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Preparation and reactivities of chiral manganese(III) and copper(II) complexes of binaphthyl Schiff bases†

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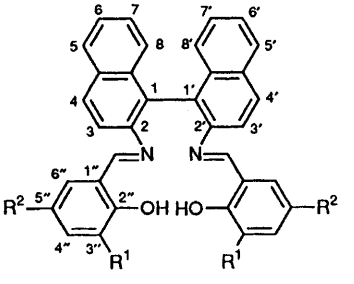
A series of chiral Schiff bases, 2,2′-bis(3-R^1-5-R^2-2-hydroxybenzylideneamino)-1,1′-binaphthyl H_2L (R^2 = Cl, R^1 = Cl, Me, Et or NO_2; R^2 = Me, R^1 = Bu^t; R^2 = NO_2, R^1 = H, Me, Et, Pr^i, Bu^t or Cl), and their complexes [CuL^1] **1** and [$Mn_2L^1{}_2(OMe)_2$] **2** (R^1 = R^2 = Cl) have been prepared. The crystal structure of the racemic form of **1** has been determined. Complex **1** is an active catalyst for the oxidation of alkenes by *tert*-butyl hydroperoxide. On the contrary, **2** is inert towards alkene epoxidation by PhIO. However, upon mixing $Mn(O_2CMe)_3{\cdot}xH_2O$ and H_2L in acetonitrile a green solution was obtained which could effect asymmetric epoxidation of alkenes by PhIO. The effects of the steric and electronic effects of the R^1 and R^2 substituents, temperature, and the addition of donors like *N*-methyl- and 2-methyl-imidazole and pyridine *N*-oxide on the catalytic activity of the Mn^{III} + (*S*)-H_2L systems towards alkene epoxidation have been investigated. When R^1 = Et and R^2 = NO_2 the best enantiomeric excesses of 58 and 43% were found for epoxidation of *cis*-β-methylstyrene to (1*S*,2*R*)-*cis*-β-methylstyrene oxide and 4-chlorostyrene to 4-(*S*)-chlorostyrene oxide respectively.

The design of new metal oxidative catalysts bearing optically active auxiliary ligands plays an important role in the development of asymmetric organic oxidation. Successful examples in this context include the asymmetric epoxidation of allylic alcohols by titanium(IV) alkoxide in the presence of optically active tartrate,[1] *cis* dihydroxylation of unfunctionalized alkenes by the OsO_4–chiral alkaloid system[2] and more recently the asymmetric epoxidation of unfunctionalized alkenes catalysed by chiral manganese(III) Schiff-base complexes.[3] Among the various chiral compounds employed in asymmetric metal catalysis, those containing C_2-symmetric binaphthyl group(s) have been widely studied.[4] In some cases effective asymmetric catalysis has been found. These include the use of ruthenium complexes of 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (binap) in asymmetric hydrogenation[5] and aluminium complexes of 1,1′-binaphthol[1] as catalysts in asymmetric Diels–Alder reactions.[6] In addition, metalloporphyrin complexes of iron and manganese incorporating the 1,1′-binaphthyl unit have also been shown to induce asymmetric epoxidation of simple alkenes by iodosylbenzene (PhIO).[7] Despite the effectiveness of this class of ligands, there has been no study on the use of non-porphyrin metal complexes of binaphthylic ligands in organic oxidation. Herein we describe the preparation of chiral 2,2′-bis(salicylideneamino)-1,1′-binaphthyl derivatives H_2L and their copper(II) and manganese(III) complexes, and the use of these chiral complexes in epoxidation of alkenes by *tert*-butyl hydroperoxide and PhIO.



	R^1	R^2
H_2L^1	Cl	Cl
H_2L^2	Me	Cl
H_2L^3	Et	Cl
H_2L^4	H	NO_2
H_2L^5	Me	NO_2
H_2L^6	Et	NO_2
H_2L^7	Pr^i	NO_2
H_2L^8	Bu^t	NO_2
H_2L^9	Cl	NO_2
H_2L^{10}	Bu^t	Me

Experimental

Instrumentation

The IR spectra were recorded on a Shimadzu IR-470 spectrometer, NMR spectra on a JEOL GSX-270 spectrometer in deuteriochloroform unless otherwise stated, with tetramethylsilane as internal standard at ambient temperature, mass spectra on a Finnigan MAT 95 high-resolution mass spectrometer and UV spectra on a Perkin-Elmer UV/VIS/NIR Lambda 19 spectrometer. Optical rotations were measured at ambient temperature with an Optical Activity AA-1000 automatic polarimeter (*c* in g per 100 cm^3). Analytical HPLC was performed on a Beckmann model 331 HPLC system with a model 163 variable UV/VIS detector. Chiral HPLC measurements were performed on a commercial column (Daicel Chemical Industries, Ltd., Chiralcel OJ). Analytical GC was performed on a Hewlett-Packard 5890 series II system equipped with a HP 5890A flame ionization detector and a HP 3395 integrator. The measurements were performed on a commercial chiral column (J & W Scientific, Cyclodex-B, 30 m × 0.25 mm internal diameter, 0.25 mm film). The CD spectra were measured with a JASCO 720 spectrophotometer. Magnetic susceptibility was determined at ambient temperature by using the Evan's method with deuteriochloroform as solvent.

† *Non-SI unit employed:* $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

Materials

The (*R*)- and (*S*)-2,2′-diamino-1,1′-binaphthyls were obtained from Fluka. A racemic sample was prepared according to the literature procedure.[8] Various substituted salicylaldehydes used in the syntheses were prepared by literature procedures.[9] Manganese(III) acetate dihydrate from Aldrich was dried *in vacuo* before use. Iodosylbenzene was prepared by hydrolysis of iodobenzene diacetate (Aldrich) in NaOH solution. *m*-Chloroperoxybenzoic acid (50 or 70%) was obtained from Merck. Dichloromethane and acetonitrile used for catalytic epoxidation were distilled from CaH_2 and stored over 4 Å molecular sieves in the dark. All olefinic substrates for catalytic epoxidation were from Aldrich or Fluka and were purified either by vacuum distillation or by passing through activated alumina. *trans*-Stilbene was recrystallized from ethanol and dried *in vacuo*. *cis*-β-Methylstyrene was prepared by hydrogenation of 1-phenyl-1-propyne (Aldrich) using Lindler catalyst.[10] Racemic styrene oxide was obtained from Fluka and distilled before use, (*S*)-(−)-styrene oxide from Aldrich (used without further purification) and *trans*-β-methylstyrene oxide, cyclohexene oxide, *cis*- and *trans*-stilbene oxide from Aldrich (distilled or purified by silica gel chromatography before use). All other epoxides required for determination of product yield and enantiomeric excess (e.e.) were independently prepared from the corresponding alkene and *m*-chloroperoxybenzoic acid in dichloromethane.[11]

Preparations

(*S*)-2,2′-Bis(3,5-dichloro-2-hydroxybenzylideneamino)-1,1′-binaphthyl, (*S*)-H_2L^1. A mixture of 3,5-dichlorosalicylaldehyde (0.32 g, 1.67 mmol) and (*S*)-2,2′-diamino-1,1′-binaphthyl (0.2 g, 0.7 mmol) in ethanol (10 cm^3) was stirred at room temperature for 3 h during which the diimine formed was precipitated as an orange solid. The crude product was filtered off, washed with ethanol and recrystallized from dichloromethane–diethyl ether to give an orange crystalline solid (0.36 g, 81.2%), m.p. 174 °C (decomp.); $[\alpha]_{589}^{24.0}$ +674.6 (*c* 0.816, toluene); λ_{max}(MeCN)/nm 230 (log ε_{max} 4.87), 227 (4.61), 323 (4.38), 372 (4.33) and 470 (2.63); $\tilde{\nu}$(Nujol)/cm^{-1} 3290–3650 (OH) and 1611 (C=N); δ_H(270 MHz, $CDCl_3$) 7.08 [1 H, d, *J*(H$^{4''}$H$^{6''}$) 2.44, H$^{4''}$)], 7.18 (1 H, d, *J* 8.31, H^5 or H^8), 7.26 [1 H, d, *J*(H$^{4''}$H$^{6''}$) 2.44, H$^{6''}$), 7.28–7.31 (1 H, m, H^6 or H^7), 7.44–7.50 (1 H, m, H^6 or H^7), 7.59 [1 H, d, *J*(H^{3}H^4) 8.79, H^4], 7.97 (1 H, d, *J* 8.06, H^5 or H^8), 8.11 [1 H, d, *J*(H^{3}H^4) 8.78 Hz, H^3], 8.55 (1 H, s, CH=N) and 12.76 (1 H, s, OH); δ_C(67.9 MHz, $CDCl_3$) 116.8, 120.4, 122.4, 123.1, 126.4, 126.5, 127.3, 128.5, 129.7, 130.5, 132.5, 132.9, 133.1, 142.8, 155.4 and 160.4 (Found: C, 64.5; H, 3.40; N, 4.15. Calc. for $C_{34}H_{20}Cl_4N_2O_2$: C, 64.8; H, 3.20; N, 4.45%).

The compound (*R*)-H_2L^1 was prepared by the same method. Starting with (*R*)-2,2′-diamino-1,1′-binaphthyl (0.2 g, 0.7 mmol) and 3,5-dichlorosalicylaldehyde (0.32 g, 1.67 mmol), the desired compound was obtained after recrystallization from dichloromethane–diethyl ether (0.34 g, 77%); $[\alpha]_{589}^{24.0}$ −670.9 (*c* 0.812, toluene). It exhibits identical spectral properties to those of its (*S*) isomer.

3-*tert*-Butyl-5-methylsalicylaldehyde. 2-*tert*-Butyl-4-methylphenol (3 g, 18.3 mmol) was dissolved in anhydrous toluene (10 cm^3) then stirred under a nitrogen atmosphere. Tin(IV) chloride (0.25 cm^3, 2.1 mmol) was added, followed by 2,6-dimethylpyridine (1 cm^3, 8.6 mmol). The mixture was stirred at room temperature for 20 min and paraformaldehyde (1.1 g, 36.7 mmol) added. The resulting mixture was heated at 100 °C for 8 h. On cooling, it was poured into water (100 cm^3), acidified to pH 2 with HCl and extracted with diethyl ether (2 × 50 cm^3). The ether extracts were combined, washed with a saturated NaCl solution, dried (Na_2SO_4) and concentrated. The yellow liquid so obtained was cooled in ice and the crystalline yellow solid was filtered off and washed with cold hexane (3 g, 85%). Recrystallization from diethyl ether–dichloromethane gave a product melting at 73–74 °C; δ_H(90 MHz, $CDCl_3$) 1.41 (9 H, s, Bu^t), 2.30 (3 H, s, 5-Me), 7.15–7.17 (1 H, m, H^4), 7.31–7.34 (1 H, m, H^6), 9.78 (1 H, s, aldehyde) and 11.61 (1 H, s, OH); δ_C(22.5 MHz, $CDCl_3$) 20.5 (5-Me), 29.3 [C(*C*H$_3$)$_3$], 34.8 [*C*(CH$_3$)$_3$], 120.5, 128.1, 131.4, 135.4, 138.0, 159.2 (2-OH) and 197.0 (aldehyde).

2,2′-Bis(3-*tert*-butyl-2-hydroxy-5-methylbenzylideneamino)-1,1′-binaphthyl, H_2L^{10}. A mixture of 2,2′-diamino-1,1′-binaphthyl (20 mg, 0.07 mmol) and 3-*tert*-butyl-5-methylsalicylaldehyde (30 mg, 0.16 mmol) in glacial acetic acid (6 cm^3) was heated at 60 °C for 2 h. The acetic acid was removed *in vacuo*. Addition of diethyl ether to the residue induced precipitation of the required compound as a yellow solid (36 mg, 80%). Recrystallization from EtOH–CH_2Cl_2 afforded a pure product, m.p. > 210 °C; $\tilde{\nu}$(Nujol)/cm^{-1} 3055 (OH) and 1622 (C=N); δ_H(270 MHz, $CDCl_3$) 1.20 (9 H, s, Bu^t), 2.17 (3 H, s, 5″-Me), 6.77 [1 H, d, *J*(H$^{4''}$H$^{6''}$) 1.71, H$^{4''}$], 6.99 [1 H, d, *J*(H$^{4''}$H$^{6''}$) 1.95, H$^{6''}$], 7.27–7.46 (3 H, m), 7.53 [1 H, d, *J*(H^{3}H^4) 8.79, H^4], 7.94 [1 H, d, *J* 8.30, H^5 or H^8], 8.03 [1 H, d, *J*(H^{3}H^4) 8.79 Hz, H^3], 8.50 (1 H, s, CH=N) and 12.64 (1 H, s, OH); δ_C(67.5 MHz, $CDCl_3$) 20.6 (5″-Me), 29.1 [C(*C*H$_3$)$_3$], 34.6 [*C*(CH$_3$)$_3$], 117.3, 118.7, 125.5, 126.3, 126.6, 126.8, 128.1, 129.0, 129.7, 130.1, 130.9, 132.5, 133.3, 137.0, 144.2, 158.2 and 162.5 (Found: C, 83.6; H, 7.10; N, 4.40. Calc. for $C_{44}H_{44}N_2O_2$: C, 83.5; H, 7.00; N, 4.40%).

The (*S*) isomer was prepared by the same method as its racemic form starting with (*S*)-2,2′-diamino-1,1′-binaphthyl (0.1 g, 0.35 mmol) and 3-*tert*-butyl-5-methylsalicylaldehyde (0.15 g, 0.8 mmol). However, the product thus obtained was very soluble in diethyl ether, so instead of recrystallization the crude product was purified by column chromatography using alumina as absorbent and light petroleum (b.p. 40–60 °C)–diethyl ether (8:2 v/v) as eluent. The yellow waxy solid (0.21 g, 94%) exhibited identical spectral properties to those of its racemic form; $[\alpha]_{589}^{15.5}$ 301.6 (*c* 0.67, toluene).

General procedure for (*S*)-2,2′-bis(3-alkyl-5-chloro-2-hydroxybenzylideneamino)-1,1′-binaphthyl. 3-Alkyl-5-chlorosalicylaldehyde (0.8 mmol) and (*S*)-2,2′-diamino-1,1′-binaphthyl (0.1 g, 0.35 mmol) were dissolved in a mixture of absolute ethanol (7 cm^3) and glacial acetic acid (1 cm^3) and stirred at room temperature under anhydrous conditions for 4 h. The orange product was filtered off, washed with absolute ethanol and recrystallized from EtOH–CH_2Cl_2.

(S)-2,2′-*Bis*(5-*chloro*-3-*ethyl*-2-*hydroxybenzylideneamino*)-1,1′-*binaphthyl*, (*S*)-H_2L^3. Yield 0.16 g (74%). λ_{max}(MeCN)/nm 276 (log ε_{max} 4.73), 321 (4.47) and 370 (4.42); $\tilde{\nu}$(Nujol)/cm^{-1} 1604 and 1570 (C=N); δ_H(270 MHz, $CDCl_3$) 1.02 [3 H, t, *J*(H$^{7''}$H$^{8''}$) 7.41, 3 H$^{8''}$], 2.40 [2 H, q, *J*(H$^{7''}$H$^{8''}$) 7.41, 2 H$^{7''}$], 6.93 [1 H, d, *J*(H$^{4''}$H$^{6''}$) 2.75, H$^{4''}$], 7.01 [1 H, d, *J*(H$^{4''}$H$^{6''}$) 2.75, H$^{6''}$], 7.20–7.46 (3 H, m), 7.52 [1 H, d, *J*(H^{3}H^4) 8.79, H^4], 7.93 (1 H, d, *J* 8.24, H^5 or H^8), 8.04 [1 H, d, *J*(H^{3}H^4) 8.79 Hz, H^3], 8.46 (1 H, s, CH=N) and 12.28 (1 H, s, OH); δ_C(67.9 MHz, $CDCl_3$) 13.2 (C$^{8''}$), 22.3 (C$^{7''}$), 117.2, 119.2, 122.8, 125.9, 126.5, 127.0, 128.2, 128.5, 129.0, 130.1, 131.7, 132.6, 133.2, 134.1, 143.8, 157.4 and 161.4 (Found: C, 73.95; H, 4.75; N, 4.35. Calc. for $C_{38}H_{30}Cl_2N_2O_2$: C, 73.9; H, 4.90; N, 4.50%).

(S)-2,2′-*Bis*(5-*chloro*-2-*hydroxy*-3-*methylbenzylideneamino*)-1,1′-*binaphthyl*, (*S*)-H_2L^2. Yield 0.18 g (87%). $\tilde{\nu}$(Nujol)/cm^{-1} 1603 and 1570 (C=N); δ_H(270 MHz, $CDCl_3$) 2.00 (1 H, s, Me), 6.97–7.03 (2 H, m, H$^{4''}$ and H$^{6''}$), 7.20–7.48 (3 H, m), 7.55 [1 H, d, *J*(H^{3}H^4) 9.06, H^4], 7.96 (1 H, d, *J* 8.05, H^5 or H^8), 8.07 [1 H, d, *J*(H^{3}H^4) 9.06 Hz, H^3], 8.49 (1 H, s, CH=N) and 12.21 (1 H, s, OH); δ_C(67.9 MHz, $CDCl_3$) 15.3 (Me), 117.2, 119.1, 122.6, 125.9, 126.5, 127.1, 128.2, 128.3, 128.5, 129.0, 130.1, 132.6, 133.2, 133.3, 143.8, 157.7 and 161.3 (Found: C, 72.9; H, 4.30; N, 4.50. Calc. for $C_{36}H_{26}Cl_2N_2O_2$: C, 73.35; H, 4.45; N, 4.75%).

General procedure for (*S*)-bis(3-alkyl- or (*S*)-bis(3-chloro-2-hydroxy-5-nitrobenzylideneamino)-1,1′-binaphthyl. (*S*)-2,2′-Diamino-1,1′-binaphthyl (0.1 g, 0.35 mmol) and 3-alkyl-5-nitrosalicylaldehyde (0.80 mmol) were dissolved in a mixture of absolute ethanol (7 cm^3) and glacial acetic acid (1 cm^3) and stirred under anhydrous conditions at room temperature for 4 h. The crude yellow product was filtered off, washed with ethanol and recrystallized from an appropriate solvent.

(S)-*Bis*(2-*hydroxy*-3-*methyl*-5-*nitrobenzylideneamino*)-1,1′-*binaphthyl*, (*S*)-H_2L^5. The crude product was recrystallized from acetic acid–ethanol–dichloromethane (0.17 g, 79%); $[\alpha]_{589}^{22.0}$ +642.7 (*c* 0.470, toluene); $\tilde{\nu}$(Nujol)/cm^{-1} 2000–3500 (br, OH), 1603 (C=N), 1510 and 1334 (NO_2); δ_H(270 MHz, $CDCl_3$) 2.07 (3 H, s, Me), 7.23 (1 H, d, *J* 8.55, H^5 or H^8), 7.27–7.54 (2 H, m, H^6 and H^7), 7.69 [1 H, d, *J*(H^3H^4) 8.85, H^4], 7.96 [1 H, d, *J*($H^{4''}H^{6''}$) 2.75, $H^{4''}$], 8.01 (1 H, d, *J* 7.94, H^5 or H^8), 8.07 [1 H, d, *J*($H^{4''}H^{6''}$) 2.74, $H^{6''}$], 8.15 [1 H, d, *J*(H^3H^4) 8.85 Hz, H^3], 8.75 (1 H, s, CH=N) and 13.38 (1 H, s, OH); δ_C(67.5 MHz, $CDCl_3$) 15.4 (Me), 116.4, 117.2, 125.9, 126.4, 126.6, 127.4, 127.9, 128.2, 128.4, 129.9, 130.5, 132.9, 133.1, 139.1, 142.2, 160.2 and 164.9 (Found: *m*/*z*, 610.1846. $C_{36}H_{26}N_4O_6$ requires *m*/*z*, 610.1852).

The (*R*) isomer was prepared by the same method. It exhibits identical spectral properties and gives an optical rotation of $[\alpha]_{589}^{19.5}$ −640.6 (*c* 0.240, toluene).

(S)-*Bis*(3-*ethyl*-2-*hydroxy*-5-*nitrobenzylideneamino*)-1,1′-*binaphthyl*, (*S*)-H_2L^6. The crude product was recrystallized from acetic acid–ethanol–dichloromethane (0.17 g, 76%); $[\alpha]_{589}^{21.0}$ +573.3 (*c* 0.658, toluene); λ_{max}(MeCN)/nm 276 (log ε_{max} 4.78), 313 (4.68), 371 (4.49) and 456 (3.23); $\tilde{\nu}$(Nujol)/cm^{-1} 2000–2570 (br, OH), 1602 (C=N), 1510 and 1330 (NO_2); δ_H(270 MHz, $CDCl_3$) 1.07 (3 H, t, *J* 7.33, CH_2CH_3), 2.46 (2 H, q, *J* 7.33, CH_2CH_3), 7.23–7.53 (3 H, m), 7.68 [1 H, d, *J*(H^3H^4) 8.85, H^4], 7.96 [1 H, d, *J*($H^{4''}H^{6''}$) 2.75, $H^{4''}$], 8.00 (1 H, d, *J* 8.24, H^5 or H^8), 8.06 [1 H, d, *J*($H^{4''}H^{6''}$) 2.75, $H^{6''}$], 8.15 [1 H, d, *J*(H^3H^4) 8.85, $H^{3''}$], 8.73 (1 H, s, CH=N) and 13.46 (1 H, s, OH); δ_C(67.5 MHz, $CDCl_3$) 12.8 (CH_2CH_3), 22.4 (CH_2CH_3), 116.4, 117.3, 125.9, 126.4, 126.5, 126.6, 127.4, 128.4, 129.8, 130.5, 133.0, 133.1, 133.7, 139.3, 142.2, 160.3 and 164.7 (Found: C, 71.2; H, 4.65; N, 8.50. Calc. for $C_{38}H_{30}N_4O_6$: C, 71.45; H, 4.75; N, 8.75%).

The (*R*) isomer was prepared by the same method. It exhibits identical spectral properties and gives an optical rotation of $[\alpha]_{589}^{19.5}$ −576.4 (*c* 0.330, toluene).

(S)-*Bis*(2-*hydroxy*-3-*isopropyl*-5-*nitrobenzylideneamino*)-1,1′-*binaphthyl*, (*S*)-H_2L^7. The crude product was recrystallized from acetic acid–ethanol–dichloromethane (0.14 g, 60%); $[\alpha]_{589}^{23.0}$ +502.1 (*c* 0.354, toluene); $\tilde{\nu}$(Nujol)/cm^{-1} 2000–3495 (br, OH), 1582, 1602 (C=N), 1518 and 1333 (NO_2); δ_H(270 MHz, $CDCl_3$) 1.08 [6 H, m, $CH(CH_3)_2$], 3.06 [1 H, m, $CH(CH_3)_2$], 7.26–7.52 (3 H, m), 7.67 [1 H, d, *J*(H^3H^4) 8.85, H^4], 7.99–8.01 (2 H, m, $H^{4''}$ and H^5 or H^8), 8.06 [1 H, d, *J*($H^{4''}H^{6''}$) 2.75, $H^{6''}$], 8.15 [1 H, d, *J*(H^3H^4) 8.85 Hz, H^3], 8.74 (1 H, s, CH=N) and 13.56 (1 H, s, OH); δ_C(67.5 MHz, $CDCl_3$) 21.7 [$CH(CH_3)_2$], 26.7 [$CH(CH_3)_2$], 116.4, 117.4, 124.6, 125.8, 126.4, 126.5, 127.5, 128.4, 129.8, 130.5, 133.1, 133.2, 138.2, 139.5, 142.2, 160.4 and 164.4 (Found: *m*/*z*, 666.2479. $C_{40}H_{34}N_4O_6$ requires *m*/*z*, 666.2478).

(S)-*Bis*(3-tert-*butyl*-2-*hydroxy*-5-*nitrobenzylideneamino*)-1,1′-*binaphthyl*, (*S*)-H_2L^8. The crude product was recrystallized from ethanol–dichloromethane (0.15 g, 66%); $[\alpha]_{589}^{22.5}$ +238.0 (*c* 0.748, toluene); λ_{max}(MeCN)/nm 278 (log ε_{max} 4.72), 314 (4.64), 372 (4.49) and 456 (3.45); $\tilde{\nu}$(Nujol)/cm^{-1} 1980–3500 (br, OH), 1602, 1582 (C=N), 1509 and 1324 (NO_2); δ_H(270 MHz, $CDCl_3$) 1.18 (9 H, s, Bu^t), 7.34–7.54 (3 H, m, H^5 or H^8 and H^6 and H^7), 7.71 [1 H, d, *J*(H^3H^4) 8.85, H^4], 8.00 (1 H, d, *J* 8.24, H^5 or H^8), 8.07 (2 H, s, $H^{4''}$ and $H^{6''}$), 8.15 [1 H, d, *J*(H^3H^4) 8.85 Hz, H^3], 8.75 (1 H, s, CH=N) and 14.21 (1 H, s, OH); δ_C(67.5 MHz, $CDCl_3$) 28.6 [$C(CH_3)_3$], 35.0 [$C(CH_3)_3$], 115.8, 117.6, 125.1, 126.4, 126.5, 126.7, 127.6, 128.4, 130.3, 130.5, 133.2, 133.3, 138.9, 139.3, 141.4, 159.7, and 166.4. (Found: C, 72.35; H, 5.50; N, 7.85. Calc. for $C_{42}H_{38}N_4O_6$: C, 72.60; H, 5.50; N, 8.05%).

(S)-*Bis*(3-*chloro*-2-*hydroxy*-5-*nitrobenzylideneamino*)-1,1′-*binaphthyl*, (*S*)-H_2L^9. The crude product was recrystallized from acetic acid–ethanol–dichloromethane (0.16 g, 71%); $[\alpha]_{589}^{24.0}$ +781.9 (*c* 0.252, toluene); $\tilde{\nu}$(Nujol)/cm^{-1} 2000–3500 (br, OH), 1621, 1564 (C=N), 1525 and 1341 (NO_2); δ_H(270 MHz, $CDCl_3$) 7.17–8.17 (8 H, m), 8.73 (1 H, s, CH=N) and 13.93 (1 H, s, OH); δ_C(67.5 MHz, $CDCl_3$) 116.1, 122.4, 126.5, 127.0, 127.7, 128.3, 128.4, 128.6, 130.0, 131.0, 133.0, 133.2, 136.2, 138.1, 141.5, 154.7 and 159.2 (Found: *m*/*z*, 650.0765. $C_{34}H_{20}Cl_2N_4O_6$ requires *m*/*z*, 650.0756).

(S)-*Bis*(2-*hydroxy*-5-*nitrobenzylideneamino*)-1,1′-*binaphthyl*, (*S*)-H_2L^4. The crude product was recrystallized from acetic acid–ethanol (0.11 g, 54%); $[\alpha]_{589}^{23.5}$ +594.6 (*c* 0.326, toluene); $\tilde{\nu}$(Nujol)/cm^{-1} 2020–3355 (br, OH), 1608, 1585 (C=N), 1519 and 1337 (NO_2); δ_H(270 MHz, $CDCl_3$) 6.74 [1 H, d, *J*($H^{3''}H^{4''}$) 9.23, $H^{3''}$], 7.23 (1 H, d, *J* 8.46, H^5 or H^8), 7.30–7.55 (2 H, m, H^6 and H^7), 7.74 [1 H, d, *J*(H^3H^4) 8.97, H^4], 8.02 (1 H, d, *J* 8.21, H^5 or H^8), 8.07 [1 H, dd, *J*($H^{3''}H^{4''}$) 9.10, *J*($H^{4''}H^{6''}$) 2.57, $H^{4''}$], 8.19 [1 H, d, *J*(H^3H^4) 8.98, H^3], 8.24 [1 H, d, *J*($H^{4''}H^{6''}$) 2.57 Hz, $H^{6''}$], 8.81 (1 H, s, CH=N) and 13.19 (1 H, s, OH); δ_C(67.5 MHz, $CDCl_3$) 115.9, 118.1, 118.2, 126.4, 126.8, 127.6, 128.1, 128.2, 128.5, 130.4, 130.6, 133.1, 139.7, 141.8, 159.6, 166.3 (Found: C, 69.55; H, 3.80; N, 9.45. Calc. for $C_{34}H_{22}N_4O_6$: C, 70.1; H, 3.80; N, 9.60%).

[CuL^1] 1. A mixture of $Cu(O_2CMe)_2$ (0.1 g) and H_2L^1 (0.25 g) in ethanol (50 cm^3) was refluxed for 0.5 h to afford a green solution. The solvent was evaporated and the residue extracted with CH_2Cl_2 (2 × 25 cm^3). The volume of the combined extracts was reduced to *ca.* 10 cm^3. Addition of an excess of methanol induced immediate precipitation of [CuL^1] as a green solid, which was recrystallized by slow evaporation of a CH_2Cl_2–MeOH mixture (Found: C, 59.0; H, 2.70; N, 4.10. Calc. for $C_{34}H_{18}Cl_4CuN_2O_2$: C, 59.0; H, 2.60; N, 4.05%).

(*S*)-[$Mn_2L^1_2(OMe)_2$] 2. To a solution of (*S*)-H_2L^1 (0.1 g, 0.18 mmol) in dichloromethane (20 cm^3) was added a solution of $Mn(O_2CMe)_3{\cdot}2H_2O$ (0.08 g, 0.31 mmol) in methanol (5 cm^3). The mixture was stirred at 40 °C for 1 h then allowed to stand at room temperature. Upon slow evaporation of solvent, a dark green crystalline solid was deposited. The solid was filtered off, washed with cold methanol and dried (0.11 g, 49%): λ_{max}(MeCN)/nm 266 (log ε_{max} 4.76), 350 (4.03) and 390 (3.82); $\tilde{\nu}$(Nujol)/cm^{-1} 1601 (C=N), 1030 (Mn–O–Mn); μ_{eff} 3.95 μ_B per manganese atom; *m*/*z* 1429 (M^+), 1398 (M^+ − OMe) and 1366 (M^+ − 2OMe) (Found: C, 57.6; H, 3.10; N, 4.1. Calc. for $C_{35}H_{21}Cl_4MnN_2O_3{\cdot}H_2O$: C, 57.8; H, 3.15; N, 3.85%).

Crystallography

Crystal data. $(C_{34}H_{18}Cl_4CuN_2O_2)_2{\cdot}2H_2O{\cdot}CH_3COCH_3$, M = 1499.78, triclinic, space group $P\bar{1}$, a = 12.844(5), b = 14.748(6), c = 18.706(4) Å, α = 107.89(3), β = 89.95(3), γ = 100.11(3)°, U = 3314(2) Å^3, D_c = 1.48 g cm^{-3}, Z = 2, F(000) = 1500, μ(Mo-Kα) = 10.2 cm^{-1}.

A crystal of dimensions 0.05 × 0.20 × 0.50 mm was used for data collection on an Enraf-Nonius diffractometer (graphite-monochromatized Mo-Kα radiation, λ = 0.7107 Å) using the θ–2θ scan mode ($2\theta_{max}$ = 45°) at 298 K. Intensity data were corrected for Lorentz and polarisation effects; empirical absorptions were based on ψ scans of five strong reflections. 8629 Unique reflections were obtained, 4944 of which were considered observed ($|F_o| \geqslant 2.0\,\sigma|F_o|$) and used in structure refinement. The structure was solved by Patterson and Fourier methods and subsequent refinement by full-matrix least squares was performed using the NRCVAX program.[12] There are two independent molecules of complex **1** per unit cell. The final

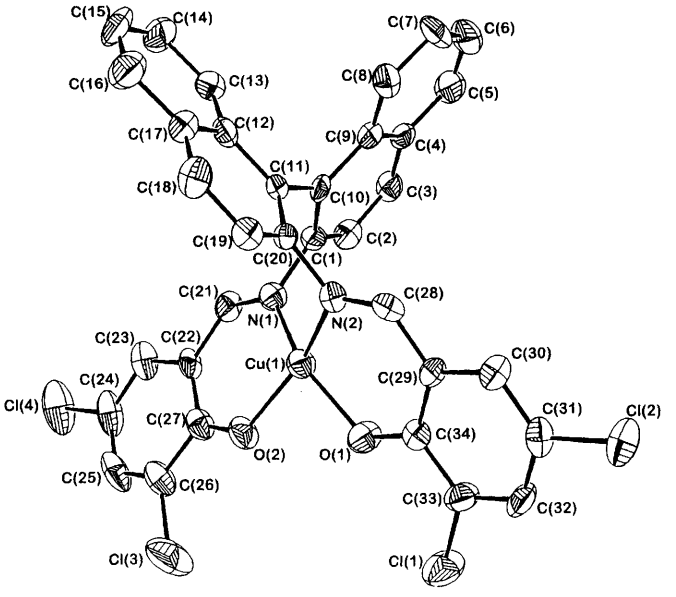


Fig. 1 A perspective view of one of the enantiomers of [CuL^1] **1**

least-squares refinement was calculated with 830 parameters and converged to $R = 0.05$, $R' = 0.048$ and $S = 1.68$ with weights based on counting statistics. The hydrogen atoms were placed in calculated positions and were not refined. The final difference map showed residual extrema in the range 0.680 to -0.50 e Å^{-3}. The atomic coordinates of non-hydrogen atoms are listed in Table 1, selected bond distances and angles in Table 2.

Alkene oxidation

Catalysed by [CuL^1] 1. In a typical run a mixture of organic substrate (0.2 g, ≈2 mmol) and the oxidant Bu^{t}O$_2$H (80%, 2 cm^3) in dichloromethane (10 cm^3) was stirred at 0 °C. Complex **1** (25 mg, 0.05 mmol) was added and the mixture stirred for 8–12 h. A blank containing the same amount of solvent, substrate and Bu^{t}O$_2$H but without the metal catalyst was simultaneously stirred under the same conditions. The reaction was quenched by addition of a saturated solution of Na_2SO_3 (10 cm^3) at 0 °C. The organic product was extracted with diethyl ether, dried with Na_2SO_4 and filtered. The aliquot was then subjected to GC analyses, and the products quantified by the internal standard method. The yield of the catalytic oxidation was calculated based on the amount of substrate used.

Catalysed by Mn^{III} + H$_2$L. All catalytic oxidation reactions were carried out at either 0 °C or room temperature under an argon atmosphere. In a typical run the olefinic substrate (0.85 mmol), manganese(III) acetate dihydrate (4 mol%) and the compound H_2L (4 mol%) were mixed in acetonitrile (5 cm^3). The mixture was stirred at room temperature for 20 min. For reactions at 0 °C, the mixture was stirred at 0 °C for 15 min more. Iodosylbenzene, PhIO (0.43 mmol), was added to the substrate–catalyst mixture and the system stirred until all of it had dissolved. The epoxide product and iodobenzene formed were quantified by gas chromatography using the internal standard method and the epoxide yield for the PhIO epoxidation was based on the amount of iodobenzene formed. The epoxide products of the catalytic oxidation of stilbenes were analysed by ^{1}H NMR spectroscopy using 1,1-diphenylethylene as internal standard.

Enantiomeric excess of epoxide products. The enantiomeric excesses of the styrene oxide, 4-chlorostyrene oxide and *cis*-β-methylstyrene oxide products were determined on a commercial chiral GC column (J & W Scientific, Cyclodex-B, 30 m × 0.25 mm internal diameter, 0.25 mm film). For *trans*-stilbene oxide the e.e. was determined on a commercial chiral HPLC column (Daicel Industries Ltd., Chiralcel OJ). All other epoxide products, were first purified by column chromatography and their e.e.s determined by ^{1}H NMR spectroscopy in the presence of tris[3-(heptafluoropropylhydroxymethylene)-D-camphorato]europium(III) {camphor = (*R*)-(+)-1,7,7-trimethylbicyclo-[2.2.1]heptan-2-one}, [Eu(hfc)$_3$]. The absolute configuration of the enriched isomer in the styrene oxide product was determined by comparison with an authentic sample, (*S*)-styrene oxide (Aldrich). The absolute configuration of the enriched isomer in the 4-chlorostyrene oxide products was determined by comparing the [Eu(hfc)$_3$]-shifted ^{1}H NMR spectra of the products with a previously reported spectrum of a sample enriched with (*R*)-4-chlorostyrene oxide.[13] For the *cis*-β-methylstyrene oxide products the absolute configuration of the enriched enantiomer was determined by matching the order of elution of the two enantiomers on the Cyclodex-B column with that provided by Professor Jacobsen:[14] first peak, (1*R*,2*S*)-(+)-*cis*-β-methylstyrene oxide; second peak, (1*S*,2*R*)-(−)-*cis*-β-methylstyrene oxide. The assignments of absolute configuration to the enriched enantiomer in the three types of epoxide product were further supported by optical rotation measurements.

Relative reactivity of styrenes in epoxidation mediated by Mn^{III} + H$_2$L^6 or H$_2$L^1. In a typical competition reaction, equimolar amounts of styrene and substituted styrene (0.3 mmol each) were mixed in acetonitrile (5 cm^3) containing the appropriate GC internal standards. The initial amounts of the two olefins were determined by GC. The compound $Mn(O_2CMe)_3 \cdot 2H_2O$ and the compound H_2L (4 mol %) were added to the solution and the mixture stirred at room temperature for 20 min. With H_2L^6 the substrate–catalyst mixture was stirred at 0 °C for 15 min more. Iodosylbenzene (0.15 mmol) was then added and the mixture stirred until all of it had dissolved. The final amounts of the two olefins were determined by GC. The relative reactivity was calculated according to equation (1) where Y_i and Y_f are the amounts of

$$\frac{k_{\text{substituted styrene}}}{k_{\text{styrene}}} = \frac{\log (Y_f/Y_i)}{\log (X_f/X_i)} \qquad (1)$$

substituted styrene before and after reaction and X_i and X_f are the corresponding amounts of styrene.[15]

Results and Discussion

The compound (*R*)- or (*S*)-H_2L^1 was prepared by a one-pot reaction of (*R*)- or (*S*)-2,2′-diamino-1,1′-binaphthyl respectively with 3,5-dichlorosalicylaldehyde in absolute ethanol at room temperature. The optically active forms are stable and no significant racemization was found to occur at temperatures below 90 °C. Reaction of $Cu(O_2CMe)_2$ with H_2L^1 in refluxing ethanol afforded the complex [CuL^1] **1** in high yield. The optically active forms of **1** were prepared from the pure *R*(−) and *S*(+) forms of H_2L^1. The structure of the racemic form of **1** has been established by X-ray crystal analysis. In each asymmetric unit there are two independent molecules, **A** and **B**, a perspective view of one of which is shown in Fig. 1. The ligand behaves like other tetradentate salicylideneimine ligands. The co-ordination geometry of Cu is distorted tetrahedral. The most intriguing structural feature is the seven-membered twist-boat ring formed from the two imine nitrogen atoms N(1) and N(2), the two naphthalene rings and the copper atom. Importantly, the measured dihedral angles of 75.5(1) (molecule A) and 74.1(1)° (B) between the two naphthalene rings are comparable to the values of 65.6° in [Ru(OCOCMe$_3$)$_2$\{(*S*)-binap\}][16] and 87.59(5)° in the related 2,2′-bis(pyridine-2-carboxamido)-1,1′-binaphthyl ligand.[17]

Reaction of a mixture of H_2L^1 and $Mn(O_2CMe)_3 \cdot 2H_2O$ in

Table 1 Atomic coordinates of non-hydrogen atoms of complex **1** (the atomic coordinates of the water and acetone molecules are not included)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu(1A)	0.249 12(8)	0.017 79(6)	0.488 74(5)	Cu(1B)	0.247 11(8)	0.474 99(6)	1.004 41(5)
N(1A)	0.325 3(4)	0.027 2(4)	0.581 8(3)	N(1B)	0.186 6(4)	0.495 4(4)	0.916 2(3)
N(2A)	0.164 2(4)	−0.111 6(4)	0.470 6(3)	N(2B)	0.340 7(4)	0.601 2(4)	1.043 1(3)
O(1A)	0.250 5(4)	0.006 4(3)	0.385 3(3)	O(1B)	0.235 2(4)	0.457 0(3)	1.100 0(3)
O(2A)	0.262 1(4)	0.153 2(3)	0.512 1(3)	O(2B)	0.226 5(4)	0.338 7(3)	0.959 6(3)
C(1A)	0.362 5(6)	−0.057 7(5)	0.586 2(4)	C(1B)	0.156 0(5)	0.587 8(4)	0.926 5(4)
C(2A)	0.472 0(6)	−0.057 7(5)	0.586 1(4)	C(2B)	0.047 1(6)	0.590 7(5)	0.925 8(4)
C(3A)	0.509 0(6)	−0.139 2(5)	0.582 2(4)	C(3B)	0.014 5(6)	0.676 9(5)	0.944 0(4)
C(4A)	0.438 0(6)	−0.226 0(5)	0.576 9(4)	C(4B)	0.087 0(6)	0.763 7(5)	0.966 5(4)
C(5A)	0.475 0(6)	−0.314 0(6)	0.566 1(4)	C(5B)	0.054 2(6)	0.856 5(5)	0.992 3(4)
C(6A)	0.404 1(7)	−0.396 7(6)	0.557 3(5)	C(6B)	0.126 4(7)	0.940 3(5)	1.015 1(5)
C(7A)	0.296 3(7)	−0.397 6(5)	0.558 5(5)	C(7B)	0.233 3(7)	0.938 5(5)	1.012 6(4)
C(8A)	0.258 0(6)	−0.314 3(5)	0.569 3(4)	C(8B)	0.268 8(6)	0.851 8(5)	0.987 5(4)
C(9A)	0.329 1(6)	−0.225 7(5)	0.578 1(4)	C(9B)	0.196 3(6)	0.762 3(5)	0.964 6(4)
C(10A)	0.290 5(5)	−0.138 4(5)	0.585 5(3)	C(10B)	0.230 9(5)	0.669 6(5)	0.942 4(4)
C(11A)	0.174 5(5)	−0.136 5(4)	0.591 5(4)	C(11B)	0.346 9(5)	0.666 5(4)	0.938 7(4)
C(12A)	0.124 7(6)	−0.143 6(5)	0.658 2(4)	C(12B)	0.404 2(5)	0.695 3(5)	0.881 6(4)
C(13A)	0.182 3(6)	−0.141 2(5)	0.722 9(4)	C(13B)	0.355 7(6)	0.715 7(5)	0.821 5(4)
C(14A)	0.132 7(7)	−0.145 6(6)	0.786 8(4)	C(14B)	0.414 6(7)	0.738 0(6)	0.766 6(4)
C(15A)	0.022 7(7)	−0.150 4(6)	0.788 9(4)	C(15B)	0.523 7(6)	0.743 4(6)	0.768 3(4)
C(16A)	−0.035 4(6)	−0.151 7(6)	0.728 3(4)	C(16B)	0.572 7(6)	0.725 4(6)	0.824 0(4)
C(17A)	0.014 5(6)	−0.147 5(5)	0.661 5(4)	C(17B)	0.515 5(6)	0.700 0(5)	0.882 1(4)
C(18A)	−0.045 0(6)	−0.146 5(5)	0.599 3(4)	C(18B)	0.564 5(5)	0.674 7(5)	0.939 1(4)
C(19A)	0.002 9(6)	−0.138 0(5)	0.535 7(4)	C(19B)	0.508 9(6)	0.643 5(5)	0.990 9(4)
C(20A)	0.113 2(6)	−0.130 8(4)	0.534 1(3)	C(20B)	0.399 5(5)	0.639 0(5)	0.989 7(4)
C(21A)	0.359 0(6)	0.107 6(5)	0.635 6(4)	C(21B)	0.156 8(6)	0.427 7(5)	0.853 6(4)
C(22A)	0.340 9(6)	0.201 6(4)	0.637 2(4)	C(22B)	0.163 8(5)	0.327 3(5)	0.835 8(4)
C(23A)	0.377 5(6)	0.277 7(5)	0.703 9(4)	C(23B)	0.129 6(6)	0.268 3(5)	0.762 4(4)
C(24A)	0.371 2(6)	0.370 8(5)	0.708 1(5)	C(24B)	0.126 0(6)	0.170 7(5)	0.743 4(4)
C(25A)	0.327 1(7)	0.390 0(5)	0.648 7(5)	C(25B)	0.155 5(6)	0.129 0(5)	0.795 4(4)
C(26A)	0.293 1(6)	0.317 7(5)	0.584 4(4)	C(26B)	0.189 3(6)	0.186 5(5)	0.866 6(4)
C(27A)	0.297 4(6)	0.219 3(5)	0.574 9(4)	C(27B)	0.196 3(6)	0.289 1(5)	0.890 8(4)
C(28A)	0.138 4(6)	−0.173 7(5)	0.405 1(4)	C(28B)	0.367 2(6)	0.648 2(5)	1.113 5(4)
C(29A)	0.165 6(5)	−0.159 5(5)	0.334 4(4)	C(29B)	0.329 3(6)	0.613 4(5)	1.175 2(4)
C(30A)	0.131 4(6)	−0.238 4(5)	0.269 6(4)	C(30B)	0.360 1(6)	0.678 8(6)	1.248 4(4)
C(31A)	0.147 8(6)	−0.229 5(5)	0.200 7(4)	C(31B)	0.335 4(7)	0.650 9(7)	1.309 7(4)
C(32A)	0.196 7(6)	−0.142 5(5)	0.192 2(4)	C(32B)	0.278 8(7)	0.559 2(7)	1.302 5(4)
C(33A)	0.231 6(6)	−0.064 9(5)	0.254 4(4)	C(33B)	0.247 9(6)	0.495 3(6)	1.232 0(4)
C(34A)	0.218 5(5)	−0.069 9(5)	0.328 2(4)	C(34B)	0.268 9(6)	0.519 3(6)	1.164 9(4)
Cl(1A)	0.295 2(2)	0.043 1(2)	0.243 5(1)	Cl(1B)	0.175 60(2)	0.381 3(2)	1.223 6(1)
Cl(2A)	0.101 0(2)	−0.326 1(2)	0.119 5(1)	Cl(2B)	0.374 9(2)	0.731 4(2)	1.397 8(1)
Cl(3A)	0.239 0(2)	0.342 92(15)	0.509 6(2)	Cl(3B)	0.225 1(2)	0.134 4(2)	0.932 0(1)
Cl(4A)	0.416 4(2)	0.463 58(16)	0.790 4(2)	Cl(4B)	0.081 5(2)	0.096 3(1)	0.653 5(1)

Table 2 Selected bond distances (Å) and angles (°) of [CuL^1] **1**

Cu(1A)–N(1A)	1.953(5)	Cu(1B)–N(1B)	1.951(5)
Cu(1A)–N(2A)	1.954(4)	Cu(1B)–N(2B)	1.954(5)
Cu(1A)–O(1A)	1.891(5)	Cu(1B)–O(1B)	1.889(5)
Cu(1A)–O(2A)	1.885(4)	Cu(1B)–O(2B)	1.895(5)
N(1A)–C(21A)	1.301(8)	N(1B)–C(21B)	1.290(8)
N(2A)–C(28A)	1.287(8)	N(2B)–C(28B)	1.299(9)
N(1A)–C(1A)	1.441(9)	N(1B)–C(1B)	1.440(8)
N(1A)–Cu(1A)–N(2A)	98.1(2)	N(1A)–Cu(1A)–O(1A)	149.4(2)
N(2A)–Cu(1A)–O(1A)	93.4(2)	N(1A)–Cu(1A)–O(2A)	93.6(2)
N(1A)–C(1A)–C(10A)	119.4(6)	N(2A)–C(20A)–C(11A)	118.6(6)
N(1B)–Cu(1B)–N(2B)	97.6(2)	N(1B)–Cu(1B)–O(1B)	151.6(2)
N(2B)–Cu(1B)–O(1B)	93.7(2)	N(1B)–Cu(1B)–O(2B)	93.4(2)
N(1B)–C(1B)–C(10B)	120.0(6)	N(2B)–C(20B)–C(11B)	119.5(6)

methanol–dichloromethane at 50 °C afforded a deep green solution, from which a dark green crystalline solid was obtained. Both elemental analyses and the mass spectrum established the empirical formula of the green solid to be [$Mn_2L^1{}_2(OMe)_2$] **2**. This empirical formula has also been inferred from a partial X-ray crystal analysis of the dark green crystals,[18] although due to their poor quality a complete structural solution is not feasible. Complex **2** is paramagnetic and has an effective magnetic moment of 3.95 μ_B per manganese atom at room temperature. This value is lower than the spin-only value of 4.9 μ_B for high-spin Mn^{III}. It is likely that in the manganese(III) Schiff-base complexes dimer formation tends to lower the effective magnetic moment as a result of coupling. The two optically active forms were prepared from the *R*(−) and *S*(+) forms of H_2L^1. As shown in Fig. 2, their ORD curves are mirror images but are different from that of the free H_2L^1. The UV/VIS absorption spectrum of **2** measured in acetonitrile is shown in Fig. 3.

Catalytic alkene oxidation by [CuL^1] 1

Complex **1** was found to catalyse alkene oxidation in the presence of *tert*-butyl hydroperoxide and the results are summarized in Table 3. Styrene was oxidized to a mixture of

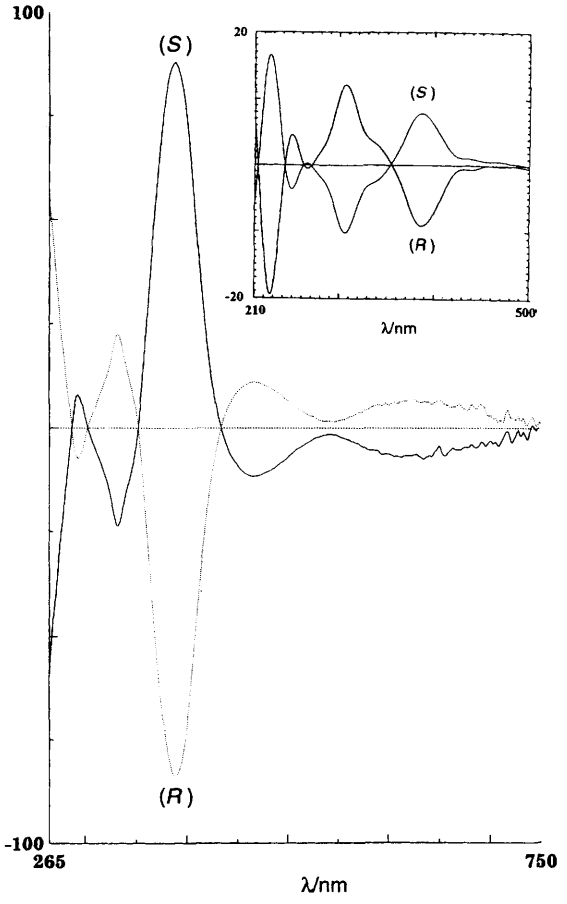


Fig. 2 The ORD spectra of the (*R*) and (*S*) forms of $[Mn_2L^1{}_2(OMe)_2]$. The insert shows the corresponding spectra of the two forms of H_2L^1 in dichloromethane

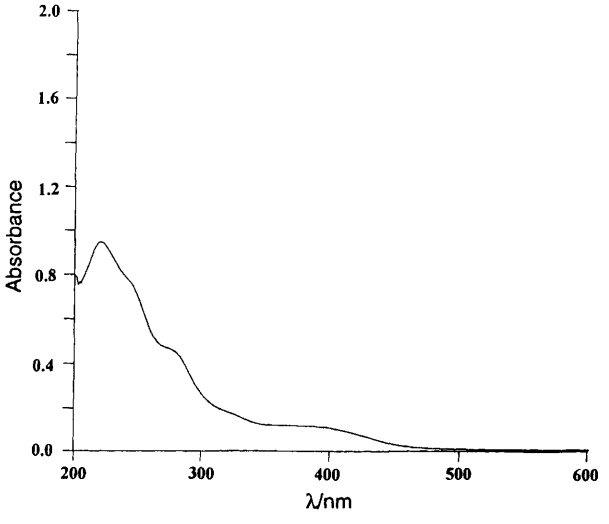


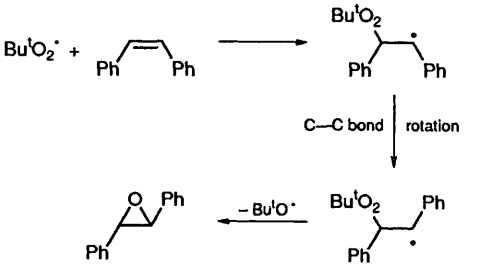
Fig. 3 The UV/VIS spectra of the green solution obtained from $Mn(O_2CMe_2)_3{\cdot}2H_2O$ with (*S*)-H_2L^1 in acetonitrile

styrene oxide and benzaldehyde in a ratio of 5:1. Norbornene (bicyclo[2.2.1]hept-2-ene) was oxidized to *exo*-norbornene oxide exclusively. Oxidation of cyclohexene gave cyclohexen-2-one predominantly together with a small amount of cyclohexene oxide. The oxidation reaction was non-stereospecific as exemplified in stilbene oxidation where *trans*-stilbene afforded *trans*-stilbene oxide, and *cis*-stilbene gave *trans*-stilbene oxide only. It should be noted that in the *cis*-stilbene oxidation a significant amount of *trans*-stilbene was detected (entry 5 in Table 3). A similar finding was reported previously by Valentine and co-workers [19] in the catalysis by simple metal

Table 3 Oxidation of alkenes by *tert*-butyl hydroperoxide catalysed by $[CuL^1]$

Entry	Substrate	Product	Yield (%)*
1	Styrene	Styrene oxide	51
		Benzaldehyde	11
2	Norbornene	*exo*-Norbornene oxide	56
3	Cyclohexene	Cyclohexene oxide	10
		Cyclohex-2-enone	32
4	*trans*-Stilbene	*trans*-Stilbene oxide	56
		Benzaldehyde	10
5	*cis*-Stilbene	*trans*-Stilbene oxide	16
		Benzaldehyde	10
		trans-Stilbene	50

* Based on substrate consumed.



Scheme 1

salts (Mn^{III}, Fe^{III}, Co^{II}, Cu^{II}) of the oxidation of *cis*-stilbene by iodosylbenzene. These workers ascribed this result to the metal-catalysed isomerization of *cis*- to *trans*-stilbene. Given the low yields of organic epoxides and non-stereospecific nature of the *cis*-stilbene oxidation, we rationalize the oxidation as involving radical-chain reaction(s) arising from homolytic O–O bond cleavage induced by Cu^{II}. Thus reaction of *cis*-stilbene with the *tert*-butylperoxy radical would give the $Bu^tO_2CHPhCHPh^\bullet$ intermediate which undergoes C–C bond rotation before expulsion of $Bu^tO^\bullet$ (Scheme 1).

With the use of chiral (*S*)-$[CuL^1]$ as the catalyst the oxidation of styrene with Bu^tO_2H gave styrene oxide (entry 1 in Table 3) but there was no asymmetric induction. Other co-oxidants like PhIO, morpholine *N*-oxide and NaOCl in the presence of **1** were found to be ineffective towards oxidation of alkenes. For this reason, no detailed study of the Cu^{II}-catalysed oxidation was undertaken.

Catalytic alkene oxidation by manganese complexes of chiral H_2L

Complex **2** is not a good catalyst for epoxidation of alkenes by iodosylbenzene. When a mixture of styrene (1 equivalent), **2** (0.04 equivalent) and PhIO (0.5 equivalent) was stirred at room temperature under an argon atmosphere for 24 h no styrene oxide was detected. Changing the solvent to acetonitrile gave the same result. We speculated that the poor catalytic activity of **2** is due to the presence of co-ordinating methoxide ions which hamper the interaction between PhIO and Mn^{III}. In order to render the system catalytic, an equimolar amount of (*S*)-H_2L^1 and $Mn(O_2CMe)_3{\cdot}2H_2O$ was allowed to react in acetonitrile at room temperature. A dark green solution was obtained after 20 min which displayed a similar UV/VIS absorption spectrum to that of **2** (Fig. 3). The ORD curves of the green solutions obtained from $Mn(O_2CMe)_3{\cdot}2H_2O$ with (*S*)- or (*R*)-H_2L^1 are similar to that of $[Mn_2\{(S)\text{-}L^1\}_2(OMe)_2]$ and $[Mn_2\{(R)\text{-}L^1\}_2(OMe)_2]$ respectively. However, unlike **2**, the green solution is active towards alkene epoxidation by PhIO. We speculate that the green species generated *in situ* is a manganese(III) dimer but without the co-ordinated methoxide. The results of PhIO oxidation of alkenes catalysed by the

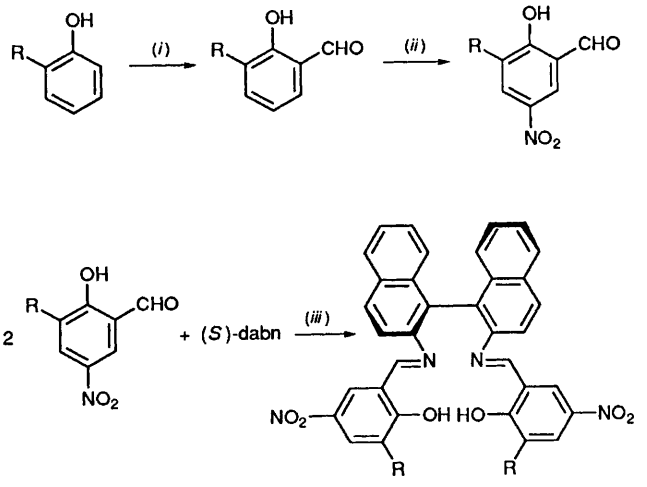
Table 4 Alkene epoxidation catalysed by the Mn^{III} + (*S*)-H_2L^1 system

Entry	Substrate	Product	Yield (%)[a]	e.e. (%)[b] (configuration)
1	Styrene	Styrene oxide	79	25 (*S*)
2	*cis*-β-Methylstyrene	*cis*-β-Methylstyrene oxide	46	34 (1*R*,2*S*)
3	*trans*-β-Methylstyrene	*trans*-β-Methylstyrene oxide	27	6 (n.d.)[c]
4	4-Chlorostyrene	4-Chlorostyrene oxide	66	31 (*S*)
5	4-Methylstyrene	4-Methylstyrene oxide	n.d.[c]	24 (*S*)
6	Oct-1-ene	Oct-1-ene oxide	18	0

[a] Based on the amount of PhI formed. [b] Determined by either ^1H NMR spectroscopy in the presence of [Eu(hfc)$_3$] or chiral column GC. [c] n.d. = Not determined.

Mn^{III} + (*S*)-H_2L^1 system are summarized in Table 4. The reaction usually took less than 30 min for completion. In all cases, epoxides are the major products. Styrene was oxidised to (*S*)-styrene oxide with 25% e.e. When (*R*)-H_2L^1 was used in the preparation of the green solution styrene was oxidized to (*R*)-styrene oxide with similar product yield but with ≈25% e.e.

Like the oxidation reactions mediated by other chiral manganese Schiff-base complexes,[20] *cis*-alkenes such as *cis*-β-methylstyrene reacted with higher yield and e.e. and are more reactive than the *trans* isomers (entries 2 and 3 in Table 4). For example, the reaction time required for *trans*-β-methylstyrene is 2 h whereas that for the *cis* counterpart is just 10 min. The e.e. is affected by electronic effects as found in the oxidation of a series of *para*-substituted styrenes. The electron-withdrawing chloro group enhances the e.e. by about 6%, whereas an electron-donating substituent decreases it slightly (entries 4 and 5 in Table 4). Oct-1-ene, an aliphatic terminal alkene, is a poor substrate in the present catalytic system.



Scheme 2 (*i*) $(CH_2O)_n$, $SnCl_4$, 2,6-dimethylpyridine, toluene; (*ii*) concentrated HNO_3, $MeCO_2H$; (*iii*) $MeCO_2H$–EtOH (1:7), room temperature. dabn = 2,2′-Diamino-1,1′-binaphthyl

Optimization of the chiral inducing effect of the auxiliary binaphthyl Schiff-base ligands

The effect of changing the $Mn(O_2CMe)_3{\cdot}2H_2O$: (*S*)-H_2L^1 mole ratio on the e.e. of the organic epoxide formed has been examined. With styrene as the substrate, changing the ratio from 1 to 2:1 had no significant effect on both the activity and enantioselectivity of the Mn^{III} + (*S*)-H_2L^1 system. The e.e. of the (*S*)-styrene oxide was unaffected.

Previously, Zhang and Jacobsen[20] reported that bulky substituents on the salicylidene ring of the Schiff-base ligand strongly affect the chiral inducing power of the manganese catalyst. In an attempt to improve the enantiodiscrimination effect of the newly developed binaphthylic Schiff-base ligand, the chloro groups in H_2L^1 were replaced by bulky alkyl substituents to give (*S*)-H_2L^{10} (R^1 = Bu^t, R^2 = Me). Disappointingly, the Mn^{III} + (*S*)-H_2L^{10} system in a molar ratio of 1:1 was found to be a poor catalytic system under similar conditions as that used for Mn^{III} + (*S*)-H_2L^1. The former took nearly 3 h for complete dissolution of PhIO and only a trace amount of racemic styrene oxide was formed. Attempts to promote the oxidation by first heating the reaction mixture did not lead to any improvement in the catalytic properties. A similar result was found when $R^1 = R^2$ = Me. Thus the inability of the dialkyl binaphthylic Schiff bases to activate Mn^{III} is not solely due to the steric effect of the alkyl substituents at the 3 position. The failure of the H_2L ($R^1 = R^2$ = Me) ligand to promote epoxidation led us to attach electron-withdrawing groups on the two phenoxy rings. Thus the two methyl groups at the 5 positions were substituted with chloro substituents to give ligands which have different steric properties in the vicinity of the manganese atom.

Under similar conditions to those used in the Mn^{III} + (*S*)-H_2L^1 catalysed epoxidation, the catalytic activities of the Mn^{III} + (*S*)-H_2L (R^1 = Me or Et, R^2 = Cl) systems were examined using 4-chlorostyrene as substrate. However, in all cases, a very low yield of racemic epoxide was found. Furthermore, the UV/VIS spectrum of a 1:1 mixture of $Mn(O_2CMe)_3{\cdot}2H_2O$ and (*S*)-H_2L^3 (R^1 = Et) in acetonitrile (stirred at 50 °C for 1 h) and that of free H_2L^3 are similar. Thus, the poor reactivity was attributed to the poor ability of (*S*)-H_2L^3 to co-ordinate to Mn^{III}.

In order to improve the co-ordination ability of the Schiff base, the compounds (*S*)-H_2L (R^1 = H, alkyl or Cl; R^2 = NO_2) were prepared (Scheme 2). The effect of (*S*)-H_2L^5 (R^1 = Me), as a chiral auxiliary ligand has been examined. Stirring a mixture of 4-chlorostyrene (1 equivalent), $Mn(O_2CMe)_3{\cdot}2H_2O$ (0.04 equivalent) and (*S*)-H_2L^5 (0.04 equivalent) in acetonitrile under an argon atmosphere for 30 min at room temperature resulted in the formation of a dark brown solution. Addition of PhIO (0.5 equivalent) gave 4-chlorostyrene oxide in 61% yield and 37% e.e. and the reaction was completed within 10 min. When *cis*-β-methylstyrene was employed as substrate an even higher enantioselectivity of 47% was observed. This result is better than that obtained with the Mn^{III} + (*S*)-H_2L^1 system.

The effect of varying the R^1 groups (Et, Pr^i, Bu^t, H or Cl) at the 3 positions of (*S*)-H_2L (R^2 = NO_2) on enantioselectivity was examined. 4-Chlorostyrene and *cis*-β-methylstyrene were used as the substrates and the results are listed in Table 5. When R^1 = Me, Et or Pr^i the reactions were completed within 20 min, whereas when R^1 = Bu^t about 2–3 h were required for complete consumption of PhIO. This indicates that the bulky *tert*-butyl group adversely affects the catalytic activity.

With *cis*-β-methylstyrene there is a slight improvement in e.e. from 47 to 50% when the substituent R^1 changes from methyl to ethyl (entries 1 and 2 in Table 5). However, when the bulkiness of the R^1 groups increase further the enantioselectivity drops as

Table 5 Epoxidation of *cis*-β-methylstyrene and 4-chlorostyrene with PhIO catalysed by the (*S*)-H_2L (R^2 = NO_2) + Mn^{III} systems, at room temperature[a]

		cis-β-Methylstyrene oxide		4-Chlorostyrene oxide	
Entry	R^1	Yield (%)[b]	e.e. (%)[c]	Yield (%)[b]	e.e. (%)[d]
1	Me	51	47	61	37
2	Et	50	50	59	36
3	Pr^i	49	33	52	19
4	Bu^t[e]	14	2	16	0
5	Cl	57	34	50	34

[a] All reactions completed within 20 min. [b] Based on amount of PhI formed. [c] (1*R*,2*S*)-*cis*-β-Methylstyrene oxide was the major product. [d] (*S*)-4-Chlorostyrene oxide was the major product. [e] Reaction time 3 h.

Table 6 Epoxidation of *cis*-β-methylstyrene and 4-chlorostyrene with PhIO catalysed by various (*S*)-H_2L (R^2 = NO_2) + Mn^{III} systems at 0 °C[a]

	cis-β-Methylstyrene oxide		4-Chlorostyrene oxide	
R^1	Yield (%)[b]	e.e. (%)[c]	Yield (%)[b]	e.e. (%)[d]
H	35	45	45	35
Me	37	47	50	41
Et	38	54	56	43
Pr^i	41	35	42	24

[a] For all reactions, manganese(III) acetate, H_2L and substrate were stirred at room temperature for 20 min and for 15 min at 0 °C before the addition of PhIO. All mixtures were stirred at 0 °C for 90 min after the addition of oxidant. [b] Determined on the basis of the PhI formed. [c] (1*R*,2*S*)-*cis*-β-Methylstyrene oxide was the major product. [d] (*S*)-4-Chlorostyrene oxide was the major product.

Table 7 Effect of donor ligand on the epoxidation of *cis*-β-methylstyrene with PhIO catalysed by the H_2L^6 + Mn^{III} catalytic system at 0 °C[a]

Donor	Amount H_2L^6 (equivalents)[b]	Yield (%)[c]	e.e. (%)[d]
Nil	0	38	54
2-Methylimidazole[e]	1	37	51
	5	24	51
N-Methylimidazole[f]	1	37	51
	5	31	44
Pyridine *N*-oxide[e]	5	43	54
	10	44	54

[a] Reactions were carried out in acetonitrile with 0.85 mmol of substrate, 0.43 mmol of PhIO and 4 mol % catalyst. In all cases, manganese(III) acetate, H_2L^7 and substrate were stirred at room temperature for 20 min, a calculated amount of donor was then added and the mixture stirred for 15 min at 0 °C before addition of PhIO. [b] Based on the amount of catalyst. [c] Yields of *cis*-β-methylstyrene oxide formed are based on PhI formed. [d] (1*R*,2*S*)-*cis*-β-Methylstyrene oxide was the major product. [e] Reaction time 1 h. [f] Reaction time 2 h.

illustrated by the 2% e.e. in the case of *tert*-butyl (entry 4 in Table 5).

When R^1 was the electron-withdrawing chloro group, *i.e.* H_2L^9, lower e.e.s were found in the epoxidation of both 4-chlorostyrene and *cis*-β-methylstyrene (entry 5 in Table 5).

The effect of decreasing the reaction temperature has also been investigated. The results are listed in Table 6. As shown, the enantioselectivity increases with decreasing temperature. Epoxidation of *cis*-β-methylstyrene with the Mn^{III} + (*S*)-H_2L^6 (R^1 = Et) system gave the best result with epoxide up to 54% e.e. at 0 °C and 58% at −20 °C.

As far as the configuration of the organic epoxide is concerned, epoxidation of styrene and *cis*-β-methylstyrene with Mn^{III} + (*S*)-H_2L^6 gave (*S*)-styrene oxide and (1*S*,2*R*)-*cis*-β-methylstyrene oxide, whereas with (*R*)-H_2L^6 the *cis*-β-methylstyrene oxide was found in the 1*R*,2*S* configuration with 54% e.e.

Efforts have been made to characterize and/or isolate the active intermediate responsible for the catalytic activity. However, no well characterized product was obtained upon heating an equimolar mixture of $Mn(O_2CMe)_3{\cdot}2H_2O$ and (*S*)-H_2L^6 in acetonitrile.

Effect of donor ligands on the catalytic activities of the manganese complexes

As reported by Katsuki and co-workers,[21] addition of a donor ligand could improve the e.e. of alkene epoxidation catalysed by chiral manganese Schiff-base complexes. In this work the effect of three donor ligands, namely *N*-methylimidazole (1-mim), 2-methylimidazole (2-mim) and pyridine *N*-oxide (pyo), on the Mn^{III} + H_2L^6 catalytic system, for *cis*-β-methylstyrene oxidation has been examined and the results are shown in Table 7. Addition of 1-mim (1 and 5 equivalents) does not affect the catalytic activity. The reaction was completed within 15 min but there was a decrease in both the e.e. and yield of the epoxide products. On the other hand, addition of just 5 equivalents of 2-mim was found to slow the reaction, which took about 90 min for completion. Presumably, the excess of 2-mim would deactivate the catalyst through binding to Mn^{III}. Although the epoxide yield decreased considerably there was only a slight decrease in e.e.

Like 1-mim, pyo did not suppress the activity of the catalyst. All PhIO reacted within 15 min. Unlike the imidazole donor, the e.e. was not affected by the *N*-oxide additive and there was a small improvement in the product yield (entries 6 and 7 in Table 7).

Epoxidation of various olefinic substrates by PhIO–Mn^{III}–H_2L^6 system

The results of PhIO epoxidation of various alkenes catalysed by the Mn^{III} + H_2L^6 system are listed in Table 8. A similar selectivity pattern has been found with the Mn^{III} + H_2L^1 system (Table 4). Electron-withdrawing substituents in *meta*- or *para*-substituted styrenes (Table 8, entries 2–4) give higher

Table 8 Epoxidation of alkenes by PhIO catalysed by the (*S*)-H_2L^6 + Mn^{III} catalytic system at 0 °C[a]

Entry	Substrate	Product	Yield (%)	e.e. (%) (configuration)
1	Styrene	Styrene oxide	59	36 (*S*)
2	3-Chlorostyrene	3-Chlorostyrene oxide	60	46 (*S*)
3	4-Chlorostyrene	4-Chlorostyrene oxide	56	43 (*S*)
4	3-Nitrostyrene	3-Nitrostyrene oxide	n.d.[b]	49 (n.d.)
5	4-Methylstyrene	4-Methylstyrene oxide	n.d.	35 (*S*)
6	*cis*-β-Methylstyrene	*cis*-β-Methylstyrene oxide	38 (*cis*-epoxide : *trans*-epoxide = 10 : 1)	54 (1*S*,2*R*)
7	*cis*-β-Methylstyrene[c,d]	*cis*-β-Methylstyrene oxide	34 (*cis*-epoxide : *trans*-epoxide = 9 : 1)	58 (1*S*,2*R*)
8	*trans*-β-Methylstyrene[d]	*trans*-β-Methylstyrene oxide	33 (no *cis*-epoxide detected)	3 (n.d.)
9	*cis*-Stilbene	*cis*-Stilbene oxide	65 (*cis*-epoxide : *trans*-epoxide = 6 : 1)	—
10	*trans*-Stilbene[d,e]	*trans*-Stilbene oxide	21 (no *cis*-epoxide detected)	1 (n.d.)
11	*cis*-Hept-2-ene	*cis*-Hept-2-ene oxide	87	—
12	*trans*-Oct-2-ene[f]	*trans*-Oct-2-ene oxide	18	—
13	Cyclohexene	Cyclohexene oxide[g]	93	—

[a] Reactions were carried out in acetonitrile (5 cm^3) with 0.85 mmol of alkene, 0.43 mmol of PhIO and 4 mol % of catalyst. All reactions were allowed to proceed for 1 h and the yields of epoxide determined by GC and reported based on the amount of PhI formed. [b] n.d. = Not determined. [c] Reaction was carried out at −20 °C. [d] Reaction for 2 h. [e] Reaction was carried out at room temperature. [f] Reaction for 3 h. [g] A small amount of cyclohexanone was detected.

Table 9 Relative reactivities of substituted styrenes in epoxidation catalysed by the H_2L^6 + Mn^{III} system

Substituted styrene	$\log(k_{substituted\ styrene}/k_{styrene})$	σ^+
4-Chloro	0	0.11
3-Chloro	−0.13	0.40
4-Methyl	0.31	−0.31
4-Methoxy	0.62	−0.78

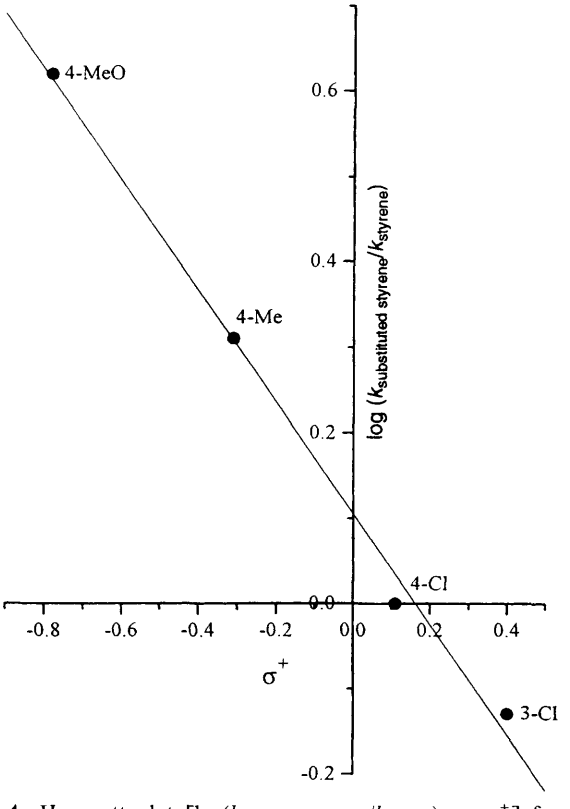


Fig. 4 Hammett plot [$\log(k_{substituted\ styrene}/k_{styrene})$ *vs.* σ^+] for the reaction of iodosylbenzene with substituted styrenes catalysed by Mn^{III} + H_2L^6

e.e.s than unsubstituted styrenes, whereas an electron-donating group (Table 8, entry 5) reduces the enantioselectivity slightly. *cis*-β-Methylstyrene remains the best substrate among the alkenes examined. The Mn^{III} + H_2L^6 system displays poor activity towards *trans* alkenes. All the *trans* substrates were found to react in a sluggish manner (about 2 h for complete reaction) and epoxides were obtained with very low e.e. and poor yield (Table 8, entries 8, 10 and 12).

Besides aryl-substituted alkenes, several aliphatic alkenes have also been tested (entries 11–13, Table 8). *trans*-Oct-2-ene afforded a low yield of epoxide. On the other hand, *cis*-hept-2-ene and cyclohexene were epoxidized in excellent yields. In the case of cyclohexene a small amount of cyclohexenone (allylic oxidation product) was formed. Attempts to determine the e.e. of *cis*-hept-2-ene oxide and *trans*-oct-2-ene oxide products failed. In both cases addition of [Eu(hfc)$_3$] to a $CDCl_3$ solution of the epoxide led to a set of overlapping multiplets and no resolved NMR signals from the two enantiomers.

Oxidation of *cis*-β-methylstyrene at 0 °C gave a 9 : 1 mixture of *cis*- and *trans*-epoxides. Furthermore, in the epoxidation of *cis*-hept-2-ene no *trans*-epoxide was detected. In the case of *cis*-stilbene a mixture of *cis*- and *trans*-epoxides was formed in a ratio of only 6 : 1.

The reactivities of a series of substituted styrenes (relative to styrene) towards PhIO catalysed by the Mn^{III} + H_2L^6 system were studied by a competition method and the results are listed in Table 9. A Hammett plot of $\log(k_{substituted\ styrene}/k_{styrene})$ *vs.* σ^+ is shown in Fig. 4. A ρ^+ value of −0.65 was found. The uniform variation of the $k_{substituted\ styrene}$ values with *para* substituents indicates that a common mechanism is operating for all substituted styrenes studied. However, the ρ^+ value is small when compared with those for reactions which involve rate-determining formation of a carbocation intermediate ($\rho^+ > -3$).[22] By comparison with ρ^+ values for concerted electrophilic reactions, such as carbene insertion into alkene double bonds ($\rho^+ = -0.62$ to -1.61)[23] or epoxidation of stilbene by peroxybenzoic acid ($\rho^+ = -1.2$),[24] it is probable that oxygen insertion into the alkene double bond in the present epoxidation reactions proceeds *via* a concerted pathway.

Conclusion

The results obtained clearly demonstrate that the newly prepared binaphthyl Schiff bases are capable of activating Cu^{II} and Mn^{III} towards catalytic oxygen-atom transfer to alkenes. Enantioselective formation of organic epoxides from the PhIO oxidation of alkenes catalysed by the Mn^{III} + H_2L system has

been demonstrated. The chiral inducing ability of the dinitro-substituted auxiliary ligands could be enhanced by attaching small alkyl groups at the 3 positions and the best ligand in this respect is H_2L^6 (R^1 = Et). Addition of donor ligands such as substituted imidazole or pyridine *N*-oxide did not result in e.e. enhancement. The small ρ^+ value obtained in the oxidation of a series of substituted styrenes suggests a concerted pathway for the Mn^{III} + H_2L system.

Acknowledgements

We acknowledge support from The University of Hong Kong and The Hong Kong Research Grants Council.

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Received 14*th August* 1995; *Paper* 5/05430C