New efficient iron catalyst for olefin epoxidation with hydrogen peroxide

Elena A. Mikhalyova, a, c Olga V. Makhlynets, a Taryn D. Palluccio, a Alexander S. Filatov, b and Elena V. Rybak-Akimova* a

Supporting information

GCMS experiments were carried out using a Shimadzu GC-17A gas chromatograph (Rxi-XLB nonpolar column) with a GCMS-QP 5050 mass detector. ESI-MS analysis was performed by electrospray mass spectrometry using a Finnigan LTQ (San Jose, CA) LCQ ion trap mass spectrometer in the positive ion detection mode. Time-resolved spectra were acquired with TgK Scientific (formerly HiTech Schientific, Salisbury, Wiltshire, UK) SF-61DX2 cryogenic Stopped-flow system equipped with J&M Diode array (Spectralytics). EPR spectra were acquired on Bruker EMX EPR spectrometer at 120 K. Cyclic voltammetry experiments were performed on a EG&G PAR 273 potentiostat using a three electrode cell with a glassy carbon working electrode and platinum wire counter- and reference electrodes.

All 1H-NMR and 13C spectra were recorded in CD3Cl solutions on a Bruker Avance III NMR spectrometer at 500 MHz for 1H-NMR and 125MHz for 13C-NMR. Chemical shifts are reported in ppm relative to TMS (for 1H-NMR) or CDCl3 (for 13C-NMR). Coupling constants are reported in Hz. Elemental analysis was performed using Carlo Erba 1106 analyzer.

All reagents were purchased from Aldrich and were used as received. Acetonitrile and ether (HPLC-grade) were purified on a commercial solvent purification system (PureSolv 400, Innovative Technologies) under nitrogen, and kept in argon-filled MBraun glove box.

Preparation of ligands and complexes.

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Bp*2HBr (2,2’-bipiperidine bis-hydrogen bromide) was prepared according to a procedure adapted from reference 1. 2,2’-bipiridine (5.5 g) was taken up in methanol (100 mL) in a 500-mL round-bottom flask fitted with a reflux condenser, and potassium hydroxide solution (2 M, 100 mL) was added; the reaction mixture warmed up upon addition of KOH. Nickel-aluminum alloy (20 g) was added in portions (ca. 5 g each). Addition must be slow (5 g in about 1 hr, in several portions), since the reaction mixture was warming up, and the reaction was accompanied by extensive gas evolution. The mixture was boiling in the process of Ni/Al addition, but this boiling should not be intensive. After addition of Ni/Al alloy was complete, the mixture was heated to reflux and stirred for ca. 36-48 hours (refluxing was stopped and the reaction mixture was kept at room temperature overnight). Final reaction mixture contained 88 % of bp and 12 % ppy (as determined by GCMS). The reaction mixture was filtered through a pad of Celite, which was washed through with a methanol-water mixture. The methanol was evaporated from combined filtrate under reduced pressure. The aqueous layer was extracted 3 times with CH2Cl2 and the combined extracts were dried over MgSO4. Evaporation of solvent and slow addition of concentrated solution of HBr (ca. 10 mL of 48 % solution in water) (to pH = 2) gave a hot slurry containing white with crystalline product. This slurry was cooled and filtered. The solid residue was washed with small amount of cold ethanol on the glass fritted funnel and air-dried, affording 5.75 g (50 %, based on 2,2’-bipiridine) of bp*2HBr.

GCMS: m/z, 84 – bp2+  

1H-NMR (D2O, 300 MHz, in agreement with reference 2): δ 3.39 (d,2H, J = 12.6 Hz); 3.29 (d, 2H, J=9.3 Hz); 3.05-2.87 (m, 2H); 2.05-1.72 (m, 6H); 1.65-1.35 (m, 6H). The positions of signals in NMR slightly differ for several portions. The main criterion was the absence of the signals from aromatic protons.
**PYBP** (1,1′-bis-(pyridine-2-ylmethyl)-2,2′bipiperidine). To a stirred mixture of 4.525 g (14.14 mmol) of bp*2HBr and 4.64 g (28.28 mmol) of picolylchloride hydrochloride in 30 mL CH$_2$Cl$_2$ and 10 mL H$_2$O, a solution of 3.6 g NaOH in 20 mL H$_2$O was added dropwise. After stirring for additional 2-4 days, 60 mL of 1M NaOH was added, and the layers were separated. Aqueous layer was extracted three times with CH$_2$Cl$_2$. Combined methylene chloride layers were dried over MgSO$_4$ and evaporated under reduced pressure, yielding semi-solid oily residue that crystallized upon cooling. In some cases, spontaneous crystallization did not occur; in these experiments, the residue was additionally dried it was dry in vacuum (0.1 bar) at 45º C, and then treated with a small amount of acetonitrile. Solid product (PYBP) was filtered and recrystallized from acetonitrile. Yield 0.948 g (19.2 %). ESI-MS (m/z): 351.36. Elemental analysis calc/found, %, for PYBP*2.8H$_2$O: C 65.9/65.9; H 8.89/8.60; N 14.0/13.7.
$^1$H-NMR (CDCl$_3$, 500 MHz): $\delta$ 8.54 (d, 2H, $J=4.75$ Hz, H$_{10}$); 7.62 (td, 2H, $J = 7.75, 1.83$ Hz, H$_{12}$); 7.46 (d, 2H, $J = 7.50$ Hz, H$_{13}$); 7.13 (dd, 2H, $J = 6.75, 5.00$ Hz, H$_{11}$); 4.265 (d, 2H, $J = 14.5$ Hz, H$_{7a}$); 3.24 (d, 2H, $J = 14.5$ Hz, H$_{7b}$); 2.83 (d, 2H, $J = 11.5$ Hz, H$_{6a}$); 2.73 (d, 2H, $J = 10.5$ Hz, H$_{2}$); 2.02 (td, 2H, $J = 11.5, 3.5$ Hz, H$_{6b}$); 1.95 (d, 2H, $J = 13.5$ Hz, H$_{3d}$); 1.74 (m, 2H, H$_{3a}$); 1.6-1.4 (m, 6H, H$_{3b}$, H$_{5a}$, H$_{5b}$); 1.25-1.1 (m, 2H, H$_{4b}$).
$^{13}$C-NMR (CDCl$_3$, 500 MHz): $\delta$ 160.43 (C$_8$); 149.04 (C$_{10}$); 136.27 (C$_{12}$); 122.67 (C$_{13}$); 121.62 (C$_{11}$); 62.32 (C$_2$); 59.56 (C$_7$); 54.80 (C$_6$); 25.65 (C$_5$); 24.98 (C$_3$); 24.79 (C$_4$).
COSY $^1\text{H} - ^1\text{H}$
[Fe(PYBP)(CH$_3$CN)$_2$](ClO$_4$)$_2$ (1). Synthesis was conducted under Ar atmosphere in the MBraun glove box. 0.121 g of Fe(ClO$_4$)$_2$$\cdot$6H$_2$O and 0.117 g of pybp were dissolved in CH$_3$CN and mixed, affording deep-purple solution. Immediately, small amount of a solid red impurity precipitated out and was removed by filtration, while the target iron(II) complex accumulated in the filtrate. Purple crystals of Fe(Pybp)(CH$_3$CN)$_2$(ClO$_4$)$_2$ were obtained by slow diffusion of ether in this solution. Yield: 65%. Elemental analysis, calc/found, %, for Fe(Pybp)(CH$_3$CN)(H$_2$O)(ClO$_4$)$_2$: C 43.4/43.6; H 5.27/5.11; N 10.5/10.2. UV-Vis: 540 nm. Cyclic Voltammetry (CVA): $E_{1/2} = 0.656$ V ($E_{F/C/Fc} = 0$); $\Delta E = 87(1)$ mV; $Ia/Ic = 0.93(3)$. The identity of the complex was confirmed by X-Ray crystallography (see below).

Catalytic Epoxidations with 1/H$_2$O$_2$ monitored by GCMS

To a 1 mL of 0.2 mM or 1 mM solution of 1, olefin (Table 1, main text) and acetic acid (when needed) were added using automatic delivery pipettes under inert atmosphere. Upon vigorous stirring of this solution, 1 mL of hydrogen peroxide (340 or 680 µL of 30 % aqueous solution in 10 mL of CH$_3$CN) was added. The mixture was stirred for 5 or 10 minutes, and a small aliquot (2-3 drops) of the reaction mixture was poured into 1 mL of ether. The solution was analyzed by GCMS. Olefin was used as an external calibration standard.

Epoxidation with labeled H$_2^{18}$O or labeled H$_2^{18}$O$_2$.

For isotope-labeling experiments, solutions of hydrogen peroxide and $^{18}$O-labeled water were prepared by mixing 73 µL H$_2$O$_2$ (70 % aqueous solution) and 97 µL H$_2^{18}$O with 10 mL of CH$_3$CN.

To a 1 mL of 0.2 mM solution of 1, 200 µmol of olefin and 57 µL of acetic acid were added. Upon vigorous stirring of this solution, 1 mL of hydrogen peroxide/H$_2^{18}$O was added. The mixture was stirred for 10 minutes, a small aliquot was poured into 1 mL of ether, and the ether solution was analyzed by GCMS.

The same experimental conditions were used in the experiment with H$_2^{18}$O$_2$ (Sigma) and unlabeled H$_2$O.

EPR studies

Purple species 1a was generated directly in the EPR tube by mixing 1 (3 mM, 0.15 mL) with H$_2$O$_2$ (30 mM, 0.15 mL) in acetonitrile at room temperature. The tube was frozen immediately after all hydrogen peroxide was injected (5 s). All EPR spectra were acquired at 120 K. EPR spectra simulation were done using SimFonia (Bruker).
Complex 1 promotes aromatic hydroxylation with H$_2$O$_2$.

**Figure S1.** Time resolved UV-vis spectra of the reaction between [1] and H$_2$O$_2$ ([1] = 1 mM, H$_2$O$_2$ = 10mM) in the presence of benzene (300 equivalents) at 20°C over 280 s. Maximum accumulation of Fe$^{III}$(OOH) was seen within 2 s after mixing reagents (red-spectrum of 1, purple-spectrum of Fe$^{III}$(OOH), blue-final spectrum of phenolate adduct). Inset: kinetic trace at 630 nm showing biexponential behavior (accumulation of the (L)Fe(III)-OOH intermediate followed by aromatic hydroxylation of benzene and the formation of the iron(III) phenolate product).
Fig. S2. Turnover number (TON) with respect to epoxide depends on the amount of acetic acid (with respect to complex 1). a,b) Reaction conditions: olefin (200 µmol), 1 (0.2 µmol), H₂O₂ (300 µmol, 30 % aqueous solution), acetic acid (1 mmol) in 2mL of CH₃CN, room temperature, 10 min.; c,d) Reaction conditions: 1-decene (400 µmol), 1 (0.2 µmol), H₂O₂ (300 µmol, 30 % aqueous solution), acetic acid (1 mmol) in 2mL of CH₃CN, room temperature, 5 min.
Isotope labeling experiments:
Catalytic epoxidation of cyclooctene (a) and 1-decene (b) with 1/H₂O₂/HOAc in the presence of H₂¹⁸O. No incorporation of the ¹⁸O label in the epoxide products was observed. Reaction conditions are described in the Experimental section (Supporting Information).

(a) GC-MS of cyclooctene + ¹⁶O-cyclooctene oxide

(b) GC-MS of 1-decene + ¹⁶O-1,2-epoxydecane.

Figure S3. No incorporation of ¹⁸O label in the epoxide products is observed in the reactions of 1 with olefin and unlabeled H₂O₂ in the presence of labeled water, H₂¹⁸O, and excess HOAc.
Figure S4. An oxygen atom from labeled H$_2^{18}$O$_2$ is incorporated into epoxide products in catalytic epoxidation of cyclooctene with 1/H$_2$O$_2$ in the presence of excess HOAc. Final (Fe:olefin:H$_2$O$_2$) ratio (1:200:10).
X-ray Diffraction Studies.

Crystals of 1 were obtained by slow diffusion of diethyl ether into an acetonitrile solution. The X-ray intensity data for the reported complex were measured on a Bruker SMART APEX CCD X-ray diffractometer system equipped with a Mo-target X-ray tube (λ = 0.71073 Å). The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The data were corrected for absorption effects using the empirical method (SADABS). The structure was solved by direct methods and refined using the Bruker SHELXTL (Version 6.14) software package. All non-hydrogen atoms were refined anisotropically. The oxygen atoms in a perchlorate anion were disordered over two rotational orientations. This disorder was modeled with two parts in a 80:20 ratio. Hydrogen atoms were included at idealized positions for structure factor calculations except water hydrogen atoms which were located on a difference Fourier map and refined with restraining equivalent isotropic displacement parameters to be 1.5 times the U_{eq} value of the oxygen atom they attached to.

Crystal data for 1: C_{26}H_{38}Cl_{2}FeN_{6}O_{9}, M = 705.37, monoclinic, P2/c, a = 8.4229(10), b = 10.4692(12), c = 17.320(2) Å, β = 94.296(2)°, V = 1523.0(3) Å³, Z = 2, T = 100(2) K, μ(Mo-Kα) = 0.733 mm⁻¹, 11362 reflection measured, 3309 unique, R_{int} = 0.0474, full-matrix least-squares refinement on F² converged at R1 = 0.0933 and wR2 = 0.1487 for 234 parameters and 2624 reflections with I > 2σ(I) (R1 = 0.0715, wR2 = 0.1390 for all data) and a GOF of 1.094.

Table S1. Crystal data and structure refinement for 1.

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Volume | 1523.0(3) Å³
---|---
Z | 2
Density (calculated) | 1.538 g/cm³
Absorption coefficient | 0.733 mm⁻¹
F(000) | 736
Crystal size | 0.29 × 0.17 × 0.04
Theta range for data collection | 1.95 to 27.00
Reflections collected | 3309
Independent reflections | 2624
Completeness to theta(max) | 0.993
Absorption correction | 'multi-scan'
Final R indices [I>2sigma(I)] | R1 = 0.0715, wR2 = 0.1390
R indices (all data) | R1 = 0.0933, wR2 = 0.1487

Notes and references