 83% yield (3.03 g). To evaluate the robustness of the catalyst, the recyclability of the system was tested, on the same scale, by simply adding fresh PO three times (total volume 7.5 mL), and we obtained a final conversion of 85% with an overall TON of 1020 (mean TOF = 85 h⁻¹). From this reaction, after purification, 6.76 g of pure PC were obtained, corresponding to a global yield of 62%. A similar experiment on the catalyst stability and recyclability was repeated, but this time by distilling out PC at the end of the reaction. The recovered solid catalyst was then used for a second cycle, yielding pure PC (80%) with 99% selectivity, showing no loss of catalytic activity.

As proposed by Pescarmona and Otten, [20], it is reasonable to assume that in the aprotic medium in which the reaction was performed, the excess of epoxide favours its coordination/activation to the iron centre, releasing Br⁻ in solution that act as nucleophile to ring open the epoxide. CO₂ insertion, followed by ring closure give the cyclic carbonate and restore the ferrate catalyst. As a further evidence of that, ESI(-)-MS spectroscopy of the solid recovered material at the end of the catalytic reaction (*vide supra*) confirmed the presence of intact FeBr₄⁻ counter-anion.

4. Conclusions

In conclusion, we synthesized a new “ferrate” salt of a pyridine-containing macrocyclic ligand which proved to be a robust and active catalyst for the cycloaddition of CO₂ to epoxides without the addition of any additive or co-catalyst. The complex proved to be active under mild conditions (38% conversion of SO at room temperature and atmospheric pressure of CO₂ in 60 h) and a competent catalyst at higher temperatures, with reasonably good TOF values (up to 132 h⁻¹ at T = 125 °C and P = 0.8 MPa), which

compares well with state of the art iron homogeneous catalysts,¹⁵ but in this case without the need of any co-catalysts. In the literature, when a combination of a Lewis acid (catalyst) and a Lewis base (co-catalyst) in the reaction between CO₂ and epoxides is employed, TOF values have been calculated usually considering the amount of the sole catalyst [33]. However, the existence of a reaction pathway catalysed by the sole Lewis base should always be considered. We have indeed shown that, under the reaction conditions employed in the present study, TBAB alone is also a competent catalyst, but higher conversions were obtained at lower catalyst loading with our ferrate complex and a 4-fold increase in the TOF was observed. Worth to note, the metal complex synthesis is straightforward, starting from cheap iron(III) bromide, to yield a stable and easy-to-handle ferrate. The scope of the reaction was investigated and the catalyst showed to be active on most of the substrates tested. Scale-up and catalyst recycle experiments were successful. Further studies to expand the scope of the reaction and elucidate the mechanism of this transformation are actually ongoing in our laboratories.

CRedit authorship contribution statement

Nicola Panza: Data curation, Writing - original draft, Visualization. **Armando di Biase:** structure determination by single crystal X-Ray Diffraction, Data curation. **Emma Gallo:** Writing - review & editing. **Alessandro Caselli:** Conceptualization, Methodology, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

There are no conflicts to declare.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at:

References

‡ Full crystal structure data of **2** are reported in the Supporting information. CCDC-2071881 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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