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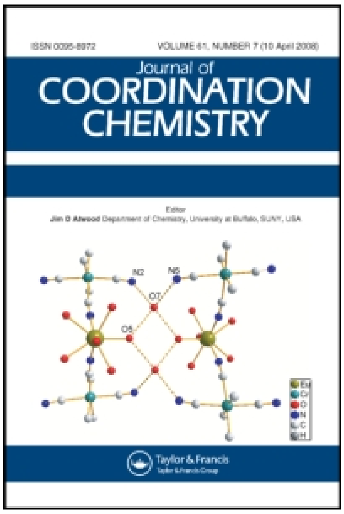

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Studies of the catalytic activity of Fe(III)(salen) complexes as epoxidation catalysts

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Studies of the catalytic activity of Fe(III)(salen) complexes as epoxidation catalysts

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Two new Fe(III)(salen) complexes, $FeL^1ClO_4 \cdot 2H_2O$ (**1**) and FeL^2ClO_4 (**2**) [$L^1 = N,N'$-ethylenebis(3-formyl-5-methylsalicylaldimine) and $L^2 = N,N'$-cyclohexenebis(3-formyl-5-methylsalicylaldimine)], have been synthesized and characterized. The catalytic activity of the complexes for epoxidation of alkenes has been investigated in the presence of two terminal oxidants PhIO and NaOCl, with two solvents CH_3CN and CH_2Cl_2. As alkenes styrene and (*E*)-stilbene have been chosen for investigation; styrene is a better substrate than electron-rich (*E*)-stilbene. The study also suggests that unlike their Mn(III) counterparts, **1** and **2** are poor epoxidation catalysts; catalysis proceeds with formation of one intermediate, rather than forming more than one intermediate depending on the terminal oxidant used. Use of exogenous neutral donor ligands such as Py, PyNO and 1-MePy is effective to improve catalytic behavior.

Keywords: Macroacyclic ligands; Fe(III) complexes; Epoxidation of alkenes

1. Introduction

Transition metal salen catalyzed epoxidation of olefins has widespread application in production of epoxides [1], an interesting class of compound [2, 3] which may be transformed into a large variety of compounds, and also for intrinsic beauty of the systems to produce variable yields and enantiomeric excess depending on steric and electronic factors of the ligands, nature of oxygen sources, nature of the substrates, solvents and even the nature of the metal ions [4–6]. Extensive work [7–21] makes it evident that Mn(III)(salen) is by far the best catalyst and competes with the enzyme, Cyt-P-450, an iron containing mono oxygenase whose activity inspired chemists to design synthetic analogues. Chemists are exploring the possibility that metals like Ti, V, Cr, etc. [22–30] may be useful, but very little attention has been paid to Fe(III)(salen) catalyzed epoxidation of olefins [31, 32], though Fe(III)-porphyrins [33–41] have already acquired special positions as synthetic analogues of Cyt-P-450. Our group is active in the study of transition metal-salen catalyzed epoxidation of olefins [42, 43], and are curious to know whether Fe(III)(salen) catalyzed epoxidation of olefins proceeds through more than one active intermediate depending on the nature of the

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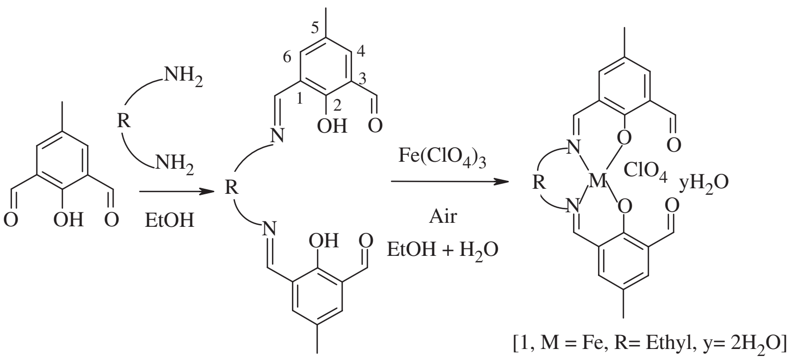

[1, M = Fe, R= Ethyl, y= 2H$_2$O]
[2, M = Fe, R=Cyclohexyl]

Scheme 1. Synthesizing Fe(III) complexes of L^1 and L^2.

oxygen source, as observed in Mn(III)(salen) catalyzed reactions [44], along with the role of donor ligands on the formation of active intermediates, effect of solvents and influence of substrates. We have synthesized Fe(III) complexes of L^1 and L^2 (scheme 1), characterized them and investigated their catalytic efficiencies as epoxidation catalysts, in presence of (i) two terminal oxidants, PhIO and NaOCl; (ii) two solvents, CH_3CN and CH_2Cl_2 and (iii) three exogenous neutral donor ligands, and report herein the results of the study to get a better understanding of the mechanistic pathways followed by Fe(III)(salen) complexes under different conditions.

2. Experimental

2.1. *Methods*

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin-Elmer 240C elemental analyzer. Infrared spectra (4000–400 cm^{-1}) were recorded at 27°C using a Shimadzu FTIR-8400S with KBr pellets. Electronic spectra (800–200 nm) were obtained at 27°C using a Shimadzu UV-3101PC with methanol as solvent and reference. The ^{1}H NMR spectra were recorded on a Bruker AC300 spectrometer. Magnetic susceptibilities were measured at 27°C using an EG and G PAR 155 vibrating sample magnetometer with Hg[Co(SCN)$_4$] as reference; diamagnetic corrections were made using Pascal's constants. Thermal analyses (TG–DTA) were carried out on a Shimadzu DT-30 thermal analyzer in flowing dinitrogen (flow rate: 30 cm^3 min^{-1}). The electrospray mass spectra were recorded on a MICROMASS Q-TOF mass spectrometer. The cyclic voltammetric measurements were carried out in dry acetonitrile solutions with 0.1 M tetraethylammonium perchlorate as supporting electrolyte employing a PAR potentiostat/galvanostat model Versa Stat-II. A three-electrode system was used in which the counter and working electrodes were platinum foils and the reference electrode was a saturated calomel electrode. GC analysis was performed on an AshcoGas Chromatograph Neon-II instrument with a flame ionization detector.

2.2. *Materials*

The reagents were obtained from commercial sources and used as received. Solvents were dried according to standard procedure and distilled prior to use. Styrene and (*E*)-stilbene were purchased from Aldrich and used in epoxidation experiments without further purification.

2.3. *Synthesis of the ligands and the complexes*

2,6-Diformyl-4-methylphenol was prepared according to the literature method [45]. The Schiff bases *N*,*N*′-ethylenebis(3-formyl-5-methylsalicylaldimine) (L^1) and *N*,*N*′-cyclohexenebis(3-formyl-5-methylsalicylaldimine) (L^2) were synthesized by similar procedure reported earlier [42, 43]. Complexes **1** and **2** were synthesized by similar procedures as described earlier [43].

2.3.1. $FeL^1ClO_4 \cdot 2H_2O$ (1).

Yield: 87% (with respect to L). Anal. Calcd for $FeL^1ClO_4 \cdot 2H_2O$: C, 44.36; H, 4.06; N, 5.17. Found: C, 44.33; H, 4.04; N, 5.18. Selected IR data (KBr, $\nu\,cm^{-1}$): 3403 $\nu(H_2O)$; 1656 $\nu(C{=}O)$; 1622 $\nu(C{=}N)$; 1544 ν(skeletal vibration); 1119, 1071, 1030, 998 $\nu(ClO_4)$. UV–Vis (CH_3CN) nm^{-1}: 520, 360, 314. ESI-MS: *m*/*z* (a.m.u): Calcd ($[FeC_{20}H_{22}N_2O_6]^+$): 464.5, experimental: 464.13. $\mu_{eff} = 5.79$ B.M. TG analysis: 0.925 mg weight loss (6.55% of 14.12 mg complex: expected weight loss: 0.938 mg) at 121°C.

2.3.2. FeL^2ClO_4 (2).

Yield: 86% (with respect to L^2). Anal. Calcd for FeL^2ClO_4: C, 51.52; H, 4.29; N, 5.01. Found: C, 51.51; H, 4.28; N, 5.03. Selected IR data (KBr, $\nu\,cm^{-1}$): 1650 $\nu(C{=}O)$; 1620 $\nu(C{=}N)$; 1545 ν(skeletal vibration); 1142, 1073, 1029, 997 $\nu(ClO_4)$. UV-Vis (CH_3CN) nm^{-1}: 518, 363, 312. ESI-MS: *m*/*z* (amu): Calcd ($[FeC_{24}H_{24}N_2O_4]^+$): 460.21, experimental: 460.12. $\mu_{eff} = 5.82$ B.M.

N.B. Perchlorate salts are potentially explosive and should be handled in small quantities with care. No problems were faced with the complexes reported herein.

2.4. *Preparation of iodosylbenzene*

It was prepared by hydrolysis of the corresponding diacetate with aqueous sodium hydroxide according to literature method [48]. In every epoxidation experiment freshly prepared PhIO was used.

2.5. *Epoxidation of alkenes catalyzed by 1 and 2*

Similar procedure was applied for all epoxidation reactions. Catalyst (1.00×10^{-2} mmol), alkene (0.300 mmol) and neutral donor ligand (0.1 mmol) were dissolved in 5 mL freshly distilled solvent (acetonitrile or dichlorometane). Under nitrogen, iodosylbenzene or sodium hypochlorite was added portion wise to the solution. The reaction mixture was then stirred at room temperature. The solution was buffered to pH 11 using NaH_2PO_4–NaOH buffer when NaOCl was used as oxidant.

Identification of the epoxide product was performed by ^{1}H NMR spectroscopy. Epoxides were prepared following the procedure described by Kochi [7] when PhIO was used as oxidant and adopting the procedure reported by Jacobsen *et al.* [10] when NaOCl was used as oxidant.

3. Results and discussion

3.1. *Synthesis procedure and characterization*

The two "side-off" compartmental ligands *N*,*N*′-ethylenebis(3-formyl-5-methyl-salicylaldimine) (L^1) and *N*,*N*′-cyclohexanebis(3-formyl-5-methylsalicylaldimine) (L^2) have been synthesized and identified by their reported physicochemical properties. Fe(III) complexes of those two ligands have been prepared following the same procedure as we reported for the corresponding Mn(III) complexes [43]. The compositions of the complexes were assigned by elemental analyses and water content was determined by thermogravimetric analysis. The IR spectral data show a shift of C=N stretching by 10 cm^{-1} in **1** and 17 cm^{-1} in **2** in comparison to that of free L^1 and L^2, a consequence of metal binding to imine nitrogens, sustaining coordination of the metal to the Schiff-base ligands. The IR data also reveal that there is no appreciable shift of C=O stretch after complexation, indicating metal ions preferentially bind to the N_2O_2 site rather than O_4 site as we observed earlier [42–45]. Even in the presence of large excess of metal ion mononuclear metal complex was isolated [42, 43]. The IR spectral data are informative regarding the coordination mode of perchlorate ligand in the two complexes. The IR spectral bands observed at 1119, 1071, 1030 and 998 cm^{-1} in the spectrum of **1** and at 1142, 1073, 1029 and 997 cm^{-1} in **2** originated from perchlorate having nearly C_{2V} symmetry, indicating bidentate coordination of perchlorate in both complexes [46]. The ESI-MS study shows the molecular ion peak for **1** at 464.13 amu and that for **2** at 460.21 amu corroborate well with the molecular compositions of $[FeL^1 \cdot 2H_2O]^+$ and $[FeL^2]^+$, for **1** and **2**, respectively. The absorption band maximum of Fe(III)(salen) is very sensitive to the nature of the substituent in the salen ligand. The parent Fe(III)(salen) complex exhibits characteristic absorption at $\lambda_{max} = 470$ nm in acetonitrile medium. In the presence of NO_2 at the 5,5′ position, blue shifting (470 to 463 nm) occurs, whereas OMe at the same position causes a red shift (470 to 500 nm); no change is observed for chloro substituent at the 5,5′ position (table 1). In our ligand system there are methyl and formyl groups at 5,5′ and 3,3′ positions, respectively, and we have observed large red shift (470 to 520 nm for **1** and 470 to 518 nm for **2**) in both complexes

Table 1. Absorption (λ_{max} nm^{-1}), magnetic moments and electrochemical data of some Fe(III)(salen) complexes.

Complex	λ_{max} (nm^{-1})	Magnetic moment at 300 K	$E_{1/2}$ *vs.* (SCE)	Ref.
[Fe(salen)Cl]	470	5.37	−0.28	[47]
[Fe(5,5′-$(NO_2)_2$-salen)Cl]	463	5.11	−0.15	[32]
[Fe(5,5′-$(Cl)_2$-salen)Cl]	470	5.14	−0.24	[47]
[Fe(5,5′-$(OMe)_2$-salen)Cl]	500	5.61	−0.35	[32]
[Fe(3,3′,5,5′-$(t\text{-}Bu)_4$-salen)Cl]	503	5.65	−0.68	[32]

in comparison with the parent Fe(III)(salen). The observed room temperature magnetic moments of 5.79 and 5.82 B.M. for **1** and **2**, respectively, suggest that in both complexes Fe(III) is high spin d^5, consistent with Fe(III)(salen) complexes reported earlier (table 1) [31, 47]. The cyclic voltammograms of **1** and **2** in dry acetonitrile exhibit only one reversible redox couple at −0.111/0.137 V and −0.156/0.152 V, respectively, indicating that only a single species is present in solution and the observed reduction potentials ($E_{1/2}$) are comparable to the earlier reported values for similar systems (table 1). The reduction potential ($E_{1/2}$) is also sensitive to the nature of the substituent in the backbone of salen.

3.2. *Epoxidation of alkenes*

The epoxidation reactions are carried out at room temperature with **1** and **2** in the presence of oxidants iodosylbenzene and sodium hypochlorite in acetonitrile or dichloromethane. Pyridine, pyridine-*N*-oxide and 1-methylimidazole are neutral donor ligands. Both complexes are highly soluble in acetonitrile, but less soluble in dichloromethane. Both complexes produce a brown solution after dissolution which fades on addition of the oxidant. When substrates are added, further fading of the color is observed. In the absence of catalyst (blank experiments) no epoxide formation is detected under our reaction condition.

3.2.1. Epoxidation of styrene. Table 2 presents the maximum conversion (%), isolated yield (%) and time required to obtain the maximum yield for styrene epoxidation with or without the addition of Py, PyNO and 1-MeIm, in the presence of PhIO and NaOCl. The data reveal that in the absence of neutral donor ligand the isolated yield of styrene epoxide in CH_2Cl_2 ranges from 18–25%, whereas better yield (30–41%) is obtained

Table 2. Epoxidation of styrene catalyzed by **1** and **2** in CH_2Cl_2 or CH_3CN using NaOCl and PhIO as oxidants.

				Conversion (%)		Epoxide yield (%)[a]	
Catalyst	Time (h^{-1})	Ligand	Solvent	PhIO	NaOCl	PhIO	NaOCl
1	2	–	CH_3CN	43	42	32	30
	2	–	CH_2Cl_2	30	23	21	18
1	2	PyNO	CH_3CN	49	44	41	39
	2	PyNO	CH_2Cl_2	41	36	32	29
1	2	Py	CH_3CN	57	54	53	48
	2	Py	CH_2Cl_2	45	41	46	41
1	2	1-MeIm	CH_3CN	42	37	38	34
	2	1-MeIm	CH_2Cl_2	39	30	28	25
2	2	–	CH_3CN	47	45	41	39
	2	–	CH_2Cl_2	36	31	25	23
2	2	PyNO	CH_3CN	61	55	54	51
	2	PyNO	CH_2Cl_2	43	37	36	32
2	2	Py	CH_3CN	75	72	68	65
	2	Py	CH_2Cl_2	57	53	52	49
2	2	1-MeIm	CH_3CN	58	50	48	47
	2	1-MeIm	CH_2Cl_2	41	33	32	28

[a] Isolated yield based on olefin.

when CH_3CN is solvent; when neutral donor ligands are used the yield of epoxide increases. In reactions catalyzed by **1** the isolated yield of styrene epoxide in CH_2Cl_2 ranges from 25–41% when NaOCl is used as oxidant, and 28–46% when PhIO is used. In reactions catalyzed by **2** the isolated yield of styrene epoxide in CH_2Cl_2 ranges from 28–49% when NaOCl is used and 32–52% when PhIO is used. When reactions are carried out in CH_3CN, **1** gives 34–48% isolated yield with NaOCl 38–53% when PhIO is used; for **2** the range is 47–65% with NaOCl and 48-68% with PhIO.

3.2.2. Epoxidation of (*E*)-stilbene. Table 3 presents the results for (*E*)-stilbene epoxidation showing that in the absence of ligand the isolated yield of (*E*)-stilbene epoxide in CH_2Cl_2 ranges from 10–18%, and 17–25% when CH_3CN is solvent; ligands increase yield of epoxide. The results (table 3) are similar to those for styrene.

3.2.3. Influence of solvent. CH_3CN is a better solvent than CH_2Cl_2 for epoxidation of styrene and (*E*)-stilbene irrespective of the catalyst as observed for Mn(III)(L^1/L^2) catalyzed reaction [44]. Here also the higher solubility of the Fe(III) complexes in CH_3CN than that in CH_2Cl_2 may be important, although minimization of formation of benzaldehyde and chlorinated products in styrene epoxidation in CH_3CN is also important for epoxidation of styrene when PhIO is oxidant.

3.2.4. Influence of substrates and terminal oxidant. In Mn(III)(L^1/L^2) catalyzed epoxidation the more electron-rich (*E*)-stilbene gives higher yield of epoxide when PhIO is oxidant; no yield is detected when NaOCl is oxidant, suggesting the possibility of another epoxidizing species, probably (salen)Mn(III)OCl, in addition to Mn(V)=O(salen) species depending on whether NaOCl or PhIO is used as oxidant.

Table 3. Epoxidation of (*E*)-stilbene catalyzed by **1** and **2** in CH_2Cl_2 or CH_3CN using NaOCl and PhIO as oxidants.

				Conversion (%)		Epoxide yield (%)[a]	
Catalyst	Time (h^{-1})	Ligand	Solvent	PhIO	NaOCl	PhIO	NaOCl
1	2	–	CH_3CN	27	25	20	17
	2	–	CH_2Cl_2	21	19	12	10
1	2	PyNO	CH_3CN	43	35	33	31
	2	PyNO	CH_2Cl_2	31	25	25	20
1	2	Py	CH_3CN	45	42	38	36
	2	Py	CH_2Cl_2	33	31	28	26
1	2	1-MeIm	CH_3CN	39	30	27	24
	2	1-MeIm	CH_2Cl_2	25	21	21	15
2	2	–	CH_3CN	32	27	25	21
	2	–	CH_2Cl_2	24	22	18	16
2	2	PyNO	CH_3CN	43	42	34	32
	2	PyNO	CH_2Cl_2	35	33	27	24
2	2	Py	CH_3CN	48	46	40	37
	2	Py	CH_2Cl_2	37	35	29	26
2	2	1-MeIm	CH_3CN	36	32	29	27
	2	1-MeIm	CH_2Cl_2	31	24	23	20

[a] Isolated yield based on olefin.

The very poor yield in (*E*)-stilbene epoxidation in comparison to styrene when NaOCl is oxidant was rationalized by the greater steric effect exerted by (*E*)-stilbene, lowering the stabilization of the (salen)Mn(III)OCl-(*E*)-stilbene adduct. For **1** and **2**, styrene is a better substrate irrespective of the oxidant with little change in yield of epoxide for styrene and (*E*)-stilbene on changing from PhIO to NaOCl. This suggests that Fe(III) complexes, unlike their Mn(III) counterpart, generate the same active intermediate on reaction with PhIO and NaOCl. We assume that Fe(III) catalyzed reactions proceed with formation of a sterically crowded intermediate similar to (salen)Mn(III)OX, which stabilizes the intermediate-substrate adduct to a greater extent with the less crowded olefin, and thus styrene becomes a better substrate than (*E*)-stilbene.

In order to determine the nature of **1** and **2** in the catalytic cycle, we studied the UV-Vis spectral changes for the complexes in the presence of PhIO (1.00×10^{-3} mmol complex in 5 mL dry acetonitrile was treated with 0.300 mmol of PhIO). Both complexes exhibit nearly identical changes in their spectral patterns after addition of PhIO, as shown in figure 1(a) and (b). The spectrum obtained 1 h after addition of PhIO shows: (i) a new shoulder at ~500 nm with disappearance of the band at ~520 nm, (ii) drastic reduction of the absorbance at ~360 nm and (iii) disappearance of the band at ~314 nm. All observations suggest the formation of a higher valent Fe(oxo) after addition of PhIO, consistent with earlier studies [31, 32]. After 1 day, the spectra obtained do not match either the original or the spectra 1 h after addition of PhIO. Fresh addition of PhIO and alkenes yielded no epoxidation. Cyclic voltammetry of both complexes 1 h after addition of PhIO failed to measure the redox potentials of the Fe(oxo) species, probably due to instability of Fe(IV) and Fe(V) species under the electrochemical conditions.

3.2.5. Influence of neutral donor ligands.

The effect of Py, PyNO, and 1-MeIm on the yield of epoxide are depicted in tables 2 and 3. In all cases conversion and yield increases in presence of ligand; with ligands, the poor catalysts **1** and **2** are converted to moderately good catalysts for epoxidation of olefins. The order of efficiency is Py > PyNO > 1-MeIm. Through electron donation the ligand stabilizes the higher valent metal oxo-species and consequently increases epoxide yield. Among the ligands,

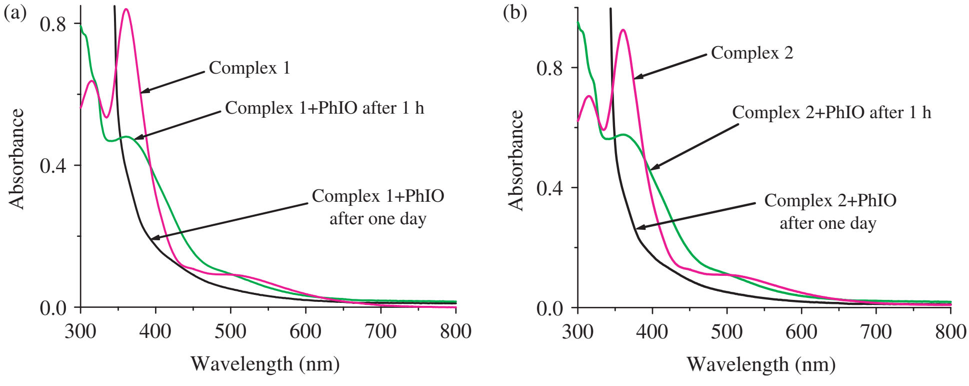

Figure 1. UV–Vis spectral pattern of complex **1** (a) and complex **2** (b): 2.00×10^{-3} M solution of complex in dry acetonitrile at 25°C, after 1 h reaction with PhIO (0.300 mmol) and after 1 day of the reaction.

1-MeIm has the highest electron-donating ability and Py the least; the order of efficiency of the ligands is reverse to their electron-donating order, suggesting steric effect. 1-MeIm exerts the largest steric effect, destabilizing the higher valent Fe(oxo) intermediate lowering epoxide yield. This explanation strengthens our earlier assumption of the formation of sterically crowded intermediate in Fe(III)-salen catalyzed epoxidation.

4. Conclusion

In summary, our results verify that epoxidation depends on metal ion. When Mn(III)(salen) was used for epoxidation of olefins two different active intermediates, [L-O-Mn(III)(salen)X] and [O=Mn(V)(salen)X], were formed depending upon oxidant. But, Fe(III)(salen) epoxidation of olefins proceeds with formation of only one active oxo intermediate irrespective of the terminal oxidant used. Fe(III)(salen) catalyzed epoxidation of olefins is not much influenced by terminal oxidant but very dependent on the nature of the substrate. The ligands play an important role for Fe(III)(salen) catalyzed epoxidation of unfunctionlized olefins, enhancing the catalytic activity. Balance of steric and electronic factors of the exogenous ligand may be crucial to obtain maximum epoxidation in Fe(III)(salen) catalyzed epoxidation of unfunctionlized olefins.

References

[1] H. Yoon, T.R. Wagler, K.J. O'Connor, C.J. Burrows. *J. Am. Chem. Soc.*, **112**, 4568 (1990).

[2] C.T. Dalton, K.M. Ryan, V.M. Wall, C. Bousquet, D.G. Gilheany. *Top. Catal.*, **5**, 75 (1998).

[3] W. Adam, K.J. Roschmann, C.R. Saha-Möller, D. Seebach. *J. Am. Chem. Soc.*, **124**, 5068 (2002).

[4] (a) T. Katsuki. *J. Mol. Catal. A: Chem.*, **113**, 87 (1996); (b) T. Katsuki. *Coord. Chem. Rev.*, **140**, 189 (1995).

[5] E.N. Jacobsen, M.H. Wu. In *Comprehensive Asymmetric Catalysis*, A. Pfaltz, E.N. Jacobsen, H. Yamamoto (Eds), Vol. 2, p. 649, Springer-Verlag, Berlin (1999).

[6] K.A. Campbell, M.R. Lashley, J.K. Wyatt, M.H. Nantz, R.D. Britt. *J. Am. Chem. Soc.*, **123**, 5710 (2001).

[7] K. Srinivasan, P. Michaud, J.K. Kochi. *J. Am. Chem. Soc.*, **108**, 2309 (1986).

[8] A.R. Oki, D.J. Hodgson. *Inorg. Chim. Acta*, **170**, 65 (1990).

[9] C. Bowers, P.K. Dutta. *J. Catal.*, **122**, 271 (1990).

[10] (a) W. Zhang, J.L. Loebach, S.R. Wilson, E.N. Jacobsen. *J. Am. Chem. Soc.*, **112**, 2801 (1990); (b) W. Zhang, E.N. Jacobsen. *J. Org. Chem.*, **56**, 2296 (1991); (c) N.H. Lee, E.N. Jacobsen. *Tetrahedron Lett.*, **32**, 6533 (1991); (d) H. Fu, G.C. Look, W. Zhang, E.N. Jacobsen, C.H. Wong. *J. Org. Chem.*, **56**, 6497 (1991); (e) E.N. Jacobsen, W. Zhang, M.L. Guler. *J. Am. Chem. Soc.*, **113**, 6703 (1991); (f) J.F. Larrow, E.N. Jacobsen, Y. Gao, Y. Hong, X. Nie, C.M. Zeep. *J. Org. Chem.*, **59**, 1993 (1994); (g) N.S. Finney, P.J. Pospisil, S. Chang, M. Palucki, R.G. Konsler, K.B. Hansen, E.N. Jacobsen. *Angew. Chem. Int. Ed. Engl.*, **36**, 1720 (1997); (h) M. Palucki, N.S. Finney, P.J. Pospisil, M.L. Guler, T. Ishida, E.N. Jacobsen. *J. Am. Chem. Soc.*, **120**, 948 (1998).

[11] (a) R. Irie, Y. Ito, T. Katsuki. *Synlett.*, 265 (1991); (b) N. Hosoya, R. Irie, T. Katsuki. *Synlett.*, 261 (1992); (c) A. Hatayama, N. Hosoya, R. Irie, Y. Ito, T. Katsuki. *Synlett.*, 407 (1992); (d) H. Sasaki, R. Irie, T. Katsuki. *Synlett.*, 300 (1993); (e) N. Hosoya, A. Hatayama, K. Yanai, H. Fuji, R. Irie, T. Katsuki. *Synlett.*, 641 (1993); (f) T. Hamada, R. Irie, T. Katsuki. *Synlett.*, 479 (1994); (g) T. Katsuki. *Coord. Chem. Rev.*, **140**, 189 (1995); (h) T. Hamada, T. Fukuda, H. Imanishi, T. Katsuki. *Tetrahedron*, **52**, 515 (1996); (i) T. Katsuki. *J. Mol. Catal. A*, **113**, 87 (1996); (j) R. Irie, T. Hashihayata, T. Katsuki, M. Akita, Y. Moro-Oka. *Chem. Lett.*, **27**, 1041 (1998); (k) T. Katsuki. *Curr. Org. Chem.*, **5**, 663 (2001); (l) C. Ohta, T. Katsuki. *Tetrahedron Lett.*, **42**, 3885 (2001); (m) T. Katsuki. *Adv. Synth. Catal.*, **244**, 131 (2002).

[12] (a) C. Linde, M. Arnold, P.O. Norrby, B. Akermark. *Angew. Chem. Int. Ed. Engl.*, **36**, 1723 (1997); (b) P.O. Norrby, C. Linde, B. Akermark. *J. Am. Chem. Soc.*, **117**, 11035 (1995); (c) P. Brandt, P-O. Norrby, A.M. Daly, D.G. Gilheany. *Chem. Eur. J.*, **8**, 4299 (2002); (d) A.M. Daly, D.G. Gilheany. *Tetrahedron: Asymmetry*, **14**, 127 (2003).

[13] L. Canali, D.C. Sherrington. *Chem. Soc. Rev.*, **28**, 85 (1999).

[14] K.P. Bryliakov, D.E. Babushkin, E.P. Talsi. *J. Mol. Catal. A*, **158**, 19 (2000).

[15] W. Adam, K.J. Roschmann, C.R. Saha-Möller, D. Seebach. *J. Am. Chem. Soc.*, **124**, 5068 (2002).

[16] M. Bandini, P.G. Cozzi, A. Umani-Ronchi. *J. Chem. Soc., Chem. Commun.*, 919 (2002).

[17] A. Chellamani, S. Harikengaram. *J. Phys. Org. Chem.*, **16**, 589 (2003).

[18] I.V. Khavrutskii, D.G. Musaev, K. Morokuma. *Inorg. Chem.*, **42**, 2606 (2003).

[19] A.R. Silva, C. Freire, B. de Castro. *New. J. Chem.*, **28**, 253 (2004).

[20] N.S. Venkataramanan, G. Kuppuraj, S. Rajagopal. *Coord. Chem. Rev.*, **249**, 1249 (2005).

[21] J.P. Collman, L. Zeng, J.I. Brauman. *Inorg. Chem.*, **43**, 2672 (2004).

[22] L. Canalai, D.C. Sherrington. *Chem. Soc. Rev.*, **72**, 603 (1999).

[23] M. Bandini, P.G. Cozzi, A. Umani-Ronchi. *J. Chem. Soc., Chem. Commun.*, 919 (2002).

[24] (a) K. Srinivasan, P. Michaud, J.K. Kochi. *J. Am. Chem. Soc.*, **108**, 2309 (1986); (b) K. Srinivasan, S. Perrier, J.K. Kochi. *J. Mol. Catal. A: Chem.*, **36**, 297 (1986).

[25] N.S. Venkatramanan, S. Premsing, S. Rajagopal, K. Pitchumani. *J. Org. Chem.*, **68**, 1506 (2002).

[26] S. Premsing, N.S. Venkatramanan, S. Rajagopal, S.P. Mirza, M. Vairamani, P.S. Rao, K. Velavan. *Inorg. Chem.*, **43**, 5744 (2003).

[27] P. Brandt, P.-O. Norrby, A.M. Daly, D.G. Gilheany. *Chem. Eur. J.*, **8**, 4299 (2002).

[28] (a) A.M. Daly, C.T. Dalton, M.F. Renehan, D.G. Gilheany. *Tetrahedron Lett.*, **40**, 3617 (1999); (b) K.M. Ryan, C. Bousquet, D.G. Gilheany. *Tetrahedron Lett.*, **40**, 3613 (1999); (c) A.M. Daly, M.F. Renehan, D.G. Gilheany. *Org. Lett.*, **3**, 663 (2001); (d) N.J. Kerriger, I.J. Langan, C.T. Dalton, A.M. Daly, C. Bousquet, D.G. Gilheany. *Tetrahedron Lett.*, **43**, 2107 (2002); (e) C.T. Dalton, K.M. Ryan, I.J. Langan, E.J. Coyne, D.G. Gilheany. *J. Mol. Catal. A*, **187**, 179 (2002); (f) A.M. Daly, D.G. Gilheany. *Tetrahedron: Assymetry*, **14**, 127 (2003); (g) E.M. Garrigle, D.M. Murphy, D.G. Gilheany. *Tetrahedron: Assymetry*, **15**, 1343 (2004).

[29] R. Sevvel, S. Rajagopal, C. Srinivasan, N.M.I. Alhaji. *J. Org. Chem.*, **65**, 3334 (2000).

[30] (a) B. Saito, T. Katsuki. *Tetrahedron Lett.*, **42**, 8333 (2001); (b) T. Tanaka, B. Saito, T. Katsuki. *Tetrahedron Lett.*, **43**, 3289 (2002).

[31] H-L. Shyu, H-H. Wei, G-H. Lee, Y. Wang. *J. Chem. Soc., Dalton Trans.*, 915 (2000).

[32] V.K. Sivasubramanian, M. Ganesan, S. Rajagopal, R. Ramaraj. *J. Org. Chem.*, **67**, 1506 (2002).

[33] B. Meunier (Ed.), *Biomimetic Oxidations Catalysed by Transition Metal Complex*, Imperical College Press, London (2000).

[34] B. Meunier (Ed.), *Metal-Oxo and Metal-Peroxo Species in Catalytic Oxidations, Structure and Bonding*, Vol. 97, Springer, Berlin (2000).

[35] P.R. Ortiz de Montelloano (Ed.), *Cytochrome P-450: Structure, Mechanism and Biochemistry*, 2nd Edn., Plenum Press, New York, (1995).

[36] (a) J.P. Collman, X. Zhang, V.J. Lee, E.S. Uffelman, J.I. Brauman. *Science*, **261**, 1404 (1993); (b) M. Sono, M.P. Roach, D. Coulter, J.H. Dawson. *Chem. Rev.*, **96**, 2841 (1996).

[37] H. Fujii. *Coord. Chem. Rev.*, **226**, 51 (2002).

[38] R.K. Hoim, R. Kennepohl, E.I. Solomon. *Chem. Rev.*, **96**, 2239 (1996).

[39] Y. Watanabe, J.T. Groves. In *The Enzyme*, D.S. Sigman (Ed.), Academic Press, San Diego, CA (1992).

[40] W. Nam, M.H. Lim, S.K. Moon, C. Kim. *J. Am. Chem. Soc.*, **122**, 10805 (2000).

[41] W. Adam, K.J. Roschmann, C.R. Saha-Moller, D. Seebach. *J. Am. Chem. Soc.*, **124**, 5068 (2002).

[42] D. Das, C.P. Cheng. *J. Chem. Soc., Dalton Trans.*, 1081 (2000).

[43] T. Chattopadhyay, S. Islam, M. Nethaji, A. Majee, D. Das. *J. Mol. Catal. A: Chem.*, **267**, 255 (2007).

[44] H. Okawa, S. Kida. *Bull. Chem. Soc. Jpn*, **16**, 1360 (1972).

[45] R.R. Gagne, C.L. Spiro, T.J. Smith, C.A. Hamann, W.R. Thies, A.D. Shiemke. *J. Am. Chem. Soc.*, **103**, 4073 (1981).

[46] A.E. Wickenden, R.A. Krause. *Inorg. Chem.*, **39**, 578 (1962).

[47] (a) M. Gerloch, J. Lewis, F.E. Mabbs, A. Richards. *J. Chem. Soc. A*, 112 (1968); (b) M. Gullotti, L. Casella, A. Pasini, R. Ugo. *J. Chem. Soc., Dalton Trans.*, 339 (1977).

[48] H. Saltzman, J.G. Sharefkin. *Org. Synth. Coll.*, **5**, 658 (1973).