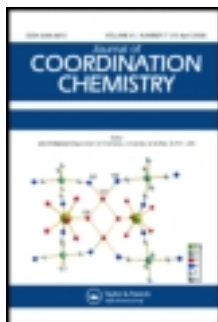


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## Mn(III) complexes with tridentate N,N,O-ligands as catalysts for the epoxidation of alkenes

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Mn(III) complexes with tridentate Schiff bases have been prepared and applied as catalyst precursors in epoxidation of alkenes using iodobenzene as an oxidant providing high conversions and high selectivities when cyclohexene derivatives were studied.

*Keywords:* Manganese; Tridentate N, N, O-; Epoxidation; Catalysis

### 1. Introduction

Epoxides are valuable and versatile intermediates in organic synthesis [1–3] and useful starting materials for the preparation of industrial chemicals such as epoxy resins, surfactants, paints, adhesives, and surface coating agents [4]. They can be efficiently obtained by metal-catalyzed oxidation of alkenes (figure 1) using a variety of oxidants such as oxygen, peroxides, hypochlorites, peracids, or iodosyl arenes. The catalyzed oxidations have the advantage of generating less waste by-products than the stoichiometric processes [4].

Schiff base manganese complexes have been extensively used as catalysts for this reaction. In particular, tetradentate salen ligands derived from salicylic aldehydes and diamines (figure 2) have been successfully applied in manganese-catalyzed epoxidation of unfunctionalized alkenes, including the asymmetric version [5–9]. Catalytic systems with tridentate N,N,O-donor ligands have been less reported than salen-based ones. Unlike salen, tridentate N,N,O-donor ligands can form species with one coordinated ligand,  $M(NNO)L_x$ , with coordination numbers from 4 to 6, and also species with two ligands  $M(NNO)_2$ . In the first case, easily available coordination sites can be generated when L are labile. In the case of  $M(NNO)_2$  complexes, a coordination vacancy should be generated by displacement of one of the arms of the ligand to allow interaction with the substrate or

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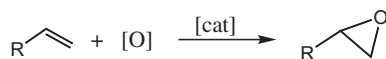


Figure 1. Epoxidation of alkenes.

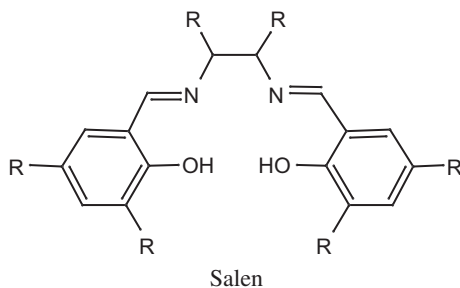
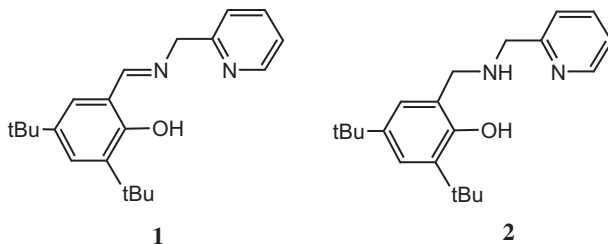


Figure 2. Salen ligands.

reagent. This pendant arm could subsequently reincorporate into the coordination sphere as an auxiliary or stabilizing ligand. In many metal-based catalytic systems, the presence of an auxiliary ligand increases the activity. For example, the addition of small amounts of the so-called donor axial ligands, such as pyridine, imidazole, or pyridine oxides, was reported to increase the yield in epoxidation of alkenes using Mn-salen catalysts [5, 10]. Furthermore, the presence of axial donors in Mn(III)-salen catalytic systems influenced the formation of the epoxide at the expense of the aldehyde by-product [11]. DFT calculations showed that cationic six-coordinate Mn(III)-salen species had a low energetic barrier for the formation of epoxide [12]. Six-coordinate Mn(III) complexes with 8-quinolinato bidentate ligands were reported to be active catalysts for epoxidation of olefins using aqueous  $\text{H}_2\text{O}_2$  as an oxidant in  $\text{AcOH}/\text{NH}_4\text{OAc}$  [13]. For these systems, a mechanism through a five-coordinate Mn-oxo species formed by dissociation of the hydroxo fragment, forming a pendant hydroxyl group, was proposed.

In this study we have investigated the preparation of manganese(III) complexes with tridentate ligands **1** and **2** (figure 3), containing phenol, imino/amino, and pyridine donors. Assuming chelate coordination through the phenoxo-imino/amino-moieties, the pyridine could act as an axial neutral ligand in a cationic six-coordinate species, with the advantage of being closer to the central metal than the free ligand. We have studied the application of these complexes as catalysts in the epoxidation of styrene and cyclohexene derivatives. Dioxo molybdenum(VI) complexes with **2** are efficient in the epoxidation of alkenes using *tert*-butyl hydroperoxide as the terminal oxidant [14].

Figure 3. N,N,O-donors **1** and **2**.

## 2. Experimental

### 2.1. General procedures

Styrene and cyclohexene were distilled over CaH<sub>2</sub> and stored under nitrogen. Dihydronaphthalene and *Z*, *E*-stilbene were used as purchased (Aldrich). PhIO [15] and **1** and **2** were prepared according to described procedures [14]. Solvents were purified through either distillation or a purification system, MBraun-SPS-800, and stored under nitrogen. IR spectra (4000–400 cm<sup>-1</sup>) were recorded on a Midac Grams/386 spectrometer in ATR or KBr. MALDI-TOF measurements of **2a** and **2b** were performed on a Voyager-DE-STR (Applied Biosystems, Framingham, MA) instrument equipped with a 337-nm nitrogen laser. All spectra were acquired in the positive ion reflector mode. Alpha-cyano-4-hydroxycinnamic acid was used as a matrix. The matrix was dissolved in MeOH at 10 mg mL<sup>-1</sup>. The complex was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mg L<sup>-1</sup>). The matrix and the samples were pre-mixed in the ratio of 2 : 1 (matrix : sample) and the mixture was then deposited (1 mL) on the stainless steel sample holder and was allowed to dry before introduction into the mass spectrometer. Three independent measurements were made for each sample. For each spectrum, 100 laser shots were accumulated. Electrospray ionization mass spectra (ESI-MS) were obtained with an Agilent Technologies mass spectrometer. Typically, a dilute solution of the compound in DMF/methanol (1:99) was delivered directly to the spectrometer source at 0.01 mL min<sup>-1</sup> with a Hamilton microsyringe controlled by a single-syringe infusion pump. The nebulizer tip operated at 3000–3500 V and 250 °C and nitrogen was both the drying and the nebulising gas. The cone voltage was 30 V. Quasi-molecular ion peaks [M–H]<sup>-</sup> (negative ion mode) or sodiated [M+Na]<sup>+</sup> (positive ion mode) peaks were assigned on the basis of the *m/z* values. Conductivity was measured with a Crison conductivity GLP equipped with a conductivity Pt cell. UV–visible spectra were recorded on a Shimadzu UV-1203 spectrophotometer.

### 2.2. Syntheses of complexes

[Mn(**1**)<sub>2</sub>Cl] (**1a**). In a round-bottomed flask under inert atmosphere, **1** (0.130 g, 0.40 mmol) was dissolved in 20 mL of ethanol and Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.147 g, 0.6 mmol) was added. The mixture was refluxed under inert atmosphere for 2 h. LiCl (0.025 g, 0.6 mmol) was then added and the mixture was refluxed under air for 2 h. The mixture was filtered off and the organic solvent evaporated. The remaining solid was redissolved in CH<sub>2</sub>Cl<sub>2</sub> and the solution was washed with aqueous sodium chloride. The organic phase was dried with sodium sulfate and evaporated to obtain a dark brown oily solid. Yield: 0.033 g (0.044 mmol, 22%). HR ESI-MS: Calcd for C<sub>42</sub>H<sub>52</sub>MnN<sub>4</sub>O<sub>2</sub> [M–Cl–2H]<sup>+</sup> *m/z* = 699.3471, found *m/z* = 699.3477. IR  $\bar{\nu}$  (ATR, cm<sup>-1</sup>): 2959, 2869, 1646, 1616, 1465, 1437, 1392, 1362, 1252, 1202, 1170, 1092, 1016, 801.  $\Lambda_M$  (acetonitrile, 4 × 10<sup>-4</sup> M) = 6.1 S·cm<sup>2</sup>·M<sup>-1</sup>.

[Mn(**1**)(OAc)<sub>2</sub>]<sub>2</sub>·2H<sub>2</sub>O (**1b**). In a round-bottomed flask, **1** (0.400 g, 1.23 mmol) and Mn(OAc)<sub>3</sub>·4H<sub>2</sub>O (0.332 g, 1.23 mmol) were dissolved in 25 mL of acetonitrile and stirred at 60 °C for 2 h. A dark brown solid was then obtained by solvent evaporation. The solid was redissolved in diethyl ether and filtered off. The filtrate was evaporated to obtain a dark brown solid. Yield: 0.226 g (0.22 mol, 36%). Anal. Calcd for C<sub>50</sub>H<sub>70</sub>Mn<sub>2</sub>N<sub>4</sub>O<sub>12</sub> (1028.98): C, 58.36; H, 6.86; N, 5.44. Found: C, 58.90; H, 6.95; N, 5.94. HR ESI-MS: calcd for (C<sub>50</sub>H<sub>65</sub>Mn<sub>2</sub>N<sub>4</sub>O<sub>10</sub>Na)<sup>+</sup> [M–H+Na]<sup>+</sup> *m/z* = 1014.3359, found *m/z* = 1014.4573;

calcd for  $(C_{44}H_{57}Mn_2N_4O_4)^+$   $[M-3OAc]^+$   $m/z=815.3140$ , found  $m/z=815.3966$ . IR  $\bar{\nu}$  (KBr,  $cm^{-1}$ ): 3418, 2959, 2867, 1753, 1663, 1588, 1570, 1469, 1433, 1392, 1250, 1202, 996, 756.

$[Mn(2)_2Cl]$  (**2a**). In a round-bottomed flask under inert atmosphere **2** (0.130 g, 0.4 mmol) was dissolved in 20 mL of ethanol and  $Mn(OAc)_2 \cdot 4H_2O$  (0.147 g, 0.6 mmol) was added. The mixture was refluxed under inert atmosphere for 1 h. LiCl (0.025 g, 0.6 mmol) was then added and the mixture was refluxed under air for 30 min. The mixture was evaporated to obtain a solid, which was washed with water. A dark violet solid was obtained after vacuum drying. Yield: 0.080 g (0.108 mmol, 54%). MALDI-TOF: calcd for  $(C_{42}H_{58}MnN_4O_2)^+$   $[M-Cl-2H]^+$   $m/z=703.3784$ , found  $m/z=703.6412$ . IR  $\bar{\nu}$  (KBr,  $cm^{-1}$ ): 3405, 3099, 2951, 1604, 1572, 1468, 1439, 1411, 1253, 1238, 956, 830, 755, 741.  $\Lambda_M$  (acetonitrile,  $4 \times 10^{-4} M$ ) =  $42.6 S \cdot cm^2 \cdot M^{-1}$ .

$[Mn(2)(OAc)_2]_x$  (**2b**). In a round-bottomed flask, **2** (0.130 g, 0.4 mmol) and  $Mn(OAc)_3 \cdot 4H_2O$  (0.107 g, 0.4 mmol) were dissolved in 15 mL of acetonitrile and stirred at 60 °C for 2 h. A dark brown solid was then obtained by solvent evaporation. The solid was redissolved in dichloromethane. Addition of hexane produced a solid, which was filtered off. The filtrate was evaporated to obtain a dark solid. MALDI-TOF: dimeric species calcd for  $(C_{42}H_{54}Mn_2N_4O_{10})^+$   $[M-2tBu]^+$   $m/z=884.2601$ , found  $m/z=884.7000$ ; trimeric species calcd for  $(C_{50}H_{68}Mn_3N_4O_{10})^+$   $m/z=1088.2714$ , found  $m/z=1088.3200$ .

### 2.3. General procedure for the epoxidation of alkenes with PhIO [5]

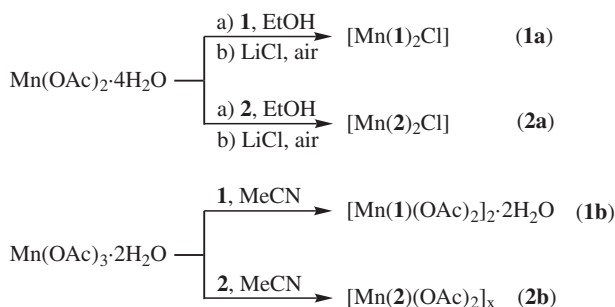
The catalyst ( $3.2 \times 10^{-2}$  mmol), PhIO (0.7 g, 3.2 mmol), substrate (1.6 mmol) and 0.3 mL of undecane as an internal standard (for styrene and cyclohexene) were placed in a purged round-bottomed flask under nitrogen (unless otherwise specified) and 8 mL of acetonitrile was added. A sample at 0 h was taken (for styrene and cyclohexene) and analyzed by GC. The mixture was stirred at 25 °C. After the indicated reaction time (table 1), the mixture was filtered through a zelite pad and analyzed by GC (styrene and cyclohexene) or by NMR spectroscopy after solvent evaporation (1,2-dihydronaphthalene, (*Z*)- and (*E*)-stilbene). The identification of the products was performed by comparison of the GC data with commercial samples, by GC-MS or by comparison with literature NMR data.

## 3. Results and discussion

### 3.1. Syntheses of complexes

Initially, the standard method of preparation of metal salen complexes starting with a Mn (II) salt was applied to the syntheses of Mn complexes with **1** and **2**. Thus,  $Mn(OAc)_2 \cdot 4H_2O$  was reacted with **1** or **2** in ethanol under inert atmosphere and after two or one hours, respectively, oxidation of Mn(II) was performed with air in the presence of lithium chloride in a ratio of Mn : ligand : LiCl 3 : 1 : 3 to furnish **1a** and **2a** (scheme 1) [16].

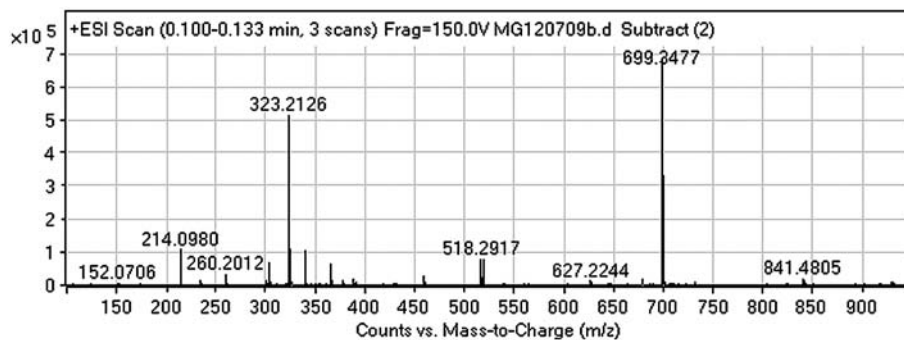
When **1** was used (complex **1a**), the IR spectrum of the final dark solid obtained showed two absorptions in the region of the azomethane stretching vibration  $\bar{\nu}$  (C=N) at  $\bar{\nu}$  1646 and  $1616 cm^{-1}$  (Supplementary material). The shift of these bands with respect to those observed in free **1** ( $1636$  and  $1590 cm^{-1}$ ) indicates coordination of the ligand to the

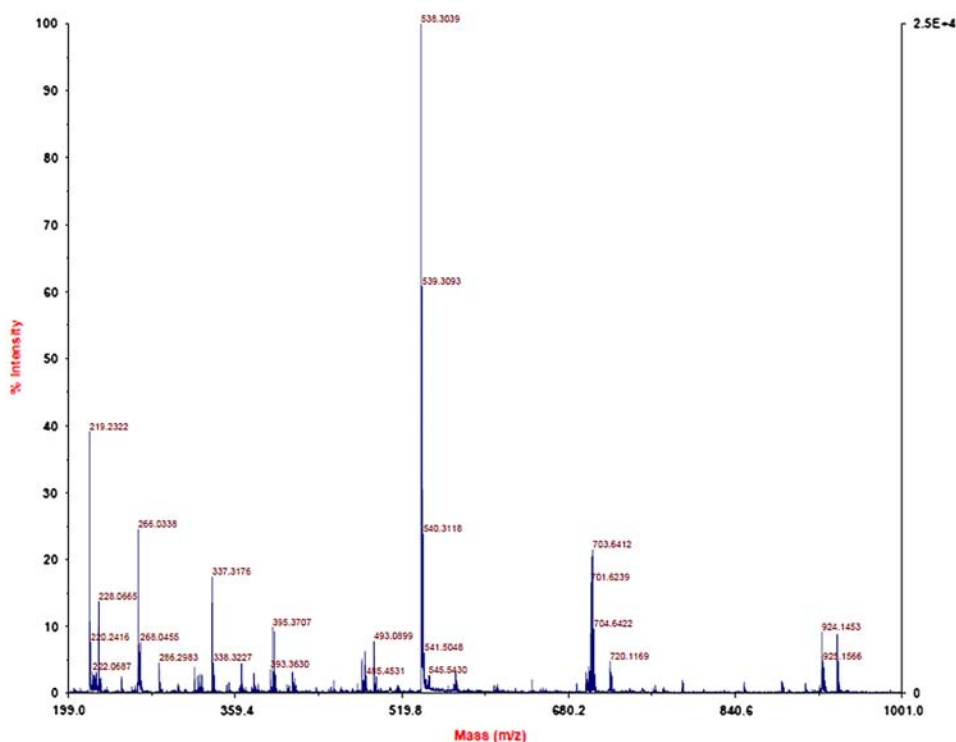
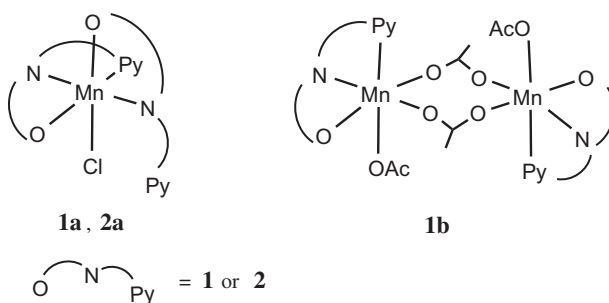
Scheme 1. Synthesis of **1a**, **1b**, **2a** and **2b**.

metal. The increase of frequency compared to that in free ligand could be attributed to a poor  $\pi$ -backbonding of this ligand [17].

Mass spectrometric analysis of **1a** showed peaks at  $m/z$  corresponding to  $[\text{Mn}(\mathbf{1})_2]^+$  (figure 4). Similar results were obtained when the ratio of Mn:ligand:LiCl used was 3 : 2 : 3. The product resulting from the reaction between  $\text{Mn(OAc)}_2 \cdot 4\text{H}_2\text{O}$  and **2** (**2a**, scheme 1) also showed a peak in the mass spectrum at  $m/z$  703.6412, attributed to  $[\text{Mn}(\mathbf{2})_2]^+$  (figure 5).

Nevertheless, the values of molar conductivity  $\Lambda_M$  in acetonitrile for **1a** and **2a**, 6.1 and  $42.6 \text{ S}\cdot\text{cm}^2\cdot\text{M}^{-1}$ , respectively, were in the range attributed to neutral species [18], indicating coordination of the chloride. Consequently, we propose the formation of the six-coordinate species  $[\text{Mn}(\text{L}-\kappa^3\text{N},\text{N},\text{O})(\text{L}-\kappa^2\text{N},\text{O})\text{Cl}]$  ( $\text{L} = \mathbf{1a}$  and  $\mathbf{2a}$ ), in which one ligand is tridentate  $\kappa^3\text{N},\text{N},\text{O}$  and the other is bidentate  $\kappa^2\text{N},\text{O}$  (one of the possible stereoisomers *mer* is depicted in figure 6). The six-coordinate Co(III) complex  $[\text{Co}(\text{III})][\text{ClO}_4]$  was reported [19], but in this case the poor coordinating perchlorate was out of the coordination sphere. The higher value of molar conductivity of **2a** compared to **1a** may be attributed to partial dissociation of chloride in solution. This dissociation was also observed for Mn–Cl–salen derivatives [20]. It was not possible to obtain good microanalysis data for **1a** and **2a**, probably due to the presence of small amounts of higher nuclearity species according to the ESI mass spectra. Reported crystal structures of related six-coordinate amino-phenolato-pyridine complexes with Co(III) [19] and Fe(III) [21] show that the tridentate ligands are coordinated in the *fac* mode. Unfortunately, it was not possible to obtain suitable crystals of these complexes to determine the X-ray structures.

Figure 4. ESI mass spectrum of **1a**.

Figure 5. MALDI TOF mass spectrum of **2a**.Figure 6. Possible molecular structures for **1a**, **2a** and **1b**.

Instead, when a Mn(III) precursor was made to react with **1** at a 1 : 1 ratio [22], the mass spectrum (figure 7) and elemental analysis of the resulting dark solid suggested the formation of a dinuclear species  $[\text{Mn}(\text{I})(\text{OAc})_2]_2 \cdot 2\text{H}_2\text{O}$  (**1b**). The strong bands at  $\bar{\nu}$   $1636\text{ cm}^{-1}$  and  $1590\text{ cm}^{-1}$  in the FTIR spectrum of free **1**, attributed to the C=N and C=C (pyridine, phenol) stretching vibrations [23], shifted to  $1663$  and  $1588\text{ cm}^{-1}$ , confirming the coordination of the ligand to the metal (Supplementary material). In comparison to the spectrum of free **1**, two medium absorptions are observed in the spectrum of **1a** at  $1570$  and  $1433\text{ cm}^{-1}$  that may be assigned to the asymmetrical and symmetrical stretching  $\bar{\nu}$  of



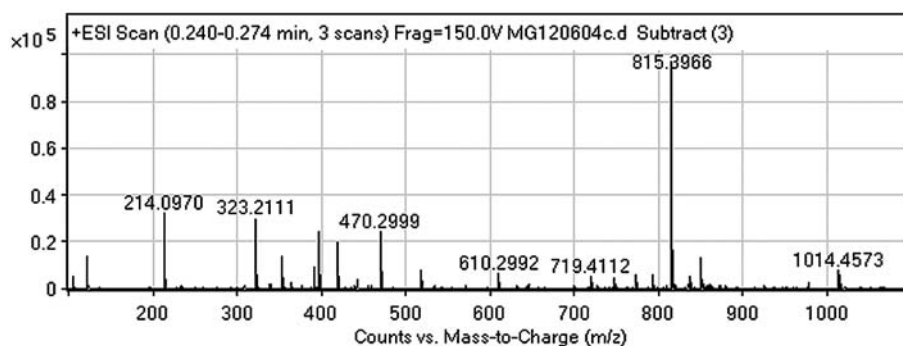


Figure 7. ESI mass spectrum of **1b**.

the CO in the acetate. According to literature data, the difference of  $137\text{ cm}^{-1}$  between these two absorptions may indicate bridging coordination [17, 24], although exchange processes may take place in the sample preparation [25]. In fact, the weak absorption at  $1753\text{ cm}^{-1}$  may indicate protonation of acetate in the presence of water. For related dimeric Mn(III) complexes, the presence of small quantities of  $\text{D}_2\text{O}$  (less than 1%) has been reported to produce the loss of about half of the bound acetate [23]. Nevertheless, the number of peaks from the ligand, which appear also in this zone, did not allow determining the presence of monodentate or free acetate [24]. The IR spectrum of the free ligand shows a broad absorption at  $\bar{\nu} 3448\text{ cm}^{-1}$  attributed to O-H stretch, which sharpens in the spectrum of **1b**, indicating the presence of water. A tentative proposal of molecular structure for **1b** is shown in figure 6.

When **2** was reacted with manganese(III) acetate dihydrate, the mass spectrum of the resulting solid showed peaks at  $m/z$  values corresponding to dimeric species, but peaks corresponding to trimeric and tetrameric species were also observed (**2b**, scheme 1). When the Mn:**2** ratio was increased to 1:2, similar mixtures of inseparable polynuclear species were detected in the MALDI-TOF mass spectrum.

### 3.2. Catalytic experiments

Complexes **1a**, **2a**, and **1b** were tested as catalysts in the epoxidation of styrene (ST), cyclohexene (Cy), 1,2-dihydronaphthalene (DHN), and (*Z*)- and (*E*)-stilbene (*Z*-STB and *E*-STB) as the model substrates. Initial experiments using **1b** and **2a** as catalysts with sodium hypochlorite [26], sodium periodate [27], and hydrogen peroxide [28] as the terminal oxidants for the epoxidation of styrene did not lead to the formation of the epoxide, so iodobenzene was selected as an oxidant. The reactions were run in acetonitrile, where this reactant is more soluble than in other organic solvents [5]. This solvent was also reported to provide better conversions and selectivities in other Mn-based catalytic systems [29]. Low selectivities in the epoxide were obtained when using styrene as a substrate, as already reported for other Mn-salen or Mn-porphyrin catalysts, and was attributed to partial polymerization [5] or the formation of other by-products (benzaldehyde) [29, 30]. Therefore, our study focused on other substrates such as stilbenes, cyclohexene, and 1,2-dihydronaphthalene. The results obtained are shown in table 1.

Table 1. Epoxidation of alkenes with PhIO and **1a**, **1b** and **2a**<sup>a</sup>.

Entry	Cat.	Substrate	% C <sub>conv</sub> <sup>b</sup>	% S <sub>epox</sub> <sup>c</sup>
1	<b>1a</b>	<i>E</i> -STB	15	100 (0/100) <sup>d</sup>
2	<b>2a</b>	<i>E</i> -STB	31	100 (0/100) <sup>d</sup>
3 <sup>e</sup>	<b>2a</b>	<i>E</i> -STB	45	70 (0/100) <sup>d</sup>
4	<b>1b</b>	<i>E</i> -STB	23	100 (0/100) <sup>d</sup>
5	<b>1a</b>	<i>Z</i> -STB	39	89 (53/47) <sup>d</sup>
6	<b>2a</b>	<i>Z</i> -STB	34	90 (47/53) <sup>d</sup>
7	<b>1b</b>	<i>Z</i> -STB	26	100 (42/58) <sup>d</sup>
8 <sup>f</sup>	<b>2a</b>	<i>Z</i> -STB	18	93 (46/54) <sup>d</sup>
9 <sup>e</sup>	<b>1a</b>	Cy	48	73
10	<b>2a</b>	Cy	52	71
11	<b>1b</b>	Cy	61	78
12 <sup>g</sup>	<b>1a</b>	DHN	53	73
13	<b>2a</b>	DHN	74	86
14 <sup>g</sup>	<b>2a</b>	DHN	72	86
15	<b>1b</b>	DHN	82	85

Notes: <sup>a</sup>Reaction conditions: catalyst 0.0037 M, molar ratio substrate/catalyst=50/1, molar ratio oxidant/substrate=2/1, solvent CH<sub>3</sub>CN V=8 mL, *t*=24 h; <sup>b</sup>determined by GC based on cyclohexene converted; <sup>c</sup>determined by <sup>1</sup>H NMR for DHN, and *Z/E*-stilbene; <sup>d</sup>determined by GC respect to epoxide formed for cyclohexene; determined by <sup>1</sup>H NMR for DHN, and *cis/trans* stilbene; <sup>e</sup>*Z/E*; <sup>f</sup>reaction run under air; <sup>g</sup>0.5 equivalents of 2,6-*tert*-butylphenol; <sup>h</sup>*t*=48 h.

The selectivities in the epoxide obtained with (*Z*)- and (*E*)-stilbene were high (70–100%), with 1,2-diphenylethanone as the by-product detected [31], although the conversions in epoxide measured by <sup>1</sup>H NMR were modest (15–39%, entries 1, 2, 4–7, table 1). When the reaction was run in the presence of air, the activity increased (45% *versus*. 31%) but the selectivity in epoxide decreased and benzaldehyde and 1,2-diphenylethanone were detected (entry 3, table 1). The reaction from *E*-stilbene was completely stereoselective producing only the (*E*)-isomer. Retention of configuration was also reported for Mn-salen complexes [5]. As for the epoxidation of *Z*-stilbene, mixtures of approx. 45/55 of *Z/E* epoxides were obtained. This suggests a radical mechanism in which the C–C bond rotation in the expected Mn–O–C–C intermediate formed competes with ring closure to form the final epoxide, thus leading to *Z/E* epoxide mixtures [5]. In fact, the addition of 0.5 equivalents of a radical scavenger (2,6-di-*tert*-butylphenol) produced a decrease in conversion (entry 8 *versus*. entry 6, table 1), as observed for Mn-salen systems [5]. In the case of **1a**, the steric effect of the substrate influenced the conversion, since it was lower for the *trans*-alkene than for the *cis*- one (entry 1 *versus*. entry 5, table 1), as also reported for porphyrin catalytic systems [32]. Nevertheless, no significant differences of conversion were observed between the *cis*- and *trans*-alkenes using **2a** and **1b** (entries 2 and 4 *versus*. entries 6 and 7, table 1).

The conversions were higher when cyclohexene and 1,2-dihydronaphthalene were epoxidated using **1a**, **2a**, and **1b**. Conversions of 48–61% and selectivities in the epoxide up to 78% were obtained in the epoxidation of cyclohexene (entries 9–11, table 1). 4-Cyclohexenone by-product was identified by GC-mass analysis. Conversions increased up to 70–80% in the epoxidation of 1,2-dihydronaphthalene using **2a** and **1b** with good selectivities towards the epoxide (entries 13 and 15, table 1). Neither the conversion nor the selectivity increased at longer reaction times using **2a** (entry 14 *versus*. entry 13, table 1). Naphthalene was identified as a by-product (*ca.* 15% selectivity) when **1a** and **2a** were used (entries 12 and 13, table 1). Using catalysts with **1** (**1a** and **1b**) the dialdehyde 2-(3-oxopropyl)benzaldehyde, product of the C=C bond cleavage, was also identified by

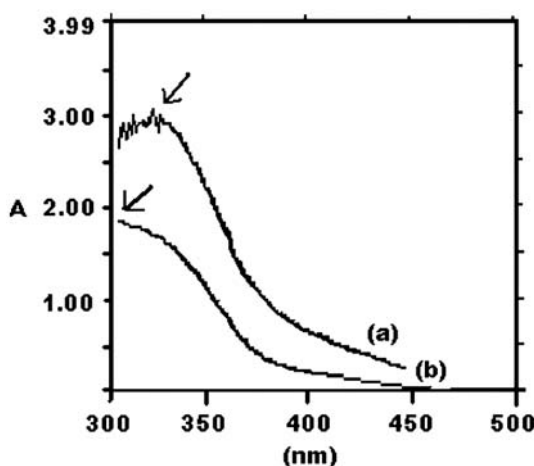


Figure 8. UV-visible spectra ( $\lambda$ , nm) of **1a** ( $4 \times 10^{-4}$  M)/PhIO (molar ratio = 1/10) in acetonitrile at (a)  $t=0$  h, (b) 24 h.

$^1\text{H}$  NMR (13% selectivity). Both the sub-products were also reported to be formed in the catalytic oxidation of 1,2-dihydronaphthalene with hydrogen peroxide using Keggin-type metal-substituted polyoxotungstates as catalysts [33].

The reactivity of **1a** with PhIO was analyzed by UV-visible spectroscopy. Complex **1a** has an absorption at  $\lambda$  322 nm ( $\epsilon$  7500) due to the  $\pi \rightarrow \pi$  electronic transition of the ligand. When PhIO was added to acetonitrile solution of **1a** ( $4 \times 10^{-4}$  M) at a molar ratio Mn/PhIO, 1/2, a weak lightening of the brown color of the solution was observed. It was analyzed after 3 h and 24 h. After 3 h, the spectrum presents a decrease in the absorption at 322 nm, probably due to the formation of a species with an absorption at  $\lambda < 300$  nm, which is unaltered after 24 h (Supplementary material). Similar changes were observed when a ratio of Mn/PhIO of 1/10 was used (figure 8). This could be indicative of the formation of an active species although no conclusive proposal can be done.

#### 4. Conclusions

New catalytic systems based on Mn(III)-tridentate complexes have been prepared and used in the epoxidation of alkenes. Tridentate ligands **1** or **2** (**L**) formed six-coordinate complexes  $[\text{Mn}(\text{L}-\kappa^3\text{N},\text{N},\text{O})(\text{L}-\kappa^2\text{N},\text{O})\text{Cl}]$  in which the chloride is coordinated, as indicated by the conductivity measurements. In the absence of this coordinating anion, formation of dimeric species with bridging acetate is proposed based on microanalysis, mass spectra, and infrared data. The lability of chloride or coordinating arms of the tridentate or bidentate **L** may account for the catalytic activity of these systems, since formation of the active species requires generation of a coordination site. Changes in the UV-visible spectrum of the solution of **1a** in the presence of PhIO indicate that reaction occurs, although no conclusive proposal of catalytic active species can be done. The best conversions with these catalytic systems were obtained for epoxidation of cyclohexene and dihydronaphthalene using iodosobenzene as a terminal oxidant (up to 82% conversion in 24 h, and selectivities in the epoxide up to 86%). The formation of allylic oxidation products such as

4-cyclohexenone or 1,2-diphenylethanone and the low stereoselectivity in the epoxidation of (*Z*)-stilbene suggest that a radical mechanism is operating in these processes, as proposed for Mn-salen catalytic systems [34, 35]. The presence of a radical scavenger produced a decrease in the conversion. As for the epoxidation of cyclohexene derivatives, the system containing the amine functionality **2a** presents slightly higher conversions than **1a**, containing imine. The dimeric catalysts **1b** provided the best results, although the increase in conversion using this catalyst was only 10%. In this case, there is a two-fold concentration of Mn in solution compared to **1a** or **2a**, which would be the reason for the increased activity if the active species was a monomer. Otherwise, the coordinative saturation of **1a** and **1b** may account for these differences. The epoxidation of styrene and stilbenes with these catalysts proceed at low conversions and selectivities.

### Supplementary material

Supplementary Data containing IR spectra, examples of NMR spectra of catalytic experiments and UV-visible spectra of **1a** and PhIO are available.

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### References

- [1] A. Somasekar Rao. *Addition Reactions with Formation of C-O Bonds: General Methods of Epoxidation*, in: *Comprehensive Organic Synthesis*, B.M. Trost, I. Fleming (Eds.), Pergamon Press, Oxford, **7**, 357 (1991).
- [2] K.A. Jørgensen. *Chem. Rev.*, **89**, 431 (1989).
- [3] T. Punniyamurthy, S. Velusamy, J. Iqbal. *Chem. Rev.*, **105**, 2329 (2005).
- [4] B.M. Choudary, M. Lakshmi Kantam, P. Lakshmi Santhi. *Catal. Today*, **57**, 17 (2000).
- [5] K. Srinivasan, P. Michaud, J.K. Kochi. *J. Am. Chem. Soc.*, **108**, 2309 (1986).
- [6] W. Zhang, J.L. Loebach, S.R. Wilson, E.N. Jacobsen. *J. Am. Chem. Soc.*, **112**, 2801 (1990).
- [7] R. Irie, K. Noda, Y. Ito, N. Matsumoto, T. Katsuki. *Tetrahedron Lett.*, **31**, 7345 (1990).
- [8] C.T. Dalton, K.M. Ryan, V.M. Wall, C. Bousquet, D.G. Gilheany. *Top. Catal.*, **5**, 75 (1998).
- [9] E.M. McGarrigle, D.G. Gilheany. *Chem. Rev.*, **105**, 1563 (2005).
- [10] J. Skarzewski, A. Gupta, A. Vogt. *J. Mol. Catal. A: Chem.*, **103**, L63 (1995).
- [11] J.P. Collman, L. Zeng, J.I. Brauman. *Inorg. Chem.*, **43**, 2672 (2004).
- [12] H. Jacobsen, L. Cavallo. *Organometallics*, **25**, 177 (2006).
- [13] S. Zhong, Y. Tan, Z. Fu, Q. Qie, F. Xie, X. Zhou, Z. Ye, G. Peng, D. Yin. *J. Catal.*, **256**, 154 (2008).
- [14] J.M. Mitchell, N.S. Finney. *J. Am. Chem. Soc.*, **123**, 862 (2001).
- [15] P. Dauban, L. Sanière, A. Tarrade, R.H. Dodd. *J. Am. Chem. Soc.*, **123**, 7707 (2001).
- [16] W. Zhang, E.N. Jacobsen. *J. Org. Chem.*, **56**, 2296 (1991).
- [17] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley & Sons, New York (1998).
- [18] W.J. Geary. *Coord. Chem. Rev.*, **7**, 81 (1971).
- [19] R. Shakya, C. Imbert, H.P. Hratchian, M. Lanznaster, M.J. Heeg, B.R. McGarvey, M. Allard, H.B. Schlegel, C.N. Verani. *Dalton Trans.*, 2517 (2006).

- [20] S. Biswas, T. Kar, S. Sarkar, K. Dey. *J. Coord. Chem.*, **65**, 980 (2012).
- [21] C. Imbert, H.P. Hratchian, M. Lanznaster, M.J. Heeg, L.M. Hryhorczuk, B.R. McGarvey, H.B. Schlegel, C.N. Verani. *Inorg. Chem.*, **44**, 7414 (2005).
- [22] M.C. Cheng, M.C.W. Chan, S.M. Peng, K.K. Cheung, C.M. Che. *J. Chem. Soc., Dalton Trans.*, 3479 (1997).
- [23] G. Eilers, C. Zettersten, L. Nyholm, L. Hammarström, R. Lomoth. *Dalton Trans.*, 1033 (2005).
- [24] G.B. Deacon, R.J. Phillips. *Coord. Chem. Rev.*, **33**, 227 (1980).
- [25] D. Martínez, M. Motevalli, M. Watkinson. *Dalton Trans.*, 446 (2010).
- [26] D. Wang, M. Wang, X. Wang, Y. Chen, A. Gao, L. Sun. *J. Catal.*, **237**, 248 (2006).
- [27] J. Huang, X. Fu, Q. Miao. *Catal. Sci. Technol.*, **1**, 1472 (2011).
- [28] M. Salavati-Niasarai, P. Salemi, F. Davar. *J. Mol. Catal. A: Chem.*, **238**, 215 (2005).
- [29] M. Bagherzadeh, M. Zare. *J. Coord. Chem.*, **65**, 4054 (2012).
- [30] M. Zakeri, M. Moghadam, I. Mohammadpoor-Baltork, S. Tangestaninejad, V. Mirkhani, A.R. Khosropour. *J. Coord. Chem.*, **65**, 1144 (2012).
- [31] Characterized by <sup>1</sup>H NMR by comparison with reported data: S. Gaillard, J. Bosson, R.S. Ramón, P. Nun, A.M.Z. Slawin, S.P. Nolan. *Chem. Eur. J.*, **16**, 13729 (2010); B. Landers, C. Berini, C. Wang, O. Navarro. *J. Org. Chem.*, **76**, 1390 (2011).
- [32] J.T. Groves, T.E. Nemo. *J. Am. Chem. Soc.*, **105**, 5786 (1983).
- [33] A.C. Estrada, M.M.Q. Simões, I.C.M.S. Santos, M.G.P.M.S. Neves, A.M.S. Silva, J.A.S. Cavaleiro, A.M.V. Cavaleiro. *Catal. Lett.*, **128**, 281 (2009).
- [34] L. Cavallo, H. Jacobsen. *Angew. Chem., Int. Ed.*, **39**, 589 (2000).
- [35] E.F. Murphy, T. Mallat, A. Baiker. *Catal. Today*, **57**, 115 (2000).