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Fighting Fenton Chemistry: A Highly Active Iron(III) Tetracarbene Complex in Epoxidation Catalysis

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Organometallic Fe complexes with exceptionally high activities in homogeneous epoxidation catalysis are reported. The compounds display Fe^{II} and Fe^{III} oxidation states and bear a tetracarbene ligand. The more active catalyst exhibits activities up to 183 000 turnovers per hour at room temperature and turnover numbers of up to 4300 at −30 °C. For the Fe^{III} complex, a decreased Fenton-type reactivity is observed compared with Fe^{II} catalysts reported previously as indicated by a substantially lower H_2O_2 decomposition and higher (initial) turnover frequencies. The dependence of the catalyst performance on the catalyst loading, substrate, water addition, and the oxidant is investigated. Under all applied conditions, the advantageous nature of the use of the Fe^{III} complex is evident.

Introduction

Fluctuating metal prices and declining resource stocks urge the chemical industry towards more abundant (and therefore, cheaper) catalyst metals for all major applications.[1] In contrast to this, most organometallic catalysts applied currently for fine chemical synthesis are based on expensive noble metals.[1c,2] Complexes of first-row transition metals, especially Fe, present a promising alternative. Fe is the most abundant transition metal in the earth's crust (4.7 wt%) and is usually considered nontoxic.[1c,3] In the human body, the ferritin system regulates the Fe concentration, which renders the majority of Fe compounds effectively harmless.[4] In addition, Fe has a diverse redox reactivity and a tunable Lewis acidic character.[1a] Smart ligand design can offer a plethora of Fe catalysts applicable to a broad range of organic transformations.[1a,5]

Expensive, toxic, or rare catalyst metals have already been replaced by Fe in a few homogeneous reactions Fe (e.g., cross-coupling reactions).[1a,b,6] For some of these systems it was found that the performance of Fe cross-coupling catalysts apparently depends on the commercial source of the Fe salts used in catalysis.[7] The most active catalysts had a higher content of trace metal impurities, which thus underlines the higher catalytic activity of these trace metals. Beside cross-coupling reactions, Fe-catalyzed hydrosilylation reactions that give anti-Markovnikov products exclusively were reported by Chirik et al.[8] These results led to enantioselective hydrosilylation catalysis and to industrial applications in cooperation with Momentive.[9] Although this example supports the hope for more active Fe-based catalysts, other Fe-based reactions require high catalyst loadings and long reaction times.[1a,b,10] Some applications that include Fe-catalyzed olefin metathesis have only been predicted in computational studies.[1a,11]

For oxidation reactions, the goal to replace existing catalysts by Fe complexes has proven to be very demanding. The main reason for this is the oxophilicity of Fe compounds and their lability under oxidative conditions.[12] Still, Fe-catalyzed C–H bond oxidations and epoxidations are feasible. Porphyrin ligands were the first to be used,[13] followed by nonheme catalysts, which have been of increasing interest during the past decade.[3b,14] Although the activity of these catalysts has improved significantly, the performance of the most active Rh and Mo complexes is still unchallenged.[15]

To find active species of nonheme Fe complexes has been a prominent goal of investigations during the last two decades.[14c,16] The predominant current opinion is that for the majority of catalyst systems the first intermediate in the formation of an active catalyst is an Fe^{III}–OOH complex.[14c,k,l] Although some studies suggest this complex to be active in epoxidation catalysis,[14a,17] Nam et al. were able to demonstrate that a Fe^{III}–OOH moiety that bears a pyridine-based ligand is not a potent oxidant for the epoxidation of olefins,[16b] which prompts the question as to the nature of the active oxidant. Investigations were conducted in great detail for nonheme

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complexes of *cis*-type geometry that resulted in a detailed mechanistic network for the formation of high-valent iron oxo complexes.[14j–l] If water is present in the reaction mixture, a water-assisted pathway for the formation of an active iron(V) oxo hydroxo complex could be proven for complexes that exhibit *cis*-labile coordination,[18] and similar results were obtained in the presence of carboxylic acid.[14j, 19] Furthermore a non-water-assisted pathway via a transitory side-on η^2-O–O complex was proposed for these complexes.[14e] The nature of the active oxidant for nonheme Fe complexes in *trans*-labile geometry, however, seems to differ. The heterolytic or homolytic cleavage of the O–O bond has been proposed to lead to iron(V) and iron(IV) oxo complexes, respectively.[20] The latter is associated with a lower selectivity because of the generation of hydroxyl radicals by homolytic O–O cleavage.

Interestingly, in most catalytic reactions Fe^{II} precatalysts are used, which mandates a preoxidation to form the iron(III) hydroperoxo species that typically involves a Fenton-type radical step.[3b, 14f, 16c, 21] This first oxidation step can potentially reduce activity and selectivity because of radical formation. To the best of our knowledge, no comparative study of structurally equivalent Fe^{II}/Fe^{III} nonheme epoxidation catalysts has been reported, which leaves an essential gap for a better understanding of effective catalyst design.

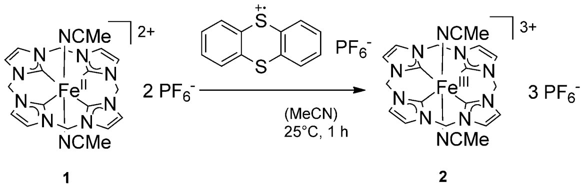
To achieve very active Fe-mediated epoxidation catalysis, our group has focused on the development of Fe complexes with N-heterocyclic carbenes (NHCs).[22] One of these complexes, which bears two carbene and two pyridine moieties (iron(II) di(*o*-imidazol-2-ylidenepyridine)methane hexafluorophosphate; $FeNCCN^{Me}$), is active in epoxidation and aromatic hydroxylation.[23] In addition to the dicarbene systems, we have reported the synthesis and reactivity of an iron(II) cyclic tetracarbene complex.[24] Herein, the activity of this complex towards epoxidation catalysis is compared with that of its oxidized counterpart to test the hypothesized leap in activity for the isostructural Fe^{III} complex.

Results and Discussion

Synthesis and characterization

Smith and Long reported an Fe^{II} monocarbene tetrapyridine complex that could be oxidized selectively to its Fe^{III} derivative using thianthrenyl hexafluorophosphate.[25] We used this approach with the cyclic tetracarbene Fe^{II} complex reported previously to obtain the corresponding Fe^{III} complex (Scheme 1).

Complex **2** is formed by an outer-sphere one-electron oxidation and isolated in 91 % yield. The purple complex was characterized by single-crystal XRD, UV/Vis spectroscopy, cyclic voltammetry, ESI-MS, and elemental analysis, which confirmed its purity and bulk composition. The electrochemical potentials match the data obtained for the Fe^{II} complex and show that the chemical oxidation with thianthrenyl hexafluorophosphate indeed yields the same product as the electrochemical oxidation reported previously.[24] Single crystals of **2** suitable for XRD were obtained by the slow diffusion of diethyl ether into an acetonitrile solution of **2**.



Scheme 1. Synthesis of **2** by the reaction of thianthrenyl hexafluorophosphate as a one-electron oxidant with **1**.

The complex exhibits an almost ideal octahedral coordination around the Fe center in which the tetracarbene ligand coordinates in the expected equatorial fashion and there are two axial acetonitrile ligands (Figure 1). The +3 oxidation state of the Fe atoms is confirmed by the number of PF_6^- anions in the unit cell.

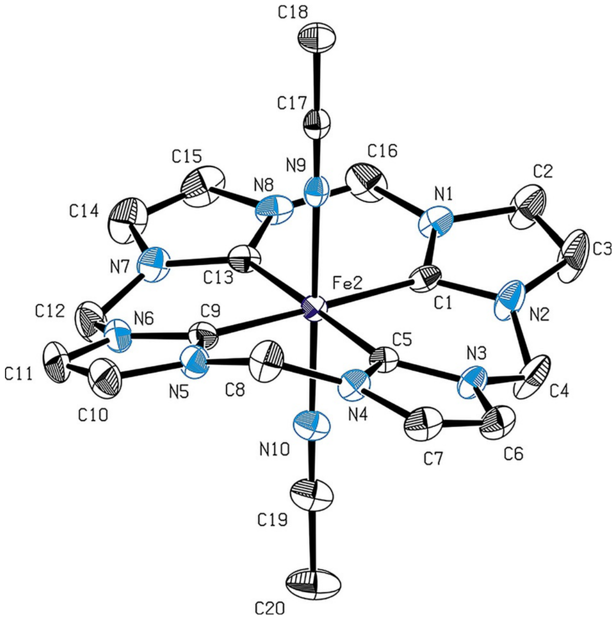


Figure 1. ORTEP-style representation of one of the two tricationic crystallographically independent molecules of **2** in the unit cell. Ellipsoids are shown at a 50 % probability level. Hydrogen atoms, co-crystallized acetonitrile molecules, and PF_6^- anions are omitted for clarity. Selected bond lengths [Å] for the shown cationic unit (values for the second independent cation are given in parentheses): Fe2–C1 = 1.937(3) (1.957(3)), Fe2–C5 = 1.944(2) (1.955(3)), Fe2–C9 = 1.944(3) (1.957(3)), Fe2–C13 = 1.941(3) (1.955(3)), Fe2–N10 = 1.914(3) (1.923(1)), Fe2–N9 = 1.929(2) (1.923(1)).

The overall geometry is not significantly different to that of the structure determined for **1**.[24] The most evident change is the slight elongation of the Fe–carbene bond after oxidation. The lengths of the Fe–carbene bonds in the crystal structure of **1** are in the range of 1.902(3)–1.912(3) Å, whereas they are 1.937(3)–1.957(2) Å for **2**. The Fe–N bond lengths are less affected: 1.930(3)–1.933(3) Å for **1** and 1.914(2)–1.929(2) Å for **2**. These bond lengths to the axial acetonitrile ligands show a significant overlap in the 3 σ confidence intervals for **1** and **2** and are interpreted as not dependent on the oxidation state of the

Fe atoms. These values are in good accord with bond lengths reported in the literature for similar compounds in these oxidation states.[5,22a,26] The bond angles around the Fe center are very close to the ideal octahedral angle with a mean deviation of 0.48° from the ideal 90° angles of adjacent coordination sites.

Epoxidation catalysis

Catalytic experiments using both the Fe^{II} (**1**) and Fe^{III} (**2**) cCCCC complexes were conducted to compare their performance as epoxidation catalysts. We used the standard conditions applied previously for FeNCCN^{Me} (2 mol% catalyst, 5 min, 25 °C)[23a] for the epoxidation of *cis*-cyclooctene to achieve the complete conversion of *cis*-cyclooctene for both **1** and **2** as catalysts (Table 1).

Table 1. Performance of iron carbene complexes in the epoxidation of cis-cyclooctene.[a]

Relative catalyst concentration [mol%]	Epoxide yield (selectivity) [%] [FeNCCN^{Me}][b]	1	2
2.0	92 (>99)	100 (>99)	100 (>99)
1.0	66 (>99)	100 (>99)	100 (>99)
0.5	–	99 (>99)	100 (>99)
0.25	–	82 (>99)	96 (>99)
0.1	4 (>99)	37 (>99)	55 (>99)

[a] Reaction conditions: *cis*-cyclooctene (269 μmol, 100 mol%), H_2O_2 (aq. 50%, 403 μmol, 150 mol%), solvent MeCN, $t=5$ min, $T=25$ °C; yields and selectivities were determined by GC–FID; reactions without catalyst did not yield any epoxide. [b] For reaction conditions refer to Ref. [23a].

No further products apart from the epoxide were detected in all ^{1}H NMR spectra and gas chromatograms. A reduction of the catalyst concentration to 0.25 mol% leads to the incomplete oxidation of the olefin with a yield of 96%. The yield of epoxide is 14% higher for **2** than **1** (82% yield). If the catalyst concentration is further lowered to 0.1 mol%, the performance difference between **2** and **1** is even more pronounced with conversions of 55 and 37%, respectively, compared to only 4% for FeNCCN^{Me}. Overall, these data show that under these conditions **2** is the best catalyst and that both tetracarbene complexes are significantly better catalysts than FeNCCN^{Me}.

Time-dependent yield studies with 0.1 mol% catalyst at room temperature showed the completion of the reaction within 30 s for both catalysts. To slow the reaction, the temperature was reduced, which increased the overall yield from 55% at 25 °C to 100% at −10 °C for **2** and from 37% at 25 °C to 97% at −10 °C for **1**. However, the initial rate of product formation is so high that it is difficult to determine initial slopes for the first 30 s for reactions of 0.1 mol% of **1** at various temperatures with the exception of reactions at −10 °C, which show a slower initial rate. Experiments with 0.1 mol% **2** are more difficult to interpret as the final yield of 100% is reached within the first two minutes at 0 °C and −10 °C, albeit with a slightly slower rate at −10 °C. To get a more interpretable set of experiments, comparable data for **2** were recorded with a relative catalyst concentration of 0.05 mol%. Here, the rate behavior in the first minutes matches that of **1** with a reduced rate at −10 °C and essentially unchanged rates for the three other experiments (Figure 2).

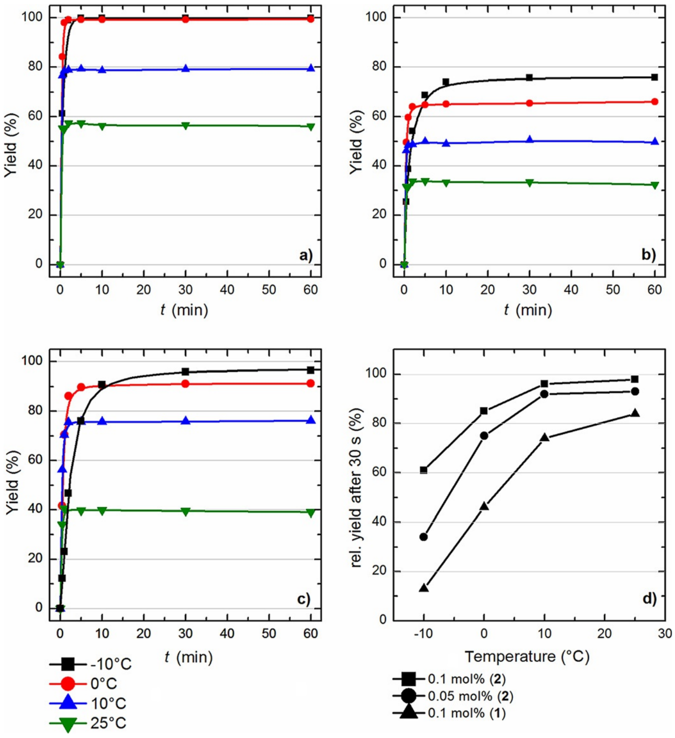


Figure 2. Temperature-dependent yield data for the epoxidation of *cis*-cyclooctene using **1** and **2** as catalysts. a) 0.1 mol% **2**, b) 0.05 mol% **2**, c) 0.1 mol% **1**, d) relative activities of **1** and **2** as indicated by relative yields after 30 s for experiments shown in a)–c), values are calculated as follows: yield(30 s)/yield(final).

In combination, these experiments show the high speed of the catalytic reactions that achieved a maximum yield within 30 min at −10 °C or even faster at higher temperatures. The increase in yields at low temperatures matches previous results and is a consequence of enhanced catalyst stability, which results in a longer catalyst lifetime.[23a] This stability effect is dominant over the expected reaction rate decrease at lower temperatures. Unfortunately, the interpretation of the time-dependent yield data is not straightforward as the initial turnover frequency (TOF) cannot be determined from the first data point at 30 s. After 30 s, the yields already approach the final yields closely and thus do not give sensible data for the initial linear slopes. However, a comparison of the relative activities between this set of experiments is feasible. For this purpose, the activity is expressed as the relative fraction of the yield that is formed within the first 30 s compared to the final yield at the respective temperature. At 25 °C these values are 84% for 0.1 mol% **1**, 98% for 0.1 mol% **2**, and 93% for 0.05 mol% **2**. At the lowest investigated temperature of −10 °C, the values are reduced significantly to 13, 61, and 34%, respectively. Between −10 and 25 °C the relative activity is highly dependent on the reaction temperature and decreases strongly with decreasing temperature. Generally, the values are lower for **1** than for **2** under identical conditions. This indicates that the oxidation state either has an immediate influence on the activity or that a lag phase in the epoxidation of *cis*-cyclooctene occurs for **1**. As expected, the values for 0.05 mol% of **2** are lower than those for 0.1 mol% of **2**.

To further decelerate the reaction, the temperature was decreased to −30 °C. However, at this temperature *cis*-cyclooctene crystallizes in acetonitrile, therefore, a change of solvent is required to guarantee homogeneous reaction conditions. A mixture of acetonitrile and methylene chloride (1:1) was used instead. These experiments show that the reaction proceeds very similarly to the experiments conducted previously in acetonitrile (Figure 3). The final yields increase significantly at −20 and −30 °C, whereas the yields for experiments at −10 and 10 °C are reduced slightly compared to that of the experiments in acetonitrile. The activity is still very high with a reaction time of 60 min at −20 °C. This increase in yield is caused by an increased catalyst lifetime from less than 30 s to 60 min upon lowering the temperature from 10 to −20 °C. At −30 °C the complete conversion of olefin is reached before the catalyst decomposes, which thus gives no information about catalyst stability.

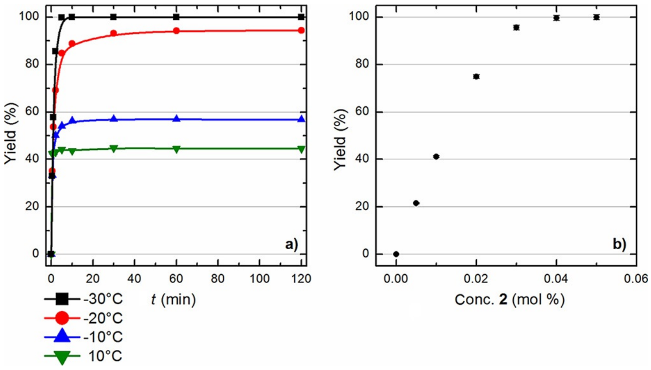


Figure 3. a) Time-dependent yield data at low temperatures for the epoxidation of *cis*-cyclooctene using 0.05 mol% of **2** as catalyst in a solvent mixture of MeCN/methylene chloride (1:1). b) Dependence of yield after 5 and 60 min on the concentration of **2**.

However, a significant decrease in activity was not detected. In the course of this reduction in temperature the yield is increased from 40 to 100%. With a catalyst concentration of 0.03 mol%, a yield of 96% is reached after 60 min at −30 °C. A further reduction of the catalyst loading lowers the yield linearly to 22% at a catalyst loading of 0.005 mol%. This corresponds to a turnover number (TON) of more than 4300 at −30 °C, which is a remarkable stability for an Fe catalyst,[14f] albeit at low temperatures.

At −40 °C, the lowest reaction temperature monitored, the activity of **1** and **2** are compared at different dilutions to investigate the initial behavior of the catalyst more clearly. For **1** an initiation phase is observable in these kinetic experiments, whereas for **2** no such initial lag phase can be detected (Figure 4).

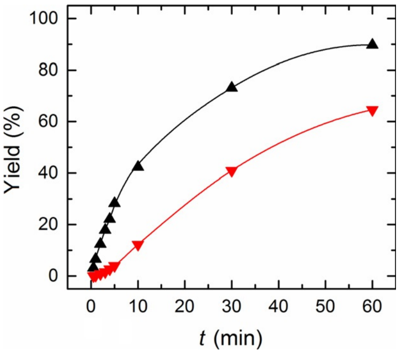


Figure 4. Time-dependent yields of catalysts (0.025 mol%) **1** (red) and **2** (black) at −40 °C in MeCN/CH_2Cl_2 (1:1). For **1** an induction period is clearly observable.

Notably, this phase is more pronounced at high dilution and only visible at temperatures lower than −10 °C. Also the global order of reaction, that is, the sum of all orders of reaction, was determined to be 2 in both cases with significantly different rate constants. The determined reaction rate after the initiation phase is lower for **1** (k_{rel}: 0.047 s^{-1} M^{-1}) than for **2** (k_{rel}: 0.25 s^{-1} M^{-1}; Figures S16–S18). Together these findings suggest strongly a preoxidation of **1** from Fe^{II} to Fe^{III} that causes a lag phase that is not necessary for **2**.

Batch reactions at 25 °C with a maximum reaction time of 10 s were conducted to determine the activity of **1** and **2** more precisely. The reaction for **2** is nearly complete in 10 s as can be seen by the yield of 51% epoxide, which is almost equal to the final yield for **2** at room temperature. In contrast, **1** yields only 14% epoxide after 10 s compared to 37% after 5 min. These values correspond to TOFs of 183 600 h^{-1} for **2** and 50 400 h^{-1} for **1**. This reactivity is unprecedented and to the best of our knowledge **2** and **1** are both more active than the most active homogeneous epoxidation catalyst to date.[15a] This leap in activity is even more pronounced in comparison to all previous Fe catalysts. The highest TOF of an Fe epoxidation catalyst ($[(bpmen)Fe(MeCN)_2]^{2+}$; bpmen = *N*,*N*′-dimethyl-*N*,*N*′-bis-(pyridin-2-ylmethyl)-1,2-diaminoethane) reported to date is 25 200 h^{-1}, which corresponds to 50% epoxide yield with 0.5 mol% catalyst after 14 s.[14f] As seen from the time-dependent yields, **2** appears to be significantly more active than **1** at room temperature with a TOF three times as high as that of **1**. This can either be explained by a dominant lag phase for **1**, which causes an underestimation of the TOF, or a significantly higher activity for **2** than **1**. Consequently, the performance of **2** in epoxidation catalysis was investigated further (Table 2).

Several common peroxides were examined as oxidants in the epoxidation of *cis*-cyclooctene. The yield of epoxide is reduced if peroxides other than H_2O_2 are applied. The use of the urea hydrogen peroxide adduct yields less epoxide because of its lower solubility in acetonitrile. Alkyl hydroperoxides are also less effective than H_2O_2. Interestingly, *tert*-butyl hydroperoxide (TBHP) is more suitable in *n*-decane solution than in aqueous conditions. As H_2O_2 is the best oxidant for the catalytic epoxidation, the influence of its relative concentration on the epoxide yield was investigated (Figure 5).

Table 2. Performance of **2** in the epoxidation of *cis*-cyclooctene using various hydroperoxides.[a]

Oxidant	Oxidant concentration [mol %]	Epoxide yield [%] (amount of **2** [mol %])
H_2O_2 (aq. 50 %)	50	47 (0.1)
H_2O_2 (aq. 50 %)	150	56 (0.1)
H_2O_2 (aq. 50 %)	300	55 (0.1)
H_2O_2 (aq. 50 %)	1000	31 (0.1)
H_2O_2 (aq. 50 %)	150	96 (0.25)
UHP[b]	150	65 (0.25)
TBHP (aq.)	150	71 (0.25)
TBHP (*n*-decane)	150	93 (0.25)
CHP[c]	150	74 (0.25)

[a] Reaction conditions: *cis*-cyclooctene (269 µmol, 100 mol %), solvent MeCN, $t=5$ min, $T=25\,^{\circ}C$; yields and selectivities were determined by GC–FID. [b] Urea hydrogen peroxide adduct. [c] Cumene hydroperoxide.

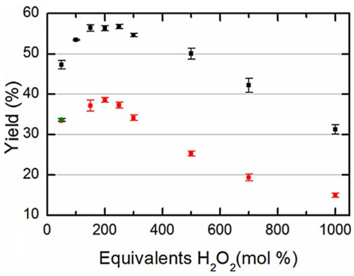


Figure 5. Influence of H_2O_2 concentration on the yield of *cis*-cyclooctene epoxidation at room temperature after 5 min. Black: 0.1 mol % of **2** used; Red: 0.1 mol % of **1** used; Green: 0.25 mol % of **1** used (50 mol % H_2O_2 only).

An increase in the H_2O_2 concentration up to 250 mol % results in slightly higher epoxide yields. The addition of further H_2O_2 decreases the epoxide yield strongly. A reduced catalyst stability emerges in the presence of large excesses of oxidant, which thus lowers the overall epoxide yield. The effect is noticeable for both **1** and **2**, albeit slightly more pronounced for **1** because of the overall lower product yields. However, if the amount of H_2O_2 is reduced below 150 mol % the yield decreases, so that at low H_2O_2 concentrations the overall yield does not reach the maximum possible yield achieved for approximately 150–300 mol % H_2O_2. This effect is probably caused by the catalytic decomposition of H_2O_2, which has been known for Fe^{II} and Fe^{III} salts for decades and is also indicated by gas formation at the very beginning of the reaction.[21,27] Consequently, the yield is limited by the H_2O_2 concentration, which does not allow for the complete conversion of the olefin. However, with 47 % yield for **2** at 50 mol % H_2O_2, the yield is quite close to the possible maximum of 50 %. If a second portion of H_2O_2 is added, the overall yield increases to 95 %. This shows that the catalyst is still active and the lowered yield is not an effect of reduced activity or stability. Compared to the $Fe^{II}NCCN^{Me}$ system reported previously, which shows a more pronounced H_2O_2 decomposition, **2** does not exhibit a strong Fenton reactivity, indicated by its lower H_2O_2 decomposition.[23a] As noted previously, the yields are decreased for **1** in comparison to **2** with maximum yields of 39 % at 200 mol % H_2O_2 and 34 % at 50 mol % H_2O_2, respectively. These reduced yields at low oxidant concentrations again show a competitive decomposition of H_2O_2. Even at higher catalyst concentrations of 0.25 mol % the decomposition of H_2O_2 is more pronounced for **1** than for **2**, which again yields epoxide. Under these conditions, the activity of **1** is no longer dependent on the catalyst concentration as a result of a much faster decomposition of H_2O_2 by the catalyst. These findings show that the oxidation state of the catalyst is the main factor that determines the decomposition of H_2O_2. Consequently, it can be assumed that a Fenton step is at least partly responsible for the significantly lower yields of the Fe^{II} complex compared to that of the Fe^{III} complex. This effect of the oxidation state has been known for classical Fe salts used as Fenton reagents.[21] These findings, in combination with kinetic studies at $-40\,^{\circ}C$, suggest strongly that a first oxidation from Fe^{II} to Fe^{III} is required for the reaction to proceed, which indicates that **2** is the first step of **1** towards the formation of an active species in epoxidation reactions.

Stability is one of the biggest challenges for the applicability of Fe epoxidation catalysts.[16b,f,18a,23a] Many Fe complexes decompose rather quickly in aqueous H_2O_2 solution and remain active only for a short period of time.[14e,f,23a] Although this problem has been known for a while, other factors also impact stability of Fe catalysts. To better understand the influence of the reaction conditions on catalyst stability, the influence of water in the reaction mixture was investigated. As a result of the use of aqueous H_2O_2, the catalytic system contains water necessarily. However, additional equivalents of water result in noticeable effects (Figure 6). The epoxide formation decreases from 53 to 42 % if 10 equivalents water relative to *cis*-cyclooctene are added. This influence is quite unexpected as **2** is remarkably stable in undried acetonitrile, yet under oxidative conditions the reaction appears to be somewhat sensitive to water. The experiments with TBHP presented in Table 2 may be rationalized by the effect of water. To verify that the noticeable decrease in yields is in fact a stability effect rather than an activity effect, time-dependent yield data were collected with 0.1 mol % **2** at $-10\,^{\circ}C$. In the case of the addition of

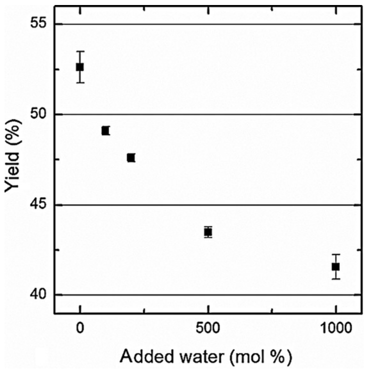
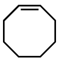
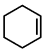
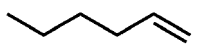
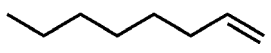
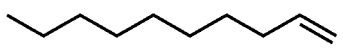
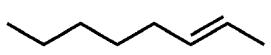
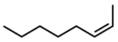
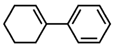
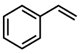


Figure 6. Influence of added water on the yield of *cis*-cyclooctene epoxidation at room temperature using 0.1 mol % **2** and 150 mol % H_2O_2 (50 % in H_2O) after 5 min.

1000 mol % water, the product formation is unaffected initially. However, after 5 min the reaction terminates and reaches only 94 % epoxide yield (see Supporting Information). Experiments without the addition of water show higher yields and longer periods of activity (Figure 2). This behavior might be considered quite unusual on first glance as most nonheme Fe catalysts exhibit enhanced activity if water is added to the reaction mixture as a water-assisted pathway in the formation of the active species is generally accepted for these catalysts.[14c,e] However, Que and co-workers showed that this only holds true for catalysts that exhibit *cis*-labile coordination. These complexes are able to undergo a water-assisted O–O cleavage in the intermediate iron hydroperoxo complex to form a Fe^{V} oxo hydroxo complex, which is the active species in the epoxidation. Thus the product yield increases upon the addition of water because of the more facile formation of the active catalyst.[14c,e] Through the addition of $H_2{}^{18}O$, it was found that one of the oxygen atoms originates from water in solution, that is, ^{18}O, in *cis* complexes. Through a tautomerization, this ^{18}O is subsequently partially incorporated into the epoxide. In contrast, **2** exhibits *trans* coordination, in which case a decrease in product yield is observed. This shows that the water-assisted pathway does not apply to **2**, which is expected from previous studies on complexes of this coordination geometry.[14e] This is also corroborated by the lack of incorporation of ^{18}O upon the addition of 1000 mol % $H_2{}^{18}O$, which again shows that a water-assisted pathway does not apply.

Various cyclic and acyclic alkyl and aryl alkenes were used as substrates in epoxidation reactions catalyzed by **2** (Table 3). For all substrates no diol formation is observed. The highest epoxide yields are obtained for cyclic olefins, of which *cis*-cyclooctene yields the most epoxide. The other cyclic olefins cyclohexene and 1-phenyl cyclohexene yield 92 and 93 %, respectively, which shows that the latter is much more easily epoxidized compared to styrene. These general trends for aryl-substituted alkenes are in agreement with the literature, with a slight improvement compared to the $Fe^{II}NCCN^{Me}$ catalyst.[23a] Of the substrates examined for epoxidation, acyclic terminal olefins are the most difficult to epoxidize, with comparable yields for 1-hexene, 1-octene, and 1-decene. However, the internal olefin 2-octene leads to the second highest yield of the eight substrates tested with a distinctively different result for the two geometric isomers. In this particular case, epoxidation of the *Z* isomer is favored over that of the *E* isomer with epoxide yields of 93 and 67 %, respectively. This selectivity is typical for Fe epoxidation catalysts and has been reported previously.[14e] The overall preference of more highly substituted alkenes over terminal alkenes and the decreased yields for aryl alkenes as well as the high selectivities indicate the electrophilic nature of the active species.[28]

Table 3. Catalytic epoxidation of alkenes with **2** in MeCN with H_2O_2.[a]

Alkene	Epoxide yield (selectivity) [%]
	100 (>99) 53 (>99)[b]
	91 (>99)
	35 (>99)
	39 (>99)
	36 (>99)
	67 (>99)
	93 (>99)
	93 (95)
	46 (93)
	59 (>99)

[a] Reaction conditions: alkene (134 μmol, 100 mol %), H_2O_2 (aq. 50 %, 202 μmol, 150 mol %), 0.375 mol % of **2**, solvent MeCN-d_3, t = 30 min, T = −10 °C; yields and selectivities were determined by ^1H NMR spectroscopy using external standards. [b] 0.1 mol % of **2**, t = 5 min, T = 25 °C.

Conclusions

Iron tetracarbene systems are applied as homogeneous epoxidation catalysts with H_2O_2 as the oxidant. In particular, the Fe^{III} derivative has an exceptionally high activity at ambient temperatures and below. The less active Fe^{II} compound is still on par with the most active homogeneous organometallic catalysts described previously that usually contain much more expensive metals (e.g., Re, Mo, etc.). Oxidant decomposition by radical pathways is reduced significantly if the Fe^{III}-based catalyst is used. This difference in behavior can be attributed to the difference in oxidation state. An initiation phase for the Fe^{II} complex indicates a need for a first oxidation to form an Fe^{III} complex.

These encouraging results support the view that Fe-based organometallic catalysts are able to compete successfully with other catalysts based on (much) more expensive metals. The metal oxidation state, the ligand sphere, temperature, and solvent apparently allow fine-tuning to reach optimal reaction conditions. To further improve this system, catalyst immobilization through the ligand sphere (to allow easy catalyst recycling) and the reduction of catalyst decomposition (to further increase the turnover number) have to be the focus of research efforts.

Experimental Section

General remarks

CAUTION: H_2O_2 and organic peroxides are potentially explosive if highly concentrated and exposed to heat or mechanical impact. All chemicals were purchased from commercial suppliers and were used without further purification. Complex **1** and thianthrenyl hexafluorophosphate were synthesized according to the literature procedures.[24,29] ^1H NMR spectra were recorded by using a Bruker Avance DPX 400. Chemical shifts are given in parts per million (ppm), and the spectra were referenced by using the residual solvent shifts as internal standards ([D_3]MeCN, $^{1H}\delta$ = 1.94 ppm). A Thermo Scientific LCQ/Fleet spectrometer by Thermo Fisher Scientific was used to collect ESI-MS data, and elemental analysis was obtained from the microanalytical laboratory of TUM. GC with flame ionization detection (FID) measurements were performed by using a Varian CP-3800 equipped with an Optima 5-Amin column (FID; 1.50 μm; 30 m × 0.32 mm) with *p*-xylene and indane as external standards. $H_2^{18}O$ (97 % ^{18}O) was used as purchased, and reaction results were quantified by GC–MS by using a HP 5890A and a mass-selective detector HP 5970 (Hewlett–Packard) equipped with a DB225-MS column (30 m × 0.250 mm; 0.25 μm film, Agilent Technologies). Temperature-controlled experiments were cooled by using Julabo FP 40 and FP 50 cryostats with an external temperature probe.

Single-crystal XRD

Single crystals of **2** ($C_{20}H_{22}F_{18}FeN_{10}P_3$, MW: 893.23 g mol^{-1}) suitable for XRD were obtained by the slow diffusion of diethyl ether into an acetonitrile solution of **2**. The intense red crystal exhibits a triclinic crystal system in the space group $P\bar{1}$ (No. 2) with the cell parameters $a = 11.9510(3)$ Å, $b = 12.2706(3)$ Å, $c = 16.6742(4)$ Å, $\alpha = 86.321(1)^\circ$, $\beta = 73.341(1)^\circ$, and $\gamma = 84.714(1)^\circ$ ($Z = 3$). Diffraction experiments were conducted at 123 K. The final quality factors of refinement were $R1 = 0.0394$, $wR2 = 0.0977$, and GOF = 1.021.

Synthesis of *trans*-diacetonitrile[calix[4]imidazolyl]iron(III) hexafluorophosphate (2)

Thianthrenyl hexafluorophosphate (144 mg, 0.40 mmol) and **1** (300 mg, 0.40 mmol) were dissolved in acetonitrile (10 mL). The resulting purple solution was stirred at RT for 1 h. The first fraction of sequential precipitation with diethyl ether yielded a purple solid. The precipitate was subsequently washed twice with diethyl ether and dried in vacuo. Yield: 91 %, 325 mg. ESI-MS ([*M*]$^+$): *m/z* (%): 439.88 [**2**$-2\,$MeCN$-3\,PF_6^-+F^-+HCOO^-]^+$ (100), 565.53 [**2**$-2\,$MeCN$-2\,PF_6^-+HCOO^-]^+$ (30), 539.68 [**2**$-2\,$MeCN$-2\,PF_6^-+F^-]^+$ (25), 197.47 $[M-2\,\mathrm{MeCN}-3\,PF_6^-+F^-]^{2+}$ (4); elemental analysis calcd (%) for $C_{20}H_{22}F_{18}FeN_{10}P_3$ (Mw: 893.23 g mol^{-1}): C 26.89, H 2.48, N 15.68, S 0.00; found: C 27.21, H 2.45, N 15.42, S < 0.1.

Catalytic procedures

Batch reactions were conducted in 4 mL solvent. Unless otherwise noted, the solvent for epoxidation reactions was HPLC-grade acetonitrile. A stock solution of catalyst (**1**: 1.0 mg mL^{-1}; **2**: 1.2 mg mL^{-1}; in acetonitrile) was prepared and added according to the stoichiometry to a preformed solution of *cis*-cyclooctene (0.2687 mmol, 35.25 mg, 100 mol %) and H_2O_2 (0.403 mmol, 22.91 μL, 50 % in H_2O, 150 mol %) in acetonitrile to give a total reaction volume of 4 mL. Variations of oxidation agents were used according to stoichiometry using 0.403 mmol of oxidant. For all reactions, control experiments without the use of a catalyst were performed as a reference. The reactions were aborted by the addition of electrolytically precipitated activated MnO_2 as a H_2O_2-decomposition agent. After filtration over activated neutral alumina, two GC samples were prepared for each experiment using 200 μL filtrate, 500 μL external standard solution (*p*-xylene and indane 4 mg mL^{-1} in *i*PrOH) and 800 μL *n*-hexane. Time-dependent yield experiments were conducted in a total volume of 12 mL using the same stoichiometry and concentrations. The reactions were started by the addition of the catalyst solution, and samples were taken and immediately added to MnO_2. GC samples were prepared by the same procedure as for batch reactions. For each time-dependent experiment, reference reactions without the use of catalyst were conducted.

^{1}H NMR experiments were conducted in [D$_3$]MeCN with the same stoichiometry in doubled absolute concentrations. The total reaction volume was 1 mL with the use of a stock solution of catalyst of 2.4 mg mL^{-1} in [D$_3$]MeCN. This solution was cooled to −10 °C and added to a preformed solution of 0.1343 mmol of olefin (100 mol %) and 0.202 mmol H_2O_2 (22.91 μL, 50 % in H_2O, 150 mol %) at −10 °C. After 30 min the reaction was aborted by the addition of activated MnO_2, and the external standards benzene or pyridine were added. After filtration over neutral activated alumina, ^{1}H NMR spectra of the samples were recorded. The products were quantified by the integral ratios of the respective olefin, diol, and epoxide protons.

Supporting Information

UV/Vis data, CV data, and XRD data for **2** in CIF format as well as supplementary catalysis data that includes ^{1}H NMR spectra can be found online. CCDC-963849 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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Keywords: carbene ligands · epoxidation · homogeneous catalysis · iron · peroxides

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