

# Selective epoxidation of unfunctionalized olefins catalyzed by unsymmetric Mn(III)–Schiff base complexes

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## Abstract

The selective epoxidation of unfunctionalized olefins (styrene, cyclohexene,  $\alpha$ -methylstyrene) catalyzed by unsymmetric Schiff base-Mn(III) complexes Mn(CBP-phen-XSal)Cl [X = H, Cl, Br, NO<sub>2</sub>, CH<sub>3</sub>, OCH<sub>3</sub>] **1** and the symmetric analogs Mn(III)(CBP-R-CBP)Y [R = CH<sub>2</sub>CH<sub>2</sub>, CH(CH<sub>3</sub>)CH<sub>2</sub>, C<sub>6</sub>H<sub>4</sub>, Y = Cl, OAc] **2** was investigated under mild conditions with iodosylbenzene as the terminal oxidant. The results showed that: the unsymmetric complexes Mn(III)(CBP-phen-XSal)Cl are effective catalysts in catalytically selective olefin epoxidation, superior to the symmetric analogs; with X = Cl, Br, the catalytic effectiveness was higher, X = strong electron-withdrawing group (NO<sub>2</sub>) or electron-releasing (OCH<sub>3</sub>) lowered the catalytic effectiveness; the highest percent yields of the three olefins were 73%, 98% and 92%, respectively. © 1997 Elsevier Science B.V.

**Keywords:** Olefin epoxidation; Manganese; Schiff base

## 1. Introduction

Transition-metal catalyzed oxidation of hydrocarbons is of synthetic as well as of biochemical interest [1]. In recent years, transition-metal Schiff base complexes have been receiving growing attention as models for enzyme-catalyzed oxidation reactions, for example, as catalysts for selective epoxidation of alkenes [2–4]. As models to mimic the function of cytochrome *p*-450, the transition-metal Schiff base system has several advantages: (a) ready availability, (b) low cost, (c) high epoxidation activity towards a wide range of unfunctional-

ized olefins. This should make it a very attractive candidate for laboratory and industrial use. In the past few years, various transition-metal–Schiff base complexes including Mn(III) [5], Fe(III) [6], Ni(II) [7], Cr(III) [2], Ru(III) [3], etc. have been used as the catalyst for epoxidation of olefins. Iodosylbenzene, sodium hypochlorite, *tert*-butyl peroxide, hydrogen peroxide, etc., were used as monooxygen sources for the catalyst to transfer oxygen to the olefin. One of the most promising examples among these transition metal complexes for epoxidation of unfunctionalized olefins with iodosylbenzene (PhIO) as the terminal oxidant are the bis(salen)-manganese(III) complexes developed by Kochi et al. [5].

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However, in comparison with the structurally-varied, well-developed metalloporphyrins [8], the readily available Schiff base complexes remain an area of considerable untapped potential in spite of their high effectiveness in catalysis. More exploitation and examination of structurally interesting Schiff base complexes on catalysis are warranted, in order to find more effective catalysts to be employed in organic reactions and to gain more insight into the behavior of the catalyst.

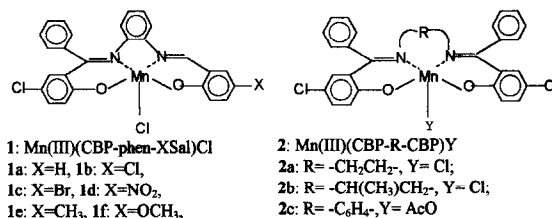
In this paper, the one-side variable unsymmetric Mn(III)–Schiff base complexes Mn(III)(CBP-phen-XSal)Cl were evaluated as catalysts for selective epoxidation of unfunctionalized olefins (styrene, cyclohexene and  $\alpha$ -methylstyrene) using PhIO as oxidant under mild conditions. For comparison the symmetric analogs Mn(III)(CBP-R-CBP) were also studied.

## 2. Experimental

### 2.1. Materials and instruments

Unless otherwise noted, commercial materials were used as received. Acetonitrile, styrene, cyclohexene,  $\alpha$ -methylstyrene, chlorobenzene and iodobenzene were purified by standard procedures prior to use. Styrene oxide [9–11], cyclohexene oxide [9–11],  $\alpha$ -methylstyrene oxide [9–11], and iodobenzene [12] were prepared according to literature procedures.

Elemental analysis was carried out on a Carlo Erba 1106 elemental analyzer. Infrared spectra were recorded on a Nicolet DX-10 FT-IR spectrometer.  $^1\text{H-NMR}$  spectra were obtained on a Varian FT-80A NMR spectrometer ( $\text{CDCl}_3$ , TMS). FAB mass spectra were taken on a ZAB-HS mass spectrometer. X-ray photoelectron spectra were measured on a PHI-550 spectrometer using  $\text{MgK}\alpha$  irradiation. The analysis of catalytic products was conducted on a Varian 3400 Gas chromatograph fitted with a Shimadzu CR-3A data processor using a  $15\text{ m} \times 0.33\text{ mm}$  OPLOT-R capillary column.



Scheme 1.

### 2.2. Synthesis of the Mn(III)–Schiff base complexes

The Schiff base ligands were synthesized according to the literature procedure [13]. Manganese complexes were prepared similarly with the procedure [14] in a mixture of dichloromethane and methanol. Elemental analysis and spectral characterization were found to be in good agreement with the formulae (Scheme 1).

### 2.3. Catalytic epoxidation of olefins and the analysis of products

Epoxidation of olefins using various Mn(III) catalysts were carried out in a 10 ml Schlenk tube under argon by mixing the test olefin (0.9 mmol), catalyst (0.0225 mmol) and iodobenzene (0.1 g, 0.45 mmol) in 5 ml acetonitrile. The contents were stirred at room temperature for 3 h, then the GC internal standard (chlorobenzene) was added and the mixture was subjected to GC analysis.

## 3. Results and discussion

### 3.1. Epoxidation of olefins catalyzed by the unsymmetric Mn(III) complexes 1a–1f

The catalysts 1a–1f were unsymmetric Mn(III)–Schiff base complexes, structurally remarkably different from those previously reported. Two different components, one from 5-chloro-2-hydroxybenzophenone (CBP) and the other from 5-substituted salicylaldehyde derivatives (XSal) are linked with the two amino

groups of 1,2-diaminobenzene(phen). In this way, the XSal moiety (see Scheme 1) was variable by changing the 5-substituent to affect the central Mn(III) ion, specifically to affect the behavior of the catalyst while keeping the left moiety. To our knowledge, the reported transition metal–Schiff base complexes as epoxidation catalysts are all structurally symmetric. The substituents from the aldehydes in the Schiff base ligand were symmetric and varied simultaneously, so that the modulation of the catalyst activity by substituents involves two similar substituents at the same time. Regarding the unsymmetric Schiff base complexes **1**, the substituents in the Schiff base ligands could be altered one at a time, permitting finer modulation of the catalyst activity by substituents with divergent electron properties. Some interesting behavior of the complexes as epoxidation catalyst are anticipated.

The epoxidation of unfunctionalized olefins (styrene, cyclohexene and  $\alpha$ -methylstyrene) catalyzed by various unsymmetric Mn(III)–Schiff base complexes (**1a–1f**) was investigated in acetonitrile. The results listed in Table 1 indicated that the examined unsymmetric complexes Mn(III)(CBP-phen-Xsal)Cl (**1a–1f**) were effective catalysts for selective epoxidation. The epoxidation reaction was selective with predominant formation of the desired epoxides. For

most catalysts the epoxide yields were fairly good. Complexes **1b**, **1a** and **1c** extended the highest epoxide yield of styrene, cyclohexene and  $\alpha$ -methylstyrene, respectively.

Concerning the selective epoxidation of olefins catalyzed by Mn(III)–Schiff base complexes with PhIO as oxidant, the oxygen-rebound mechanism had been suggested by Kochi et al. [5]: the Mn(III) complex first picks up an oxygen atom from the oxidant (PhIO) and converts to an oxomanganese species (V), which is the catalytically active species that transfers the oxygen to the olefinic double bond. This process is repeated with manganese shuttling between the Mn(III) and O = Mn(V) state. Besides this redox pathway, O = Mn(V) and Mn(III) can dimerize and form an  $\mu$ -oxo manganese(IV) species, which is an inactive species and whose formation leads to depletion of the catalytically active species (Scheme 2).

The percent yield is expressed relative to PhI formed, but PhI could also be formed in absence of the olefin [5], and the catalytically active species oxomanganese(V) could perform some side reactions during epoxidation. Thus the percent yield largely reflects the selectivity of epoxidation. The highest percent yields of epoxidation catalyzed by these unsymmetric catalysts for styrene, cyclohexene and  $\alpha$ -methylstyrene were 73%, 98% and 92%, respec-

Table 1  
Epoxidation of unfunctionalized olefins catalyzed by Mn(III)(CBP-phen-5-XSal)Cl complexes

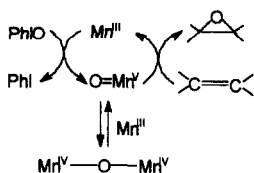
Complexes	Styrene oxide yield (mmol (%))	Cyclohexene oxide yield (mmol (%))	$\alpha$ -methylstyrene oxide yield (mmol (%))
<b>1a</b>	0.26 (70)	0.30 (84)	0.28 (92)
<b>1b</b>	0.28 (73)	0.27 (98)	0.27 (89)
<b>1c</b>	0.23 (66)	0.24 (96)	0.32 (90)
<b>1d</b>	0.20 (55)	0.27 (83)	0.18 (69)
<b>1e</b>	0.21 (66)	0.22 (84)	0.28 (85)
<b>1f</b>	0.10 (40)	0.14 (58)	0.17 (68)
<sup>a</sup>	(37)	(67)	(45)

Epoxidations were conducted in acetonitrile at room temperature under argon for 3 h with a molar ratio of substrate:iodosylbenzene:catalyst = 2:1:0.05, PhIO = 0.45 mmol.

The yield was determined by capillary GC integration against an internal quantitative standard (chlorobenzene). Percent yields were based on iodobenzene formed.

During epoxidation, benzaldehyde, 2-cyclohexene-1-ol and benzophenone were byproducts for styrene, cyclohexene and  $\alpha$ -methylstyrene, respectively.

<sup>a</sup>(5,5'-(NO<sub>2</sub>)<sub>2</sub> Salen)Mn(III)PF<sub>6</sub> evaluated by Kochi et al. [5].



Scheme 2.

tively. The optimal catalyst for epoxidation evaluated by Kochi was  $[5,5'-(\text{NO}_2)_2(\text{Salen})\text{PF}_6]$ . The corresponding percent yields catalyzed by this catalyst were only 37%, 67% and 45%, respectively. It indicated that the oxomanganese(V) species from the unsymmetric complexes was more reactive with the olefin to form epoxide than with other species to result in byproducts. For the three test olefins with a given catalyst, the order was cyclohexene  $\approx$   $\alpha$ -methylstyrene  $>$  styrene in terms of percent yield and yield. We ascribed the order, to some extent, to the fact that the isolated double bond in cyclohexene is relatively electron-rich and more apt to react with the electrophilic oxomanganese species with respect to the conjugated double bond in  $\alpha$ -methylstyrene and styrene. Though  $\alpha$ -methylstyrene is more hindered than styrene in epoxidation, the better results suggested that the electronic factor plays a more important role than the steric factor in the catalytic epoxidation reaction. A similar effect has been observed by Groves with Fe(III)-porphyrins as catalyst [15].

The substituent effect was interesting. Neither strong electron-withdrawing group ( $\text{NO}_2$ , complex 1d) nor strong electron-releasing group ( $\text{OCH}_3$ , complex 1f) on 5 position favored the

formation of epoxide. The catalytic effectiveness decreased considerably. However, complexes 1b and 1c which have halogen substituents (Cl, Br) on 5 position generally exhibited better catalytic behavior. It appears that the strong electron-withdrawing or electron-releasing groups in the unsymmetric catalyst have a negative effect on stabilization of high valent oxomanganese(V), on inhibition of dimerization via  $\mu$ -oxo complex formation and on diminution of oxidative ligand self-destruction, while the 5-halogen substituent shows a positive effect on them. It is well known that polyhalogenated porphyrin complexes are much more stable in catalytically oxidation of hydrocarbons [16]. The stabilization order of 5,5'-substituted  $[\text{Cr}(\text{III})\text{Salen}]\text{OTf}$  observed by Kochi during catalytic epoxidation was  $\text{Cl}, \text{H} \gg \text{OCH}_3 > \text{NO}_2$ . In terms of effectiveness the substituent effect of catalysts 1 could be put into the order as  $\text{Cl}, \text{Br}, \text{H} > \text{CH}_3 \gg \text{NO}_2 > \text{OCH}_3$ . So, presumably the positive effect of the 5-halogen substituent was largely on diminution of oxidative ligand self-destruction. In addition, the chloro substituent on 5-chloro-2-hydroxybenzophenone contributes a positive effect to the unsymmetric catalyst.

### 3.2. Epoxidation catalyzed by symmetric complexes (2a–2c)

The interesting catalytic behavior of the unsymmetric complexes prompted us to examine the effect of their symmetric analogs. Complexes (2a–2c) were synthesized and used as the catalyst for epoxidation under the aforemen-

Table 2  
Epoxidation of unfunctionalized olefins catalyzed by complexes 2

Complexes	Styrene oxide yield (mmol (%))	Cyclohexene oxide yield (mmol (%))	$\alpha$ -methylstyrene oxide yield (mmol (%))
2a	0.18 (59)	0.23 (70)	0.20 (82)
2b	0.16 (47)	0.21 (82)	0.23 (87)
2c	0.17 (45)	0.09 (26)	0.23 (65)

Epoxidations were conducted in acetonitrile at room temperature under argon for 3 h with a molar ratio of substrate:iodosylbenzene:catalyst = 2:1:0.05,  $\text{PhIO} = 0.45$  mmol.

The yield was determined by capillary GC integration against an internal quantitative standard [chlorobenzene]. Percent yields were based on iodobenzene formed.

tioned conditions. The results are presented in Table 2. It is easy to see that the epoxide yields and the percent yields catalyzed by **2a**, **2b** and **2c** for the three olefins are all lower than those of **1a**. **1a** and **2c**, which are more closely related than **1a** with **2a** or with **2b** in structure, showed the largest difference in catalytic efficacy. It is obvious that the asymmetry plays an interesting role in enhancing the catalytic effectiveness. Unfortunately, so far we haven't found out a satisfactory approach to account for the different behavior between the unsymmetric complexes and the corresponding symmetric ones in catalytic epoxidation. Active work is under way.

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