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Synthesis, physico-chemical studies and solvent-dependent enantioselective epoxidation of 1,2-dihydronaphthalene catalysed by chiral Ruthenium(II) Schiff base complexes. I

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Abstract

Ruthenium(II) chiral Schiff base complexes **1**–**10** and their precursor ligands derived from L-amino acids viz. L-leucine, L-histidine with salicylaldehyde, 3-*tertiary*-butyl-, 3,5-di-*tertiary*-butyl-, 3,5 dichloro- and 3,5-dinitrosalicylaldehyde are reported. The characterization of the ligands and complexes was accomplished by various appropriate physico-chemical studies, namely, microanalysis, IR-, UV/Vis-, ^{1}H, $^{31}P\{^{1}H\}$ NMR, CD spectroscopy, optical rotation, conductance measurement and cyclic voltammetry. The complexes thus synthesised were used as catalysts for enantioselective epoxidation of 1,2-dihydronaphthalene. The effect on enantioselectivity and chemical conversions to epoxide were studied in different solvents viz. acetonitrile, dichloromethane and fluorobenzene along with change of the substituents on ligands and different terminal oxidants. The less polar nature of solvent as well as the donating group attached on the catalysts favours enantioselectivity, while PhIO was the oxidant of choice. The enantiomeric excess of the resulting epoxide was evaluated by chiral cyclodex BDA capillary column.

Keywords: Enantioselective; Epoxidation; Catalyzed; Chiral Schiff base; Ruthenium; Complexes

1. Introduction

Enantioselective epoxidation of olefins presents a powerful strategy for the synthesis of enantiomerically enriched epoxides that are very important building blocks for the synthesis of enantiomerically pure complex molecules [1–4]. Asymmetric induction in allyl alcohols for the production of corresponding epoxy alcohols with enantiomeric excesses greater than 90% were first achieved by Rossiter et al. [5], Katsuki and Sharpless [6], Johnson and Sharpless [7] and Martin et al. [8]. An intrinsic limitation of this system is the essentiality of coordinating functional group on the substrate in order to show high enantioselection. Therefore, ultimate challenge in this area still remains for non-functionalised olefins where the chiral recognition is based solely on non-bonding interaction between substrate and catalyst. The most important early contribution in this respect was made by Groves and Myers [9] where they used Fe(III)

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porphyrin as catalyst with mild oxidants. The best selectivities are achieved with *cis* olefins and other substituted olefins by Chang [10], Zhang et al. [11], Jacobsen et al. [12,13] and Zhang and Jacobsen [14], and Sasaki et al. [4] and Irie [15] using optically active salen Mn(III) complexes.

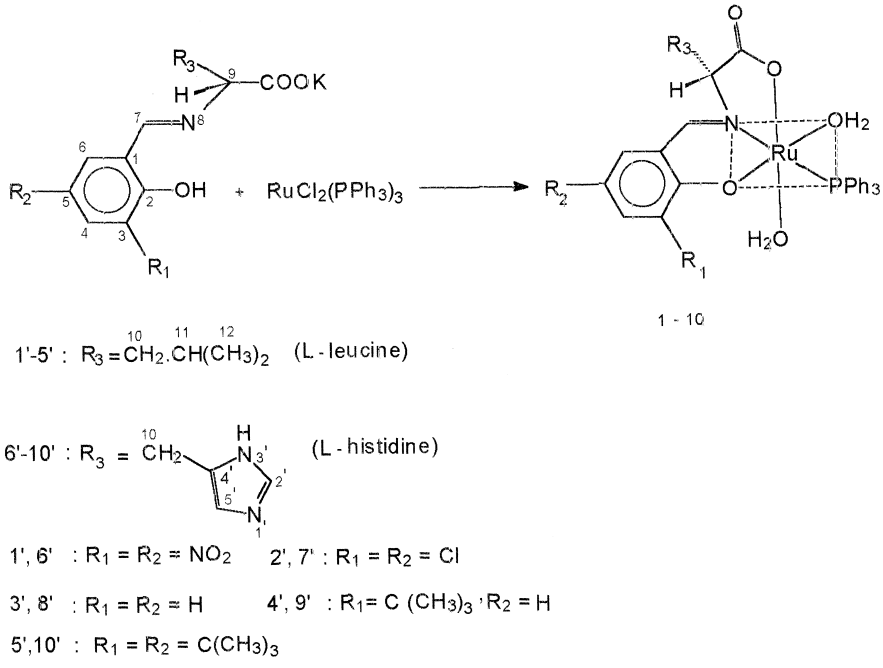
In continuation to our earlier work on enantioselective epoxidation of prochiral non-functionalised olefins using Ru(III), Ru(II), Mn(III), Co(II) and Ni(II) chiral Schiff base complexes [16–20], we are reporting here the synthesis, physicochemical studies of chiral Ru(II) Schiff base complexes and their utility for enantioselective epoxidation of 1,2-dihydronaphthalene in acetonitrile, dichloromethane and fluorobenzene in order to see the difference in enantioselectivity in different solvent with respect to the donating or withdrawing group on the ligand moiety of the catalysts. Various terminal oxidants viz. NaOCl, H_2O_2, O_2 (with sacrificial aldehyde), *m*-chloroperbenzoic acid were also tried. However, PhIO came out to be the oxidant of choice.

2. Experimental

$RuCl_3 \cdot 3H_2O$ (Johnson and Matthey), PPh_3, L-leucine, L-histidine (Sisco), salicylaldehyde, 3,5-dichloro-, 3,5-dinitrosalicylaldehyde (Aldrich) were used as such. The metal complex $[RuCl_2(PPh_3)_3]$ [21], 3-*tertiary*-butyl- and 3,5-di-*tertiary*-butyl salicylaldehyde were prepared by the known method [22]. All the chiral Schiff bases derived from appropriate salicylaldehyde with L-leucine and L-histidine (**1′**–**10′**, Scheme 1) were synthesised by known methods [23].

The characterisation of the chiral Schiff bases was done by microanalysis, IR- and ^1H NMR spectroscopy.

*N-(3,5-Dinitrosalicylidine) L-leucine **1′***. Yield 70%; Calcd. for $C_{13}H_{14}N_3O_7K$: C, 42.97; H, 3.88; N, 11.56. Found: C, 42.95; H, 3.85; N,



Scheme 1. Synthesis of the complexes **1**–**10**.

11.52; IR (KBr) cm^{-1}, 1625 ν(H–C=N); ^{1}H NMR (CD_3OD) δ ppm, 8.91 (d, $J = 2$ Hz, C_4 aromatic), 8.73 (s, 1 H, C_7, azomethine), 8.67 (d, $J = 2$ Hz, C_6 aromatic), 4.38–4.31 (2d, $J = 6$ Hz, 1 H, C_9 asymmetric), 1.91–1.82 (dd, $J = 8$ and 6 Hz, 2 H, C_{10}), 1.78–1.65 (m, 1 H, C_{11}), 1.02 (d, $J = 6$ Hz, 6 H, C_{12}).

N-(3,5-Dichlorosalicylidine) L-leucine ***2′***. Yield 60%; Calcd. for $C_{13}H_{14}NO_3Cl_2K$: C, 45.62; H, 4.12; N, 4.09. Found: C, 45.59; H, 4.10; N, 4.05; IR (KBr) cm^{-1} 1620 ν(H–C=N); ^{1}H NMR (CD_3OD) in δ ppm, 8.41 (s, 1 H, C_7, azomethine), 7.46 (dd, $J = 2$ Hz, 1 H, C_4 aromatic), 7.28 (d, $J = 2$ Hz, 1 H, C_6 aromatic), 4.24–4.17 (dd, $J = 6$ Hz, 1 H, C_9 asymmetric), 1.85–1.75 (dd, $J = 6$ Hz, 2 H, C_{10}), 1.73–1.61 (m, 1 H, C_{11}), 1.0 (d, $J = 6$ Hz, 6 H, C_{12}).

N-(Salicylidine) L-leucine ***3′***. Yield 60%; Calcd. for $C_{13}H_{16}NO_3K$: C, 57.11; H, 5.89; N, 5.12. Found: C, 57.09; H, 5.85; N, 5.10; IR (KBr) cm^{-1} 1620 ν(H–C=N); ^{1}H NMR (CD_3OD) in δ ppm, 8.38 (s, 1 H, C_7, imine), 7.32–7.24 and 6.81–6.69 (two sets of m, 4 H, C_{3-6} aromatic) 4.06–3.99 (dd, $J = 6$ Hz, C_9, 1 H, asymmetric), 1.83–1.75 (dd, $J = 6$ Hz, 2 H, C_{10}), 1.71–1.60 (m, 1 H, C_{11}), 0.97 (d, $J = 6$ Hz, 6 H, C_{12}).

N-(3-tertiary-Butyl salicylidine) L-leucine ***4′***. Yield 65%; Calcd. for $C_{17}H_{24}NO_3K$: C, 61.97; H, 7.34; N, 4.25. Found: C, 61.94; H, 7.31; N, 4.21; IR (KBr) cm^{-1} 1620 ν(H–C=N); ^{1}H NMR (CD_3OD) δ ppm, 8.39 (s, 1 H, C_7 azomethine), 7.30 and 7.8 (dd, $J = 2$ Hz, 1 H, C_6 aromatic), 7.18 (dd, $J = 2$) and 7.4 Hz (1 H, C_4 aromatic), 6.79 (t, $J = 7.8$ and 7.4 Hz, 1 H, C_5 aromatic), 3.98–3.91 (dd, $J = 7$ Hz, 1 H, C_9 asymmetric), 1.70 (m, 1 H, C_{11}), 1.85–1.75 (dd, $J = 6.4$ Hz, 2 H, C_{10}), 1.37 (s, 9 H, *t*-butyl), 0.99 (d, $J = 6.6$ Hz, 6 H, C_{12}).

N-(3,5-ditertiary-Butyl salicylidine) L-leucine ***5′***. Yield 60%; Calcd. for $C_{21}H_{32}NO_3K$: C, 65.41; H, 8.36; N, 3.63. Found: C, 65.38; H, 8.32; N, 3.60; IR (KBr) cm^{-1} 1620 ν(H–C=N); ^{1}H NMR (CD_3OD) δ ppm, 8.37 (s, 1 H, C_7, azomethine), 7.28 (d, $J = 2$ Hz, 1 H, C_6 aromatic), 6.96 (d, $J = 2$ Hz, 1 H, C_4 aromatic), 3.96–3.89 (dd, $J = 6$ Hz, 1 H, C_9 asymmetric), 1.67 (m, 1 H, C_{11}), 1.82–1.72 (dd, $J = 6$ Hz, 2 H, C_{10}), 1.36 and 1.40 (2s, 18 H, *t*-butyl), 0.96 (d, $J = 6$ Hz, 6 H, C_{12}).

N-(3,5-Dinitrosalicylidine) L-histidine ***6′***. Yield 70%; Calcd. for $C_{13}H_{10}N_5O_7K$: C, 40.31; H,2.60; N, 18.08. Found: C, 40.28; H, 2.57; N, 18.06; IR (KBr) cm^{-1} 1620; ^{1}H NMR (CD_3OD) δ ppm, 9.23 (d, $J = 2$ Hz, 1 H, C_4, aromatic), 8.96 (s, 1 H, C_7 and C_5 imine), 8.81 (d, $J = 2$ Hz, 1 H, C_6 aromatic), 7.69 and 6.92 (2s, 2 H, $C_{2'}$ and $C_{5'}$ imidazole), 4.48–4.41 (dd, $J = 6$ Hz, 1 H, C_9 asymmetric), 3.38 (d, $J = 6$ Hz, 2 H, C_{10}).

N-(3,5-Dichlorosalicylidine) L-histidine ***7′***. Yield 65%; Calcd. for $C_{13}H_{10}N_3O_3Cl_2K$: C, 42.63; H, 2.75; N, 11.47. Found: C, 42.60; H, 2.72; N, 11.43; IR (KBr) cm^{-1} 1620 ν(H–C=N); ^{1}H NMR (CD_3OD) in δ ppm, 7.94 (s, 1 H, C_7, imine), 7.65 and 6.88 (2s, 2 H, $C_{2'}$ and $C_{5'}$ imidazole), 7.50 (d, $J = 2$ Hz, 1 H, C_4 aromatic), 7.22 (d, $J = 2$ Hz, 1 H, C_6 aromatic), 4.36–4.28 (dd, $J = 6$ Hz, 1 H, C_9 asymmetric), 3.35 (d, $J = 6$ Hz, 2 H, C_{10}).

N-(Salicylidine) L-histidine ***8′***. Yield 70%; Calcd. for $C_{13}H_{12}N_3O_3K$: C, 52.51; H, 4.06; N, 14.13. Found: C, 52.48; H, 4.04; N, 14.10; IR (KBr) cm^{-1} 1625 ν(H–C=N); ^{1}H NMR (CD_3OD) δ ppm, 8.10 (s, 1 H, C_7, imine), 7.54 and 6.79 (2s, 2 H, $C_{2'}$ and $C_{5'}$ imidazole), 7.45–6.72 (m, 4 H, C_{3-6} aromatic), 4.17–4.11 (dd, $J = 6$ Hz, 1 H, C_9 asymmetric), 3.30 (d, $J = 6$ Hz, 2 H, C_{10}).

N-(3-tertiary-Butyl salicylidine) L-histidine ***9′***. Yield 65%; Calcd. for $C_{17}H_{20}N_3O_3K$: C, 57.76; H, 5.70; N, 11.88. Found: C, 57.72; H, 5.67; N, 11.83; IR (KBr) cm^{-1} 1625 ν(H–C=N); ^{1}H NMR (CD_3OD) δ ppm, 8.10 (s, 1 H, C_7, imine), 7.53, 6.78 (2s, 2 H, $C_{2'}$ and $C_{5'}$ imidazole), 7.28 (d, $J = 2$ Hz, 1 H, C_6 aromatic), 7.24 (d, $J = 2$ Hz, 1 H, C_4 aromatic), 6.72 (m, 1 H, C_5 aromatic), 4.10–4.03 (dd, $J = 5$ Hz, C_9 asymmetric), 3.33 (d, $J = 5$ Hz, 2 H, C_{10}), 1.39 (s, 9 H, *t*-butyl).

N-(3,5-diter-Butylsalicylidine) L-histidine ***10′***. Yield 60%; Calcd. for $C_{21}H_{28}N_3O_3K$:C, 61.58;

H, 6.89; N, 10.25. Found: C, 61.53; H, 6.86; N, 10.21; IR (KBr) cm^{-1} 1620 ν(H–C=N); ^1H NMR (CD_3OD) δ ppm, 7.91 (s, 1 H, C_7, imine), 7.32 and 6.69 (2s, 2 H, $C_{2'}$ and $C_{5'}$ imidazole), 7.22 (d, $J = 2$ Hz, 1 H, C_6 aromatic), 6.98 (d, $J = 2$ Hz, 1 H, C_4 aromatic) 4.04–3.97 (dd, $J = 4$ and 6 Hz, 1 H, C_9 asymmetric), 3.35 (d, $J = 6$ Hz, 2 H, C_{10}), 1.37 and 1.41 (2s, 18 H, *t*-butyl).

2.1. Preparation of the catalysts **1**–**10**

Complexes **1**–**10** were synthesised by using following general procedure (Scheme 1).

Methanolic solution of the appropriate chiral Schiff bases (0.1 mmol) was added to a degassed hot acetone solution containing [$RuCl_2(PPh_3)_3$] (0.1 mmol) and the resulting solution was refluxed for 8 to 9 h in argon atmosphere. The progress of the reaction was monitored on TLC. After completion of the reaction, the solution was filtered and concentrated on rotatory evaporator and then precipitated by diethyl ether. The complexes were filtered washed again by diethyl ether to remove excess of triphenyl phosphine. The complexes were recrystallized in methanol/dichloromethane and dried in vacuo. Yield, 60–70%. All the complexes are dark green in colour.

The analytical data for the complexes is given below.

R(−)SALdinitroleu Ru ***1***. Calcd. for $C_{31}H_{32}N_3O_9PRu$: C, 51.52; H, 4.46; N, 5.81. Found: C, 51.49; H, 4.42; N, 5.76. IR (KBr) cm^{-1} 1580 ν(H–C=N), 3400 ν(OH) 1100 and 1170 δ(OH); $^{31}P\{^1H\}$ NMR (CD_3OD) δ ppm 29.70; UV/Vis (nm) (MeOH) λ_{max} (ε), 210 (2093), 224 (1629), 262 (540), 336 (378); CD λ_{max} ($\Delta\varepsilon$), (CH_2Cl_2) 225 (+2.5), 345 (−2), 423 (−1.7), 550 (−0.5); $[\alpha]_D^t = -42.1$; configuration (*R*); Λ_M (CH_2Cl_2) 3 mho cm^{-1} $nmol^{-1}$; $\Delta Epa = +0.68$, $\Delta Epc = -0.12$ V.

R(−)SALdichloroleu Ru ***2***. Calcd. for $C_{31}H_{32}NO_5Cl_2PRu$: C, 53.07; H, 4.59; N, 1.99. Found: C, 53.04; H, 4.55; N, 1.96; IR (KBr) cm^{-1} 1580 ν(H–C=N), 3400 ν(OH) 1100 and 1170 δ(OH); $^{31}P\{^1H\}$ NMR (CD_3OD) δ ppm 29.52; UV/Vis (nm) (MeOH) λ_{max} (ε), 212 (4361), 236 (5628), 258 (5629), 298 (3136), 342 (1662), 608 (253); CD λ_{max} ($\Delta\varepsilon$), (CH_2Cl_2) 355 (+1.5), 375 (−2), 600 (−0.4); $[\alpha]_D^t = -18.9$; configuration (*R*); Λ_M (CH_2Cl_2) 4 mho cm^{-1} mol^{-1}; $\Delta Epa = +0.70$, $\Delta Epc = -0.15$ V.

R (−) SALleu Ru ***3***. Calcd. for $C_{31}H_{34}NO_5PRu$: C, 58.85; H, 5.41; N, 2.21. Found: C, 58.82; H, 5.39; N, 2.19; IR (KBr) cm^{-1} 1580 ν(H–C=N), 3400 ν(OH) 1100 and 1170 δ(OH); $^{31}P\{^1H\}$ NMR (CD_3OD) δ ppm 29.38; UV/Vis (nm) MeOH λ_{max} (ε), 234(3032), 264 (3069), 300 (2899), 356 (1496), 657 (273); CD λ_{max} ($\Delta\varepsilon$) (CH_2Cl_2) 327 (−5.7), 370 (−6.2), 440 (−9.2), 635 (−0.8); $[\alpha]_D^t = -7.1$; configuration (*R*); Λ_M (MeOH), 4 mho cm^{-1} mol^{-1}; $\Delta Epa = +0.71$, $\Delta Epc = -0.17$ V.

R(−) SALterBuleu Ru ***4***. Calcd. for $C_{35}H_{42}NO_5PRu$: C, 61.03; H, 6.14; N, 2.03. Found: C, 61.01; H, 6.11; N, 2.01; IR (KBr) cm^{-1} 1585 ν(H–C=N), 3400 ν(OH), 1100 and 1170 δ(OH); $^{31}P\{^1H\}$ NMR (CD_3OD) δ ppm 29.36; UV/Vis. (nm) (MeOH) λ_{max} (ε), 234 (5761), 256 (5625), 340 (2433), 600 (708); CD λ_{max} (CH_2Cl_2) 305(−2.6), 380(−5.5) 420 (−6.6), 585 (+0.8); $[\alpha]_D^t = -11.9$; configuration (*R*); Λ_M (MeOH) 3 moh cm^{-1} mol^{-1}; $\Delta Epa = +0.76$, $\Delta Epc = -0.19$ V.

R (−) SALDiterBuleu Ru ***5***. Calcd. for $C_{39}H_{50}NO_5PRu$: C, 62.88; H, 6.76; N, 1.88. Found: C, 62.85; H, 6.74; N, 1.84; IR (KBr) cm^{-1} 1585 ν(H–C=N), 3400 ν(OH), 1100 and 1170 δ(OH); $^{31}P\{^1H\}$ NMR (CD_3OD) δ ppm 29.30; UV/Vis.(nm) (MeOH) λ_{max} (ε), 236 (6086), 258 (6045), 348 (2823), 504 (468), 622 (680); CD λ_{max} ($\Delta\varepsilon$) (CH_2Cl_2) 320 (+5.9), 390 (−8.7), 450 (−7.8); $[\alpha]_D^t = -20.5$. Configuration (*R*); Λ_M (CH_2Cl_2) 4 mho cm^{-1} mol^{-1}; $\Delta Epa = +0.80$ V, $\Delta Epc = -0.23$ V.

R(−) SALdinitrohis Ru ***6***. Calcd. for $C_{31}H_{28}N_5O_9PRu$: C, 49.86; H, 3.77; N, 9.37. Found: C, 49.82; H, 3.73; N, 9.35; IR (KBr)

cm^{-1} 1580 ν(H–C=N), 3400 ν(OH), 1100 and 1170 δ(OH); $^{31}P\{^1H\}$ NMR (CD_3OD) δ ppm 29.80; UV/Vis.(nm) (MeOH) λ_{max} (ε), 230 (3710), 256 (3657), 358 (2380), 408 (1644); CD λ_{max} ($\Delta\varepsilon$) (CH_2Cl_2) 325 (+2.0), 415 (+3.6), 494 (−3.3); $[\alpha]_D^t = -20.5$. Configuration (*R*); Λ_M (CH_2Cl_2) 3 mho cm^{-1} mol^{-1}; ΔEpa = +0.67 V, ΔEpc = −0.12 V.

R(−)SALdichlorohis Ru ***7***. Calcd. for $C_{31}H_{28}N_3O_5Cl_2PRu$: C, 51.32; H, 3.89; N, 5.79. Found: C, 51.30; H, 3.86; N, 5.75; IR (KBr) cm^{-1} 1590 ν(H–C=N), 3400 ν(OH), 1100 and 1170 δ(OH); $^{31}P\{^1H\}$ NMR (CD_3OD) δ ppm 29.56; UV/Vis (nm) (MeOH) λ_{max} (ε), 214 (2667), 236 (3101), 264 (3190), 300 (2487), 364 (1089), 584 (471); CD λ_{max} ($\Delta\varepsilon$), (CH_2Cl_2) 278 (+6.3), 310 (+3), 450 (−3.6), 592 (−1.9); $[\alpha]_D^t = -19.3$; configuration (*R*); Λ_M (MeOH) 3 mho cm^{-1} mol^{-1}; ΔEpa = +0.69, ΔEpc = −0.14 V.

R (−) SALhis Ru ***8***. Calcd. for $C_{31}H_{29}N_3O_5PRu$: C, 56.79; H, 4.45; N, 6.40. Found: C, 56.72; H, 4.42; N, 6.37; IR (KBr) cm^{-1} 1580 ν(H–C=N), 3400 ν(OH), 1100 and 1170, δ(OH); $^{31}P\{^1H\}$ NMR (CD_3OD) δ ppm 29.42; UV/Vis (nm) MeOH λ_{max} (ε), 212 (3021), 232 (3470), 262 (3462), 340 (1969), 598 (692); CD λ_{max} ($\Delta\varepsilon$) (CH_2Cl_2) 275 (+8), 345 (+1.5), 445 (−5.4), 645 (−1); $[\alpha]_D^t = -25.9$; configuration (*R*); Λ_M (MeOH), 4 mho cm^{-1} mol^{-1}; ΔEpa = +0.72, ΔEpc = −0.18 V.

R(−) SALterBuhis Ru ***9***. Calcd. for $C_{35}H_{38}N_3O_5PRu$: C, 58.98; H, 5.37; N, 5.89. Found: C, 58.93; H, 5.34; N, 5.85; IR (KBr) cm^{-1} 1580 ν(H–C=N), 3400 ν(OH), 1100 and 1170, δ(OH); $^{31}P\{^1H\}$ NMR (CD_3OD) δ ppm 29.40; UV/Vis. (nm) (MeOH) λ_{max} (ε), 212 (2704), 232 (3118), 262 (3153), 354 (1865), 694 (360); CD λ_{max} (CH_2Cl_2) 308 (+9), 355 (+9.5), 404 (+2.5), 455(−4.8), 665 (−1.5); $[\alpha]_D^t = -13.5$; configuration (*R*); Λ_M (MeOH) 3 moh cm^{-1} mol^{-1}, ΔEpa = +0.75, ΔEpc = −0.12 V.

R (−) SALditerBuhis Ru ***10***. Calcd. for $C_{39}H_{46}N_3O_5PRu$: C, 60.92; H, 6.03; N, 5.46. Found: C, 60.89; H, 6.00; N, 5.42; IR (KBr) cm^{-1} 1590 ν(H–C=N), 3400 ν(OH), 1100 and 1170, δ(OH); $^{31}P\{^1H\}$ NMR (CD_3OD) δ, ppm 29.35; UV/Vis.(nm) (MeOH) λ_{max} (ε), 212 (2853), 236 (3209), 260 (3250), 284 (2872), 358 (2067), 728 (472); CD λ_{max} ($\Delta\varepsilon$) (CH_2Cl_2) 315 (+7.8), 355 (+7.4), 405 (+3), 465 (−4.5), 635 (+0.7); $[\alpha]_D^t = -28.6$. Configuration (*R*); Λ_M (MeOH) 4 mho cm^{-1} mol^{-1}, ΔEpa = +0.85 V, ΔEpc = −0.24 V.

2.2. Methods

Microanalysis of the complexes was done on Perkin Elmer model 1106. Molar conductance was measured at room temperature on a Digisun Electronic Conductivity Bridge DI-909. The IR spectra were recorded on Biorad FTS-40 spectrophotometer in KBr/nujol mull. Electronic spectra were recorded on Shimadzu UV/Visible recording spectrophotometer Model 160. ^1H NMR 200 MHz and $^{31}P\{^1H\}$ NMR 81 MHz were recorded on Bruker FX-200 NMR spectrophotometer in $CDCl_3$. Cyclic voltammetry, differential pulse voltammogram were recorded with a Princeton Applied Research (PAR) instrument using tetrabutyl ammonium perchlorate as supporting electrolyte in dichloromethane. The optical rotation of the complexes in methanol was measured by polarimeter Atago, Japan. The CD spectra were recorded in dichloromethane by Jasco Machine Model J-20, Japan. The purity of the solvent, substrate and analysis of the product was determined by GLC using Shimadzu GC 14B coupled with PC using 2 M long, 3 mm ID, 4 mm OD stainless steel column packed with SE30, 5% mesh size 60 to 80 with FID detector. Column temperature programmed between 70° to 150°C and injection temperature 200°C with nitrogen carrier gas flow 30 ml/min. Synthetic standard of the product was used to determine yields by comparison of peak height and area. The optical yield of the product was determined by Chiraldex BDA chiral capillary column.

*2.3. Epoxidation of 1,2-dihydronaphthalene by catalyst **1**–**10***

Enantioselective epoxidation of 1,2-dihydronaphthalene by the catalyst **1**–**10** were attempted under homogenous system with iodosyl benzene as oxidant by the following procedure: The chiral catalyst, (0.02 mmol), 1,2-dihydronaphthalene (1.00 mmol), and *n*-tridecane (0.10 mmol) as GLC internal standard were dissolved in 1.5 ml dichloromethane/fluorobenzene/acetonitrile. The reaction was initiated by the addition of iodosyl benzene (1.00 mmol) and stirred at constant speed in inert atmosphere at 0°C. After each intervals of 1 h, an aliquot was taken from the reaction mixture quenched with PPh_3 and analysed by GLC. After completion of reaction, the solvent was removed and product was separated by short silica gel column (60–120 mesh) using hexane: dichloromethane as eluent. Evaluation of enantiomeric excess was done by GC on chiral capillary column BDA.

3. Results and discussion

The complexes **1**–**10** were isolated as dark green neutral solids using corresponding potassium salt of dianionic terdentate ligands (**1′**–**10′**) (spectral and analytical data given in Section 2) with interaction of Ru(II) metal ion in acetone/methanol. The remaining coordination sites of the octahedral ruthenium are occupied by triphenyl phosphine and two molecules of water. The presence of $^{31}P\{^1H\}$ signal in CD_3OD between 29.3–29.8 ppm suggested that triphenyl phosphine is *trans* to the nitrogen of the Schiff bases. The analytical data, molar conductance, ^1H and $^{31}P\{^1H\}$ NMR data of the complexes are given in Section 2 and are in accordance to the suggested representative energy minimised structure of the complex **10** (Fig. 1).

IR spectra of the complexes show strong bands near 1590–1580 cm^{-1} assigned to the coordinated azomethine group which overlap with the bands due to asymmetric carboxylato group. In free ligand, this band lie at higher

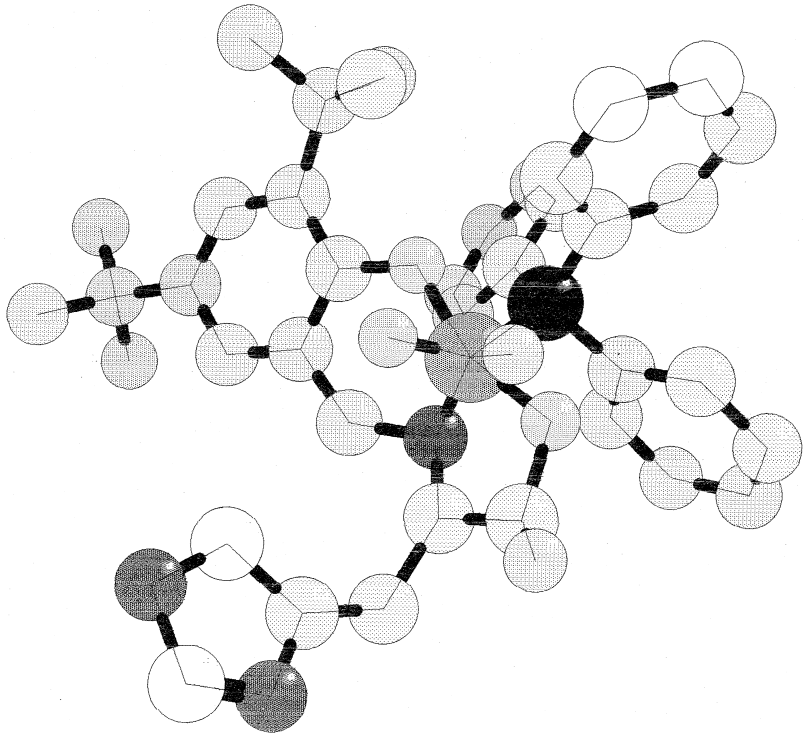


Fig. 1. Representative energy minimised molecular model for the complex **10** (H-atoms are omitted for the sake of clarity).

wave number. A broad band at 3280 cm^{-1} in the ligand is due to phenolic OH, after complexation this band disappears showing the coordination of phenolic oxygen to ruthenium. The micro analysis of the complexes suggests the presence of two molecules of water hence, broad band near 3400–3300 cm^{-1} along with deformation modes of water lie at 1100 and 1170 cm^{-1}. In the far IR region bands at 550, 350 are due to ν(Ru–P) and ν(Ru–N), respectively.

The electronic spectra of the complexes were recorded in methanol show high intensity charge transfer band near 210–260 nm while MLCT bands lie at 336–408 nm. The position of LMCT band depends on the substituents attached to the salicylaldehyde moiety of the catalysts as well as the R group attached to the amino acid [24]. The band near 598 to 610 are assigned to the forbidden ligand field transitions.

CD spectra of the complexes were recorded in dichlomethane. Data regarding CD is given in Section 2. In the charge transfer region, the bands $d \rightarrow \pi^*$ with negative Cotton effect fall in the range 423–465 nm and high intensity $\pi \rightarrow \pi^*$ transition are seen at 256–370 nm. In case of histidine complexes **9**, **10**, the $d \rightarrow \pi^*$ band appeared in lower energy region (455 and 465 nm) than their counterpart luecine complexes (420 and 450 nm), respectively. This trend is consistent with the inductive effect of the substituents R on the ligand π levels [16,23] and is shown in (Fig. 2). The dd bands of these complexes lie near 550–655 nm.

The cyclic voltammogram of the complexes **1**–**10** recorded in dichloromethane shows the system to be quasi reversible one electron transfer and the oxidation potential of Ru(II)/Ru(III) couple lie in the range +0.67 to +0.85 V vs. Ag/AgCl. From cyclic voltammogram, the $E_{1/2}$ value of Ru(II)/Ru(I) reduction couple falls in the range −0.12 to −0.24 V which mainly depends on the substituents attached to the ligand moiety of complexes.

3.1. Enantioselective epoxidation of 1,2-dihydronaphthalene

3.1.1. Solvent effect

Enantioselective epoxidation of 1,2-dihydronaphthalene catalysed by the catalysts **1**–**10** was carried out in fluorobenzene, dichloromethane and acetonitrile using PhIO as oxidant. Higher chemical yields were obtained in fluorobenzene for the complexes **5** and **10** accompanied by relatively larger ee values. By changing the solvent from fluorobenzene to acetonitrile

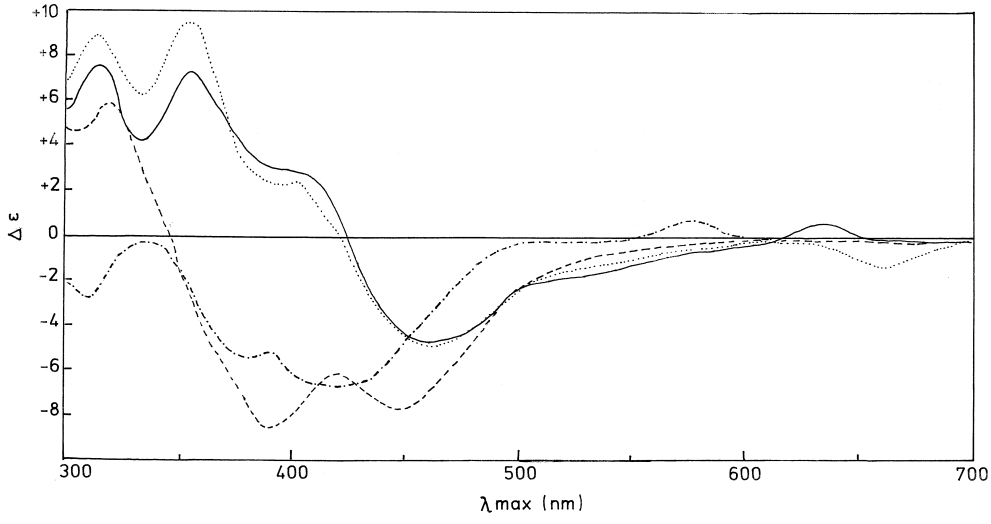


Fig. 2. CD spectra of the complexes **4** (- · - · -), **5** (- - - -), **9** (· · · · · · · · · · · · · · ·) and **10** (————) in dichloromethane.

Table 1
Data for enantioselective epoxidation of 1,2-dihydronaphthalene catalysed by chiral Ru(II) Schiff base complexes

Catalyst[a]	Solvent	Time (h)	% Conversion[b]	ee[c]	Configuration
1/6	Fluorobenzene	10	50/55	29/32	1S, 2R
	Dichloromethane	10	36/40	20/21	1S, 2R
	Acetonitrile	10	30/35	18/19	1S, 2R
2/7	Fluorobenzene	10	54/60	32/38	1S, 2R
	Dichloromethane	10	41/45	22/25	1S, 2R
	Acetonitrile	10	36/42	18/20	1S, 2R
3/8	Fluorobenzene	10	60/65	35/42	1S, 2R
	Dichloromethane	10	45/52	26/28	1S, 2R
	Acetonitrile	10	39/48	20/22	1S, 2R
4/9	Fluorobenzene	10	66/72	39/48	1S, 2R
	Dichloromethane	10	48/ 55	28/32	1S, 2R
	Acetonitrile	10	42/50	21/25	1S, 2R
5/10	Fluorobenzene	10	70/80	45/58	1S, 2R
	Dichloromethane	10	58/62	30/36	1S, 2R
	Acetonitrile	10	49/55	25/29	1S, 2R

[a]Organic phase, fluorobenzene/dichloromethane/acetonitrile (1.5 ml); Catalyst (0.02 mmol); 1,2-dihydronaphthalene (1.0 mmol); PhIO, (1.00 mmol); *n*-tridecane (0.1 mmol) (internal standard for gas chromatography).
[b]1,2-Dihydronaphthalene epoxide only.
[c]1,2-Dihydronaphthalene epoxide separated by short silica gel column using hexane: dichloromethane (9:1) as eluent and used for determination of ee values by chiraldex BDA capillary column.

through dichloromethane, the induced changes in ee values are from 45 → 30 → 25 and 58 → 32 → 29 with a similar trend in chemical yields 70 → 58 → 49, 80 → 62 → 55, respectively (Table 1). Catalysts **4** and **9** gave better conversion and ee values while low conversions were ob-

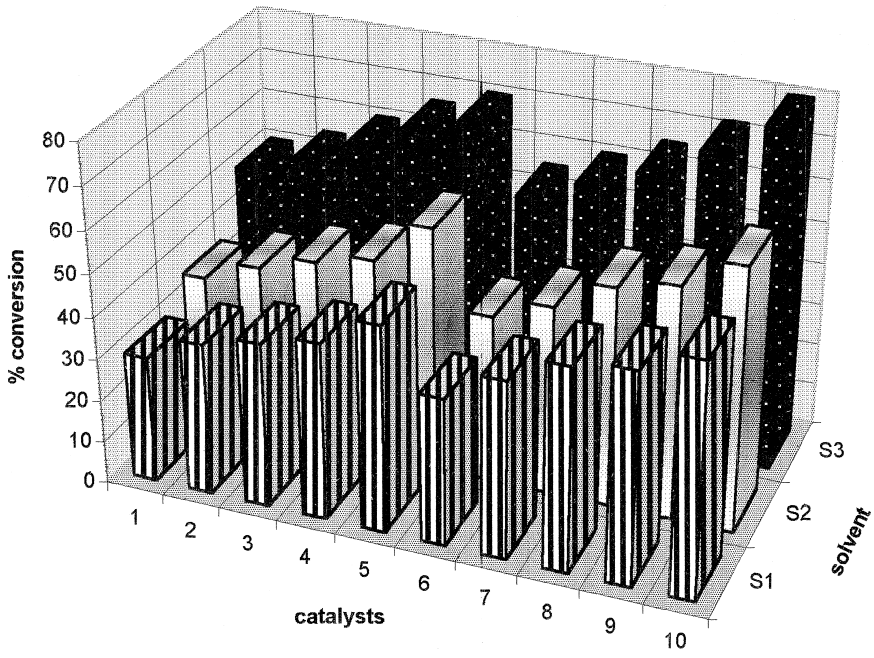


Fig. 3. Bar diagram representing the % conversion of epoxide by the catalyst **1**–**10** in the solvents viz. $\mathbf{S}_1$ (acetonitrile), $\mathbf{S}_2$ (dichloromethane) and $\mathbf{S}_3$ (fluorobenzene).

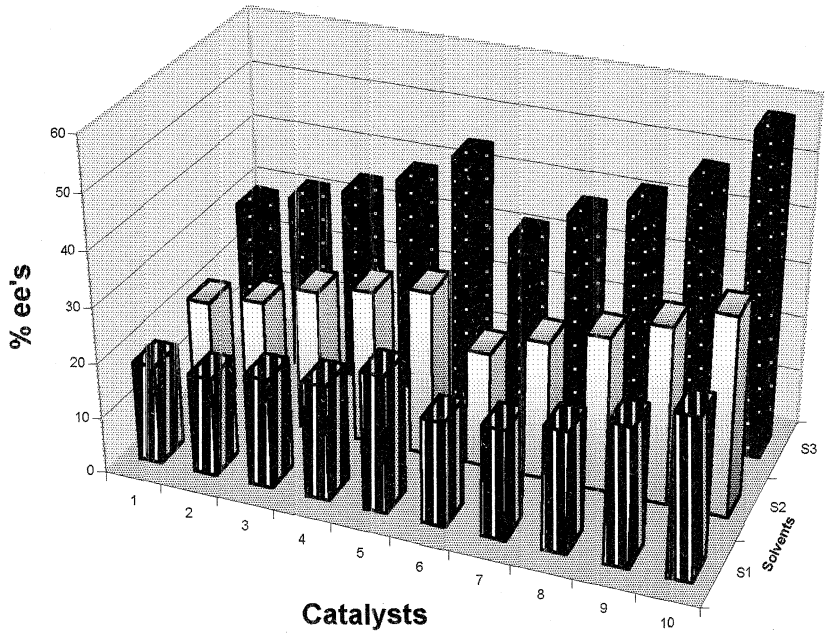


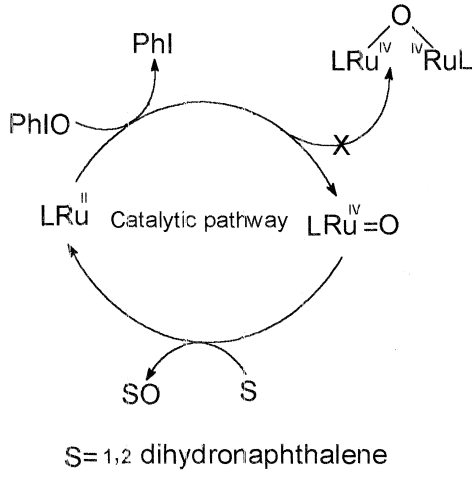
Fig. 4. Bar diagram representing the % ee of epoxide by the catalyst **1**–**10** in the solvents viz. $\mathbf{S}_1$ (acetonitrile), $\mathbf{S}_2$ (dichloromethane) and $\mathbf{S}_3$ (fluorobenzene).

tained in the catalysts **1** and **6**. On the basis of chemical yield and ee values, effectiveness of the solvents may be arranged in the following order, fluorobenzene > dichloromethane > acetonitrile which is in the reverse order of increasing polarity (Figs. 3 and 4).

3.1.2. Effect of substituents on ligands

Over all trend in ee values and chemical yields suggest that ligands derived from L-histidine with electronically rich salicylaldehyde are better catalysts than their counter part derived from L-leucine. The substituents on salicylaldehyde also suggests that an increased electron density around the metal ion by means of *t*-butyl group are more active and selective than lower electron densities by means of electron withdrawing NO_2 group. Therefore, the stability and lability of the intermediate Ru(IV) oxo which is very much dependent on the electron density on the metal center play a significant role in all these cases.

A separate set of catalytic reaction was conducted under identical conditions in absence of substrate. The oxidised metal product was isolated by precipitation and characterised by IR spectroscopy and elemental analysis as reported



Scheme 2. Possible mechanism for catalytic epoxidation reaction.

Table 2
Effect of oxidants in epoxidation reaction in fluorobenzene at 0°C

Catalyst	Oxidant	Time (h)	% conversion[a]	% epoxide
5(10)	NaOCl	24	10(15)[b]	2(3)
	H_2O_2	24	–	–
	O_2	24	–	–
	m-chloroperbenzoic acid	24	40(70)[c]	8(6)

[a]Reaction was monitored for 24 h on GC using *n*-tridecane as internal standard for the calculations of total % conversion and % conversion to the epoxide.
[b]Along with some unidentified products naphthalene diol was also detected.
[c]Diol was the major product.

earlier [25]. The analytical data supports the formation of $LRu^{(IV)}=O$ species rather than diamagnetic LRu–O–RuL dimeric complex. Hence, it would be logical to presume that during catalysis $LRu^{(IV)}=O$ species is forming as reactive intermediate which transfers its oxygen to give product epoxide (Scheme 2). As far as the mechanism of enantioselection is concerned, the product distribution (see the ee values, Table 1) suggest that both chiral and nonchiral path is operative as reported earlier [26].

3.1.3. Effect of oxidant

All the complexes were screened for their enantioselective epoxidation of a representative substrate 1,2-dihydronaphthalene with divergent oxidants like NaOCl, H_2O_2, O_2 (with sacrificial reductant isobutyraldehyde) and *m*-chloroper benzoic acid. Data for representative catalyst **5** and **10** is summarised in Table 2. Except for NaOCl where 10–15% conversions were obtained with 2–3% epoxide selectivity, all other oxidants failed to perform clean epoxidation. Selectivity was even poorer in case of the oxidant *m*-chloroperbenzoic acid with a large percentage converted into dihydronaphthalene diol. Rest of the alkene, however, could be isolated back unaltered at the end of the reaction. The oxidants like H_2O_2 and O_2 failed to give any conversion. The enantioselectivities were found to be between 0–2% for the epoxide formed in all these cases. The system works well only with iodosyl benzene as terminal oxidant.

4. Conclusion

Several variables that effect the enantioselectivity in the epoxidation of unfunctionalized alkenes by amino acid based Schiff base complexes as catalysts were investigated in the present study. Complexes **6**–**10** derived from L-histidine are better catalysts than the complexes of L-leucine **1**–**5** and 3,5-di-*tertiary*-butyl salicylaldehyde based catalysts shows better conversion and enantioinduction than the catalysts having electron withdrawing groups on ligand moiety. Furthermore, aromatic solvent, i.e., fluorobenzene is found to be better solvent than more polar dichloromethane and acetonitrile. As far as oxidant is concerned, only PhIO was able to perform epoxidation reaction. Other commonly used oxidants like H_2O_2, NaOCl, O_2 and *m*-chloroperbenzoic acid were either inactive or gave product other than epoxides.

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