



# Iron complexes with nitrogen bidentate ligands as green catalysts for alcohol oxidation



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## ABSTRACT

The iron(II) complexes  $[\text{Fe}(\text{N-N})_3](\text{OTf})_2$  (N-N = 2,2'-bipyridine, 1,10-phenanthroline and substituted derivatives) were employed as catalyst precursors for the oxidation of primary and secondary alcohols, including glycerol. The single-crystal structure of  $[\text{Fe}(\text{bipy})_3](\text{OTf})_2$  was determined by X-ray crystallography. The catalytic reactions were performed using either  $\text{H}_2\text{O}_2$  or *tert*-butylhydroperoxide (TBHP) as oxidizing agent, in mild experimental conditions: with all catalysts employed, secondary alcohols were oxidized to the corresponding ketones with up to 100% yields, whereas other substrates gave lower conversions. Indications on the nature of the catalytically active species, which is probably formed via dissociation of a nitrogen ligand from the iron center, were obtained from NMR and ESI-MS spectra.

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## 1. Introduction

The recent development of transition-metal promoted organic synthesis has largely focussed on the replacement of catalysts based on precious metals with first row transition-metal compounds. The urgency towards this target lies on the limited availability as well as high price of platinum group metals on one hand and on their relevant toxicity on the other. Among the possible candidates, iron has been emerging as the most attractive substitute due to its large availability, moderate price and low toxicity; last but not least, iron compounds are environmentally benign [1]. The enormous increase of research on iron-based catalysis is witnessed by a growing number of publications, among which some very recent examples concern olefin hydrogenation [2] and epoxidation [3], reduction of carboxylic acid derivatives [4], amination of alcohols [5], alkynes trimerization [6] and diazidation of olefins [7].

Since iron catalysts have a relevant role in biological redox systems, it is not surprising that the most important iron-promoted processes so far developed include oxidation reactions [8]. In particular, regarding the oxidation of alcohols to carbonyl compounds, which is a fundamental transformation in organic synthesis, iron-based catalysts are promising substitutes for the traditional

stoichiometric methods on one hand, and precious metal promoted oxidation on the other. Use of iron catalysts in association with green oxidants such as peroxides, the reduced products of which (alcohols or water) are generally non-toxic [9], is expected to provide highly sustainable oxidation processes.

Apart from early reports of alcohol oxidation catalyzed by iron salts [10], which proved sometimes effective but often poorly selective, more recent papers describe the use of very efficient catalysts based on the association of iron with various polydentate nitrogen-donor ligands [11] including porphyrines [12]. In contrast, examples of alcohol oxidation catalyzed by iron complexes with bidentate ligands with either N or N,O donor atoms are less common [13].

We became interested in the development of iron-based oxidation catalysts which should combine appreciable catalytic activity and selectivity with simple and low-cost catalyst synthesis: in other words, catalyst precursors having cheap, ready available coordinated ligands. In addition, use of Fe(II) low spin complexes would offer the opportunity of gaining information on the evolution of the catalytically active species by means of NMR studies. In fact, the mechanistic details of iron-promoted oxidations are still unclear, in spite of recent efforts to shed light on this subject [14].

A further reason which called our attention towards alcohol oxidation lies in our interest on selective glycerol oxidation, a process of high applicative importance: after developing iridium-based catalysts for the conversion of glycerol to dihydroxyacetone, we recently reported the first example of such reaction

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promoted by an iron catalyst, *i.e.*  $[\text{Fe}(\text{BPA})_2(\text{OTf})_2]$  (BPA = bis(2-pyridinylmethyl)amine) [15].

In the following we describe our results in the oxidation of primary and secondary alcohols, including glycerol, catalyzed by iron complexes with 1,10-phenanthroline, 2,2'-bipyridine and substituted derivatives, using either hydrogen peroxide or TBHP as oxidant in very mild reaction conditions.

## 2. Experimental

### 2.1. General

All the chemicals were reagent grade and were used as received from the commercial suppliers, with the exception of naphthalene, used as GC standard, which was recrystallized from ethanol.

### 2.2. Instrumental

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded either on a Varian 500 spectrometer operating at 500 MHz and 125.68 MHz, respectively, or on a Jeol EX400 spectrometer operating at 400 MHz and 100.4 MHz, respectively; chemical shifts were measured relative to the residual solvent signal. Resonances were assigned with reference to COSY and HSQC spectra.

ESI-MS spectra were obtained by an ion-trap instrument (ESI-MS Bruker Esquire 4000) equipped with an electrospray ion source. The instrument performed with 10.0 psi nebulizer pressure, end-plate offset  $-500\text{ V}$ , capillary 4000 V and capillary exit at 113.3 V. The drying gas ( $\text{N}_2$ ) flow was  $5\text{ L min}^{-1}$  and the spectral range was from  $m/z = 100$  to 1200.

The chemical yields of the catalytic reactions were determined by integration of the  $^1\text{H}$  NMR signals and/or by GC analysis on an Agilent 6850 instrument with helium as carrier gas and a TCD detector.

### 2.3. Synthesis of the iron complexes

#### 2.3.1. Synthesis of $[\text{Fe}(\text{bipy})_3](\text{OTf})_2$ (1)

A round-bottomed flask was charged with acetonitrile (3 mL) and  $\text{Fe}(\text{OTf})_2$  (0.56 mmol), the yellow solution so obtained immediately turned dark red upon addition of bipy (1.12 mmol). The reaction mixture was stirred at r.t. for 30 min and then concentrated to 1/3 of the initial volume. Addition of diethylether caused precipitation of a dark red solid, which was filtered and washed with ether. Yield 73%.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ,  $25^\circ\text{C}$ ):  $\delta$  8.56 (d, 2H,  $\text{H}_3$  and  $\text{H}_{3'}$ ), 8.13 (t, 2H,  $\text{H}_4$  and  $\text{H}_{4'}$ ), 7.42 (m, 4H,  $\text{H}_5$  and  $\text{H}_{5'}$ ,  $\text{H}_6$  and  $\text{H}_{6'}$ ).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{CN}$ ,  $25^\circ\text{C}$ ):  $\delta$  160.0 ( $\text{C}_2$  and  $\text{C}_{2'}$ ), 155.0 ( $\text{C}_6$  and  $\text{C}_{6'}$ ), 139.5 ( $\text{C}_4$  and  $\text{C}_{4'}$ ), 128.3 ( $\text{C}_5$  and  $\text{C}_{5'}$ ), 124.8 ( $\text{C}_3$  and  $\text{C}_{3'}$ ).

#### 2.3.2. Synthesis of $[\text{Fe}(\text{phen})_3](\text{OTf})_2$ (2)

Same procedure as for **1** but with ligand phen. Yield 71%.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ,  $25^\circ\text{C}$ ):  $\delta$  8.65 (d, 2H,  $\text{H}_2 + \text{H}_9$ ), 8.29 (s, 2H,  $\text{H}_5 + \text{H}_6$ ), 7.69 (d, 2H,  $\text{H}_4 + \text{H}_7$ ), 7.63 (dd, 2H,  $\text{H}_3 + \text{H}_8$ ).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{CN}$ ,  $25^\circ\text{C}$ ):  $\delta$  156.2 ( $\text{C}_4 + \text{C}_7$ ), 149.7 (C–N quat.), 137.4 ( $\text{C}_2 + \text{C}_9$ ), 130.5 (C quat.), 128.1 ( $\text{C}_5 + \text{C}_6$ ); 126.0 ( $\text{C}_3 + \text{C}_8$ ).

#### 2.3.3. Synthesis of $[\text{Fe}(\text{DMbipy})_3](\text{OTf})_2$ (3)

Same procedure as for **1** but with ligand DMbipy (DMbipy = 4,4'-dimethyl-2,2'-bipyridine). Yield 80%.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ,  $25^\circ\text{C}$ ):  $\delta$  8.38 (s, 2H,  $\text{H}_3$  and  $\text{H}_{3'}$ ), 7.21 (br, 4H,  $\text{H}_5$  and  $\text{H}_{5'}$ ,  $\text{H}_6$  and  $\text{H}_{6'}$ ), 2.59 (s, 6H, Me).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{CN}$ ,  $25^\circ\text{C}$ ):  $\delta$  158.9 ( $\text{C}_2$  and  $\text{C}_{2'}$  or  $\text{C}_4$  and  $\text{C}_{4'}$ ), 153.3 ( $\text{C}_5$  and  $\text{C}_{5'}$  or  $\text{C}_6$  and  $\text{C}_{6'}$ ), 151.2 ( $\text{C}_2$  and  $\text{C}_{2'}$  or  $\text{C}_4$  and  $\text{C}_{4'}$ ), 128.3 ( $\text{C}_5$  and  $\text{C}_{5'}$  or  $\text{C}_6$  and  $\text{C}_{6'}$ ), 124.7 ( $\text{C}_3$  and  $\text{C}_{3'}$ ), 20.3 (Me).

#### 2.3.4. Synthesis of $[\text{Fe}(\text{DMphen})_3](\text{OTf})_2$ (4)

Same procedure as for **1** but with ligand DMphen (DMphen = 4,7-dimethyl-1,10 phenanthroline). Yield 75%.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ,  $25^\circ\text{C}$ ):  $\delta$  8.38 (s, 2H,  $\text{H}_2 + \text{H}_9$ ), 7.51 (s, 2H,  $\text{H}_5 + \text{H}_6$ ), 7.44 (s, 2H,  $\text{H}_3 + \text{H}_8$ ), 2.89 (s, 6H, Me).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{CN}$ ,  $25^\circ\text{C}$ ):  $\delta$  156.2 ( $\text{C}_5 + \text{C}_6$ ), 150.4 (C quat.), 148.6 (C quat.), 131.1 (C quat.), 127.5 ( $\text{C}_3 + \text{C}_8$ ), 125.5 ( $\text{C}_2 + \text{C}_9$ ), 18.9 (Me).

### 2.4. X-ray crystal structure analysis

Data collection of **1** was performed at the X-ray diffraction beamline (XRD1) of the Elettra Synchrotron of Trieste (Italy), with a Pilatus 2M image plate detector. The experiment was performed at 100 K (nitrogen stream supplied by an Oxford Cryostream 700) with a monochromatic wavelength of 0.700 Å through the rotating crystal method. The diffraction data were indexed, integrated and scaled using program XDS [16]. The structure was solved by direct methods using SIR2014 [17]. Fourier analysis and refinement with the full-matrix least-squares method based on  $F^2$  were performed with SHELXL-2014 [18]. One triflate anion was found disordered over two positions with refined occupancies of 0.850(3)/0.150(3), sharing one oxygen atom. Hydrogen atoms were placed at calculated positions with isotropic U factors equal to 1.2 times the equivalent U factor of the bonded atom.

Crystallographic data:  $\text{C}_{32}\text{H}_{24}\text{F}_6\text{FeN}_6\text{O}_6\text{S}_2$ ,  $M = 822.54$ , monoclinic, space group  $\text{C}2/c$ ,  $a = 36.417(3)$ ,  $b = 11.123(2)$ ,  $c = 17.554(3)$  Å,  $\beta = 111.83(3)^\circ$ ,  $V = 6601(2)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_c = 1.655\text{ g cm}^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 0.674\text{ mm}^{-1}$ ,  $F(000) = 3344$ ,  $\theta$  range =  $1.19$ – $28.23^\circ$ . Final  $R1 = 0.0624$ ,  $wR2 = 0.1671$ ,  $S = 1.073$  for 508 parameters and 15945 reflections, 8154 unique [ $R(\text{int}) = 0.0279$ ], of which 7795 with  $I > 2\sigma(I)$ , max positive and negative peaks in  $\Delta F$  map 1.787,  $-1.512$  e. Å<sup>-3</sup>. CCDC reference number 1473638.

### 2.5. Procedure for the catalytic reactions

#### 2.5.1. Oxidation of alcohols catalyzed by $[\text{Fe}(\text{OTf})_2]/\text{N}-\text{N}$ "in situ"

A round-bottomed flask was charged with the solvent (3.0 mL),  $\text{Fe}(\text{OTf})_2$  (0.050 mmol) and the nitrogen ligand (0.10 mmol). After addition of the substrate (2.5 mmol), the oxidant was added dropwise under stirring, at r.t. After the desired time the reaction mixture was cooled at  $-18^\circ\text{C}$  and subsequently analyzed by GC and/or NMR.

#### 2.5.2. Oxidation of alcohols catalyzed by $[\text{Fe}(\text{N}-\text{N})_3](\text{OTf})_2$

In a round-bottomed flask the solvent (3.0 mL) and the catalyst precursor  $[\text{Fe}(\text{N}-\text{N})_3](\text{OTf})_2$  (0.050 mmol) were introduced, followed by the substrate (2.5 mmol). For reactions performed at temperatures higher than r.t., the resulting solution was heated in a thermostatted bath to the desired temperature. Slow addition of the oxidant was then carried out under stirring. After the desired time the reaction mixture was cooled at  $-18^\circ\text{C}$  and subsequently analyzed by GC and/or NMR.

#### 2.5.3. Oxidation of glycerol catalyzed by $[\text{Fe}(\text{N}-\text{N})_3](\text{OTf})_2$

Glycerol (2.5 mmol) was introduced into a round-bottomed flask, followed by the solvent (3.0 mL) and the iron catalyst (0.050 mmol). For reactions performed at temperatures higher than r.t., the resulting solution was heated in a thermostatted bath to the desired temperature. The oxidant was then added dropwise under vigorous stirring. After the appropriate time the reaction mixture was cooled at  $-18^\circ\text{C}$  and subsequently analyzed by GC and/or NMR.

### 2.6. Analysis of the reaction mixtures

Qualitative analysis was accomplished by  $^1\text{H}$  and  $^{13}\text{C}$  NMR; the resonances were compared with those of authentic samples

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