ELSEVIER

Journal of Molecular Catalysis A: Chemical 110 (1996) 33–40

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

Asymmetric catalytic epoxidation of styrene by dissymmetric Mn(III) and Ru(III) chiral Schiff base complexes synthesis and physicochemical studies

R.I. Kureshy *, N.H. Khan*, S.H.R. Abdi, A.K. Bhatt

Central Salt & Marine Chemicals Research Institute, Bhavnagar 364002, Gujarat, India

Received 2 November 1995; accepted 26 January 1996

Abstract

Some dissymmetric Mn(III) and Ru(III) chiral Schiff base complexes derived from 1*R*,2*R*(−)1,2-diaminocyclohexane with 3-acetyl-4-hydroxy-6-methyl-2-pyrone and salicylaldehyde, 5-chloro-5-methoxy-and 5-nitrosalicylaldehyde have been synthesized. The characterization of the complexes was accomplished by microanalysis, IR, UV–Vis, CD spectroscopy, conductance measurements, magnetic susceptibility, optical rotation and electrochemical studies. The asymmetric epoxidations catalyzed by the complexes were examined with styrene using the terminal oxidant, iodosylbenzene to assess the stereoselectivity in the epoxidation of styrene by changing substituents on the catalyst. In all cases the *R* form of the catalyst resulted in *S*(−) form of the product as a dominant enantiomer. Optical yield of the resulting epoxide was determined by GLC using chiral capillary column/ ^{1}H NMR using Eu(hfc)$_3$ as a chiral shift reagent.

Keywords: Asymmetric epoxidation; Epoxidation; Dissymmetric complexes; Schiff bases; Styrene; Manganese; Ruthenium

1. Introduction

Synthesis of an excellent chiral metal complex as catalyst for asymmetric epoxidation of non-functionalized olefins has been of great importance to the current development in synthetic chemistry [1–3]. Metalloporphyrins [4–7], heme enzymes such as cytochrome C peroxidase [4,8] and salen complex catalysts have been extensively studied as a model system of oxygen activation from the point of mechanistic and biological interest.

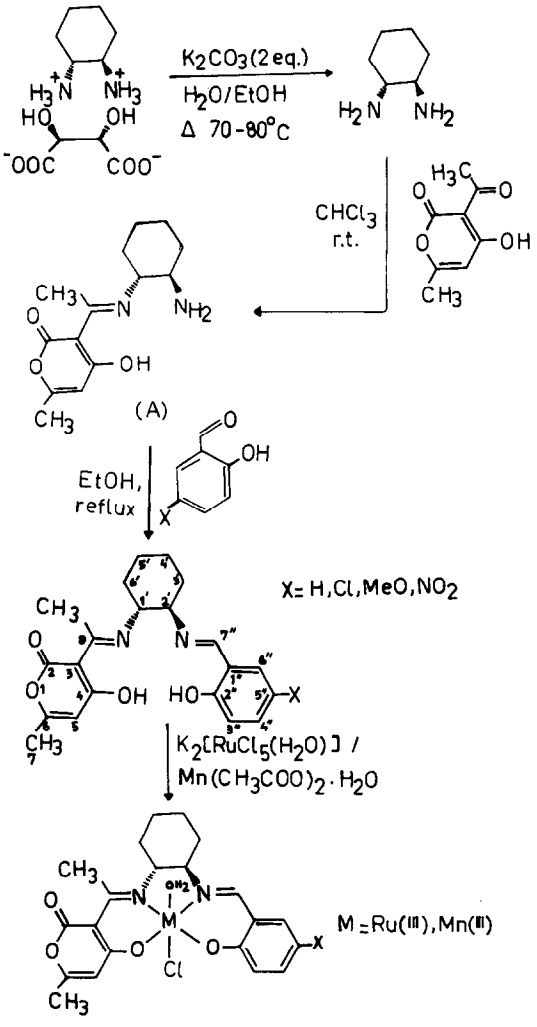
The recent introduction of optically active salen Mn(III) catalysts (hereafter referred to as Jacobsen catalyst) have greatly enhanced progress in the asymmetric epoxidation of simple olefins [9–13]. Especially the epoxidation of cis olefins conjugated with alkenyl, alkynyl or aryl group shows high enantioselectivity, Katsuki et al. [14] also reported Salen Mn(III) complexes bearing a six stereogenic centre with a bulky chiral group at the orthoposition of the salicylaldehyde moiety affected the asymmetric induction. In these the selection of the enantiomeric faces of prochiral substrates was proposed to be directed by steric interaction with the bulky substituents of the ligands and the

* Corresponding authors.

PII S1381-1169(96)00040-4

substrate approaching the metal centres. The mechanism of chiral induction was not elucidated.

In continuation of our earlier work on the enantioselective epoxidation of styrene derivatives by chiral Ru(II) Schiff base complexes [15,16] we are reporting here the synthesis and characterisation of dissymmetric chiral Schiff base complexes of Mn(III) and Ru(III) metal ions derived from 1*R*,2*R*-(−)-cyclohexanediamine and 3-acetyl-4-hydroxy-6-methyl-2-pyrone with salicylaldehyde, 5-chloro-, 5-methoxy- and 5-nitrosalicylaldehyde (Scheme 1). These



Scheme 1.

catalysts were evaluated for their catalytic activity in enantioselective epoxidation of styrene using iodosylbenzene as oxidant.

2. Experimental

$RuCl_3 \cdot 3H_2O$ (Johnson Matthey), salicylaldehyde, 5-chloro-, 5-methoxy-, 5-nitrosalicylaldehyde, 3-acetyl-4-hydroxy-6-methyl-2-pyrone, styrene and tris(3-(heptafluoropropylhydroxymethylene)camphorato-(+)-europium(III)) (Aldrich) were used as received. 1*R*,2*R*-(−)-cyclohexanediamine was resolved from the *cis–trans* isomer by the reported procedure [17]. The metal complex $K_2[RuCl_5(H_2O)]$ was prepared by a published method [18].

2.1. Synthesis of the dissymmetric chiral Schiff bases

Monotartrate salt of 1*R*,2*R*-(−)-cyclohexanediamine (29.7 g, 0.112 mol) and K_2CO_3 (31.2 g, 0.225 mol) was dissolved in 150 ml of distilled water with stirring. Ethanol (60 ml) was added and the resulting cloudy mixture was heated to reflux at 70–80°C for 8 h. Heating was discontinued and 3-acetyl-4-hydroxy-6-methyl-2-pyrone (16.8 g, 0.112 mol) dissolved in chloroform was added and the solution was stirred for further 6–8 h at room temperature. The precipitate was filtered off. The filtrate was concentrated and treated with CH_2Cl_2 to yield a light yellow compound we refer to as (A) Scheme 1.

Compound A (0.264 g, 0.001 mol) and the appropriate aldehyde (0.001 mol) were taken up in ethanol and the mixture was allowed to reflux on a steam bath for 6–8 h (TLC checked). Solvent was removed on a rotary evaporator and the resulting mass was triturated with 40–60 petroleum ether to give the desired Schiff base ligand.

1*R*,2*R*-(−)-3[1[2-(2-Hydroxy-5-

nitrophenyl)methylene]amino] 1′,2′-cyclohexylidene]4-hydroxy-6-methyl-2-pyrone (DISSAL NO_2) yield 65%, mp 215°C. ^{1}H NMR ($CDCl_3$): δ, 1.43–1.91 (m, 8H, $(CH_2)_4$ H'_3 to H'_4), 2.05 (s, 3H, CH_3, H_7], 3.09–3.29 (bs, 3H, H_8), 3.40–3.50 (m, 2H, H'_1 and H'_2), 6.76–7.36 (m, 3H, phenyl, H''_3, H''_4 and H''_6), 8.32 (s, 1H, N=CH H''_7), 12.76 (bs, 1H aromatic OH) and 14.39 (bs, 1H, OH keto/enol). ^{13}C{^{1}H} NMR (CH_2Cl_2), δ, 18.73, 23.99, 33.59 $(CH_2)_4$, 58.26 (C–CH_3), 73.2 (CH_3–C=N), 96.7 (CH_3–C–O), 107–133 (aromatic), 161.13 (Me–C=N), 163.06 (–C–OH), 166 (H–C=N), 175.75 (>C=O). Calcd. for $C_{21}H_{23}N_3O_6$: C, 61.01; H, 5.60; N, 10.16. Found C, 60.98, H, 5.58; N, 10.13. IR (KBr): ν(C=N) = 1625 cm^{-1}.

1*R*,2*R*-(−)-3[1[2-(2-Hydroxy-5-chlorophenyl)methylene]amino]-1′,2′-cyclohexylidene]4-hydroxy-6-methyl-2-pyrone (DISSAL Cl) yield 62%, mp 200°C. ^{1}H NMR ($CDCl_3$): δ, 1.42–1.90 (m, 8H, $(CH_2)_4$ H'_3 to H'_6), 2.03 (s, 3H, CH_3, H_7], 3.06–3.28 (bs, 3H, H_8), 3.39–3.48 (m, 2H, H'_1 and H'_2), 6.75–7.34 (m, 3H, phenyl, H''_3, H''_4 and H''_6) 8.30 (s, 1H, N=CH, H''_7), 12.75 (bs, 1H aromatic OH) and 14.38 (bs, 1H, OH keto/enol). ^{13}C{^{1}H} NMR (CH_2Cl_2), δ, 18.59, 23.97, 33.59 $(CH_2)_4$, 58.23 (C–CH_3), 73.0 (CH_3–C=N), 96.7 (CH_3–C–O), 107–133 (aromatic), 161.13 (Me–C=N), 163.08 (–C–OH), 166.2 (H–C=N), 175.72 (>C=O). Calcd. for $C_{21}H_{23}N_2O_3Cl$: C, 65.20; H, 5.99; N, 7.24. Found C, 65.17, H, 5.98; N, 7.23. IR (KBr): ν(C=N) 1630 cm^{-1}.

1*R*,2*R*-(−)-3[1[2-(2-Hydroxy-5-methoxyphenyl)methylene]amino]-1′,2′-cyclohexylidene]4-hydroxy-6-methyl-2-pyrone (DISSAL MeO) yield 70%, mp 110°C. ^{1}H NMR ($CDCl_3$): δ, 1.50–1.98 (m, 8H, $(CH_2)_4$ H'_3 to H'_6), 2.08 (s, 3H, CH_3, H_7], 3.13–3.30 (bs, 3H, H_8) 3.45–3.55 (m, 2H, H'_1 and H'_2), 6.80–7.40 (m, 3H, phenyl, H''_3, H''_4 and H''_6), 8.32 (s, 1H, N=CH, H''_7), 12.82 (bs, 1H aromatic OH) and 14.42 (bs, 1H, OH keto/enol). ^{13}C{^{1}H} NMR (CH_2Cl_2), δ, 18.8, 24.03, 33.62 $(CH_2)_4$, 58.29 (C–CH_3), 73.5 (CH_3–C=N), 96.7 (CH_3–C–O), 108–134 (aromatic), 162.5 (*Me*–C=N), 163.50 (–*C*–OH), 166.50 (H–*C*=N), 176.20 (C=O). Calcd. for $C_{22}H_{26}N_2O_5$: C, 66.32; H, 6.57; N, 7.03. Found C, 66.30, H, 6.53; N, 7.01. IR (KBr): ν(C=N) 1625 cm^{-1}.

1*R*,2*R*-(−)-3[1[2-(2-Hydroxyphenyl)methylene]amino]-1′,2′-cyclohexylidene]-4′-hydroxy-6′-methyl-2-pyrone (DISSAL) yield 68%, mp 141°C. ^{1}H NMR ($CDCl_3$): δ, 1.45–1.92 (m, 8H, $(CH_2)_4$ H'_3 to H'_6), 2.04 (s, 3H, CH_3, H_7], 3.10–3.25 (bs, 3H, H_8) 3.38–3.49 (m, 2H, H'_1 and H'_2), 6.85–7.36 (m, 3H, phenyl, H''_3, H''_4 and H''_6) 8.37 (s, 1H, N=CH, H''_7), 12.75 (bs, 1H aromatic OH) and 14.30 (bs, 1H, OH keto/enol). ^{13}C{^{1}H} NMR (CH_2Cl_2), δ, 18.39, 23.50, 33.50 $(CH_2)_4$, 58.20 (C–CH_3), 73.40 (CH_3–C=N), 96.7 (CH_3–C–O), 107–133 (aromatic), 160.5 (Me–C=N), 162.50 (–C–OH), 165.50 (H–C=N), 175.3 (>C=O). Calcd. for $C_{21}H_{24}N_2O_3$: C, 71.54; H, 6.86; N, 7.94. Found C, 71.52; H, 6.83; N, 7.92. IR (KBr): ν(C=N) 1630 cm^{-1}.

2.2. *Preparation of dissymmetric chiral Schiff base complexes of Mn(III) metal ion* ***1–4***

Appropriate amount of the chiral Schiff bases (0.001 mol) dissolved in ethanol containing KOH 0.5 M (4 ml) was vigorously stirred at reflux till the mixture is homogeneous under inert atmosphere. A solution of $Mn(CH_3COO)_2 \cdot 4H_2O$ (0.490 g, 0.002 mol) in 10 ml of water was then added slowly and the resulting solution was refluxed for 8–10 h. The reaction was allowed to cool to room temperature. A solution containing 0.127 g of LiCl in a minimum quantity of water was added and the mixture was stirred at room temperature under aerobic conditions. TLC analysis at that stage showed a single spot with no evidence of free ligand. The resulting dark brown solution was filtered and concentrated on rotary evaporator. The residue were redissolved in dried CH_2Cl_2 and filtered. Water was removed by using a separating funnel and the organic phase was concentrated on rotary evaporator till dryness. The complexes thus obtained were recrystallised from acetoni-

trile. Generally the yields for all the complexes were in the range of 58–62%.

The analytical data for the complexes is given below:

2.2.1. (R,R)-(−)-DISSAL NO_2 Mn

Calcd. for $C_{21}H_{23}N_3O_7ClMn$: C, 48.53; H, 4.46; N, 8.08. Found: C, 48.50; H, 4.42; N, 8.04. IR (KBr) cm^{-1}: 1580 ν(H–C=N), 3300 ν(OH), 1100, 1170 δ(OH). UV–Vis (nm) (MeOH) λ_{max} (ε), 310 (2500), 420 (2419), 576 (235); CD λ_{max} ($\Delta\varepsilon$) (MeOH) 420 (+2), 465 (−0.9), 530 (+3); $[\alpha]_D^t = -68.4$. Configuration (*R*); Ω_m (MeOH) 5 mho cm^{-1} mol^{-1}; μ_{eff} (BM) 4.8.

2.2.2. (R,R)-(−)-DISSAL Cl Mn

Calcd. for $C_{21}H_{23}N_2O_4Cl_2Mn$: C, 51.13; H, 4.70; N, 5.67. Found: C, 51.09; H, 4.67; N, 5.64. IR (KBr) cm^{-1}: 1590 ν(H–C=N), 3300 ν(OH), 1100, 1170 δ(OH). UV–Vis (nm) (MeOH) λ_{max} (ε): 300 (2500), 349 (2499), 406 (844); CD λ_{max} ($\Delta\varepsilon$) (MeOH): 345 (−9.5), 405 (−2.7), 480 (−1); $[\alpha]_D^t = -48.67$. Configuration (*R*); Ω_m (MeOH): 4 mho cm^{-1} mol^{-1}, μ_{eff} (BM) 4.85.

2.2.3. (R,R)-(−)-DISSAL MeO Mn

Calcd. for $C_{22}H_{24}N_2O_4ClMn$: C, 52.34; H, 5.19; N, 5.54. Found: C, 52.31; H, 5.17; N, 5.52. IR (KBr) cm^{-1}: 1590 ν(H–C=N), 3300 ν(OH), 1100, 1170 δ(OH). UV–Vis (nm) (MeOH) λ_{max} (ε): 320 (2500), 423 (2450); CD λ_{max} ($\Delta\varepsilon$) (MeOH): 345 (−5.3), 375 (−7.5), 430 (−3) 580 (+0.9); $[\alpha]_D^t = -89.75$. Configuration (*R*); Ω_m (MeOH): 3 mho cm^{-1} mol^{-1}; μ_{eff} (BM) 4.95.

2.2.4. (R,R)-(−)-DISSAL Mn

Calcd. for $C_{21}H_{24}N_2O_4$ ClMn : C, 54.97; H, 5.27; N, 6.10. Found: C, 54.95; H, 5.25; N, 6.08. IR (KBr) cm^{-1}: 1380 ν(H–C=N), 3300 ν(OH), 1100, 1170 δ(OH). UV–Vis (nm) (MeOH) λ_{max} (ε): 270 (2500), 395 (1434); CD λ_{max} ($\Delta\varepsilon$) (MeOH): 400 (−5), 470 (−0.7), 570 (+1); $[\alpha]_D^t = -110.05$. Configuration (*R*); Ω_m (MeOH): 4 mho cm^{-1} mol^{-1}; μ_{eff} (BM) 4.85.

2.3. Preparation of dissymmetric chiral Schiff base complexes of the Ru(III) metal ion 5–8

The dissymmetric chiral Schiff bases (0.001 mol) dissolved in ethanol were refluxed with $K_2[RuCl_5(H_2O)]$ (0.374 g, 0.001 mol) under argon atmosphere for 8–10 h. After completion of reaction (determined by TLC) the solutions were filtered and concentrated on a rotary evaporator. The complexes were again dissolved in dried acetonitrile and filtered to the remove the excess of KCl. Solvent was reduced to 10 ml on a rotary evaporator and the desired complexes were precipitated by diethyl ether and recrystallised from acetonitrile (yield 62–65%).

2.3.1. (R,R)-(−)-DISSAL NO_2 Ru

Calcd. for $C_{21}H_{23}N_3O_7ClRu$: C, 44.57; H, 4.09; N, 7.42. Found: C, 44.53; H, 4.06; N, 7.40. IR (KBr) cm^{-1}: 1570 ν(H–C=N), 3300 ν(OH), 1100, 1170 δ(OH). UV–Vis (nm) (MeOH) λ_{max} (ε): 300 (2500), 419 (2486) 561 (660); CD λ_{max} ($\Delta\varepsilon$) (MeOH): 380 (+5.5), 435 (+6.0), 570 (+1); $[\alpha]_D^t = -54.81$. Configuration (*R*); Ω_m (MeOH): 4 mho cm^{-1} mol^{-1}; μ_{eff} (BM) 1.99.

2.3.2. (R,R)-(−)-DISSAL Cl Ru

Calcd. for $C_{21}H_{23}N_2O_4$ Cl_2Ru: C, 46.76; H, 4.29; N, 5.19. Found: C, 46.72; H, 4.27; N, 5.16. IR (KBr) cm^{-1}: 1590 ν(H–C=N), 3300 ν(OH), 1100, 1170 δ(OH). UV–Vis (nm) (MeOH) λ_{max} (ε): 270 (2500), 398 (1980), 597 (255); CD λ_{max} ($\Delta\varepsilon$) (MeOH): 385 (−0.5), 430 (+3.0), 520 (−1.0); $[\alpha]_D^t = -98.14$. Configuration (*R*); Ω_m (MeOH): 3 mho cm^{-1} mol^{-1}; μ_{eff} (BM) 2.00.

2.3.3. (R,R)-(−)-DISSAL MeO Ru

Calcd. for $C_{22}H_{26}N_2O_6$ ClRu: C, 47.96; H, 4.75; N, 5.08. Found: C, 47.94; H, 4.73; N, 5.06. IR (KBr) cm^{-1}: 1590 ν(H–C=N), 3300 ν(OH), 1100, 1170 δ(OH). UV–Vis (nm)

(MeOH) λ_{max} (ε): 300 (2500), 401 (2150), 678 (394); CD λ_{max} ($\Delta\varepsilon$) (MeOH): 370 (+5.3), 440 (+8.5), 520 (−1.0); $[\alpha]_D^t = -82.39$. Configuration (*R*); Ω_m (MeOH): 4 mho cm^{-1} mol^{-1}; μ_{eff} (BM) 2.04.

2.3.4. (R,R)-(−)-DISSAL Ru

Calcd. for $C_{21}H_{24}N_2O_4ClRu$: C, 49.95; H, 4.79; N, 5.54. Found: C, 49.92; H, 4.75; N, 5.52. IR (KBr) cm^{-1}: 1575 ν(H–C=N), 3300 ν(OH), 1100, 1170 δ(OH). UV–Vis (nm) (MeOH) λ_{max} (ε): 310 (2500), 385 (1792), 580 (235); $[\alpha]_D^t = -42.85$. Configuration (*R*); Ω_m (MeOH): 3 mho cm^{-1} mol^{-1}; μ_{eff} (BM) 2.06.

2.4. Methods

Elemental analysis of the complexes were done on a Carlo Erba Analyser Model 1106. Molar conductance was measured at room temperature on a Digisun electronic conductivity bridge model DI-909. The IR spectra were recorded on Carl Zeiss Specord M-80 spectrophotometer in KBr. Electronic spectra were recorded on Shimadzu UV–Vis recording spectrophotometer model 160. ^1H NMR 99.55 MHz and $^{13}C\{^1H\}$ 24.99 MHz were done on a JEOL FX100 NMR spectrometer in $CDCl_3$ and CH_2Cl_2. The purity of the solvent, substrate and analysis of the product was determined by GLC using Shimadzu GC-9A couple with C-R-3A recorder using 2 m long, 3 mm ID, 4 mm OD stainless steel column packed with SE30, 5% 60–80 mesh, with FID detector, column temperature programmed between 70 and 170°C, injector temperature 200°C, with nitrogen carrier gas flow 30 ml/min. Synthetic standards of the product were used to determine yields by comparison of the peak height and area. The optical yield of the product was determined by chiral γ-cyclodextrin propionyl capillary GC column G-PN type. Cyclic voltammetry, differential pulse voltammograms were recorded with a Princeton Applied Research (PAR) instrument using tetrabutyl ammonium tetrafluoroborate as supporting electrolyte in acetonitrile. The magnetic moment measurements were done at 298 K by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant and experimental susceptibilities were corrected for diamagnetism. The optical rotation of the complexes in dichloromethane was measured by polarimeter AtagO, Japan. The CD spectra were recorded in MeOH by Jasco model J-20, Japan.

*2.5. Epoxidation of styrene by the catalysts **1–8***

The epoxidation of styrene by the catalysts **1–8** with iodosylbenzene was carried out by the following procedure: The chiral catalyst (0.01 mmol), styrene (1 mmol) and n-tridecane (0.1 mmol) as GLC internal standard were dissolved in 2.5 ml acetonitrile. The reaction was initiated by the addition of iodosylbenzene (0.1 mmol) and stirred at constant speed in inert atmosphere at 25°C. After each 15 min interval, an aliquot was taken from the reaction mixture, quenched with PPh_3 and analysed by GLC. After the reaction was completed the solvent was removed and the product styrene oxide was separated from the reaction mixture using short silica gel column using hexane:dichloromethane (9:1) as eluent. The enantiomeric excess was determined by chiral γ-cyclodextrin GC capillary column. The product sample was taken up in $CDCl_3$ for the ^1H NMR measurements using the chiral shift reagent $Eu(hfc)_3$ for further determination of the enantiomeric excess.

3. Results and discussion

The neutral complexes **1–8** were isolated as solids using dissymmetric tetradentate ligands with the interaction of Ru(III) and Mn(II) metal ions in ethanol followed by a slower air oxidation in presence of a large excess of coordinating anion to form Mn(III) chelate. The magnetic moment is in the range 4.8–4.95 BM for the complexes **1–4**, which is consistent with their formulation as high spin Mn(III) complexes, while μ_{eff} values for Ru(III) dissymmetric com-

plexes fall between 1.9–2.06 BM indicating the presence of Ru(III) ion with a spin paired $4d^5$ electronic configuration.

A strong band near 1620–1630 cm^{-1} in all the dissymmetric chiral Schiff bases undergoes a decrease in frequency of about 30–40 cm^{-1} after complexation [19], indicating coordination through azomethine nitrogen. Two bands at 1100 and 1170 cm^{-1} along with a broad band at 3300 cm^{-1} appear in all the complexes due to δ(O–H) and ν(O–H), respectively, of coordinated water [20].

The electronic spectra of the complexes in methanol show highly intense UV bands which are usually ligand centered and lie in the range 270 ($\varepsilon = 2500$) and 320 ($\varepsilon = 2500$) nm while the MLCT band fall between 385 ($\varepsilon = 1722$) to 420 ($\varepsilon = 2419$) nm and the position of MLCT band depends on the substituent X = H, NO_2, Cl, MeO. The energy of the band decreases as (*R*,*R*) DISSAL NO_2 > (*R*,*R*) DISSAL > (*R*,*R*) DISSAL Cl > (*R*,*R*) DISSAL MeO. These values are in consistent with that reported earlier [21]. The band near 561 ($\varepsilon = 660$) and 678 ($\varepsilon = 394$) is assigned to the forbidden ligand field transitions of Ru(III) and Mn(III), respectively. The CD spectra of the complexes **1–8** were recorded in methanol. Two representative

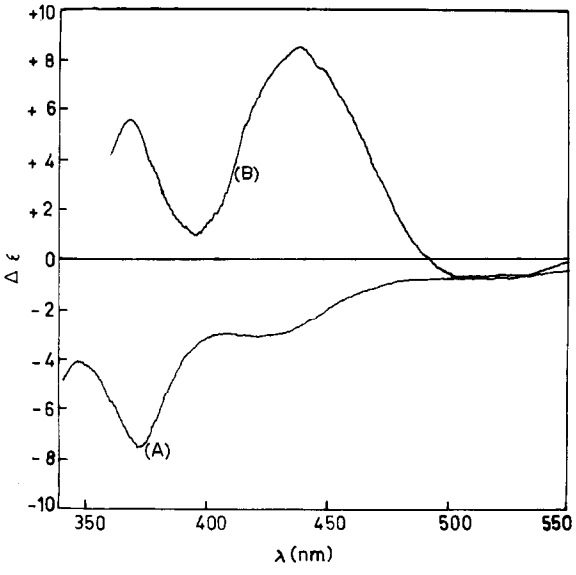


Fig. 1.

CD spectra Fig. 1(A) (*R*,*R*) DISSAL MeO Mn, (B) (*R*,*R*) DISSAL MeO Ru show that both the complexes have the same absolute configuration but complex (A) is stereospecifically coordinated to Mn so that the gauche chelate ring is in the δ conformation while complex (B) has the λ conformation with a minor contribution from the δ isomer. This preferred conformation and configuration depends on the steric interaction

Table 1
Enantioselective styrene epoxidation catalyzed by (*R*,*R*) DISSAL Mn(III) and Ru(III) complexes

Catalyst [a]	Epoxide [b] yield (%)	Reaction [c] time (min)	ee (%) [d]
1. (*R*,*R*) DISSAL NO_2 Mn	42	180	29 (*S*)
2. (*R*,*R*) DISSAL Cl Mn	28	150	10 (*S*)
3. (*R*,*R*) DISSAL MeO Mn	22	90	56 (*S*)
4. (*R*,*R*) DISSAL Mn	29	60	34 (*S*)
5. (*R*,*R*) DISSAL NO_2 Ru	24	30	48 (*S*)
6. (*R*,*R*) DISSAL Cl Ru	26	150	45 (*S*)
7. (*R*,*R*) DISSAL MeO Ru	30	120	58 (*S*)
8. (*R*,*R*) DISSAL Ru	28	90	18 (*S*)

[a] Organic phase, CH_3CN; catalyst, 0.01 mmol; styrene, 1.0 mmol, PhIO, 0.1 mmol; 0.1 mmol; n-tridecane (internal standard for gas chromatography).

[b] Styrene conversions (%) were the same as the epoxide yield as only a trace amount of benzaldehyde side product was detected, except in the case of catalyst **5** where aldehyde found was 2%.

[c] Reaction time was determined on the basis of the evolution of the epoxide peak on GC. An aliquot (100 μl) from each catalytic run was taken every 15 min and quenched with triphenylphosphine (100 μl, 0.1 mmol).

[d] Styrene oxide was separated from the reaction mixture using a short silica gel column using hexane:dichloromethane (9:1) as eluent. *S*-Styrene oxide was found to be in excess in all of the cases determined by using (+)-tris-Eu(hfc)$_3$ chiral NMR shift reagent/γ-cyclodextrin capillary GC column.

between substituents at the azomethine carbon and the size of the metal ions.

In the liquid field region, CD bands near 520 (−1), 580 (+0.6) of opposite sign are displayed and assigned to both d–d bands and spin forbidden ligand bands. A blue shift is seen in these bands which depends [21] on the donor strength of the substituent at para position of the salicylaldehyde moiety. The charge transfer region of the spectra shows $d \rightarrow \pi^*$ bands between 405 (−2.7) to 470 (−0.7) nm and the high intensity $\pi \rightarrow \pi^*$ transition are seen at 345–370 nm.

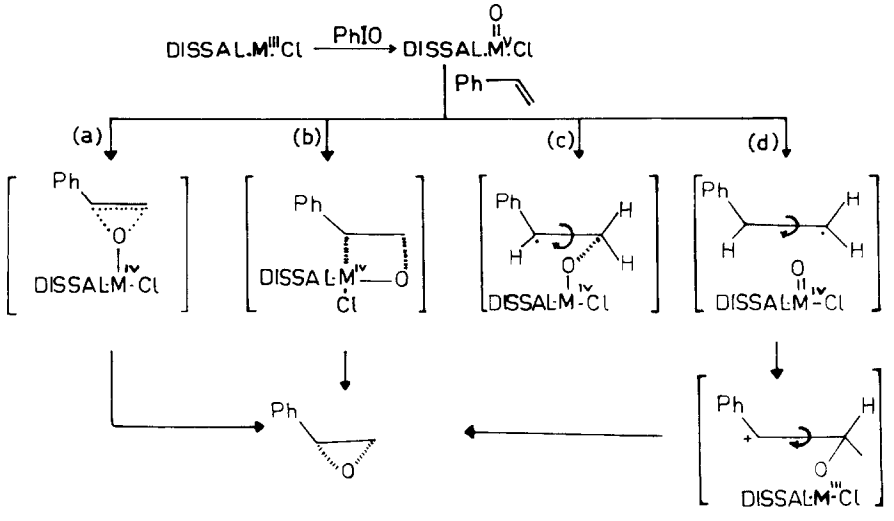
The cyclic voltammetry of the complexes **1–8** in acetonitrile is a one electron reduction process. The reduction couple of Mn(III)/Mn(II) observed in the range of −0.12 to −0.52 V while Ru(III)/Ru(II) lie between −0.21 and −0.55 V. The reduction potential shows a positive shift when a withdrawing group is on the para position of the salicylaldehyde and vice versa. The same trend was also reported earlier [21].

3.1. Enantioselective epoxidation

Enantioselective epoxidation of styrene has been investigated with complexes **1–8**, as catalyst and PhIO as oxidant. The results are summarised in Table 1. In absence of the catalysts the styrene was scarcely oxygenated by iodosylbenzene alone under the identical reaction conditions.

The enantiomeric excesses for the resulting epoxide separated by silica gel column chromatography were determined by GLC using γ-cyclodextrin column and also by ^{1}H NMR performed in the presence of a chiral shift reagent tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium(III) Eu(hfc)$_3$. When the *R*-(−)-forms of the catalyst **1–8** were employed (*S*)-styrene oxide was obtained as the dominant enantiomer.

The mechanism of oxo-transfer (Scheme 2) seems to be dependent on substrate, metal and ligand, currently it cannot be explained by a single mechanism [7,15]. In all our catalytic runs only traces of benzaldehyde were formed, except in the case of catalyst **5** (benzaldehyde 2%), which suggests that formation of epoxide is mostly through either concerted direct oxygen atom transfer (a) or oxametallaoxetane (b). However, the presence of a trace amount of benzaldehyde suggests a parallel free radical carbocationic route is also in operation (d). The routes (c) and (d) are also responsible for the



Scheme 2. Possible mechanisms of oxotransfer from high-valent oxo-Mn/oxo-Ru DISSAL in the epoxidation of styrene: (a) direct oxygen atom transfer, (b) metallaoxetane formation, (c) free radical addition and successive fast ring closure, and (d) single-electron transfer followed by collapse to a radical or a carbocation.

loss in enantiomeric excess by rotation about the C–C single bond in the intermediate.

With most of the catalysts screened, only moderate enantiomeric excesses were observed. The highest values of 58% and 56% ee's were found with catalysts **7** and **3** and 48% and 45% with **5** and **6**, respectively. Although chemical yields of epoxides are in very close range 22–42%. In the case of Mn complexes **1–4** more electron withdrawing group on ligand gave higher epoxide yields while in the case of Ru with the same ligand systems the trend is reversed. However, no such effect is seen in ee's. Interestingly highest ee's were obtained both with Mn and Ru complexes where there is methoxy group on the ligand system.

Acknowledgements

Two of us (RIK and NHK) are thankful for financial assistance from CSIR Young Scientist Project, DST Young Scientist Project and Third World Academy of Sciences.

References

[1] T. Nagata, K. Imagawa, T. Yamada and T. Mukaiyama, Chem. Lett. (1995) 1259.
[2] E.N. Jacobsen, Asymmetric Catalytic Epoxidation of Unfunctionalized Olefins, in I. Ojima (Ed.), Catalytic Asymmetric Synthesis, VCH, New York, 1993, Ch. 4.2, p. 159.
[3] K. Konishi, K. Oda, K. Nishida, T. Aida and S. Inoue, J. Am. Chem. Soc., 114 (1992) 1313.
[4] Y. Naruta, F. Tani, N. Ishihara and K. Maruyama, J. Am. Chem. Soc., 113 (1991) 6865.
[5] B. Boitrel, A. Lecas and E. Rose, J. Chem. Soc., Chem. Commun. (1989) 349.
[6] K. Konishi, K. Miyazaki, T. Aida and S. Inove, J. Am. Chem. Soc. 112 (1990), 5639.
[7] K.A. Jorgensen and B. Schiott, Chem. Rev., 90 (1990) 1483.
[8] J.T. Groves and R.S. Myers, J. Am. Chem. Soc., 105 (1993) 5791.
[9] R. Irie, K. Noda, Y. Ito, N. Matsumoto and T. Katsuki, Tetrahedron Asymm., 2 (1991) 481.
[10] N. Hosoya, R. Irie and T. Katsuki, Synth. Lett., (1993) 261.
[11] E.N. Jacobsen, W. Zhang and M.L. Guller, J. Am. Chem. Soc., 113 (1991) 6703.
[12] E.N. Jacobsen, W. Zhang, L.C. Muci, J.R. Ecker and L. Deng, J. Am. Chem. Soc., 113 (1991) 7063.
[13] W. Zhang and E.N. Jacobsen, J. Org. Chem., 86 (1991) 2296.
[14] H. Sasaki, R. Irie, T. Hamada, K. Suzuki and T. Katsuki, Tetrahedron, 50 (1994) 11827.
[15] R.I. Kureshy, N.H. Khan, S.H.R. Abdi and K.N. Bhatt, Tetrahedron Asymm., 4 (1993) 1693.
[16] R.I. Kureshy, N.H. Khan and S.H.R. Abdi, J. Mol. Catal., 96 (1995) 117.
[17] J.F. Larrow, E.N. Jacobsen, Y. Gao, Y. Hong, X. Nie and C.M. Zepp, J. Org. Chem. 59 (1994), 1939.
[18] E.E. Mercer and R.R. Buckley, Inorg. Chem., 4 (1965) 1692.
[19] D.A. Edwards and R. Richards, J. Chem. Soc., Dalton Trans. (1975) 637.
[20] M.A. Bangres, M. Gonzales, M.E. Peres and R.J. Ruano, Polyhedron, 5 (1986) 1371.
[21] K. Nakajima, K. Kojima, M. Kojima and J. Fujita, Bull. Chem. Soc. Jpn., 63 (1990) 2620.