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Review

Asymmetric epoxidation of unsaturated hydrocarbons catalyzed by ruthenium complexes

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Contents

Abstract

Ruthenium complexes of various chiral ligands viz. porphyrins, Schiff-base, polypyridyl, pyridinebisoxazolines and pyridinebisimidazoline are known to perform asymmetric epoxidation of unfunctionalized alkenes with moderate to high enantioselectivity. The advancement of asymmetric epoxidation catalyzed by ruthenium chiral complexes has not been systematically reviewed till date. Hence, the subject of this review comprises the use of chiral complexes as catalysts for performing enantioselective epoxidation of olefins using various precursor oxidants. The catalytic ability and intriguing aspects of the ruthenium based catalyst complexes in asymmetric epoxidation under homogeneous reaction along with the mechanistic details are systematically reviewed in this article. This review highlights most recent investigations on the catalytic systems with chiral ruthenium complexes for olefin epoxidation.

Keywords: Ruthenium complex; Alkene epoxidation; Enantioselectivity; Chiral ligands

1. Introduction

The synthetic value of enantiopure epoxides is well established and a very substantial amount of research on the synthetic methods for their production has been carried out. In this regard transition metal complexes catalyzed asymmetric epoxidation [1–4] of unfunctionalized olefins is of increasing significance in synthetic chemistry as it offers an effective and elegant possibility for synthesis of enantiomerically pure compounds. Ruthenium complexes by virtue of their wider range of stable, but chemically accessible oxidation states have been the subject of much research in the area of hydrocarbon oxidation [4]. Moreover, chiral ruthenium complexes are known to perform enantioselective epoxidation of unfunctionalized alkenes. However, advancement of this intriguing area has not been systematically reviewed till date. Hence, the catalytic ability and the intriguing aspects of the ruthenium based catalyst

Abbreviations: bipy, 2,2′-bipyridine; 2,6-DCPNO, 2,6-dichloropyridine *N*-oxide; edta, ethylenediminetetraacetate; hedtra, *N*-hydroxyethylethylenediminetriacetate; Me_3tacn, 1,4,7-trimethyl,1,4,7-triazacyclononane; pac, polyaminocarboxylate; pybim, pyridinebisimidazoline; pybox, pyridinebisoxazoline; pz, pyrazine; tacn, 1,4,7-triazacyclononane; TMP, tetramethylporphyrin; TPEPP, *meso*-tetrakis(pentafluorophenyl)porphyrin

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complexes in asymmetric epoxidation under homogeneous reaction along with the mechanistic details are systematically reviewed in this article. The chiral ruthenium catalysts used in this widely encountered enantioselective transformation are presented in this review in a logical manner, according to the ligand type and structure; moreover, they are directed to specific unsaturated substrates. The review also considers the effectiveness of the chiral ruthenium complexes towards achieving enantioselective epoxidation of olefins in relation to the nature of the precursor oxidants.

2. Ruthenium complexes as oxo-transfer catalysts

The importance of ruthenium complexes for promoting studies towards development of oxo-transfer catalysts has been well established in the literature [4]. Ruthenium complexes containing a variety of ligands including macrocyclic, polypyridyl, polyaminopolycarboxylate donors, Schiff-base and porphyrins are reported to activate precursor oxidants like O_2, H_2O_2, ClO^-, pyridine-*N*-oxide, iodosylbenzene, oxone and *t*-BuOOH for carrying out hydrocarbon oxidation. A brief overview on the oxo-functionalisation of organic substrates using different groups of ruthenium complexes as catalysts is presented below.

A macrocyclic tertiary amine ligand was reportedly [5] the first ligand that afforded stability to high-valent ruthenyl (Ru=O) complexes in the oxidation states IV, V and VI. This sterically encumbered $[Ru^{IV}(tacn)(bipy)(O)]^{2+}$ complex was a selective oxidant for alkene epoxidation.

Polypyridyl complexes [6–9] of ruthenium are of special interest in regard to their applications as oxo-transfer catalyst because they are coordinatively well defined and chemically stable under catalytic conditions of hydrocarbon oxidation. A number of mechanistic pathways have been proposed, but mechanistic uncertainty remains. However, like cytochrome P450, these complexes reportedly act as oxidants to epoxidize olefins via oxygen atom transfer reactions and hydroxylate alkanes via radical reactions.

Polyaminocarboxylate (pac) ligands are somewhat similar in their donor character to many metalloenzymes, which utilize carboxylate and amine to bind to the metal center. The catalytic ability of Ru-pac complexes towards performing oxidation of a variety of organic compounds using various precursor oxidants has been well documented in the literature [10]. Ru^{III}-(pac)/*t*-BuOOH system catalytic system epoxidized stilbenes effectively, but not in stereoretentive manner as reported in the stilbene oxidation by Ru^{V}(edta)(O) complex with the loss of stereochemistry for *cis*-stilbene. A large amount of *trans*-epoxide versus *cis*-epoxide (5.5:1) was reportedly observed to form from *cis*-stilbene, whereas *trans*-stilbene was converted to trans-epoxide only [10b]. This indicates a predominantly radical character of the Ru^{III}(hedtra)/*t*-BuOOH epoxidation process. The loss of stereochemistry via the radical addition pathway had been explained in terms of competition between rotation with the radical intermediate with that of ring-closure to form the epoxide product.

Reports on the application of ruthenium complexes containing Schiff bases ligands in the catalysis of hydrocarbon oxidation are also available in the literature [11–15]. These complexes reportedly catalyze the epoxidation of olefins with PhIO, but are ineffective in hydroxylating saturated hydrocarbons. For arenes, oxidative cleavage of the C=C double bond was the major reaction pathway.

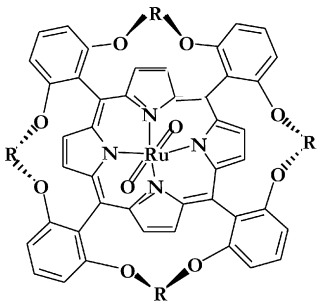
Metalloporphyrins act as excellent catalysts for the transfer of oxygen from different oxidants, in resemblance of cytochrome P450. An in-depth overview of the chemistry of metalloporphyrins as oxidation catalysts in chemical and biological systems underlying mechanistic features and the practical techniques for the synthesis of metalloporphyrins is available in a book edited by Montanari and Casella [14]. However, catalytic schemes containing ruthenium porphyrin complexes are very few [15,16]. The Ru^{VI}-$(TMP)(O)_2$ complex reportedly catalyzes the aerobic epoxidation of olefins at room temperature and normal pressure [15a], whereas, alkane oxidation was reportedly achieved by [Ru(TPEPP)(CO)]/2,6–DCPNO system [15b]. Perhalogenated ruthenium porphyrins were efficient catalysts for the oxygenation of hydrocarbons including secondary alkanes [16a] and benzene [16b]. A mechanism is proposed whereby the oxidation of the Ru^{III} precursor to a reactive oxo species is the rate-determining step.

3. Choice of chiral ligands

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. Many chiral ligands (with variety of donor atoms) viz. porphyrins, pyridinebisoxazolines, pyridinebisimidazoline, Schiff-base, polypyridyl, chiral phosphine, tartrate derivatives and phosphinooxazolines are known today and used comprehensively for asymmetric catalytic reactions. The efficacy of ruthenium catalyst complexes of various chiral ligands toward asymmetric olefin epoxidation is discussed sequentially in the following sections.

4. Asymmetric epoxidation catalyzed by chiral ruthenium-porphyrin complexes

Chiral metalloporphyrins have constituted an important class of catalysts for asymmetric epoxidation of alkenes. A rigid macrocyclic core and modifiable periphery make them attractive cut-out for building chiral catalysts. Several different strategies have been adopted in which optically active groups are appended to the macrocyclic ring of metalloporphyrins [17]. Chiral groups attached to porphyrins in various geometries could yield high enantioselectivities. However, studies on metalloporphyrin catalysts are limited mostly to the porphyrin complexes of iron and manganese. In 1996, the first example of a homochiral ruthenium porphyrin complex (**1**) employed in asymmetric epoxidation of styrene, was reported by Gross et al. [18].



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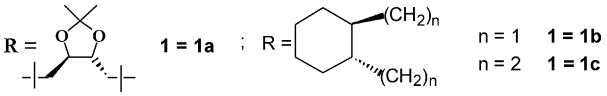
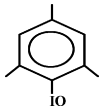
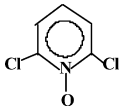
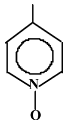
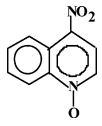


It had been reported that the enantioselectivity of epoxide formation was highly solvent dependent, however, an effect of terminal oxidant [19] on the enantioselectivity was also noticed (Table 1). A Hammett plot of enantiomeric excess (ee) in the **1** catalyzed epoxidation of substituted styrenes was linear when 2,6-dichloropyridine-*N*-oxide was used as oxidant, but in the case of iodosylbenzene the corresponding plot was curved. Although no attempt was made [19] to fit the relative reactivity data, k_{rel} ($k_Y/k_H = \log(Y_f/Y_i)/\log(H_f/H_i)$, where Y_f and Y_i are the final and initial quantities of substituted styrenes; H_f and H_i are the final and initial quantities of styrene) to Hammett substituent constants (σ^+), the chemical yields [19] reported for the **1** catalyzed epoxidation of styrene and various *para*-substituted styrenes with 2,6-dichloropyridine-*N*-oxide [19] indicate that the Hammett plot ($\log k_{rel}$ versus σ^+) would be non-linear. The stoichiometric oxidation of styrenes by dioxoruthenium(VI) porphyrins exhibits [32,33] a non-linear ($\log k_{rel}$ versus σ^+) Hammett relationship. Therefore, observance of non-linearity in a Hammett plot favors the intermediacy of high-valent dioxoruthenium(VI) species in the case of the **1**/DCPNO epoxidation system [19]. An oxoruthenium(V) intermediate had also been implicated as the active species in alkane oxidation using the [Ru(TPEPP)(CO)]/2,6-DCPNO system [15b]. Nonetheless, the involvement of intermediate(s) other than **1** cannot be eliminated when pyridine-*N*-oxides were used as primary oxidants. A Ru-PhIO intermediate species (in place of high-valent Ru-oxo species) could be involved in the epoxidation step when iodosyl benzene (PhIO) was used as oxidant. The intermediacy of such a species in iodosyl benzene O-atom transfer catalyzed by Ru-complex had been reported earlier [7a]. Moreover, change in the solution structure of metalloporphyrin involving a specific association with aromatic solvent molecule was proposed to be the reason for observing superior enantioselectivity in benzene (Table 1). The observance of non-linearity in the Hammett plot of enantiomeric excess (ee) in the **1** catalyzed epoxidation of substituted styrenes in the case of iodosylbenzene [19] is suggestive of the fact that the olefin approach and its orientation to the Ru-PhIO intermediate species is not governed by the electronic effect exerted by the substituents on the *para* position of the aromatic ring of the approaching styrenes.

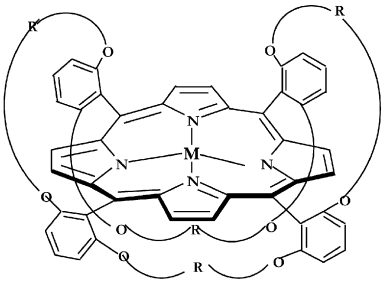
Recently, Le Maux et al. reported [20] two new ruthenium complexes (**1b**) containing C_2-symmetric chiral porphyrins bearing cyclohexyl substituents at the *ortho*-position of the *meso*-phenyl groups and, their use in the catalytic asymmetric epoxidation of styrene derivatives with 2,6-dichloropyridine-*N*-oxide. The results shown in Table 2 suggest that the presence of various cyclohexane rings as chiral entities on metalloporphyrins not only improved the efficacy of the catalytic system, but also govern both the reactivity and the enantioselectivity. The low yield and poor enantioselectivity observed for R = short armed ($n = 1$) chiral cyclohexyl group probably indicates the upper limit of the level of steric encumbrance that can be tolerated in a reactive homochiral porphyrin complex. Shortening the size of the ring viz. cyclopentane, cyclobutane, and cyclopropane rings, could be a good option to deal with above problem as reported previously in the case of asymmetric hydrogenation with the chiral phosphines [21–23].

A series of D_2-symmetric chiral *trans*-dioxo porphyrinatoruthenium(VI) complexes (**2a**–**c**) was reported by Che and co-workers [24].

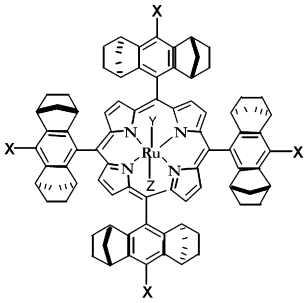
Table 1
Effect of oxidant and solvent on **1a**-$Ru^{VI}(O)_2$-catalyzed asymmetric epoxidation of styrene[a]

Solvent	Oxidant									
										
	% ee	% Yield	% ee	% Yield	% ee	% Yield	% ee	% Yield	% ee	% Yield
Benzene	42	47	29	6	50	20	54	0.4	49	3
Dichloromethane	4	11								
m-Xylene[b]					54	29				

Taken from Ref. [19].
[a] **1** = 1 μmol, oxidant = 330 μmol, styrene = 330 μmol, time 2 h, temp. = 25 °C.
[b] 5 h.



2 (M = $Ru^{VI}(O)_2$)



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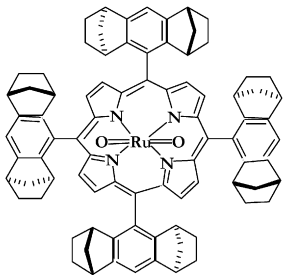

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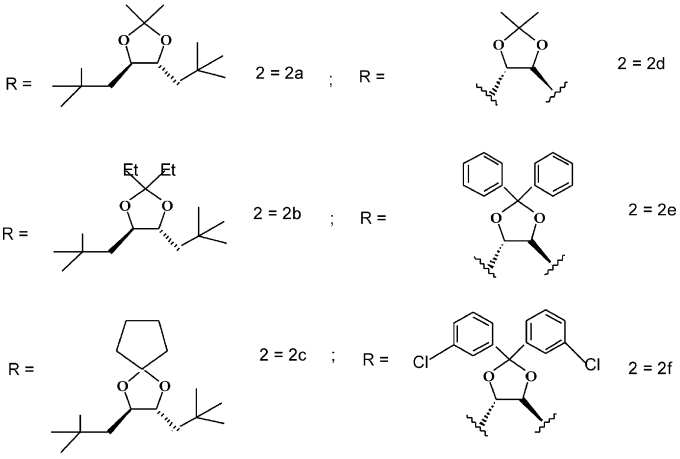
for 3 = 3a, x = H, y = CO, z = MeOH; 3b, x = CF_3, y = CO, z = MeOH; 3c, x = H, y = z = Cl



At room temperature in the presence of pyrazole, **2a** stoichiometrically oxidized aromatic olefins to the corresponding epoxide with moderately high enantioselectivity (Table 3). However, in the absence of pyrazole a lesser enantioselectivity (40%) was observed (Table 3). Decrease in enantioselectivity was reportedly explained in terms of formation of Ru(II)-species (Scheme 1) in the reacting system that racemized the chiral epoxide by an epoxide ring-opening pathway previously suggested by Grove et al. [25].

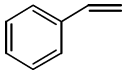
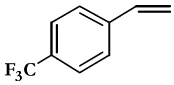
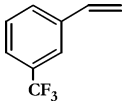
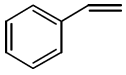
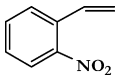
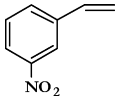
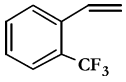
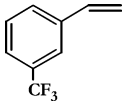
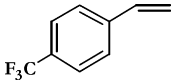
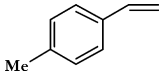
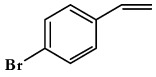
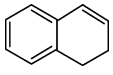
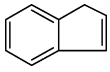
Solvent dependence studies on the rate of epoxidation of *trans*-β-methylstyrene by **2a** provided a value of the second-order rate constant in benzene ($9.04 \times 10^{-4}\,M^{-1}\,s^{-1}$) almost twice that obtained in dichloromethane ($4.15 \times 10^{-4}\,M^{-1}\,s^{-1}$) at 25 °C. The observed stereoselectivity in the case of epoxidation of *cis*- and *trans*-β-methyl styrenes is suggestive that the rate limiting step is involved with the association of C=C bond with Ru=O which governs the product enantioselectivity. More members of D_2-symmetric ruthenium porphyrins complexes (**2d–f**) were reported by Gross and Ini [26], which exhibited high enantioselective induction in the **2d** catalyzed epoxidation of terminal and *trans*-disubstituted olefins using 2,6-dichloropyridine-*N*-oxide, but significantly poorer chiral induction for *cis*-olefins. The epoxidation of styrene and its *m*- and *p*-chloro-substituted derivatives proceeded with 79–83% ee (Table 4).

Berkessel et al. in 1997 reported [27] the synthesis and reactivity of an enantiomerically pure D_4-ruthenium carbonyl porphyrin complex **3**.

The complex could not be prepared in good yield by following the standard procedure of refluxing ruthenium carbonyl ($[Ru_3(CO)_{12}]$) with the porphyrin ligand in an inert solvent. Complex **3a** was prepared [27] with very high yield by refluxing $Ru_3(CO)_{12}$ with the corresponding porphyrin ligand in phenol. The asymmetric epoxidation of olefins catalyzed by **3a** using 2,6-dichloropyridine *N*-oxide (2,6-DCPNO) as oxidant was carried out at room temperature in benzene under argon. The product yield and enantioselectivity were encouraging (Table 5), however, decrease in product yield and enantioselectivity was also observed when iodosylbenzene was used as a terminal oxidant. Other oxidant like hydrogen peroxide, sodium hypochloride and 'oxone' ($KHSO_5$) showed no reaction under the specified reaction conditions. The same group has recently reported [28] that improved results could be achieved by putting substituents on the remote position of the porphyrin ligand. Introduction of a CF_3 substituent in the remote position (**3b**) resulted in high turnover numbers (up to 14,200) with an ee value of 80% in alkene epoxidation with 2,6-dichloropyridine *N*-oxide in benzene at room temperature.

Che and coworkers reported [29] for the first time that a chiral *trans*-dioxo(D_4-porphyrinato)ruthenium(VI) complex (**4**) could effect enantioselective epoxidation of a prochiral alkene (Table 6) using dioxygen as oxidant. This complex exhibited catalytic activity toward aerobic enantioselective epoxidation of prochiral alkenes with an enantioselectivity up to 72% ee (Table 6) under an oxygen pressure of 8 atm. Using iodosylbenzene as terminal oxidant catalytic ability of both $[Ru^{II}(por^*)(CO)(EtOH]$ and $[Ru^{VI}(por^*)(O)_2]$ were examined [30] for the asymmetric epoxidation of alkenes, and the results (Table 7) of the studies revealed that for same substrate a similar product distribution and ee values were obtained for both the catalytic and stoichiometric reactions. No solvent dependence on enantioselectivity was observed while changing the solvent from dichloromethane to benzene (Table 7). Similar 'ee' values and 'absolute configuration' of epoxide products were obtained both from stoichiometric (Table 6) and catalytic (Table 7) epoxidations of aromatic olefins. This suggests that the $[Ru^{VI}(por^*)(O)_2]$ complex is the predominantly active intermediate species which transfers an oxo-atom to the C=C bond of un-functionalized olefins in the catalytic process [30].

Table 2
Results of asymmetric epoxidation of alkenes catalyzed by **1b**[a]

Catalyst	Alkene	Yield (%)	Turnover	% ee (absolute configuration)
$Ru(O)_2$ ($n=1$)		62	204	7.5 (*R*)
		2.5	8	8 (*R*)
		0	–	–
$Ru(O)_2$ ($n=2$)		84.5	276	23 (*R*)
		32.6	107	17(*R*)
		15	50	30 (*R*)
		84	276	18 (*R*)
		74	244	32 (*R*)
		30	97	24 (*R*)
		43	144	27 (*R*)
		40	132	21 (*R*)
		22	72	35 (1*S*,2*R*)
		0	–	–

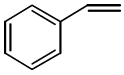
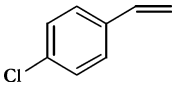
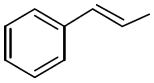
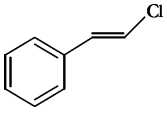
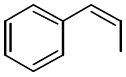
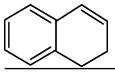
Taken from Ref. [20].
[a] A mixture containing alkene (330 μmol), 2,6-dichloro pyridene *N*-oxide (330 μmol), and catalyst (1 μmol) in degassed benzene was stirred at room temperature for 2.5 h.

The kinetics of stoichiometric epoxidation of *para*-substituted styrenes by $[Ru^{VI}(por^*)(O)_2]$ exhibited linear dependence of the observed rate constant values with the alkene concentration, and the second-order rate constants fall in the narrow range ($2.1 \times 10^{-3} - 9.7 \times 10^{-3}\ M^{-1}\ s^{-1}$ at 25 °C). The rate-determining step of oxygen atom transfer was proposed to be involved with the formation of a loosely bound radical intermediate [30]. This radical type intermediate could plausibly explain the formation of *trans*-epoxide from *cis*-methylstyrene as bond rotation of this carbon center radical resulted in loss of stereoselectivity. The linearity of Hammett plots observed for the epoxidation of of *para*-substituted styrenes by of *para*-substituted styrenes further supports the formation of the above radicaloid intermediate in the oxo-transfer process [30].

Recently, Che and co-workers [31] reported highly efficient asymmetric epoxidation of alkenes catalyzed by a D_4-symmetric ruthenium(IV) porphyrin complex (**3c**) prepared from **3a** in refluxing CCl_4. Styrene, substituted styrenes and some conjugated *cis*-disubstituted alkenes are efficiently converted to their corresponding epoxide in the presence of **3c** as catalyst and 2,6-dichloropyridine-*N*-oxide as precursor oxidant (Table 8) at room temperature. Gradual decrease in catalytic activity **3c** with successive uses had been reportedly explained [31] in terms of formation of less reactive ruthenium(II)-carbonyl species.

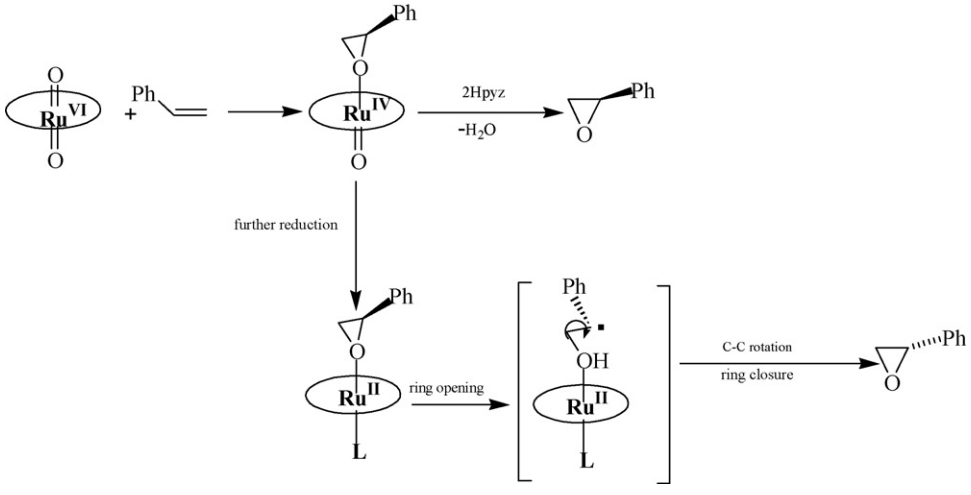
A comparison of the results of styrene epoxidation catalyzed by Ru-porphyrin complexes for which data are available is shown in Table 9. The observed net effect of changing the struc-

Table 3
Stoichiometric epoxidation of aromatic alkenes by **2a**[a]

Alkene	Solvent	% epoxide yield	% ee (absolute configuration)
	C_6H_6	64	62 (*R*)
	C_6H_6	62	40 (*R*)
	CH_2Cl_2	39	41 (*R*)
	CH_3CN	13	33 (*R*)
	C_6H_6	75	60 (*R*)
	C_6H_6	90 (>99% *trans*)	67 (1*S*,2*R*)
	C_6H_6(0 °C)	90 (>99% *trans*)	70 (1*S*,2*R*)
	CH_2Cl_2	58 (>99% *trans*)	32 (1*S*,2*R*)
	EtOAc	82 (>99% *trans*)	38 (1*S*,2*R*)
	C_6H_6	70	76 (1*S*,2*R*)
	C_6H_6	75 (>99% *cis*)	40 (1*S*,2*R*)
	CH_2Cl_2	68 (95% *cis*, 5% *trans*)	18 (1*S*,2*R*)
	C_6H_6	88	20 (1*S*,2*R*)

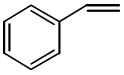
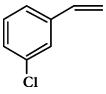
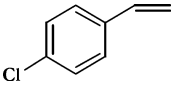
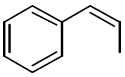
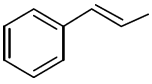
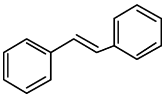
Taken from Ref. [24].
[a] **2a** = 0.015 – 0.03 mmol; pyrazole = 0.3 mmol; alkene = 1 mmol. The reacting solution (in degassed benzene) was stirred at room temperature for 12 h.

ture by introducing electron-withdrawing moieties or non-planar distortion of the porphyrin ligand on the reactivity of O-donor intermediate in Ru-porphyrin catalyzed styrene epoxidation (Table 9) is evident in regard to epoxide yield, turnovers and enantioselectivity. The results for a range of alkenes (Table 10) with the same oxidant 2,6-dichloropyridine-*N*-oxide further suggest that the D_2-symmetric ruthenium(IV)-porphyrin complex is much less active than the D_4-symmetric ruthenium(IV)-porphyrin complex. Although complex **3c** appears to be the best in all respect, no definitive assignment of the active intermediate was available [31]. Intermediacy of a species other than high-valent oxo-ruthenium(VI) complex had been proposed [31] for the **3c** catalyzed epoxidaton of alkenes with 2,6-dichloropyridine-*N*-oxide as precursor oxidant. The reportedly observed linearity of Hammett correlation plot [31] in contrast to a nonlinear Hammett relationship proposed for stoichiometric oxo-transfer from dioxoruthenium(VI) to styrene and substituted styrenes [32,33], further supports the above argument. A loosely bound O-bonded [P*Ru···O–N–Cl_2Py] species (milder oxidant than the corresponding dioxoruthenium(VI) species) affording



Scheme 1.

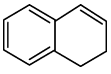
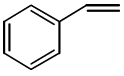
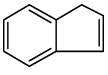
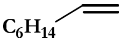
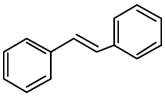
Table 4
Epoxidation of aromatic alkenes catalyzed by **2f** in toluene at −10 °C[a]

Substrate	% ee	TON
	79[a]	551
	81	226
	83	191
	57	244
	69	487
	38	242

Taken from Ref. [26].
[a] **2f** = 0.165 μmol, 2,6-dichloropyridine-*N*-oxide 165 μmol.
Olefin = 165 μmol.
Time = 48 h.

a product like transition state during transfer of oxygen atom to alkenes might be operative in the catalytic process. A far better enantioselectivity is observed in the case of **3c** catalyzed epoxidation of styrene (Table 9) than that observed in stoichiometric oxo-transfer from the corresponding dioxoruthenium(VI) complex.

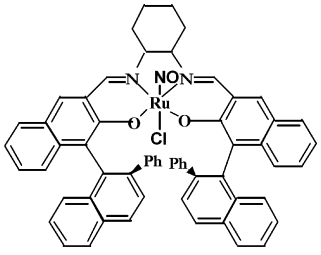
Table 5
Results of epoxidation of prochiral olefins **3a** catalyzed by using 2,6-DCPNO in benzene[a]

Alkene	% conversion	% epoxide yield	ee
	90	85	71
	80[b]	65	72
	35[c]	25	71
	9[d]	4	71
	10[e]	7	69
	80[f]	65	64
	80[g]	52	62
	100	79	70
	65	55	54
	6	5	28
	6	5	0

Taken from Ref. [27].
[a] **3** = 315 nmol, substrate = 315 μmol, oxidant = 315 μmol, time = 2 days, reaction temperature = 25 °C.
[b] In toluene.
[c] Oxidant = 2,6-dibromopyridine *N*-oxide.
[d] Oxidant = *N*-methylmorpholine *N*-oxide.
[e] In methanol-ethyl acetate (2:1 v/v).
[f] In CH_2Cl_2.
[g] Ethyl acetate.

5. Asymmetric epoxidation catalyzed by chiral ruthenium-Schiff-base complexes

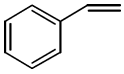
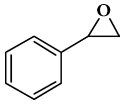
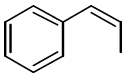
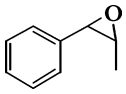
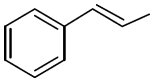
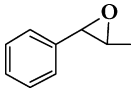
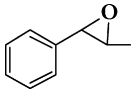
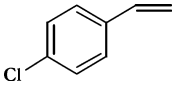
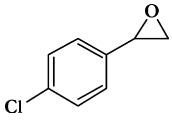
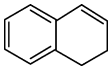
The chemistry of metal complexes containing Schiff-base ligands is of enduring significance, since they have common features with metalloporphyrins with respect to their electronic structure and catalytic activities that mimic enzymatic hydrocarbon oxidation. Further, preparation of chiral Schiff-base ligands by condensation of readily available chiral amines with aldehydes/ketones is much easier when compared to the very lengthy steps involved in the synthesis of chiral porphyrin ligands. Among several catalytic systems, the manganese Schiff-base catalysts, have emerged as powerful species for the asymmetric oxidation of unfunctionalized olefins [34,35]. Studies with ruthenium complexes containing Schiff-base ligands in the catalysis of asymmetric epoxidation are noticeably few in the literature. Katsuki and co-workers [36] first reported the synthesis and catalytic application of ruthenium(II)-complex (**5**) containing chiral tetradentate (N2O2) 'salen' type Schiff-base ligand in the asymmetric epoxidation of conjugated olefins in the presence of various terminal oxidants.



5

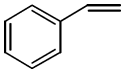
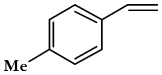
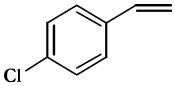
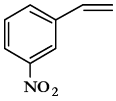
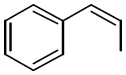
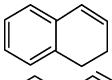
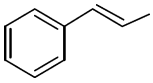
Complex **5** was found to be an efficient catalyst (Table 10) for the epoxidation of conjugated olefins under irradiation of visible light, and 2,6-Cl_2pyNO appeared to be the most useful oxidant amongst the various terminal oxidants viz. PhIO, $NaIO_4$. $KHSO_5$, NaOCl and tetramethylpyrazine *N*,*N*′-dioxide used in the epoxidation studies [36b]. The results of catalytic epoxidation (Table 11) revealed that complex **5** in the presence of 2,4-dichloropyridine *N*-oxide is capable of effecting high asymmetric induction irrespective of substitution patterns of olefins in ethereal solvents. As seen in Table 10 the solvent of choice was dependent on the substrate used, however, in most cases reactions advanced smoothly in diethyl ether and benzene and, high enantioselectivity was observed, whereas, use of polar solvent like acetone, ethyl acetate and acetonitrile epoxidation retarded epoxidation [36b]. Upon irradiation nitrosyl ligand of **5** dissociates to produce a five-coordinated active species which reacts with terminal oxidant to form **5**-oxo species with an open asymmetric coordination sphere around the oxen atom, which is perhaps responsible for the observed high asymmetric induction [36b] in the epoxidation of conjugated olefins irrespective of their substitution pattern.

Table 6
Enantioselective epoxidation of alkenes by **4**-$Ru^{VI}(O)_2$[a]

Substrate	Product	Stoichiometric[a]		Catalytic aerobic[b]	
		% yield	% ee	TON	% ee (configuration)
		61	65	10	70 (*R*)
		64	72	20 21	69 (1*R*,2*S*) 73 (1*R*,2*S*)
		5	–	2 3	– –
		66[c]	20[c]	–	–
		71	45	11	52 (*R*)
		61	71	14	56

Taken from Ref. [29].
[a] Stochiometric reactions were conducted in CH_2Cl_2 at room temperature for 12 h, **3**-$Ru^{VI}(O)_2$ = 4 mg, substrate 200 mg, pyrazole 50 mg.
[b] Catalytic reaction were performed in CH_2Cl_2 at room temperature under oxygen pressure (ca. 8 atm) for 22–24 h, catalyst = 4 mg, substrate = 40 mg.
[c] In benzene.

Table 7
Catalytic epoxidation of alkenes by PhIO with **3a**-Ru^{II}(CO)(EtOH) (A) and **4**-$Ru^{VI}(O)_2$ (B) as catalysts[a]

Substrate	Catalyst	Solvent	Epoxide	
			% Yield	% ee (configuration)
	A	CH_2Cl_2	71	55 (*R*)
	A	C_6H_6	57	63 (*R*)
	B	CH_2Cl_2	52	51(*R*)
	A	CH_2Cl_2	51	40
	A	C_6H_6	35	40
	B	CH_2Cl_2	41	38
	A	CH_2Cl_2	51	41(*R*)
	A	C_6H_6	66	51(*R*)
	B	CH_2Cl_2		
	A	CH_2Cl_2	53	54
	A	C_6H_6	40	52
	B	CH_2Cl_2	59 (*cis:trans* = 9.9)	58 *cis* (1*R*,2*S*)
	A	C_6H_6	52 (*cis:trans* = 6.3)	52 *cis* (1*R*,2*S*)
	B	CH_2Cl_2	53 (*cis:trans* = 11)	55 *cis* (1*R*,2*S*)
	A	CH_2Cl_2	62	30
	A	C_6H_6	46	62
	A	CH_2Cl_2	45	16 *trans*
	A	C_6H_6	41	17 *trans*
	B	CH_2Cl_2	31	13 *trans*
	A	CH_2Cl_2	55	8
	B	CH_2Cl_2	61	7

Taken from Ref. [30].
[a] A mixture of substrate (100 mg), PhIO (50 mg) and catalyst (2 mg) was stirred in CH_2Cl_2 with restriction of air [30].

Table 8
Asymmetric epoxidation of alkenes catalyzed by **3c-Ru^{IV}** in the presence of 2,6-DCPNO[a]

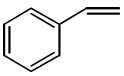
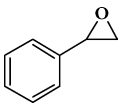
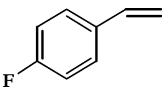
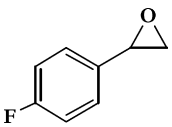
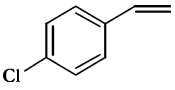
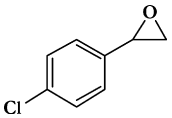
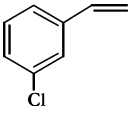
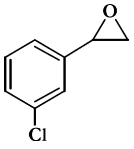
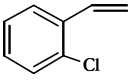
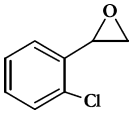
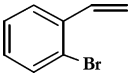
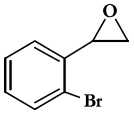
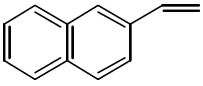
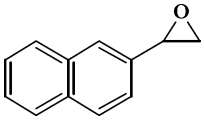
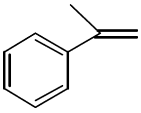
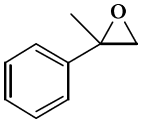
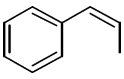
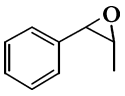
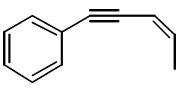
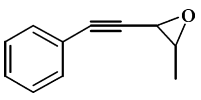
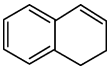
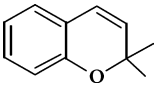
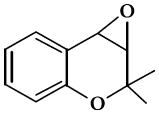
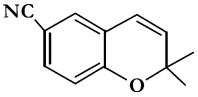
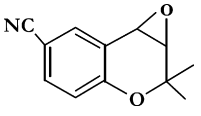
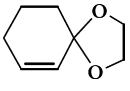
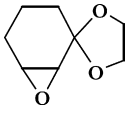
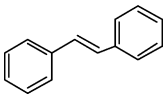
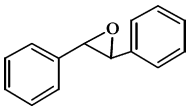
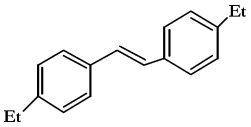
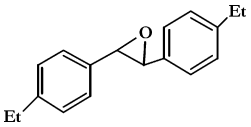
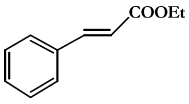
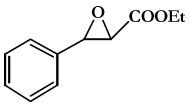
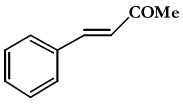
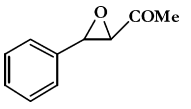
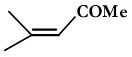
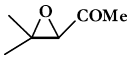
Substrate	Product	Time (h)	% conversion	% epoxide yield (TON)	% ee (absolute configuration)
		1.5	100	84 (875)	69 (*R*)
		1.5	100	92 (980)	71 (*R*)
		4	100	88 (930)	65 (*R*)
		4	90	96 (940)	72 (*R*)
		4	80	97 (836)	52 (*R*)
		4	100	96 (968)	50 (*R*)
		3	68	96 (803)	72 (*R*)
		5	60	80 (790)	24 (n.d)
		3	100	98 (990)	68 (1*R*,2*S*)
		2	90	86 (700)	70 (n.d)
		3	100	78 (890)	80 (1*R*,2*S*)[b]
		1	100	91 (900)	65 (n.d)
		2	90	85 (860)	67 (n.d.)
		12	36	94 (440)	35 (2*R*,3*S*)

Table 8 (*Continued*)

Substrate	Product	Time (h)	% conversion	% epoxide yield (TON)	% ee (absolute configuration)
		16	21	98 (270)	30(1*R*,2*R*)
		16[c]	72	88 (620)	14 (n.d)
		16	18	95 (220)	16 (n.d)
		16	48	96 (635)	14 (n.d)
		16	30	95 (360)	28 (n.d)

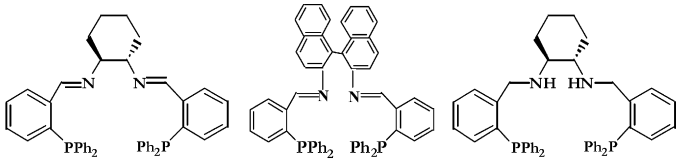
Taken from Ref. [31].

[a] A mixture containing alkene (0.5 mmol),2,6-DCPNP (0.55 mmol) and **3c** (0.5 μmol) in degassed benzene was stirred at room temperature.

[b] With [Ru^{II}(D_4-Por*)(CO)] as co-catalyst, the chiral epoxide was obtained in 81% yield and 71% ee after 48h reaction in C_6H_6.

[c] Temperature = 40 °C. n.d = not determined.

A new family of ruthenium(II)-complexes containing tetracoordinating chiral Schiff-base ligands (**6a–c**) with N2P2 donors was reported by Mezzetti et al. [37]. Their work [37] was the first example of the asymmetric epoxidation over ruthenium complexes employing hydrogen peroxide as terminal oxidant.

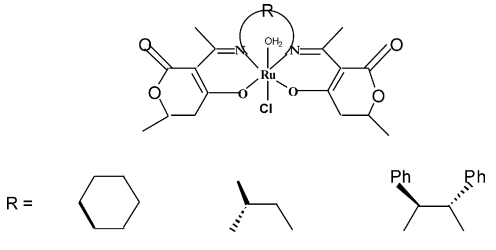


6a **6b** **6c**

Results of asymmetric epoxidation of alkenes with hydrogen peroxide catalyzed by five-coordinated ruthenium complexes containing the chiral ligands above are summarized in Table 12. The results in Table 12 indicate that [Ru^{II}(**6a**)Cl]$^+$ is a better catalyst than [Ru^{II}(**6a**)(H_2O)Cl]$^+$ complex. Chloride abstraction appears to be necessary to initiate catalytic activity as the dichloro [Ru(PNNP)Cl_2] species was reportedly found inactive under the specified turn-over conditions. This is further suggestive of the fact that activation of H_2O_2 is governed by the oxo-philicity of the five-coordinated [Ru^{II}(**6a**)Cl]$^+$ complex. Either reduced oxo-philicity (of [Ru^{II}(**6b**)Cl]$^+$) or reduced stability (of [Ru^{II}(**6c**)Cl]$^+$) decreased the efficiency of the catalytic system [37b]. The observed stereospecificity suggests that the reported epoxidation reaction [37b] predominantly proceeded through a non-radical pathway. No reaction was found to occur with NaOCl, whereas, use of $NaIO_4$, *t*-BuOOH and [NBu_4]HSO_5 resulted in oxidation products other than the epoxide.

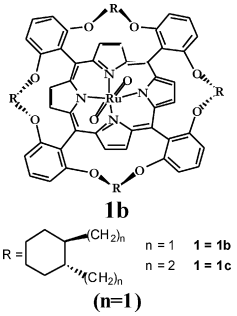
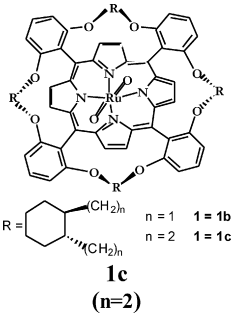
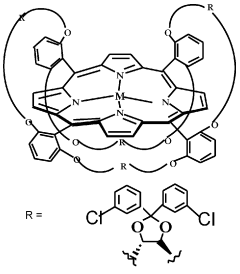
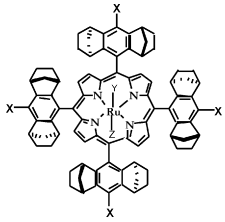
Very recently the same group has reported [37c] the use of the five-coordinate 16-electron [RuCl(PNNP)]$^+$ species and their octahedral analogues [RuCl(L)(PNNP)]$^+$ in the enantioselective atom transfer reactions, in which oxene or carbene are transferred from ruthenium to the non-coordinated substrate. The [RuCl(PNNP)]$^+$ catalysts perform cyclopropanation of 1-octene in the presence of ethyl diazoacetate with excellent *cis*- and enantioselectivity. A different mode of enantioselective atom transfer has been reported in the hydroxylation and electrophilic fluorination of 1,3-dicarbonyl compounds, in which the oxene or F^+-transfer agent attacks a ruthenium-bound substrate.

A series of new tetradentate Schiff-base ligands derived by interacting dehydroacetic acid (3-acetyl-6-methylpyran-2,4-dione) with various diamines, and the catalytic ability of their corresponding ruthenium(III) complexes (**7a–c**) to effect the asymmetric epoxidation of styrene and substituted styrenes has been reported by Kureshy et al. [38].



7a **7b** **7c**

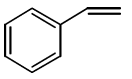
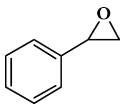
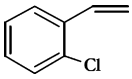
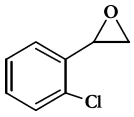
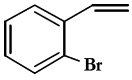
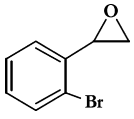
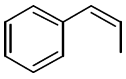
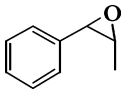
Table 9
Comparison of results of styrene epoxidation catalyzed by **1b**, **2f**, **3a** and **3c** in the presence of 2,6-DCPNO

Ru complex	Reaction conditions	% epoxide yield	TON[a]	% ee	Remarks
 **1b**	Cat:Ox:Substrate = 1 μmol: 330 μmol:330 μmol. Reaction was run for 2.5 h at room temperature in degassed benzene	62	204	7.5	Ref. [20]. The reactivity and enantioselectivity are strongly dependent on the arms of the chiral cyclohexyl entity. The short arm ($n = 1$) gives small chiral cavity and weak reactivity. Epoxide yield is of significance, but poor enantioselectivity
 **1c** **(n=2)**	Cat:Ox:Substrate = 1 μmol: 330 μmol:330 μmol. Reaction was run for 2.5 h at room temperature in degassed benzene	84	276	23	
 **2f**	Cat:Ox:Substrate = 0.165 μmol: 165 μmol:165 μmol. Reaction was run for 48 h reaction at −10 °C in toluene under argon	55	551	79	Ref. [26]. Higher enantioselectivity achieved at non-ambient reaction condition. Comparatively lower epoxide yield noticed at much higher reaction time.
 **3a** **(x = H, y = CO, z = MeOH)**	Cat:Ox:Substrate = 0.315 μmol: 315 μmol:315 μmol. Reaction was run for 48 h reaction at 25 °C in benzene under argon	79	790	70	Ref. [27]. Better catalyst in regard to epoxide yield, enantioselectivity and TON, but very high reaction time
3c (x = H, $y = z$ = Cl). Prepared from 3a in refluxing CCl_4	Cat:Ox:Substrate = 0.5 μmol: 0.55 mmol:0.5 mmol. Reaction was run for 1.5 h reaction at 25 °C in benzene under argon	84	875	69	Ref. [31]. Best catalyst. Non-intermediacy of dioxoruthenium(VI) species

[a] Moles of product per mole of catalyst.

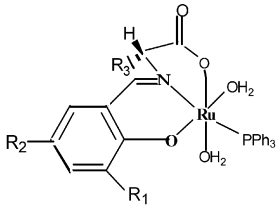
The ruthenium(III)-complexes (**7a–c**) efficiently catalyze the epoxidation of styrene and substituted styrenes by the combined use of dioxygen and sacrificial reductant isobutyraldehyde (Table 13) [38]. Although there is some minor improvement in conversion yield and 'ee' values in the presence of both dioxygen and pyridine *N*-oxide, the role of this oxidant was not obvious in the proposed catalytic cycle [38]. However, it is coordinated to the ruthenium center during the catalytic process.

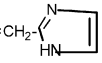
Table 10
$[Ru^{IV}(D_2\text{-Por*})Cl_2]$ and $[Ru^{IV}(D_4\text{-Por*})Cl_2]$ catalyzed asymmetric epoxidations[a]

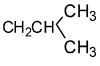
Alkene	Product	$[Ru^{IV}(D_2\text{-Por*})Cl_2]$				$[Ru^{IV}(D_4\text{-Por*})Cl_2]$			
		t (h)	% Conv.	% Yield epoxide	% ee (absolute configuration)	*t* (h)	% Conversion	% yield epoxide	% ee (absolute configuration)
		24	50	82	32 (*R*)	1.5	100	84	69 (*R*)
		24	48	94	52 (*R*)	4	80	97	52 (*R*)
		24	50	92	41 (*R*)	4	100	96	50 (*R*)
		24	15	80	10 (1*R*,2*S*)	3	100	98	68 (1*R*,2*S*)

Taken from Ref. [31].
[a] Reaction conditions are same as in Table 8.

The same group had reported [39] a number of ruthenium(II) complexes (**8**–**11**) containing tridentate chiral Schiff-base ligand derived from L-amino acids with salicylaldehyde and phenyl ring-substituted salicylaldehydes.

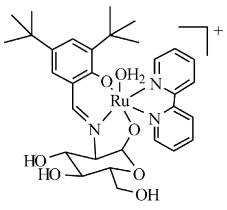


for 8; $R_1 = H$, $R_2 = H$ and $R_3 =$  **for 9;** $R_1 = H$, $R_2 = H$ and $R_3 =$ 

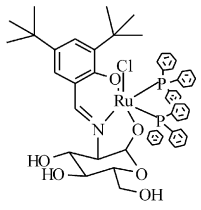
for 10; $R_1 = H$, $R_2 = H$ and $R_3 =$  **for 11;** $R_1 = H$, $R_2 = H$ and $R_3 =$ 

Complexes **8**–**11** were reported [39a,39b] to be the active catalysts towards the enantioselective epoxidation of styrene and aromatic ring substituted styrenes in the presence of iodosyl benzene as terminal oxidant (Table 14). The results in Table 14 suggest that **8** is the most efficient catalyst in the case of styrene epoxidation with iodosylbenzene as a precursor oxidant. Better results both in terms of conversion yield and enantioselectivity were achieved by modifying the chiral ligands in **8**–**11** using substituents on the phenyl ring of the salicylaldehyde moiety [39a,b]. Other oxidants like H_2O_2, NaOCl, O_2 and *m*-CPBA were either inactive or produced predominantly non-epoxide products [39b]. Surprisingly, above catalytic system were quite less efficient towards epoxidation of 1,2-dihydronapthalene [39c].

Very recently, Chatterjee et al. reported [40] a novel family of ruthenium(III) epoxidation catalyst complexes (**12** and **13**) using a tridentate chiral Schiff-base ligand (TDL*) derived from condensing chiral D-glucose amine with 3,5-ditertiarybutyl salicylaldehyde. The TDL* controls the enantiomeric induction, whereas, π-acidic bipy or PPh_3 influences the reactivity of the catalyst.



12



13

This new family of chiral ruthenium catalytic system runs under mild conditions. The results (Table 15) of the epoxida-

Table 11
Asymmetric epoxidation of conjugated olefins with **5** as a catalyst[a]

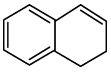
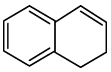
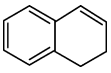
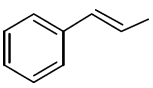
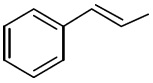
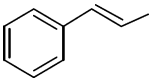
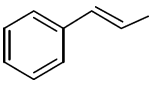
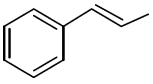
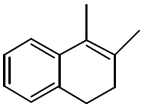
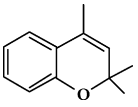
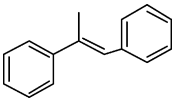
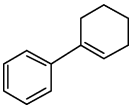
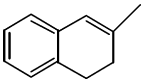
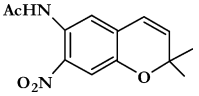
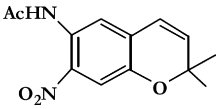
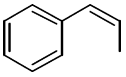
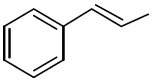
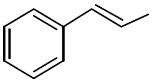
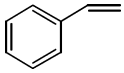
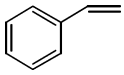
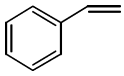
Entry	Substrate	*t* (h)	% Yield (epoxide)	% ee	Absolute configuration
1[b]		2	51	87	(1*S*,2*R*)
2[b]		6	70	81	(1*S*,2*R*)
3[e]		2	48	80	(1*S*,2*R*)
4[a]		2	26	86	(1*S*,2*S*)
5[a]		32	64	75	(1*S*,2*S*)
6[c]		7	60	81	(1*S*,2*S*)
7[b]		6	28	82	(1*S*,2*S*)
8[b]		20	75	80	(1*S*,2*S*)
9[c]		28	32	82	–
10[c]		16	54	97	3*S*
11[c]		17	83	86	(1*R*,2*R*)
12[c]		22	62	79	(1*R*,2*S*)
13[c]		22	74	88	–
14[a]		5	54	98	(3*S*,4*S*)
15[b]		16	59	97	(3*S*,4*S*)
16[b]		30	60	89	(1*S*,2*R*)
17[b]		72	52	87	(1*R*,2*R*)
18[c]		40	64	85	(1*R*,2*R*)

Table 11 (*Continued*)

Entry	Substrate	*t* (h)	% Yield (epoxide)	% ee	Absolute configuration
19[c]		7	30	83	(*S*)
20[c]		14	63	71	(*S*)
21[b]		12	34	79	(*S*)

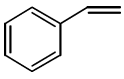
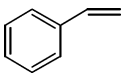
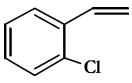
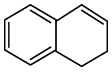
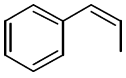
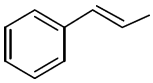
Taken from Ref. [36b].

[a] Reaction was carried out in ether at room temperature under irradiation of visible light. **5** = 2.0 μmol; 2,6-DNPNO = 100 μmol; substrate = 100 μmol.

[b] The reaction was carried out in benzene with 2,6-DNPNO as a terminal oxidant.

[c] The reaction was carried out in dioxane with tetramethylpyrazine *N*,*N*′-dioxide as a terminal oxidant.

Table 12
Asymmetric epoxidation of olefins catalyzed by [Ru^{II}(**6a**)Cl] and Ru^{II}(**6a**)(H_2O)Cl] complexes

Alkene	[Ru^{II}(**6a**)Cl][a]				[Ru^{II}(**6a**)(H_2O)Cl][a]			
	t (h)	% conversion	% yield epoxide	% ee (absolute configuration)	*t* (h)	% Conversion	% yield epoxide	% ee (absolute configuration)
	6	35	81	37 (*S*)	6	39	68	30 (*S*)
	6	34[b]	50[b]	40 (*S*)	–	–	–	–
	2	48	94	52 (*R*)	4	18	53	12
	2	100	55	41 (1*S*,2*R*)	2	84	50	25(1*S*,2*R*)
	6	22	72	4	6	6	70	22
	4	26	62	25 (1*R*,2*R*)	3	14	52	10 (1*R*,2*R*)

Taken from Ref. [37a,b].

[a] Reaction was carried out in CH_2Cl_2 at room temperature under argon atmosphere. Catalyst = 9.6 μmol; H_2O_2 = 6.86 mmol; substrate = 0.96 mmol.

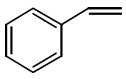
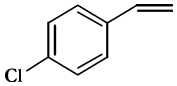
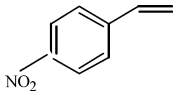
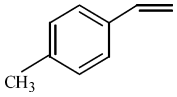
[b] The reaction was carried out in dichlorobenzene.

tion studies clearly revealed the catalytic ability of **12** and **13** to perform the epoxidation of unfunctionalized alkenes with high enantioselectivity using *t*-BuOOH as terminal oxidant. The efficacy of the **12** [40a] in terms of product yield is better when compared with that of **13**, however, notably high asymmetric induction by **13** (up to 94% of ee observed for 4-chlorostyreneoxide) to the epoxidation of styrenes with *t*-BuOOH was observed [40b]. Since, carbohydrates are naturally occurring enantiomeric pure compounds, and such chiral ligands (H_2TDL*) could be prepared in one step from commercially available starting materials, the results above are of significance in the design and development of more sugar-based ligands and their corresponding metal complexes for catalytic application in various asymmetric synthesis.

6. Asymmetric epoxidation by chiral monooxo ruthenium(IV)-polypyridyl complexes

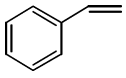
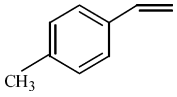
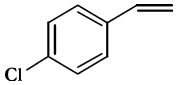
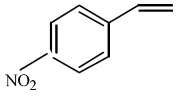
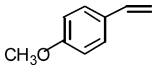
Polypyridyl complexes of ruthenium are of great significance as they are coordinatively stable both in higher and lower oxidation states, and a variety of ruthenium-oxo complexes containing polypyridyl ligands are known to be effective stoichiometric agents for alkene epoxidation [9]. In this context ruthenium(IV)-oxo complexes containing chiral ligands **14** and **15** that afford

Table 13
Asymmetric epoxidation of styrenes catalyzed by **7a-c**

Alkene	7a			7b		7c	
	t (h)	% conversion	% ee (absolute configuration)	% conversion	% ee (absolute configuration)	% conversion	% ee (absolute configuration)
	24[a]	90	18 (*R*)	85	24 (*R*)	95	20 (*S*)
	24[b]	75	12 (*R*)	72	20 (*R*)	83	20 (*S*)
	24[a]	92	19 (*R*)	70	26 (*R*)	90	22 (*S*)
	24[b]	69	14 (*R*)	65	22 (*R*)	78	30 (*S*)
	24[a]	55	23 (*R*)	55	30 (*R*)	62	24(*S*)
	24[b]	48	19 (*R*)	50	25 (*R*)	55	24(*S*)
	24[a]	75	16 (*R*)	70	22 (*R*)	80	20 (*S*)
	24[b]	70	11 (*R*)	65	17 (*R*)	70	15 (*S*)

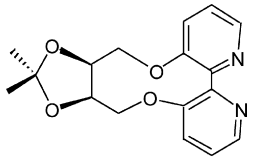
Taken from Ref. [38].
[a] Reaction was carried out in in CH_2Cl_2 at room temperature. catalyst = 6 μmol; pyridine *N*-oxide = 240 μmol; substrate = 2 mmol. 1 atm of O_2, isobutyraldehyde = 2 mmol.
[b] The reaction was carried out without pyridine *N*-oxide.

Table 14
Asymmetric epoxidation of styrenes catalyzed by **8**–**10**

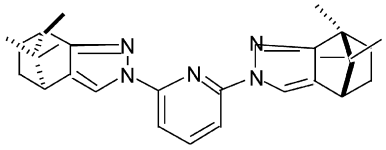
Alkene	**8**[a]		**9**[b]		**10**[b]	
	% conversion	% ee (absolute configuration)	% conversion	% ee (absolute configuration)	% conversion	% ee (absolute configuration)
	30	53 (*S*)	38	33 (*S*)	32	28 (*S*)
	25	60 (*S*)	45	36 (*S*)	40	32 (*S*)
	32	50 (*S*)	53	38 (*S*)	48	35 (*S*)
	45	75 (*S*)	59	45 (*S*)	52	38 (*S*)
	32	54 (*S*)	–	–	–	–

Taken from Ref. [39a,b].
[a] Reaction was carried out in degassed CH_2Cl_2 at room temperature; [catalyst] = 0.01 M; [iodosylbenzene] = 0.25 M [substrate] = 0.5 M; reaction time = 30 min.
[b] Reaction was carried out in degassed fluorobenzene at 0 °C; catalyst = 0.02 mmol, iodosylbenzene = 1 mmol; substrate = 1 mmol, reaction time = 120 min.

enantioselective epoxidation of unfunctionalized olefins were first reported by Che and co-workers [41].



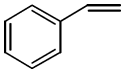
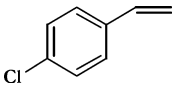
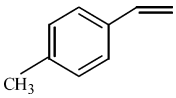
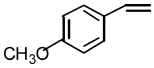
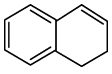
14



15

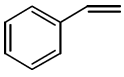
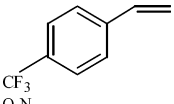
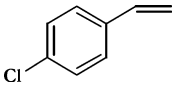
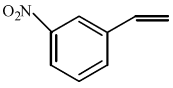
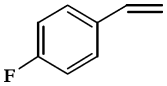
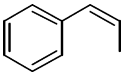
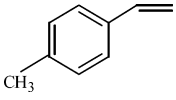
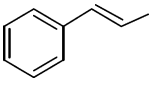
The results of stoichiometric oxidation of styrene by [Ru^{IV}(**14**)(Me_3tacn))O] resulted in only 9% ee [41b]. This low enantiomeric excess (ee) was attributed to the chirality of the ligand (**14**) which is too remote from the Ru=O moiety. The reaction of [Ru^{IV}(**15**)(bipy))O] with aryl alkenes in acetonitrile resulted in epoxide as the major product together with minor amount of aldehydes, and induced moderate enantioselectivity (Table 16). Detailed kinetic studies revealed that the reaction of [Ru^{IV}(**15**)(bipy))O] with alkenes is second-order in nature, and the values of second-order rate constant (*k*) lie in the range

Table 15
Asymmetric epoxidation of alkenes catalyzed by **12** and **13**

Alkene	12			13		
	% conversion[a]	% selectivity of epoxide	% ee	% conversion[b]	% selectivity of epoxide	% ee
	74	84	42	51	84	84
	75	87	39	59	76	94
	73	83	45	57	68	87
	72	79	37	56	73	90
	(32)	90	45	33	85	65
	(59)	92	47	44	89	67

Taken from Ref. [40a,b].
[a] Reaction was carried out in CH_2Cl_2 at room temperature; [catalyst] = 0.01 mmol; *t*-BuOOH = 1 mmol; substrate = 1 mmol; reaction time = 18 h.
[b] Reaction time = 12 h.

Table 16
Asymmetric epoxidation of alkenes by [Ru^{IV}(**15**)(bipy))O][a]

Alkene	% Cy.	% epoxide	% ee	Alkene	% Cy.	% epoxide	% ee
	78	58	37		72	63	37
	77	62	38		79	72	35
	78	60	36		81	33 (*cis*-epoxide) 17 (*trans*-epoxide)	30
	80	39	39		78	33 (*trans*-epoxide)	12

Taken from Ref. [41c].
[a] Reaction was carried out in CH_3CN under nitrogen atmosphere at 25 °C; [Ru^{IV}(**15**)(bipy))O] = 0.05 mmol; substrate = 1–2 mmol; reaction time = 12 h.

Table 17
Asymmetric epoxidation of *trans*-stilbene catalyzed by **16a**

Run	Oxidant	Catalyst:Oxidant:Substrate /mmol	Solvent	*T* °C	*t* (h)	% yield (epoxide)	ee
1	PhIO	0.025:1.5:0.5	Toluene	25	96	67	24
2	$PhI(OAc)_2$	0.025:1.5:0.5	Toluene	25	96	80	63
3	$PhI(OAc)_2$	0.025:1.5:0.5	Toluene	0	96	63	74
4	$PhI(OAc)_2$	0.025:1.5:0.5	Benzene	25	96	43	52
5	$PhI(OAc)_2$	0.025:1.5:0.5	CH_2Cl_2	25	96	40	36
6	NaIO4	0.025:2.5:0.5	Toluene	5	96	Trace	–
7	O_2/*t*-BuCHO	0.025:2.5:0.5	Toluene	25	96	67	5
8	*t*-BuOOH	0.025:2.0:0.5	CH_2Cl_2	25	72	38	16

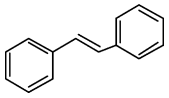
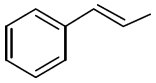
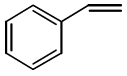
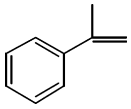
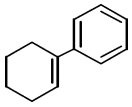
Taken from Ref. [43].

Table 18
Asymmetric epoxidation of *trans*-stilbene catalyzed by **16a**[a]

Run	Ratio of substrate:oxidant:H_2O	Solvent	*t* (h)	% conversion	% yield (epoxide)	ee
1	1:3:0	Toluene	96	97	80	63
2	1:6:0	Toluene	<63	100	80	53
3	1:6:0	Anhyd.toluene	67	12	11	–
4	1:6:6	Anhyd.toluene	3.5	100	80	46
5	1:6:3	Anhyd.toluene	3	100	80	43
6	1:3:3	Anhyd.toluene	26	100	83	49
7	1:3:6	Anhyd.toluene	5.5	82	63	29
8	1:1:1	Anhyd.toluene	25	55	53	71
9	1:6:6	THH/Anhyd.toluene (4: 6)	25	99	25	–
10	1:6:6	Dioxan/Anhyd.toluene (4: 6)	2	100	60	59
11	1:6:6	*t*-BuOH/Anhyd.toluene (4: 6)	1	100	84	57

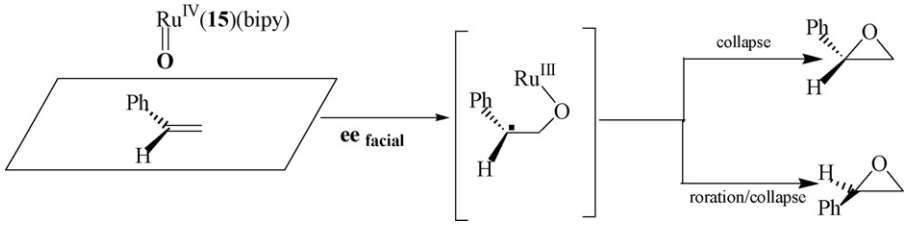
Taken from Ref. [45].
[a] Catalyst = 0.025 mmol, oxidant = $PhI(OAc)_2$; substrate = *trans*-stilbene = 0.5 mmol, reaction was performed at room temperature.

Table 19
Results of asymmetric epoxidation of olefins catalyzed by **16a**[a]

Run	Substrate	*t* (h)	% Conversion	% yield (epoxide)	ee
1		1	100	84	57
2		5	100	86	27
3		45	100	48	5
4		23	100	73	11
5		1	100	81	7

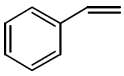
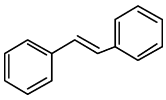
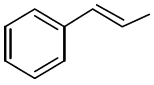
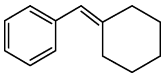
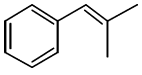
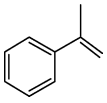
Taken from Ref. [45].
[a] Reaction was performed in a solvent mixture containing anhydrous toluene (6 ml) and *t*-BuOH (4 ml) at room temperature. Catalyst = 0.025 mmol, $PhI(OAc)_2$ = 1.5 mmol, substrate = 0.5 mmol, H_2O = 1.5 mmol.

0.046–0.42 $M^{-1}\,s^{-1}$ at 25 °C [41c]. Activation parameters, in particular large negative values of activation entropy ($\Delta S^{\neq}$) are consistent with the associative nature of activation for the reaction of [Ru^{IV}(**15**)(bipy))O] with alkenes. The small variations of the reported rate constant values (k = 0.19 $M^{-1}\,s^{-1}$ for *p*-chlorostyrene and 0.22 $M^{-1}\,s^{-1}$ for *p*-methyl styrene at 25 °C) [41c] disfavors the participation of either an alkene-derived cation radical or carbocation intermediate. However, the authors by invoking total substituent effect (TE) radical parameters [42] into their kinetic results, proposed the rate limiting formation of a benzylic radical intermediate [41c]. A facial selectivity through side-on approach that brings about the observed enantioselectivity was proposed [41c] by considering that the Ru=O axis is orthogonal to the molecular plane of **15** but collinear to 'bipy' in [Ru^{IV}(**15**)(bipy))O]; the oxo-moiety is thus sterically encumbered and only one face of the Ru=O site is exposed for the



Scheme 2.

Table 20
[a]Asymmetric epoxidation of alkenes with H_2O_2 catalyzed by **23** and **16b**

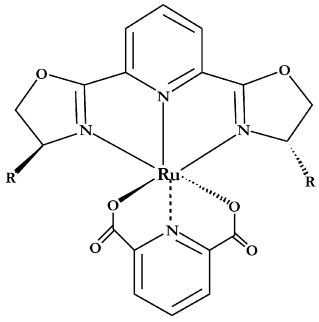
Alkene	**23**			**16b**		
	% conversion	% selectivity of epoxide	% ee	% conversion	% selectivity of epoxide	% ee
	100	77	26	100	70	31
	100	100	71	100	100	67
	100	100	56	100	82	58
	100	100	58	100	99	68
	100	79	62	100	91	72
	100	69	2	100	52	13

Taken from Refs. [47,51].
[a] Reaction was carried out in *tert*-amyl alcohol at room temperature; [catalyst] = 0.025 mmol; H_2O_2 = 1.5 mmol; substrate = 0.5 mmol; reaction time = 12 h.

olefinic approach. Because of the non-concerted nature of reaction, the product enantioselectivity (% ee) is not established at the first irreversible C–O bond formation. The reduction of product enantioselectivity also likely takes place by the formation of the opposite enantiomeric epoxide via rotation/collapse pathway (Scheme 2), and hence, the stereoselectivity of the epoxide ring-closure is also important in controlling the overall product enantioselectivity [41c].

7. Asymmetric epoxidations catalyzed by chiral Ru-oxazoline complexes

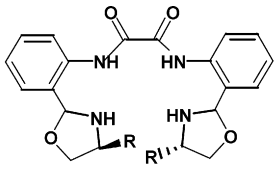
In 1997, Nishiyama et al. reported [43] a new catalyst design by introducing dual closed meridional stereotopes around the metal center using bis(oxazolinyl)pyridine (pybox) and pyridine-2,6-dicarboxylate (pydic). Because of the π-acceptor property of dicarboxylic group and oxazoline rings, these ligands are suitable for the preparation of stable metal complexes. The [Ru(pybox)(pydic)] (**16**) complex was found to effect catalytic epoxidation of olefins accompanied by asymmetric induction [43].



16a R = ^{i}Pr; **16b** R = Ph; **16c** R = CH_3

Considering *trans*-stilbene as a test substrate, the catalytic ability of **16** in achieving alkene epoxidation was examined using various precursor oxidants and the results (Table 17) suggest that bis(acetoxy)iodobenzene was the best oxidant amongst the terminal oxidants used.

Application of chiral oxalamides ligands (**17**) prepared from 2-(2-aminophenyl)oxazolines in asymmetric epoxidation of olefins using $RuCl_3$ and $NaIO_4$ was reported by End and Pfaltz [44].



17a-d

17a R = Me; 17b R = ^{iso}Pr; 17c R = ^{tert}Bu; 17d R= Ph

Amongst the oxalamides examined, **17b** was the most active ligand. The results showed that in the asymmetric epoxidation of *trans*-stilbene the ee value of the epoxide was very low in the beginning but increased significantly with prolonged reaction time. However, by subjecting the catalytic species to interact with the oxidant for a period before addition of the substrate, a significant improvement of the catalytic performance with 74% yield and 69% ee was achieved [44].

Unfortunately, both the catalytic systems above [43,44] revealed very low reactivity (70–96 h were needed for full conversion) and limited applicability (successful epoxidation was only achieved with *trans*-stilbene as substrate). Nonetheless, further investigation of **16** was continued because of the easy accessibility of pyridinebisoxazoline (pybox) ligands from natural occurring amino acids [43]. In 2003, Beller et al.

Table 21
Comparison of results of styrene epoxidation catalyzed by various chiral complexes of ruthenium

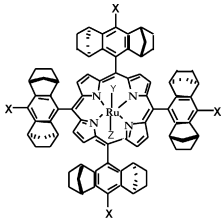
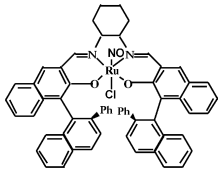
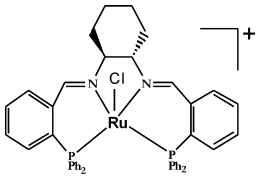
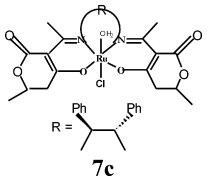
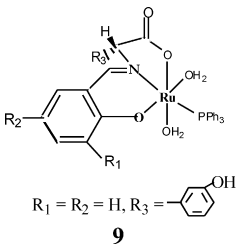
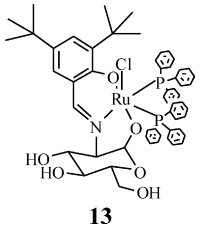
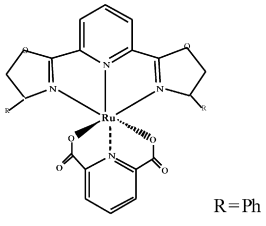
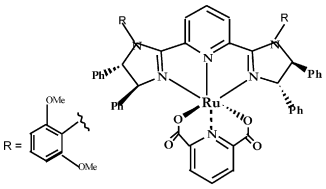
Ru complex	Reaction conditions	% epoxide yield	TON[a]	% ee	Remarks
 **(x = H, y = z = Cl)** **3c**	Cat:Ox:Substrate = 0.5 μmol:0.55 mmol: 0.5 mmol. Reaction was run for 1.5 h at 25 °C in benzene under argon. Ox = 2,4-DCPNO	84	875	69	Ref. [31]. Best catalyst. Non-intermediacy of dioxoruthenium(VI) species. Multi-step tedious synthesis of chiral porphyrin ligands
 **5**	Cat:Ox:Substrate = 2.0 μmol:0.1 mmol: 0.1 mmol. Reaction was run for 12 h at room temperature in benzene under argon. Ox = 2,4-DCPNO	34	17	75	Ref. [36]. Poor yield and turnover, reasonably high enantioselectivity. Synthesis of chiral ligand involved more than one step
 **6a**	Cat:Ox:Substrate = 9.6 μmol:6.86 mmol: 0.96 mmol. Reaction was run for 6 h at room temperature in CH_2Cl_2 under argon. Ox = H_2O_2	81	81	37	Ref. [37a]. Poor yield and turnover, reasonably high enantioselectivity. Catalytic system comprises of green precursor oxidant. Synthesis of chiral ligand is not involved more than one step
 **7c**	Cat:Ox:Substrate = 6.0 μmol:240 μmol: 2.0 mmol. Reaction was run for 24 h at room temperature in CH_2Cl_2 under argon. Ox = pyridine *N*-oxide	95	317	20	Ref. [38]. High epoxide yield and reasonably good turnover. Poor enantioselectivity. Synthesis of chiral ligand involved condensation of enantiomerically pure diaamine with dehydroacetic acid
 **9**	Cat:Ox:Substrate = 20.0 μmol:1.0 mmol: 1.00 mmol. Reaction was run for 2 h at 0 °C in degassed fluorobenzene. Ox = iodosylbenzene	38	19	33	Ref. [39]. Low turnover and enantioselectivity. Reaction condition is not ambient. One step synthesis of chiral ligand using enantiomerically pure amino acid
 **13**	Cat:Ox:Substrate = 10.0 μmol:1.0 mmol: 1.0 mmol. Reaction was run for 12 h at room temperature in CH_2Cl_2. Ox = *t*-BuOOH	47	47	84	Ref. [40b]. Moderate yield and low turnover, but high enantioselectivity. One step synthesis of chiral ligand using naturally occurring sugar based compound
 **16b**	Cat:Ox:Substrate = 0.025 mmol:1.5 mmol: 0.5 mmol. Reaction was run for 12 h at room temperature in CH_2Cl_2. Ox = H_2O_2	70	71	31	Ref. [47]. High epoxide yield, but low turnover and enantioselectivity. Catalytic system comprises of green precursor oxidant. Synthesis of chiral ligand is not complicated

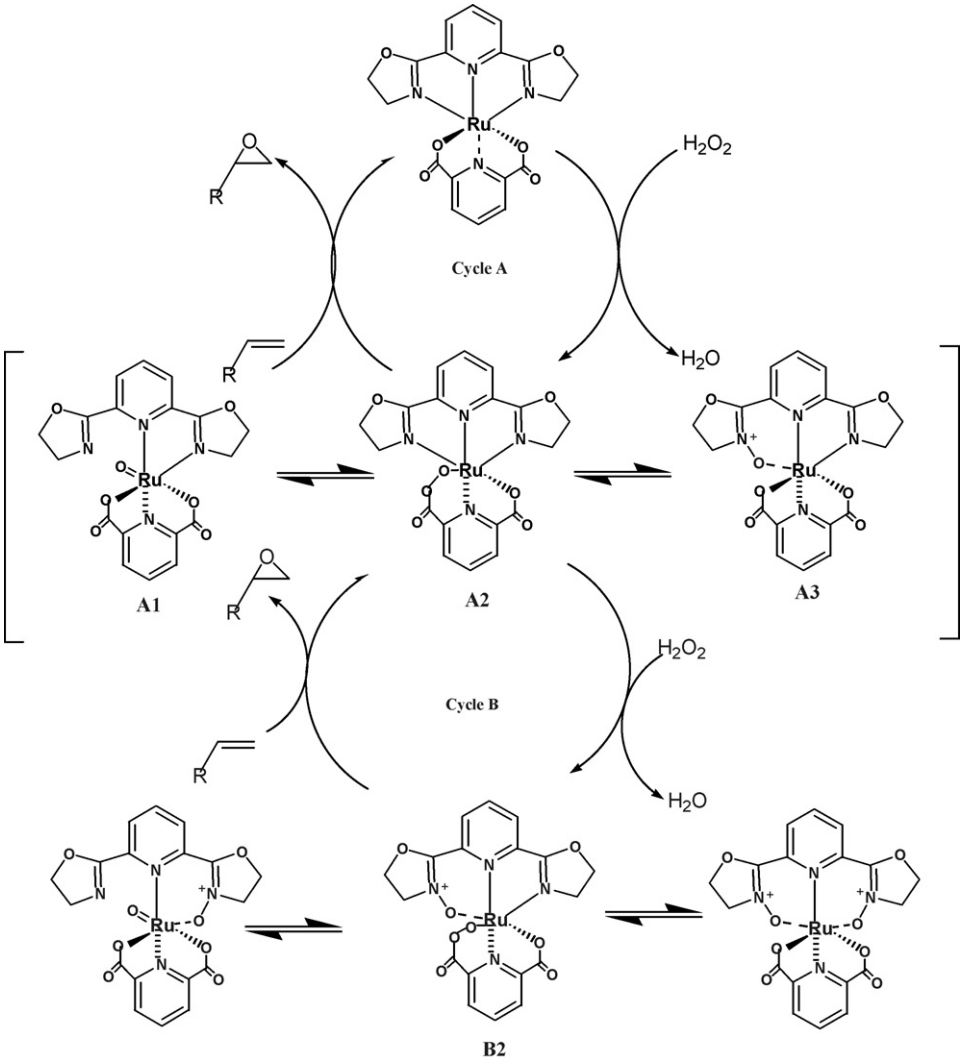
Table 21

Ru complex	Reaction conditions	% epoxide yield	TON[a]	% ee	Remarks
 **24**	Cat:Ox:Substrate = 25.0 μmol: 1.5 mmol:0.5 mmol. Reaction was run for 12 h at room temperature in *tert*-amyl alcohol. Ox = H_2O_2	77	15	26	Ref. [51]. High epoxide yield, but low turnover and enantioselectivity. Catalytic system comprises of green precursor oxidant. Synthesis of chiral ligand is not complicated

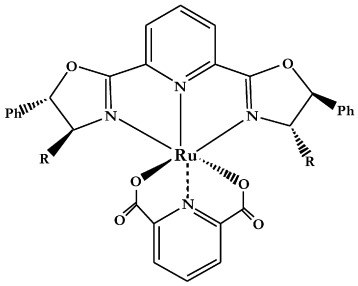
[a] Moles of product per mole of catalyst.

[45] reported an improved protocol for the ruthenium(pybox)-catalyzed asymmetric alkene epoxidation. The addition of a stoichiometric amount of water increased the ee value to 71% in the case of epoxidation of *trans*-stilbene at a low concentration of $PhI(OAc)_2$, however, increasing the concentration of oxidizing agent ($PhI(OAc)_2$) resulted in an elevated yield but a reduced enantioselectivity (Table 18). The results in Table 18 suggest that water played a crucial role in the reaction, presumably due to the enabling of the oxidation of 18-electron [Ru(***S***,***S***-$^{i}Pr_2$-pybox)(pydic)] **16a** via a ligand dissociation [46]. Applicability of catalyst **16a** in the epoxidation of olefinic substrates other than *trans*-stilbene, had also been explored [45]. Table 19 reveals that except for *trans*-stilbene the reaction gave poor enantioselectivity for other olefins.

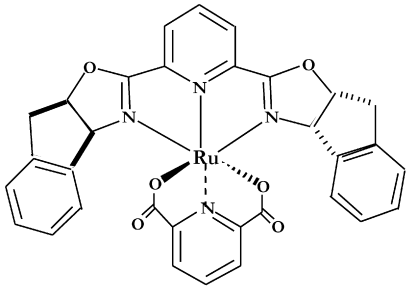
The use of *t*-BuOOH as terminal oxidant instead of $PhI(OAc)_2$ in the asymmetric epoxidation of alkenes catalyzed by **16** and its modified versions (**18** and **19**) showed highly encouraging results achieving epoxide yield up to 97% with a feasible ee value of 65% at room temperature [47].



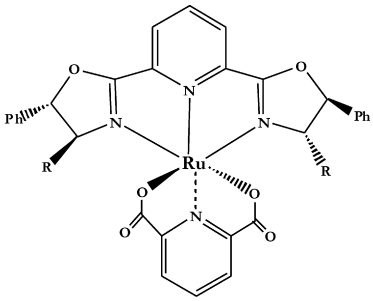
Scheme 3.



18



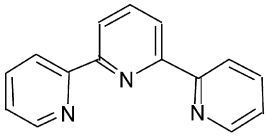
19



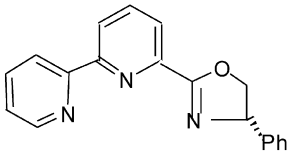
20

(for pybox n = 0; pyboxazine n = 1)

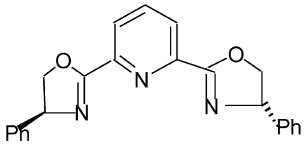
The same group later reported the use of H_2O_2 in the catalytic systems above [48]. Very recently, they have shown [48b] that using [Ru(pybox)(pydic)] (**16**, **18**, **19**) and [Ru(pyboxazine)(pydic)] (**20**) as catalysts, the asymmetric epoxidation of mono-, 1,1-di, *cis*- and *trans*-1,2-di, tri- and tetra-substituted aromatic olefins with versatile functional groups can be achieved in good to excellent yield (up to 100%) with moderate to good enantioselectivities (50–80% ee). Usage of two different meridional ligands significantly simplified the structural variations electronically and sterically around the metal center. The presence of weak organic acid and electron-withdrawing groups on the catalyst enhanced the catalytic performance [48b]. On the basis of mechanistic studies and density functional theory calculations, the intermediacy of a novel *N*-oxide type intermediate was proposed [48b]. Mechanistic implications concerning the intermediacy of mono-*N*-oxide species along with the putative oxoruthenyl [$L_1L_2Ru{=}O$] species, have been further consolidated [49]. While performing catalysis of olefin epoxidation with 30% aqueous H_2O_2 [49] using various [Ru(L_1)(L_2)] complexes where $\mathbf{L}_1$ = **21a–c** and $\mathbf{L}_2$ = **22a–c**, they observed that the catalyst complexes that contain 'pyridyl' ligand showed extraordinarily high reactivity.



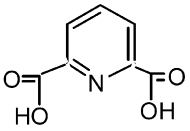
21a



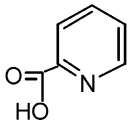
21b



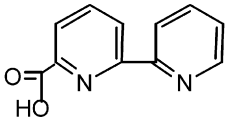
21c



22a



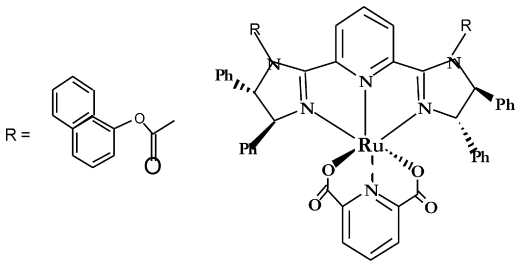
22b



22c

Further, considering the stereoselective performance of chiral ruthenium complexes containing non-racemic 2,2′-bipyridines including 6-[(4*S*)-4-phenyl-4,5-dihydro-oxazol-2-yl]-[2,2′]bipyridine (**21b**), the following reaction pathway (Scheme 3) for ruthenium catalyzed enantioselective epoxidation was proposed [49].

Further to the success of the pybox type of ligands, Beller et al. introduced another novel class of *N*,*N*,*N*-tridentate pyridinebisimidazoline ligands (abbreviated as 'pybim') in the ruthenium catalyzed asymmetric epoxidation of olefins [50,51]. The introduction of nitrogen in place of oxygen in the 'pybox' ligand would provide a more flexible ligand scaffold, which might be easily varied by *N*-derivatization to tune the reactivity as well stereoselectivity in the catalytic asymmetric epoxidation.



23

The newly developed pybim complexes of ruthenium (**23**) exhibited comparable reactivity (Table 20) and enantioselectivity to those obtained by using corresponding 'pybox' complexes. The facile synthesis of the pybim ligands together with the *easy-to-tune* facility makes them a suitable toolbox for application to a number of other catalytic asymmetric reactions.

8. Summary and outlook

The work described in this review firstly confirms the observation that chiral ruthenium complexes are particularly well adapted as asymmetric devices for asymmetric epoxidation. This review has systematically summarized the performance of chiral ruthenium complexes that effect asymmetric epoxidations in homogeneous conditions. Considering styrene as a test substrate, best performing Ru-catalytic systems from each group discussed in the preceding sections, are compared in Table 21.

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. However, some important observations are briefly outlined in the last column of the Table 21. Under ambient conditions **3c** appears to be most effective with regard to epoxide yield, enantioselectivity, turnover and reaction time among the other Ru-catalysts shown in Table 21. This catalytic system is also versatile in the epoxidation of various alkenes [31]. However, the tedious preparation and high cost of porphyrin ligands are major bottlenecks for its application in organic synthesis. In this regard the heterogenization of homogeneous chiral catalysts is an attractive solution as it affords the repetitive use of catalyst and facilitates product-catalyst separation [52]. Encapsulation of Ru-porphyrin complex in ordered molecular sieves (MCM-41 and MCM-45) showed enhanced reactivity in the asymmetric epoxidation of olefins [31,53]. In this regard there is a very recent review article [54] on the progress made in asymmetric catalysis in the nanopores of mesoporous materials and periodic mesoporous organosilicas (PMOs) highlighting factors like confinement effect, linkage and micro-environment in nanopores that influence the activity and enantioselectivity of asymmetric catalysis. This would also be of significance in developing heterogenized Ru-based asymmetric epoxidation catalytic systems.

Developing catalytic routes for the asymmetric epoxidation using environmentally cleaner reagents such as air or hydrogen peroxide is another opportunity for future research in this demanding area. Although significant results have been obtained very recently using H_2O_2 as a green oxidant [37,48,51], there is still a need for a new and improved ligand, which can be conveniently prepared from inexpensive and commercially available starting materials and most importantly would form ruthenium catalysts that are highly efficient, productive and versatile for a wide range of alkenes.

There remain substantial unresolved mechanistic issues in the Ru-catalyzed asymmetric epoxidations. Although oxo-transfer from Ru=O species to the alkenes is generally suggested, this is not the only active species. There is now firm evidence supporting multiple competing oxygen transfer species. A consensus on the relative selectivity of this species and Ru=O has not yet been established. More importantly, for such potential oxo-transfer species the substrate approach trajectory has hardly been explored. The mechanism of oxygen atom transfer from catalytic active intermediate (usually high-valent metal-oxo complex) to the organic substrate is still an open question. Several mechanisms have been proposed depending on several factors like oxidant, coordinating ligand, substrate, solvent. The results obtained with a specific system cannot be extended to other systems. Thus a unified mechanism is an interesting, yet to be achieved, objective. There is great scope for an increased understanding of the mechanistic possibilities concerning the nature of the active oxidant involved in the epoxidation step, the effect of ligand structure and primary oxidant, which should lead to further improvements in catalyst design and/or reaction conditions.

Acknowledgments

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