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Enantioselective catalytic epoxidation of styrenes by iodosylbenzene using chiral ruthenium(II) Schiff base complexes

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Abstract

Chiral ruthenium(II) Schiff base complexes **1–3** derived from L-histidine with salicylaldehyde, 5-chloro and 5-methoxy salicylaldehyde were prepared and used for catalytic enantioselective epoxidation of non-functionalised olefins, viz., styrene, 3-methyl-, 3-methoxy-, 3-chloro- and 3-nitrostyrene, with iodosylbenzene as an oxidant, giving the highest ee (80%) for nitrostyrene with catalyst **3**. Each catalyst/substrate combination was examined under epoxidation conditions and the results for catalysts **1–3** are presented as Hammet plots. The existence of a possible intermediate and the mechanism of chiral induction are discussed. The stacking/charge transfer interaction between the substrate and triphenyl phosphine of chiral Ru(II) catalyst at oxo-transfer stage seem to function favouring *S*(−) styrene oxide as dominant enantiomer.

Keywords: Enantioselectivity; Epoxidation; Ruthenium; Schiff bases; Styrene

1. Introduction

Enantioselective epoxidation is of fundamental importance as a versatile intermediary functionality in synthetic chemistry and many efforts have been directed towards the exploitation of highly enantioselective epoxidation reactions of olefins [1–4]. Many efforts have been made on highly catalytic enantioselective epoxidation of allylic alcohols using $Ti(OiPr)_4$/diethyl tartrate/t-butyl hydroperoxide system [5] but the study of enantioselective epoxidation of olefins which do not bear a coordinating functional group is still a topic of current interest [6–9].

Several modified chiral metalloporphyrins [10], heme enzymes such as cytochrome *c* peroxidase [11] and chiral salen manganese(III) complexes [3,7,8,9,12,13] have been reported to exhibit catalytic enantioselective oxidation with good optical yields. Substantially higher enantioselectivities are observed in the oxidation of styrenes and *cis*-, *trans*-β-methyl styrenes to their corresponding oxides [14] with cytochrome P-450_{cam}.

In order to explore the detailed mechanistic analysis of an efficient catalyst we have synthesized and characterised the chiral Ru(II) Schiff base complexes using the chiral ligands derived from L-histidine with salicylaldehyde, 5-chloro- and 5-methoxysalicylaldehyde, and the asymmetric epoxidation of styrene 3-chloro-, 3-methyl-, 3-methoxy- and 3-nitrostyrene by iosodylbenzene which constitute good enantioselective non-enzymatic olefin epoxidation catalysts thus far reported in which asymmetric induction results solely from

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non-bonded interaction [4,6]. The mechanism of oxygen transfer and chiral induction has been discussed in terms of stacking/charge transfer interactions between substrate and triphenylphosphine of the ruthenium(II) chiral catalyst.

2. Experimental

All reagents were of analytical grade, commercially available, and used as received. $RuCl_3 \cdot 3H_2O$ was from Johnson Matthey triphenylphosphine (Sisco), salicylaldehyde, 5-chloro-, 5-methoxysalicylaldehyde L-histidine, styrene, 3-chloro, 3-methyl-, 3-methoxy- and 3-nitrostyrene, tris (3-(heptafluoropropylhydroxymethylene) camphorato (+) europium(III) (Aldrich) were used as received.

All manipulations in the synthesis were carried out with the use of vacuum line and Schlenk tube. All solvents, after drying over the appropriate drying agents, were vacuum transferred. All the chiral Schiff bases, Sal–His, 5-Cl·Sal–His and 5-MeO·Sal–His [15], the starting complex $RuCl_3(PPh_3)_3$ [16] were prepared by published procedures. Authentic styrene oxide (Aldrich), and the 3-chloro-, 3-methyl-, 3-methoxy-, 3-nitrostyrene oxides were prepared according to the published methods [17]. The complexes prepared were: Ru(Sal–His)$(PPh_3)(H_2O)_2$ (**1**), Ru(5Cl·Sal–His)$(PPh_3)(H_2O)_2$ (**2**), Ru(5MeO·Sal–His)$(PPh_3)(H_2O)_2$ (**3**).

A hot solution of the appropriate Schiff base ligand (0.348 g, 0.382 g, 0.362 g, 1.0 mmol in dry methanol 20 cm^3) was added to a solution of $RuCl_2(PPh_3)_3$ (0.959 g, 1.0 mmol in dry acetone 50 cm^3). The reaction mixture was refluxed on a steam bath till completion of the reaction 6–8 h, checked on TLC. After that the solution was filtered and subsequently concentrated to 10 cm^3. The desired complex was precipiated and washed by the addition of oxide-free diethyl ether. The complexes were recrystallised from methanol/dichloromethane and dried in vacuo (yields 68% for **1**, 69% for **2** and 68% for **3**.

1. Analysis: found (calculated) $C_{31}H_{31}N_3O_5PRu$: C, 56.4 (56.6); H, 4.7 (4.8); N, 6.4 (6.4)%; IR (KBr) cm^{-1}, 1600 ν (H–C=N) + $\nu_{asy}(COO^-)$, 1440 $\nu_{syn}(COO^-)$, 3300 ν(OH), 1620, 620 δ(OH). Far IR (Nujol) 510 ν(Ru–P), 340 ν(Ru–N), ^1H NMR ($CDCl_3$) δ 2.17 (–CH,t), 8.12 (–CH=N,s), 6.12–7.17. 7.40 (phenyl, histidine ring, m). $^{13}C\{^1H\}$ NMR (ppm) CH_2Cl_2, 54.90 (–CH), 198.0 (COO^-), 159.2 (–CH=N), 131.1, 128.10, 126.3 (phenyl and histidine ring). $^{31}P\{^1H\}$ NMR (CH_2Cl_2), 32.0 (pph_3,s) UV/Vis (nm) (CH_2Cl_2) λ_{max} (ϵ), 320 (2499), 376 (1988), 664 (410); C.D. λ_{max} ($\Delta\epsilon$) (CH_2Cl_2) 580 (+8.1), 440 (−2.1), 370 (+1.1); $[\alpha]_d^t = -92.0$; configuration (*R*) Λ_M (methanol) 5 mho cm^{-1} mol^{-1}; C.V. oxidation V (ΔE_p mV) Ru(II)/Ru(III) +0.88 (190), reduction $V(\Delta E_p$ mV) Ru(II)/Ru(I) −0.20 (160).

2. Analysis: found (calculated) $C_{31}H_{30}ClN_3O_5PRu$: C, 53.7 (53.8); H, 4.4 (4.4); N, 6.1 (6.1)%/ IR (KBr) cm^{-1}: 1590 ν(H–C=N) + $\nu_{asy}(COO^-)$, 1435 $\nu_{sym}(COO^-)$, 3310 ν(OH), 1625, 620 δ (PH). Far IR (Nujol): 510 ν(Ru–P), 340 ν(Ru–N), ^1H NMR ($CDCl_3$), δ 2.32 (CH,t), 8.20 (CH=N,s), 6.30–7.20, 7.45 (phenyl, histidine ring, m). $^{13}C\{^1H\}$ NMR (ppm), CH_2Cl_2. 54.90 (–CH), 198.0 (COO^-), 160.4 (–CH=N), 132.1, 129.1, 127.4 (phenyl and histidine ring) $^{31}P\{^1H\}$ NMR CH_2Cl_2 31.8 (PPh_3,s); UV/Vis (nm) (CH_2Cl_2) $\lambda_{max}(\epsilon)$ 325 (2500), 385 (2238), 649 (873): C.D.$\lambda_{max}(\Delta\epsilon)$ (CH_2Cl_2) 585 (+1.1), 445 (−1.25), 380 (+3.8), $[\alpha]_D^t = -77.6$; configuration (*R*), Λ_M (CH_3OH), 4 mho cm^{-1} mol^{-1}: C.V. oxidation V (ΔE_p, mV) (Ru(II)/Ru(III) +0.76 (90), reduction V (ΔE_p, mV) Ru(II)/Ru(I) −0.17 (120).

3. Analysis: found (calculated) $C_{32}H_{33}N_3O_6$ PRu; C, 55.6 (55.9); H, 4.5 (4.8); N, 6.0 (6.1). IR (KBr): 1605 ν (H–C=N) + $\nu_{asy}(COO^-)$, 1430 $\nu_{sym}(COO^-)$, 3350 ν(OH), 1615, 615 δ(OH); Far IR (Nujol) 515 ν(Ru–P), 345 ν (Ru–N): ^1H NMR ($CDCl_3$) δ 2.08 (CH,t) 8.10 (H–C=N,s) 6.00–7.1, 7.35 (phenyl and histidine ring, m). $^{13}C\{^1H\}$ NMR (ppm) (CH_2Cl_2) 54.2

(–CH), 197.2 (COO^-) 158.5 (H–C=N), 130, 128.1, 127 (phenyl, histidine ring), $^{31}P\{^1H\}$ NMR (CH_2Cl_2) 32.8 (PPh_3,s): UV/Vis (nm) CH_2Cl_2 μ_{max} (ϵ): 317 (2499), 346 (2498), 380 (1870), 719 (643): C.D. λ_{max} ($\Delta\epsilon$) CH_2Cl_2 570 (+0.80), 445 (−1.25), 360 (+2.5), $[\alpha]_D^t$ = −74.2; configuration (*R*) Λ_M (CH_3OH) 3 mho cm^{-1} mol^{-1}; C.V. oxidation V (ΔE_p, mV) Ru(II)/Ru(III); +0.90 (152); reduction V (ΔE_p, mV) Ru(II)/Ru(I); −0.26 (150).

3. Methods

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 a Carl Zeiss Specord M-80 spectrophotometer as Nujol mull on KBr pellets. Electronic spectra were recorded on a Shimadzu UV/Vis recording spectrophotometer model 160. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were obtained on a JEOL FX-100 NMR spectrometer in $CDCl_3$ operating at 99.55, 24.99 and 40.27 MHz respectively. The purity of solvent, substrate and analysis of the product was determined by GLC using Shimadzu GC-9A coupled with C-R/3A recorder using 2 m long, 3 mm ID, 4 mm OD stainless steel column packed with SE 30, 5% mesh size 60 to 80 with FID detector, column temperature programmed between 70 and 170°C and injector temperature 200°C with nitrogen carrier gas flow 30 ml/min. Synthetic standards of the products were used to determine yields by comparison of peak height and area. Cyclic voltammograms, differential pulse voltammograms were recorded with a Princeton Applied Research (PAR) instrument using tetrabutyl ammonium 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.

3.1. Epoxidation of styrenes by the catalyst **1–3**

The epoxidation reaction by the catalysts and iodosylbenzene was carried by the given procedure: the chiral catalyst (0.01 M) styrene or substituted styrene (0.5 M) and n-tridecane (0.05 M) as GLC internal standard were dissolved in degassed dry CH_2Cl_2 (2.5 cm^3). Reaction was initiated by the addition of iodosyl benzene (0.25 M) and stirred at constant speed in inert atmosphere at low temperature (in the dark). After each interval of 10 min an aliquot was taken from the reaction mixture and analysed by GLC. After the reaction had gone to completion the solvent was removed and the organic material was taken up in diethyl ether which was subsequently removed and the sample was taken in $CDCl_2$ for ^1H NMR studies. Chiral shift reagent Eu(hfc)$_3$ was employed to the above sample for calculating enantiomeric excess.

4. Results and discussion

The chiral catalysts **1–3** were isolated as neutral complexes in good yield using a straightforward synthetic route [18,19] involving condensation of L-histidine with salicylaldehyde, 5-chloro- and 5-methoxysalicylaldehyde followed by insertion of ruthenium(II) center.

The epoxidations catalysed by **1–3** were examined with styrene, 3-chloro-, 3-methyl-, 3-methoxy- and 3-nitrostyrene as substrate and iodosylbenzene as oxidant in dichloromethane in order to assess the enantioselectivities in epoxidation by changing the substituent either on the catalyst or on substrate, respectively. All the complexes showed catalytic activity and characteristic enantioselectivity, as summarised in Table 1. The styrenes were difficult to be oxygenated by iodosylbenzene in absence of the catalyst under the identical conditions.

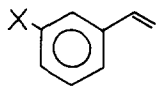
Optical yields for these reactions were conveniently measured using the chiral shift reagent tris[3-(heptafluoropropylhydroxymethylene) (+)-camphorato]europium(III) Eu(hfc)$_3$. In all

Table 1
Data for enantioselective epoxidation of styrenes by chiral Ru(II) Schiff base complexes

Schiff complex no.	Catalyst[b]	$XC_6H_4CH=CH_2$[c] X=	Reaction time/min	Conversion to epoxide (%)	ee (%)	Config.[a]
1	[(Sal–His) (triphenylphosphino) diaquo ruthenium(II)[d]	H	30	30	53	*S*
		CH_3	30	25	60	*S*
		Cl	30	32	50	*S*
		NO_2	30	45	75	*S*
		OCH_3	30	32	54	*S*
2	[(5-Cl·Sal–His) (triphenylphosphino) diaquo ruthenium(II)[e]	H	90	41	38	*S*
		CH_3	90	35	22	*S*
		Cl	90	44	44	*S*
		NO_2	90	55	70	*S*
		OCH_3	90	32	32	*S*
3	[(5-MeO·Sal–His) (triphenylphosphino) diaquo ruthenium(II)[f]	H	30	44	58	*S*
		CH_3	30	30	55	*S*
		Cl	30	48	72	*S*
		NO_2	30	60	80	*S*
		OCH_3	30	27	45	*S*

[a]Configurations of epoxide of styrene and substituted styrenes were determined by comparison with authentic optically pure oxides.
[b]0.01 M of the catalysts were used.

[c]$XC_6H_4CH=CH_2$ =



[d]Sal–$HisH_2$ = [4-(2-salicylidineaminato)-2-carboxyethyl]imidazole.
[e]5-Cl·Sal–$HisH_2$ = [4-(5-chloro-2-salicylideneaminato)-2-carboxyethyl]imidazole.
[f]5-MeO·Sal–$HisH_2$ = [4-(5-methoxy-2-salicylidineaminato)-2-carboxyethyl]imidazole.

of the cases ^1H NMR shows a set of three peaks with a doublet of doublets and two triplits between δ 2.6–3.2 ppm assigned to the product epoxide. The peak for the H trans to the phenyl ring appearing at $\approx$3 ppm was shifted downfield and was split into two sets of triplets between δ 3.8–4.4 ppm when treated with several equivalents of the chiral shift reagent [Eu(hfc)$_3$]. The less downfield shifted the *R* isomer peak which was confirmed by the increase in the respective peak intensities when enantiomerically pure *S*(−) and *R*(+) styrene oxide was added to the test samples, respectively.

The employment of *R* form of the catalyst **1–3** resulted in the formation of *S*(−) styrene oxide as dominant enantiomer. Good optical yields were obtained with the catalysts **3** and **1** with an enantiomeric excess recorded in the case of electron deficient 3-nitrostyrene of 80% (catalysed by **3**) and 75% (catalysed by **1**). These values are consistent with those reported for the chiral Mn(III) Schiff bases [3,7,13].

The mechanism for determining absolution configuration of the product *S*(−) styrene epoxide from the *R* form of the catalyst can be understood by an idealised molecular model construction of the Ru(II) oxo complex (Fig. 1). Inspection of this model reveals that the substrate styrene approach to give the *R*(+) form (route A) of the product is prohibited due to steric constraints which become more pronounced for ring-substituted styrenes. In addition to the steric feasibility to form *S*(−) styrene oxide (route B) there is a distinct possibility of π–π^* interaction between phenyl rings of styrene and triphenyl phosphine present in the catalyst. Higher ee's in case of electron withdrawing substituent on styrene phenyl ring as in case of nitrostyrene further

strengthen this presumption. The role of electron donating or withdrawing groups on the phenyl group of the Schiff base in the catalyst **1–3** can be explained on the basis of metal mediated electron transfer to the triphenylphosphine phenyl ring and the stability of catalytically active oxo species.

The results obtained for enantioselectivity for each catalyst and substrate are presented as Hammet plots (Fig. 2a, 2b) which show a clear trend with respect to the substituents either on *para* or *meta* position. In all the cases with electron donating groups on the catalyst and electron withdrawing group on substrate lead to higher enantioselectivities (ees) in epoxidation and this corresponds to a remarkable selectivity difference $\Delta(\Delta G^*)$ 0.95 KCl/mol for catalyst **3**. Further, that there is only trace amount formation of arylacetoaldehyde in all the catalytic runs suggests the rate of H rearrangement (Fig. 3 path a) is much lower than the rate of oxygen attack (Fig. 3 path c) and thus giving the higher epoxide formation. Furthermore, racemisation of the product (epoxide) can occur if the rate of attack of oxygen on carboncationic species (Fig. 3, path c) is some-

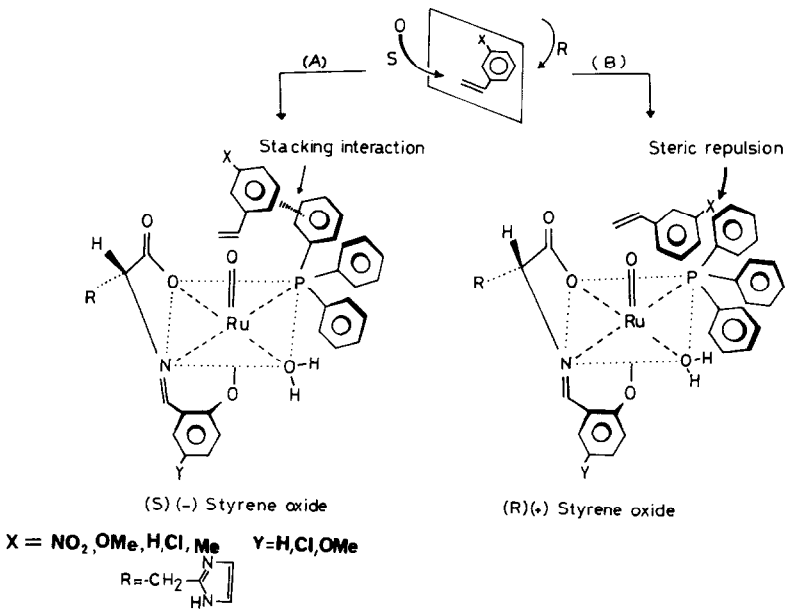


Fig. 1.

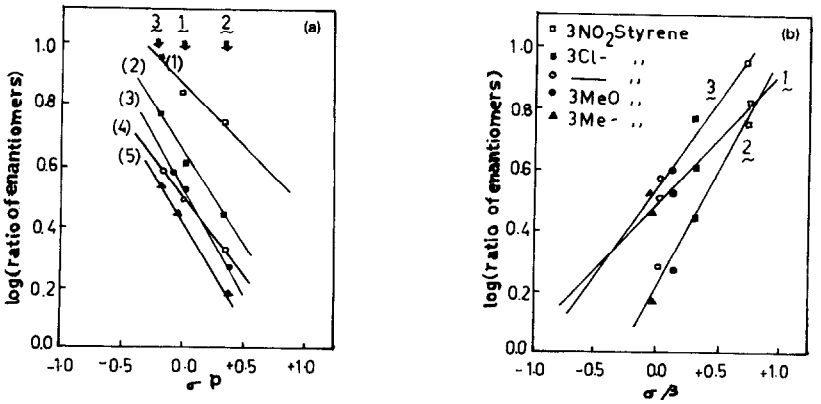
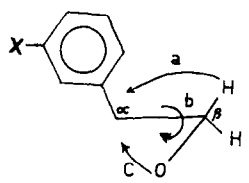


Fig. 2.



X = H, Cl, OMe, Me, NO_2

Fig. 3.

what lower than the rotation of the C_α–B_β bond of styrene (Fig. 3 path b). The rate of oxygen attack and the rate of rotation along the C_α–C_β bond would however depend upon the stability of carboncationic species. It is evident from the ees in our catalytic runs, that the presence of an electron donating group on styrene yielded lower ees via rapid electron transfer to the C_α cation from the styrene phenyl ring thus stabilising the cation and so lowering the oxygen attack. By contrast, in the oxidation of the electron deficient styrenes, slower electron transfer and simultaneous rapid oxygen attack on the very unstable cation greatly increased the ees. This proposed mechanism is based on the product distribution formed in our catalytic runs. However, the other route e.g. concerted oxygen addition or oxametallocyclic formation and formation of a cyclic radical, cannot be entirely ruled out as discussed in our previous communication [18].

5. Conclusion

In this paper we have elucidated the catalytic enantioselectic epoxidation of styrene and substituted styrenes using chiral ruthenium(II) Schiff base complexes with iodosylbenzene as oxidant and have obtained good chiral induction in the oxidation of electron deficient nitrostyrene with 80% ee with catalyst **3**. The correlation between the optical yield and electronic properties of the substrate and catalysts used are explained with respect to the proposed mechanism through stacking/CT interaction between the substrate and PPh_3 of the ruthenium(II) catalyst at the oxo transfer stage resulted in the formation of $S(-)$ styrene oxide as the dominant enantiomer.

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