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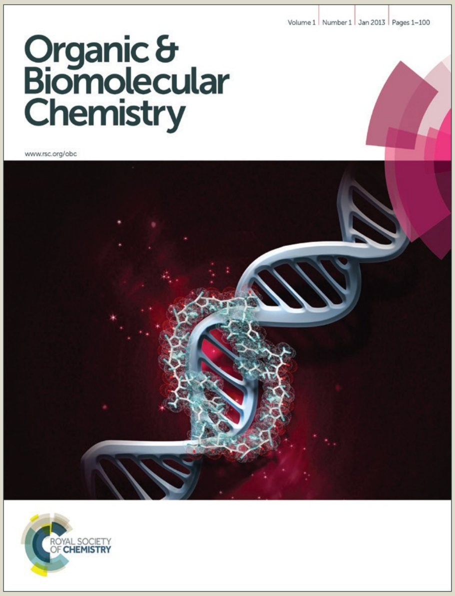

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ARTICLE

Alcohol Oxidation with H_2O_2 Catalyzed by a Cheap and Promptly Available Imine Based Iron Complex.

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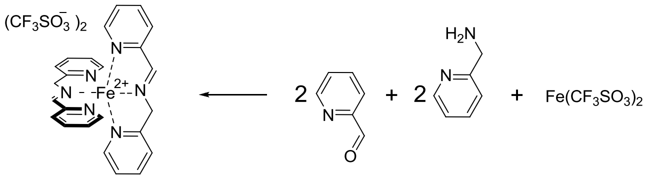
Giorgio Olivo,[a,b] Simone Giosia,[a] Alessia Barbieri,[a] Osvaldo Lanzalunga[a] and Stefano Di Stefano*[a]

We previously reported that the iminopyridine iron (II) complex **1**, easily and quantitatively obtainable *in situ*, can activate H_2O_2 to form a powerful oxidant, capable of aliphatic C-H bond hydroxylation. In the present study we expand the application of this catalyst to the oxidation of a series of alcohols to the corresponding carbonyl compounds. The oxidation of aliphatic alcohols proceedes smoothly, while that of benzylic alcohols is shown to be challenging. Some collected pieces of evidence suggest a preferency of the oxidizing species for the aromatic ring instead for the alcoholic moiety. The decrease of the electron density in the aromatic ring shifts the oxidation from the aromatic towards the alcoholic moiety. Quite surprisingly, preferential oxidation of cyclohexanol versus benzylic alcohol was achieved, showing an unprecedented selectivity.

Introduction

Alcohol oxidation is a fundamental reaction in organic synthesis, since it converts readily available alcohols into valuable carbonyl compounds, prone to further functionalization. Accordingly, several methodologies have been developed over the years to perform such reaction. However, most of them rely on toxic and/or polluting reagents, such as CrO_3 or hypervalent iodine.[1,2] The rising environmental concerns in our society call for greener methodologies that require more efficient and sustainable processes. In this context, the use of a non-polluting catalyst in combination with a readily available and waste-free terminal oxidant (such as H_2O_2 or O_2) is an optimal choice. Great advances have been achieved in the last decades by replacing toxic and/or rare transition metals with cheaper and more environmentally friendly ones. For instance, the Cu/air/TEMPO catalytic systems pioneered by Stahl[3,4] or the tungsten oxide/phase transfer catalysts developed by Noyori[5] gave brilliant results. Catalytic systems based on iron complexes and hydrogen peroxide are highly attractive in this regard, due to the large availability and low environmental impact of the iron coupled with the high atom-economy of H_2O_2.[6] Indeed, aminopyridine iron complexes have been recently demonstrated to promote effective and highly selective oxidation reactions, mimicking natural nonheme iron oxygenases.[7–14] Iron-catalyzed alcohol oxidation with H_2O_2 has been first explored by Beller and coworkers,[15–18] and in the last decade several iron complexes have been reported to mediate alcohol oxidation with H_2O_2[19–25] or *t*-BuOOH.[26] Also manganese-based catalysts in combination with H_2O_2 provided promising results in alcohol oxidation.[27–30]

In this scenario, we exploited the imine chemistry[31–34] to simplify the catalyst structure and to prepare the simple iminopyridine iron complex **1** that was found to be an effective catalyst for aliphatic C-H oxidation with H_2O_2.[35] Very gratifyingly we obtained results comparable to the ones reported for far more sophisticated catalysts.[34,36–38] Conveniently, complex **1** can be easily and quantitatively prepared *in situ* by the self-assembly of cheap and commercially available 2-picolylaldehyde **2**, 2-picolylamine **3** and $Fe(CF_3SO_3)_2$ added in acetonitrile solution in a 2:2:1 ratio (see Scheme 1).¶ Most interestingly, we found that catalyst **1** operates through a mechanism fully devoid of free diffusing radical intermediates, and hence is able of stereoretentive oxidations.[39] The oxidation is metal-based, and the H_2O_2 activation mechanism follows a path different from that generally observed for iron nonheme based imine catalysts.[34,40]



1 **2** **3**

Scheme 1: *In situ* formation of complex **1** by self-assembly of **2**, **3** and $Fe(CF_3SO_3)_2$.

The good results obtained in hydrocarbon oxidation under mild reaction conditions prompted us to extend our study to the

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[a] Dipartimento di Chimica, Università degli Studi di Roma "La Sapienza" and Istituto CNR di Metodologie Chimiche (IMC-CNR), Sezione Meccanismi di Reazione, c/o Dipartimento di Chimica, Università degli Studi di Roma "La Sapienza", P.le A. Moro 5, I-00185 Rome, Italy.
[b] Current address: Institut de Química Computacional i Catàlisi (IQCC) and Departament de Química, Universitat de Girona, Campus de Montilivi, 17071 Girona, Spain.
*E-mail: stefano.distefano@uniroma1.it;

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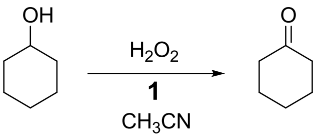
oxidation of the alcoholic function, and the data collected in such investigations are reported in the present paper.

Results and discussion

With our imine-based iron complex **1** in hand, we initially carried out a set of cyclohexanol to cyclohexanone oxidation by H_2O_2 exploring different reaction conditions (Scheme 2 and Table 1). The reaction is clean, with cyclohexanone as the only product (see GC chromatograms in the ESI). At first, the effect of catalyst loading was investigated. A marked enhancement of catalytic activity is evident on the increase of catalyst loading from 0.5 to 1 mol%, while further increase to 3 mol% and even to 5 mol% has a moderate impact (the yield increases from 67 to 74 % and from 74 to 76%, respectively, entries 1-4 of Table 1), suggesting a saturation behaviour for the catalytic activity versus catalyst loading. As reported also for other nonheme iron complexes,[7] slow addition of the oxidant is crucial (compare entries 2 and 5) in order to avoid high H_2O_2 concentration, which leads to unproductive consumption by disproportionation. Further increase of the addition time does not have any significant impact (entry 6).

Acetic acid does not exert any beneficial effect (see entry 7), in line with what observed in aliphatic C-H oxidation mediated by **1**.[39] Increase of the oxidant amount leads to higher yields, up to 74% with 2.5 equivalents (entry 8), but the same effect is not observed with an additional increase of the oxidant to 3.5 equivalents (entry 9). The combination of a higher catalyst loading (3 mol%) with 2.5 equivalents of the oxidant led to a decrease in efficiency, probably due to cyclohexanone overoxidation (entry 10). Any change of the reaction temperature from 25°C has a negative impact on the outcomes (compare entry 2 with entries 11 and 12, respectively). Catalyst **1** performances are negatively affected when a co-solvent is added to acetonitrile, even though a residual and sometimes satisfactory efficiency is retained with oxidatively robust ethyl acetate or trifluoroethanol (TFE).

From the above screening, the conditions described in entry 8 (slow addition of 2.5 molar equivalents of H_2O_2, 1 mol % catalyst **1**, 25 °C, CH_3CN) were selected and adopted in the oxidation of a series of alcohol substrates.



Scheme 2

At first, the effect of the alcohol ring size was evaluated in cyclopentanol and cycloheptanol oxidation, while 2-methylcyclohexanol and 2,6-dimethylcyclohexanol enabled to assess the impact of substrate steric hindrance on the catalytic efficiency (Table 2). Both cyclopentanol and cycloheptanol are oxidized slightly less efficiently than cyclohexanol.

Table 1. Oxidation of cyclohexanol to cyclohexanone catalyzed by complex **1**.[a]

entry	cat load (mol %)	H_2O_2 (eq.)	temp (°C)	co-solv (20%)	conv (%)[b]	yield (%)[b,c]
1	0.5	1.5	25	-	51	45
2	1	“	“	-	86	67
3	3	“	“	-	86	74
4	5	“	“	-	92	76
5	1[d]	“	“	-	42	41
6	1[e]	“	“	-	88	67
7	1[f]	“	“	-	39	29
8	1	2.5	“	-	93	74
9	“	3.5	“	-	92	57
10	3	2.5	“	-	100	70
11	1	1.5	0	-	70	58
12	“	1.5	40	-	84	59
13	1	1.5	25	CH_2Cl_2	57	47
14	“	“	“	AcOEt	70	58
15	“	“	“	acetone	30	12
16	“	“	“	TFE	70	51
17	“	“	“	*t*-amyl alcohol	59	42

[a] All the reagents were added at time t = 0 apart from the oxidant (H_2O_2) which is added during the first 30 min from start by a syringe pump, in CH_3CN. The reactions were quenched at 90 min from start. [b] GC conversions and yields defined as (mol unrecovered substrate/mol substrate)×100 and (mol product/mol substrate) respectively; average of three determinations (error ±2%). [c] when % mol catalyst is 1 numeric values of yield and TON coincide. [d] H_2O_2 added in one aliquot from start. [e] H_2O_2 added during 60 min from start. [f] Reaction carried out in the presence of 50% AcOH.

As for the substitution impact, an increase of the steric hindrance around the hydroxyl function leads to a definite reduction of the catalytic activity, which decreases in the series cyclohexanol (entry 8, Table 1), 2-methylcyclohexanol and 2,6-dimethylcyclohexanol (Table 2). Competitive oxidations carried out on 1:1 cyclohexanol/2-methylcyclohexanol and cyclohexanol/2,6-dimethylcyclohexanol mixtures led to the consistent molar ratios of cyclohexanone/2-methylcyclohexanone (1.36) and cyclohexanone/2,6-dimethylcyclohexanone (1.68), clearly supporting the steric origin of the selectivity.

Varying results have been obtained when the reaction was carried out on the linear alcohol. Oxidation of 3-pentanol to 3-pentanone proceeds smoothly (Table 2) as well as the oxidation of cyclohexanol to cyclohexanone (Table 1, entry 8). However, the presence of a methyl group in the β position leads to a marked decrease in efficiency (4-methyl-2-butanol, Table 2). 2-Decanol was found to be scarcely soluble in CH_3CN and 20% CH_2Cl_2 was required to carried out the reaction in homogeneous conditions. The presence of the co-solvent leads

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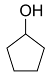
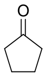
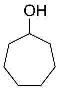
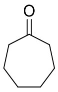
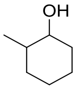
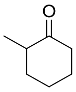
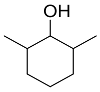
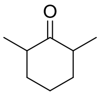
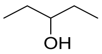
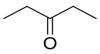
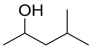
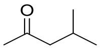
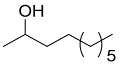
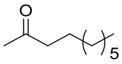
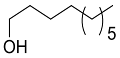
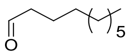
to a significant yield decrease, as already found for cyclohexanol (see entry 13 in Table 1).

Table 2. Oxidation of aliphatic alcohols to the corresponding ketones with H_2O_2 catalyzed by complex **1** in CH_3CN at 25 °C.[a]

Substrate	conv (%)	product	yield (%)
	77		54
	67		56
	73		54
	51		38
	80		76
	57		50[c]
	62		34[c]
	61		20[c,d]

[a] Reaction condition as in entry 8 of Table 1. GC conversions and yields defined as (mol unrecovered substrate/mol substrate)×100 and (mol product/mol substrate) respectively, average of three determinations (error ±2%). Numeric values of yield and TON coincide. [b] reaction carried out in CH_3CN/CH_2Cl_2 80:20. [c] Ketone product is accompanied by lower amounts of C-H oxidation products. [d] Carboxylic acid is also detected

Primary alcohols are less prone to oxidation, and this is reflected in the low yield obtained in 1-decanol oxidation.

Eventually, oxidation of cyclohexanol to cyclohexanone and cycloheptanol to cycloheptanone were carried out in preparative scale (500 mg of substrate) under the optimized conditions. The reaction proceeds smoothly at this scale with no losses in efficiency, yielding 67% and 50% of ketone products, respectively (see ESI for procedures). Conveniently, the ketone could be easily obtained pure after a quick filtration on a one inch SiO_2 layer with dichloromethane,[§] demonstrating the good potential of such catalyst for synthetic purpose.

At this point we turned our attention to benzylic alcohol substrates. Oxidation of benzyl alcohols to carbonyl compounds is usually more facile than oxidation of aliphatic ones since the hydrogen atom transfer (HAT) process from the α-C-H(OH) bond to the metal-based oxidant (a mechanism similar to that proposed for the oxidation of benzylic alcohols promoted by the active species of cytochrome P450[41]) is facilitated by the low BDE of the benzylic α-C-H(OH) bond.[42] In addition, HAT from benzyl alcohols is also favored by the stabilization of the partial positive charge developing on the benzylic carbon in the TS due to polar effects.[43,44] Surprisingly, disappointing results have been obtained in the oxidation of these substrates with catalyst **1**. Primary benzyl alcohol and secondary 1-phenylethanol are sluggishly oxidized into the corresponding carbonyl compounds, with poor mass balances (see entry 1 and 2 of Table 3, respectively). We speculated that the highly electrophilic oxidizing species[39] formed by reaction of **1** with H_2O_2 would preferentially hydroxylate the aromatic ring, forming a phenol which would strongly coordinate to the iron center leading to catalyst deactivation. Such a process has been already described with other nonheme iron oxidation catalysts, for which a metal-based oxidation has been firmly established.[45–48] In support of this hypothesis, in the GC-MS chromatograms we observed peaks assigned to aromatic oxidation byproducts in comparable amounts to the one of the desired ketones. Moreover, when cyclohexanol oxidation was carried out in the presence of equimolar amounts of toluene or benzene, catalytic activity dramatically dropped down (10% and 11% cyclohexanone yield, respectively), reinforcing the idea of competitive aromatic ring oxidation with subsequent catalyst deactivation.[‡] In order to investigate further this effect we performed the oxidation of a series of 4-substituted-1-phenylethanols, regularly varying the electron density of the aromatic ring. The results are reported in the entries 3-7 of Table 3. The yield of the ketone product steadily increases on increasing the electron withdrawing power of the substituent. Such trend is at odds with the ease of alcohol oxidation, since the most electron rich substrate is usually the most prone to oxidation.[29] However, it can be rationalized in terms of the ease of competitive aromatic oxidation. The more electron donating is the substituent, the more prone to oxidation is the aromatic ring, with respect to the alcoholic moiety. Indeed, the same trend can be observed for the mass balance of the reaction, indicating that the withdrawal of electron density from the aromatic ring tends to switch the preferential oxidation site from the arene to the benzylic position. A similar behavior has been observed in the oxidation of alkylaromatic substrates.[49] On the other hand, the presence of an electron withdrawing group on the aromatic moiety could weaken the binding between the phenol function derived from aromatic oxidation with the active form of the iron complex, resulting in a less efficient deactivation of the catalyst.

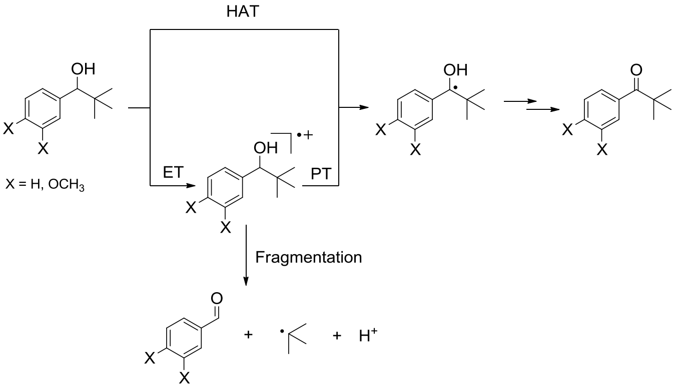
Eventually we investigated the plausibility of an electron transfer (ET) oxidation mechanism, akin to the one recently reported for sulfoxidation[50] and *N*-demethylation of *N*,*N*-dimethylanilines processes[51,52] catalyzed by nonheme iron(IV)-oxo complexes. In the case of 1-phenyl-2,2-dimethylpropanol oxidation, an ET mechanism would form a radical cation which undergoes rapid fragmentation to yield benzaldehyde, in competition with proton transfer and ketone formation (Scheme

3).[53] When oxidation of such a substrate was carried out in the presence of catalyst **1**, no trace of benzaldehyde was detected. Even when the more reducing 1-(3',4'-dimethoxy)phenyl-2,2-dimethylpropanol was used as a substrate, no trace of the corresponding aldehyde was found in the product mixture. Therefore, an ET oxidation mechanism can be reasonably ruled out.

In contrast with the above findings and the reports of the incompatibility of aromatic rings with nonheme iron mediated oxidations, some iron-based alcohol oxidation catalysts have been recently reported to efficiently convert benzylic alcohols into the corresponding carbonyl compounds.[19,23,24,26] However, competitive aromatic oxidation occurs whenever a high-valent iron species is clearly implicated in the oxidation mechanism.[45–48,54]

At this point, a competitive oxidation experiment between equimolar amounts of the expected more reactive 1-phenylethanol and cyclohexanol was carried out. Although not high in absolute value, yield in cyclohexanone (16 %) doubles the one in acetophenone (8 %). The latter is a very peculiar feature of catalyst **1** which seems to prefer the oxidation of a substrate less activated from both an enthalpic (BDE α-C-H(OH) = 92.8 and 85.1 kcal/mol for cyclohexanol and 1-phenylethanol, respectively)[42] and polar effects (Scheme 4).

For the sake of comparison, the same competitive experiment was carried out under the same conditions in the presence of complex **4** ([(TPA)Fe(CF_3SO_3)$_2$], which is known to oxidize benzyl alcohol.[55] In this case the inverse result was obtained, with cyclohexanone yield being almost half of the acetophenone one (10 % and 17 %, respectively), in accordance with BDE-based prediction. The results of the last two experiments emphasize a very specific character of catalytic properties of complex **1**, but the reasons for this unusual behavior are not fully disclosed at this stage. Nevertheless one possible explanation for the inversion of selectivity going from **1** to **4** could be ascribed to the lower steric accessibility of the iron center in the former. A rather sterically encumbered pentacoordinated oxidizing species is indeed supposed to form from reaction of **1** with H_2O_2 thanks to the detach of one of the pyridyl arm of the complex.[39] Such an oxidizing species would



Scheme 3

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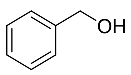
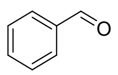
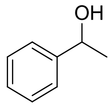
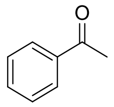
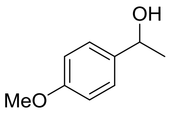
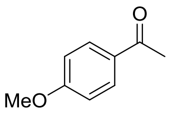
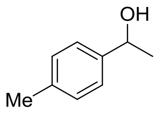
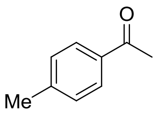
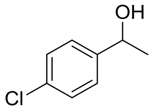
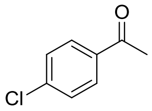
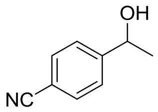
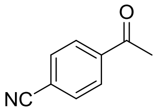
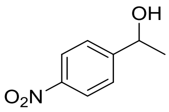
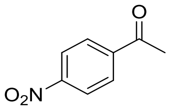
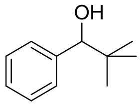
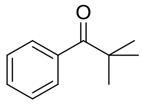
Table 3. Oxidation of benzylic alcohols to the corresponding aldehydes or ketones with H_2O_2 catalyzed by complex **1**.[a]

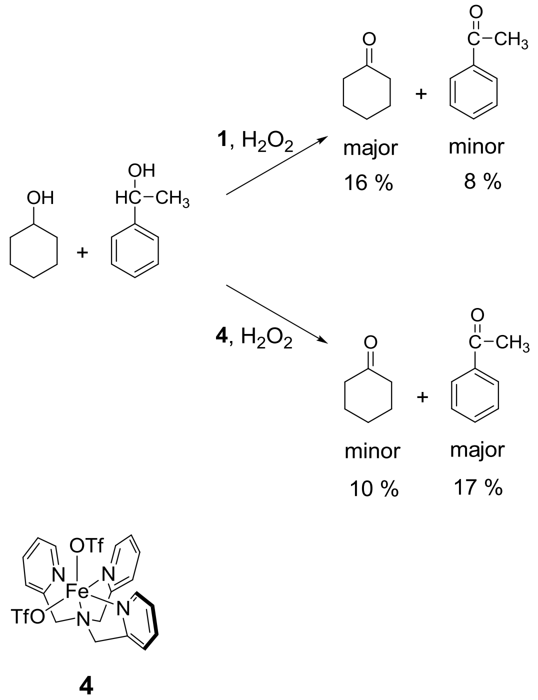
Entry	substrate	conv (%)	product	yield (%)
1[b]		51		21
2[b]		58		9
3[b]		80		5
4[b]		65		6
5[b]		36		11
6		55		29
7		53		30
8[b]		68		14

[a]Reaction condition as in entry 8 of Table 1. GC conversions and yields defined as (mol recovered product/mol substrate)×100 and (mol product/mol substrate) respectively, average of three determinations (error ±2%). Numeric values of yield and TON coincide. [b]dihydroxyl derivatives appear in the mass spectra of the product mixture, see ESI.

be more sterically demanding than the one generated by reaction of the tetracoordinated **4** with H_2O_2. We carried out competitive oxidations on 1:1 mixtures of cyclohexanol and 2-methylcyclohexanol and of cyclohexanol and 2,6-dimethylcyclohexanol in the presence of complex **4**. Such oxidations led to ratios cyclohexanone/2-methylcyclohexanone 0.68 and cyclohexanone/2,6-dimethylcyclohexanone 1.25, respectively. Comparison with the related ratios obtained in the presence of complex **1**, 1.36 and 1.68 (see above), respectively, points out to a possible steric origin of the selectivity properties of catalyst **1**.

Conclusions

In conclusion, we carried out a series of aliphatic and benzylic alcohol oxidations with H_2O_2 catalyzed by the readily available complex **1**. We obtained moderate-to-good yields in the case of aliphatic secondary alcohols, depending on substrate steric hindrance. Primary alcohols react sluggishly in comparison with secondary ones, and probably competitive C-H oxidation reactions takes place. Benzylic alcohols are oxidized only in low yields, due to competitive aromatic hydroxylation reactions. Interestingly, in a competitive oxidation experiment, less reactive cyclohexanol is oxidized preferentially with respect to 1-phenylethanol. The cause of this unprecedented selectivity is not fully clear at this stage, and are currently under investigation in our laboratory.



Scheme 4

Experimental

In a typical oxidation experiment $Fe(CF_3SO_3)_2(CH_3CN)_2$ (1.09 mg, 2.50 μmol), picolylamine (from a ~0.1 M CH_3CN solution, 5.0 μmol) and picolylaldehyde (from a ~0.1 M CH_3CN solution, 5.0 μmol) were mixed in a vial at 25°C. Substrate (250 μmol) and CH_3CN were then added up to a total volume of 700 μL. A ~0.7 M CH_3CN solution of H_2O_2 (diluted from a 35% w/w H_2O_2 commercial solution) was added over 30 minutes by syringe pump under vigorous stirring, and left reacting for additional 60 minutes. At this point an internal standard was added (bibenzyl, 125 μmol) and the reaction mixture was filtered over a short pad of SiO_2 with 2 mL of AcOEt. The filtered solution was subjected to GC or evaporated to furnish the product mixture.

When the reaction was carried out on 0.5-gram scale, the filtration was performed with CH_2Cl_2, and the pure ketone product was collected after the silica plug.

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Notes and references

¶ Complex **1** was previously characterized by means of a series of techniques including X-ray diffraction, ^1H NMR and UV-vis spectroscopy, elemental analysis, ESI-MS, cyclic voltammetry (see ref 35 and 39). Complex **1** was shown to have a high stability in acetonitrile solution even at very low concentrations (UV-vis titrations, see ref 35). Furthermore, complex **1** was also shown to be highly stable also in the oxidative reaction conditions by means of coupled UV-vis and ESI-MS investigations: although it slowly undergoes oxidative degradation paths during the reaction, remains the most abundant iron containing species and the most catalytically active species along large part of the reaction timecourse (see ref 39).

§ Unreacted alcohol remains on the silica layer.

‡ A comparable decrease of cyclohexanone yield was also observed when the cyclohexanol oxidation catalyzed by **1** was carried out in the presence of 10 % mol phenol.

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Graphical abstract

A cheap and easily available catalyst for alcohol oxidations with unexpected selectivity features.