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Chiral Ru(II) Schiff base complex-catalysed enantioselective epoxidation of styrene derivatives using iodosyl benzene as oxidant. II

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Abstract

Six-coordinated chiral Ru(II) Schiff base complexes of the type $[RuLX(Y)_2]$ where L = terdentate chiral Schiff bases derived from L-tyrosine, L-phenylalanine with salicylaldehyde, 3-*tertiary*-butyl-, 3,5-di-*tertiary*-butyl-, 3,5-dichloro- and 3,5-dinitrosalicylaldehyde, $X = PPh_3$ and $Y = H_2O$ have been investigated as catalysts for enantioselective epoxidation of styrene, 4-chloro-, 4-nitro- and 4-methylstyrene in fluorobenzene in order to explore the efficiency of catalytic system by varying the substituents on the ligand moiety of the catalysts as well as on the substrates using iodosyl benzene as terminal oxidant. Much better results were obtained with catalyst **5** and **10** with 4-nitrostyrene. The enantiomeric excess of the resulting epoxide was evaluated by chiral capillary column. © 1999 Elsevier Science B.V. All rights reserved.

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

1. Introduction

Catalytic enantioselective epoxidation of non-functionalised alkenes has emerged as the most preferred route in order to obtain chirally enriched epoxides required as intermediate for chiral bioactive compounds [1,2]. In recent years after the pioneering research by Jacobsen et al. [3], Zhang et al. [4] and Zhang and Jacobsen [5] with NaOCl, several other oxidants such as iodosyl benzene [6], molecular oxygen [7], H_2O_2 [8], Bu_4 NIO_4 [9], dimethyl dioxirane [10] and *m*-chloroperbenzoic acid [11] were also explored.

In continuation of our earlier work on enantioselective epoxidation of prochiral non-functionalized olefins using Ru(III), Ru(II), Mn(III), Co(II) and Ni(II) chiral Schiff base complexes [12–15], we are reporting here chiral Ru(II) Schiff base complex-catalysed enantioselective epoxidation of styrene and substituted styrenes in fluorobenzene using iodosyl benzene as oxidant of choice. The difference in enantioselectivity by varying the substituents on the substrate as well as on the catalysts is also explored. Further, the role of *N*-coordinating and *O*-coordinating additives on catalytic activity of these complexes was studied.

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2. Experimental

$RuCl_3 \cdot 3H_2O$ (Johnson and Matthey), PPh_3, L-tyrosine, L-phenylalanine (Sisco), Salicylaldehyde, 3,5-dichloro-, 3,5-dinitrosalicylaldehyde (Aldrich) were used as such. The metal complex $[RuCl_2(PPh_3)_3]$ [16], 3-tertiary-butyl- and 3,5-ditertiary-butyl salicylaldehyde were prepared by the known method [17]. All the chiral Schiff bases derived from salicylaldehyde substituted salicylaldehyde with L-tyrosine and L-phenylalanine and were synthesized by known methods [18].

The characterisation of the chiral Schiff bases was done by microanalysis, IR- and [^{1}H] nuclear magnetic resonance (NMR) spectroscopy.

2.1. N-(3,5-Dinitrosalicylidine) L-tyrosine 1′

Yield 65%; m.p. > 250°C. Calculated, for $C_{16}H_{12}N_3O_8K$: C, 46.49; H, 2.93; N, 10.17. Found: C, 46.43; H, 2.90; N, 10.13; IR (KBr) cm^{-1} 1620 ν(H–C = N); ^{1}H NMR (CD_3OD) δ ppm, 9.20 (d, $J = 2$ Hz, 1 H, C_4 aromatic), 8.94 (s, 1 H, C_7 imine), 8.79 (d, $J = 2$ Hz, 1 H, C_6 aromatic), 6.68–6.80 (m, 4 H, aromatic), 4.01–4.08 (dd, $J = 4$ Hz, 1 H, C_9 asymmetric), 3.33 (d, $J = 4$ Hz, 2 H, C_{10}).

2.2. N-(3,5-Dichlorosalicylidine) L-tyrosine 2′

Yield 65%; m.p. 210°C. Calculated for $C_{16}H_{12}NO_4Cl_2K$: C, 48.99; H, 3.08; N, 3.57. Found: C, 48.95; H, 3.04; N, 3.54; IR (KBr) cm^{-1} 1625 ν(H–C = N); ^{1}H NMR (CD_3OD) in δ ppm, 7.70 (s, 1 H, C_7, imine), 7.59 (d, $J = 2$ Hz, 1 H, C_4 aromatic), 7.41 (d, $J = 2$ Hz, 1 H, C_6 aromatic), 6.65–6.72 (m, 4 H, aromatic), 3.94–4.00 (dd, $J = 4$ Hz, 1 H, C_9 asymmetric), 3.30 (d, $J = 4$ Hz, 2 H, C_{10}).

2.3. N-(Salicylidine) L-tyrosine 3′

Yield 65%; m.p. > 250°C. Calculated for $C_{16}H_{14}NO_4K$: C, 59.43; H, 4.36; N, 4.33. Found: C, 59.39; H, 4.32; N, 4.30; IR (KBr) cm^{-1} 1625 ν(H–C = N); ^{1}H NMR (CD_3OD) in δ ppm, 7.83 (s, 1 H, C_7 imine,), 6.61–7.09 (m, 8 H, aromatic), 3.97–4.04 (dd, $J = 4$ Hz, C_9, 1 H, asymmetric), 3.26 (d, $J = 4$ Hz, 2 H, C_{10}).

2.4. N-(3-tertiary-Butylsalicylidine) L-tyrosine 4′

Yield 64%; m.p. 170°C. Calculated for $C_{20}H_{22}NO_4K$: C, 63.30; H, 5.84; N, 3.69. Found: C, 63.26; H, 5.80; N, 3.65; IR (KBr) cm^{-1} 1625 ν(H–C = N); ^{1}H NMR (CD_3OD) δ ppm, 7.94 (s, 1 H, C_7 imine), 6.58–7.27 (m, 7 H, aromatic), 3.89–3.96 (dd, $J = 4$ Hz, 1 H, C_9 asymmetric), 3.27 (d, $J = 4$ Hz, 2 H, C_{10}), 1.41 (s, 9 H, *t*-butyl).

2.5. N-(3,5-ditertiary-Butylsalicylidine) L-tyrosine 5′

Yield 60%; m.p. 94°C. Calculated, for $C_{24}H_{30}NO_4K$: C, 66.18; H, 6.94; N, 3.22. Found: C, 66.14; H, 6.90; N, 3.17; IR (KBr) cm^{-1} 1625 ν(H–C = N); ^{1}H NMR (CD_3OD) δ ppm, 7.90 (s, 1 H, C_7, imine), 7.18 (d, $J = 2$ Hz, 1 H, C_6), 6.96 (d, $J = 2$ Hz, 1 H, C_4), 6.58–6.74 (m, 4 H, aromatic), 3.85–3.92 (dd, $J = 4$ Hz, 1 H, C_9 asymmetric), 3.24 (d, $J = 4$ Hz, 2 H, C_{10}), 1.36 and 1.42 (2s, 18 H, *t*-butyl).

2.6. N-(3,5-Dinitrosalicylidine) L-phenylalanine 6′

Yield 60%; m.p. > 250°C. Calculated, for $C_{16}H_{12}N_3O_7K$: C, 48.36; H, 3.04; N, 10.57. Found: C, 48.30; H, 3.01; N, 10.52; IR (KBr) cm^{-1} 1625; ^{1}H NMR (CD_3OD) δ ppm, 9.14 (d, 1 H, $J = 2$ Hz, C_4 aromatic), 8.91 (s, 1 H, imine C_7), 8.78 (d, 1 H, $J = 2$ Hz, C_6 aromatic), 7.28 (m, 5 H, phenyl), 4.34–4.27 (dd, 1 H, $J = 4$ Hz, C_9 asymmetric), 3.15 (d, 2 H, $J = 4$ Hz, C_{10}).

2.7. N-(3,5-Dichlorosalicylidine) L-phenylalanine 7′

Yield 67%; m.p. 78°C. Calculated, for $C_{16}H_{12}NO_3Cl_2K$: C, 51.07; H, 3.21; N, 3.72.

Found: C, 51.04; H, 3.18; N, 3.69; IR (KBr) cm^{-1} 1625 ν(H–C = N); ^{1}H NMR (CD_3OD) in δ ppm, 7.79 (s, 1 H, imine, C_7), 7.42 (d, 1 H, $J = 2$ Hz, C_6 aromatic), 7.98 (d, 1 H, $J = 2$ Hz, C_4 aromatic), 7.27 (m, 5 H, phenyl), 4.31–4.24 (dd, 1 H, $J = 4$ Hz, C_9 asymmetric), 3.12–3.00 (d, 2 H, $J = 4$ Hz, C_{10}).

2.8. N-(Salicylidine) L-phenylalanine 8′

Yield 70%; m.p. 186°C. Calculated, for $C_{16}H_{14}NO_3K$: C, 62.52; H, 4.59; N, 4.56. Found: C, 62.48; H, 4.53; N, 4.51; IR (KBr) cm^{-1} 1620 ν(H–C = N); ^{1}H NMR (CD_3OD) δ ppm, 7.78 (s, 1 H, imine, C_7), 7.19 (m, 5 H, phenyl), 6.78 (m, 4 H, C_3–C_6 aromatic), 4.10–4.03 (dd, $J = 4$ Hz, 1 H, C_9 asymmetric), 3.06 (d, $J = 4$ Hz, 2 H, C_{10}).

2.9. N-(3-tertiary-Butylsalicylidine) L-phenylalanine 9′

Yield 60%; m.p. 174°C. Calculated, for $C_{20}H_{22}NO_3K$: C, 66.09; H, 6.10; N, 3.85. Found: C, 66.04; H, 6.06; N, 3.82; IR (KBr) cm^{-1} 1620 ν(H–C = N); ^{1}H NMR (CD_3OD) δ ppm, 7.93 (s, 1 H, imine, C_7), 7.22 (m, 5 H, phenyl), 6.98–6.66 (m, 3 H, C_4–C_6 aromatic), 4.07–4.00 (dd, $J = 4$ Hz, 1 H, C_9 asymmetric), 3.13 (d, $J = 4$ Hz, 2 H, C_{10}), 1.41 (s, 9 H, *t*-butyl).

2.10. N-(3,5-diter-Butylsalicylidine) L-phenylalanine 10′

Yield 65%; m.p. 82°C. Calculated for $C_{24}H_{30}NO_3K$: C, 68.64; H, 7.20; N, 3.34. Found: C, 68.61; H, 7.18; N, 3.30; IR (KBr) cm^{-1} 1625 ν(H–C = N); ^{1}H NMR (CD_3OD) δ ppm, 7.91 (s, 1 H, imine, C_7), 7.20 (m, 5 H, phenyl), 7.17 (d, $J = 2$ Hz, 1 H, C_6 aromatic), 6.94 (d, $J = 2$ Hz, 1 H, C_4 aromatic), 4.05–3.98 (dd, $J = 4$ Hz, 1 H, C_9 asymmetric), 3.12 (d, $J = 4$ Hz, 2 H, C_{10}), 1.40 and 1.36 (2s, 18 H, *t*-butyl).

3. Preparation of the catalysts 1–10

To a hot degassed solution of [$RuCl_2(PPh_3)_3$] (0.1 mmol) in 25 ml acetone was added methanolic solution of appropriate chiral Schiff bases (0.1 mmol) in 10 ml and was allowed to reflux under argon for 8–9 h. After completion of the reaction on thin-layer chromatography (TLC), the solution was filtered, concentrated and precipitated by diethyl ether. The complexes were thoroughly filtered, washed with excess of diethyl ether to remove liberated triphenyl phosphine. The complexes were recrystallized in methanol/dichloromethane and dried in vacuo. Yield 60–65%.

The analytical data for the complexes are as follows.

3.1. R(−)SAL dinit tyro Ru 1

Calculated for $C_{34}H_{30}N_3O_{10}PRu$: C, 52.85; H, 3.91, N, 5.44. Found: C, 52.80; H, 3.89; N, 5.40. IR (KBr) cm^{-1} 1580 ν(H–C = N), 3400 ν(OH) 1100, 1170 δ(OH); $^{31}P\{^1H\}$ NMR(CD_3OD) δ ppm 29.80; UV/Vis (nm) (MeOH) λ_{max} (ε), 210(2189), 226(1885), 336(1415); CD λ_{max} ($\Delta\varepsilon$), (CH_2Cl_2) 410(+2.7), 480(+1.5), 540(−1.4); $[\alpha]_D^t$ = −6.5; Configuration (*R*); Λ_M (MeOH) 3 mho cm^{-1} mol^{-1}; ΔEpa = +0.64, ΔEpc = −0.10 V.

3.2. R(−)SAL dichloro tyro Ru 2

Calculated for $C_{34}H_{30}NO_6Cl_2PRu$: C, 54.37; H, 4.02, N, 1.86; Found: C, 54.30; H, 4.00; N, 1.82 IR (KBr) cm^{-1} 1585 ν(H–C = N), 3400 ν(OH) 1100, 1170 δ(OH); $^{31}P\{^1H\}$ NMR (CD_3OD) δ ppm 29.60; UV/Vis (nm) (MeOH) λ_{max} (ε), 210(2008), 226(1727), 350(176), 598(37); CD λ_{max} ($\Delta\epsilon$), (CH_2Cl_2) 310(+1.7), 355(−2.2), 415 (−2.1); $[\alpha]_D^t$ = −7.3; Configuration (*R*); Λ_M (MeOH) 4 mho cm^{-1} mol^{-1}; ΔEpa = +0.66, ΔEpc = −0.13 V.

3.3. R(−)SAL tyroru 3

Calculated for $C_{34}H_{32}NO_6PRu$: C, 59.82: H, 4.73: N, 2.05. Found: C, 59.78: H, 4.70: N, 2.01; IR (KBr) cm^{-1} 1580 ν(H–C = N), 3400 ν(OH) 1100, 1170 δ(OH); $^{31}P\{^1H\}$ NMR (CD_3OD) δ ppm 29.20; UV/Vis (nm) MeOH λ_{max} (ε), 210(1976), 224(1692), 370(1162); CD λ_{max} ($\Delta\varepsilon$) (CH_2Cl_2) 285(+4.5), 315(−2.4), 355(+2.5), 405(−5.9), 568(+0.9); $[\alpha]_D^t$ = −23.4; Configuration (*R*); Λ_M(MeOH), 3 mho cm^{-1} mol^{-1}; ΔEpa = +0.67, ΔEpc = −0.15 V.

3.4. R(−)SAL terBu tyro Ru 4

Calculated for $C_{38}H_{40}NO_6PRu$: C, 61.78; H, 5.46; N, 1.90. Found: C, 61.75; H, 5.42; N, 1.86; IR (KBr) cm^{-1} 1585 ν(H–C = N), 3400 ν(OH), 1100, 1170 δ (OH); $^{31}P\{^1H\}$ NMR (CD_3OD) δ, ppm 29.32; UV/Vis (nm) (MeOH) λ_{max} (ε), 234(5779), 350(2234), 502(322), 518(322), 654(552); CD λ_{max} (CH_2Cl_2) 290(−2.4), 355(−3.8), 435(+5.0) 550(−0.8); $[\alpha]_D^t$ = −13.6; Configuration (*R*); Λ_M (MeOH) 3 moh cm^{-1} mol^{-1}; ΔEpa = +0.71, ΔEpc = −0.17 V.

3.5. R(−)SAL diterBu tyro Ru 5

Calculated for $C_{42}H_{48}NO_6PRu$: C, 63.46; H, 6.09; N, 1.76. Found: C, 63.43; H, 6.06; N, 1.72; IR (KBr) cm^{-1} 1580 ν(H–C = N), 3400 ν(OH), 1100, 1170 δ(OH); $^{31}P\{^1H\}$ NMR (CD_3OD) δ, ppm 29.12; UV/Vis (nm) (MeOH) λ_{max} (ϵ), 232(6430), 354(3035), 660(830); CD λ_{max} ($\Delta\varepsilon$) (CH_2Cl_2) 284(−2.0), 335(−1.2), 412(−4.5), 534(−1.2); $[\alpha]_D^t$ = −30.2; Configuration (*R*); Λ_M (MeOH) 4 mho cm^{-1} mol^{-1}; ΔEpa = +0.76, ΔEpc = −0.21 V.

3.6. R(−)SAL dinit pheala Ru 6

Calculated for $C_{34}H_{30}N_3O_9PRu$: C, 53.96; H, 4.00; N, 5.55. Found: C, 53.92; H, 3.97; N, 5.52; IR (KBr) cm^{-1} 1580 ν(H–C = N), 3400 ν(OH) 1100, 1170 δ(OH); $^{31}P\{^1H\}$ NMR (CD_3OD) δ ppm 29.90; UV/Vis (nm) (MeOH) λ_{max} (ε), 236(6852), 262(5844), 338(3473); CD λ_{max} ($\Delta\varepsilon$), (CH_2Cl_2) 380(+4.1), 405(−2.0), 500(−1.3); $[\alpha]_D^t$ = −13.2; Configuration (*R*); Λ_M (MeOH) 4 mho cm^{-1} mol^{-1}; ΔEpa = +0.64, ΔEpc = −0.11 V.

3.7. R(−)SAL dichloro pheala Ru 7

Calculated for $C_{34}H_{30}NO_5Cl_2PRu$: C, 55.51; H, 4.11; N, 1.90. Found: C, 55.48; H, 4.09; N, 1.88; IR (KBr) cm^{-1} 1585 ν(H–C = N), 3400 ν(OH) 1100, 1170 δ(OH); $^{31}P\{^1H\}$ NMR (CD_3OD) δ ppm 29.40; UV/Vis (nm) (MeOH) λ_{max} (ϵ), 212(2089), 226(1729), 358(1217), 610 (47); CD λ_{max} ($\Delta\varepsilon$), (CH_2Cl_2) 340(−1.4), 355(+1.2), 385(−1.8), 422(−1.0), 630 (−1); $[\alpha]_D^t$ = −6.8; Configuration (*R*); Λ_M (MeOH) 4 mho cm^{-1} mol^{-1}; ΔEpa = +0.67, ΔEpc = −0.14 V.

3.8. R(−)SAL pheala Ru 8

Calculated for $C_{34}H_{32}NO_5PRu$: C, 61.26; H, 4.84; N, 2.10. Found: C, 61.23; H, 4.80; N, 2.08; IR (KBr) cm^{-1} 1585 ν(H–C = N), 3400 ν(OH) 1100, 1170 δ(OH); $^{31}P\{^1H\}$ NMR (CD_3OD) δ ppm 29.30; UV/Vis (nm) MeOH λ_{max} (ϵ), 234(5612), 258(5534), 328(2011), 508(181), 606(335); CD λ_{max} ($\Delta\varepsilon$) (MeOH) 330(−4.1), 370(−6.2), 440(−6.0), 600(−1.0); $[\alpha]_D^t$ = −15.0; Configuration (*R*); Λ_M (MeOH), 4 mho cm^{-1} mol^{-1}; ΔEpa = +0.68, ΔEpc = −0.16 V.

3.9. R(−)SAL terBu pheala Ru 9

Calculated for $C_{38}H_{40}NO_5PRu$: C, 63.18; H, 5.58; N, 1.94. Found: C, 63.15; H, 5.54; N, 1.91; IR (KBr) cm^{-1} 1585 ν(H–C = N), 3400 ν(OH), 1100, 1170 δ(OH); $^{31}P\{^1H\}$ NMR (CD_3OD) δ ppm 29.33; UV/Vis (nm) (MeOH) λ_{max} (ε), 210(5845), 234(6263), 260(6108) 344-(2982), 656(631); CD λ_{max} (MeOH) 280-(+11.0), 325(+8.9), 392(−8.0), 445(−8.2),

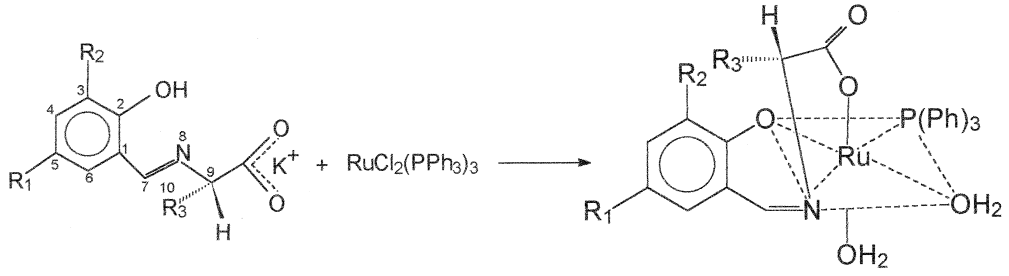
580(−1.0); $[\alpha]_D^t = -6.9$; Configuration (*R*); Λ_M (MeOH) 4 moh cm^{-1} mol^{-1}; ΔEpa = +0.72, ΔEpc = −0.19 V.

3.10. R(−)SAL diterBu pheala Ru 10

Calculated for $C_{42}H_{48}NO_5PRu$: C, 64.77; H, 6.21; N, 1.80. Found: C, 64.74; H, 6.17; N, 1.76; IR (KBr) cm^{-1} 1585 ν(H–C = N), 3400 ν(OH), 1100, 1170 δ(OH); $^{31}P\{^1H\}$ NMR (CD_3OD) δ ppm 29.20; UV/Vis (nm) (MeOH) λ_{max} (ε) 234(6304), 260(6051), 350(2761); CD λ_{max} ($\Delta\varepsilon$) (MeOH) 282(+13.2), 328(+13.0), 395(−10.7), 450(−8.8), 620 (−1.5); $[\alpha]_D^t = -17.9$; Configuration (*R*); Λ_M (MeOH) 3 mho cm^{-1} mol^{-1}; ΔEpa = +0.77, ΔEpc = −0.22 V.

3.11. Methods

Microanalysis of the complexes was done on a 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 a Bio-Rad FTS-40 spectrophotometer in KBr/nujol mull. Electronic spectra were recorded on a Hewlett-Packard Diode Array spectrophotometer Model 8452A. ^1H NMR 200 MHz and $^{31}P\{^1H\}$ NMR 81 MHz were recorded on a Bruker FX-200 NMR spectrophotometer in CD_3OD. 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 using a Jasco Machine Model J-20 Japan. The purity of the solvent, substrate and analysis of the product was determined by gas–liquid chromatography (GLC) using a 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 an FID detector. Column temperature programmed between 70° and 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 a Chiraldex GTA chiral capillary column.



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

*3.12. Epoxidation of styrene derivatives by catalysts **1–10***

Enantioselective epoxidation of styrene, 4-chloro-, 4-methyl, 4-nitrostyrene by the catalysts **1–10** were attempted in a homogeneous system with iodosyl benzene by the following procedure. The chiral catalyst, (0.02 mmol), substrate, (1 mmol), and *n*-tridecane (0.1 mmol) as GLC internal standard were dissolved in 1.5 ml fluorobenzene. The reaction was initiated by the addition of iodosyl benzene (1 mmol) and stirred at constant speed in an inert atmosphere at 0°C. After each interval of 30 min, 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 a short silica gel column (60–120 mesh) using hexane: dichloromethane as eluent. Evaluation of enantiomeric excess was done by GC on chiral capillary column GTA.

4. Results and discussion

The chiral catalysts **1–10** were isolated as neutral six coordinated solids in good yield using straightforward synthetic route involving the condensation of L-tyrosine and L-phenylalanine with salicylaldehyde, 3,5-dichloro-, 3,5 dinitro-, 3-*tertiary*-butyl- and 3,5-di-*tertiary*-butyl salicylaldehyde followed by insertion of Ru(II) center (Scheme 1). The analytical data for the complexes are given in Section 2.

4.1. Enantioselective epoxidation of styrene derivatives

Enantioselective epoxidation of styrene, 4-chloro-, 4-methyl- and 4-nitrostyrene catalysed by the catalysts **1–10** was investigated in fluorobenzene using PhIO as oxidant. Within a short reaction time, the highest chemical conversion to epoxide (66–72%), together with a remark-

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

Catalyst[a]	Substrate	Time (min)	Percentage of conversion[b]	ees[c]	Configuration
1/6	styrene	120	28/22	22/18	*S*
	4-chlorostyrene	120	35/28	28/23	*S*
	4-methylstyrene	120	49/40	32/27	*S*
	4-nitrostyrene	120	60/52	36/32	*S*
2/7	styrene	120	32/28	28/22	*S*
	4-chlorostyrene	120	40/36	33/27	*S*
	4-methylsytrene	120	48/43	39/33	*S*
	4-nitrostyrene	120	55/57	42/35	*S*
3/8	styrene	120	38/32	33/28	*S*
	4-chlorostyrene	120	45/40	36/32	*S*
	4-methylstyrene	120	53/48	38/35	*S*
	4-nitrostyrene	120	59/52	45/38	*S*
4/9	styrene	120	40/36	39/33	*S*
	4-chlorostyrene	120	50/46	42/35	*S*
	4-methylstyrene	120	60/51	40/33	*S*
	4-nitrostyrene	120	65/57	47/39	*S*
5/10	styrene	120	45/40	40/35	*S*
	4-chlorostyrene	120	60/54	35/30	*S*
	4-methylstyrene	120	66/60	32/26	*S*
	4-nitrostyrene	120	72/66	50/42	*S*

[a] Organic phase, fluorobenzene (1.5 ml); catalyst (0.02 mmol); styrene, 4-chloro-, 4-metyl- and 4-nitrostyrene (1.0 mmol); PhIO (1 mmol); 0.1 mmol *n*-tridecane (internal standard for GC).
[b] Styrene oxide only.
[c] Styrene oxide separated by short silica gel column using hexane:dichloromethane (9:1) as eluent and used for determination of ee values by chiraldex GTA capillary column.

able chemoselectivity towards epoxidation reaction, was obtained in case of nitrostyrene with catalyst **5** and **10** while catalyst **4** gave 50% of chlorostyrene oxide. Low conversions were obtained in the case of styrene (22–45%) (Table 1). Enantiomeric excess of the isolated epoxide was evaluated by chiraldex GTA capillary column. Absolute configuration of the product epoxide was confirmed by comparison with authentic chirally pure epoxide in case of styrene while for other substrates, by analogy.

Results obtained for conversion to epoxide and ees for each catalyst and substrate are shown in Figs. 1 and 2 which show a clear trend that catalysts **1**–**5** derived from L-tyrosine are better catalysts than those derived with L-phenylalanine **6**–**10**. Furthermore, catalysts with electron-donating group gave better conversion and ees with the substrate containing electron-withdrawing group. In all the cases, employment of *R* form of the catalyst *S* form of the product was obtained [12], which in agreement with the mechanism reported earlier under identical conditions.

In order to understand the sense of chiral induction, a hypothetical model for probable catalytic intermediate species was constructed using bond lengths and angles reported in literature for the related compounds. Energy minimisation was accomplished by using DTMM program followed by docking of the substrate Fig. 3. Out of the various approaches tried, the approach shown in the Fig. 3 is energetically more feasible and suggests that triphenyl phosphine rings play a role in directing the substrate towards metal center of the catalyst **5**. Highest conversions and ee values obtained in case of catalyst **5** and **10** where electron-donating *t*-butyl group is present, with the electronically deficient substrate like nitrostyrene further strengthening this hypothesis. It also shows that the groups on salicylaldehyde moiety effect the

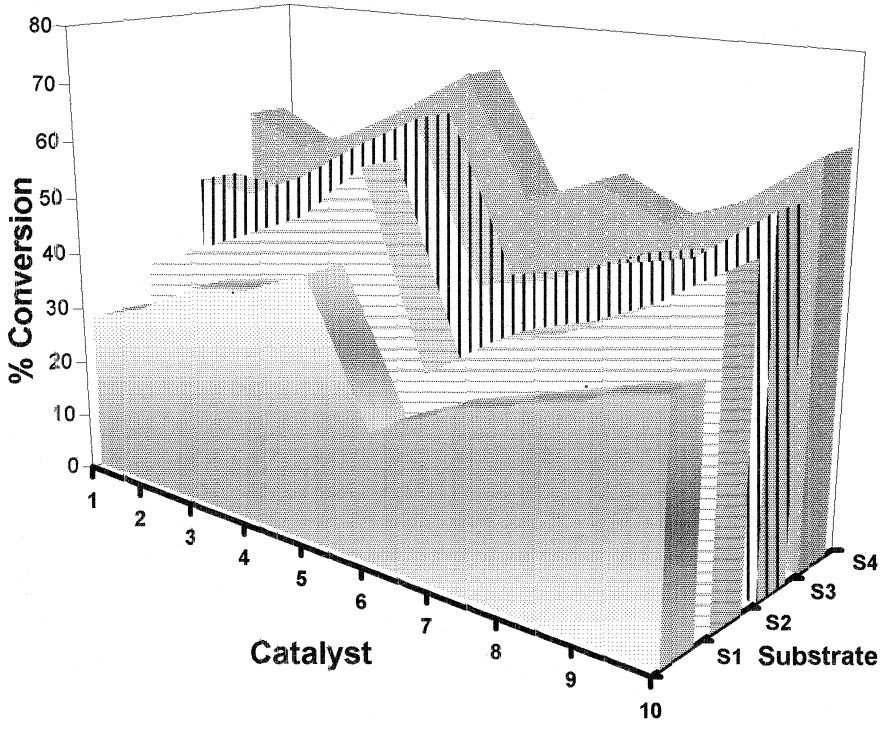


Fig. 1. 3-D view representing the percentage of conversion of epoxide by the catalysts **1**–**10** for the substrate S_1 = styrene, S_2 = 4-chlorostyrene, S_3 = 4-methylstyrene and S_4 = 4-nitrostyrene in fluorobenzene.

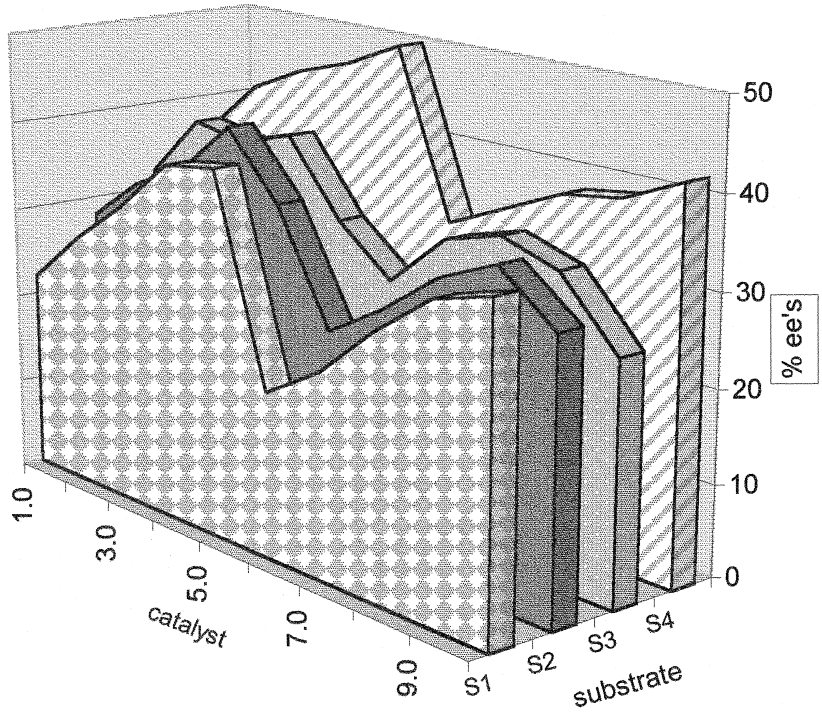


Fig. 2. 3-D view representing the percentage of ee values of epoxide by the catalysts **1**–**10** for the substrate S_1 = styrene, S_2 = 4-chlorostyrene, S_3 = 4-methylstyrene and S_4 = 4-nitrostyrene in fluorobenzene.

electron density of triphenyl phosphine rings through metal ions. This approach does not allow the chiral center on catalyst and substrate close enough in order to allow absolute chiral induction which is reflected in the experimental results (ees 18, 22% to 42, 50%).

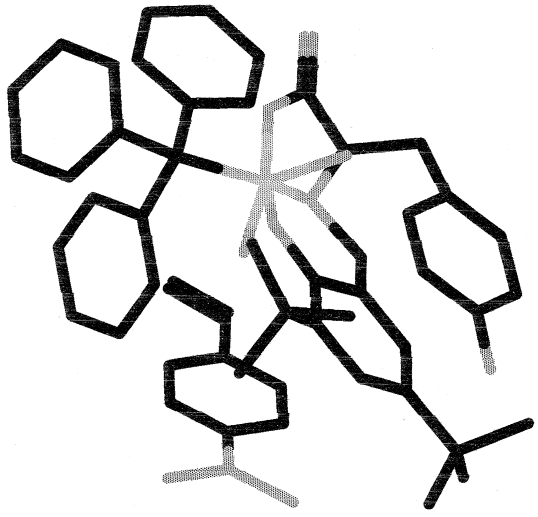


Fig. 3. Representative energy-minimised molecular model showing the mode of approach of the substrate 4-nitrostyrene in the complex **5** (H atoms are omitted for the sake of clarity).

As the complexes of the type **1**–**10** are known to show substitution of water molecule with *N*-coordinating ligands [19], it was desirable to study their effect on catalytic activity. Thus, *N*-methylimidazole and pyridine *N*-oxide were taken as representative additives for these reactions. However, there seems to be no appreciable effect on overall conversion or enantioselectivity.

5. Conclusion

Several amino acid-based Schiff base complexes were investigated as catalysts for the enantioselective epoxidation of styrene, 4-chloro-, 4-methyl- and 4-nitrostyrene in the present study. Complexes **1**–**5** derived from L-tyrosine are better catalysts than the complexes

of L-phenylalanine **6**–**10**. Catalysts **5** and **10** with 3,5-di-*tertiary*-butyl salicylaldehyde-based catalysts show better conversion and enantioinduction with nitrostyrene than the catalysts having electron-withdrawing groups on ligand moiety. As far as oxidant is concern, only PhIO was able to perform epoxidation reaction. Other 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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