



Oxidation of alkenes with non-heme iron complexes: suitability as an organic synthetic method



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ABSTRACT

In the course of a preliminary study to determine the preparative value and the synthetic applications of the non-heme iron(II) complexes Fe(**bpmen**)(OTf)₂ and Fe(**tpa**)(OTf)₂, in particular the oxidation of alkenes by using hydrogen peroxide as the terminal oxidant, we have found significant differences in catalyst behavior. After several attempts it was clear that the preparative relevance of the oxidation processes was linked to the concentration of the catalyst and optimal results were obtained when the concentration value was 5 mol %. At that concentration, the Fe(**bpmen**)(OTf)₂ catalyst mostly gave rise to mixtures of the epoxide and the *trans*-dihydroxylation products formed by water-assisted hydrolytic cleavage of the epoxides. Furthermore, the use of the tripodal ligand **tpa** led to *cis* dihydroxylation products. When deactivated olefins were used as substrates for the oxidation reaction, the *cis*-diols were obtained exclusively, although with modest conversions, regardless of the catalyst used.

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1. Introduction

Current methodology to achieve the catalytic *cis*-dihydroxylation of alkenes with preparative significance in organic synthesis is mainly focused on osmium and ruthenium compounds. However, some of the reagents used for this purpose are expensive, rather volatile and toxic. Accordingly, the development of alternative catalysts for the *cis*-1,2-dihydroxylation of alkenes is very challenging.¹

Inspired by the active site of iron oxidation enzymes, chemists have designed a wide variety of complexes that could mimic these metalloenzymes functionally, with the final goal of designing catalysts to achieve the oxidation of alkanes^{2–16} and alkenes.^{17–33} It has been seen that the most effective non-heme iron catalysts are those possessing nitrogen-based tripodal or linear tetradentate ligands, such that two *cis* labile sites available for coordination with exogenous ligands become available (Fig. 1). During the last twenty years, the preparation of a series of organic ligands that incorporate the key features of the non-heme active iron site of the Rieske dioxygenases, bacterial enzymes that perform the enantioselective *cis*-dihydroxylation of arene and alkene double bonds, has led to the characterization of several non-heme iron complexes and their application to dihydroxylation processes.^{34–39} However, most of

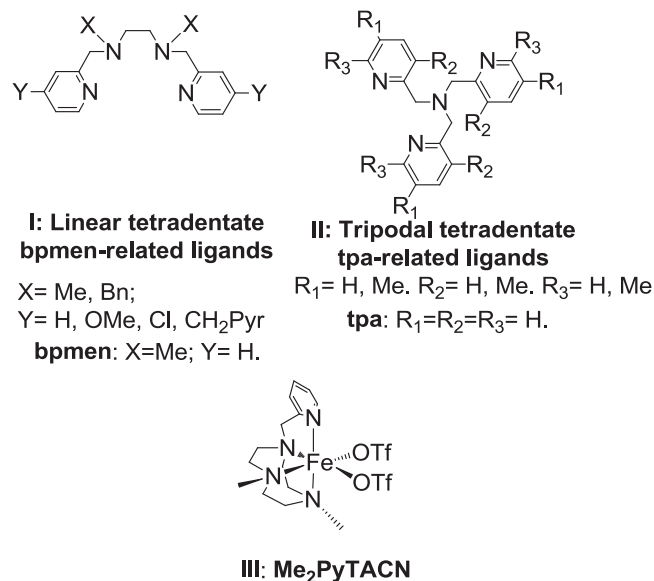


Fig. 1. Examples of the organic ligands used in the non-heme iron catalysis.

this effort has been developed by bioinorganic groups mainly interested in understanding enzyme mechanisms.⁴⁰

In an investigation of the oxidation of alkenes by non-heme iron enzyme mimics⁴¹ in the course of a preliminary study to determine

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the preparative value and synthetic applications of the non-heme iron complexes derived from the above-mentioned linear nitrogen-based tetradentate ligands, in particular the oxidation of alkenes by using hydrogen peroxide as the terminal oxidant, we focused our interest on bpmen iron(II) complexes and their capacity to oxidize steroids, monoterpenes and polycyclic aromatic hydrocarbons.^{42–44}

In this work, we study the preparative significance of the *cis*-dihydroxylation of alkenes by using the non-heme iron complexes Fe(**bpmen**)(OTf)₂ **I** (**bpmen**: bispicolyl-*N,N'*-methylethylenediamine) and Fe(**tpa**)(OTf)₂ **II** (**tpa**: tripicolylamine, –OTf: trifluoromethanesulphonate) (Fig. 1).

2. Results and discussion

Use of the **bpmen** system (**I**, Fig. 1) in epoxidation reactions for preparative purposes was first described by Jacobsen.^{22a} Later, the oxidation of olefins to *cis*-diols by using **tpa** catalysts (**II**, Fig. 1) under conditions of limiting substrate was described by Que and

Nam to have high conversion efficiency; however, these authors worked on substrates with a 0.12 mmol scale. Although some epoxide was also generated, those complexes represented the first examples of iron catalysts capable of olefin *cis*-hydroxylation.³⁸

We chose the *cis*-jasmane **1** as a peculiar and interesting substrate because its structure contains both a rich *cis*-alkene and a cyclic deactivated double bond. The oxidation of **1** (0.5 mmol) in the open air with hydrogen peroxide (1.2 equiv) in the presence of Fe(**bpmen**)(OTf)₂ (5 mol %) in CH₃CN at room temperature proved to be a regio- and stereoselective process. However, it afforded the *threo* diol **2** as the only oxidation product with 80% yield and 94% conversion (Table 1, entry 1). Furthermore, when the concentration of the catalyst was decreased to 0.2 mol %, the conversion of the oxidation reaction fell to 10% and, again, the diol **2** was obtained but in only 6% yield (Table 1, entry 2). After several attempts, it was clear that the preparative relevance of the process depended on the catalyst concentration, and optimal results were obtained for catalyst concentration values of 5 mol %. When the reaction was run under an inert atmosphere (Ar), we did not observe any substantial

Table 1
Iron (II) complex-catalyzed dihydroxylation of (*Z*)-Jasmane and (*E*)-Jasmane. Studies of the competition between dihydroxylation and epoxide hydrolytic cleavage

Entry	Substrate	Catalyst	Method ^a	Conversion (%) ^b	Products (yield %) ^c
1		Fe(bpmen)(OTf) ₂	A	94%	 2 (80%)
2		Fe(bpmen)(OTf) ₂	D	10%	 2 (6%)
3		Fe(bpmen)(OTf) ₂	A ^d	90%	 2 (79%)
4		Fe(bpmen)(OTf) ₂	A	100%	 2 (12%) 4 (50%)
5		Fe(bpmen)(OTf) ₂	A	100%	 7 (70%)
6		Fe(bpmen)(OTf) ₂	C	100%	 2 (30%) 4 (30%)
7		Fe(tpa)(OTf) ₂	A	85%	 7 2 (70%) <i>erythro:threo</i> = 2:1
8		Fe(tpa)(OTf) ₂	A	75%	 2 (80%)

^a The different procedures (A–D) are described in Experimental section. Typical experiments were performed using 0.5 mmol of starting material. Additionally, most of the tests were carried out at a scale of 2 mmol in order to test the preparative scale of the methodology.

^b Conversion was determined by GC or ¹H NMR analysis of the crude product.

^c Isolated yield based on the starting substrate.

^d The reaction was carried under a nitrogen atmosphere.

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