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## PAPER

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## Synthesis of cyclic carbonates from epoxides and carbon dioxide catalyzed by an easy-to-handle ionic iron(III) complex†

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We report the successful utilization of monometallic, ionic iron( $\mu$ )– and iron( $\mu$ )–N<sub>2</sub>O<sub>2</sub>–ligand-systems as highly active homogeneous catalysts for the conversion of CO<sub>2</sub> with different epoxides to cyclic carbonates. The catalytic tests were performed using propylene oxide (PO) and a range of nine substituted epoxides. Terminal monosubstituted oxides react quantitatively.

## Introduction

Being the final product of all the energy-producing processes involving carbon-based substances (*e.g.* burning fossil- and biofuels), carbon dioxide is omnipresent in our atmosphere. Its concentration is continuously increasing since the beginning of the industrial revolution, representing in 2004 77% of the total anthropogenic greenhouse gases with an emission of 38 gigatonnes.<sup>1</sup> This nearly endless availability and *de facto* "renewability" together with a low toxicity make it a perfect C1-synthon for organic synthesis.<sup>2,3</sup>

In recent years many attempts have been made to use the thermodynamically stable  $CO_2$  in the synthesis of valuable chemicals and several processes could be actually industrialized. Some of them with a promising future like *e.g.* the synthesis of urethane derivatives, cyclic carbonates and polycarbonates. Older industrial processes like the synthesis of hydroxy-benzoic acids, the production of urea and methanol still play an important role in the "positive image" of the  $CO_2$ -chemistry.<sup>4</sup>

Epoxides can be seen as high-energy starting materials which are ideal for engaging a reaction (catalytic or not) with the inert  $CO_2$ . One class of fully "atom-efficient", biodegradable products gained from this reaction includes on the one

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**Scheme 1** Possible products of the reaction of CO<sub>2</sub> and epoxides.

hand cyclic carbonates and on the other hand aliphatic polycarbonates (Scheme 1).<sup>5</sup>

Cyclic carbonates increasingly find an industrial application like *e.g.* their use as non-toxic, polar, high boiling-point solvents, as electrolytes in lithium ion batteries or as reactive intermediates (*e.g.* in ring-opening polymerizations, reactions with amines, alcohols, thiols, and carboxylic acids).<sup>6</sup>

For a successful industrial utilization, the conversion of  $CO_2$  and epoxides to cyclic carbonates requires, as a catalytic system, mostly a synergetic combination of a Lewis acid and a Lewis base. Most of the catalytic systems reported earlier in the literature needed high temperatures and pressures to achieve reasonable conversions, limiting in some way the practicability of the synthesis. However, new promising approaches published within the last decade showed that high cyclic carbonate yields could be reached using mild operating conditions.<sup>7-10</sup> Generally speaking a wide range of compounds can be used as catalysts, encompassing onium salts (with or without supplementary metal salts), some ionic liquids, organocatalysts (bases), metal halides, metal oxides and transition metal complexes.<sup>11,12</sup> For the latter a wide range of elements have been successfully tested as catalysts in the "CO2-involving" formation of cyclic carbonates. They are

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ranging from complexes of the "less toxic" zinc and aluminium to the more problematic tin, cobalt and chromium.<sup>11–13</sup> The two latter metals are currently the most promising candidates despite a high toxicity causing an effective separation of the catalyst to be paramount.

Iron-systems have the advantage of displaying a low intrinsic toxicity but also a high catalytic activity in the conversion of  $CO_2$  and epoxides to carbonates.<sup>14-16</sup> In this contribution we investigated the catalytic activity of the iron-N<sub>2</sub>O<sub>2</sub>-systems 2, 3 and 4 towards different epoxides and CO<sub>2</sub>.

## **Results and discussion**

#### Synthesis of the catalysts

The synthesis of the catalytic Fe(n)- and Fe(m)-systems 2 and 3 is shown in Scheme 2. The ligand 1 is formed by condensation of *ortho*-phenylene diamine and ethyl 2-cyano-3-ethoxyacrylate in yields of up to 92%. According to a procedure introduced by Jäger<sup>17,18</sup> ligand 1 reacts with  $Fe(OAc)_2$  in DMF, pyridine being added afterwards as a weak coordinating ligand.

The obtained iron(II) complex 2 is air-stable for weeks. Although it can be taken from elemental analysis that the iron should be pentacoordinated, it is known from the literature to be six-fold coordinated *via* an intermolecular interaction involving the nitrile substituent of a neighbouring molecule, as suggested by the splitting of the  $\nu$ (CN) absorption band in the IR spectra.<sup>17–19</sup> Compound 2 can be further oxidized under mild conditions by iodine to afford the iron(III)–N<sub>2</sub>O<sub>2</sub>-system 3. As many iron(III)-based systems are paramagnetic, reliable spectroscopic NMR data are not easily available and the structure of the complexes has to be ascertained *via* elemental analysis and MS-ESI. UV-visible-, infrared- and electron spin resonance spectroscopy provide also complementary information on ligand and coordination geometry. For instance complex 3 forms a deep brown solution in acetonitrile with



Scheme 2 Synthesis of the iron catalysts 2 and 3



Fig. 1 ESR spectra of complex 3 in the solid state and in  $\text{CH}_3\text{CN}$  solution recorded at 123 K.

two intense bands at  $\lambda_{\max}(\varepsilon) = 300 \text{ nm} (32739 \text{ M}^{-1} \text{ cm}^{-1})$  and 353 nm (22 272 M<sup>-1</sup> cm<sup>-1</sup>) which can be tentatively assigned to  $\pi$ - $\pi$ \* intra-ligand transitions localized predominantly on phenyl ring and conjugated –CN moieties.<sup>20,21</sup> In addition the analysis of powder ESR spectra of complex 3 reveals features regularly found in the literature for iron(m) complexes even though a definitive attribution of the Landé *g* effective factors remains complicated.<sup>22</sup>

The X-band spectrum (Fig. 1) displays a strong isotropic signal at  $g_{\text{eff}}$  = 4.1793 and two broad signals of lower intensity at  $g_{\rm eff}$  = 2.1383 and  $g_{\rm eff}$  = 2.0056. According to the literature<sup>23–25</sup> these data suggest the presence in the solid of two iron(m) complexes with different coordination geometries around the metal. For instance, the presence of a high-spin Fe<sup>3+</sup>-complex  $(3d^5, S = 5/2)$  in a distorted environment would account for the isotropic signal around  $g \approx 4.^{25}$  This coordination geometry around the iron can be either octahedral (with one weak axial ligand) or square pyramidal/trigonal bipyramidal. In contrast, a second low spin  $Fe^{3+}$  (S = 1/2) complex in a more symmetric environment could be responsible for the broad signal around  $g \approx 2.1$ . This species would display an octahedrally coordinated iron(m) with two pyridines in axial positions. The shoulder at  $g_{\rm eff}$  = 2.0056 can be attributed to a low-spin, octahedrally coordinated iron(m) with one pyridine and one nitrile in axial positions. This hypothesis is further backed by the spectra of complex 3 in acetonitrile measured at 123 K. The isotropic signal at  $g_{\text{eff}}$  = 4.1793 together with a second signal of lower intensity at  $g_{\text{eff}}$  = 2.0056 speaks in favour of two different coordination geometries around the iron(m) centers. The weakening/broadening of the shoulder at g = 2.0056 supports its attribution to an iron(m) complex with pyridine and ligand's nitrile in axial positions, the competition between nitrile of a neighbouring ligand and acetonitrile being displaced in favour of the latter.

Changing the base in favour of *N*-methylimidazole (*N*-MeIm) yields the related  $iron(n)-N_2O_2/N$ -MeIm-complex 4. The synthesis is shown in Scheme 3.

Single crystals suitable for a structure determination were obtained from the reaction mixture, by leaving it standing at



Scheme 3 Synthesis of the iron catalyst 4.

room temperature. After one night small deep red crystals were formed. Crystals of compound **4** are triclinic, crystallizing in the space group  $P\bar{1}$  (no. 2). (Crystallographic data of the structure have been deposited at the Cambridge Crystallographic Database Centre, supplementary publication Nos. CCDC 906827.) The thermal ellipsoid plot of **4** is shown in Fig. 2 whereas crystallographic data, selected bond lengths and angles of **4** are listed in Tables **1** and **2**, respectively.



Fig. 2 ORTEP drawings (50% probability) of 4. For clarity, hydrogen atoms have been removed.

#### Table 1 Crystallographic data for 4

Chemical formula	C <sub>29</sub> H <sub>35</sub> FeN <sub>9</sub> O <sub>5</sub>
Formula mass	645.51
Crystal system	Triclinic
a/Å	9.6875(7)
b/Å	10.7398(8)
c/Å	15.2491(11)
$\alpha / ^{\circ}$	100.4530(10)
$\beta / ^{\circ}$	97.6860(10)
$\gamma/\circ$	91.2450(10)
Unit cell volume/Å <sup>3</sup>	1544.5(2)
Temperature/K	173(2)
Space group	$P\overline{1}$ (No. 2)
No. of formula units per unit cell. Z	2
No. of reflections measured	23 122
No. of independent reflections	7165
Rint	0.0294
Final $R_1$ values $(I > 2\sigma(I))$	0.0406
Final w $R(F^2)$ values $(I > 2\sigma(I))$	0.1094
Final $R_1$ values (all data)	0.0501
Final $wR(F^2)$ values (all data)	0.1159
( ( dutu)	

Table 2 Selected bond lengths (Å) and angles (°) for 4

Fe(1)-N(1) Fe(1)-N(2) Fe(1)-N(5) Fe(1)-N(7)	2,1285(17)
Fe(1)-N(2) Fe(1)-N(5) Fe(1)-N(7)	
Fe(1)-N(5) Fe(1)-N(7)	2.1070(17)
Fe(1)-N(7)	2.1827(17)
	2.2217(17)
Fe(1)-O(1)	2.0647(14)
Fe(1)-O(3)	2.0834(14)
C(4)-N(3)	1.149(3)
C(1)-O(1)	1.244(2)
C(1)-O(2)	1.346(2)
C(2)-C(3)	1.413(3)
C(1)-C(2)	1.427(3)
C(2)-C(4)	1.423(3)
C(3)-N(1)	1.311(3)
C(7)-N(1)	1.416(3)
O(1)-Fe(1)-O(3)	107.23(6)
O(1)-Fe(1)-N(2)	165.39(6)
O(3)-Fe(1)-N(2)	87.21(6)
O(1)-Fe(1)-N(1)	87.17(6)
O(3)-Fe(1)-N(1)	165.39(6)
N(2)-Fe(1)-N(1)	78.32(6)
O(1)-Fe(1)-N(5)	89.84(6)
O(3)-Fe(1)-N(5)	90.05(6)
N(2)-Fe(1)-N(5)	92.46(7)
N(1)-Fe(1)-N(5)	92.51(7)
O(1)-Fe(1)-N(7)	87.13(6)
O(3)-Fe(1)-N(7)	87.21(6)
N(2)-Fe(1)-N(7)	91.42(7)
N(1)-Fe(1)-N(7)	91.14(7)
N(5)-Fe(1)-N(7)	175.13(7)

Complex 4 displays octahedral coordination geometry around the metal center with two *N*-methylimidazole molecules in the axial position and the N<sub>2</sub>O<sub>2</sub>-ligand occupying the equatorial plane. One molecule of dimethylformamide per iron complex is present in the molecular structure, showing weak interactions with the ligands' nitrile groups as suggested in Fig. 2 (more details, with intermolecular distances, can be found in the ESI<sup>†</sup>). The diverse interactions with the CN groups have a logical effect on the IR-spectrum, leading to an overlap in the related C=N stretching band region. Owing to the fact that compound 4 is coordinatively saturated and that the DMF-ligand interactions remain weak, the splitting of the resulting  $\nu$ (CN) measured in the spectrum is smaller than in the case of the pyridine complex 2, Fe(N<sub>2</sub>O<sub>2</sub>)Py (8 cm<sup>-1</sup>  $\nu$ s. 17 cm<sup>-1</sup>).

The overall structure of 4 is comparable to the iron(n)– $N_2O_2/Py$  complex, Fe( $N_2O_2$ )Py<sub>2</sub>\*Py, investigated by Jäger *et al.*<sup>26</sup> The iron atom occupies the center of an octahedron, slightly distorted from the ideal geometry (distortion from the mean  $N_2O_2$ -plane: 3.1 pm), the  $N_2O_2$  ligand being almost planar as in Jäger's complex and in Fe–salen derivatives.<sup>27</sup> The bond lengths found within the  $N_2O_2$  coordination sphere are within a small range, the Fe–O bonds being a tad shorter than the Fe–N ones: Fe(1)–N(1) and Fe(1)–N(2) with 2.1285(17) Å and 2.1070(17) Å while Fe(1)–O(1) and Fe(1)–O(3) amount to 2.0647(14) Å and 2.0834(14) Å respectively. As expected from the literature, the Fe–N apical bonds are, with Fe(1)–N(7), 2.2217 Å, and Fe(1)–N(2), 2.18127 Å, longer than the equatorial ones and similar to those found in the connected homoleptic

complex  $[Fe(NMi)_6][PF_6]$ .<sup>28</sup> The four (NO)–Fe angles within the plane suggest an influence of the ethyl ester groups on the coordination environment at the metal center. The angle O(3)–Fe–O(1) which involves both ester groups is the widest with 107.2° whereas the opposite angle, N(1)–Fe–N(2), can be seen as compressed with only 78.3°.

The two remaining N–Fe–O angles are similar, around 87.2°. The angle involving iron and the two axial nitrogens of the imidazoles amounts to 175.13(7)°, towards values found in N4–iron/*N*-methylimidazole systems like *e.g.* iron porphyrins or phthalocyanins,<sup>29</sup> whereas the Jäger's Fe–pyridine complex displays a N–Fe–N angle of 170.31°. The interatomic distances measured within this ligand class<sup>30</sup> illustrate the strong interaction with the metal center: as an example, all the C–C distances involving C(2) are in a narrow range (around 1.42 Å) while the C–N involving the coordinating nitrogens (*e.g.* C3–N1) are significantly shorter than the standard C–N bonds found in amines (C(3)–N(1): 1.311(3) Å instead of 1.45 Å).<sup>31</sup>

Unfortunately attempts to oxidize complex 4 with iodine in order to isolate an iron(m)(*N*-MeIm) complex analogue to 3, also with solvents other than DMF (*e.g.* THF and CHCl<sub>3</sub>), did not succeed, delivering only complex mixtures. Likewise, trying to oxidize compound 3 by bubbling air through the solution and vigorous stirring delivered no clear results.

#### Catalytic tests with propylene oxide

The catalytic screening of iron(II) complex 2 and iron(III) complexes 3 and 4 involving propylene oxide and carbon dioxide was performed in 70 ml autoclaves under solvent-free conditions. Standard reaction time was 20 h. The results are summarized in Table 3. In agreement with similar studies,<sup>32–34</sup> the conversions were directly determined using <sup>1</sup>H-NMR spectroscopy with an internal standard, a swift and reliable analytical method for such samples if one considers the sometimes tedious separation of the final cyclic carbonate (*e.g.* a complex distillation step).<sup>34,35</sup>

Catalyst 2 alone showed no reactivity towards the  $CO_2$  conversion (entry 2). The co-catalyst TBAB alone showed a conversion of 35% (entry 1), which is not surprising knowing that

Entry	Catalyst	Mol%	<i>p</i> /bar	$T/^{\circ}\mathrm{C}$	% Yield <sup>b</sup>	TON <sup>c</sup>
1	TBAB	1	50	80	35	35
2	2	1	50	80		_
3	2 TBAB	0.2	35	80	37	185
4	2 TBAB	1	50	80	91	91
5	3	0.5	50	80	99	198
6	3	0.2	50	80	99	495
7	3	0.2	50	50	76	380
8	3	0.2	50	100	96	480
9	3	0.1	35	80	69	690
10	3	0.2	2	80	36	180
11	4	0.2	50	80	_	_
12	4 TBAB	0.2	50	80	75	375
13	4 TBAB	1	50	80	94	94

<sup>*a*</sup> Reaction time 20 h. <sup>*b*</sup> Yields by NMR. <sup>*c*</sup> TON = mol<sub>PC</sub>/mol<sub>KAT</sub>.

onium salts are on their own active towards this reaction.<sup>36,37</sup> A synergetic effect can be seen considering the reaction with a combined catalyst and a co-catalyst (entry 3 + 4). 0.2 mol% of the catalyst-co-catalyst mixture showed a yield of 37% cyclic carbonate (entry 3) and 1 mol% a conversion of even 91% (entry 4). After oxidation with iodine, the iron(III) complex 3 displays a much higher activity than the iron catalyst in the lower oxidation state 2 (entries 5 and 6). The reasons for the observed increased reactivity leading to a quantitative conversion of propylene oxide are manifold: (i) two pyridine molecules in the coordination sphere of the complex are able to act as co-catalysts, (ii) a higher Lewis acidity of the metal centre and (iii) the ionic character of complex 3 which comprises an iodide anion also able to interact with an epoxide. It can be easily seen that within complex 3, all the catalytic components needed for a successful insertion of CO<sub>2</sub> into an epoxidic ring are present and that no supplementary co-catalyst or the challenging synthesis of a co-catalyst anchored to the ligand is needed.<sup>38-40</sup> In order to find the optimal reaction conditions, different reaction temperatures and catalyst concentrations were tested. At 50 °C with 0.2 mol% of 3 the reaction only produces 76% of propylene carbonate (entry 7). The reaction at 100 °C is not that effective as at 80 °C with a yield of 96%, caused by a slow degradation of the catalyst, which makes catalyst recycling problematic (entry 8). At 80 °C the reaction can be easily performed to deliver high yields of cyclic carbonates permitting potential catalyst recycling.

Lowering the catalyst concentration to only 0.1 mol% leads to a lower yield of propylene carbonate of 69% but logically rises the TON up to 690 (entry 9). Best conversion was achieved with a catalyst concentration of 0.2 mol% and a temperature of only 80  $^{\circ}$ C (entry 6).

Low-pressure experiments were carried out in a 70 ml autoclave continuously connected to a gas cylinder *via* a backpressure regulating valve, pressing 2 bar of  $CO_2$  into the reaction mixture. After heating the reaction mixture for 20 h, 36% of the propylene oxide was converted to propylene carbonate (entry 10).

Complex 4 as  $iron(\pi)$  complex shows no catalytic activity without the addition of a cocatalyst, as already shown with complex 2 (entries 2 and 11). Only the addition of a cocatalyst (in this case again TBAB) leads to a conversion to propylene carbonate with a satisfactory yield (75%) (entry 12). The higher PC yield observed with compound 4 and TBAB at low catalyst loadings (entries 12 and 3) can be tentatively explained by the higher nucleophilicity of *N*-methylimidazole (compared to pyridine) and/or an active role in the ring opening of the epoxide.

The reactions with propylene oxide and **3** proceed fast. In Fig. 3 a typical diagram displaying temperature and pressure against reaction time is represented. The dashed line shows the reaction with catalyst **3**, the continuous one shows the reaction with **2** and TBAB as a co-catalyst. The reaction in the presence of **2** needs 20 h to reach a comparable conversion to the reaction with **3** after 3 hours.



**Fig. 3** Comparison of the recorded pressures during the reaction of propylene oxide and  $CO_2$  with the catalysts **2** (Fe( $\mathfrak{n}$ ) + TBAB) and **3** (Fe( $\mathfrak{m}$ )).

Compared to other iron catalysts in the literature, the amount of iron used in our conversions is lower. Moreover, the examples from the literature used co-catalysts like tetrabutylammonium bromide (TBAB), tetrabutylammonium iodide and bis(triphenylphosphine)-iminium (TBAI) chloride (PPNCl), which are not necessary with our most effective catalyst system 3. Related studies with iron catalysts were published by Rieger and co-workers<sup>15</sup> (quantitative conversion of PO: 1 mol% Fe(II)-catalyst, TBAB as a co-catalyst, 100 °C, 15 bar CO<sub>2</sub>, 2 h), the research group of Williams<sup>14</sup> (91% conversion of PO: 1 mol% iron in Fe(II)-catalyst, 1 mol% PPNCl, 25 °C, 1 atm CO<sub>2</sub>, 48 h) and Kleij et al.<sup>16</sup> (96% conversion of PO: 1 mol% iron in Fe(III)-catalyst, 5 mol% TBAI, 25 °C, 2 bar CO<sub>2</sub>, 18 h).

Both catalysts show a very high selectivity in the formation of cyclic carbonates. IR analysis of the products displayed neither  $\nu_{as}(C=O)$  vibration typical for polycarbonate  $(1752 \text{ cm}^{-1})^{41}$  nor a massive stretching  $\nu(C-O)$  band (around 1050 cm<sup>-1</sup>) typical for polyethers, potential products of a ring opening polymerisation of the epoxide. Absorption bands related to potential traces of 1,2-diols as hydrolysis' products ( $\nu(OH)$  and  $\delta(OH)$  at 3600–3650 cm<sup>-1</sup> and around 1600 cm<sup>-1</sup> respectively)<sup>42</sup> were not observed.

Time resolved *in situ* IR spectroscopy, ran with a Mettler Toledo React-IR 45m, supports that the formation of cyclic carbonate from propylene oxide using our catalysts does not involve the degradation of a prior formed polycarbonate.<sup>43,44</sup>

To check the possibility of recycling catalyst 3, five successive runs with propylene oxide were started. After every experiment the resulting propylene carbonate was distilled and the residue catalyst was collected and reused in the next batch following the standard procedure (80 °C, 50 bar  $CO_2$ , 20 h, catalyst concentration 0.2 mol%). The catalyst loss was evened up by proportionally lowering the added amount of propylene oxide in order to maintain the catalyst-to-epoxide ratio (1:500).

Fig. 4 shows the yields per experiment. The first use of catalyst 3 is the most successful one, with a yield of 99%. The following batches display yields between 78% and 91%, showing that 3 can be reasonably recycled after removing the reaction product.



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Fig. 4 Yields in recycling experiments of catalyst 3 (0.2 mol%) with propylene oxide at 80  $^\circ$ C and 50 bar.

#### Tests with other epoxides

To point out the broad applicability of the ionic catalyst 3, we performed a broader screening using a range of commercially available epoxides. The results of the cyclization with CO<sub>2</sub>, ran under an optimized reaction temperature of 80 °C and a catalyst concentration of 0.2 mol%, are listed in Table 4. Yields were estimated by <sup>1</sup>H NMR using an internal standard (tetrachloroethane and, if not possible, chloroform) to quantify the catalytic activity. Under the selected conditions no conversion was found using epoxides with more than one bulky substituent like 1,2-epoxy-2-methylpropane, 2,3-epoxy-2-methylbutane and cyclohexene oxide (entries 8-10). But also a sterically more hindered mono-substituted epoxide like 3,3-dimethyl-1,2epoxybutane showed no conversion to the corresponding cyclic carbonate (entry 7). This suggests either an unfavourable competition between coordination of the epoxide and decoordination of a pyridine molecule at the iron centre or, if a coordination indeed takes place, an ineffective nucleophile attack of the iodide anion at the epoxide. The mechanism of the reaction is under further study and details on its exact nature together with kinetic data will be reported in due course.

The other monosubstituted epoxides showed very high yields of their cyclic carbonates, 1,2-epoxyhexane and 2,3-epoxypropyl benzene could be for instance quantitatively converted (entry 2 + 6). The other mono-substituted epoxides like styrene oxide, epichlorhydrine, 2,3-epoxypropyl phenyl ether and allyl glycidyl ether delivered also the desired cyclic carbonates in nearly quantitative yields (entries 1, 3–5).

## Conclusion

We reported a highly selective iron-based, easy-to-handle catalytic system for the conversion of epoxides with  $CO_2$  to cyclic carbonates. Based on a ligand system reported by Jäger *et al.* in the early eighties, we were able to synthesize iron( $\pi$ ) and iron( $\pi$ ) complexes on a multi-gram scale from commercially available starting materials (Fe( $\pi$ ) only with pyridine as a ligand). The three complexes were firstly tested for the

Table 4 CO<sub>2</sub>/epoxide coupling catalysed by iron-system 3<sup>a</sup>

Entry	Epoxide	Product	<i>p</i> /bar	% Conversion <sup>b</sup>	TON <sup>c</sup>
1	Ph	Ph	50	96	480
2	Ph	Ph	50	100	500
3	Ph <sup>0</sup>		35	98	490
4	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~		50	99	495
5	ci		35	95	475
6	Bu		50	100	500
7	t-Bu		50	_	_
8	$\checkmark$		50	_	_
9	$\checkmark$		50	_	—
10	$\bigcirc$	<i>f</i>	50	_	_

<sup>*a*</sup> Reaction conditions: catalyst loading 0.2 mol%, reaction time 20 h, reaction temperature 80 °C. <sup>*b*</sup> Conversion by <sup>1</sup>H-NMR with an internal standard. <sup>*c*</sup> TON =  $mol_{cycl.carb}/mol_{KAT}$ .

conversion of propylene oxide. The iron( $\pi$ ) complexes 2 and 4 need a rather high catalyst concentration and the addition of a co-catalyst to fulfil the reaction. The more active iron( $\pi$ ) system 3 demonstrates a high activity without co-catalysts in a short reaction time. The screening tests were extended to a wider range of epoxides and showed the very high catalytic activity of this system towards terminal, mono-substituted epoxides and CO<sub>2</sub>. Kinetics of the reaction and spectroscopic investigation of the mechanism are the topic of ongoing studies.

## **Experimental section**

#### General

All reactions were performed under argon using standard Schlenk techniques. The chemicals were purchased from Sigma Aldrich except  $Fe(OAc)_2$  (abcr), pyridine (AppliChem) and iodine (Roth). Propylene oxide and pyridine were dried over CaH<sub>2</sub> before their use. <sup>1</sup>H-NMR spectra were obtained

with a Varian Inova instrument equipped with an Oxford magnet (9.4 T, 400 MHz for <sup>1</sup>H). IR spectra were obtained with a Varian 660-IR FT-IR Spectrometer. Elementary analysis was performed with a CHNS-Analyser from the company Elementar. The ESR measurements were recorded in perpendicular mode on an X-band Joel Jes Fa 200 spectrometer equipped with a cylindrical mode cavity and a liquid helium cryostat. The ESR measurements were performed in guartz tubes at 123 K (9.45 GHz, 1 mW microwave power). The analysis and simulation of the ESR data was done with the Jes-Fa Series software package (Version 2.2.0). Mass spectra were measured with a Bruker ApexOe hybrid 9.4 T FT-ICR. UV-Vis spectra were measured with an MCS 501 UV-NIR (Zeiss). The X-ray analyses were performed on a Bruker Apex II Quazar diffractometer. 2124 frames were collected with an irradiation time of 1 s per frame. Integration of the data proceeded with SAINT, the data were corrected for Lorentz- and polarisation effects, and an experimental absorption correction with sadabs was performed.45 For searches relating to single-crystal X-ray diffraction data, the Cambridge Structural Database was used.46 Crystallographic data have been deposited at the Cambridge Crystallographic Database Centre (CCDC), supplementary publications No. CCDC 906827. Figures were prepared with the appropriate software of the CCDC, MERCURY 3.0 (Build RC5) for Windows<sup>47</sup>. Ligand 1 and the iron(II) catalyst 2 were synthesized according to a literature procedure.<sup>17</sup>

Fe(m) complex 3. Complex 2 (3.0 g, 6.16 mmol) was dissolved in 30 ml of pyridine. Afterwards iodine (780 mg, 3.07 mmol) was added and the solution was stirred for 48 h at room temperature. The solvent was removed under reduced pressure leaving 3 as a dark brown solid (4.24 g, 99%). IR (KBr): 1611 cm<sup>-1</sup> ( $\nu$ (C=C),  $\nu$ (C=N)), 2205 cm<sup>-1</sup> ( $\nu$ (C=N)). MS: (ESI+) m/z (%): 408.1 (58)  $[M-2Py-I]^+$ , 487.1 (100)  $[M-Py-I]^+$ , 816.1 (31)  $[2(M-2Py-I)]^+$ , 847.1 (63)  $[2(M-2Py-I)^+OMe]^+$ . HR-MS: (ESI+) m/z (%) calcd for  $C_{18}H_{16}FeN_4O_4^+$ : 408.0516, found: 408.0516 (58); calcd for  $C_{19}H_{19}FeN_4O_5Na^+$ : 462.0597, found: 462.0599 (29); calcd for C<sub>23</sub>H<sub>21</sub>FeN<sub>5</sub>O<sub>4</sub><sup>+</sup>: 487.0938, found: 487.0939 (100); calcd for C36H32Fe2N8O8: 816.1038, found: 816.1041 (31); calcd for C37H35Fe2N8O9: 847.1222, found: 847.1221 (63). Anal. calcd for C<sub>28</sub>H<sub>26</sub>FeIN<sub>6</sub>O<sub>4</sub>: C, 48.51; H, 3.78; N, 12.12, found: C, 49.11; H, 3.95; N, 12.61, UV/Vis (acetonitrile):  $\lambda_{\text{max}}(\varepsilon) = 300 (32739), 353 \text{ nm} (22272 \text{ mol}^{-1})$  $dm^{3} cm^{-1}$ ).

**Fe(II) complex 4.** The ligand **1** (3.12 g, 8.81 mmol) was dissolved in 35 ml DMF and Fe(OAc)<sub>2</sub> (1.53 mg, 8.81 mmol) was added. The reaction mixture was heated to 75 °C and stirred for half an hour. Afterwards *N*-methylimidazole (1.45 g, 17.62 mmol) was added and the reaction mixture was stirred at 75 °C for 1 h. Then it was cooled to room temperature and left standing without stirring overnight. Deep red crystals were collected by filtration and dried (4.09 g, 6.33 mmol, 72%). IR (KBr): 1612 cm<sup>-1</sup> ( $\nu$ (C=C),  $\nu$ (C=N)), 2196 cm<sup>-1</sup>, 2187 cm<sup>-1</sup> ( $\nu$ (C=N)). MS: (ESI+) *m*/*z* (%): 408.0 (10) [M-2*N*-MeIm], 409.0 (9) [M-2*N*-MeIm + H]<sup>+</sup>, 490.0 (8) [M-*N*-MeIm]. HR-MS: (ESI+) *m*/*z* (%) calcd for C<sub>18</sub>H<sub>16</sub>FeN<sub>4</sub>O<sub>4</sub>Na: 431.0413, found: 431.0417 (13);

calcd for  $C_{19}H_{19}FeN_4O_5Na$ : 462.0597, found: 462.0601 (12); calcd for  $C_{22}H_{22}FeN_6O_4$ : 490.1046, found: 490.1049 (100); calcd for  $C_{36}H_{32}Fe_2N_8O_8$ : 816.1036, found: 816.1044 (22). Anal. calcd for  $C_{29}H_{35}FeN_9O_5$ : C, 53.96; H, 5.47; N, 19.53, found: C, 53.81; H, 5.606; N, 19.37.

#### Autoclave tests

The tests were performed in a screening test-bench consisting of 70 ml autoclaves (mat. 1.4571 (SS 316Ti), 70 ml,  $p_{\rm max}$  200 bar, T<sub>max</sub> 250 °C) equipped with magnetic stirrers and P, T-Acquisition via multi-meters (Agilent 34970A Data Acquisition/Data Logger Switch Unit + 34901A 20 Channel Multiplexer) and PCs. The heating was performed with an aluminium heating block controlled via the electronic contact thermometer of the magnetic stirrers. The dried autoclaves were filled with the catalyst and set under vacuum for 1 h. Afterwards the epoxide was added under argon *via* one of the autoclave's ports and the reaction mixture was pressurized with CO<sub>2</sub>. This procedure was chosen owing to the low reactivity of complexes 2, 3 and 4 with epoxides alone (no ring opening polymerisation of the epoxides was observed under the chosen experimental conditions). With all epoxides except propylene oxide the autoclave was cooled to 0 °C during the CO<sub>2</sub> loading ensuring that enough CO<sub>2</sub> was available for the reaction (CO<sub>2</sub>/epoxide molar ratio around 3). Once the autoclave was heated, pressure and temperature were recorded every 30 seconds during the whole reaction time. After the reaction the autoclaves were cooled down, slowly vented in a fume hood, opened and the products collected. The analysis was done via <sup>1</sup>H-NMR and FT-IR spectroscopy. The reproducibility of a typical reaction was assessed via performing numerous tests with complex 3 and PO (2-3 runs for each entry/ entries 5-10) and found an overall very good reproducibility. The rest of the runs, performed with the other epoxidic substrates and catalysts, are single experiments performed within the same screening campaign.

#### Low-pressure experiment

A first low pressure screening test was performed in a standard glass equipment with two high performance reflux condensers at -20 °C, partly filled with metallic Raschig rings to enhance the cooling efficiency, with moderate success. Hence the low-pressure experiments were carried out in a 70 ml autoclave permanently connected during the reaction to a gas cylinder pressing 2 bar CO<sub>2</sub> into the mixture. The gaseous propylene oxide is kept in the autoclave by means of a back pressure regulator. The dried autoclave is operated the same way as for the high pressure experiments: filled with catalyst 3 and propylene oxide under an argon atmosphere, at 2 bar CO<sub>2</sub> pressurized and heated for the same reaction time. Afterwards the products were analyzed by <sup>1</sup>H-NMR spectroscopy.

#### In situ IR experiments

The experiments were carried out in a "home-made" stainless steel 316Ti autoclave (mat. 1.4571, 150 ml,  $p_{\text{max}}$  300 bar,  $T_{\text{max}}$  200 °C, magnetic stirring, aluminium heating block with TIC).

This vessel is equipped with a "sidewise-attached" diamond probe sensor (DiComp<sup>TM</sup> window) and coupled *via* a Sentinel<sup>TM</sup> K4 conduit to a ReactIR 45m from Mettler-Toledo. The reaction was monitored with the dedicated software iCIR (version 4.2). The autoclave was flushed with argon. Afterwards 10 ml of dichloromethane and 40 ml of propylene oxide were added. The autoclave was closed and heated to 80 °C. A cartridge was installed at one of the autoclave's accesses and also flushed with argon. Then the catalyst was dissolved in 15 ml of dichloromethane, and injected into the cartridge. When the reaction mixture reached the desired temperature, the background for the measurement was collected. Afterwards the measurement was started and the catalyst solution was pressed into the reaction mixture with 50 bar of CO<sub>2</sub>.

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