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# Highly efficient asymmetric epoxidation of alkenes with a novel chiral complex of ruthenium(III) containing a sugar based ligand and triphenylphosphines

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**Abstract**

Mixed-ligand complexes of ruthenium(III) containing tridentate chiral Schiff-base ligands ($H_2TDL^*$s) derived from condensation of either D-glucose amine or L-alanine with 3,5-di-tertiarybutylsalicyldehyde, and triphenylphosphine ($PPh_3$) or 2,2′-bipyridine (bipy) have been synthesized. The ruthenium(III)-complexes, $[Ru^{III}Cl(TDL_1^*)(PPh_3)_2]$ {($H_2TDL_1^*$ = *N*-3, 5-di-(tertiarybutyl)salicylidine-D-glucosamine)},(**1**) $[Ru^{III}Cl(TDL_2^*)(PPh_3)_2]$ $H_2TDL_2^*$ = {*N*-3, 5-di-(tertiarybutyl)salicylidine-L-alanine} (**2**) and $[Ru^{III}(TDL_2^*)(bipy)H_2O]Cl$ (bipy = 2,2′-bipyridine) (**3**) were characterized by analytical, spectral (UV–vis and IR), molar conductivity, magnetic moment and electrochemical studies. Complex **1** exhibited remarkable enantioselcetivity toward epoxidation of unfunctionalized alkenes using *tert*-butylhydroperoxide (*t*-BuOOH) as terminal oxidant. Styrene, 4-chlorostyrene, 4-methylstyrene, 4-methoxystyrene, 1-methylcyclohexene and 1,2-dihydronaphthalene were effectively converted to their organic epoxides in the 70–95% ee at ambient temperature. A lesser enantioselectivity was observed when complexes **2** and **3** were used in the epoxidation of enlisted alkenes under identical experimental conditions. A mechanism involving intermediacy of a high-valent Ru(V)-oxo species is proposed for the catalytic epoxidation process.


*Keywords:* Ruthenium complex; *t*-BuOOH; Alkenes; Epoxidation; Enantioselectivity

## 1. Introduction

Transition metal complexes catalyzed asymmetric epoxidation of simple alkenes remains a current interest as it offers an efficient and elegant possibility for synthesis of enantiomerically pure compounds [1]. In the field of asymmetric catalysis, manganese Schiff base catalysts [2] have successfully extended the scope of the epoxidation reaction to unfunctionalised alkenes, however, Mn-catalyzed reactions often require 2.5–5 mol% catalyst with low product turnover (seldom exceeding 100), and the instability of such chiral Mn-complexes remains to be addressed [2]. Thus, there is a considerable interest in the development of alternative catalytic systems. In this regard, ruthenium complexes by virtue of their wider range of stable, but chemically accessible oxidation states have been subject of many recent investigations [3–8]. Ruthenium complexes of various chiral ligands, viz. porphyrins, Schiff-base, polypyridyl, pyridinebisoxazolines (pybox), pyridinebisimidazoline (pybim) are recently known to perform asymmetric epoxidation of unfunctionalized alkenes with moderate to high enantioselectivity.

In general, the choice and synthesis of a suitable chiral controller ligand is the crucial step in the development of a new catalyst for enantioselective reactions. Although many chiral ligands (with variety of donor atoms), viz. porphyrins [3], pyridinebisoxazolines [4], pyridinebisimidazoline [5], Schiff-base [6], polypyridyl [7], chiral phosphine (PNNP) [8], tartrate derivatives [9] and phosphinooxazolines [10] are known today and used comprehensively for asymmetric catalytic reactions, there is still an increasing need for new and improved ligands which can afford the following advantages; that the ligand should conveniently be prepared from the commercially available starting materials and most importantly that the cat-

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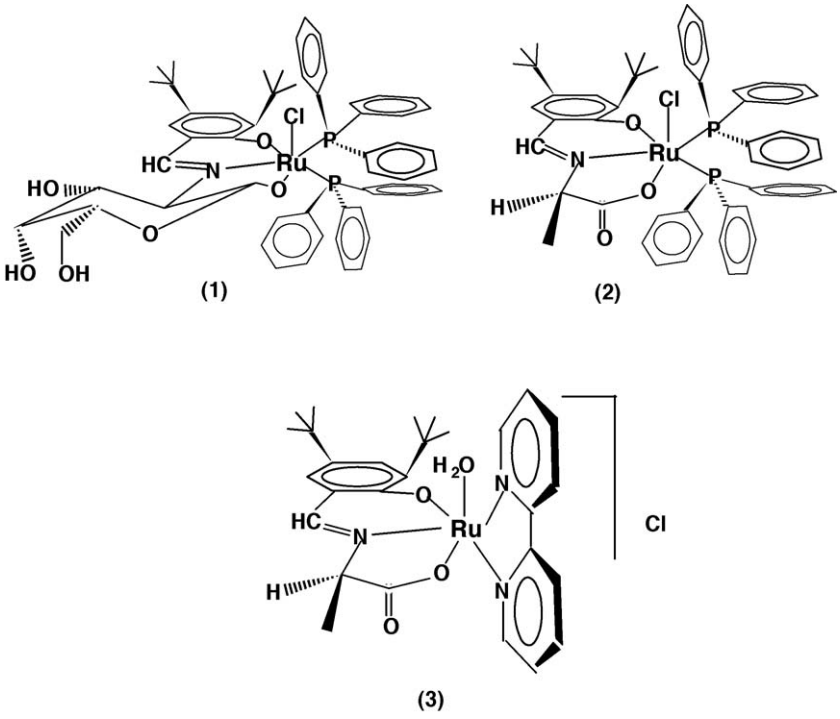



Fig. 1. Schematic representation of complexes **1**–**3**.

alysts prepared from the ligand should be highly selective, efficient and productive. In this content we are attracted to the chiral ligands derived from carbohydrates which are naturally occurring enantiomerically pure compounds ("chiral pool") [11] Furthermore, reports on the asymmetric epoxidation of olefins catalyzed by transition metal complexes containing sugar-based ligands are few in the literature [12]. Very recently, we have reported [13] the synthesis and catalytic activity of a novel ruthenium complex that contains a tridentate (O,N,O) chiral ligand, *N*-3,5-ditertiarybutylsalicylidine-D-glucosamine (hereafter designated as $H_2TDL_1^*$) derived from the condensation of a saccharide containing a $NH_2$ group (D-glucose amine) with 3,5-di-(tertiarybutyl)salicylaldehyde [13]. We have shown [14] that the $[Ru^{III}(TDL_1^*)(bipy)H_2O]Cl$ (bipy = 2,2′-bipyridine) catalyst complex in presence of *tert*-butylhydroperoxide (*t*-BuOOH) as terminal oxidant, epoxidizes styrenes and other alkenes with moderate enantioselectivity (37–47%). In order to examine the effect of changes in the parent ($H_2TDL^*$) as well as ancillary (XY) ligands on the efficacy and selectivity of $[Ru^{III}Cl(TDL^*)(XY)]$ catalyzed alkene epoxidation reaction, we have synthesized the following ruthenium complexes, $[Ru^{III}Cl(TDL_1^*)(PPh_3)_2]$ (**1**), $[Ru^{III}Cl(TDL_2^*)(PPh_3)_2]$ (**2**) and $[Ru^{III}(TDL_1^*)(bipy)H_2O]Cl$ (**3**) (where $H_2TDL_1^*$ = *N*-3, 5-di-(tertiarybutyl)salicylidine-D-glucosamine, $H_2TDL_2^*$ = *N*-3, 5-di-(tertiarybutyl)salicylidine-L-alanine and bipy = 2,2′-bipyridyl) in the present investigation. Pictorial representation of **1**–**3** is shown in Fig. 1. We report herein, the syntheses, characterization and catalytic activity of such ruthenium(III) complexes towards epoxidation of styrenes and other alkenes using *t*-BuOOH as terminal oxidant.

## 2. Experimental

### 2.1. Synthesis of chiral ligands ($H_2TDL^*$)

The sugar based Schiff-base chiral ligand, *N*-3,5-di-(tertiarybutyl)salicylidine-D-glucosamine ($H_2TDL_1^*$) was prepared by following the procedure reported earlier [13]. The ligand, *N*-3,5-di-(tertiarybutyl)salicylidine-L-alanine ($H_2TDL_2^*$) was prepared by following method. To an argon purged methanolic solution (15 ml) of KOH (420 mg), amino acid (660 mg) was dissolved by strong agitation, and the solution was kept in ice-water bath. 3,5,-di-(tertiarybutyl)salicyldehyde (1.17 g) dissolved in methanol (10 ml) was then rapidly added to the ice-cooled alkaline solution of the amino acid, and the colour of the solution immediately turned yellow. The reaction mixture was stirred for 5 min and then subjected to evaporation at rota-evaporator. A mixture of hexane (10 ml) and di-ethylether (10 ml) was added to the residue and then filtered to remove the remaining amino acid salt. Evaporation of the filtrate yielded the desired ligand which was kept in a desiccator over $CaCl_2$. Yield, 70%. m.p 145 °C.

### 2.2. Synthesis of $[Ru^{III}Cl(TDL_1^*)(PPh_3)_2]$ (1)

Synthesis of $[Ru^{III}Cl(TDL_1^*)(PPh_3)_2]$ (**1**) was carried out by interacting $[RuCl_2(PPh_3)_3]$ complex was prepared by following the literature procedure [15] with $H_2TDL_1^*$. To a hot methanolic solution $H_2TDL_1^*$ solid sample of $[RuCl_2(PPh_3)_3]$ was added under stream of air to ensure the complete dissolution of the precursor complex. The resultant greenish solution was kept under

reflux for 8 h till it turned dark green, then cooled at room temperature and filtered to remove any undissolved particle. The filtrate was evaporated to dryness and the product complex was recystallized from dichloromethane and finally dried in desiccator over $CaCl_2$. Yield (75%). Anal. calculated for $C_{57}H_{61}NO_6P_2RuCl$: Calc. C, 65.0; H, 5.8; N, 1.3. Found. C, 65.8; H, 5.3; N, 1.3.

### 2.3. Synthesis of $[Ru^{III}Cl(TDL_2^*)(PPh_3)_2]$ (2)

$[Ru^{III}Cl(TDL_2^*)(PPh_3)_2]$ (**2**) was prepared in a manner similar to adopted for the synthesis of complex-**1**, except $H_2TDL_2^*$ was used in place of $H_2TDL_1^*$. Yield, 76%. Anal. calculated for $C_{54}H_{55}NO_3P_2RuCl$: Calc. C, 67.3; H, 5.7; N, 1.5. Found. C, 67.1; H, 5.7; N, 1.5.

### 2.4. Synthesis of $[Ru^{III}(TDL_2^*)(bipy)H_2O]Cl$ (3)

Precursor compound $K_2[RuCl_5]$ was prepared by following a literature procedure [16]. A methanolic solution of $K_2[RuCl_5]$ (1 mmol) and $H_2TDL_2^*$ (1 mmol) was refluxed for 12 h. 2,2′-Bipyridine (1 mmol) was added subsequently to the hot green solution and, refluxing was continued for another 8 h. The resultant solution was evaporated to dryness and the solid product was washed with water and recystallized in dichloromethane. Yield (70%). Anal. calculated for $C_{28}H_{35}N_3O_4RuCl$: Calc. C, 54.8; H, 5.7; N, 6.8. Found. C, 55.0; H, 6.1; N, 6.2.

### 2.5. Instrumentation

The UV–vis electronic absorption spectra were obtained on a Perkin Elmer (Model Lambda 35) spectrophotometer. IR spectra were collected on a Perkin Elmer (Model 783) spectrometer using KBr pellets. Electrochemical measurements were carried out in acetonitrile medium using tetraethylammoniumperchlorate (TEAP) as supporting electrolyte. A CH Electrochemical Instruments (CHI-660B) equipped with a platinum working electrode and Ag/AgCl as reference were used for this purpose. NMR studies were performed on a Bruker 300AC NMR spectrometer in $CD_3OD$. Magnetic susceptibility was measured by using a PAR-155 vibrating sample magnetometer. A Perkin-Elmer 240C elemental analyzer was used to collect microanalytical (C,H,N) data.

### 2.6. Procedure of catalytic studies

In a typical experiment 0.01 mmol of the catalyst complex, 1.0 mmol of 70% aqueous *t*-BuOOH oxidant and 1.0 mmol of substrate in 5 ml of $CH_2Cl_2$ were rapidly magnetically stirred at room temperature (25 °C). At the end of the reaction an internal standard (decane) was added and an alliquot was taken for GC analysis. GC analysis were performed with a Carlo Erba GC $8000^{Top}$ series on Tenax column fitted with FID. GC parameters were quantified with authentic samples of product prior to the analysis. The enantiopurity of epoxides was estimated by HPLC analysis (Shimadzu SPD-M10A equipped with diode array detector) was carried out for estimation of enantiomeric excess (ee) using Chiralcel OD-H column (mobile phase = 90% *n*-hexane/10% isopropyl alcohol). In all cases, conditions for determination of enantiomeric excess were set up with racemic epoxides.

## 3. Results and discussion

### 3.1. Characterization of ruthenium complexes

Complexes **1–3** (Fig. 1) have been characterized by analytical, spectral (UV–vis and IR), molar conductivity, magnetic moment and electrochemical studies (Table 1). In the absorption spectra of **1–3**, a number of bands are observed in the UV–vis region. The band appearing in the UV region are characterized by intra-ligand charge transition, whereas, bands displayed in the visible region are attributed to the ligand to metal charge transfer bands ($\pi \rightarrow t_{2g}$ origin). The basis of assignments is the spectral data reported for similar type of ruthenium(III)-complexes of ligands containing N,O and P donor atoms [14,17,18]. The IR spectra of the complexes exhibited bands usual for coordinated Schiff-base ligands (viz. 1620–1640 $cm^{-1}$ for C=N stretch). The magnetic moments of complexes **1–3** indicate the low-spin $d^5$ configurations (idealized $t_{2g}^5$, $S = 1/2$). Conductance data (Table 1) established that the complex **3** is 1:1 electrolyte nature, whereas, complexes **1** and **2** are non-electrolyte in solution.

Cyclic voltammogram of **1–3** in displayed quasi-reversible $Ru^{III}/Ru^{II}$ redox couples with a peak-to-peak separation ($\Delta E$) values lie in the range 80–120 mV. A representative cyclic voltammogram is displayed in Fig. 2 and the $E_{1/2}$ values corresponding to the $Ru^{III}/Ru^{II}$ redox couple estimated from the cyclic voltammetric studies are listed in Table 1. The $E_{1/2}$ value

Table 1
Spectral (UV–vis and IR), molar conductance, magnetic moment and electrochemical data of **1–3**

| Complex | UV–vis $\lambda_{max}$ (nm) ($\varepsilon$/$mol^{-1}$, $dm^3$, $cm^{-1}$) | IR ($cm^{-1}$) | $\Lambda_M$ in MeOH (ohms$^{-1}$ $cm^2$ $mol^{-1}$) | $\mu_{eff}$ (B.M) | $E_{1/2}$ ($Ru^{III}/Ru^{II}$) (V against Ag/AgCl) | $\Delta E$ (mV) |
|---|---|---|---|---|---|---|
| 1 | 623 (1475), 350 (4776) | 3650, 3055, 2954, 1957, 1577, 1479, 1435, 1252, 1186, 1118, 721, 695 | 19.5 | 1.91 | 0.30 | 118 |
| 2 | 687 (2202), 349 (9182) | 3467, 3055, 2954, 1956, 1609, 1481, 1435, 1251, 1182, 1118, 997, 929, 750, 722, 695, 539, 456 | 17.2 | 1.87 | 0.37 | 122 |
| 3 | 660 (1290), 347 (10640), 263 (28754) | 3460, 2960, 1642, 1610, 1440, 1310, 1242, 1172, 1030, 760, 730 | 93.6 | 1.93 | 0.32 | 106 |

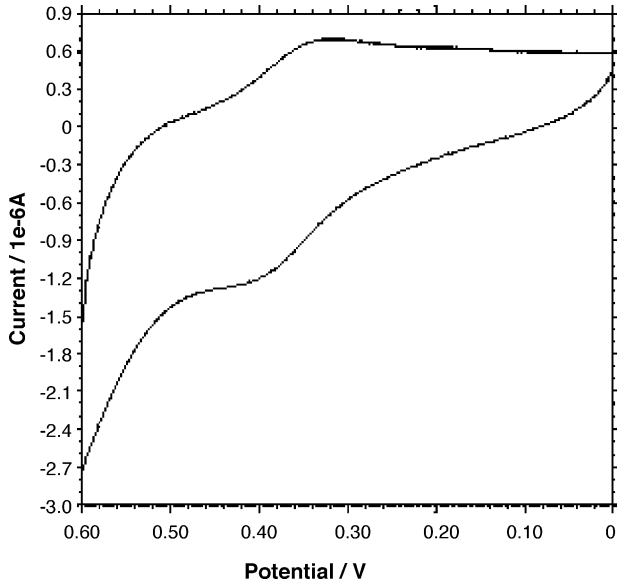



Fig. 2. Cyclic voltammogram of **2** in $CH_3CN$.

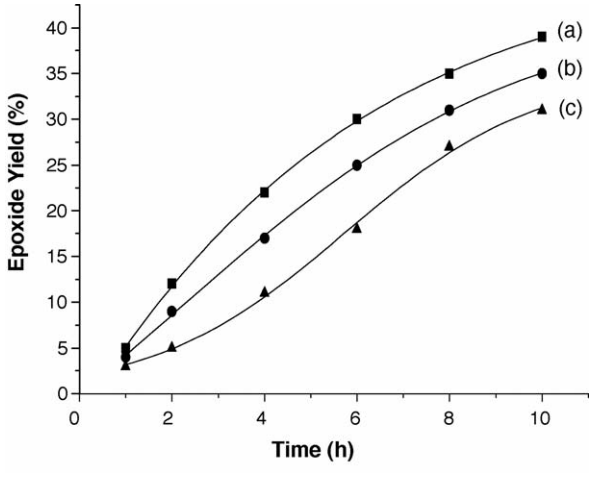



Fig. 3. Time course for the ruthenium complexes catalyzed epoxidation of styrene at room temperature. (a) **2** as catalyst, (b) **1** as catalyst and (c) **3** as catalyst.

of **1** is more cathodic than that of **2**. This is qualitatively consistent with superior electron withdrawing ability of carboxylate group in $TDL_2^{*2-}$ compared to glycosidic oxygen donor in $TDL_1^{*2-}$. Coordination of glycosidic O atom enhances the electron density on the ruthenium center and shifts the oxidation potential to a more negative as observed for **1** as compared to **2** in the present case.

### 3.2. Catalysis of alkene epoxidation

The results of oxidation of styrenes and other alkenes catalyzed by **1–3** using *t*-BuOOH as a terminal oxidant are summarized in Table 2. In all cases, epoxides were found to be the major product, however, minor amounts of benzaldehyde was also obtained in each case (Table 2). As shown in the time course of the enantioselective epoxidation of styrene using complexes **1–3** (Fig. 3), the epoxide formation followed a slow reaction progress with less than 3–5% epoxide formation in the first 1 h.

Catalytic activity of **1–3** was evaluated using 4-chlorostyrene as test substrate. We have carried out four successive reactions by sequential adding of fresh substrate (1.0 mmol) and *t*-BuOOH (1.0 mmol) to the catalytic mixture at an interval of 10 h for a period of 40 h and the decrease in product yield in each case are summarized in Table 3. As seen in Table 3, the catalytic activity of **1–3** decreases with successive uses, however, overall enantioselectivity was found to be identical with that observed in a single catalytic run. During the course of the reaction, however, the activity of the catalytic process goes down considerably since an increasing amount of *t*-BuOH formed in the catalytic process competes in parallel with *t*-BuOOH for the same coordination site in the catalyst complexes (**1–3**). However, no significant changes observed in the spectral features of the **1–3** at the end of the catalytic runs essentially suggests that **1–3** are reasonably stable under the specified turnover conditions. Further, the drop

Table 2
Results of epoxidation of styrenes at ambient conditions[a]

| Substrate | Product | 1 | | 2 | | 3 | |
|---|---|---|---|---|---|---|---|
| | | Yield[b,c] (%) | ee | Yield[b,c] (%) | ee | Yield[b,c] (%) | ee |
| Styrene | Styrene oxide | 43 | 84 | 47 | 57 | 45 | 40 |
| | Benzaldehyde | 8 | | 17 | | 11 | |
| 4-Chlorostyrene | 4-Chlorostyrene oxide | 45 | 94 | 47 | 61 | 47 | 37 |
| | 4-Chlorobenzaldehyde | 14 | | 15 | | 10 | |
| 4-Methylstyrene | 4-Methylstyrene oxide | 39 | 87 | 40 | 58 | 42 | 40 |
| | 4-Methylbenzaldehyde | 18 | | 18 | | 9 | |
| 4-Methoxystyrene | 4-Methoxystyrene oxide | 41 | 90 | 37 | 52 | 41 | 35 |
| | 4-Methoxybenzaldehyde | 15 | | 15 | | 12 | |
| 1-Methylcyclohexene | 1-Methylcyclohexene oxide | 33 | 65 | 35 | 56 | 37 | 41 |
| 1,2-Dihydronaphthalene | 1,2-Dihydronapthalene oxide | 44 | 67 | 43 | 55 | 49 | 42 |

[a] See experimental for turn-over conditions.
[b] Based on substrate concentration.
[c] After 12 h.

Table 3
Results of four consecutive run for the **1–3** catalyzed epoxidation of 4-chlorostyrenes at ambient conditions[a]

| Catalytic run | Reaction time (h) | Catalyst | | | | | |
|---|---|---|---|---|---|---|---|
| | | **1** | | **2** | | **3** | |
| | | Yield | ee | Yield | ee | Yield | ee |
| Run-1 | 10 | 43 | 94 | 47 | 61 | 45 | 37 |
| Run-2 | 10 | 37 | 92 | 39 | 58 | 31 | 39 |
| Run-3 | 10 | 29 | 91 | 24 | 60 | 28 | 36 |
| Run-4 | 10 | 19 | 95 | 17 | 57 | 19 | 35 |

of epoxide yield is evidently associated with the over-oxidation of epoxide under specified conditions. Over-oxidation of epoxide was evidenced by an independent experiment using authentic sample of styrene epoxide (employed as substrate in place of styrene). Reaction of styrene epoxide (1.0 mmol) with *t*-BuOOH (1.0 mmol) and **1–3** (0.01 mmol) in dichloromethane at room temperature resulted in depletion of styrene epoxide (10–15%) in the reaction mixture within 12 h, and benzaldehyde was found to be predominant reaction product as evidenced gas chromatographically.

Treatment of complexes **1–3** with *t*-BuOOH has been considered to give the corresponding Ru(V)-oxo complex. Spectral changes that occurred upon addition of *t*-BuOOH to the solution of catalyst complexes **1–3** (as shown typically in Fig. 4) is attributed to the formation of Ru(V)-oxo species. It had been reported earlier [19] that in the UV–vis spectra, the characteristic $d_{xy} \rightarrow d_{\pi^*}$ charge transition band of Ru(V)-oxo complexes appears in the wave length range 420–450 nm. The UV–vis spectra of the ensuing solution obtained by reacting precursor catalyst complexes (**1–3**) with *t*-BuOOH showed spectral features comparable to that of Ru(V)-oxo complexes reported earlier [19]. The IR spectra of the solid mass obtained by evaporation of the resultant solution (that showed the spectra of $Ru^{V}$-oxo species) exhibited bands in the range 850–865 $cm^{-1}$, which are assignable to $\nu_{Ru=O}$ stretch [19]. These bands were not found in the IR spectra of complexes **1–3** themselves. However,

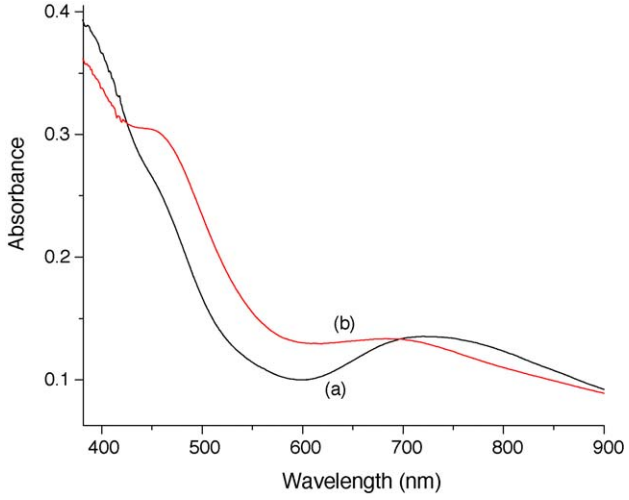



Fig. 4. Spectra of (a) **2** ($1 \times 10^{-4}$ M) and (b) **2** + *t*-BuOOH to in $CH_2Cl_2$.

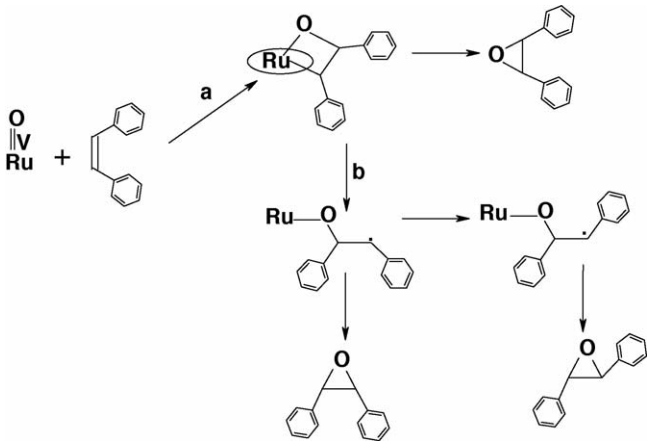
Table 4
Results of epoxidation of *cis*-stilbene and *trans*-stilbene catalyzed by the **1–3** at ambient conditions

| Substrate | Product | Yield (%)[a] | | |
|---|---|---|---|---|
| | | Catalyst | | |
| | | **1** | **2** | **3** |
| *cis*-Stilbene | *cis*-Stilbeneoxide | 40 | 42 | 41 |
| | *trans*-Stilbeneoxide | <1 | 12 | 10 |
| | Benzaldehyde | 15 | 17 | 12 |
| *trans*-Stilbene | *cis*-Stilbeneoxide | Not detected | Not detected | Not detected |
| | *trans*-Stilbeneoxide | 44 | 43 | 46 |
| | Benzaldehyde | 12 | 15 | 10 |

[a] Identification and quantification of epoxides of stilbenes were carried out by following an earlier report on the $^1$H NMR analysis of stilbene epoxides (Ref. [20]), wherein, the peaks at 3.90 and 4.31 ppm were assigned to *trans*-stilbene oxide and *cis*-stilbene oxide, respectively.

IR spectral bands concerning coordination of other ligands (viz. $TDL^{*2-}$, bipy and $PPh_3$) were found to be similar to those noted in the IR spectra of precursor complexes **1–3**. This essentially indicates that the coordinated ligands in the catalyst complexes **1–3** are reasonably stable and remain unchanged during catalytic process under the specified conditions.

In order to know the stereoselectivity of the epoxidation process and the nature of intermediate formed in the oxygen atom transfer from Ru(V)-oxo species to alkenes, *cis*-stilbene was used as a probe. The stereo-retentive product formation, i.e. *cis*- to *cis*-epoxide and *trans*- to *trans*-epoxide (Table 4), suggests that in case of complex-**1** catalyzed epoxidation, the reaction proceeds via formation of a metallaoxetane intermediate (path 'a' in Scheme 1). On the other hand, a mixture of epoxides was produced (Table 4) during epoxidation of *cis*-stilbene when **2** and **3** were used as catalyst. It seems plausible to postulate that transfer of oxo-atom to olefins could also involve a radicaloid intermediate species which would allow a limited amount of rotation through –C–C– bond prior to the epoxide formation (path 'b' in Scheme 1). The enantioselectivity of the reaction is plausibly determined by enantioface selectivity in the metallaoxetane formation. The sense of chirality induced is controlled




Scheme 1. Pathways for epoxide formation.

Table 5
Comparison of **1**/*t*-BuOOH catalytic system with other related systems for asymmetric oxidation of syrene to styrene epoxide

| Catalytic system | Yield (%) | ee (%) | Time (h) | Reference |
|---|---|---|---|---|
| **1**–**3**/*t*-BuOOH | 43–47 | 42–84 | 12 | Present work |
| $[Ru^{IV}(D_4\text{-}Por^*)Cl_2]/Cl_2PyNO$[a] | 84 | 69 | 1.5 | [3] |
| $[Ru^{II}(S,S'\text{-}Pr_2\text{-}pybox)(pydic)]/PhI(OAc)_2$[b] | 48 | 5 | 45 | [4a] |
| $[Ru^{II}(R,R'\text{-}(2\text{-}nap)_2\text{-}pybox)(pydic)]/H_2O_2$[c] | 59 | 48 | 12 | [4b] |
| $[Ru^{II}(S,S'\text{-}Ph_2\text{-}pybox)(pydic)]/t\text{-}BuOOH$[d] | 56 | 30 | 36 | [4c] |
| $[Ru^{II}(pybim)(pydic)]/H_2O_2$[e] | 76 | 42 | 12 | [5b] |
| $[Ru^{II}(salen)(NO^+)]$/TMPDO/light[f] | 34 | 79 | 14 | [6a] |
| $[Ru^{II}(salen)(NO^+)]$/DMPNO/light[g] | 30 | 83 | 12 | [6b] |
| $[Ru^{IV}(terpy)(cxhn^*)O]$[h] | 68 | 0 | 12 | [7a] |
| $[Ru^{IV}(Me_3tacn)(cbpy^*)O]$[i] | 56 | 9 | 12 | [7a] |
| $[Ru^{IV}(PPz^*)(bipy)O]$[j] | 58 | 37 | 12 | [7b] |
| $[Ru^{IV}(Cn)(diopy^*)O]$[k] | 65 | 9 | 12 | [7c] |
| $[Ru^{II}Cl(PNNP)]/H_2O_2$[l] | 81 | 37 | 6 | [8] |
| $[Ru^{II}S^1(PPh_3)(H_2O)_2]/PhIO$[m] | 30–44 | 38–58 | 0.5–1.5 | [21a] |
| $[Ru^{II}S^2(PPh_3)(H_2O)_2]/PhIO$[n] | 28–40 | 22–40 | 2 | [21b] |

[a] $D_4$-Por*, $D_4$-symmetric chiral porphyrin. Reaction conditions: catalyst = 0.5 μmol; oxidant = 0.55 mmol, substrate = 0.5 mmol; solvent = benzene; temp., room temperature.

[b] pybox, Pyridinebisoxazoline; pydic, pyridyl dicarboxylate. Reaction conditions: catalyst = 0.025 mmol; oxidant = 1.5 mmol; substrate = 0.5 mmol; solvent = $^t$BuOH/toluene; temp., room temperature.

[c] $(2\text{-nap})_2$-pybox, $(2\text{-Napthyl})_2$-pyboxazine; pydic, pyridyl dicarboxylate. Reaction conditions: catalyst = 0.025 mmol; oxidant = 1.5 mmol; substrate = 0.5 mmol; solvent = 2-methylbutan-2-ol; temp., room temperature.

[d] Reaction conditions: catalyst = 0.025 mmol; oxidant = 1.5 mmol; substrate = 0.5 mmol; solvent = *t*-BuOH; temp., room temperature.

[e] pybim, Pyridinebisimidazoline; pydic, pyridyl dicarboxylate. Reaction conditions: catalyst = 0.025 mmol; oxidant = 1.5 mmol; substrate = 0.5 mmol; solvent = *tert*-amyl alcohol; temp., room temperature.

[f] TMPDO, tetramethyl pyrazine *N*,*N*′-dioxide. Reaction conditions: catalyst = 2 μmol; oxidant = 0.1 mmol; substrate = 0.1 mmol; solvent = dioxane, the whole reaction mixture was stirred under illumination of visible light (100 W halogen lamp) at room temperature.

[g] MPNO, dimethyl pyridine *N*-oxide. Reaction conditions: catalyst = 2 μmol; oxidant = 0.1 mmol; substrate = 0.1 mmol; solvent = benzene, the reaction was carried out under incandescent light (100 V, 60 W) at room temperature.

[h] terpy, 2,2′,6′,2″-Terpyridine; cxhn, *N*,*N*,*N*′,*N*′-tetramethyl-1,2-diaminocyclohexane. Reaction conditions: $[Ru^{IV}(terpy)(cxhn)O]$ = 30 mg; substrate = 0.1 ml; solvent = acetonitrile (2 ml); temp. = 25 °C.

[i] $Me_3tacn$, 1,4,7-trimethyl-1,4,7-triazacyclononane; cbpy, (−)-3,3′-[(4*S*-trans)-1,3-dioxolane-4,5-dimethyl]-2,2′-bipyridine. Reaction conditions: $[Ru^{IV}(Me_3tacn)(cbpy)O]$ = 30 mg; substrate = 0.1 ml; solvent = acetonitrile (2 ml); temp. = 25 °C.

[j] $PPz^*$, 2,6-bis[(4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methanoindazol-2-yl]pyridine; bipy, 2,2′-bipyridine. Reaction conditions: $[Ru^{IV}(PPz^*)(bipy)O]$ = 50 μmol; substrate = 1 mmol; solvent = acetonitrile; temp. = 25 °C.

[k] Cn, *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane; $diopy^*$ = *R*,*R*′-3,3′-(1,2-dimethylethylenedioxy)-2,2′-bipyridine. Reaction conditions: $[Ru^{IV}(Cn)(diopy^*)O]$ = 30 μmol; substrate = 2 mmol; solvent = acetonitrile; temp. = 25 °C.

[l] PNNP, (*N*,*N*′-bis{*o*-diphenylphosphino)benzylidene}-(1*S*,2*S*)-diiminocyclohexane. Reaction conditions: catalyst = 9.6 μmol; oxidant = 6.86 mmol; substrate = 0.96 mmol; solvent = dichloromethane; temp., room temperature.

[m] Schiff-base ligand prepared from condensation of L-histidine with salicylaldehyde, 5-chloro and 5-methoxy salicylaldehyde. Reaction conditions: [catalyst] = 0.01 M; [oxidant] = 0.25 Ml; [substrate] = 0.5 M; solvent = dichloromethane; temp., room temperature.

[n] Schiff-base ligand prepared from condensation of amino-acids, viz. L-tyrosine, L-phenylalanine with salicylaldehyde, 3-*tert*-butyl-, 3,5,-di-*tert*-butyl, 3,5-dichloro and 3,5-dinitro salicylaldehyde. Reaction conditions: catalyst = 0.02 mmol; oxidant = 1 mmol; substrate = 1 mmol; solvent = fluorobenzene; temp. = 0 °C.

by the asymmetric center(s) at the sugar or amino acid part of the coordinated $TDL^{*2-}$ ligands. The high asymmetry-inducing ability of **1** is attributed to the location of asymmetric centers of the sugar moiety of $TDL_1^{*2-}$ ligand proximal to Ru=O bond, for which they can interact deeply with the incoming alkene and effect high enantioface selection.

Considering styrene as a test substrate, the results of the present work are compared in Table 5 with a number of prior studies on alkene epoxidation using chiral ruthenium complexes. Since, product yield and enantioselectivity are dependent on so many factors like, nature of oxidant, variability of solvent, reaction time and most importantly the nature of the active intermediate formed in the catalytic process, it is difficult to make any significant comparison of one system with another. The efficacy of the present catalytic system in terms of product yield seems to be reasonably good considering the moderate epoxide yield (28–40%) reported in the literature [6,21,22] for styrene epoxidation employing ruthenium catalyst complexes that contain Schiff-base type ligands. However, most striking result comes from the comparison of the enantiomeric excess (ee) of the epoxide. The results in Table 5 convincingly demonstrates that the present catalytic system (**1**–**3**/*t*-BuOOH), particularly **1** is indeed prospective in regard to its high symmetry-inducing ability in epoxidation of syrenes.

## 4. Conclusion

The finding of this work is summarized along with indications of future prospect. A new family of chiral ruthenium catalysts that run under mild conditions has been developed. The chiral ligands ($H_2TDL^*$) could be prepared in one step from commercially available starting materials. The results of the present

studies clearly reveal the ability of **1**–**3** to achieve enantioselective epoxidation of unfunctionalized alkenes using *t*-BuOOH as terminal oxidant. The notable feature of this work is the remarkably high enantioselectivity (up to 94% for 4-chlorostyrene oxide) in the complex-**1** catalyzed epoxidation of alkenes with *t*-BuOOH.

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## References

[1] (a) M. Beler, C. Bolm (Eds.), Transition Metals for Organic Sínthesis, second ed., Wiley-VCH, Weingheim, 2004;
(b) E.N. Jacobson, A. Pfaltz, H. Yamomoto (Eds.), Comprehensive Asymmetric Catálysis, vol. II, Springer, Berlin, 1999.
[2] (a) E.N. Jacobson, Catalytic Asymmetric Synthesis (Ed: 1. Ojima), VCH, New York, 1993;
(b) T. Katsuki, Coord. Chem. Rev. 140 (1995) 189.
[3] R. Zhang, W.-Y. Yu, K.-Y. Wong, C.-M. Che, J. Org. Chem. 66 (2001) 8145.
[4] (a) M.K. Tse, S. Bhor, M. Klawonn, C. Dobler, M. Beller, Tetrahedron Lett. 44 (2003) 7479;
(b) M.K. Tse, C. Dobler, S. Bhor, M. Klawonn, W. Magerlien, H. Hugl, M. Beller, Angew. Chem. Int. Ed. 43 (2004) 5255.
[5] (a) G. Anilkumar, S. Bhor, M.K. Tse, M. Klawonn, B. Bitterlich, A. Grotevendt, M. Beller, Terahedron Aysmmetry 16 (2005) 3536;
(b) S. Bhor, G. Anilkumar, M.K. Tse, M. Klawonn, C. Dobler, B. Bitterlich, A. Grotevendt, M. Beller, Org. Lett. 7 (2005) 3393.
[6] (a) K. Nakata, T. Takeda, J. Mihara, T. Hamada, R. Irie, T. Katsuki, Chem. Eur. J. 7 (2001) 3776;
(b) T. Takeda, R. Irie, Y. Shinoda, T. Katsuki, Synlett (1999) 1157.
[7] (a) W.-C. Cheng, W.-Y. Yu, J. Zhu, K.-K. Cheung, S.-M. Peng, C.-K. Poon, C.-M. Che, Inorg. Chim. Acta 242 (1996) 105;
(b) W.-H. Fung, W.-Y. Yu, C.-M. Che, J. Org. Chem. 63 (1998) 7715;
(c) W.-Y. Yu, W.-H. Fung, J.-L. Zhu, K.-K. Cheung, K.-K. Ho, C.-M. Che, J. Chin. Chem. Soc. 46 (1999) 341.
[8] R.M. Stoop, A. Mezzetti, Green Chem. (1999) 39.
[9] D. Seebach, A.K. Beck, A. Heckel, Angew. Chem. Int. Ed. 1 (2001) 92.
[10] G. Helmchen, A. Pfaltz, Acc. Chem. Res. 33 (2000) 336.
[11] D. Steinborn, H. Junicke, Chem. Rev. 100 (2000) 4283.
[12] J. Zhao, X. Zhou, A.M. Santos, E. Herdtweck, C.C. Romao, F.E. Kuhn, J. Chem. Soc. Dalton Trans. (2003) 3736.
[13] D. Chatterjee, S. Basak, A. Mitra, A. Sengupta, J. Le Bras, J. Muzart, Catal. Commun. 6 (2005) 459.
[14] D. Chatterjee, S. Basak, A. Mitra, A. Sengupta, J. Le Bras, J. Muzart, Inorg. Chim. Acta 359 (2006) 1325.
[15] S.F. Colson, S.D. Robinson, Inorg. Chim. Acta 149 (1988) 13.
[16] E.E. Mercer, R.R. Buckley, Inorg. Chem. 4 (1965) 1692.
[17] W.-H. Leung, C.-M. Che, Inorg. Chem. 28 (1989) 4619.
[18] D. Chatterjee, A. Mitra, R.E. Shepherd, Inorg. Chim. Acta 357 (2004) 980.
[19] C.-M. Che, Ti-F. Lai, K.-Y. Wong, Inorg. Chem. 26 (1987) 2289.
[20] R.E. Shepherd, Inorg. Chim. Acta 209 (1993) 201.
[21] (a) R.I. Kureshy, N.H. Khan, S.H.R. Abdi, J. Mol. Catal. A: Chem. 96 (1995) 117;
(b) R.I. Kureshy, N.H. Khan, S.H.R. Abdi, S.T. Patel, P. Iyer, J. Mol. Catal. A: Chem. 150 (1999) 175.
[22] W.-H. Leung, C.-M. Che, Inorg. Chem. 28 (1989) 4619.