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A Highly Potential Analogue of Jacobsen Catalyst with In-built Phase Transfer Capability in Enantioselective Epoxidation of Nonfunctionalized Alkenes

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A new analogue of Jacobsen Mn^{III} SALEN epoxidation catalysts having in-built phase transfer capability by means of introducing tertiary amino alkyl groups at the 5,5′-position of the Salen ligand were used as catalysts for the liquid-phase enantioselective epoxidation of 2,2-dimethyl-6-cyano chromene, indene, and styrene in the presence of O-coordinating axial bases with NaOCl as an oxidant under biphasic reaction conditions. Excellent conversions were obtained with catalyst loading in the range 0.4–2.0 mol% in all alkenes, but high chiral induction (EEs > 99%) was obtained only in the case of 2,2-dimethyl-6-cyano chromene. The enhanced activity of these complexes is attributed to the presence of *t*-alkyl amines in the Salen ligand, imparting in-built phase transfer capability to the catalyst.

Key Words: **enantioselective; chiral; epoxidation; nonfunctionalized alkenes; phase transfer; homogeneous catalysis; manganese.**

INTRODUCTION

Chiral epoxides are used as building blocks for the synthesis of many pharmaceuticals and fine chemicals (1, 2). Direct oxygen atom transfer to alkenes employing homogeneous inorganic metal-complex-based catalysts is emerging as an important strategy for the synthesis of chiral epoxides. The choice of an appropriate chiral ligand and metal is central to the design of efficient catalysts for this application. In this context, the reactivity and selectivity of Mn^{III} SALEN systems (3–5) are observed to be remarkable. These catalyst systems are known to be sensitive to a dissymmetric diamine bridge derived from a C_2 symmetric 1,2-diamine as well as bulky substituents at the 3,3′-position of the salicylide ligand. It is further reported (6) that the presence and nature of substituents at 5,5′-positions of the salicylide ligand can also influence enantioselectivity during epoxidation. Substituents on the ligand influence catalyst performance through steric and electron effects, with the former determining the enantioselective pathway for the substrate molecule and the latter affecting the reactivity of the oxo intermediates formed during the reaction. Furthermore, in Mn^{III} SALEN-based catalysts, employing NaOCl as an oxidant, the addition of pyridine N-oxide derivatives improves (6) both catalyst turnover and enantioselectivity, as in these cases the catalyst resides entirely in the organic phase of the two-phase reaction medium; water-insoluble pyridine N-oxide derivatives bearing hydrophobic substituents such as 4-phenylpyridine N-oxide (4-PPyN-O) and 4-(3-phenylpropyl) pyridine-N-oxide (4-PPPyN-O) also act as phase transfer catalysts in transporting HOCl from aqueous to organic phase (6). Based on this understanding and specific requirements for biphasic epoxidation systems, we synthesized a new analogue of Jacobsen's catalysts, **1a**–**1c** and **2a**–**2c**, which have in-built phase transfer capability. Due to this in-built feature, these catalysts show high epoxidation activity even when PyN–O and 1,4-dioxane are used as axial bases with NaOCl as an oxidant, thus avoiding the requirement of expensive substituted pyridine N-oxide under biphasic conditions.

EXPERIMENTAL METHODS

^{1}H NMR spectra were recorded in $CDCl_3$ using a Bruker F113V, 200-MHz spectrometer. IR spectra were recorded on a Biorad FTS-40 spectrophotometer in KBr/nujol mull. Electronic spectra were recorded in dichloromethane using a UV–vis spectrometer (HP Diode Array Spectrophotometer model 8452A). The optical rotation (Atago, Japan) and CD spectra (Jasco Machine J-20, Japan) were recorded in dichloromethane. Melting points were determined with capillary apparatus and are reported without further correction.

All the solvents used were procured from Merck and purified by known procedures (7). Indene and styrene were passed through a pad of neutral alumina before use. 2,2-Dimethyl-6-cyano chromene (8) and 3,5-di-*t*-Bu salicylaldehyde were synthesized by reported procedure (9). The purity of the solvents, alkenes, and reaction products was

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determined by gas chromatography (GC) using a Shimadzu GC model 14B having a stainless steel column (2 m long, 3 mm i.d., 4 mm o.d.) packed with 5% SE30 (mesh size 60–80) and FID detector. Ultrapure nitrogen was used as carrier gas with a flow rate of 30 ml/min and the injection port temperature was kept at 200°C. For styrene and indene analysis, the column temperature was programmed to between 70 and 150°C while for chromenes it was kept isothermal at 150°C. Synthetic standards of the products were used to determine yields by comparison of peak height and area. The optical yield of the product was determined by GC using a Chiraldex GTA chiral capillary column, by ^{1}H NMR using a chiral shift reagent, (+)Eu(hfc)$_3$, or by HPLC (Shimadzu SCL-10AVP) using a Chiralcel column OJ.

Magnetic susceptibility measurements were carried out as per the procedure reported by Evans (10). The inner tube (~2.5 mm i.d.) was filled with the known concentration of sample solution in $CDCl_3 + \sim 2\%$ TMS, while the outer tube was filled with $CDCl_3 + 2\%$ TMS. A paramagnetic shift observed in a TMS resonance line was used to calculate χ_M using Eq. [1].

$$\chi_M = 3\Delta f/2\pi f_m + \chi_0 + \chi_0(d_0 - d_s)/m, \qquad [1]$$

where Δf = frequency separation between the TMS lines, f_m = frequency at which the proton resonance is studied, and m = mass of the substance. The magnetic moment was calculated from χ_M using Eq. [2].

$$\mu_{eff} = \sqrt{\chi_M T}. \qquad [2]$$

Synthesis of Metal Complex Catalysts

A four-step synthetic strategy was followed for the synthesis of catalysts **1a**–**1c** and **2a**–**2c** (Scheme 1). 3-*t*-Bu-2-hydroxy benzaldehyde, 3THB, was chloromethylated by modified procedure to yield 3TB5CMB, which was allowed to react with an appropriate secondary amine to yield **1″a**–**1″c**. On condensation of **1″a**–**1″c** with (+)(1*S*, 2*S*)1,2-diaminocyclohexane/(+)(1*R*, 2*R*)1,2-diphenyl-1,2-diaminoethane in 2 : 1 molar ratio, ligands **1′a**–**1′c** and **2′a**–**2′c** were formed which were then complexed with Mn^{III} to give **1a**–**1c** and **2a**–**2c**, respectively.

Synthesis of 3-t-Bu-5-(chloro-methyl)-2-hydroxy benzaldehyde (3TBSCMB). 3TBSCMB was synthesized by modifying the procedure reported in the literature (11, 12). 3-*t*-Bu-2-hydroxy benzaldehyde (26.8 g; 150 mmol) and paraformaldehyde (10.0 g; 333 mmol) was added to precooled (5–10°C) concentrated hydrochloric acid (100 ml) and the resulting emulsion was stirred for 48 h with slow bubbling of HCl gas for 6 h, following which the reaction mixture was extracted with Et_2O. The organic phase was washed carefully with saturated aqueous $NaHCO_3$ and brine and dried over Na_2SO_4. This was further concentrated in vacuum to get 3TBSCMB as a white crystalline solid (yield, 33.2 g, 97%; m.p. 63–65°C). The CHN analysis, IR, and ^{1}H NMR data of the sample are in agreement with those reported earlier (11, 12).

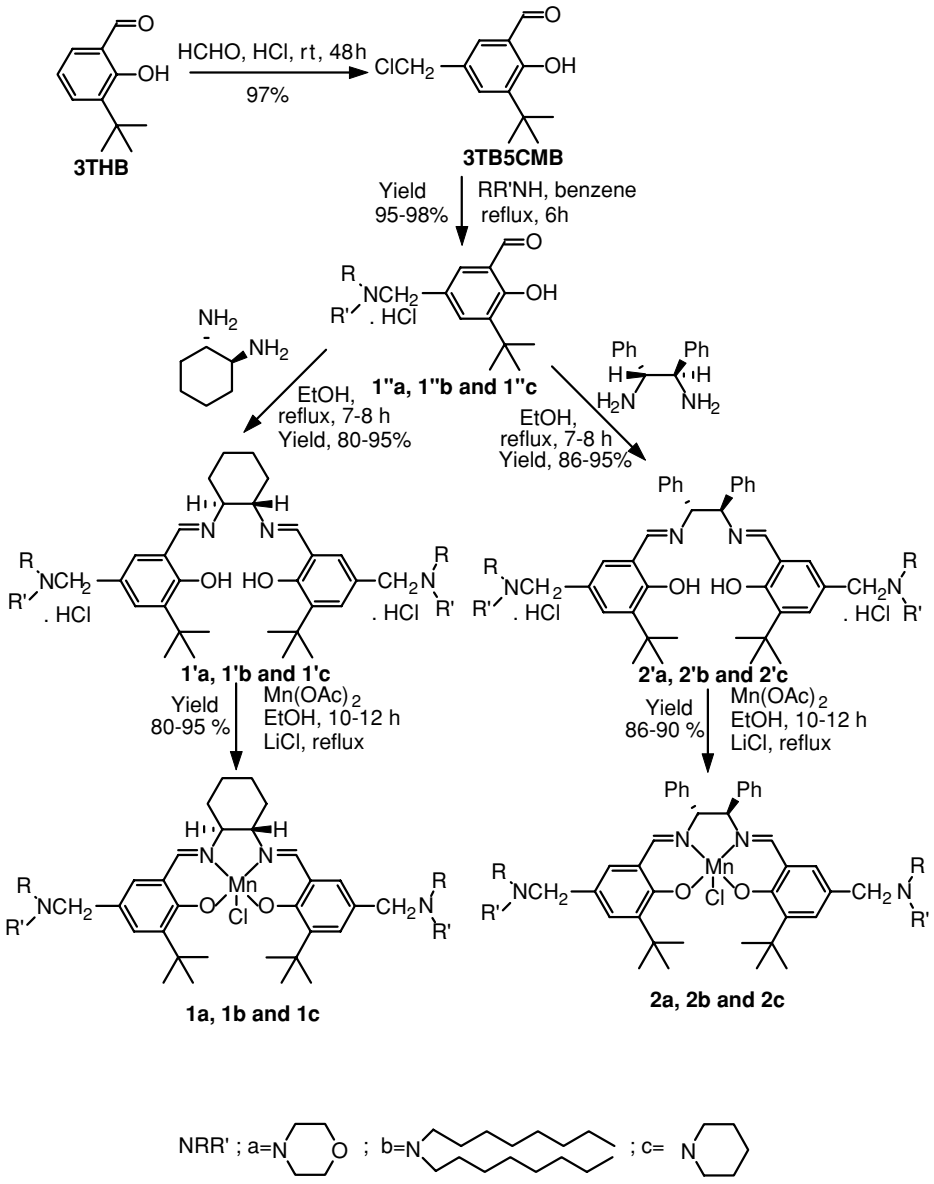
*Synthesis of **1″a–1″c**.* An appropriate secondary amine (20 mmol) in 20 ml of benzene was added dropwise to a stirring solution of 3TBSCMB (4.53 g; 20 mmol) in 20 ml of dry benzene. The resulting hazy solution was allowed to reflux with stirring for 6 h. The products **1″a** and **1″c** were obtained as a white crystalline solid while **1″b** was a viscous oil. These products were characterized and the data are given in Table 1.

*Synthesis of chiral Schiff base ligands **1′a–1′c** and **2′a–2′c**.* To a solution of **1″a**–**1″c** (10 mmol, 2 equivalent) in absolute EtOH (10 ml) was added a 10-ml solution of (1*S*,2*S*)(+)1,2-diaminocyclohexane/(1*R*,2*R*)(+) diphenyldiaminoethane (5 mmol, 1 equivalent). The resulting mixture was allowed to reflux for 7–8 h. The progress of the reaction was monitored on TLC. The solvent was partially removed under reduced pressure on a rotary evaporator and the yellow products **1′a**–**1′c** and **2′a**–**2′c** were precipitated by hexane. Analytical data for these compounds are given in Table 1. ^{1}H NMR data are supplied as supplementary material.

*Synthesis of chiral Mn^{III} Schiff base complexes **1a–1c** and **2a–2c**.* An ethanolic solution of (10 ml) $Mn(CH_3COO)_2 \cdot 4H_2O$ (10 mmol) was added to a solution of **1′a**–**1′c**/**2′a**–**2′c** (5 mmol) in absolute ethanol (50 ml) under N_2 atmosphere. The resulting brown mixture was refluxed for 7–8 h, following which the reaction mixture was cooled to room temperature and solid LiCl (0.64 g, 15 mmol) was added to it and stirred for an additional 4 h while the reaction mixture was exposed to air and filtered. The solvent was completely evaporated from the filtrate and the resulting residue was extracted with dichloromethane (100 ml). The organic phase was washed with water and dried over Na_2SO_4. The drying agent was removed by filtration and the solution concentrated to yield the desired complex. Characterization of catalysts was done by CHN analysis, optical rotation, magnetic susceptibility, and FAB mass spectral analysis (Table 1). Electronic and CD spectral data are supplied as supplementary materials.

Enantioselective Epoxidation Reaction

Enantioselective epoxidation reactions were performed according to the established procedure (13) using 2 mol% of the complexes **1a**–**1c** and **2a**–**2c** with 6-cyano-2,2-dimethylchromene, styrene, and indene (1.29 mmol) as a substrate in 1 ml of dichloromethane in the presence of O-coordinating ligands, namely, pyridine N-oxide (PyN-O), 4-phenyl pyridine N-oxide (PPyN-O), 4-(3-phenyl propyl pyridine N-oxide) (PPPyN-O), morpholine N-oxide (MorNO), 1,4 dioxane (1,4-D), and dimethyl sulphoxide (DMSO) (0.13 mmol) using NaOCl (2.75 mmol) in four equal portions as an oxidant at 0°C. The progress of the reaction was monitored by GC analysis of the products. After completion of reaction the solvent was removed, the



SCHEME 1. Synthesis of complexes **1a**–**1c** and **2a**–**2c**.

product was separated by a short silica gel (60–120 mesh) column using a hexane:dichloromethane mixture as an eluent, and enantiomeric excesses (EEs) were determined.

RESULTS AND DISCUSSION

Product yields, EEs, and turnover frequency for Mn^{III} SALEN complexes, **1a**–**1c** and **2a**–**2c**, with substrates 6-cyano-2,2-dimethyl-2*H*-chromene, indene, and styrene are given in Table 2. Quantitative yields were obtained in all the alkenes studied with these complexes in 1.5–7 h. The results obtained with 6-cyano-2,2-dimethyl-2*H*-chromene are encouraging, with >99% yield and 97–99% EEs. The catalyst **2b** was observed to give the highest EEs (84%) for indene. However, of styrene, the EEs were not encouraging (36–54%); nevertheless, the catalysts **2a**–**2c** were found to give higher EE values than **1a**–**1c**. In all the catalytic runs, configuration of the dominant enantiomer of the product is the same as that of the catalyst used.

A Jacobsen catalyst with 2 mol% catalyst loading using 4-PPyN-O as axial base is reported (13–15) to give 96% conversion with 97% EEs for 6-cyano-2,2-dimethyl-2*H*-chromene in 9 h. However, the catalysts **1a**–**1c** and **2a**–**2c** take only 6–7 h to give >99% conversion and 97–99% EEs under similar reaction conditions even with simple PyN-O (Table 2, entries 7–12) as axial base. It is to be noted that the catalysts reported here do not require expensive hydrophobic 4-PPyN-O, possibly due to in-built phase transfer capability of the catalyst rendered by the amino alkyl group in the salicylide ligand. Furthermore, a catalyst loading of

TABLE 1

Physicochemical Characterization Data of the Compounds

Compound[a]	M.P. (°C)	Yield (%)	$[\alpha]_D^{27}$ (CH_2Cl_2)	μ_{eff} (B.M.)	FAB mass (*m*/z)	% Microanalysis found (calcd)		
						C	H	N
1″a	189–191	98	—	—	—	61.28 (61.24)	7.68 (7.66)	4.44 (4.47)
1″b	—	97	—	—	—	71.80 (71.87)	10.40 (10.70)	3.02 (3.00)
1″c	224–226	95	—	—	—	65.40 (65.49)	8.30 (8.35)	4.43 (4.49)
1′a	176–178	85	+340 ($c = 0.07$)	—	—	64.65 (64.68)	8.21 (8.23)	7.92 (7.94)
1′b	190–191	95	+158 ($c = 0.10$)	—	—	73.46 (73.45)	10.88 (10.86)	5.49 (5.53)
1′c	177–179	88	+342 ($c = 0.07$)	—	—	68.43 (68.47)	8.84 (8.85)	7.93 (7.99)
2′a	135	90	−125 ($c = 0.08$)	—	—	68.70 (68.74)	7.42 (7.47)	6.92 (6.97)
2′b	138–139	86	−110 ($c = 0.07$)	—	—	75.57 (75.61)	10.03 (10.08)	5.02 (5.04)
2′c	196–198	90	−129 ($c = 0.08$)	—	—	72.05 (72.09)	7.97 (8.01)	6.98 (7.01)
1a	240[b]	88	+339 ($c = 0.04$)	4.80	720	63.26 (63.30)	7.48 (7.50)	7.77 (7.75)
1b	190	92	+240 ($c = 0.10$)	4.85	1028	72.36 (72.34)	10.27 (10.31)	5.40 (5.45)
1c	240[b]	89	+218 ($c = 0.07$)	4.85	717	70.69 (70.72)	7.32 (7.37)	6.84 (6.88)
2a	240[b]	92	−287 ($c = 0.04$)	4.80	818	67.39 (67.45)	6.80 (6.84)	6.79 (6.84)
2b	182	91	−123 ($c = 0.10$)	4.80	1126	74.52 (74.57)	9.54 (9.59)	4.93 (4.97)
2c	238	90	−193 ($c = 0.08$)	4.85	814	70.70 (70.72)	7.33 (7.37)	6.86 (6.88)

[a] (**1″a**) 3-*t*-Bu-2-hydroxy-5-(methylene-N morpholino) benzaldehyde hydrochloride, (**1″b**) 3-*t*-Bu-2-hydroxy-5-(methylene-N,N-dioctylamino) benzaldehyde hydrochloride, (**1′c**) 3-*t*-Bu-2-hydroxy-5-(methylene-N piperidino) benzaldehyde hydrochloride, (**1′a**) (*S*,*S*)-[[2,2′-][(1,2-cyclohexanediyl) bis(nitrilomethylidyne)] bis[4-(methylene-N-morpholino)-6-(1,1-dimethylethyl)phenol]] dihydrochloride, (**1″a**) 3-*t*-Bu-2-hydroxy-5-(methylene-N morpholino) benzaldehyde hydrochloride, (**1″b**) 3-*t*-Bu-2-hydroxy-5-(methylene-N,N-dioctylamino) benzaldehyde hydrochloride, (**1″c**) 3-*t*-Bu-2-hydroxy-5-(methylene-N piperidino) benzaldehyde hydrochloride, (**1′a**) (*S*,*S*)-[[2,2′-][(1,2-cyclohexanediyl) bis(nitrilomethylidyne)] bis[4-(methylene-N-morpholino)-6-(1,1-dimethylethyl)phenol]] dihydrochloride, (**1′b**) (*S*,*S*)-[[2,2′-][(1,2-cyclohexanediyl) bis(nitrilomethyli-dyne)] bis[4-(methylene-N,N′-dioctylamino)-6-(1,1-dimethylethyl)phenol]] dihydrochloride, (**1′c**) (*S*,*S*)-[[2,2′-][(1,2-cyclohexanediyl) bis(nitrilomethylidyne)] bis[4-(methylene-N-piperidino)-6-(1,1-dimethylethyl)phenol]] dihydrochloride, (**2′a**) (*R*,*R*)-[[2,2′-][(1,2-diphenyl 1,2-ethanediyl] bis(nitrilomethylidyne)] bis[4-(methylene-N-morpholino)-6-(1,1-dimethylethyl)phenol]] dihydrochloride, (**2′b**) (*R*,*R*)-[[2,2′-][(1,2-diphenyl-1,2-ethanediyl) bis(nitrilomethylidyne)] bis[4-(methylene-N,N′-dioctylamino)-6-(1,1-dimethylethy) phenol]] dihydrochloride, (**2′c**) (*R*,*R*)-[[2,2′-][(1,2-diphenyl 1,2-ethanediyl] bis(nitrilomethylidyne)] bis[4-(methylene-N-piperidino)-6-(1,1-dimethylethyl)phenol]] dihydrochloride, (**1a**) chloro-(*S*,*S*)-[[2,2′-][(1,2-cyclohexanediyl) bis(nitrilomethylidyne) bis[4-(methylene-N-morpholino)-6-(1,1-dimethylethyl)phenolato]]-[N,N′,O,O′]manganese(III), (**1b**) Chloro-(*S*,*S*)-[[2,2′-][(1,2-cyclohexanediyl) bis(nitrilomethylidyne)] bis[4-(methylene-N,N′-dioctylamino)-6-(1,1-dimethylethyl)phenolato]]-[N,N′,O,O′]manganese(III), (**1c**) chloro-(*S*,*S*)-[[2,2′-][(1,2-cyclohexanediyl) bis(nitrilomethylidyne)-bis[4-(methylene-N-piperidino)-6-(1,1-dimethylethyl) phenolato]]-[N,N′,O,O′]manganese(III), (**2a**) chloro-(*R*,*R*)-[[2,2′-][(1,2-diphenyl 1,2-ethanediyl) bis(nitrilomethylidyne)] bis[4-(methylene-N-morpholino)-6-(1,1-dimethylethyl)-phenolato]]-[N,N′,O,O′]manganese(III), (**2b**) chloro-(*R*,*R*)-[[2,2′-][(1,2-diphenyl 1,2-ethanediyl) bis(nitrilomethylidyne)] bis[4-(methylene-N,N-dioctylamino)-6-(1,1-dimethylethyl)-phenolato]]-[N,N′,O,O′]manganese(III), (**2c**) chloro-(*R*,*R*)-[[2,2′-][(1,2-diphenyl-1,2-ethanediyl) bis(nitrilomethylidyne)] bis[4-(methylene-N-piperidino)-6-(1,1-dimethylethyl)phenolato]]-[N,N′,O,O′]manganese(III).

[b] Decomposed.

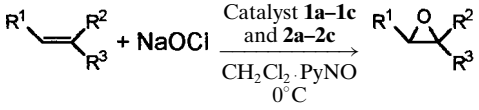
0.4 mol% is sufficient to achieve reported conversion and selectivity within 6 h. However, reduction in catalyst loading (0.2 mol%) caused an increase in overall reaction time (24 h) with a marginal decrease in EEs. This shows that amino alkyl groups at 5- and 5′-positions on the salicylide ligand have electronic and steric features favorable to conversion and enantioselectivity.

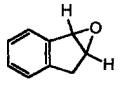
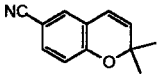
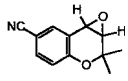
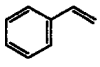
In order to evaluate the performance of our catalyst with various O-coordinating axial bases, epoxidation of styrene (as a representative substrate) was carried out under the above-described reaction conditions. In contrast to reported findings (6), 4-PPyN-O and 4-PPPyN-O axial bases (Table 3, entries 21–24) slow down (42–60% conversion in 24–30 h) the epoxidation reaction significantly without affecting EEs values. On the other hand, in O-donor ligands, PyN-O (Table 3, entries 19, 20, and 25–30) with catalysts **1a** and **2a** gave epoxidation conversion >99% of styrene in 5–7 h. Therefore, it is inferred that by introducing phase transfer capability into the catalyst itself, hydrophobic axial base ligands such as 4-PPyN-O and 4-PPPyN-O are no longer needed. A water-soluble O-coordinating axial base such as 1,4-dioxane (Table 3, entries 27 and 28) is good enough to enhance the epoxidation reaction rate with marginally or no decrease in enantioselectivity.

Mn^V=O complexes are often proposed (4, 16–19) as intermediates in Mn^{III}SALEN-catalyzed epoxidation of alkenes. Collins and Gordon-Wylie (20) have reported stable monomeric $Mn^V[\eta^4$-HMPA-B$]^{-4}$[O] which show well-resolved ^{1}H NMR spectra in diamagnetic region. In order to trap the intermediate oxo species in the case of catalysts used in the present study, we oxidized **1b** with ozone both at −78°C and at room temperature in CH_2Cl_2. This turned into green complex [**A**] within 10 min but failed to give a diamagnetic NMR. A UV–vis spectrum of [**A**] shows the formation of a band at 656 nm (Fig. 1). The complex [**A**] is paramagnetic and is stable (no color or UV–vis

TABLE 2

Product Yield, EEs, and TOF for Enantioselective Epoxidation of Nonfunctionalized Alkenes Catalyzed by 1a–1c and 2a–2c[a]

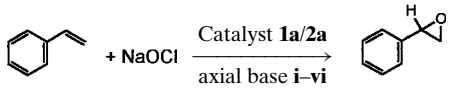


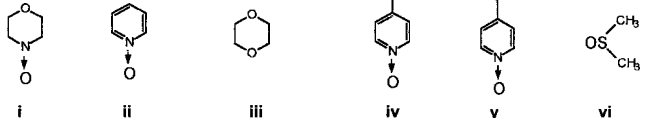
Entry	Catalyst	Substrate	Time	Product	Yield (%)[b]	EE (%)[c]	TOF[d] × 10^{-3}
1 (2)	**1a** (**2a**)		6.0 (5.0)		99 (99)	69[e] (68)[f]	2.29 (2.75)
3 (4)	**1b** (**2b**)		5.0 (4.5)		97 (98)	71[e] (84)[f]	2.69 (3.02)
5 (6)	**1c** (**2c**)		6.5 (7.0)		>99 (99)	53[e] (68)[f]	2.11 (1.96)
7 (8)	**1a** (**2a**)		6.0 (7.0)		>99 (99)	>99[g] (97)[h]	2.29 (1.96)
9 (10)	**1b** (**2b**)		6.0 (6.5)		>99 (99)	99[g] (98)[h]	2.29 (2.11)
11 (12)	**1c** (**2c**)		6.5 (7.0)		>99 (99)	99[g] (97)[h]	2.11 (1.96)
13 (14)	**1a** (**2a**)		5.0 (5.5)		98 (99)	39[i] (50)[j]	2.72 (2.50)
15 (16)	**1b** (**2b**)		4.5 (1.5)		99 (99)	36[i] (51)[j]	3.06 (9.17)
17 (18)	**1c** (**2c**)		5.5 (6.0)		99 (99)	39[i] (54)[j]	2.50 (2.29)

[a] Reactions were performed in CH_2Cl_2 (1 ml) with catalyst, 2 mol%; substrate, 1.29 mmol, pyridine N-oxide, 0.13 mmol; NaOCl, 2.75 mmol.
[b] Determined by GC.
[c] By ^1H NMR using chiral shift reagent (+)Eu(hfc)$_3$/chiral capillary column GTA-type/chiral HPLC column OJ.
[d] Turnover frequency is calculated by the expression (product)/(catalyst) × time mol^{-1} cat^{-1} s^{-1}.
[e] Epoxide configuration, 1*S*,2*R*.
[f] Epoxide configuration, 1*R*,2*S*.
[g] Epoxide configuration, 3*S*,4*S*.
[h] Epoxide configuration, 3*R*,4*R*.
[i] Epoxide configuration, *S*.
[j] Epoxide configuration, *R*.

TABLE 3

Effect of Different Axial Bases on Enantioselective Epoxidation by Complexes 1a[a] (2a)





Entry	Axial bases	Conversion (%)[b]	Time (h)	EE (%)[c]	TOF × 10^{-3}
19 (20)	PyN-O	>99 (99)	5.0 (5.5)	39 (50)	2.75 (2.50)
21 (22)	4-PPyN-O	42 (60)	30.0 (24)	40 (51)	0.19 (0.35)
23 (24)	PPPyN-O	60 (50)	24.0 (24)	48 (55)	0.35 (0.29)
25 (26)	MorN-O	>99 (99)	6.5 (7)	36 (50)	2.12 (1.96)
27 (28)	1,4-D	98 (99)	6.5 (7)	38 (50)	2.09 (1.96)
29 (30)	DMSO	98 (99)	5.5 (5.5)	38 (49)	2.47 (2.50)

[a] Reactions were carried out in CH_2Cl_2 (1 ml) with catalyst (2 mol%), substrate (1.29 mmol), axial bases (0.13 mmol), NaOCl (2.75 mmol), 0°C.
[b] Determined on GC.
[c] From comparing RT of the authentic sample of *R*-styrene oxide on GC using a γ-type chiral capillary column.

spectral change) for over a week at −78°C, for 24 h at 4°C, and for 3 h at room temperature. The green solution turns brown on the addition of styrene, which gave a spectrum (Fig. 1) very similar to the original complex **1b** (Fig. 1), suggesting the involvement of a paramagnetic Mn^{IV}=O species in the oxygen atom transfer step.

To further support the paramagnetic nature of the intermediate Mn^{IV}=O, magnetic moment was measured for the solutions undergoing these transformations. It is reported

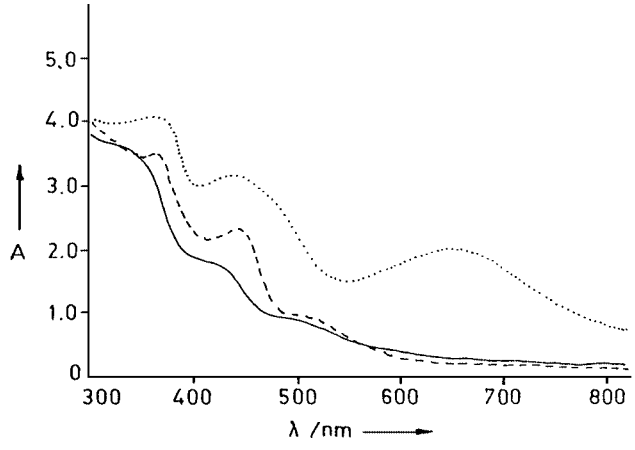


FIG. 1. Absorption spectra obtained with 1 mM solution in CH_2Cl_2 of **1b** (dashed line), with O_3 bubbled in **1b** solution (green complex) (dotted line), and after the addition of styrene in green solution (solid line).

TABLE 4

Magnetic Susceptibility Data for the Complex 1b under Different Conditions

Entry	Experiment	μ_{eff} (B.M.) with respect to time[a]				
		Immediately	10 min	30 min	180 min	24 h
31	**1b** + NaOCl	4.88	4.27	3.88	2.91	N.D.
32	**1b** + NaOCl + PyNO	4.66	4.64	4.29	3.87	N.D.
33	**1b** + styrene + PyNO + NaOCl	5.21	4.31	4.24	4.19	4.12
34	**1b** + PyNO + NaOCl 3 h + styrene	3.98	3.97	3.80	3.00	2.15

[a] In the sequence they were added.

that (20–22) in a Mn^{III}SALEN-catalyzed epoxidation reaction the central metal ion undergoes several changes in its oxidation state, i.e., Mn^{III}, Mn^{IV}, Mn^{V}, dimeric species in the presence of PhIO, NaOCl as oxidant, and PyN-O as axial base.The magnetic moment of the complex **1b** upon addition of NaOCl (no green color observed) decreased from 4.88 to 4.27, 3.88 and 2.91 B.M. at 10, 30, and 180 min, respectively (Table 4, entry 31), indicating the initial formation of catalytically active monomeric Mn^{IV}=O species which get dimerized (Table 4, entry 31, 2.91 B.M.) to catalytically inactive Mn^{IV}–O–Mn^{IV}. A similar observations were reported by Adam *et al.* (21). The low magnetic moment value of 2.91 B.M. can be explained due to antiferromagnetic coupling in a high-spin Mn^{IV}–O–Mn^{IV} dimer. The presence of PyN–O in **1b** and a NaOCl mixture slows down the formation of the Mn^{IV}–O–Mn^{IV} dimer (Table 4, entry 32). Further, after the addition of NaOCl to the mixture of **1b** + styrene + PyN-O, there is an initial increase in μ_{eff} value (Table 4, entry 33, 5.21 B.M.) and then it remains constant (4.31–4.12 B.M.) over a period of 24 h under refrigeration (Table 4, entry 33). The initial rise in the magnetic moment is attributed to the formation of Mn^{III}–O–Mn^{IV}, as also reported earlier (22), with use of EPR techniques, which later disproportionate to form high-spin d^3 monomeric Mn^{IV}=O species. Therefore, it further strengthens the view that the use of PyN-O with NaOCl prevents the formation of the catalytically inactive Mn^{IV}–O–Mn^{IV} dimer and acts as a favorable and steady oxidant (16). The complete conversion of styrene to styrene oxide strengthens our view that Mn^{IV}=O is involved in the catalytic cycle. However, if the substrate is added 3 h after addition of NaOCl to **1b** + PyN-O (Table 4, entry 34), the epoxidation reaction progresses slowly and stops before completion, with a marked decrease in magnetic moment 2.15 B.M.

CONCLUSION

We have described the synthesis of chiral Mn^{III}SALEN complexes having in-built phase transfer capability, which are very active and selective catalysts for enantioselective epoxidation of styrene, indene, and 6-cyano-2,2-dimethyl-2*H*-chromene using NaOCl as an oxidant in the presence of PyN-O as axial base. Also, by using magnetic moment studies by the Evans method, paramagnetic NMR, and UV–vis spectral analysis, we have successfully demonstrated the formation of catalytically active Mn^{IV}=O species during epoxidation reaction.

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