

**Asymmetric Epoxidation of Styrene by Novel Chiral Ruthenium(II)
Schiff Base Complexes, Synthesis and Characterization.**

**Rukhsana I. Kureshy*, Noor-ul H. Khan, Sayed H.R. Abdi and
Ketan N. Bhatt**

Discipline of Coordination Chemistry & Homogeneous Catalysis
Central Salt & Marine Chemicals Research Institute,
Bhavnagar 364002, India

(Received in UK 22 April 1993)

Abstract: Synthesis of some novel Chiral Ru(II) Schiff base complexes of the type $[RuL(PPh_3)(H_2O)_2]$ 1-6 where L = Chiral Schiff bases derived from salicylaldehyde² and L-amino acids namely, L-alanine, L-valine, L-Serine, L-Arginine, L-Cystein and L-aspartic acid are reported. The characterisation of the complexes has been accomplished by microanalysis, IR-, UV/visible, $[^1H]$, $[^{13}C]$ and $[^{31}P]$ NMR spectroscopy, conductance measurements, electrochemical studies, optical rotation and circular dichroism spectroscopy. The conformational aspects regarding the asymmetric arrangement of substituents R at amino acid moiety of the Schiff bases around Ru(II) metal ion has been discussed. The complexes show quasireversible behaviour and the redox potential of Ru(II)/Ru(I) couple lie in the range -0.34 to -0.18 volts.

In the asymmetric epoxidation of styrene by the complexes 1 - 6 and idosylbenzene, we observed that on employment of the R form of the catalyst resulted in the formation of (S) styrene oxide as dominant enantiomer by GLC and NMR. Enantiomeric excess for the resulting epoxides were determined by $[^1H]$ NMR spectroscopy using Chiral shift reagent, tris[3-(heptafluoropropyl hydroxymethylene) - (+) camphoratol europium(III), Eu(hfc)₃.

Introduction

Enantioselective epoxidation of simple olefins constitutes a challenging and important synthetic problem¹. Indeed, the stereoselectivity of known chiral reagents and catalysts is generally interpreted solely in terms of steric considerations. So far, the effect of varying the electronic properties of chiral catalysts has never been systematically assessed in a practical system^{2,3}, although this is largely because known effective catalysts tend not to be synthetically or structurally well suited to electronic tuning.

There has been relatively little progress in catalytic asymmetric oxidation, especially for substrates not bearing coordinative functional groups⁴. Thus it is desirable to design and synthesize novel oxidising chiral catalysts bearing different substituents to study the effects on enantioselectivity by accomplishing prochiral selection of a simple substrate solely dependent upon weak nonbonding interactions.

In continuation of our earlier work^{5,6} we are reporting first the synthesis and characterisation of Chiral Ru(II) Schiff base complexes (Fig.1) and next the asymmetric epoxidation of styrene with their Ru(II) complexes and iodosylbenzene as oxidant³. On the basis of the results obtained, we discuss the mechanisms of oxygen transfer and chiral induction.

Results and Discussion

The neutral complexes 1 - 6, were isolated using a dianion terdentate ligand with interaction of Ru(II) metal ion in acetone/methanol. However, the chiral Schiff bases derived from L-aspartic acid and L-cystein could also coordinate through the COO^- and S group thus may behave as tetradentate. The remaining coordination sites are occupied by triphenyl phosphine

and two molecules of water giving an octahedral geometry around ruthenium. The complexes are listed in Table-I together with their microanalysis and molar conductance.

The IR spectra Table-II show strong bands typical of Schiff base complexes in $1605 - 1590 \text{ cm}^{-1}$ region, assigned to the azomethine group (H-C=N) which overlaps with asymmetric COO^- stretching modes. This band undergoes a shift to lower energy by $15-30 \text{ cm}^{-1}$ from that of the free ligand inferring coordination through the azomethine and carboxylato groups⁷. The analytical data suggest the presence of two molecules of water which show broad absorption at $3400 - 3300 \text{ cm}^{-1}$ along with the deformation and rocking modes of water at 1620 and 620 cm^{-1} . Other significant bands are listed in Table-II. In far IR region bands at 555 and 350 cm^{-1} is due to $\nu(\text{Ru-P})$ and $\nu(\text{Ru-N})$ respectively.

The electronic spectra of the complexes 1 - 6 recorded in dichloromethane show a broad intense charge transfer, i.e. MLCT, band from $t_2(\text{Ru}) \rightarrow \pi^* \text{L}$ at 590 ($\epsilon = 1008$) to 674 ($\epsilon = 385$) nm Table-III. The position of the LMCT band depends on the substituents attached to the aminoacid moiety of the Schiff base⁸. The energy of the bands decreases in the order $\text{Sal - Asp} > \text{Sal - Cys} > \text{Sal - ala} > \text{Sal - val} > \text{Sal - Arg} > \text{Sal - Ser}$ which is in consonance to those reported earlier^{5,6}. The sharp, highly intense UV peaks are usually ligand centered and lie in the range 285 ($\epsilon = 2500$) and 411 ($\epsilon = 2500$) nm.

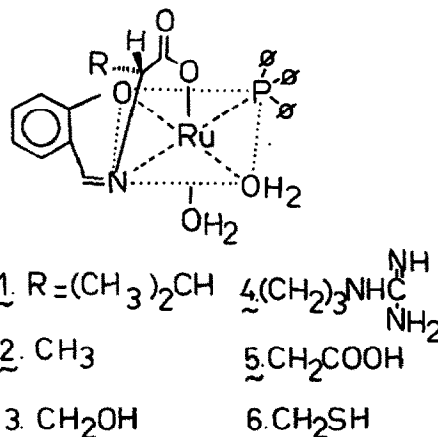


Fig. 1

Table - I Elemental analysis, molar conductance, absolute configuration and optical rotation of Chiral Ru(II) Schiff base complexes.

Complexes	Analysis % found (calculated)			Molar conductance (Λ M) Ohm ⁻¹ cm ² mol ⁻¹ (MeOH 298k)	Absolute configura- tion	[α] ^t deg. cm ⁻² D ^D _g ⁻¹ (CH ₂ Cl ₂)
	C	H	N			
1	58.00 (58.24)	4.99 (5.19)	2.01 (2.11)	5	R	-116.2
2	56.98 (57.04)	4.20 (4.61)	2.08 (2.37)	8	R	-136.3
3	56.14 (56.65)	4.17 (4.75)	2.10 (2.35)	4	R	-142.8
4	54.97 (55.10)	5.00 (5.22)	8.00 (8.29)	6	R	-130.0
5	55.00 (55.13)	4.17 (4.28)	2.00 (2.20)	4	R	-153.8
6	53.99 (54.11)	4.60 (4.53)	2.11 (2.24)	7	R	+58.32

Table-II Selected IR absorption bands and electrochemical data of chiral Ru(II) Schiff base complexes

Complexes	ν (H-C=N) + ν asy(CO \bar{O})	ν (C=O)	ν (Ru-P)	ν (Ru-N)	Oxidation, V (ΔE_p , mV) ^a (Ru(II)/Ru(III))	Reduct- ion, V (ΔE_p , mV) ^a Ru(II)/ Ru(I)
1	1605(s)	1720	535	345	+0.68(177)	-0.34(104)
2	1610(s)	1715	540	340	+0.72(94)	-0.30(172)
3	1600(s)	1720	550	340	+0.79(80)	-0.31(125)
4	1590(s)	1705	545	345	+0.65(71)	-0.22(95)
5	1605(s)	1725	540	340	+0.82(100)	-0.29(78)
6	1595(s)	1730	550	345	+0.70(112)	-0.18(90)

^aPt electrode is the working electrode, solvent is CH₂Cl₂, supporting electrolyte is tetrabutyl ammonium perchlorate (0.001M), the reference electrode is Ag/AgCl.

C.D.spectra of all the complexes were recorded in dichloromethane (Table - III). Three representative C.D.spectra Fig.2 of chiral Ru(II) Schiff base complexes containing the ligands derived from (A) L-ala, (B) L - Ser and (C) L-Cys show that although all the aminoacids have the same absolute configuration, the complexes (A) and (B) are stereospecifically coordinated to the metal ion so that the gauche chelate ring is located in δ form with a very small preference for the λ form but the complex (C) preferred only the λ conformation. Similar relationship among C.D.spectra were reported elsewhere^{8,9}.

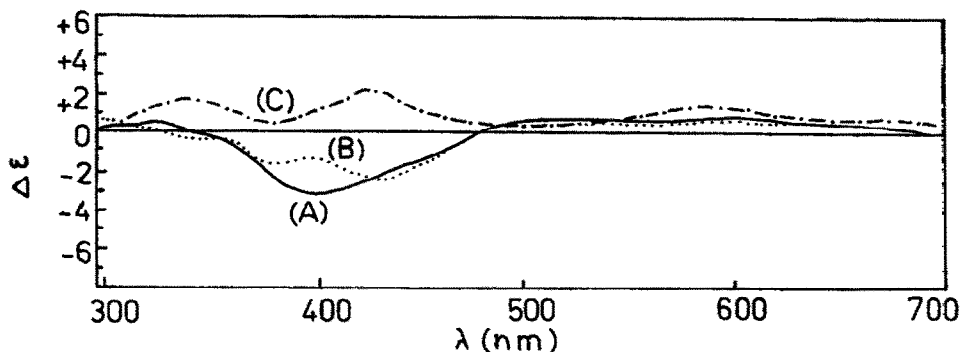


FIG.2

C.D. bands with positive cotton effect lie in the range 580 - 590 nm in the ligand field region and are assignable to both the d-d bands and spin forbidden ligand bands. A blue shift is seen in these bands which mainly depends^{5,8} on the donor strength of the R group attached to the aminoacid moiety of the Schiff base. In the charge transfer region the band $d \rightarrow \pi^*$ fall in the region 405 - 470 nm and high intensity $\pi \rightarrow \pi^*$ (azomethine) transition are seen at 300 - 395 nm. A shift in charge transfer and ligand transition with azomethine substituents is consistent with the inductive effect of the substituent R on ligand π - levels¹⁰.

[¹H] NMR spectra of the complexes recorded in CDCl₃ show a triplet in the range 3.40 - 3.58 ppm for asymmetric proton while a doublet at 2.10 - 2.18 ppm assignable to -CH₂ protons in the complexes 3, 4, 5 and 6. Complexes 1 and 2 also show signals due to -CH₃ protons near 1.28 - 1.25 ppm. The azomethine proton at 8.0 ppm in all chiral Schiff bases undergoes a down field shift after complexation with metal ion and lie at 8.10 - 8.23 ppm respectively inferring the involvement of azomethine nitrogen atom in coordination (Table - IV). The resonance signals in the range 7.27 - 7.71 ppm are assigned to the phenyl protons of triphenylphosphine and salicylaldehyde moiety.

¹³C[¹H] chemical shift data for all the complexes is listed in Table -IV. The resonance signal due to the carbon of carboxylate group as well as that for the azomethine carbon atom undergo a down field shift relative to those of free chiral Schiff bases which infers that in the complexes the ligand functioned as terdentate O-N-O. However, the signals due to the stereogenic carbon atom and ring

Table-III Electronic and C.D.spectral data of Chiral Ru(II) Schiff base complexes.

Complexes	abs λ_{\max} ($\epsilon \text{ M}^{-1} \text{ cm}^{-1}$)	C.D. λ_{\max} ($\Delta\epsilon \text{ M}^{-1} \text{ cm}^{-1}$)
1	609(1273), 393(2363)	580(+0.9), 405(-3.0), 300(+0.5)
2	603(1077), 393(2369)	585(+0.9), 406(-3.1), 305(+0.6)
3	674(385), 345(1972) 285(2500)	580(+0.8), 435(-2.3), 380(-1.6)
4	611(959), 393(2388)	580(+0.4), 470(-0.5), 395(-0.3)
5	590(1008), 395(2380)	590(+0.7), 395(-0.2), 330(+0.7)
6	599(977), 411(2500)	590(+1.5), 415(+2.2), 350(+1.7)

Table-IV [^1H] and ^{13}C [^1H] Chemical Shift data of Chiral Ru(II) Schiff base complexes.

Complexes	^1H]NMR Assignment (ppm)			^{13}C [^1H] NMR Assignment (ppm)		
	-CH	-CH=N	Aromatics	-CH	-CO $\bar{\text{O}}$	Aromatics
1	3.40	8.10	7.27-7.34	62.5	199.9	128,6-130.1
2	3.42	8.12	7.29-7.36	63.8	200.4	128.7-132.0
3	3.41	8.11	7.29-7.36	62.7	199.1	129.0-131.0
4	3.41	8.14	7.38-7.42	67.4	204.4	128.5-133.2
5	3.44	8.16	7.40-7.46	66.1	201.3	128.6-134.8
6	3.45	8.17	7.60-7.71	68.2	203.2	128.4-134.5

carbon fall in the range 62.5 - 73.61, 128.5 - 134.8 ppm. In the case of complexes 1 and 2 a singlet in the range 22 - 24.02 ppm is due to methyl carbon atom while a singlet at 30.20 - 31.00 ppm assignable to $-\text{CH}_2$ carbon atom for the complexes 4 - 6. All these results are inconsonance with those reported earlier^{11,12}.

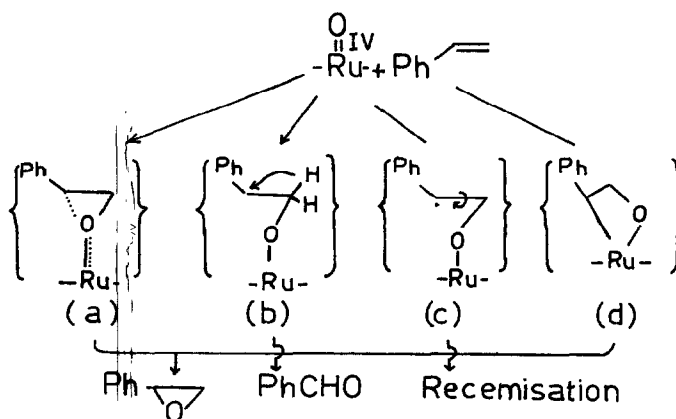
$^{31}\text{P}\{^1\text{H}\}$ NMR spectra in dichloromethane show only one signal in the range 29.5 to 32.5 ppm reflects that there is only one triphenyl phosphine which is trans to azomethine nitrogen atom^{13,14}.

The cyclic voltammogram of the complexes 1 - 6 recorded in CH_2Cl_2 shows the system to be quasi reversible one electron transfer and the oxidation potential of Ru(II)/Ru(III) couple lie in the range +0.65 to + 0.82 volts vs Ag/AgCl. From cyclic voltammogram the $E_{1/2}$ value of Ru(II)/Ru(I) reduction couple fall in the range -0.18 to -0.34 volts which mainly depend on the R group attached to aminoacid moiety of the Schiff base complexes (Table-II).

Stereoselective Epoxidation

A typical selective epoxidation by the catalysts 1 - 6 and iodosylbenzene was performed according to the following procedure. The chiral catalyst (1 μmol), styrene (500 μmol) and n-tridecane (50 μmol) as GLC internal standard were dissolved in degassed dry CH_2Cl_2 (2.5 ml). Reaction was initiated by the addition of PhIO (100 μmol) and stirring at a constant speed in inert atmosphere at 4°C in the dark. At appropriate intervals, aliquots taken from the reaction mixture and analysed by GLC. Results are summarised in Table-V. Without any catalysts, the styrene was hardly oxygenated by iodosylbenzene alone under the identical reaction conditions.

Enantiomeric excesses for the resulting epoxides were determined by ^1H NMR spectroscopy performed in the presence of a chiral shift reagent, tris [3-(heptafluoropropyl hydroxy methylene -(+)-camphorato)europium(III), $\text{Eu}(\text{hfc})_3$. When the (R) - forms of the catalysts 1 - 6 were used (S)-styrene oxide were formed as a dominant enantiomer.



Scheme-A

In all the catalytic runs [Scheme - A] only trace amounts of benzaldehyde were found suggesting the addition of oxygen mostly via either concerted oxygen addition (a) or oxametallacyclic (d) formation which predominantly form epoxide rather than carbocationic intermediate (c) yielding benzaldehyde as major product. Furthermore in cases where there is absolute enantiomeric induction, the possibility of opening of oxametallacyclic intermediate to form a cyclic radical (c) and rotation of styrene $C_{\alpha} - C_{\beta}$ bond rotation can not be ruled out.

However, the construction of molecular models for these complexes (S form) Fig.3 suggests route (A) is more favourable as it stabilises the cyclic intermediate through stacking interactions between phenyl rings of styrene and PPh_3 present in the catalyst while the other orientation is less preferred due to the steric constraint thus restricting the formation of R styrene oxide.

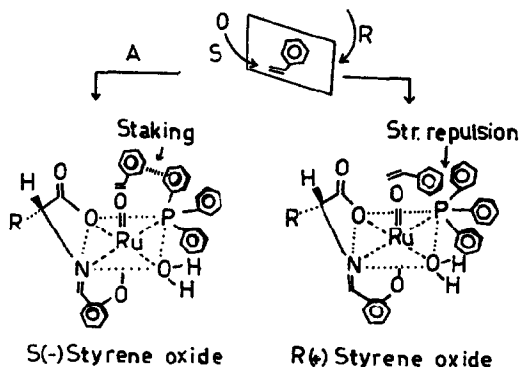


FIG.3
Molecular model of styrene in vicinity over the catalysts (1-6) in the transition state of oxygen transfer

Table - V Data for Asymmetric Epoxidation of Styrene by Chiral Ru(II) Schiff base complexes.

Catalysts ^b	Reacn. time, min.	% Conversion to Epoxide	ee, %	Confign ^a
1	30	12	80	S
2	30	17	68	S
3	120	38	50	S
4	30	15	70	S
5	60	16.5	65	S
6	60	14	76	S

^aMajor configuration of the epoxides of styrene was determined by comparison with authentic optically pure oxides, ^b(1 μ mol) of the catalyst was used.

Good optical yields were obtained in the oxidation of styrene in case of all the catalysts (1 - 6), specially complex 1 and 6 which yielded excellent enantiomeric excesses Table V. However, it is difficult to draw any conclusion for the role of substituents R in yielding higher enantiomeric excess.

Experimental

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ was from Johnson and Mathey, PPh_3 (Sisco), salicylaldehyde, L-alanine (L-ala), L-valine (L-val), L-Serine (L-Ser) L-Arginine (L-Arg), L-Aspartic acid (L-Asp), tris[3-(heptafluoropropyl)hydroxy methylene -(+) camphorato] europium(III) (Aldrich) were used as such. All the chiral Schiff bases derived from salicylaldehyde and L-aminoacids were prepared by the reported procedure^{5,6}. The metal complex $[\text{RuCl}_2(\text{PPh}_3)_3]$ was synthesized by the known method¹⁵.

Preparation of the complexes 1 - 6

To degassed hot solution of acetone containing (1.0 mmol) of $[\text{RuCl}_2(\text{PPh}_3)_3]$ was refluxed with methanolic solution of the chiral Schiff bases (1.0 mmol) for 8 to 9 hrs in argon atmosphere. After completion of reaction as checked by TLC, the solution was filtered under argon atmosphere. The filtrate was concentrated on rotatory evaporator and then precipitated by diethyl ether. The complexes were filtered and washed with diethyl ether to remove excess of PPh_3 . The complexes were recrystallized in methanol/dichloromethane and dried in vacuo. Yield 60 - 65%. All the complexes are dark green in colour.

Physical Measurements

Microanalysis 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 DI-909. The IR spectra were recorded on Carl Zeiss Specord M-80 spectrophotometer in nujol mull/KBr. Electronic spectra were recorded on a Shimadzu UV/visible recording spectrophotometer model 160. ^1H , ^{13}C [^1H] and ^{31}P [^1H] NMR spectra were obtained on a Jeol FX-100 NMR spectrometer in CDCl_3 and chloroform using $[\text{Si}(\text{CH}_3)_4]$ as internal standard and operating at 99.55, 24.99 and 40.27 MHz. The purity of the solvent, substrate and analysis of the product was determined by GLC using Shimadzu GC-9A coupled with C-R.3A recorder using 2M long, 3mm I-D, 4 mm O.D. stainless steel column packed with SE30, 5%, mesh size 60 to 80 with FID detector, column temperature programmed between 70 to 170°C and injector temperature 200°C with nitrogen carrier gas flow 30 ml/min. Synthetic standards of the product was used to determine yields by comparison of peak height and area. Cyclic voltammogram, differential pulse voltammogram were recorded with a Princeton Applied Research (PAR) instrument using tetrabutylammonium perchlorate as supporting electrolyte in dichloromethane. The optical rotation of the complexes in dichloromethane was measured by polarimeter Atago, JAPAN. The C.D. spectra were recorded in dichloromethane by Jasco Machine Model J-20 JAPAN.

Reference

1. E.N.Jacobsen, W.Zhang, A.R.Muci, J.R.Ecker and L.Deng., *J. Am. Chem. Soc.* 1991, **113**, 7063.
2. J.T.Groves, P.Viski, *J. Org. Chem.* 1990, **55**, 3628.
3. Y.Naruta, F.Tani, K.Maruyama, *Chem. Lett.* 1989, 1269.
4. M.G.Finn, K.B.Sharpless, *An Asymmetric Synthesis* J.D.Morrison, Ed.,¹ Academic Press; New York, 1985, Vol.5, Chapter 8.
5. M.M.Taqi Khan, R.I.Kureshy and N.H.Khan, *Tetrahedron Asymmetry*, 1991, **2**, 1015.
6. M.M.Taqi Khan, N.H.Khan and R.I.Kureshy, *Tetrahedron Asymmetry*, 1992, **3**, 403.
7. D.A.Edwards and R.Richards, *J. Chem. Soc.Dalton Trans.*, 1975, 637.
8. K.Nakajima, K.Kojima, M.Kojima, J.Fujita, *Bull. Chem. Soc., Jpn.* 1990, **63**, 2620.
9. Y.Sasaki and M.Miyashita, *Inorg. Chim. Acta.*, 1991, **15**, 183.
- 10 L.J.Boucher, *Inorg. Nucl. Chem.*, 1974, **36**, 531.
11. K.Okamoto, M.Takari, T.Yonemura, T.Konno and J.Hidaka, *Inorg. Chim. Acta.* 1990, **31**, 175.
12. P.A.Hunt and B.P.Straughan, A.A.M.Ali, R.K.Harris and B.J.Say, *J. Chem. Soc., Dalton Trans.* 1990, 2131
13. C.Bianchini, P.J.Perez, M.Peruzzini, F.Zanobini and A.Vacca, *Inorg.Chem.*, 1991, **30**, 2790
14. F.M.Conroy - Lewis, A.D.Redhouse and S.J.Simpeen, *J. Organomet. Chem.*, 1990, **399**, 307.
15. T.F.Calson and S.D.Robinson, *Inorg. Chim. Acta.* 1988, **149**, 13.