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Iron Complex with Ionic Tag-Catalyzed Olefin Reduction under Oxidative Conditions—A Different Reaction for Iron

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An iron(III) complex with ionic tags was applied to the reduction of alkenes in imidazolium-based ionic liquids (ILs) under oxidative conditions. The catalyst is very efficient to promote reactions of biomass derivatives. At least ten recycling reactions were performed without any loss of catalytic activity. Some important mechanistic insights for this new reaction are also provided based mostly on electrospray ionization quadrupole-time of flight mass spectrometry (ESI-QTOF-MS).

Introduction

The search for new, sustainable, inexpensive, efficient, nontoxic, recyclable, and eco-friendly catalysts is a global reality owing to climate, safety, and security reasons.[1] In this sense, both the development of new Fe catalysts and the discovery of new reactions for this metal are fundamental goals in modern catalysis. The state-of-the-art of Fe-catalyzed reactions is found in many reports and literature surveys,[2,3] including Fe-catalyzed reduction processes.[4] Nowadays, it is commonly agreed upon that Fe is a very attractive transition metal for catalytic processes as it is virtually non-toxic, abundant, and relative easy to handle. All of the aforementioned features of Fe-based catalysts boost ongoing efforts from many research groups towards new alternatives to Pd, Ru, Pt, Rh, and other metals in catalysts.

Ionic liquids (ILs), especially those based on the imidazolium cation (Figure 1), play an important role for environmental acceptability.[5] For some time, these salts were regarded as promising candidates for green and sustainable processes,[6] and nowadays they are successfully used in many industrial processes.[7] Their unique physicochemical properties render these salts very attractive media to efficiently support a plethora of catalysts. And, as one can expect, ILs are of special interest in the use of catalysts that bear ionic tags.[8]

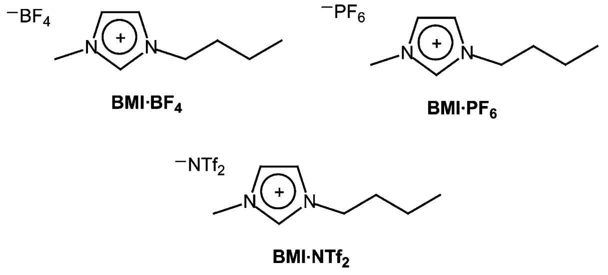

Figure 1. Imidazolium-based ILs commonly used in catalysis.

In this context, catalysts with ionic tags are outstanding alternatives to traditional systems.[9] The combination of catalyst-containing ionic tags and ILs are, without doubt, a powerful and promising combination, which usually afford outstanding results.[10] Recently, we described the synthesis, characterization and application of a new Fe catalyst with ionic tags (Figure 2) as the promoter of olefin epoxidation using air or H_2O_2 as the oxidizing agent.[11] Owing to the high affinity of the ionophilic ligand and the metal center, at least ten recycling reactions could be performed with no loss of activity.

As a result of our interest in chemical transformations in ILs[12] and our experience with MS to investigate reaction mechanisms,[13] we decided to investigate olefin reductions in IL media submitted to unusual conditions, that is, under oxidative conditions. Herein, we report our findings on this new reaction catalyzed by Fe catalyst **1**. During the execution of our previously reported work on olefin epoxidation,[11] we found that under the best conditions to perform the oxidation reaction—air (oxidizing agent, 1.5 MPa), **1** (1 mol%), 90 °C, BMI·NTf$_2$ (1 mL, BMI = 1-*n*-butyl-3-methylimidazolium, NTf$_2$ = bis(trifluoromethylsulfonyl)imide), 24 h—it was possible to reduce the olefin instead of oxidizing it just by adding methanol to the reaction medium. To the best of our knowledge, this is the first report of Fe catalysis for this type of reaction.[14]

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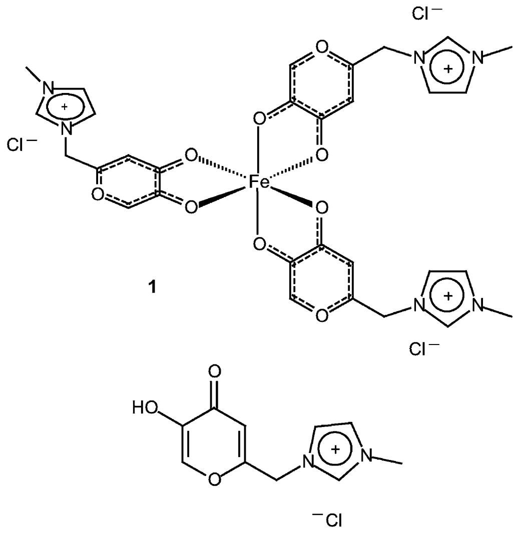

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Figure 2. Fe complex **1** with ionic tags and the ionophilic ligand **2**.[11]

Results and Discussion

First, we chose to investigate methyl oleate as the model compound to perform the reduction[15] as the importance of hydrogenated oils, fats, and biodiesel derivatives is well known.[12a,16] By using **1**, we were able to perform the reduction of methyl oleate (under an oxidative atmosphere) by adding methanol to the reaction media (Scheme 1). Other reaction conditions remained the same as those previously optimized for air epoxidation,[11] that is, 1.5 MPa of synthetic air at 90 °C with 1 mol% of **1** for 24 h.

Methyl stearate was obtained in 83–85 % yield independent of the IL used. However, BMI·PF$_6$ and BMI·BF$_4$ turned dark, which is an indication of anion degradation (HF formation). Thus, we decided to keep BMI·NTf$_2$ as the ionic media for this study.

To verify the efficiency of the system in the performance of the reduction reaction, biodiesel derived from soybean oil was also used in a mixture of methyl esters of oleic acid (18:1), linoleic acid (18:2), and linolenic acid (18:3) in the presence of **1** with BMI·NTf$_2$ as the reaction media for 24 h. The reduction occurred almost quantitatively. It is likely that olefin isomerization in linolenic and linoleic methyl ester derivatives occurs under the tested conditions, which has been recently reported elsewhere with Ru or Rh as catalysts[17a] and for some commercially available Fe derivatives.[17b] The conjugated olefins probably hydrogenate faster than the isolated olefin, which may explain the quantitative yield observed for this reaction.

Recycling reactions that used methyl oleate as the model substrate were performed, and the results are displayed in Figure 3. After the reaction, the product could be easily separated by decantation. If necessary, hexane was used to extract any remaining product.

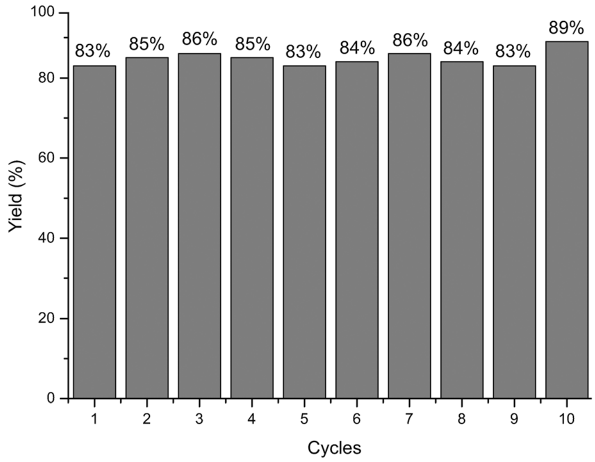
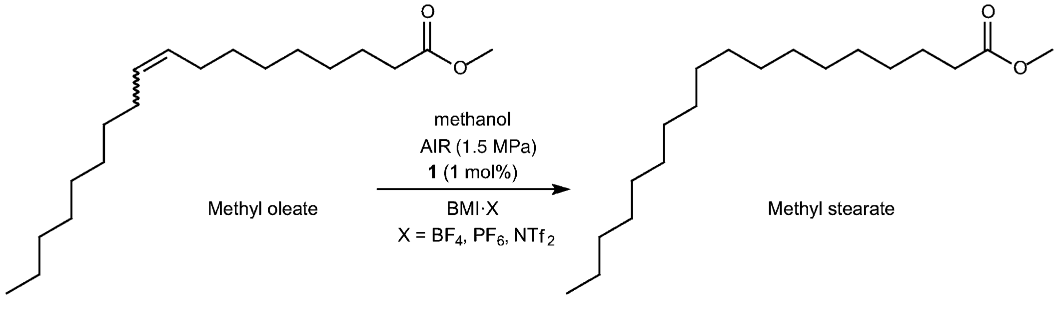


Figure 3. Recycling of **1**. No loss of activity was noted after 10 runs.

Inductively coupled plasma (ICP) analysis revealed that the use of **1** (with three ionic tags) greatly prevents catalyst leaching, and as little as 2 ppm of Fe was detected in the oil phase. This indicates the efficient anchorage of **1** in BMI·NTf$_2$. Moreover, the activity of **1** remains unchanged even after ten runs. It is worth remembering that **1** is used at low concentrations (65 μM, 1 mol%) for all reactions, whereas Fe catalysts are commonly used up to 10 mol%. Some exceptions are also found. For example, Chirick et al. used 0.3 mol% of Fe^0 to perform hydrogenation reactions.[4e]

To gain insight into the generality of this catalytic system, it was applied to reduction reactions of several other substrates from biomass, and the results are summarized in Table 1.

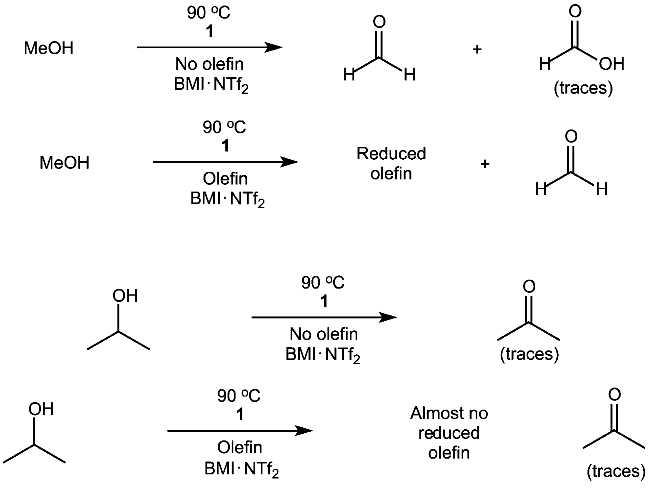


Scheme 1. Methyl oleate reduction catalyzed by the Fe complex **1** with imidazolium tags.

Table 1. Reduction reactions[a] under oxidative conditions by using **1**.

Entry	Substrate	Product yield[b] [%]
1	soybean oil	89
2	biodiesel (from soybean oil)	99
3	rapeseed oil	87
4	corn oil	85
5	sunflower oil	89
6	castor oil	81[c]
7	oleic acid	84
8	1-hexadecene	81
9	1-decene	78
10	styrene	–[d]
11	cyclohexene	–

[a] Complex **1** supported in BMI•NTf$_2$, methanol (2 mL), synthetic air (1.5 MPa), 24 h, 90 °C. [b] Yields of completely hydrogenated products only. [c] Also 11 % of transesterification reaction and a partial oxidation of the OH group in the side chain were observed. [d] Only polymerized product.



Scheme 2. Alcohol oxidation experiments using synthetic air as the oxidant (1.5 MPa).

Notably, the reaction occurred in the presence of multiple double bonds, which were found in different proportions in the tested substrates (Table S1, Supporting Information). Reduction reactions occurred in good to excellent yields (81–99 %). The use of castor oil as the substrate resulted in a biodiesel derivative as a consequence of a partial transesterification reaction, and a partial oxidation of the side-chain OH group from ricinoleic acid was observed (Table 1, Entry 6). We believe that the difference in solubility of the tested substrates in ILs (biphasic catalysis) may be why almost quantitative yields were not observed for all reactions. It is important to highlight that we have recently shown that the difference in the solubility of reagents and products in ILs can modulate the selectivity of the hydrogenation of polyunsaturated substrates.[12a,d] The use of styrene (Table 1, entry 10) resulted only in the polymerized product (almost quantitative) as observed without methanol.[11] The use of volatile olefins (cyclohexane) produced no result (Table 1, entry 11). However, heavier olefins (Table 1, entries 8 and 9) gave good results.

To gain insight into the mechanism of this new reaction, some experiments were performed in the presence and absence and of the olefin (methyl oleate). Initially, two alcohols were tested: methanol and isopropanol. In the absence of olefin, the catalytic system oxidized methanol to a mixture of formaldehyde and traces of formic acid, which reduced the metal center, as shown by the MS experiments. Isopropanol was also oxidized to acetone, but in insignificant amounts (Scheme 2).

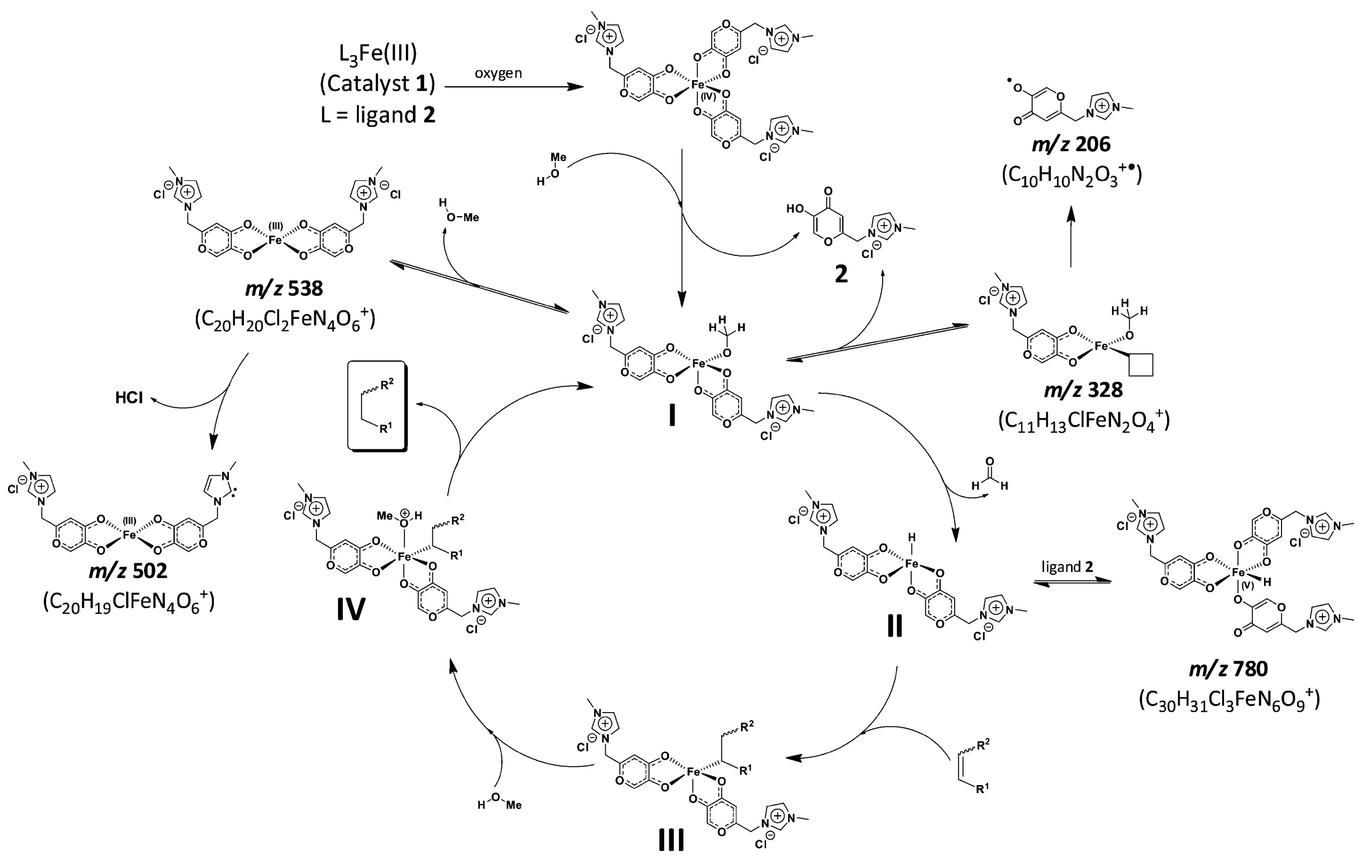
The use of methanol in the presence of methyl oleate afforded the reduced compound and formaldehyde (detected by GC). Isopropanol gave poor results (Scheme 2). The obtained results were expected; it has been described that steric hindrance, owing to the presence of different ligands, prevents the coordination of branched alcohols (such as isopropanol) to the cationic Fe center[18] and that less hindered alcohols such as methanol are capable of coordination. Structurally different ligands have shown a similar steric hindrance effect.[18]

Based on the obtained results, we propose the catalytic cycle in Scheme 3. High-resolution electrospray ionization quadrupole-time of flight mass spectrometry (ESI-QTOF-MS, in W mode for higher accuracy and resolution) measurements were performed to allow a better understanding of the catalytic cycle for this transformation.

First, oxygen oxidizes the Fe center from Fe^{III} to a high-valent state. In the presence of methanol, the oxidized complex dissociates and an alcohol molecule coordinates to form **I** (Scheme 3). At this stage, the hydrogen slated for abstraction is transferred to the metal center and the oxidation of the alcohol occurs to result in the metal hydride **II**. This step, **I**→**II**, may be a result of the rearrangement of an initially formed iron-oxo complex from alcohol coordination, which is similar to a previously proposed transition state with hydrogen migration in catalytic asymmetric epoxidations with chiral Fe porphyrins.[20] After that, olefin coordination followed by hydride transfer leads to **III**. Then, another methanol molecule coordinates. Species **IV** then undergoes substrate protonation and eliminates the reduced substrate, which restores the catalytically active species **I**.

Intentionally, we have briefly discussed the metal oxidation state in the proposed catalytic cycle. Nevertheless, some important insights must be highlighted:

(i) Methanol seems to be the best alcohol. Primary alcohols such as ethanol or *n*-butanol can also be used (lower yields were observed), but not as efficiently as methanol.
(ii) The reaction does not occur without synthetic air in the reactor (1.5 MPa). This indicates that it is necessary to force the oxidation (by O_2) of the metal center (high-valent Fe) to form the metal hydride species through the oxidation of the primary alcohol.
(iii) As a consequence, a high-valent Fe center is necessary to facilitate the formation of both **I** and **II** as it is an electron-deficient Fe center.[21] Probably, a mixture of Fe^{IV} and Fe^{V} species are involved in the cycle. Additionally, it has been proposed that high-valent Fe^{IV} cations with electron-defi-



Scheme 3. Proposed catalytic cycle for olefin reduction catalyzed by **1** in the presence of methanol. Major ions detected in ESI(+)-QTOF-MS experiments are indicated by their *m/z* values, and propositions for their origins from intermediates of the catalytic cycle are shown.

cient porphyrin ligands may exhibit a greater propensity for electron transfer to an olefin.[22]

(iv) It was proposed for thiolate-ligated enzymes (cytochrome family) that electron donation from the ligand to the metal center (Fe) increases the basicity of the iron-oxo group, which thereby allows a hydrogen atom to be abstracted from C–H bonds.[23] This hypothesis is very important, mostly because it helps to explain the high reactivity of cytochrome P-450 in C–H bond activation reactions.[24] In our case, supposedly, this logical increase in the Lewis acidic character of the high-valent Fe species, facilitates the hydride transfer to form **II**.

MS experiments produced outstanding results to support most of these aforementioned insights and the proposed catalytic cycle. By monitoring the reaction in a methanolic solution by on-line direct infusion ESI(+)-QTOF-MS, we were able to detect some interesting ions, which were then structurally characterized by collision-induced dissociation (CID) product ion spectrum experiments (ESI-QTOF-MS/MS). It is important to remember that it is necessary to force the oxidation of the Fe^{III} to form a high-valent metal center (Fe^{IV} or Fe^{V}) and to allow the olefin reduction to take place. Otherwise, the reaction does not occur. In many reports, the oxidation of the metal is forced with air (or pure O_2) or with H_2O_2.[2–4] In this sense, we have studied these two oxidizing agents to evaluate the differences. Overall, we observed very similar results, but the intensities of the signals in the MS spectra showed slight changes, which allowed us to select the most intense signals to perform structural characterization by ESI-QTOF-MS/MS.

We were able to detect a high-valent Fe^{V} species with three ionophilic ligands that also contains a metal–hydride bond ($m/z = 780$) formed by air oxidation. Representative ESI(+)-QTOF mass spectra are shown in Figure 4. Common losses such as of HCl and the ligand could be observed in the product ion spectrum (Figure 4a). The characteristic isotope pattern and exact mass measurement (Figure 4b and c) point firmly to the interception of a derivative of intermediate **II** (Scheme 3). Thus, it is expected that **II** can form as shown in the equilibrium described in Scheme 3.

Other important species have been detected and characterized by product ion spectrum experiments. We have also detected a Fe^{III} species (Scheme 3, $m/z = 328$, Figure S1) from the alcohol oxidation as discussed above. Naturally, the presence of O_2 in the reaction mixture (or other oxidizing agents) forces the Fe to oxidize again. The species that gives rise to the peak at $m/z = 328$ is similar to **I** as proposed and shown in Scheme 1. Features such as the isotopic pattern of the signal, its low *m/z* error and its fragmentation (Figure S1) all corroborate the proposed structure. A neutral loss of a radical methoxy group ($CH_3O^{\bullet}$, 31 Da) occurs to form an ion of $m/z = 297$. A fragment ion of $m/z = 206$ (Scheme 3) is attributed as charac-

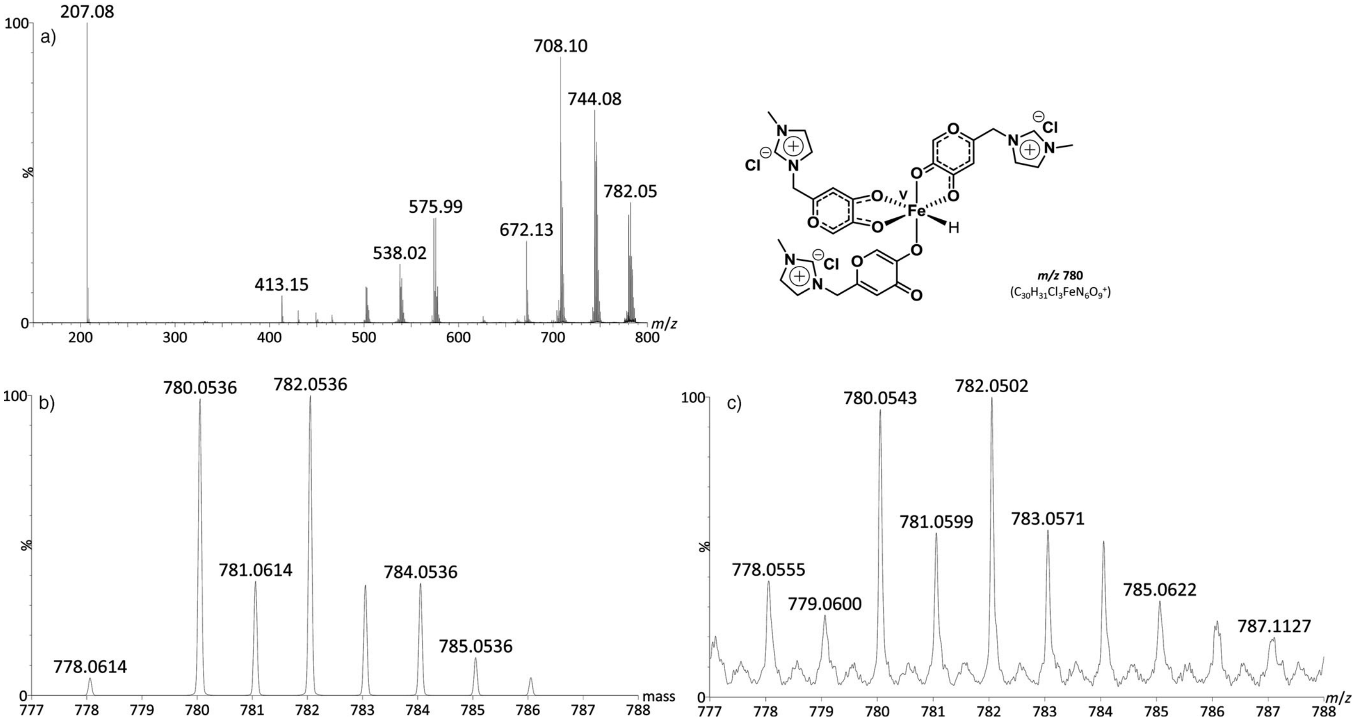


Figure 4. a) ESI(+)-QTOF product ion spectrum of $m/z = 780$ from a reaction mixture of **1** dissolved in methanol and heated (open system). b) Simulated isotope pattern for $[C_{30}H_{31}Cl_3FeN_6O_9]^+$. c) Expansion between $m/z = 777–788$ of the spectrum (calcd. $m/z = 780.0536$; found $m/z = 780.0543$, error +0.9 ppm).

teristic of the ionophilic ligand and detected as a cation radical species in accordance with a radical loss. Notably, without the presence of an oxidizing agent, such as H_2O_2 (or by heating the alcoholic solution in air to force the oxidation), no metal hydride signal has been found. Nevertheless, in the presence of any of those oxidants, we detected signals that corroborate the presence of a Fe–H bond and a high-valent Fe center (Figures 4 and 5).

In the presence of any of the oxidizing agents, an ion of $m/z = 538$ was detected and structurally characterized by ESI(+)-QTOF-MS/MS (Figure S2). The ion was attributed to a Fe^{III} species bound to two ligands. This ion can be formed by the loss of methanol from **I** (Scheme 3). The isotope pattern for the ion of $m/z = 538$ is in excellent agreement with that of the simulated spectrum for $[C_{20}H_{20}Cl_2FeN_4O_6]^+$ (Figure S2). The product ion of $m/z = 538$ shows a loss of HCl to form a carbene ion of $m/z = 502$ (Scheme 3, Figure S3). As already described, carbene formation can be almost completely inhibited in the presence of protic solvents such as methanol.[25] This ion was not found in solution, but only as a result of direct HCl loss in the collision-induced dissociation in the gas phase, which has been previously demonstrated for imidazolium derivatives.[26]

All of these results indicate that some parallel reactions occur simultaneously, such as: (i) direct alcohol oxidation (to form Fe^{II}) and (ii) the reaction proposed in Scheme 3; both of which include alcohol

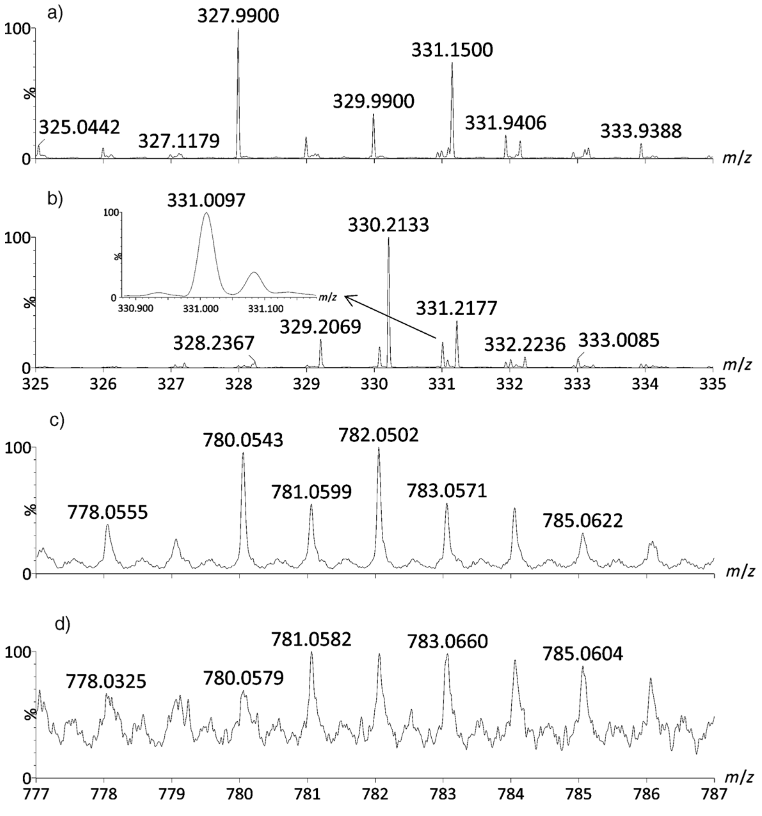


Figure 5. ESI(+)-QTOF mass spectra demonstrating an isotope pattern shift resulting from the incorporation of deuterium atoms to ions of $m/z = 328$ and 780, which result from reactions performed in CD_3OD compared to those in CH_3OH. Expansion around $m/z = 328$ for reactions performed in a) CH_3OH and b) CD_3OD. Inset in (b) shows an expansion around the $m/z = 331$ ion ($C_{11}H_{10}D_3ClFeN_2O_4^+$). Expansion around $m/z = 780$ for reactions performed in c) CH_3OH and d) CD_3OD.

oxidation and seem to be favored under the developed conditions, otherwise we would not observe good yields of the reduced olefin.

As observed by all ESI(+)-QTOF product ion spectra, the proposed mechanism is acceptable but may be more complex than those five steps suggested. Envisaging that the detected transient intermediates of $m/z = 328$ (Scheme 3, Figure 5) and $m/z = 780$ (Scheme 3, Figure 4) contain atoms that are indeed derived from the methanol present in the reaction mixture, we decided to perform the same on-line monitoring with CD_3OD (99.96 %) instead of CH_3OH to confirm the proposed species and to guarantee these species are not artifacts. Isotopic labeling proved to be a powerful and elegant tool in MS.[27]

Thus, by repeating the reaction with CD_3OD instead of CH_3OH, isotopomeric ions of $m/z = 331$ (three deuterium atoms) were analogously monitored and characterized (Figure 5 a and b). This elegant experiment demonstrated that the neutral loss to form the ion of $m/z = 297$ is attributed to a radical $CD_3O^{\bullet}$ (34 Da), instead of $CH_3O^{\cdot}$ (31 Da) previously observed (see Figure S4) for the reaction performed in CH_3OH, thus confirming the presence of the alcohol moiety in the proposed structure (Scheme 3). Also, by monitoring the ion of $m/z = 780$, we were able to observe a shift in its isotope pattern between reactions performed in CH_3OH and CD_3OD (Figure 5 c and d), which strongly indicates the incorporation of a deuterium atom. This atom could be bound to the Fe center, indicating a Fe–D bond instead of a Fe–H bond observed for the experiment performed in CH_3OH.

Conclusions

We have described a new reduction reaction catalyzed by a Fe complex with ionic tags, which acts as a pre-catalyst to form the active species in situ. The optimized reaction resulted in good to excellent yields of the reduced products. Ten recycling reactions could be conducted with no loss of activity. Based on experiments and MS measurements, a catalytic cycle that includes a high-valent Fe was proposed. All results point towards the proposed catalytic cycle, but they also indicate that the reaction may be more complex than shown here. Nevertheless, the isotopic labeling experiments are in agreement with the proposed species, which indicate that the proposed catalytic cycle is appropriate. Finally, this new Fe-catalyzed reaction has the potential to open a new avenue of possibilities towards greener and sustainable processes, and at the same time boosting the development of Fe chemistry.

Experimental Section

The Supporting Information contains full experimental details and product characterizations.

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Keywords: ionic liquids · isotopic labeling · iron · mass spectrometry · reduction

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