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Efficient and Selective Oxidation of Primary and Secondary Alcohols Using an Iron(III)/Phenanthroline Complex: Structural Studies and Catalytic Activity

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An efficient catalytic system for the oxidation of alcohols has been developed by using iron(III) catalyst $[Fe(phen)_2Cl_2]NO_3$ (1) (phen = 1,10-phenanthroline) and H_2O_2 as terminal oxidant. A series of primary and secondary alcohols were oxidized into aldehydes and ketones in good yields and excellent

Introduction

The selective oxidation of alcohols remains an important transformation for organic synthesis and the chemical industry.^[1] Numerous catalytic systems that use transition metals such as Co,^[2] Mn,^[3] Au,^[4] Cu,^[5] Mo,^[6] Ru,^[7] and Pd^[8] have been reported. However, most of these systems suffer from high reagent load, harsh reaction conditions, high cost, toxicity of the metal, or they form unwanted waste. From both environmental and economic points of view, the search for effective catalytic oxidation processes that use clean, inexpensive terminal oxidants, such as molecular oxygen or hydrogen peroxide, is highly attractive.^[9] Iron is a cheap and less toxic metal; iron and hydrogen peroxide together is an ideal green combination because water is the only byproduct formed in this transformation.^[10] Recently, iron has become broadly used in many oxidation processes such as epoxidation,^[11] sulfoxidation,^[12] hydrox-

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selectivities after a short reaction time. The mononuclear iron(III) complex [Fe(phen)₂Cl₂]NO₃ was characterized by several independent methods. The X-ray structure shows distorted octahedral geometry around the Fe^{III} center, which is in a high-spin state (S = 5/2) according to Mössbauer study.

ylation,^[11d,13] and oxidation of arenes to phenols.^[14] In general, chemoselectivity is the key issue for these reactions due to potential nonselective Fenton- or Gif-type chemistry.^[15] Although alcohol oxidations catalyzed by iron complexes have been investigated in many systems,^[15d,15f,16] no general method has been discovered so far and improvements that use clean and safe oxidation procedure are still needed. Thus a catalytic system with iron metal holds a promising future with regards to sustainability and selective transformations.

Polypyridine derivatives, such as 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), and 2,2':6',2''-terpyridine (tpy), have attracted substantial interest in recent years.^[17] 1,10-Phenanthroline ligands have been extensively utilized for the complexation of metal cations, particularly those of the d and f blocks. For the structure–reactivity correlation and the investigation of the mechanistic pathway, the chemistry of Fe–phenanthroline-catalyzed oxidations was extensively studied in the nineteenth century.^[18–21]

Herein, we present a novel catalytic system for the efficient oxidation of primary and secondary aliphatic alcohols. The system is based on a synthesized iron(III) complex $[Fe(phen)_2Cl_2]NO_3$ (1) and uses H_2O_2 as terminal oxidant and aqueous solution as solvent. The synthesis, crystal structure, and UV/Vis, IR, and Mössbauer spectroscopy studies of the complex are also reported.

Results and Discussion

Synthesis of [Fe(phen)₂Cl₂]NO₃ (1)

Complex 1 was synthesized by adding 1,10-phenanthroline into a solution of $FeCl_3$ in acetic acid and water (60:40 v/v). Ammonium ceric nitrate (CAN) was added into the Date: 29-08-12 15:13:36

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reaction mixture to maintain the Fe^{III} oxidation state. Compound **1** was isolated in good yield (80%) as red crystals. The complex is sufficiently stable in air and in the presence of moisture. It is soluble in almost all solvents such as methanol, ethanol, dichloromethane, acetonitrile, dimethylformamide, and dimethyl sulfoxide. The synthetic procedure is summarized in Scheme 1.

$$\begin{array}{c} \text{1 equiv. FeCl}_{3} \\ + \text{2 equiv. phen} \\ + \text{1 equiv. CAN} \end{array} \xrightarrow{\text{AcOH/H}_{2}O} [Fe(phen)_{2}Cl_{2}]NO_{3} \\ \hline 1 \end{array}$$

Scheme 1.

Description of the Crystal Structure

Structural analysis reveals that the crystal lattice of 1 consists of a mononuclear [Fe(phen)₂(Cl)₂]NO₃ unit. An Oak Ridge thermal ellipsoid plot (ORTEP) with an atom numbering scheme of 1 is shown in Figure 1. Bond lengths and angles relevant to the coordination sphere around Fe^{III} are listed in Table 1. The coordination polyhedron around each Fe^{III} is best described as a distorted octahedron with an N_4Cl_2 core. The distortion from the ideal octahedral geometry is due to the different bite angles of nitrogen atoms of phen units and the deviation of the refined angles (90/180°) at the metal centers (Table 1). The coordination includes two chelated symmetrical bidentate ligated by four N atoms along with two coordinated Cl atoms in mutual cis orientation in 1. The angle $97.36(4)^{\circ}$ between the two coordinated chlorine atoms around the Fe^{III} center as Cl2-Fe1-Cl2* indicates the cisoid representation of the structure. The Fe-N/Cl bond lengths range from 2.132(3) to 2.2683(10) Å, and the difference Δ between the longest and shortest Fe–N/Cl bonds is 0.1363 Å. Comparative values of Fe–N and Fe–Cl bond lengths of 2.250(11) and 2.246(4) Å,

respectively, were found for the ferrous complex $[Fe(phen)_2Cl_2][FeCl_4]$, which indicates a high-spin (HS) state.^[22]



Figure 1. An ORTEP of $[Fe(phen)_2Cl_2]NO_3$ (1) with atom-numbering scheme and 30% probability ellipsoids for all non-hydrogen atoms.

Table 1. Selected bond lengths [Å] and angles [°] for 1.

| 2.175(3) | Fel-N1* | 2.175(3) |
|-----------|---|--|
| 2.132(3) | Fe1-Cl2 | 2.2683(10) |
| 2.132(3) | Fe1-Cl2* | 2.2683(10) |
| | | |
| 76.72(10) | N1-Fe1-N2* | 90.29(10) |
| 84.82(10) | N2-Fe1-N2* | 162.50(11) |
| 90.29(10) | N1*-Fe1-N2* | 76.72(10) |
| 89.33(7) | Cl2-Fe1-N2 | 95.49(7) |
| 170.63(7) | Cl2-Fe1-N2* | 96.04(8) |
| 170.63(7) | Cl2*-Fe1-N2 | 96.04(8) |
| 97.36(4) | Cl2*-Fe1-N1* | 89.33(7) |
| 95.49(8) | | |
| | 2.175(3) 2.132(3) 2.132(3) 76.72(10) 84.82(10) 90.29(10) 89.33(7) 170.63(7) 170.63(7) 97.36(4) 95.49(8) | 2.175(3) Fe1-N1* 2.132(3) Fe1-Cl2 2.132(3) Fe1-Cl2* 76.72(10) N1-Fe1-N2* 84.82(10) N2-Fe1-N2* 90.29(10) N1*-Fe1-N2* 89.33(7) Cl2-Fe1-N2 170.63(7) Cl2-Fe1-N2* 97.36(4) Cl2*-Fe1-N1* 95.49(8) |

Intermolecular C–H···O, intermolecular C–H···Cl hydrogen bonds, and π ··· π interactions in 1 consolidate the interlocking between adjacent molecular moieties to result in 3D supramolecular structures (Figure 2). The relevant noncovalent forces and the parameters are shown in Table S1 in the Supporting Information.



Figure 2. Projection of the crystal packing showing a supramolecular network of monomeric units of 1.



UV/Vis and IR Spectroscopic Studies of 1

UV/Vis spectroscopic studies of 1 were performed with a pink methanolic solution (10^{-4} M) . In the spectrum, initially there are two bands that appear at 231 and 259 nm with high absorbance values. This indicates the presence of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions for the C=N chromophore of the phen moiety coordinated to Fe^{III}. Although Fe^{III} is a 3d⁵ system, the intense pink color of the solution is due to charge-transfer absorption. After initial measurements, the solution was kept for a few weeks with gradual color changes from pink to red, and then to intense red. Simultaneously, a band at 508 nm with maximum absorbance (2.12) appeared. The UV/Vis measurement was taken over a 3 h period with an increase in the absorbance at 508 nm band that indicates the presence of Fe^{II} in solution (Figure 3).



Figure 3. UV/Vis spectrum of the iron compound $(1 \rightarrow 4 \text{ indicates} \text{ successive absorption bands of iron compound in methanol after 30 min interval; inset: absorption bands in the visible region).$

In IR spectrum of 1, a sharp and intense band at 1384 cm^{-1} , indicates the presence of ionic nitrate.^[23] The v(C=N) stretching vibrations of phen bound to metal ion are seen at 1517 (s) and 1426 (s) cm⁻¹. All other characteristic ligand vibrations are in the 1600–600 cm⁻¹ region.

Alcohol Oxidation Experiments

The synthesized catalyst was tested for alcohol oxidation by using benzyl alcohol as a model substrate (Table 2, Scheme 2). We first investigated the effect of oxidants and then solvents. The desired benzaldehyde was only obtained in moderate to high conversion and selectivity in the presence of *tert*-butyl hydroperoxide (TBHP) as oxidant (88, 41, and 60%, respectively; Table 2, entries 1–3). Molecular oxygen showed no reactivity under the same reaction conditions, whereas H_2O_2 demonstrated an improvement in the conversion with moderate selectivity (Table 2, entries 7–9).

Table 2. Oxidation of benzyl alcohol: optimization of the catalytic system. $^{\left[a\right] }$

| Entry | Solvent | Oxidant | 2/3 ^[b] ratio | % Conv.[c] |
|-------|-------------------|----------|---------------------------------|------------|
| 1 | MeCN | TBHP | 10:1.0 | 88 |
| 2 | toluene | TBHP | 10:1.2 | 41 |
| 3 | alkaline water | TBHP | 10:1.4 | 60 |
| 4 | MeCN | O_2 | 10:1.6 | 8 |
| 5 | toluene | O_2 | 10:3.0 | 13 |
| 6 | alkaline water | O_2 | 10:1.0 | 24 |
| 7 | MeCN | H_2O_2 | 10:1.5 | 65 |
| 8 | MeCN/acetic acid | H_2O_2 | 10:2.8 | 72 |
| 9 | buffer $(pH = 1)$ | H_2O_2 | 10:0.1 | 98 |
| 10 | buffer $(pH = 2)$ | H_2O_2 | 10:2 | 90 |
| 11 | buffer $(pH = 4)$ | H_2O_2 | 10:2.9 | 60 |
| 12 | buffer $(pH = 1)$ | TBHP | 2.5:10 | 90.1 |
| 13 | buffer $(pH = 1)$ | O_2 | 10:1 | 16 |

[[]a] Reaction conditions: see the Exp. Section. [b] Chemoselectivity ratio (see Scheme 2). [c] Conversion and yield were determined by GC analysis; average of two runs.



Scheme 2.

It has recently been reported that a carefully pH-controlled solution of iron-based oxidation catalyst enhances the selectivity.^[11a,11b] Similarly, when we used acidic buffer solution (pH = 1) as a solvent, both conversion and selectivity increased to 98 and 99%, respectively (Table 2, entry 9). Changing the pH value from 1 to 2 and 4 (Table 2, entries 10 and 11) resulted in lower selectivity as the amount of acid increased. These results are in agreement with previous work.^[24,25] A maximum in the oxidation rate is observed at a pH that corresponds to the lowest H₂O₂ decomposition rate.^[26,27] Moreover, this pH range corresponds to the highest stability zone of the soluble Fe^{III}(OH)⁺² complex.^[26,27] By decreasing the pH (more acidic media), the concentration of stable ferric ions (Fe⁺³) increases at the expense of the concentration of the Fe⁺² species,^[28] whereas by increasing the pH (more basic media) the insoluble ferric hydroxides precipitate.

Next, we investigated the concentration effect of the oxidant. Here, the hydrogen peroxide addition rate as well as the total amount of oxidant was varied. The best results were obtained by employing 2.0 equiv. of H_2O_2 , which were added to the reaction mixture within 10 min (89% conversion, 75% yield).

The efficiency of the catalyst was studied by using structurally diverse secondary and primary alcohols under the optimized reaction conditions. As Table 3 shows, α , β -unsaturated primary alcohols, such as allylic and benzylic alcohols, can be selectively oxidized to the corresponding aldehydes in excellent yields. Similarly, α , β -saturated primary alcohols such as 1-octanol and 1-undecanol produced their corresponding aldehyde in moderate yield (52–56%; Table 3, entries 1–3). The capability of the catalyst to oxid-

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ize primary aliphatic alcohols into carbonyl products in very good yield is worth noting. Following the success of oxidizing primary alcohols selectively, we tested the reaction of secondary alcohols. Secondary aliphatic alcohols were oxidized selectively to the corresponding ketones in excellent yields (70–100%; Table 3, entries 4–9). Not only α , β -unsaturated secondary alcohols, such as phenyl propanol (95%; Table 3, entry 4) and 1-phenylethanol (96% yield, 99% selectivity; Table 3, entry 10) were easily converted but also sterically demanding secondary alcohols, such as those in entries 6 and 7 in Table 3, were converted to a moderate degree.

The catalyst displays an interesting regioselectivity for a vicinal diol such as 1-phenyl-1-ethanediol. Only the secondary hydroxy group is oxidized, which leaves the primary alcohol function intact (Table 3, entry 12). 2-Hydroxyacetophenone was observed as the main product (75%), and only a small amount of mandelic acid (15%) was obtained. Also, 2-thiophenemethanol (entry 13) was smoothly oxidized to the corresponding acid with high conversion and selectivity. In general, it is considered to be a difficult substrate for most oxidation systems that involve transition metals because of their strong coordination ability with the sulfide group. It is worth noting that the sulfide group that is susceptible to oxidation remained here unreacted.

Next we investigated the oxidation of allylic alcohols by testing the reactivity of cinnamyl alcohol (Table 3, entry 10). By using the standard conditions (3 mol-% of catalyst, 2.2 equiv. of H_2O_2 , 60 min), we obtained a high conversion (91%) but a moderate selectivity (83%) to cinnamaldehyde.

To understand the mechanism of our system, we performed a concentration/time graph for the oxidation of the benzyl alcohol (see the Supporting Information). After addition of the oxidant, the formation of benzaldehyde started immediately. Then a linear consumption of benzyl alcohol occurred, followed by formation of aldehyde. After 10 min of reaction time, some degradation was observed with lower selectivity. However, potential side products such as benzoic acid were detected with low concentration. Next, we performed additional reactions by using a radical inhibitor [i.e., (2,2,6,6-tetramethylpiperidinyl)-N-oxyl (TEMPO)] to exclude a radical pathway. In the presence of TEMPO (1 equiv.), we observed a higher influence on the reactivity. Here, benzaldehyde is obtained in 42% yield with 99% selectivity. However, TEMPO is a well-known ligand in iron-catalyzed oxidations.^[9a,9e] Hence, we postulate that the decrease in reactivity is due to a change in the iron complex rather than an inactivation of radical species. In summary, under our experimental conditions, the oxidation of alcohols should not be induced by a Fenton free-radical diffusion pathway.

We performed ESI-MS measurements to obtain more insights into the molecular nature of the active catalyst and its precursors. The spectrum of a freshly prepared complex 1 in acetonitrile showed in positive-ion mode a peak of m/z486.0096 that corresponded to [Fe(phen)₂Cl₂]. Then, we subjected a sample of the reaction mixture after 15 min of reaction to ESI-MS measurements. The appearance of a Table 3. Oxidation of various alcohols into aldehydes and $ketones.^{\left[a\right] }$

| C | OH 1.5 mol-% Fe(pho buffer, 2.2 equiv. | $(H_2O_2)^2$ | | |
|-------|---|--------------|---------------------------|-----------------------------|
| Entry | Substrate | t (min) | Yield ^[b] % | Select. ^[c] % |
| 1 | ОН | 30 | 97 | 98 |
| 2 | ОН | 60 | 65 | 90 |
| 3 | ОН | 120 | 62 | 91 |
| 4 | OH | 30 | 95 ^[d] | 99 |
| 5 | ОН | 60 | 96 | 99 |
| 6 | | 60 | 93 | 99 |
| 7 | но | 120 | 65 | 99 |
| 8 | OH | 120 | 73 | 99 |
| 9 | ОН | 120 | 69 | 99 |
| 10 | ОН | 60 | 91 | 83 |
| 11 | ОН | 120 | 35 | 99 |
| 12 | он он | 60 | 81 | 75 |

[a] Reaction conditions: see the Exp. Section. [b] Conversion and yield were determined by GC–MS (using decane as internal standard) and ¹H NMR spectroscopy; average of two runs. [c] Chemoselectivity. [d] Isolated yield.

30

90

99

peak at m/z 378.09 that corresponded to [Fe(phen)(benzyl alcohol)Cl] confirms the coordination of the substrate to the complex. Although the experiment was repeated twice, we could not detect H₂O₂ coordination. It is worth noting that the oxidation of alcohols to the corresponding carbonyl compounds is known to take place by high-valent metal complexes.^[1a,29] Therefore, alcohol oxidation with

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this system could be achieved by means of high-valent iron species. However, further studies of this mechanism are on-going.

⁵⁷Fe Mössbauer Spectroscopy

Mössbauer spectra of 1 were recorded at variable temperatures over the temperature range 300–77 K with a relatively high maximum Doppler velocity (Figure 4). Spectra could be fitted to one singlet with isomer shift δ = $0.36(1) \text{ mm s}^{-1}$ at 77 K, which is typical for an iron(III) ion in the HS state, S = 5/2. No spin-state crossover and no ordered phase was observed over the range of investigated temperatures and velocities. This measurement thus confirms the success of our synthesis without coprecipitation of the reduced complex [Fe(phen)₂Cl₂] by comparison of its hyperfine parameters at 77 K ($\delta = 1.02 \text{ mm s}^{-1}$ and $\Delta E_{\Omega} =$ 3.15 mm s⁻¹), which are typical of a ferrous material.^[30] Coprecipitation of the starting salt can also be excluded (δ = 0.53 mm s⁻¹).^[31] This result is in agreement with the crystal structure, which reveals only one iron site. It is worth noting that the Mössbauer parameters of 1 compare well with the isomer shift of the ferric complex [Fe(phen)₂Cl₂]ClO₄ recorded at 80 K ($\delta = 0.39 \text{ mm s}^{-1}$).^[32]



Figure 4. ⁵⁷Fe Mössbauer spectrum of 1 at 77 K.

Conclusion

We report a convenient and efficient method for the oxidation of benzylic and aliphatic primary and secondary alcohols by using an iron-based catalyst with hydrogen peroxide as terminal oxidant. This methodology can also be applied to more steric compounds like *endo*-fenchyl alcohol, menthol, or cyclopropyl(phenyl)methanol. After a short reaction time (30 min up to 120 min), the desired carbonyl compounds are obtained in moderate to very good yields (35–98%) and excellent selectivity (80–99%). Mechanistic investigations reveal that diffusion free radicals are not significantly involved in the oxidation.

Experimental Section

General: All solvents and chemicals are commercially available and were used as received or synthesized according to procedures in the literature. Aqueous H₂O₂ (30%) from Sigma-Aldrich was used as received. NMR spectra were measured with a Variant 300 spectrometer at 300 MHz (¹H) and 75 MHz (¹³C). All spectra were recorded in CDCl₃ or $[D_6]DMSO$, and chemical shifts (δ) are reported in ppm relative to tetramethylsilane referenced to the residual solvent peaks. Spectra were measured at room temperature. High-resolution mass spectrometry experiments (ESI) were performed with a time-of flight mass spectrometer equipped with an electrospray ion source (Bruker microTOF). All analyses were carried out in a positive-ion mode. The sample solutions were introduced by continuous infusion with the aid of a syringe pump at a flow rate of 180 µL min⁻¹. The instrument was operated at end plate offset -500 V and capillary -4500 V. Nebulizer pressure was 0.8 bar (N_2) , and the drying gas (N_2) flow was 7 Lmin⁻¹. Capillary exit and skimmer 1 were 90 and 30 V, respectively. Sodium formate was used for mass calibration for a calibration range of m/z 100–2000. Drying gas temperature was set to 220 °C. Elemental analyses (carbon, hydrogen, and nitrogen) were performed with a Perkin-Elmer 2400 CHNS/O elemental analyzer. IR spectrum was recorded (KBr discs, 4000–300 cm⁻¹) with a Perkin–Elmer RX1 FTIR spectrometer. Ground-state absorption was measured with a JASCO V-530 UV/Vis spectrophotometer. The software used for the simulations was Bruker Daltonics Data Analysis (version 3.3) Reaction products were isolated and analyzed quantitatively by means of GC (Agilent 6890 chromatograph, Agilent 19091 J-413 capillary column 0.32 mm \times 30 m \times 0.25 mm, FID detector) using decane as internal standard. Products were identified by GC-MS analyses (Agilent 6890N equipped with Agilent 5973 mass selective detector) and DB-innowax 19091 1-102 capillary columns (200 mm \times 24 m \times 0.31 mm). ⁵⁷Fe Mössbauer spectra were recorded in transmission geometry with a constant acceleration mode conventional spectrometer equipped with a 20 mCi ⁵⁷Co(Rh) source and a Reuter Stokes proportional counter. The sample was sealed in aluminum foil and spectra were recorded at room temperature and 77 K with a liquid nitrogen cryostat Optistat DN from Oxford instruments. The spectra were fitted with Recoil 1.05 Mössbauer Analysis software.^[33] The isomer shift values are given with respect to α -Fe at room temperature.

Synthesis: Mononuclear complex [Fe(phen)₂Cl₂]NO₃ (1) was prepared using a 1:2:1 mol ratio of iron(III) chloride, 1,10-phenanthroline, and ammonium ceric nitrate (CAN). A typical synthesis is described in the following: A solution of phen (0.396 g, 2 mmol) in acetic acid/water (6:4, 5 mL) was added dropwise to a solution of FeCl₃·6H₂O (0.270 g, 1 mmol) in the same solvent (10 mL) while slowly stirring (450 rpm) the solution. Then solid CAN (550 mg, 1 mmol) was added portionwise into the pink solution and stirring was continued for an additional 30 min. The pink solution turned red, and the supernatant liquid was kept in air for slow evaporation. After 7-10 days, complex 1 was separated out, washed with hexane, and dried under vacuum over a silica gel dessicator. Yield (based on metal salt): 0.2178 g (80%). $C_{24}H_{16}Cl_2FeN_5O_3$ (1, 549.18): calcd. C 52.48, H 2.93, N 12.75; found C 52.54, H 2.99, N 12.81. IR (KBr pellet): $\tilde{v} = 1384$ (s), 1426 (m), 1517 (s) cm⁻¹. The complex is soluble in almost all solvents such as methanol, ethanol, dichloromethane, acetonitrile, dimethylformamide, and dimethyl sulfoxide.

X-ray Crystallography: A summary of the crystallographic data and structure refinement parameters is given in Table 4. Single crystals (size $0.07 \times 0.09 \times 0.12$ mm) of 1 were obtained by slow evapora-

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tion of the reaction mixture in an acetic acid/water solution. Red crystals suitable for X-ray crystallographic analysis were selected following examination under a microscope. Diffraction data 250(2) K were collected with a Kappa CCD diffractometer using Mo- K_{α} radiation ($\lambda = 0.71073$ Å). Systematic absence led to the identification of space group C2/c (15). Of the 10159 unique reflections, 3335 with $I > 2\sigma(I)$ were used for structure solutions. The structure was solved by direct methods, and the structure solution and refinement were based on $|F|^2$. All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas hydrogen atoms were placed in calculated positions when possible and given isotropic U values 1.2 times that of the atom to which they are bonded. At convergence the final residuals were R1 = 0.0775; wR2 = 0.2882 with $I > 2\sigma(I)$, goodness-of-fit = 1.399. The final differences Fourier map showed the maximum and minimum peak heights at 2.499 and -0.505 e Å⁻³ with no chemical significance. All calculations were carried out using SHELXL-97.[34] CCDC-818508 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.

Table 4. X-ray crystallographic data of [Fe(phen)₂Cl₂]NO₃ (1).

| Empirical formula $C_{24}H_{16}Cl_2N_5O_3Fe$ M_r 549.17 T [K] 250(2) λ [Å] 0.71073 Crystal system monoclinic Space group $C2/c$ (15) a [Å] 15.559(3) b [Å] 13.588(3) c [Å] 12.905(3) a [°] 90 β [°] 101.501(3) γ [°] 90 V [Å ³] 2673.4(9) Z 4 $D_{calcd.}$ [Mg m ⁻³] 1.364 e [mm ⁻¹] 0.797 $F(000)$ 1560 Crystal size [mm ³] 0.07 × 0.09 × 0.12 θ range [°] 2.01 to 28.36 Index ranges $-17 \le h \le 20$ $-18 \le k \le 15$ $-15 \le l \le 17$ Reflections collected 10159 Independent reflections 3335 [R(int) = 0.0169] Completeness to $\theta = 28.36^{\circ}$ 99.6% Absorption correction multiscan Max./min. transmission 0.775/0.673 Refinement method full-matrix least-squares on F^2 Data/res | | |
|---|--|------------------------------------|
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| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | <i>T</i> [K] | 250(2) |
| Crystal system monoclinic Space group $C2/c$ (15) a [Å] 15.559(3) b [Å] 13.588(3) c [Å] 12.905(3) a [°] 90 β [°] 101.501(3) γ [°] 90 β [°] 101.501(3) γ [°] 90 V [Å3] 2673.4(9) Z 4 $D_{calcd.}$ [Mg m ⁻³] 1.364 ε [mm ⁻¹] 0.797 $F(000)$ 1560 Crystal size [mm³] 0.07 × 0.09 × 0.12 θ range [°] 2.01 to 28.36 Index ranges $-17 \le h \le 20$ $-18 \le k \le 15$ $-15 \le l \le 17$ Reflections collected 10159 Independent reflections 3335 [R(int) = 0.0169] Completeness to $\theta = 28.36^{\circ}$ 99.6% Absorption correction multiscan Max./min. transmission 0.775/0.673 Refinement method full-matrix least-squares on F^2 Data/restraints/parameters 3335/0/177 Goodness-of-fit on F^2 1.399 Fi | λ[Å] | 0.71073 |
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| a [Å] 15.559(3) b [Å] 13.588(3) c [Å] 12.905(3) a [°] 90 β [°] 101.501(3) γ [°] 90 γ [Å] 2673.4(9) Z 4 $D_{calcd.}$ [Mg m ⁻³] 1.364 ϵ [mm ⁻¹] 0.797 $F(000)$ 1560 Crystal size [mm³] 0.07 × 0.09 × 0.12 θ range [°] 2.01 to 28.36 Index ranges $-17 \le h \le 20$ $-18 \le k \le 15$ $-15 \le l \le 17$ Reflections collected 10159 Independent reflections 3335 [R(int) = 0.0169] Completeness to $\theta = 28.36^{\circ}$ 99.6% Absorption correction multiscan Max./min. transmission 0.775/0.673 Refinement method full-matrix least-squares on F^2 Data/restraints/parameters 3335/0/177 Goodness-of-fit on F^2 1.399 <td>Space group</td> <td>C2/c (15)</td> | Space group | C2/c (15) |
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| $ \begin{split} \beta \begin{bmatrix} \bar{e} \end{bmatrix} & 101.501(3) \\ \gamma \begin{bmatrix} e \end{bmatrix} & 90 \\ V \begin{bmatrix} A^3 \end{bmatrix} & 2673.4(9) \\ Z & 4 \\ D_{calcd.} \begin{bmatrix} Mg m^{-3} \end{bmatrix} & 1.364 \\ \varepsilon \begin{bmatrix} mm^{-1} \end{bmatrix} & 0.797 \\ F(000) & 1560 \\ Crystal size \begin{bmatrix} mm^3 \end{bmatrix} & 0.07 \times 0.09 \times 0.12 \\ \theta \ range \begin{bmatrix} e \end{bmatrix} & 2.01 \ to \ 28.36 \\ Index \ ranges & -17 \le h \le 20 \\ -18 \le k \le 15 \\ -15 \le l \le 17 \\ Reflections \ collected & 10159 \\ Independent \ reflections \\ Absorption \ correction & multiscan \\ Max./min. \ transmission & 0.775/0.673 \\ Refinement \ method & full-matrix \ least-squares \ on \ F^2 \\ Data/restraints/parameters & 3335/0/177 \\ Goodness-of-fit \ on \ F^2 & 1.399 \\ Final \ R \ indices \ [I > 2\sigma(I)] & R1 = 0.0775, \ wR2 = 0.2882 \\ R \ indices \ (all \ data) & R1 = 0.0812, \ wR2 = 0.2962 \\ Largest \ diff. \ peak/hole \ [e \ Å^{-3}] & 2.499/-0.505 \\ \end{split} $ | a [°] | 90 |
| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | β[°] | 101.501(3) |
| V [Å ³] 2673.4(9) Z 4 $D_{calcd.}$ [Mg m ⁻³] 1.364 ε [mm ⁻¹] 0.797 $F(000)$ 1560 Crystal size [mm ³] 0.07 × 0.09 × 0.12 θ range [°] 2.01 to 28.36 Index ranges $-17 \le h \le 20$ $-18 \le k \le 15$ $-15 \le l \le 17$ Reflections collected 10159 Independent reflections 3335 [R(int) = 0.0169] Completeness to $\theta = 28.36^{\circ}$ 99.6% Absorption correction multiscan Max./min. transmission 0.775/0.673 Refinement method full-matrix least-squares on F^2 Data/restraints/parameters 3335/0/177 Goodness-of-fit on F^2 1.399 Final R indices [I > $2\sigma(I)$] $R1 = 0.0775, wR2 = 0.2882$ R indices (all data) $R1 = 0.0812, wR2 = 0.2962$ Largest diff. peak/hole [e Å ⁻³] 2.499/-0.505 | γ [°] | 90 |
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| $\begin{array}{llllllllllllllllllllllllllllllllllll$ | F(000) | 1560 |
| $\begin{array}{lll} \theta \mbox{ range } [^{o}] & 2.01 \mbox{ to } 28.36 \\ \mbox{Index ranges} & -17 \leq h \leq 20 \\ & -18 \leq k \leq 15 \\ & -15 \leq l \leq 17 \\ \mbox{Reflections collected} & 10159 \\ \mbox{Independent reflections} & 3335 \mbox{ [}R(\mbox{int}) = 0.0169\mbox{]} \\ \mbox{Completeness to } \theta = 28.36^{\circ} & 99.6\% \\ \mbox{Absorption correction} & multiscan \\ \mbox{Max./min. transmission} & 0.775/0.673 \\ \mbox{Refinement method} & full-matrix least-squares on F^2 \\ \mbox{Data/restraints/parameters} & 3335/0/177 \\ \mbox{Goodness-of-fit on F^2} & 1.399 \\ \mbox{Final R indices $[I > 2\sigma(I)]$} & R1 = 0.0775, wR2 = 0.2882 \\ \mbox{R indices $(all data)$} & R1 = 0.0812, wR2 = 0.2962 \\ \mbox{Largest diff. peak/hole $[e \ A^{-3}]$} & 2.499/-0.505 \\ \end{array}$ | Crystal size [mm ³] | $0.07 \times 0.09 \times 0.12$ |
| Index ranges $-17 \le h \le 20$ $-18 \le k \le 15$ $-15 \le l \le 17$ Reflections collected10159Independent reflections3335 [R(int) = 0.0169]Completeness to $\theta = 28.36^{\circ}$ 99.6%Absorption correctionmultiscanMax./min. transmission0.775/0.673Refinement methodfull-matrix least-squares on F^2 Data/restraints/parameters3335/0/177Goodness-of-fit on F^2 1.399Final R indices $[I > 2\sigma(I)]$ $R1 = 0.0775, wR2 = 0.2882$ R indices (all data) $R1 = 0.0812, wR2 = 0.2962$ Largest diff. peak/hole [e Å-3]2.499/-0.505 | θ range [°] | 2.01 to 28.36 |
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| $\begin{array}{c} -15 \leq l \leq 17 \\ \mbox{Reflections collected} & 10159 \\ \mbox{Independent reflections} & 3335 [R(int) = 0.0169] \\ \mbox{Completeness to } \theta = 28.36^{\circ} & 99.6\% \\ \mbox{Absorption correction} & multiscan \\ \mbox{Max./min. transmission} & 0.775/0.673 \\ \mbox{Refinement method} & full-matrix least-squares on F^2 \\ \mbox{Data/restraints/parameters} & 3335/0/177 \\ \mbox{Goodness-of-fit on F^2} & 1.399 \\ \mbox{Final R indices $[I > 2\sigma(I)]$} & R1 = 0.0775, wR2 = 0.2882 \\ \mbox{R indices (all data)$} & R1 = 0.0812, wR2 = 0.2962 \\ \mbox{Largest diff. peak/hole $[e Å^{-3}]$} & 2.499/-0.505 \\ \end{array}$ | | $-18 \le k \le 15$ |
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| Data/restraints/parameters $3335/0/177$ Goodness-of-fit on F^2 1.399 Final R indices $[I > 2\sigma(I)]$ $R1 = 0.0775, wR2 = 0.2882$ R indices (all data) $R1 = 0.0812, wR2 = 0.2962$ Largest diff. peak/hole [e Å-3] $2.499/-0.505$ | Refinement method | full-matrix least-squares on F^2 |
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| | Largest diff. peak/hole [eÅ ⁻³] | 2.499/-0.505 |

General Method for the Oxidation of Alcohols: Complex [Fe(phen)₂-Cl₂]NO₃ (1.5 mol-%, 0.022 mmol) was added to a 50 mL roundbottomed flask followed by buffer solution (3 mL; HCl/KH buffer solution pH = 1). After addition of the substrate (1.5 mmol) and the internal standard (decane, 200 μ L), the mixture was vigorously stirred at 55 °C. The reaction started by adding the first drop of hydrogen peroxide. The oxidant (2.2 equiv.) was added through a syringe pump. After a time (t = 30-120 min), the reaction was quenched by the addition of sodium sulfite (Na₂SO₃), and a sample was directly taken and subjected to GC analysis.

Isolation of 1-Phenyl-1,2-ethanediol: The crude product was purified by silica gel chromatography using a mixture of *n*-hexane and ethyl acetate as eluent (gradient from 3:1 to 2:1). ¹H NMR (300 MHz, CDCl₃): δ = 7.95–7.90 (m, 2 H), 7.67–7.59 (m, 1 H), 7.54–7.46 (m, 2 H), 4.89 (s, 2 H), 3.55 (br., 1 H) ppm.

MS Studies: HR-MS (ESI-TOF) spectrum of **1** (Figure S3 in the Supporting Information): $[C_{24}H_{16}N_4Cl_2Fe]$, $[M + H]^+$: m/z calcd. 486.0087; found 486.0095 (error 1.78 ppm). New species were observed in the reaction mixture spectrum (Figure S4 in the Supporting Information): $[C_{12}H_8N_2CIFeOC_7H_7]$, $[M + H]^+$: m/z calcd. 378.022; found 378.0217 (error 1.36 ppm). Areas m/z 372–391 are presented in the insets of Figures S3 and S4 in the Supporting Information.

Supporting Information (see footnote on the first page of this article): Experimental details such as general procedure for the benzyl alcohol oxidation, time effect, catalyst amount, ESI mass spectrum for **1** and for the reaction mixture.

Acknowledgments

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- a) F. Cavani, J. H. Teles, *ChemSusChem* 2009, 2, 508–534; b)
 R. A. Sheldon, J. K. Kochi, *Metal-Catalyzed Oxidation of Organic Compounds*, Academic Press, New York, 1981.
- [2] a) T. Iwahama, S. Sakaguchi, Y. Nishiyama, Y. Ishii, *Tetrahe-dron Lett.* **1995**, *36*, 6923–6930; b) V. B. Sharma, S. L. Jain, B. Sain, *Tetrahedron Lett.* **2003**, *44*, 383–386.
- [3] a) F. Minisci, F. Recupero, G. F. Pedulli, M. Lucarini, J. Mol. Catal. A 2003, 63, 204–205; b) F. Minisci, C. Punta, F. Recupero, J. Mol. Catal. A 2006, 251, 129–149.
- [4] a) H. Guo, A. Al-Hunaiti, M. Kemell, S. Rautiainen, M. Leskelä, T. Repo, *ChemCatChem* 2011, *3*, 1872–1875; b) H. Guo, M. Kemell, A. Al-Hunaiti, S. Rautiainen, M. Leskelä, T. Repo, *Catal. Commun.* 2011, *12*, 1260–1264.
- [5] a) I. E. Marko, P. R. Giles, M. Tsukazaki, S. M. Brown, C. J. Urch, Science 1996, 274, 2041–2044; b) Y. Wang, J. L. DuBois, B. Hedman, K. O. Hodgson, T. D. P. Stack, Science 1998, 279, 534–537; c) P. Chaudhuri, M. Hess, U. Florke, K. Wieghardt, Angew. Chem. 1998, 110, 2340; Angew. Chem. Int. Ed. 1998, 37, 2217–2220; d) I. E. Marko, A. Gautier, I. C. Regnaut, P. R. Giles, M. Tsukazaki, C. J. Urch, S. M. Brown, J. Org. Chem. 1998, 63, 7576–7577; e) I. E. Marko, P. R. Giles, M. Tsukazaki, I. C. Regnaut, A. Gautier, S. M. Brown, C. J. Urch, J. Org. Chem. 1999, 64, 2433–2439; f) P. Chaudhuri, M. Hess, J. Müller, K. Hildenbrand, E. Bill, T. Weyhermüller, K. Wieghardt, J. Am. Chem. Soc. 1999, 121, 9599–9610; g) I. E. Marko, A. Gautier, J. L. Mutonkole, R. Dumeunier, A. Ates, C. J. Urch, S. M. Brown, J. Organomet. Chem. 2001, 624, 344–347.
- [6] R. B. Daniel, P. Alsters, R. Neumann, J. Org. Chem. 2001, 66, 8650–8653.
- [7] a) M. Matsumoto, N. Watanabe, J. Org. Chem. 1984, 49, 3435–3436; b) K. Yamaguchi, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, J. Am. Chem. Soc. 2000, 122, 7144–7145; c) H. Shimizu, S. Onitsuka, H. Egami, T. Katsuki, J. Am. Chem. Soc. 2005, 127, 5396–5414; d) S. Mori, M. Takubo, K. Makida, T.



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Yanase, S. Aoyagi, T. Maegawa, Y. Monguchi, H. Sajiki, *Chem. Commun.* **2009**, 5159–5161.

- [8] a) B. A. Steinhoff, S. R. Fix, S. S. Stahl, J. Am. Chem. Soc. 2002, 124, 766–767; b) Y. Uozumi, R. Nakao, Angew. Chem. 2003, 115, 201–204; c) J. A. Mueller, A. Cowell, B. D. Chandler, M. S. Sigman, J. Am. Chem. Soc. 2005, 127, 14817–14824; d) T. Chen, J.-J. Jaing, Q. Xu, M. Shi, Org. Lett. 2007, 9, 865–868.
- [9] For Hydrogen peroxide oxidation systems, see: a) F. Shi, M. K. Tse, M.-M. Pohl, J. Radnik, A. Brückner, S. Zhang, M. Beller, J. Mol. Catal. A 2008, 292, 28-35; b) F. Shi, M. K. Tse, Z. Li, M. Beller, Chem. Eur. J. 2008, 14, 8793-8797; c) F. Shi, M. K. Tse, M.-M. Pohl, A. Brückner, S. Zhang, M. Beller, Angew. Chem. 2007, 119, 9022; Angew. Chem. Int. Ed. 2007, 46, 8866-8868; d) M. Nakanishi, C. Bolm, Adv. Synth. Catal. 2007, 349, 861-864; e) É. Balogh-Hergovich, G. Speier, J. Mol. Catal. A 2005, 230, 79-83; f) S. E. Martin, A. Garrone, Tetrahedron Lett. 2003, 44, 549-552. Oxygen activation systems: g) W. Yin, C. Chu, Q. Lu, J. Tao, X. Liang, R. Liu, Adv. Synth. Catal. 2010, 352, 113-118; h) A. J. Pearson, Y. Kwak, Tetrahedron Lett. 2005, 46, 5417-5419; i) A. Gosh, F. Tiago de Oliveira, T. Yano, T. Nishioka, E. S. Beach, I. Kinoshita, E. Münck, A. D. Ryabov, C. P. Horwitz, T. J. Collins, J. Am. Chem. Soc. 2005, 127, 2505–2513; j) N. Wang, R. Liu, J. Chen, X. Liang, Chem. Commun. 2005, 5322-5324; k) S. E. Martin, D. F. Surez, Tetrahedron Lett. 2002, 43, 4475-4479, and references therein.
- [10] H. Adolfsson, Modern Oxidation Methods, 2nd ed., Wiley, New York, 2011.
- [11] a) K. Schröder, B. Join, A. J. Amali, K. Junge, X. Ribas, M. Costas, M. Beller, *Angew. Chem.* 2011, *6*, 1461–1465; *Angew. Chem. Int. Ed.* 2011, *6*, 1425–1429; b) K. Schröder, K. Junge, A. Spannenberg, M. Beller, *Catal. Today* 2010, *157*, 364–370; c) E. Rose, E. Gallo, N. Raoul, L. Bouche, A. Pille, A. Caselli, O. J. Lequin, *J. Porphyrins Phthalocyanines* 2010, *14*, 646–659; d) P. Das, L. Que Jr, *Inorg. Chem.* 2010, *41*, 9479–9485.
- [12] a) C. O. Kinen, L. I. Rossi, R. H. de Rossi, J. Org. Chem. 2009, 74, 7132–7139; b) C. O. Kinen, L. J. Rossi, R. H. de Rossi, Green Chem. 2009, 11, 223–228; c) J. Legros, C. Bolm, Chem. Eur. J. 2005, 11, 1086–1092; d) J. Legros, C. Bolm, Angew. Chem. 2004, 31, 4321–4324; Angew. Chem. Int. Ed. 2004, 43, 4225–4228; e) J. Legros, C. Bolm, Angew. Chem. 2003, 44, 5645–5647; Angew. Chem. Int. Ed. 2003, 44, 5487–5489.
- [13] a) M. A. Bigi, S. A. Reed, M. C. White, *Nat. Chem.* 2011, *3*, 216–222; b) P. D. Oldenburg, Y. Feng, I. Pryjonska-Ray, D. Ness, L. Que Jr, *J. Am. Chem. Soc.* 2010, *132*, 17713–17723; c) M. Chen, M. C. White, *Science* 2010, *327*, 566–571; d) Y. Feng, C.-Y. Ke, G. Xue, L. Que Jr, *Chem. Commun.* 2009, 50–52; e) L. Gómez, I. Garcia-Bosch, A. Company, J. Benet-Buchholz, A. Polo, X. Sala, X. Ribas, M. Costas, *Angew. Chem.* 2009, *31*, 5830–5833; *Angew. Chem. Int. Ed.* 2009, *48*, 5720–5723.
- [14] a) R. Molinari, T. Poerio, *Appl. Catal. A* 2011, *393*, 340–347;
 b) G. Mi, J. Li, J. Zhang, B. Chen, *Kor. J. Chem. Eng.* 2010, *27*, 1700–1706;
 c) B. S. Rana, B. Singh, R. Kumar, D. Verma, M. K. Bhunia, A. Bhaumik, A. K. Sinha, *J. Mater. Chem.* 2010, *20*, 8575–8581;
 d) O. V. Makhlynets, P. Das, S. Taktak,

M. Flook, R. Mas-Ballest, E. V. Rybak-Akimova, L. Que Jr, *Chem. Eur. J.* **2009**, *15*, 13171–13180; e) X. Chen, J. Zhang, X. Fu, M. Antonietti, X. Wang, *J. Am. Chem. Soc.* **2009**, *131*, 11658–11659.

- [15] a) H. J. H. Fenton, Chem. News 1876, 33, 190; b) H. J. H. Fenton, Proc. Chem. Soc. 1894, 10, 157–158; c) C. Walling, Acc. Chem. Res. 1998, 31, 155–157; d) D. H. R. Barton, D. Doller, Acc. Chem. Res. 1992, 25, 504–512; e) M. J. Perkins, Chem. Soc. Rev. 1996, 25, 229–236; f) D. H. R. Barton, B. Hu, D. K. Taylor, R. U. R. Wahl, J. Chem. Soc. Perkin Trans. 2 1996, 1031–1041.
- [16] a) A. Al-Hunaiti, T. Niemi, A. Sibaouih, P. Pihko, M. Leskelä, T. Repo, *Chem. Commun.* **2010**, *46*, 9250–9252; b) W. Yin, C. Chu, Q. Lu, J. Tao, X. Liang, R. Liu, *Adv. Synth. Catal.* **2010**, *352*, 113–118.
- [17] G. Chelucci, R. P. Thummel, Chem. Rev. 2002, 102, 3129-3170.
- [18] S. Menage, J. M. Vincent, C. Lambeaux, G. Chottard, A. Grand, M. Fontecave, *Inorg. Chem.* **1993**, *32*, 4766–4773.
- [19] S. Ménage, J. M. Vincent, C. Lambeaux, M. Fontecave, J. Mol. Catal. A 1996, 113, 61–75.
- [20] O. N. Gritsenko, mc="2" G. N. Nesterenko, A. A. Shteinman, *Russ. Chem. Bull.* **1995**, 44, 2415–2417.
- [21] V. S. Kulikova, O. N. Gritsenko, A. A. Shteinman, *Mendeleev Commun.* 1996, 6, 119–120.
- [22] H. J. Goodwin, M. Mc Partlin, H. A. Goodwin, *Inorg. Chim. Acta* 1977, 25, 74.
- [23] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry, John Wiley & Sons, New York, 1997.
- [24] D. F. Bishop, G. Stern, M. Fleischmann, S. Marshall, Ind. Eng. Chem. Process Res. Dev. 1968, 7, 110–117.
- [25] H. R. Eisenhauer, J. Water Pollut. Control Fed. 1964, 36, 1116– 1128.
- [26] W. Feuerstein, E. Gilbert, H. Heberle, Vom Wasser 1981, 56, 34.
- [27] C. F. Base, R. E. Mesmer, *The Hydrolysis of Cations*, Willey/ Interscience, New York, **1976**, pp. 226–237.
- [28] M. Pourbaix, Atlas d'Équilibres Électrochimiques, Gauthier-Villars, Paris, 1963, pp. 409–411.
- [29] D. H. R. Barton, S. D. Bévière, B. M. Chabot, W. Chavasiri, D. K. Taylor, *Tetrahedron Lett.* **1994**, *35*, 4681–4684.
- [30] R. L. Collins, R. Pettit, W. A. Baker, *Inorg. Nucl. Chem.* 1966, 28, 1001–1010.
- [31] A. P. Ginsberg, M. B. Robin, Inorg. Chem. 1963, 2, 817-822.
- [32] R. R. Berret, B. W. Fitzsimmons, A. Owusu, J. Chem. Soc. A **1968**, *90*, 2044–2048.
- [33] K. Lagarec, D.G. Rancourt, *Recoil*, Mössbauer Spectral Analysis software for Windows 1.0, Department of Physics, University of Ottawa, Canada, 1998.
- [34] SHELXTL, v. 5.10, Bruker Analytical X-ray Instruments Inc., Karlsruhe, Germany, 1997.

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Using high-spin iron(III) complex $[Fe(phen)_2Cl_2]NO_3$ (1) (phen = 1,10-phenanthroline) and H_2O_2 as terminal oxidant, a series of primary and secondary alcohols were oxidized into aldehydes and ketones in good yields and excellent selectivities after a short reaction time.



Selective Alcohol Oxidation

Efficient and Selective Oxidation of Primary and Secondary Alcohols Using an Iron(III)/Phenanthroline Complex: Structural Studies and Catalytic Activity

Keywords: Homogeneous catalysis / Oxidation / Iron / Alcohols / Ketones