University of Groningen

Highly selective single-component formazanate ferrate(II) catalysts for the conversion of CO₂ into cyclic carbonates

Kamphuis, Aeilke J; Milocco, Francesca; Koiter, Luuk; Pescarmona, Paolo; Otten, Edwin

Published in:
Chemsuschem

DOI:
[10.1002/cssc.201900740](https://doi.org/10.1002/cssc.201900740)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Final author's version (accepted by publisher, after peer review)

Publication date:
2019

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Kamphuis, A. J., Milocco, F., Koiter, L., Pescarmona, P., & Otten, E. (2019). Highly selective single-component formazanate ferrate(II) catalysts for the conversion of CO₂ into cyclic carbonates. *Chemsuschem*, 12(15), 3635-3641. <https://doi.org/10.1002/cssc.201900740>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

CHEMISTRY & SUSTAINABILITY

CHEM **SUS** CHEM

ENERGY & MATERIALS

Accepted Article

Title: Highly selective single-component formazanate ferrate(II) catalysts for the conversion of CO₂ into cyclic carbonates

Authors: Aeilke J. Kamphuis, Francesca Milocco, Luuk Koiter, Paolo Pescarmona, and Edwin Otten

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *ChemSusChem* 10.1002/cssc.201900740

Link to VoR: <http://dx.doi.org/10.1002/cssc.201900740>

WILEY-VCH

www.chemsuschem.org

A Journal of

Highly selective single-component formazanate ferrate(II) catalysts for the conversion of CO₂ into cyclic carbonates

Aeilke J. Kamphuis,^{§[a]} Francesca Milocco,^{§[b]} Luuk Koiter,^[b] Paolo P. Pescarmona^{*[a]} and Edwin Otten^{*[b]}

Abstract: The development of new families of active and selective single-component catalysts based on earth-abundant metal is of interest from a sustainable chemistry perspective. In this context, we report anionic mono(formazanate) iron(II) complexes bearing labile halide ligands, which possess both Lewis acidic and nucleophilic functionalities, as novel single-component homogeneous catalysts for the reaction of CO₂ with epoxides to produce cyclic carbonates. The influence of the halide ligand and the electronic properties of the formazanate ligand backbone on the catalytic activity were investigated by employing complexes **1–3** with and without an additional nucleophile. Very high selectivity was achieved towards the formation of the cyclic carbonate product for various terminal and internal epoxides without the need of a co-catalyst.

Introduction

The use of carbon dioxide as a C₁-feedstock to produce useful chemicals is highly desirable due to its low cost and its non-toxic and non-flammable nature.^[1] One of the biggest challenges associated with the use of CO₂ as a chemical building block is to overcome its high thermodynamic stability. This can be achieved by reacting CO₂ with compounds that are sufficiently high in free energy to result in exergonic reactions. Examples thereof include the hydrogenation of CO₂ to formic acid or methanol,^[1c,2] and the 100% atom-efficient reaction of CO₂ with epoxides to produce cyclic carbonates (CCs) and/or polycarbonates (PCs, Scheme 1).^[3] Both products are relevant for a number of applications.^[4] In particular, CCs are used as green solvents, in electrolytes for Li-ion batteries, and as greener alternatives to toxic reagents such as phosgene.^[5] Another crucial challenge in the fixation of carbon dioxide into CCs and PCs is the development of suitable catalysts, with the purpose of reaching high conversion rates of epoxides and to control the reaction selectivity so that only one of the two products is obtained,^[3]

thus minimising separation costs. Among the many classes of homogeneous and heterogeneous catalysts that have been studied for the reaction of CO₂ with epoxides,^[3,4,6] the binary catalyst systems involving a Lewis acid (e.g. a metal centre) and a nucleophile (e.g. a halide) generally achieve the highest activity and selectivity.^[7] Several metal complexes have been developed, especially based on Al,^[8] Zn,^[9] Co,^[10] Cr.^[11] Recently, growing attention has been dedicated to Fe catalysts.^[12, 13] The use of the latter metal is very attractive due to its abundance, low cost and relatively low toxicity.^[14] The Lewis acid centre and the nucleophilic species can be provided by two distinct components (e.g. a metal complex and an organic halide) or be incorporated in a single compound (i.e. a bifunctional catalyst). Examples of bifunctional iron-based catalysts include complexes based on Fe(II)^[13e,15] or Fe(III)^[13a-c,13f,16] with multidentate ligands containing N and/or O donor atoms. A limitation of these systems is that, particularly in the case of conversion of internal epoxides, an additional nucleophilic co-catalyst is typically required to achieve high activity and/or selectivity towards the cyclic carbonate product.

Here, we report for the first time the use of Fe(II) formazanate complexes as active and selective single-component homogeneous catalysts for the selective conversion of CO₂ and epoxides into the corresponding cyclic carbonates. In contrast to β -diketiminates, which have been widely used as ligands in metal complexes with application as homogeneous catalysts,^[17] the structurally related formazanates ligands (based on a NNCNN backbone) are much less explored.^[18] Recently, some of us^[19] and Holland et al.^[20] reported formazanate iron complexes, including a stoichiometric reaction with CO₂ to give isocyanate,^[21] but the application of formazanate iron complexes in catalysis has, to the best of our knowledge, not been described so far.

Scheme 1. Catalysed reaction of CO₂ with epoxides.

Results and Discussion

The mono(formazanate) ferrate(II) dihalide catalysts, [(PhNNC(Ar)NNPh)FeX₂][−] (Ar = C₆H₄(*p*-Me) (**1**), C₆F₅ (**2**), C₆H₄(*p*-OMe) (**3**); X = Cl, Br, I) were synthesised via a modified procedure of a route previously reported by some of us.^[19b] This new procedure uses a one-pot approach that circumvents the isolation of formazanate alkali metal salts, thus allowing to use ligand substitution patterns that would otherwise lead to decomposition (for example, C₆F₅-substituents engage in

[a] A. J. Kamphuis, Prof. Dr. P. P. Pescarmona
Chemical Engineering Group, Engineering and Technology Institute
Groningen (ENTEG)
University of Groningen
Nijenborgh 4, 9747 AG Groningen, The Netherlands
E-mail: p.p.pescarmona@rug.nl

[b] F. Milocco, L. Koiter, Prof. Dr. E. Otten
Stratingh Institute for Chemistry
University of Groningen
Nijenborgh 4, 9747 AG Groningen, The Netherlands
E-mail: edwin.otten@rug.nl

§ These authors contributed equally

Supporting information (SI) for this article is given via a link at the end of the document.

CCDC 1889271, 1889272 and 1889273 contain 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.

nucleophilic aromatic substitution).^[22] Thus, simply mixing the formazans **1H-3H** with a tetrabutylammonium halide, a base ($\text{KN}(\text{SiMe}_3)_2$) and FeX_2 in THF under inert atmosphere allowed isolation of compounds **1-3** in good yield (60-85%) (Scheme 2).

Scheme 2. Synthesis of compounds **1-3**.

Single-crystal X-ray diffraction of the new compounds **2Br/I** and **3Br** (Figure S1) showed geometries close to tetrahedral (τ_4 in the range of 0.91-0.93), similar to those of the previously reported **1Cl/Br** ($\tau_4^{[23]} = 0.89\text{-}0.90$).^[19b] The Fe-N bond lengths of **2Br/I** and **3Br** (see Table S2) are comparable with those of **1Cl/Br**, in agreement with a Fe(II) high-spin ($S = 2$). Compounds **1-3** were characterised in $\text{THF-}d_8$ solution via ^1H and ^{19}F NMR spectra (see SI), which show broad paramagnetically shifted peaks, the number of which is consistent with C_{2v} symmetry. The electrochemical behaviour of compounds **2Br** and **3Br** was studied by cyclic voltammetry in THF solution (0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ electrolyte, see SI). An anodic scan of **3Br** shows an irreversible oxidation at a peak potential of +0.04 V vs $\text{Fc}^{0/+}$, which is attributed to the $\text{Fe}^{\text{II/III}}$ redox couple in analogy to what has been observed previously for **1Br** ($E_{p,a} = +0.05$ V vs $\text{Fc}^{0/+}$).^[19b] A second oxidation is observed at +0.42 V vs $\text{Fc}^{0/+}$, which is likely due to bromide oxidation.^[24] The cyclic voltammogram of the C_6F_5 -substituted complex **2Br** shows an $\text{Fe}^{\text{II/III}}$ couple that is shifted to higher potential by more than 100 mV ($E_{p,a} = +0.16$ V vs $\text{Fc}^{0/+}$). The iron oxidation potential can be used as an indication of the Lewis acidity of the complex, suggesting that the Fe-centre in **2Br** is a stronger Lewis acid compared to the corresponding sites in **1Br** and **3Br**, as expected when an electron withdrawing group is introduced in the ligand backbone. The halides in **1Br** were shown to be labile and can be replaced by 4 eq. of 4-methoxyphenyl isocyanide to give the octahedral cationic complex $[\text{LFe}(\text{CNC}_6\text{H}_4(p\text{-OMe}))_4][\text{Br}]$.^[19b] This feature is promising for the application of this class of complexes as catalysts for the reaction of CO_2 with epoxides. In this context, the ability of these iron formazanates to activate epoxides was investigated by performing an in situ NMR study. Treatment of a $\text{THF-}d_8$ solution of **1Br** with successive amounts of 1,2-epoxyhexane (1 to 25 eq.) led to a slight shift in the ^1H NMR spectrum of the signals of the formazanate moiety (Figure S8), while the resonances of the epoxide were hardly affected (Figure S9). Although the changes are relatively minor, we interpret them as indication of an equilibrium involving the exchange of bromide with epoxide, albeit shifted towards the starting materials. A similar experiment with pyridine, which is a

stronger Lewis base than epoxyhexane, indeed resulted in extensive broadening of the pyridine resonances when 1 eq. was used, while the peaks sharpen when 25 eq. were added (Figure S10-11). These data are consistent with the notion that bromide exchange in **1Br** is facile, but the extent of bromide displacement depends on the nature of the added base. Addition of CO_2 (1 bar) to the NMR tube containing **1Br** and epoxyhexane (25 eq.) produced a small amount of cyclic carbonate after standing at room temperature for 2 h. Warming up to 60 °C overnight led to complete conversion of CO_2 (based on ^{13}C NMR), together with an increase of the amount of cyclic carbonate (Figure 1).

Figure 1. ^1H NMR spectrum of **1Br** + 1,2-epoxyhexane (25 eq.) + CO_2 (1 bar) ($\text{THF-}d_8$, 400 MHz, 25 °C), selected peaks.

Encouraged by these initial studies, complexes **1Cl/Br/I** were evaluated as catalysts for the reaction of CO_2 with 1,2-epoxyhexane in solvent-free conditions at 90 °C, 12 bar CO_2 . The experiments were run using 0.25 mol% of Fe complex, both with and without the corresponding tetrabutylammonium halide as co-catalyst (Table 1, entries 1-6). Notably, all three formazanate complexes (**1Cl/Br/I**) are active without requiring the addition of a co-catalyst (Table 1, entries 1, 3 and 5). This demonstrates that a halide ligand in these ferrate(II) complexes is sufficiently labile to act as nucleophile causing ring-opening of the epoxide, resulting in a bifunctional catalytic behaviour. A similar mechanism based on a labile metal-halide bond was proposed for (anionic) Fe(III) catalysts.^[16f] Virtually complete selectivity (>99%) towards the cyclic carbonate was observed in all cases. When the corresponding tetrabutylammonium halide was used as co-catalyst in combination with complexes **1Cl/Br/I**, the epoxide conversion could be further improved (Table 1,

entries 2, 4 and 6). Comparing these results with the activity of the tetrabutylammonium halides under the same conditions but in the absence of iron formazanates (entries 16-18), showed that the presence of the iron complexes leads to substantially increased conversion, thus confirming their catalytic activity.

Table 1. Reaction of 1,2-epoxyhexane with CO₂ catalysed by Fe(II) formazanate complexes (1-3).

#	Catalyst	Co-catalyst	Conv. (%) ^[a]	TON ^[b]
1	1Cl	-	12	48
2	1Cl	Bu ₄ NCl	19	76
3	1Br	-	36	144
4	1Br	Bu ₄ NBr	50	200
5	1I	-	21	84
6	1I	Bu ₄ NI	28	112
7	2Br	-	24	96
8	2Br	Bu ₄ NBr	41	164
9	2I	-	24	96
10	3Br	-	28	112
11	3Br	Bu ₄ NBr	39	156
12 ^[c]	1Br	-	47	188
13 ^[c]	1Br	Bu ₄ NBr	61	244
14 ^[c,d]	1Br	-	>99	100
15 ^[c,e]	1Br ^[e]	-	69	-
16	-	Bu ₄ NCl	3	-
17	-	Bu ₄ NBr	4	-
18	-	Bu ₄ NI	5	-

Reaction conditions: 30 mmol epoxide, 3 mmol mesitylene as internal standard, 0.25 mol% Fe complex relative to the epoxide; 0.25 mol% co-catalyst relative to the epoxide (if applicable), 90 °C, 12 bar CO₂ pressure, 2 h. The Fe complexes (and co-catalysts, if used) are fully soluble at room temperature in the reaction mixture. Selectivity towards the cyclic carbonate was >99% in all cases as confirmed by ¹H NMR spectroscopy (see SI). [a] Conversion calculated based on the ¹H NMR signals of the carbonate product and epoxide substrate (see SI); all runs were conducted in (at least) duplicate, the reported conversion being an average. [b] Turnover number expressed as mol of converted epoxide per mol of catalyst complex. [c] Using anhydrous 1,2-epoxyhexane. [d] 1.00 mol% of complex 1Br relative to the epoxide. [e] Recycled catalyst from entry 14.

Among the three formazanate complexes (1Cl/Br/I), the activity increased in the order of X = Cl⁻ < I⁻ < Br⁻, both in the presence or absence of a co-catalyst. This trend can be understood considering that the overall catalytic activity depends on the nucleophilicity of the halide, its leaving group ability (see

Scheme 3 for proposed reaction mechanism) and its interaction with the Lewis acid (i.e. the halide lability from the iron centre).^[3c,8c,25] In the aprotic medium in which the reaction was carried out, the nucleophilicity increases in the order of I⁻ < Br⁻ < Cl⁻, whereas the leaving group ability decreases in the same order. It can be concluded that in this system bromide provides the best balance between nucleophilicity, leaving group ability and lability from the iron centre, thereby leading to the highest catalytic activity. In addition to studying the effect of the anionic nucleophilic species on the catalytic activity, the influence of the cationic counterpart was also investigated. Performing the benchmark reaction (equal conditions to Table 1, entry 3) with an analogue of complex 1Br with PPN (bis(triphenylphosphine)iminium) as counteranion showed no significant difference in catalytic activity (34% conversion).

Scheme 3. Proposed mechanism for the reaction of CO₂ and epoxide catalysed by Fe(II) formazanate complexes (1-3).

To further investigate the potential of iron formazanate catalysts in this reaction, the influence of the substituents in the ligand backbone was studied by preparing and testing compounds 2Br, 2I and 3Br. The electron-withdrawing C₆F₅ substituent present in compounds 2Br/I is expected to lead to a more Lewis acidic Fe centre in comparison to that in complexes 1, whereas the electron-donating *p*-methoxy group of 3Br will generate the opposite effect. When comparing the catalytic activity of complex 1Br (entries 3 and 4) with 2Br (entries 7 and 8) and 3Br (entries 10 and 11), it is clear that all iron complexes are active catalysts, both with and without added co-catalyst, and that both electron-withdrawing and -donating groups have a detrimental effect on activity. The lack of a clear correlation between a single parameter (i.e. the Lewis acidity of the metal centre) and catalytic activity is not surprising given the complex balance between the parameters that determine the activity of the

system (such as halide dissociation from the metal centre, substrate binding, product release). Complexes **1Br** and **2Br** were also tested using lower loading relative to the epoxide. Under these conditions, a decrease in conversion was observed but a higher TON could be reached (see Table S5).

Many homogeneous metal-based catalysts employed in the reaction of CO₂ with epoxide are air- and moisture-sensitive,^[9a] requiring drying of the reagents in order to prevent their deactivation. In the case of the iron formazanate complexes, we investigated the effect of using pre-dried, N₂-saturated 1,2-epoxyhexane on the activity of catalyst **1Br** (Table 1, entries 12 and 13). An increase in conversion of around 11% was observed in comparison with the test with untreated 1,2-epoxyhexane (entries 3 and 4, respectively). These results indicate that, though working with anhydrous reagents is beneficial, the formazanate catalyst is not affected in a major way by adventitious water. This is an important asset, as for practical applications the addition of a drying step would lead to significant undesirable costs.

Of all the formazanate complexes examined, **1Br** showed the highest catalytic activity towards the benchmark reaction of CO₂ with 1,2-epoxyhexane, both with and without additional nucleophile. Hence, we chose this complex as single-component catalyst to expand the scope of the reaction by testing various terminal and internal epoxides (Table 2; for the substrate scope with complex **2Br** see Table S4).

For 1,2-epoxyhexane, the conversion after 18 h (89%) is considerably higher than after 2 h (36%, entry 3 in Table 1), showing that formazanate complex **1Br** remains active for an extended period of time. Indeed, addition of Et₂O after the reaction afforded a precipitate that contained intact **1Br** as shown by ¹H NMR spectroscopy (Figure S7). This allowed investigating the recyclability of the catalyst. First, a catalytic test with 1.0 mol% catalyst loading was carried out, which gave quantitative conversion of 1,2-epoxyhexane after 2 h (Table 1, entry 14). Subsequently, **1Br** was precipitated by addition of cold Et₂O/hexane (4:1) under N₂ atmosphere. After removal of the supernatant, the solid was washed with cold Et₂O, dried and used without further purification in a second run. Under identical conditions, the recycled catalyst afforded 69% conversion (Table 1, entry 15). It should be noted that full catalyst recovery was hampered by its solubility in the carbonate product, and further optimisation is required. Nevertheless, these results show that the recovered catalyst retains substantial activity.

When comparing the activity with different substrates, it was observed that **1Br** is especially active in the conversion of terminal epoxides, leading to high conversions (≥84%) for reactions of CO₂ with 1,2-epoxyhexane (Table 2, entry 1), epichlorohydrin (entry 3) and allyl glycidyl ether (entry 4). In the case of propylene oxide (entry 2), quantitative conversion was achieved after 18 h with a catalyst loading of 0.25 mol%, accompanied by a propylene carbonate yield of 97% (see Table 2, note [f]). Lowering the catalyst loading to 0.05 mol% resulted in a propylene carbonate yield of 43% (entry 2), with a high TON of 860. The conversion of styrene oxide (entry 5) is slightly lower than that of the other terminal epoxides, which can be related to the steric hindrance of the aromatic group.

Table 2. Substrate scope of the reaction of various terminal and internal epoxides with CO₂ to produce cyclic carbonates, catalysed by Fe(II) formazanate complex **1Br**.

#	Epoxide	Conv. (%) ^[a]	Sel. (%) ^[b]	TON ^[c]
1		89	>99	356
2 ^[f]		>99 (97 ^[d]) 55 ^[e] (43 ^[d,e])	>99	400 (388 ^[d]) 1100 ^[e] (860 ^[d,e])
3		89	98	356
4		84	>99	336
5		70	>99	280
6		32	98	128
7		18	98	72
8		2 ^[g]	>99 ^[g]	8 ^[g]

Reaction conditions: 30 mmol epoxide, 3 mmol mesitylene as internal standard, 0.25 mol% of complex **1Br** relative to the epoxide, 90 °C, 12 bar CO₂ pressure, 18 h. [a] Conversion calculated based on the ¹H NMR signals of the carbonate product and epoxide substrate (see SI). [b] Selectivity towards the cyclic carbonate product determined with FTIR analysis by comparing the C=O stretch signal of the cyclic carbonate and polycarbonate, respectively (see SI). [c] Turnover number expressed as mol of converted epoxide per mol of catalyst complex. [d] The reported value is based on yield of propylene carbonate. [e] Catalyst loading of 0.05 mol% of complex **1Br** relative to the epoxide. [f] The small discrepancy between the conversion of propylene oxide and the yield of propylene carbonate is a consequence of the high volatility of propylene oxide, which leads to evaporation of small amounts of epoxide during purging and depressurisation of the reactor (see experimental section). [g] Reaction conditions: 30 mmol epoxide, 3 mmol mesitylene as internal standard, 1.00 mol% of complex **1Cl** relative to the epoxide, 90 °C, 12 bar CO₂ pressure, 18 h.

Internal epoxides are typically more difficult to convert due to steric effects, hence, lower conversions were achieved for the reactions of CO₂ with cyclohexene oxide (entry 6) and vinylcyclohexene oxide (entry 7), while only trace amounts of carbonate product were observed with limonene oxide. Since it has been reported that for highly substituted epoxide smaller nucleophiles are preferred,^[26] **1Cl** was also tested in the reaction of CO₂ with limonene oxide. With a catalyst loading of 1.00 mol%, **1Cl** gave ca. 2% conversion to the corresponding carbonate (entry 8). Although the reaction is very slow, this result demonstrates that formazanate complexes promote the

conversion of this challenging substrate even in the absence of a co-catalyst.

Interestingly, very high selectivity towards the cyclic carbonate product was achieved also with the cyclohexene-type epoxides, which are known to be prone to polymerisation.^[27] Typically, in the case of other single-component bifunctional catalysts, the polycarbonate is the major product obtained from the reaction between CO₂ and cyclohexene oxide, and the addition of a separate nucleophile is required to form the cyclic product selectively (see Table S6 for a detailed comparison with other bifunctional iron-based catalysts in the literature).^[13a,13c,15c,16a,16b]

Conclusions

We presented the first example of formazanate Fe complexes as homogeneous catalysts for the fixation of CO₂ into cyclic carbonates via reaction with epoxides. The main assets of these complexes are: (i) their ability to act as single-component catalysts, thus obviating the need for an additional nucleophile; and (ii) their remarkable selectivity towards the cyclic carbonate product even in the conversion of internal epoxides such as (substituted) cyclohexene oxides, which generally tend to yield polycarbonates. More generally, this work indicates that anionic metal complexes with loosely bound halide ligands may provide a new entry into single-component transition metal catalysts for CO₂-fixation into organic carbonates.

Experimental Section

General Considerations.

The synthesis of the complexes was carried out under nitrogen using standard glovebox, Schlenk, and vacuum-line techniques. THF (Aldrich, anhydrous, 99.8%) was dried by percolation over columns of Al₂O₃ (Fluka); toluene and hexane (Aldrich, anhydrous, 99.8%) were passed over columns of Al₂O₃ (Fluka), BASF R3-11-supported Cu oxygen scavenger, and molecular sieves (Aldrich, 4 Å). THF-*d*₈ (Euriso-top) was vacuum transferred from Na/K alloy and stored under nitrogen. The compounds **1H**,^[28] **3H**,^[29] PhNNC(C₆F₅)H^[30] and FeBr₂(THF)₂^[31] were synthesised according to literature procedures. Ligand **2H** was prepared according to a slightly-adapted version of a literature method^[32] (see SI for the detailed description). Aniline (Sigma-Aldrich, 99%), hydrochloric acid (Boom B.V., 37-38%), glacial acetic acid (Imsure, 100%), sodium hydroxide (pellets, Acros), sodium nitrite (Sigma-Aldrich), acetone (Boom B.V., technical grade), methanol (Boom B.V., technical grade), hexane (Boom B.V., technical grade), CDCl₃ (Euriso-top), tetrabutylammonium bromide (Sigma-Aldrich, 99%), tetrabutylammonium chloride (Sigma-Aldrich, 99%), tetrabutylammonium iodide (Sigma-Aldrich, 98%), FeI₂ (Alfa Aesar, anhydrous, 97%), potassium bis(trimethylsilyl)amide (Sigma-Aldrich, 95%) were used as received. KH (Sigma-Aldrich, 30 wt% dispersion in mineral oil) was washed several times with hexane to free them from the mineral oil and subsequently dried *in vacuo* to obtain a fine powder. NMR spectra were recorded on a Varian Oxford 300 MHz, Varian Mercury 400 MHz, Inova 500 MHz, or Bruker 600 MHz spectrometer. The ¹H and ¹³C NMR spectra were referenced internally using the residual solvent resonances and reported in ppm relative to TMS (0 ppm). FTIR spectra were recorded using a Shimadzu IR tracer-100 equipped with an ATR sample unit with a frequency range of 4000-

600 cm⁻¹, a resolution of 4 cm⁻¹ and 64 scans. Cyclic Voltammetry was performed using a three-electrode setup with a silver wire pseudo-reference electrode and a platinum disk working electrode (CHI102, CH Instruments; diameter = 2 mm). The platinum working electrode was polished before the experiment using an alumina slurry (0.05 µm), rinsed with distilled water, and subjected to brief ultrasonication to remove any adhered alumina microparticles. The electrodes were then dried in an oven at +75 °C overnight to remove any residual traces of water. The CV data were calibrated by adding decamethylferrocene as a THF solution at the end of the experiments. There is no indication that the addition of decamethylferrocene influences the electrochemical behaviour of the products. All electrochemical measurements were performed at ambient temperatures under an inert N₂ atmosphere in THF containing 0.1 M [Bu₄N][PF₆] as the supporting electrolyte. Data were recorded with Autolab NOVA software (version 2.1-2). UV-vis spectra were recorded in a THF solution (~10⁻⁵ M) using an Agilent Cary 8454 UV-Visible spectrophotometer.

Synthesis of the iron complexes.

[Bu₄N][(PhNNC(*p*-tol)NNPh)FeCl₂] (1Cl). To a solution of **1H** (276.3 mg, 1.0 eq, 0.88 mmol) in 20 mL of THF, tetrabutylammonium chloride (244.3 mg, 1.0 eq, 0.88 mmol), potassium bis(trimethylsilyl)amide (203.0 mg, 1.1 eq, 0.97 mmol) and FeCl₂ (111.4 mg, 1.0 eq, 0.88 mmol) were added as a solid. The dark purple mixture was stirred for 3 days after which the volatiles were removed *in vacuo*. The product was extracted in THF (2 x 6 mL) and slow diffusion of hexane into the THF solution afforded dark purple crystals which were filtered and washed with toluene and hexane giving **1Br** as product (473.8 mg, 0.69 mmol, 79% yield). The ¹H NMR spectrum was in agreement with the literature.^[19b]

[Bu₄N][(PhNNC(*p*-tol)NNPh)FeBr₂] (1Br). To a solution of **1H** (572.2 mg, 1.0 eq, 1.82 mmol) in 25 mL of THF, tetrabutylammonium bromide (586.7 mg, 1.0 eq, 1.82 mmol), potassium hydride (89.0 mg, 1.2 eq, 2.20 mmol) and FeBr₂·(THF)₂ (655.0 mg, 1.0 eq, 1.82 mmol) were added as a solid. The dark purple mixture was stirred for 3 days after which the volatiles were removed *in vacuo*. The product was extracted in THF (2 x 25 mL) and slow diffusion of hexane into the THF solution afforded dark purple crystals which were filtered and washed with toluene and hexane giving **1Br** as product (1024.2 mg, 1.33 mmol, 73% yield). The ¹H NMR spectrum was in agreement with the literature.^[19b]

[Bu₄N][(PhNNC(*p*-tol)NNPh)FeI₂] (1I).^[33] To a solution of **1H** (565.9 mg, 1.0 eq, 1.80 mmol) in 25 mL of THF, tetrabutylammonium iodide (664.7 mg, 1.0 eq, 1.80 mmol), potassium hydride (87.4 mg, 1.2 eq, 2.20 mmol) and FeI₂ (556.1 mg, 1.0 eq, 1.80 mmol) were added as a solid. After stirring at r.t. for 1 day the volatiles were removed *in vacuo*. The product was extracted in THF (2 x 20 mL) and slow diffusion of hexane into the THF solution afforded a dark purple powder which was filtered and washed with toluene and hexane giving **1I** as product (826.6 mg, 1.14 mmol, 63% yield). ¹H NMR (400 MHz, THF-*d*₈, 25 °C): δ = 36.34 (3H, *p*-tol CH₃), 30.07 (4H, Ph *m*-CH), 25.15 (2H, *p*-tol *m*-CH), 2.73 (8H, NBu₄⁺, CH₂), 2.47 (8H, NBu₄⁺, CH₂), 1.37 (8H, NBu₄⁺, CH₂), 0.83 (12H, NBu₄⁺, CH₃), -8.79 (2H, Ph *p*-CH), -9.42 (2H, *p*-tol *o*-CH), -24.49 (4H, Ph *o*-CH) ppm. Anal. Calcd. for C₃₅H₄₆N₅I₂Fe: C 49.96, H 6.17, N 8.09; found: C 50.58, H 6.81, N 7.13.

[Bu₄N][(PhNNC(C₆F₅)NNPh)FeBr₂] (2Br). To a solution of **2H** (858.7 mg, 1.0 eq, 2.20 mmol) in 30 mL of THF, tetrabutylammonium bromide (695.0 mg, 0.98 eq, 2.16 mmol), potassium bis(trimethylsilyl)amide (478.8 mg, 1.1 eq, 2.40 mmol) and FeBr₂·(THF)₂ (791.7 mg, 1.0 eq, 2.20 mmol) were added as a solid. The reaction mixture was stirred for 3 days after which the volatiles were removed *in vacuo*. The product was washed with toluene (20 mL) and subsequently extracted in THF (2 x 15 mL) and slow

diffusion of hexane into the orange-brown THF solution at r.t. afforded dark brown solid which was filtered and washed with toluene and hexane giving **2Br** as product (1266.0 mg, 1.49 mmol, 69% yield). ^1H NMR (400 MHz, $\text{THF}-d_6$, 25°C): δ = 23.76 (4H, Ph *m*-CH), 4.44 (8H, NBu_4^+ , CH_2), 2.95 (8H, NBu_4^+ , CH_2), 2.19 (8H, NBu_4^+ , CH_2), 1.31 (12H, NBu_4^+ , CH_3), -5.54 (2H, Ph *p*-CH), -16.70 (br, 4H, Ph *o*-CH) ppm. ^{19}F -NMR (376 MHz, $\text{THF}-d_6$, 25°C): δ = -125.12 (1F, C_6F_5 *p*-CF), -130.24 (2F, C_6F_5 CF), -157.72 (2F, C_6F_5 CF) ppm. Anal. Calcd. for $\text{C}_{35}\text{H}_{46}\text{N}_5\text{Br}_2\text{Fe}$: C 49.61, H 5.47, N 8.26; found: C 49.36, H 5.53, N 7.86.

[Bu₄N][(PhNNC(C₆F₅)NNPh)FeI₂] (2I). To a solution of **2H** (267.4 mg, 1.0 eq, 0.69 mmol) in 15 mL of THF, tetrabutylammonium iodide (253.0 mg, 1.0 eq, 0.69 mmol), potassium bis(trimethylsilyl)amide (158.2 mg, 1.1 eq, 0.75 mmol) and FeI₂ (218.7 mg, 1.0 eq, 0.69 mmol) were added as a solid. After stirring the reaction mixture for 3 days, the volatiles were removed *in vacuo*. The product was washed with hexane and toluene and subsequently extracted in THF. Slow diffusion of hexane into the orange-brown THF solution at r.t. afforded dark brown solid which was filtered and washed with toluene and hexane giving **2I** as product (393.4 mg, 0.42 mmol, 61% yield). ^1H NMR (400 MHz, $\text{THF}-d_6$, 25°C): δ = 27.98 (4H, Ph *m*-CH), 2.26 (8H, NBu_4^+ , CH_2), 1.94 (8H, NBu_4^+ , CH_2), 1.72 (8H, NBu_4^+ , CH_2), 1.22 (12H, NBu_4^+ , CH_3), -5.02 (2H, Ph *p*-CH) ppm. ^{19}F -NMR (376 MHz, $\text{THF}-d_6$, 25°C): δ = -123.58 (1F, C_6F_5 *p*-CF), -128.89 (2F, C_6F_5 CF), -158.55 (2F, C_6F_5 CF) ppm. Anal. Calcd. for $\text{C}_{35}\text{H}_{46}\text{N}_5\text{I}_2\text{Fe}$: C 44.65, H 4.93, N 7.44; found: C 44.42, H 4.88, N 7.39. *The peak of Ph *o*-CH is not visible due to paramagnetic line broadening.

[Bu₄N][(PhNNC(C₆H₄(*p*-OMe)NNPh)FeBr₂] (3Br). To a solution of **3H** (660.8 mg, 1.0 eq, 2.00 mmol) in 30 mL of THF, tetrabutylammonium bromide (644.7 mg, 1.0 eq, 2.00 mmol), potassium bis(trimethylsilyl)amide (462.0 mg, 1.1 eq, 2.20 mmol) and FeBr₂·(THF)₂ (719.7 mg, 1.0 eq, 2.00 mmol) were added as a solid. The reaction mixture was stirred for 3 days after which the volatiles were removed *in vacuo*. The product was extracted in THF (2 x 20 mL) and slow diffusion of hexane into the fuchsia THF solution at r.t. afforded dark purple solid which was filtered and washed with toluene and hexane giving **3Br** as product (1342.9 mg, 1.71 mmol, 85% yield). ^1H NMR (400 MHz, $\text{THF}-d_6$, 25°C): δ 26.24 (4H, Ph *m*-CH), 24.11 (2H, $\text{C}_6\text{H}_4\text{OCH}_3$ *m*-CH), 9.38 (3H, $\text{C}_6\text{H}_4\text{OCH}_3$ *p*-OCH₃), 2.82 (8H, NBu_4^+ CH_2), 1.30-2.00 (16H, NBu_4^+ CH_2), 0.91 (12H, NBu_4^+ CH_3), -7.27 (2H, $\text{C}_6\text{H}_4\text{OCH}_3$ *o*-CH), -8.93 (2H, Ph *p*-CH), -19.76 (br, 4H, Ph *o*-CH) ppm. Anal. Calcd for $\text{C}_{36}\text{H}_{53}\text{N}_5\text{OBr}_2\text{Fe}$: C 54.91, H 6.79, N 8.89; found: C 54.79, H 6.43, N 8.61.

Catalytic tests.

The catalytic experiments were conducted in a high-throughput CO₂ reactor unit, constructed by ILS-Integrated Lab Solutions GmbH. This CO₂ reactor unit consists of: (a) a 10-reactors block that allows performing 10 reactions simultaneously in individually-stirred batch reactors in separate batch reactors (84 mL volume each, 30 mm internal diameter); and (b) a single batch reactor with the same dimensions and equipped with a borosilicate glass window to allow visualisation of the phase behaviour within the reactor. The unit can operate in a temperature range of 20-200 °C and a pressure range of 1-200 bar. For each test, 30.0 mmol epoxide, 3.0 mmol mesitylene as internal standard and the appropriate amounts of catalyst and co-catalyst (when used) were weighed into a glass vial (46 mL volume, 30 mm external diameter) equipped with a magnetic stirring bar and a screw cap containing a silicone/PTFE septum. The glass vials were then transferred into the 10-reactors block and each septum was pierced with two thin syringe needles to allow gas to flow in and out of the vials. The reactors block was subsequently closed. The parallel batch reactors were first purged 3 times with 5 bar N₂, after which they were pressurised to 10 bar CO₂. 10 min were waited before depressurising the reactors to atmospheric

pressure in order to prevent damage to the Viton O-rings. After reaching atmospheric pressure, another 10 min were waited. Next, the reactors were pressurised with 10 bar CO₂. After reaching this pressure, the reactors block was heated to 90 °C, which resulted in a final pressure of approximately 12 bar in each batch reactor. The process of purging, pressurising and heating the reactors block took approximately 1 h. The start of the reaction was defined as the moment at which the magnetic stirring was switched on, after reaching the desired reaction temperature and pressure. The reactions were carried out at 900 rpm stirring speed for either 2 or 18 h. At the end of the reaction, the magnetic stirring and the reactor heating were switched off and the water cooling system was turned on to cool down the reactors block. Upon reaching room temperature, the reactors were depressurised. The process of cooling down and depressurising the reactors block took approximately 45 min. After reaching atmospheric pressure, the reactors block was opened and the vials were removed. Small aliquots of each sample were used for ^1H NMR and FTIR analyses.

The recycling tests were conducted in the visualisation reactor of the high-throughput CO₂ reactor unit at 90 °C, 12 bar CO₂ pressure, 2 h, following the same catalytic testing procedure reported above. 1,2-Epoxyhexane and mesitylene were previously dried on molecular sieves and degassed under N₂. For the first run, 30.0 mmol epoxide, 3.0 mmol mesitylene as internal standard and 1.0 mol% of **1Br** relative to the epoxide were employed. After the reaction, cold Et₂O and hexane (in ratio 4:1) were added under N₂. The fuchsia-coloured mixture was stirred until a precipitate formed. Then, the stirring was stopped and the supernatant was decanted. The obtained solid was washed with cold Et₂O and dried obtaining a dark-purple solid, which was directly used in the second catalytic run without any further purification. For the second run, 30.0 mmol epoxide and 3.0 mmol mesitylene were added to the recovered catalyst and the recycling test was carried out under the same conditions as in the first run.

The description of the synthesis of ligand **2H**, the characterisation of the complexes and the ^1H NMR and FTIR spectra used to quantify the conversions and yields of the catalytic tests are provided in the Supporting Information (SI).

Acknowledgements

We are thankful for the financial support of NWO for a Vidi grant to EO. We acknowledge Yasser Alassmy for scientific discussion and help in the recycling tests.

Keywords: CO₂ fixation • cyclic carbonates • homogeneous catalysis • iron • formazanate ligands

- [1] (a) Q. Liu, L. Wu, R. Jackstell, M. Beller, *Nat. Commun.* **2015**, 6, 5933; (b) J. Artz, T. E. Müller, K. Thenert, J. Kleinekorte, R. Meys, A. Sternberg, A. Bardow, W. Leitner, *Chem. Rev.* **2018**, 118, 434-504.
- [2] M. Aresta, A. Dibenedetto, A. Angelini, *Chem. Rev.* **2014**, 114, 1709-1742.
- [3] (a) S. Inoue, H. Koinuma, T. Tsuruta, *J. Polym. Sci. C Polym. Lett.* **1969**, 7, 287-292; (b) M. North, R. Pasquale, C. Young, *Green Chemistry* **2010**, 12, 1514-1539; (c) P. P. Pescarmona, M. Taherimehr, *Catal. Sci. Technol.* **2012**, 2, 2169-2187.
- [4] A. J. Kamphuis, F. Picchioni, P. P. Pescarmona, *Green Chemistry* **2019**, 21, 406-448.
- [5] (a) J. H. Clements, *Ind. Eng. Chem. Res.* **2003**, 42, 663-674; (b) T. Sakakura, K. Kohno, *Chem. Commun.* **2009**, 1312-1330.

- [6] S. Klaus, M. W. Lehenmeier, C. E. Anderson, B. Rieger, *Coord. Chem. Rev.* **2011**, 255, 1460-1479.
- [7] C. Martín, G. Fiorani, A. W. Kleij, *ACS Catal.* **2015**, 5, 1353-1370.
- [8] (a) T. Aida, S. Inoue, *J. Am. Chem. Soc.* **1983**, 105, 1304-1309; (b) X. B. Lu, R. He, C. X. Bai, *J. Mol. Catal. A: Chem.* **2002**, 186, 1-11; (c) C. J. Whiteoak, N. Kielland, V. Laserna, F. Castro-Gómez, E. Martín, E. C. Escudero-Adán, C. Bo, A. W. Kleij, *Chem. Eur. J.* **2014**, 20, 2264-2275; (d) D. O. Meléndez, A. Lara-Sánchez, J. Martínez, X. Wu, A. Otero, J. A. Castro-Osma, M. North, R. S. Rojas, *ChemCatChem* **2018**, 10, 2271-2277.
- [9] (a) D. R. Moore, M. Cheng, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2003**, 125, 11911-11924; (b) T. Ema, Y. Miyazaki, S. Koyama, Y. Yano, T. Sakai, *Chem. Commun.* **2012**, 48, 4489-4491.
- [10] R. L. Paddock, Y. Hiyama, J. M. McKay, S. T. Nguyen, *Tetrahedron Lett.* **2004**, 45, 2023-2026.
- [11] S. Mang, A. I. Cooper, M. E. Colclough, N. Chauhan, A. B. Holmes, *Macromolecules* **2000**, 33, 303-308.
- [12] For a recent review, see: F. Della Monica, A. Buonerba, C. Capacchione, *Adv. Synth. Catal.* **2019**, 361, 265-282.
- [13] (a) A. Buchard, M. R. Kember, K. G. Sandeman, C. K. Williams, *Chem. Commun.* **2011**, 47, 212-214; (b) C. J. Whiteoak, E. Martín, M. M. Belmonte, J. Benet-Buchholz, A. W. Kleij, *Adv. Synth. Catal.* **2012**, 354, 469-476; (c) M. Taherimehr, J. P. C. C. Sertã, A. W. Kleij, C. J. Whiteoak, P. P. Pescarmona, *ChemSusChem* **2015**, 8, 1034-1042; (d) D. Alhashmialameer, J. Collins, K. Hattenhauer, F. M. Kerton, *Catal. Sci. Technol.* **2016**, 6, 5364-5373; (e) F. Chen, N. Liu, B. Dai, *ACS Sustain. Chem. Eng.* **2017**, 5, 9065-9075; (f) M. Cozzolino, V. Leo, C. Tedesco, M. Mazzeo, M. Lamberti, *Dalton Trans.* **2018**, 47, 13229-13238.
- [14] (a) I. Bauer, H.-J. Knölker, *Chem. Rev.* **2015**, 115, 150309133704007; (b) A. Fürstner, *ACS Cent. Sci.* **2016**, 2, 778-789.
- [15] (a) J. E. Dengler, M. W. Lehenmeier, S. Klaus, C. E. Anderson, E. Herdtweck, B. Rieger, *Eur. J. Inorg. Chem.* **2011**, 336-343; (b) X. Sheng, L. Qiao, Y. Qin, X. Wang, F. Wang, *Polyhedron* **2014**, 74, 129-133; (c) E. Y. Seong, J. H. Kim, N. H. Kim, K.-H. Ahn, E. J. Kang, *ChemSusChem* **2019**, 12, 409-415.
- [16] (a) M. A. Fuchs, T. A. Zevaco, E. Ember, O. Walter, I. Held, E. Dinjus, M. Döring, *Dalton Trans.* **2013**, 42, 5322-5329; (b) M. Adolph, T. A. Zevaco, C. Altesleben, O. Walter, E. Dinjus, *Dalton Trans.* **2014**, 43, 3285-3296; (c) F. M. Al-Qaisi, M. Nieger, M. L. Kemell, T. J. Repo, *ChemistrySelect* **2016**, 1, 545-548; (d) E. Fazekas, G. S. Nichol, M. P. Shaver, J. A. Garden, *Dalton Trans.* **2018**, 47, 13106-13112; (e) F. Della Monica, B. Maity, T. Pehl, A. Buonerba, A. De Nisi, M. Monari, A. Grassi, B. Rieger, L. Cavallo, C. Capacchione, *ACS Catalysis* **2018**, 8, 6882-6893; (f) F. Della Monica, A. Buonerba, V. Paradiso, S. Milione, A. Grassi, C. Capacchione, *Adv. Synth. Catal.* **2019**, 361, 283-288.
- [17] (a) L. Bourget-Merle, M. F. Lappert, J. R. Severn, *Chem. Rev.* **2002**, 102, 3031-3065; (b) R. L. Webster, *Dalton Trans.* **2017**, 4483-4498.
- [18] (a) G. I. Sigeikin, G. N. Lipunova, I. G. Pervova, *Russ. Chem. Rev.* **2006**, 75, 885-900; (b) J. B. Gilroy, M. J. Ferguson, R. McDonald, B. O. Patrick, R. G. Hicks, *Chem. Commun.* **2007**, 412, 126-128; (c) M. C. Chang, T. Dann, D. P. Day, M. Lutz, G. G. Wildgoose, E. Otten, *Angew. Chem. Int. Ed.* **2014**, 53, 4118-4122.
- [19] (a) R. Travieso-Puente, J. O. P. Broekman, M.-C. Chang, S. Demeshko, F. Meyer, E. Otten, *J. Am. Chem. Soc.* **2016**, 138, 5503-5506; (b) F. Milocco, S. Demeshko, F. Meyer, E. Otten, *Dalton Trans.* **2018**, 47, 8817-8823.
- [20] (a) D. L. J. Broere, B. Q. Mercado, E. Bill, K. M. Lancaster, S. Sproules, P. L. Holland, *Inorg. Chem.* **2018**, 57, 9580-9591; (b) D. Broere, B. Mercado, J. Lukens, A. Vilbert, G. Banerjee, H. Lant, S. H. Lee, E. Bill, K. Lancaster, S. Sproules, P. Holland, *Chem. Eur. J.* **2018**, 24, 9417 - 9425.
- [21] D. Broere, B. Q. Mercado, P. L. Holland, *Angew. Chem.* **2018**, 57, 6507-6511.
- [22] R. Travieso-Puente, S. Budzak, J. Chen, P. Stacko, J. T. B. H. Jastrzebski, D. Jacquemin, E. Otten, *J. Am. Chem. Soc.* **2017**, 139, 3328-3331.
- [23] L. Yang, D. R. Powell, R. P. Houser, *Dalton Trans.* **2007**, 955-964.
- [24] (a) J. E. Anderson, C. L. Yao, K. M. Kadish, *J. Am. Chem. Soc.* **1987**, 109, 1106-1111; (b) L. Yu, X. Jin, G. Z. Chen, *J. Electroanal. Chem.* **2013**, 688, 371-378.
- [25] F. Castro-Gómez, G. Salassa, A. W. Kleij, C. Bo, *Chem. Eur. J.* **2013**, 19, 6289-6298.
- [26] A. Rehman, A. M. López Fernández, M. F. M. Gunam Resul, A. Harvey, *Journal of CO₂ Utilization* **2019**, 29, 126-133.
- [27] D. J. Darensbourg, J. C. Yarbrough, C. Ortiz, C. C. Fang, *J. Am. Chem. Soc.* **2003**, 125, 7586-7591.
- [28] J. B. Gilroy, M. J. Ferguson, R. McDonald, B. O. Patrick, R. G. Hicks, *Chem. Commun.* **2007**, 126-128.
- [29] (a) H. Tezcan, Ş. Can, R. Tezcan, *Dyes and Pigments* **2002**, 52, 121-127; (b) J. B. Gilroy, S. D. J. McKinnon, B. D. Koivisto, R. G. Hicks, *Org. Lett.* **2007**, 9, 4837-4840.
- [30] M. C. Chang, E. Otten, *Chem. Commun.* **2014**, 50, 7431-7433.
- [31] S. D. Ittel, A. D. English, C. A. Tolman, J. P. Jesson, *Inorg. Chim. Acta* **1979**, 33, 101-106.
- [32] I. G. Ryabokon, O. M. Polumbrik, L. N. Markovskii, *Zh. Org. Khim.* **1983**, 19, 230-232.
- [33] D. L. J. Broere, B. Q. Mercado, J. T. Lukens, A. C. Vilbert, G. Banerjee, H. M. C. Lant, S. H. Lee, E. Bill, S. Sproules, K. M. Lancaster, P. L. Holland, *Chem. Eur. J.* **2018**, 24, 9417-9425.

FULL PAPER

Mono(formazanate) ferrate(II) complexes bearing labile halide ligands act as single-component homogeneous catalysts for the selective conversion of CO₂ into cyclic carbonate. High selectivity was achieved towards the formation of the cyclic carbonate product for several terminal and internal epoxides without the need for a co-catalyst.

Aeilke J. Kamphuis,^[a] Francesca Milocco,^[b] Luuk Koiter,^[b] Paolo P. Pescarmona^{*,[a]} and Edwin Otten^{*,[b]}

Page No. – Page No.

Highly selective single-component formazanate ferrate(II) catalysts for the conversion of CO₂ into cyclic carbonates