A partially water-soluble cationic Mn(III)–salphen complex for catalytic epoxidation

Amir Abdolmaleki and Saeed Malek-Ahmadi

Abstract: Synthesis and application of new cationic Mn(III)–salphen complexes for catalytic epoxidation of olefins to epoxides in a homogeneous reaction media have been reported. The experimental data showed that the cationic salphen is more active than its neutral form. The acceleration of the reaction rate is attributed to the phase-transfer capability of the built-in phenazinium salt of the Mn(III)–salphen catalyst.

Key words: phase transfer, phenazinium salt, cationic Mn(III)-salphen complex, epoxidation.

Résumé : On a effectué la synthèse et examiné le domaine d'application d'un nouveau complexe cationique, le Mn(III)– salphène, pour la transformation catalytique d'oléfines en époxydes, dans un milieu réactionnel homogène. Les données expérimentales montent que le salphène cationique est plus actif que sa forme neutre. L'augmentation de la vitesse de réaction est attribuée à la capacité de transfert de charge du sel de phénazinium inclus dans le catalyseur Mn(III)–salphène.

Mots-clés : transfert de phase, sel de phénazinium, complexe cationique Mn(III)-salphène, époxydation.

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Introduction

Epoxides are versatile synthetic intermediates that can be readily converted into a large variety of useful compounds by means of a regioselective ring-opening reaction.^{1–3} Therefore, the design of new catalysts for epoxidation of alkenes constitutes an important strategy for the synthesis of pharmaceuticals and fine chemicals.^{4–6}

In the field of homogeneous catalysis, salen and salophen ligands^{4,7-11} have been investigated for many years and are among the most widely developed ligands in the catalysis toolbox of modern chemistry for a range of organic transformations. Many synthetic approaches toward metallosalen complexes are known that start off with double Schiff base precursors. These precursors commonly originate from a condensation process involving 1 equiv of a diamine and 2 equiv of salicylaldehyde or a ketone analogue. The resultant metallosalen frameworks are thermally and kinetically stable entities controlled by the presence of a tetradentate ligation mode of the N₂O₂ pocket that is characteristic of a salen ligand. This type of stabilization allows, for instance, the creation of vital catalytic intermediates generated by a change in or accommodation of a higher oxidation state of the metal ion coordinated by the salen ligand.¹²⁻¹⁵

In this area, Jacobsen and co-workers¹⁶ developed a practical epoxidation procedure using a two-phase system, with an aqueous phase containing H_2O_2 and an organic phase composed of a solution of substrates.^{10,17–20} For practical application, there has been a compelling interest in the development of catalytic epoxidation systems that can increase reaction activity in the aqueous H_2O_2 solution / organic biphasic system. Usually a pyridine *N*-oxide derivative is added to the aforementioned catalytic system to stabilize the catalyst by ligation and to increase the epoxidation reaction rate by drawing the active oxidant into the organic phase.^{21,16} Also, the addition of some phase-transfer catalysts could accelerate the epoxidation reaction in the presence of a Mn(III)–salphen catalyst.²² Moreover, it was reported that the epoxidation activity could be enhanced in the two-phase reaction medium using Mn (III)–salphen catalysts with a built-in phase-transfer capability, constructed by introducing tertiary amine unit(s) to the salen ligand.^{23–25}

Recently, Sun and co-workers found that the internal pyridinium salt of the catalyst could play a built-in phase-transfer role for the acceleration of the epoxidation in an aqueous / organic biphasic medium as 2 mol% of external pyridinium salts and ammonium halides, with a tertiary amine unit that was used.^{26,27}

In this work, the synthesis of a new phenazinium salphen and its cationic complex with Mn(III) is reported. The cationic complex Mn(III)–salphen was applied in the epoxidation of olefins to epoxides.

Experimental

General remarks

All chemicals were purchased from Merck Chemical Co. *o*-Phenylenediamine was sublimated for further purification. Other solvents and chemicals were purified by common procedures. ¹H NMR (500 MHz) spectra were obtained in deuterated dimethylsulfoxide (DMSO- d_6) on a Bruker Avance 500 instrument (Bruker, Rheinstetten, Germany), UV–vis absorption spectra were obtained in DMSO (ca. ×10⁻⁵ mol/L)

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Fig. 1. ¹H NMR spectra of cationic salphen (4).



on a JASCO-570 UV–vis spectrometer, and IR spectra were obtained as KBr pellets with a 680 plus-JASCO. Elemental analysis was also performed by Malek-Ashtar University of Technology, Tehran, Iran.

Synthesis of 2,3-diaminophenazine (1)

2,3-Diaminophenazine was prepared by using a modified procedure reported in the literature.¹⁰ In a typical experiment, 6 mL of 0.08 mol/L aq FeCl₃ solution was rapidly added into 30 mL of a 0.02 mol/L aqueous o-phenylenediamine solution with vigorous stirring. A quick color change from purpleblack to reddish-brown was observed upon the addition of FeCl₃. After 5 h at ambient temperature, a large amount of white solid was formed. The precipitate was washed three times with deionized water, then separated by centrifugation and sublimated to afford 1 as a white needlelike crystal. Yield (%): 98; mp > 300 °C. FT-IR (KBr, cm⁻¹) ν : 3394 (s), 3313 (s), 3188 (w), 1692 (m), 1633 (m), 1531 (s), 1478 (s), 1383 (m), 1371 (m), 1240 (m), 1149 (m), 891 (w), 834 (m), 772 (m), 750 (m). ¹H NMR (500 MHz, DMSO-*d*₆, ppm) δ: 8.01 (s, 2H, aromatic H), 7.715 (s, 2H, aromatic H), 7.01 (s, 2H, aromatic H), 3.43 (br, 4H, -NH₂). EI/MS m/z (C12H10N4): M+, 210. Anal. calcd for C12H10N4 (%): C 68.56, H 4.79, N 26.65; found: C 68.42, H 4.71, N 26.59.

Synthesis of salphen (2)

Compound (1) (0.21 g, 1 mmol) and 3,5-di-*tert*-butyl-2hydroxybenzaldehyde (0.468 g, 2 mmol) were dissolved in 10 mL of absolute ethanol in a 25 mL flask equipped with a magnetic stirring bar. The reaction mixture was stirred at room temperature for 12 h. The dark brown precipitate was filtered, washed with ethanol. and was purified by column chromatography. Yield (%): 82; mp 267 °C. FT-IR (KBr, cm⁻¹) ν : 3421 (w), 2956 (s), 1636 (m), 1616 (m), 1527 (m), 1442 (s), 1398 (m), 1360 (m), 1292 (m), 1251 (m), 1144 (m), 983 (m), 847 (w), 741(m). ¹H NMR (500 MHz, DMSO- d_6 , ppm) δ : 13.84 (s, 2H, HO–Ar), 8.43 (s, 2H, CH=N), 8.12, 7.91, 7.64, 7.54 (m, 10H, aromatic H), 1.48 (s, 18H, CH₃), 1.39 (s,18H, CH₃). Anal. calcd for C₄₂H₅₀N₄O₂ (%): C 78.47, H 7.84, N 8.72; found: C 78.37, H 7.73, N 7.80.

Synthesis of Mn(III) salphen (3)

In a 50 mL round-bottom flask equipped with a magnetic stirring bar, compound **1** (0.21 g, 1 mmol), 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (0.468 g, 2 mmol), Mn(OAc)₂·4 H₂O (0.245 g, 1 mmol) and an excess amount of LiCl (0.5 g) in absolute ethanol were stirred under reflux for 12 h. For oxidation of Mn(II) to Mn(III), air was bubbled into the solution during the reaction. Then the reaction mixture was cooled to room temperature and filtered. The brown solid was washed with ethanol to remove all impurities. Yield (%): 78; mp > 300 °C. FT-IR (KBr ν , cm⁻¹): 2962 (m), 2921 (m), 1648 (m), 1610 (m), 1592 (s), 1492 (m), 1445 (m), 1220 (m), 770 (w), 643 (w), 616 (w), 488 (w). UV–vis (DMSO, nm) λ_{max} : 263, 346, 447.

Synthesis of cationic salphen (4)

In a 25 mL round-bottom flask, 15 mL of methyl iodide was added to compound **2** (0.032 g, 0.05 mmol) and refluxed for 7 days. The mixture was cooled to room temperature. The unreacted methyl iodide was removed under reduced pressure. The brown solid was obtained after the removal of methyl iodide. Yield (%): 83; mp > 300 °C (decomp.). FT-IR (KBr, cm⁻¹) ν : 3417 (w), 2958 (m), 2923 (m), 2853 (m), 1653 (m), 1624 (s), 1571 (m), 1525 (m), 1457 (m), 1384 (m), 1260 (m), 1199 (w), 1169 (w), 1097 (w), 1024 (m), 800 (w), 751 (m). ¹H NMR (500 MHz, DMSO-*d*₆, ppm) δ : 13.85 (br, 2H, HO–Ar), 8.43 (s, 2H, CH=N), 8.26, 8.12, 7.93, 7.52 (m, 10H, aromatic H), 5.04 (br, 6H, CH₃–N⁺), 1.49 (s, 18H, CH₃), 1.40 (s, 18H, CH₃) (Fig. 1). Anal. calcd for C₄₄H₅₆I₂N₄O₂ (%): C 57.02, H 6.09, N 6.05; found: C 56.99, H 6.11, N 5.97.

Synthesis of cationic Mn(III)–salphen (5)

In a 25 mL round-bottom flask, 15 mL of methyl iodide was added to compound **3** (0.034 g, 0.02 mmol) and refluxed for 7 days; after this period of time, the reaction mixture was cooled to room temperature. After removal of the unreacted methyl iodide under reduced pressure, a brown solid was obtained. The residue was purified by chromatography on a silica gel column (MeOH/CH₂Cl₂, 1:8) to give the desired complex. Yield (%): 94; mp > 300 °C. FT-IR (KBr, cm⁻¹) ν : 2957 (m), 2925 (m), 2850 (m), 1650 (m), 1622 (s), 1570 (m), 1525 (m), 1460 (m), 1384 (m), 1261 (m), 1200 (w), 1171 (w), 1097 (w), 1024 (m), 799 (w), 751 (m). Anal. calcd for C₄₄H₅₄ClI₂MnN₄O₂ (%): C 52.06, H 5.36, N 5.52; found: C 51.93, H 5.27, N 5.50.

Epoxidation of olefins in the presence of Mn(III)-salphen (3) and cationic Mn(III)-salphen (5)

An aqueous solution of H₂O₂ (30%, 0.8 mmol) was added

t-Bu

t-Bu





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Results and discussion

t-Ru

t-Bu

The procedure for catalyst preparation is depicted in the Scheme 1.

2,3-Diaminophenazine (1) was synthesized by oxidation of o-phenylenediamine. In the FT-IR spectrum, the two major peaks of 2,3-diaminophenazine are observed between 3400 and 3150 cm⁻¹ owing to N–H stretching vibrations of theamino groups, which indicate the presence of NH₂ groups in the structural unit. The bands at 834 and 891 cm⁻¹ are as-

signed to the out-of-plane bending vibrations of the C–H bonds in the 1,2,4,5-tetra-substituted benzene ring of the phenazine unit. The results obtained from the ¹H NMR spectrum (δ 8.01 (m, 2H), δ 7.71 (m, 2H), δ 7.01 (s, 2H), and δ 3.43 (br, 4H, –NH₂)) support the structure of compound **1**. The elemental analysis result is consistent with the proposed chemical formula of **1**.

Synthesis of salphen (2)

Salphen (2) was synthesized by using a stoichiometric ratio of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde and 2,3-diaminophenazine (2:1) (Scheme 1) and characterized by FT-IR and ¹H NMR spectroscopies. The ¹H NMR data (CH=N in δ 8.43 ppm; δ 13.84 ppm for OH; all aromatic hydrogens in δ 8.12, 7.91, 7.64, and 7.51 ppm; and two kinds of aliphatic hydrogen of the *tert*-butyl groups in δ 1.48 and 1.39 ppm) confirm the formation of compound **2**. The FT-IR spectrum of compound **2** shows vibrational peaks at 2929 and 2959 cm⁻¹ (stretching of the methyl group of *tert*-butyl), at

	Mn(III)-salphen (3)		Cationic Mn(III)–salphen (5)	
Catalysts	Conversion (%)	Reaction time (min)	Conversion (%)	Reaction time (min)
	73	45	86	20
	75	45	91	20
	69	45	84	20
	67	45	79	20
<i>n-C</i> ₆ H ₁₃	61	45	77	20

Table 1. Epoxidation of olefins catalyzed by 1% mol Mn(III)-salphen (3) and cationic Mn(III)-salphen (5).

Scheme 2. Epoxidation of olefins.

 $\mathbb{R}^{1} \xrightarrow{\mathbb{R}^{2}} \mathbb{R}^{3} \xrightarrow{1\% \text{ mol salphen } (\mathbf{3 \text{ or } 5)}}_{\begin{array}{c} \mathrm{CH}_{2}\mathrm{Cl}_{2} \\ \mathrm{H}_{2}\mathrm{O}_{2} (30\%) \\ \mathrm{rt} \end{array}} \mathbb{R}^{1} \xrightarrow{\mathbb{R}^{2}} \mathbb{R}^{3}$

1636 cm⁻¹ (stretching of the C=N bond), and at 3421 cm⁻¹ for stretching of the OH group.

Preparation of Mn(III)–salphen (3)

Complex **3** was obtained according to the procedure shown in Scheme 1. The complex was synthesized in the presence of excess LiCl as a counterion. The Mn(II) was converted to Mn(III) via in situ oxidation and the progress of the oxidation reaction was monitored by UV–vis spectroscopy. The Mn (II)–salphen shows an absorption band at $\lambda = 420$ nm, whereas a maximum was observed at 447 nm for Mn(III)– salphen (**3**).

Cationic salphen (4)

As shown in Scheme 1, the cationic salphen (4) was prepared by reaction of salphen 2 with excess methyl iodide under reflux. The ¹H NMR spectrum of 4 supports the proposed structure (Fig. 1). The protons of CH_3^+ –N appear at 5.04 ppm, and this evidence is important because the methyl iodide protons have no chemical shift higher than 3.5 ppm.

Cationic Mn(III)-salphen (5)

Cationic Mn(III)–salphen (5) was prepared by reaction of compound 3 in the presence of excess methyl iodide as a reagent and a solvent under reflux (Scheme 1). The two CH_3^+ –N groups were formed in the salphen ligand and neutralized by two iodide anions.

Epoxidation of olefins

The epoxidation reaction of olefins (Scheme 2) was done using a 0.01 molar ratio of each of the catalysts, Mn(III)salphen (3) and cationic Mn(III)-salphen (5). The conversion was measured by GC-MS spectroscopy. The results show that the cationic Mn(III)-salphen (5) had a higher catalytic activity than the neutral Mn(III)-salphen (3) (Table 1).

The addition of excess CH₃I to the 2,3-diaminophenazine moiety and formation of the cationic Mn(III)–salphen (**5**) can considerably facilitate the epoxidation reaction of olefins, which is presumably because of the formation of the more water-soluble phenazinium groups in the structure (**5**). The neutral Mn(III)–salphen is slightly soluble in water and, consequently, shows a low catalytic activity toward the epoxidation of olefins.⁹

Conclusions

We explore the synthesis of new types of salphen complexes with built-in inherent phase-transfer capability. The complexes were synthesized in good yields and applied toward two catalytic processes. The cationic Mn(III)–salphen complex with two water-soluble phenazinium groups showed an appropriate catalytic activity for the epoxidation of olefins. This method could also be useful for the preparation of other transition-metal catalysts for organic reactions.

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References

- Martinez, L. E.; Leighton, J. L.; Carsten, D. H.; Jacobsen, E. N. J. Am. Chem. Soc. **1995** 117 (21), 5897. doi:10.1021/ ja00126a048.
- (2) Rodger, A. J. Am. Chem. Soc. **1988** 110 (18), 5941. doi:10. 1021/ja00226a002.

- (3) Schurig, V.; Betschinger, F. Chem. Rev. 1992 92 (5), 873. doi:10.1021/cr00013a006.
- (4) Canali, L.; Sherrington, D. C. Chem. Soc. Rev. 1999 28 (2), 85. doi:10.1039/a806483k.
- (5) Fan, Q.-H.; Li, Y.-M.; Chan, A. S. C. Chem. Rev. 2002 102 (10), 3385. doi:10.1021/cr010341a.
- (6) Sato, K.; Aoki, M.; Ogawa, M.; Hashimoto, T.; Noyori, R. J. Org. Chem. 1996 61 (23), 8310. doi:10.1021/jo961287e.
- (7) Leung, A.; MacLachlan, M. J. Inorg. Organometal. Polym. Mater. 2007 17 (1), 57. doi:10.1007/s10904-006-9092-1.
- (8) McGarrigle, E. M.; Gilheany, D. G. Chem. Rev. 2005 105 (5), 1563. doi:10.1021/cr0306945.
- (9) Hosseinpoor, F.; Golchoubian, H. ChemInform 2006 37 (43). doi:10.1002/chin.200643098.
- (10) Liu, S.-Y.; Nocera, D. G. *Tetrahedron Lett.* **2006** 47 (12), 1923. doi:10.1016/j.tetlet.2006.01.074.
- Wei, X.; Li, J.; Zhou, B.; Qin, S. *Transition Metal Chem.* 2004
 29 (4), 457. doi:10.1023/B:TMCH.0000027463.00158.6b.
- (12) Belokon, Y. N.; North, M.; Maleev, V. I.; Voskoboev, N. V.; Moskalenko, M. A.; Peregudov, A. S.; Dmitriev, A. V.; Ikonnikov, N. S.; Kagan, H. B. *Angew. Chem. Int. Ed.* **2004** *43* (31), 4085. doi:10.1002/anie.200454031.
- (13) Feichtinger, D.; Plattner, D. A. Angew. Chem. Int. Ed. Engl. 1997 36 (16), 1718. doi:10.1002/anie.199717181.
- (14) Finney, N. S.; Pospisil, P. J.; Chang, S.; Palucki, M.; Konsler, R. G.; Hansen, K. B.; Jacobsen, E. N. Angew. Chem. Int. Ed. Engl. 1997 36 (16), 1720. doi:10.1002/anie.199717201.
- (15) Zheng, X.; Jones, C. W.; Weck, M. J. Am. Chem. Soc. 2007 129 (5), 1105. doi:10.1021/ja0641406.
- (16) Jacobsen, E. N.; Deng, L.; Furukawa, Y.; Martínez, L. E.

Tetrahedron **1994** *50* (15), 4323. doi:10.1016/S0040-4020(01) 89369-8.

- (17) Krishna Mohan Kandepi, V. V.; Cardoso, J. M. S.; Royo, B. Catal. Lett. 2010 136 (3–4), 222. doi:10.1007/s10562-010-0332-1.
- (18) Morlanés, N.; Notestein, J. M. J. Catal. 2010 275 (2), 191. doi:10.1016/j.jcat.2010.07.010.
- (19) Reis, P. M.; Gamelas, C. A.; Brito, J. A.; Saffon, N.; Gómez, M.; Royo, B. *Eur. J. Inorg. Chem.* **2011** 2011 (5), 666. doi:10. 1002/ejic.201001065.
- (20) Stamatis, A.; Giasafaki, D.; Christoforidis, K. C.; Deligiannakis, Y.; Louloudi, M. J. Mol. Catal. Chem. 2010 319 (1–2), 58.
- (21) Hughes, D. L.; Smith, G. B.; Liu, J.; Dezeny, G. C.; Senanayake, C. H.; Larsen, R. D.; Verhoeven, T. R.; Reider, P. J. J. Org. Chem. **1997** 62 (7), 2222. doi:10.1021/jo961735i.
- (22) Kureshy, R. I.; Khan, N. U. H.; Abdi, S. H. R.; Singh, S.; Ahmed, I.; Jasra, R. V. J. Mol. Catal. Chem. 2004 218 (2), 141. doi:10.1016/j.molcata.2004.03.043.
- (23) Kureshy, R. I.; Khan, N. U. H.; Abdi, S. H. R.; Patel, S. T.; Iyer, P. K.; Jasra, R. V. *Tetrahedron Lett.* **2002** *43* (14), 2665. doi:10.1016/S0040-4039(02)00112-0.
- (24) Kureshy, R. I.; Khan, N. U. H.; Abdi, S. H. R.; Patel, S. T.; Iyer, P. K.; Subramanian, P. S.; Jasra, R. V. J. Catal. 2002 209 (1), 99. doi:10.1006/jcat.2002.3558.
- (25) Sun, Y.; Tang, N. J. Mol. Catal. Chem. 2006 255 (1–2), 171. doi:10.1016/j.molcata.2006.03.056.
- (26) He, D.; Wu, Y.; Xu, B.-Q. Eur. Polym. J. 2007 43 (9), 3703. doi:10.1016/j.eurpolymj.2007.06.038.
- (27) Wang, D.; Wang, M.; Wang, X.; Zhang, R.; Ma, J.; Sun, L. J. Mol. Catal. Chem. 2007 270 (1–2), 278. doi:10.1016/j. molcata.2007.01.052.