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Enantioselective epoxidation reaction of non-functionalised prochiral alkenes using optically resolved [brucine](*R*)-[Ru(PDTA-H)Cl] and [brucine](*S*)-[Ru(PDTA-H)Cl] complexes

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Abstract

The racemic metal complex K[Ru(PDTA-H)Cl] [1] has been resolved into its optical isomers using brucine as the resolving agent counter ion, [brucine](*S*)-[Ru(PDTA-H)Cl] (**1**) and [brucine](*R*)-[Ru(PDTA-H)Cl] (**2**) and their structures are determined by single crystal X-ray methods. Longer Ru–Cl bonds in both the complexes (2.3974(13)A in **1** and 2.415(6) in **2** along with one relatively weaker and strained chelation ring could be responsible for their catalytic activity. The CD pattern of the complex **1** shows the presence of the two isomers λ and δ with more contribution of λ form while the complex **2** acquire only λ conformation. Catalytic activity of **1** and **2** for enantioselective epoxidation of non-functionalised alkenes viz. styrene, 4-chloro-, 4-methyl-, 4-nitrostyrene, 1,2-dihydronaphthalene and indene was accomplished by using molecular oxygen and iodosyl benzene as terminal oxidant. Excellent conversions (85–89%) were obtained in case of 1,2-dihydronaphthalene with both the catalysts while catalyst **2** gave good conversion with styrene and 4-methylstyrene. The enantiomeric excess of the epoxide was determined by ^{1}H NMR using chiral shift reagent Eu(hfc)$_3$/ by chiral capillary column. The extent of enantioselectivity with respect to the substituents on substrate is shown on Hammet plot. A possible mechanism at the oxo transfer stage is also envisaged.

Keywords: Enantioselective; Epoxidation; Non-functionalised; Prochiral alkenes; Optically resolved; Ru(III)(PDTA-H)Cl; Brucine

1. Introduction

Asymmetric catalysis has emerged as one of the most promising routes for the synthesis of chiral epoxides [1] by using the transition metal complexes as catalysts. Currently, synthetic application of Sharpless asymmetric epoxidation [2,3] of allylic alcohols (functionalised alkenes) and Jacobsen [4–8], Katsuki [9,10], Mukaiyama et al. [11] and Takai et al. [12] asymmetric epoxidation of several kinds of non-functionalised alkenes with moderate to high enantioselectivity using PhIO, NaOCl, H_2O_2, molecular

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[1] PDTA = Propylene diaminetetraacetic acid.

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oxygen and periodate as oxidant have been of topical interest. However, the use of chiral Ru(III) polyaminocarboxylic acid complexes was not envisaged, although they have been extensively used for various racemic oxidation reaction [13].

With our interest in enantioselective epoxidation of prochiral alkenes [14] and to get a better mechanistic insight for the factors controlling enantioselectivity relationship with the structure of the catalyst in epoxide formation, we are reporting here the optical resolution and characterization including single crystal X-ray structures of both the enantiomer of $[Ru^{III}(PDTA\text{-}H)Cl]^-$ complex using brucine as countercation resolving agent and their catalytic activity in enantioselective epoxidation of prochiral non-functionalised alkenes, viz. styrene, 4-chloro-, 4-methyl-, 4-nitrostyrene, 1,2-dihydronaphthalene, indene using iodosyl benzene and molecular oxygen in presence of sacrificial reductant. The extent of enantioselectivity with respect to the substituents on substrate is shown by a Hammet plot. A possible mechanism at oxo transfer stage is also proposed.

2. Experimental

2.1. Methods

Microanalysis of the complexes was done on a Carlo Erba Analyzer Model 1106. Molar conductance was measured at room temperature on a Digisun electronic conductivity bridge DI-909. Electronic spectra were recorded on Shimadzu UV/Visible recording spectrophotometer Model 160. 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 water was measured by polarimeter Atago, JAPAN. The CD spectra were recorded in water by Jasco Machine, Model J-20, Japan. The progress of the catalytic epoxidation reaction and final product analysis was determined by GLC using Shimadzu GC model 14B coupled with PC using 2 m long, 3 mm 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 and 150°C and injection temperature 200°C with nitrogen carrier gas flow 30 ml/min. Synthetic standards of the product were used to determine yields by comparison of peak height and area. Optical yield of the product was determined by chiral cyclodextrin capillary column of 30M GTA/BDA and by ^1H NMR 99.55 MHz on Jeol FX-100 FT NMR spectrometer in $CDCl_3$ using chiral shift reagent $Eu(hfc)_3$.

2.2. Synthetic procedures

K[Ru(PDTA-H)Cl] was prepared from $K_2[RuCl_5(H_2O)]$ by the published method [15].

2.3. Resolution of K[Ru(PDTA-H)Cl]

Equimolar quantities of Brucine and racemic K[Ru(PDTA-H)Cl] were separately dissolved in minimum quantity of 0.01 M HCl at room temperature. The two solutions were mixed quickly which resulted into an immediate precipitation. The mixture was allowed to stand for further 30 min, filtered, washed with cold water and dried in vacuum. The solid thus obtained is referred to as complex **1**. The mother liquor on standing for a week deposited dark brown crystals in quantitative yield and is referred to as complex **2** now on.

2.4. [Brucine](S)(+)[Ru(PDTA-H)Cl] · $3H_2O$ (1)

Correspond to the formulation [Brucine][Ru(PDTA-H)Cl] · $3H_2O$. Calcd. for $C_{34}H_{48}N_4O_{15}RuCl$: C, 45.92; H, 5.44; N, 6.30. Found: C, 45.65; H, 5.40; N, 6.28. UV-VIS. (H_2O) nm (ε): 212 (14000), 263 (12000), 299 (8700), 361 (740); molar conductance in water (Λ_M) at 298 K; 180 Ω^{-1} mol^{-1} cm^2, magnetic susceptibil-

ity at 298 K $\mu_{eff} = 1.96$ BM, $[\alpha]_D^t$ (H_2O) + 133.33; CD (H_2O) nm ($\Delta\varepsilon$), 325(+8), 390 (−2.0), 550(+0.5).

2.5. [Brucine](R)(−)[Ru(PDTA-H)Cl] · 9H_2O (2)

These crystals were stable in mother liquor only and lost their crystallinity in air probably due to efflorescence. All other physical and spectral properties of this complex were same as of complex **1** except for its optical rotation $[\alpha]_D^t$ (H_2O), −188.88 and CD (H_2O), nm($\Delta\varepsilon$), 370(+3.8), 390(+4.4), 515(+0.7).

2.5.1. X-ray diffraction

Crystals of **1** were stable outside the mother liquor, whereas those of **2** had to be sealed in Lyndman glass capillary for the X-ray intensity measurements. The heavy-atom method solved the structures for both the complexes **1** and **2**. For complex **1**, the full-matrix least-squares refinement of all non-hydrogen atoms with isotropic temperature factors was carried out till the convergence reached. The full-matrix refinement with anisotropic thermal parameters was carried out in blocks. The Ru-PDTA moiety was refined at one time while the brucine molecule and the water molecules were at the other. Most of the H-atoms were seen in the difference map, the others were fixed stereochemically. The final cycles of least-squares refinements, in blocked fashion described earlier. The *R*-value for complex **1** came to 0.0224

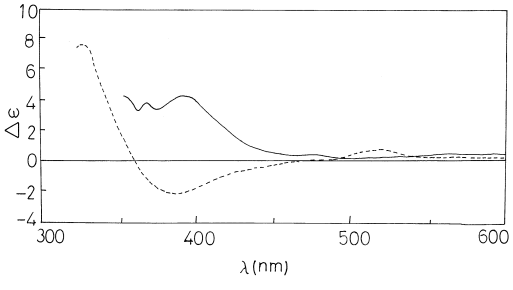
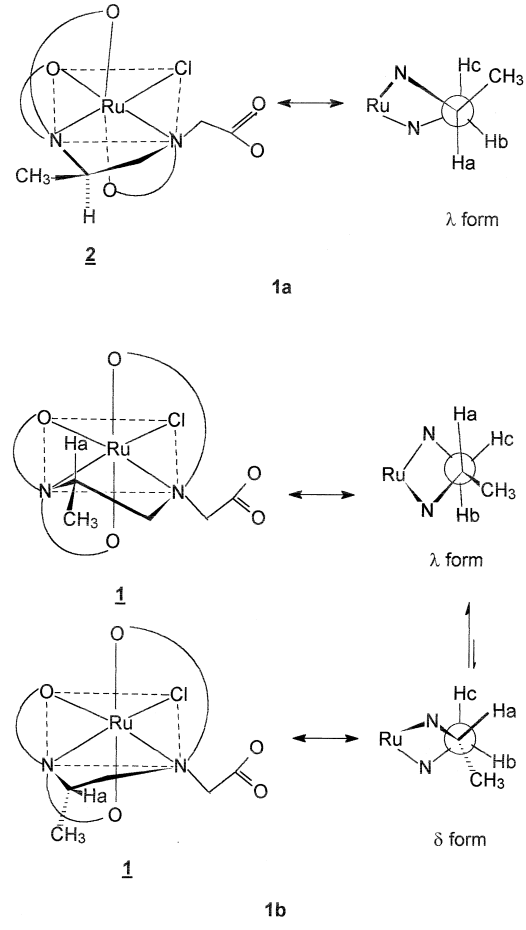


Fig. 1. CD spectra of the complexes (————)[brucine](*S*)-[Ru(PDTA-H)Cl] **1** and (— — —)[brucine](*R*)-[Ru(PDTA-H)Cl] **2** recorded in water.



Scheme 1. Probable conformational isomers in solution (water) (a) (*R*)-[Ru(PDTA-H)Cl]$^-$ in **2** and (b) (*S*)-[Ru(PDTA-H)Cl]$^-$ in **1**.

($R_W = 0.062$) while for the complex **2**, the *R*-value finally came to 0.089 ($R_W = 0.250$), as there were two pairs of crystallographically independent brucine:RuPDTA complexes in the crystal lattice. The structure development for **2**, therefore, was rather slow and the quality of the data did not allow us to carry out the anisotropic refinement of the non-hydrogen atoms. The difference Fourier revealed at least nine water molecules in the lattice (some with half the occupancies) and there were many peaks of height 1–1.5 eÅ^{-3} in the region, probably due to the disordered solvent in the region. PLUTO diagram of [Brucine](*S*)(+)[Ru(PDTA-H)Cl] and of [Brucine](*R*)(−)[Ru(PDTA-H)Cl] of complexes **1** and **2** are shown in Figs. 2 and 3,

respectively. Details of crystallographic parameter and factors responsible for chiral recognition would be communicated separately elsewhere.

*2.5.2. Aerobic enantioselective epoxidation of prochiral alkenes by the catalysts **1** and **2** (with molecular oxygen as oxidant)*

Enantioselective epoxidation of styrenes, 1,2-dihydronaphthalene and indene by the catalysts entry **1** and **2** with molecular oxygen was carried out at pH 7–8 by the following procedure: The chiral catalyst (0.006 mmol), substrate, e.g., styrenes, 1,2-dihydronaphthalene, indene (2 mmol), dissolved in 1.5 ml of 1:1 water: 1,4-dioxane was stirred with isobutyraldehyde (6 mmol) in presence of molecular oxygen at 4°C in dark. Progress of the reaction was monitored by GLC. After the reaction was completed, the solvent was removed and the product epoxide was separated from the reaction mixture using short column of basic alumina with hexane:dichloromethane (9:1) as eluent. Evaluation of enantiomeric excess was done by chiraldex GTA/BDA. Besides, the product was taken in $CDCl_3$ for ^1H NMR using chiral shift reagent $Eu(hfc)_3$ for further evaluation of enantiomeric excess.

2.5.3. With PhIO as oxidant

Enantioselective epoxidation of styrenes, 1,2-dihydronaphthalene, indene by the catalysts **1** and **2** were attempted in homogenous system with iodosyl benzene at pH 7–8 by the following procedure: The chiral catalyst, (0.02 mmol),

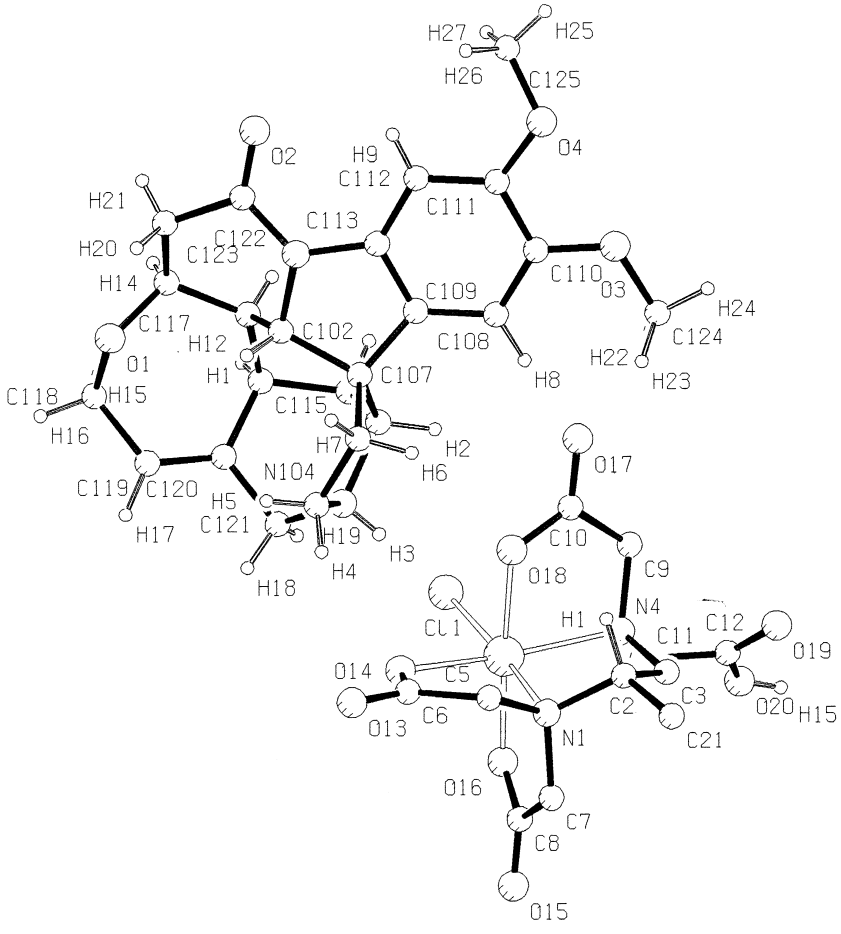


Fig. 2. PLUTO diagram of [brucine](*S*)(+)[Ru(PDTA-H)Cl] **1**.

styrenes, 1,2-dihydronaphthalene, indene (1 mmol) and *n*-tridecane (0.1 mmol) as GLC internal standard were dissolved in 1.5 ml 1:1 water:1,4-dioxane. The reaction was initiated by the addition of iodosyl benzene (1 mmol) and stirred at constant speed in an inert atmosphere at 4°C. After completion of reaction (checked by GLC), the solvent was removed and product was separated by short silica gel column (60–120 mesh) using hexane:dichloromethane as eluent. Evaluation of enantiomeric excess was done as mentioned in preceding experiment.

3. Results and discussion

The aqueous solution of the complexes **1** and **2** have similar absorption spectra while CD pattern of the two complexes are quite opposite from each other (Fig. 1). The shape of the CD spectrum in the first absorption region can be correlated to the absolute configuration and conformation of the complexes. The sign of the d–d transition in both the cases is positive and lie in the range 515 to 550 nm while the higher energy transition at 390 nm is positive in the complex **2** and negative in the complex **1**. Hence, the N–N chelate moiety seems to be fixed in λ gauche conformation in complex **2** with the methyl group disposed equatorially (Scheme 1a). This assignment is in agreement with its single crystal X-ray structure (Fig. 2), whereas, in complex **1**, there seems to be a little contribution of δ gauche form where the methyl group is disposed axially (Scheme 1b) with more contribution of λ form (equatorial methyl) (Fig. 3). This phenomenon exists in solution only and can be attributed to flip flop of the five membered chelate ring involving Ru and ethylenediamine collar of 1,2-diaminopropane moiety [16].

*3.1. Structures of **1** and **2***

Crystal structure of complex **1** contains a pair consisting of one molecule of [Ru(PDTA-H)Cl] and one molecule of brucine whereas the latter contains two such pairs which are related by an approximate non-crystallographic two-fold axis for all the atoms except for the asymmetric center. The absolute configuration of the brucine has been taken as per the earlier crystallographic determination [17]. The configurations of [Ru(PDTA-H)Cl] anions thereupon turn out to be (*S*)- in **1** and (*R*)- in **2** with respect to the asymmetric environment around carbon C2 (Figs. 2 and 3). The less soluble complex **1** contains only three solvent molecules (water) in the crystal lattice, whereas **2** is highly solvated with (at least) nine water molecules located in the solvent region of the lattice.

Selected bond distances and angles for brucine and [Ru(PDTA-H)Cl] are given in Table 1. The accuracy in the geometries are higher in the stable crystals of **1** compared to the highly solvated crystals of **2** which were mounted in a sealed glass capillary. The Ru–Cl bonds are

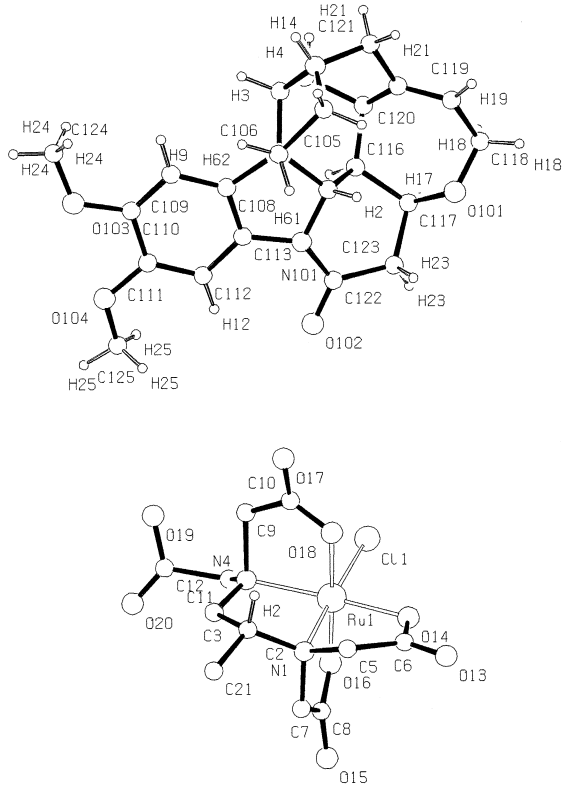


Fig. 3. PLUTO diagram of [brucine](*R*)(−)[Ru(PDTA-H)Cl] **2**.

Table 1
Selected bond lengths [Å] and angles [°] for [Ru(PDTA-H)Cl] moiety

Complex **1**		Complex **2**	
Ru1–O16	2.006(3)	Ru1–O16	1.990(2)
Ru1–O18	2.031(3)	Ru1–O18	1.950(2)
Ru1–O14	2.034(3)	Ru1–O14	2.010(2)
Ru1–N1	2.062(3)	Ru1–N1	2.080(2)
Ru1–N4	2.112(4)	Ru1–N4	2.110(2)
Ru1–Cl1	2.397(13)	Ru1–Cl1	2.414(6)
O16–Ru1–O18	176.40(2)	O18–Ru1–O16	173.7(7)
O16–Ru1–O14	94.20(2)	O16–Ru1–O14	96.3(7)
O18–Ru1–O14	88.07(13)	O18–Ru1–O14	88.7(7)
O16–Ru1–N1	83.89(12)	O16–Ru1–N1	82.8(7)
O18–Ru1–N1	93.64(12)	O18–Ru1–N1	94.2(7)
O14–Ru1–N1	83.23(13)	O14–Ru1–N1	82.8(6)
O16–Ru1–N4	95.70(2)	O16–Ru1–N4	90.1(7)
O18–Ru1–N4	81.53(14)	O18–Ru1–N4	84.3(8)
O14–Ru1–N4	164.80(11)	O14–Ru1–N4	168.0(7)
N1–Ru1–N4	86.38(13)	N1–Ru1–N4	88.0(7)
O16–Ru1–Cl1	95.44(9)	O16–Ru1–Cl1	94.4(5)
O18–Ru1–Cl1	87.19(10)	O18–Ru1–Cl1	88.8(5)
O14–Ru1–Cl1	93.18(10)	O14–Ru1–Cl1	94.6(5)
N1–Ru1–Cl1	176.29(10)	N1–Ru1–Cl1	175.9(5)
N4–Ru1–Cl1	97.33(10)	N4–Ru1–Cl1	95.1(5)

longer in both the structures (2.397(13)) Å in **1** and 2.414(6) Å in **2**), as noted to be the essential structural feature for the high lability and substitution rates at the site. The Ru–N bonds are unequal in both cases, the Ru–N1 bond (*trans* to the Cl position) is shorter by about 0.05 Å than the Ru–N2 (Table 1); also Ru–O bonds of the G-ring (ring almost parallel to the Ru–N1–N2 plane) are longer than the Ru–O bonds of the R-rings (rings approximately perpendicular to the Ru–N1–N2 plane) (Table 1) in **1** and **2**. In **1**, Ru–O18 bond also is as long as the Ru–O of the G-ring. The somewhat weaker chelation in the strained G-ring is noteworthy from the catalytic point of view, implying the availability of two *cis* positions (*trans* to two N-atoms) for the reaction to take place [18,19].

3.2. Aerobic enantioselective epoxidation

Complexes **1** and **2** have been used as catalysts for aerobic enantioselective epoxidation of styrene, 4-chloro-, 4-nitro-, 4-methylstyrene, 1,2-dihydronaphthalene, indene, using molecular oxygen in presence of isobutyraldehyde as sacrificial reductant to give their corresponding

Table 2
Data for enantioselective epoxidation of prochiral non-functionalised alkenes catalysed by novel resolved Ru(III) PDTA complexes with iodosyl benzene and molecular oxygen[a]

Catalyst[b]	Substrate	Time (h)	% Conversion[c]	ee's[d]	Configuration
Entry 1	styrene	12(24)	60(55)	45(40)	*R*
	4-chlorostyrene	12(24)	58(49)	42(36)	*R*
	4-nitrostyrene	12(24)	50(45)	35(32)	*R*
	4-methylstyrene	12(24)	70(65)	55(42)	*R*
	1,2-dihydronaphthelene	12(24)	85(80)	59(46)	1*R*, 2*S*
	indene	12(24)	65(60)	49(35)	1*R*, 2*S*
Entry 2	styrene	12(24)	75(64)	54(43)	*S*
	4-chlorostyrene	12(24)	60(58)	48(38)	*S*
	4-nitrostyrene	12(24)	55(50)	44(28)	*S*
	4-methylstyrene	12(24)	78(68)	60(48)	*S*
	1,2-dihydronaphthelene	12(24)	89(76)	65(57)	1*S*, 2*R*
	indene	12(24)	60(57)	54(48)	1*S*, 2*R*

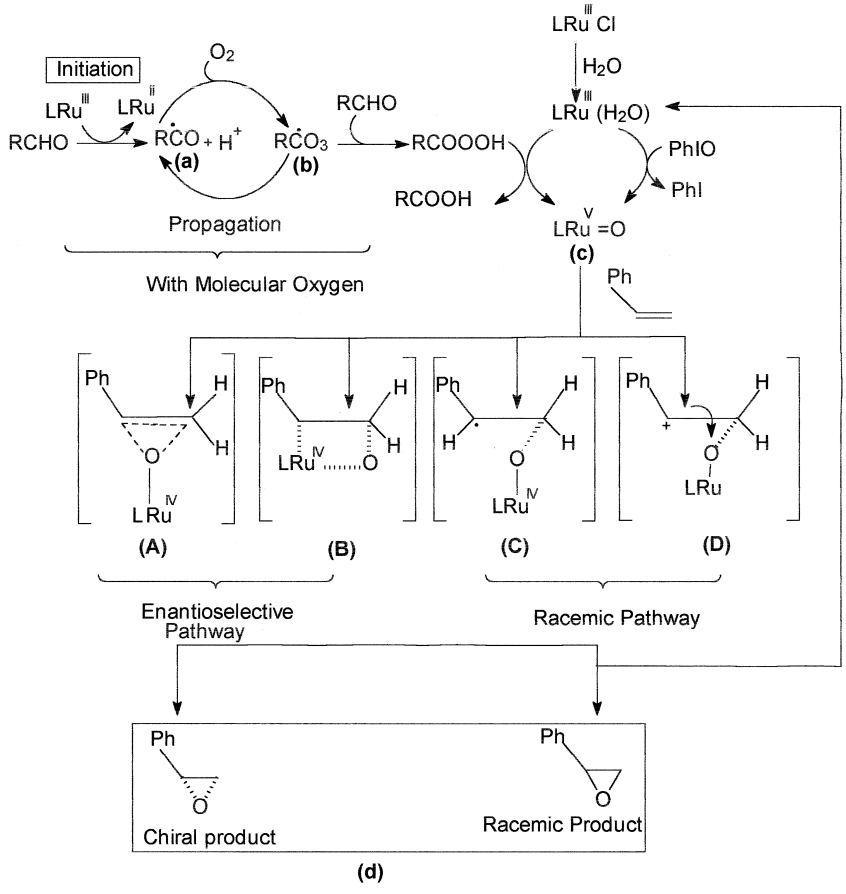
[a] Values are given in parentheses.
[b] Reaction conditions. With molecular oxygen: substrate (2 mmol), catalyst (0.006 mmol), isobutyraldehyde (6 mmol), solvent 1.5 ml (1:1) 1,4d-ioxane:water, 1 atm. O_2 at pH 7–8 at 4°C; (with PhIO) substrate (0.1 mmol), catalyst (0.02 mmol), PhIO (1 mmol), solvent 1.5 ml (1:1) 1,4d-ioxane:water at pH 7–8 at 4°C.
[c] Determined by GC analysis.
[d] Determined by Chiraldex GTA/BDA and by ^{1}H NMR using Eu(hfc)$_3$.

epoxides. Data regarding enantioselectivity are given in Table 2 (values in parentheses). The isobutyraldehyde behaves as an effective reductant to accept one oxygen atom of molecular oxygen with concomitant co-oxidation of isobutyraldehyde to carboxylic acid in the present reaction system.

A probable mechanism for the metal complex catalyzed oxygenation of styrenes is shown in Scheme 2. There seems to be two distinctive roles of the catalysts. First, the catalyst reacts with reductant isobutyraldehyde to initiate the radical chain process by generating sequentially an acyl radical (a) and acylperoxy radical (b) which acts as a carrier in a chain mechanism by reacting with another isobutyraldehye molecule to give a peroxy acid and yet another acyl radical. The peroxy acid then reacts with catalyst to form high valent metal oxo intermediate (c) which reacts with substrates to give respective epoxide (d) in a similar fashion reported earlier [20].

3.3. Enantioselective epoxidation with iodosyl benzene

Enantioselective epoxidation of styrene, 4-chloro-, 4-nitro-, 4-methylstyrene, 1,2-dihydronaphthalene and indene using the catalysts **1** and **2** was carried out with iodosyl benzene to give their respective epoxides. Results are summarized in (Table 2). In all, the catalytic runs only trace amounts of arylaldehyde were found in case of styrenes, suggesting addition of oxy-



Scheme 2. Possible mechanism for the catalytic epoxidation reactions.

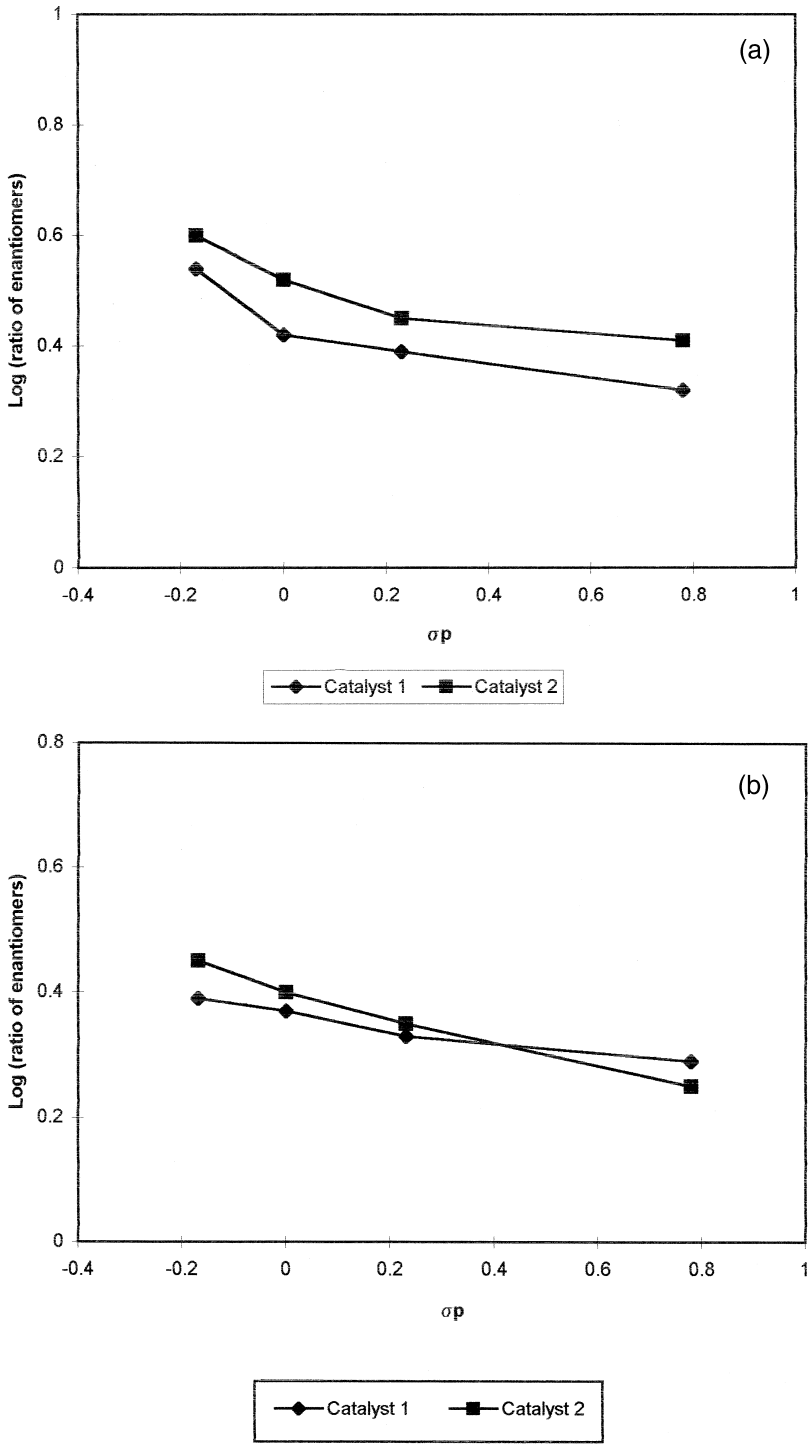


Fig. 4. (a) Hammet plot showing the extent of enantioselectivity with respect to the substituents at para position of styrene with PhIO. (b) Hammet plot showing the extent of enantioselectivity with respect to the substituents at para position of styrene with molecular oxygen.

gen via either concerted oxygen addition (A) or oxametallacyclic (B) formation which predominantly form epoxide rather than carbocationic intermediate (D) yielding arylaldehyde as major product. Further, it is evident from experimental results that there is no absolute enantiomeric induction. Therefore, some amount of recemisation is taking place by opening of oxametallacyclic intermediate or direct side on approach of the alkene at the oxo center to generate acyclic radical (C) followed by rotation of styrene C–C bond (Scheme 2).

The enantiomeric excess for the resulting epoxides separated by short column of silica gel were evaluated using chiral capillary column (Chiraldex GTA/BDA) and also by ^{1}H NMR using chiral shift reagent Eu(hfc)$_3$.

Excellent conversions were obtained in case of 1,2-dihydronaphthalene (80–89%) with catalysts **1** and **2** in the presence of both the oxidants while methylstyrene gave epoxide yield of 70–78%. Low conversion was obtained in case of nitrostyrene with both the catalysts. The highest selectivity was achieved for 1,2-dihydronaphthalene and methyl styrene with catalyst **2**. Enantiomeric excesses were better with oxidant iodosyl benzene compared to molecular oxygen.

In all the cases, employment of *S* form of the catalyst resulted in *R* form of the product as a dominant enantiomer and vice versa. This trend was already seen by Jacobsen [4–7] and Katsuki [10] for Mn(III) salen complexes using iodosyl benzene as terminal oxidant and with combined use of molecular oxygen with aldehyde [11,12].

The result obtained for enantioselectivity for each catalyst and substrate (styrenes) with both oxidants are presented on Hammet plot (Fig. 4a and b) which shows a clear trend with respect to the substituents at the para position. All the catalyst gave higher selectivity with an electron donating group on the substrates and have shown excellent chemoselectivity as no side products were detected on GLC/NMR with complete recovery of starting material after the reaction is over.

4. Conclusions

In this paper, we have presented the optical resolution of racemic metal complex Ru(PDTA-H)Cl into its optical isomers using brucine as resolving agent. The two resolved complexes were used independently for enantioselective epoxidation of styrene, 4-chloro-, 4-methyl-, 4-nitrostyrene, 1,2-dihydronaphthalene and indene in presence of PhIO and molecular oxygen using isobutyraldehyde as sacrificial reductant. Good optical yield was obtained in case of 1,2-dihydronaphthalene in presence of catalysts **1** and **2** with both the oxidants. The highest selectivity was achieved for 1,2-dihydronaphthalene and methyl styrene using catalyst **2**. Enantiomeric excess was better with iodosyl benzene rather than molecular oxygen. Chemically, the two complexes should have behaved similarly. However, experiments showed some variations in catalytic activity.

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