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Chiral manganese and iron complexes of binaphthyl Schiff bases: syntheses, crystal structures and asymmetric epoxidation of alkenes

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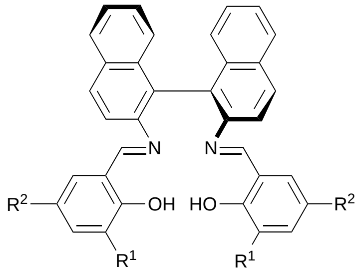
The chiral binaphthyl Schiff-base manganese complexes [MnL(X)] [H_2L = 2,2′-bis(3-R^1-5-R^2-2-hydroxybenzylideneimino)-1,1′-binaphthyl; $R^1 = R^2$ = Cl, X = O_2CMe **1**; R^1 = Et, R^2 = NO_2, X = O_2CMe **2**; $R^1 = R^2$ = Cl, X = acac (acetylacetonate) **3**] and an iron analogue [FeL(acac)] **4** ($R^1 = R^2$ = Cl) have been prepared. The crystal structures of the racemic forms of **3**·CH_2Cl_2 and **4**·$2H_2O$ exhibit non-planar *cis*-β configurations with dihedral angles of 85.5 and 72.1° respectively between the two naphthalene rings. Complexes (*R*)-**1** to **3** are active catalysts for the asymmetric epoxidation of alkenes by PhIO. The oxidation of *cis*-β-methylstyrene by (*R*)-**2** in toluene at −20 °C gave an enantiomeric excess of 76%.

The search for chiral complexes which can catalyse asymmetric oxidation has continued to attract considerable interest.[1] Recent results in asymmetric epoxidation of unfunctionalised alkenes have been achieved by Jacobsen and Katsuki[2] using chiral Schiff-base manganese complexes based on optically active 1,2-diamines. However, the binaphthyl moiety, which has been effectively deployed in other asymmetric catalysis reactions,[3] has rarely been incorporated into the Schiff base for mediating asymmetric oxidation. We recently reported that the *in situ* $Mn(O_2CMe)_3$ + (*S*)-H_2L systems [H_2L = 2,2′-bis(3-R^1-5-R^2-2-hydroxybenzylideneimino)-1,1′-binaphthyl, R^1 = Cl, H or alkyl; R^2 = Cl, NO_2 or Me] are effective catalysts for asymmetric epoxidation of alkenes by PhIO.[4] Nevertheless, there are few examples of complexes containing the binaphthyl Schiff-base ligand[5] and to our knowledge the only published crystal structure is the copper(II) complex where $R^1 = R^2$ = Cl.[4] We now report the successful synthesis of monomeric chiral manganese(III) and iron(III) binaphthyl Schiff-base complexes, and asymmetric catalysis results which show improved enantioselectivity. Crystal structures of complexes in racemic forms have been determined.

Experimental

Full instrumentation details and preparation of the chiral and racemic forms of the Schiff base have been given.[4] The compounds $Mn^{III}(O_2CMe)_3·2H_2O$ (Aldrich) and [$Fe^{III}(acac)_3$] (acac = acetylacetonate) (Strem) were dried *in vacuo* before use; [$Mn^{III}(acac)_3$] was prepared according to the literature method.[6] Iodosylbenzene was prepared by hydrolysis of iodobenzene diacetate (Aldrich) in NaOH solution. Solvents for catalytic epoxidation were purified according to standard procedures.[7] All alkene substrates used for catalytic epoxidation were from Aldrich and Fluka and purified either by vacuum distillation or by passing through activated alumina. *cis*-β-Methylstyrene was prepared by hydrogenation of 1-phenylprop-1-yne (Aldrich) using Lindler catalyst.[8] Racemic styrene oxide was obtained from Fluka and distilled before use; (*R*)-(−) styrene oxide from Aldrich was used without further purification. 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.[9]

Syntheses



H_2L^1 $R^1 = R^2$ = Cl
H_2L^2 R^1 = Et, R^2 = NO_2

[$Mn^{III}L^1(O_2CMe)$] 1. A mixture of H_2L^1 (0.5 g, 0.8 mmol) and $Mn(O_2CMe)_3·2H_2O$ (0.21 g, 0.8 mmol) in acetonitrile (30 cm^3) was heated at 60 °C for 30 min. The solvent was removed *in vacuo*. The residue was dissolved in dichloromethane (10 cm^3) and then filtered. Addition of *n*-hexane yielded a green solid. Chiral complexes were prepared by the same method using optically active ligands. Yield 0.44 g, 74% (Found: C, 58.1; H, 3.1; N, 3.8. $C_{36}H_{21}Cl_4MnN_2O_4$ requires C, 58.25; H, 2.85; N, 3.8%); $\lambda_{max}(CH_3CN)$/nm 222 (ε 87820), 274 (51740), 317 (19590) and 391 (14180 dm^3 mol^{-1} cm^{-1}); $\tilde{\nu}$(KBr)/cm^{-1} 1602 (C=N) and 1421 (O_2CMe); *m/z* 683 (*M* − O_2CMe).

[$Mn^{III}L^2(O_2CMe)$] 2. The procedure was the same as for complex **1** using $Mn(O_2CMe)_3·2H_2O$ (0.21 g, 0.8 mmol) and H_2L^2 (0.5 g, 0.8 mmol). Chiral complexes were prepared using optically active ligands. Yield 0.49 g, 81% (Found: C, 66.7; H, 4.5; N, 7.7. $C_{40}H_{31}MnN_4O_8$ requires C, 66.85; H, 4.45; N, 7.8%); $\lambda_{max}(CH_3CN)$/nm 242 (ε 80560), 274 (54620), 317 (19590), 386 (14190 dm^3 mol^{-1} cm^{-1}); $\tilde{\nu}$(KBr)/cm^{-1} 1593 (C=N), 1420 (O_2CMe) and 1315 (NO_2).

[$Mn^{III}L^1$(acac)] 3. A mixture of H_2L^1 (0.3 g, 0.5 mmol) and [$Mn(acac)_3$] (0.18 g, 0.5 mmol) in acetonitrile (30 cm^3) was refluxed for 4 h. The solution was evaporated to dryness and then dissolved in dichloromethane. Upon addition of *n*-hexane a green solid was obtained. Chiral complexes were prepared by the same method using optically active ligands. Yield 0.33 g, 85% (Found: C, 59.6; H, 3.5; N, 3.7. $C_{39}H_{25}Cl_4MnN_2O_4$ requires C, 59.9; H, 3.2; N, 3.6%); $\lambda_{max}(CH_2Cl_2)$/nm 220 (ε 104870), 273 (74720), 320 (26490) and 389 (15860 dm^3 mol^{-1} cm^{-1}); $\tilde{\nu}$(KBr)/cm^{-1} 1602 (C=N) and 1418 (acac); *m/z* 683 (*M* − acac).

[$Fe^{III}L^1$(acac)] 4. A mixture of H_2L^1 (0.5 g, 0.8 mmol) and [$Fe(acac)_3$] (0.28 g, 0.8 mmol) in acetonitrile (30 cm^3) was

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refluxed for 6 h. The resultant solution was filtered and concentrated, and dark red crystals were obtained upon standing for 1 d. Yield 0.52 g, 83% (Found: C, 59.7; H, 3.4; N, 3.6. $C_{39}H_{25}Cl_4FeN_2O_4$ requires C, 59.8; H, 3.2; N, 3.6%); λ_{max}-(CH_2Cl_2)/nm 269 (ε 75760), 360 (14960) and 445 (9020 dm^3 mol^{-1} cm^{-1}); $\tilde{\nu}$(KBr)/cm^{-1} 1604 (C=N) and 1424 (acac); *m/z* 684 (*M* − acac).

X-Ray crystallography

Crystal data for complexes **3**·CH_2Cl_2 and **4**·$2H_2O$ are collected in Table 1. For **3**·CH_2Cl_2 a green crystal of dimensions 0.25 × 0.50 × 0.50 mm was used for data collection at 25 °C on a Enraf-Nonius diffractometer (graphite-monochromatized Cu radiation, $\lambda = 1.5406$ Å) using θ–2θ scans. Intensity data ($2\theta_{max} = 130°$; *h* −16 to 16, *k* 0 to 21, *l* 0 to 18; three standard reflections measured every 3600 s showed 2% decay) were corrected for decay and for Lorentz-polarisation effects and an empirical absorption correction was made. 6513 Unique reflections were obtained from a total of 6613 measured reflections; 3592 reflections with $I > 2\sigma(I)$ were used in the structural analysis. The structure was solved by Patterson and Fourier methods[10] and subsequent refinement by full-matrix least squares was performed using the software package NRCVAX.[11] All 53 non-H atoms were refined anisotropically. Convergence for 476 variable parameters by least-squares refinement was reached at $R = 0.077$ and $R' = 0.087$ with a goodness of fit of 2.17, $(\Delta/\sigma)_{max} = 0.01$. The final Fourier-difference map was featureless, with residual extrema of 0.89 and −0.67 e $Å^{-3}$ respectively.

For complex **4**·$2H_2O$ a purple-brown crystal of dimensions 0.20 × 0.15 × 0.35 mm was used for data collection at 25 °C on a Enraf-Nonius diffractometer (graphite-monochromatized Mo-Kα radiation, $\lambda = 0.7107$ Å) using ω-2θ scans. Intensity data ($2\theta_{max} = 44°$; *h* 0 to 12, *k* −18 to 18, *l* −21 to 21; three standard reflections measured every 300 showed decay of 7.95%) were corrected for decay and for Lorentz-polarisation effects and an empirical absorption correction was made. 9397 Unique reflections were obtained from a total of 9972 measured reflections; 5494 reflections with $I > 3\sigma(I)$ were used in the structural analysis. The structure was solved by direct methods (SIR 92[12]), expanded by the Fourier method and refined by full-matrix least squares using the software package TEXSAN.[13] Two formula units constitute a crystallographic asymmetric unit. All 100 non-H atoms, including the oxygen atoms of the four water molecules, were refined anisotropically. Hydrogen atoms of the water molecules were not located. Convergence for 937 variable parameters by least-squares refinement was reached at $R = 0.045$ and $R' = 0.050$ with a goodness of fit of 2.07, $(\Delta/\sigma)_{max} = 0.04$. The final Fourier-difference map was featureless, with residual extrema of 0.80 and −0.45 e $Å^{-3}$ respectively.

CCDC reference number 186/632.

Alkene oxidation

All catalytic oxidation reactions were carried out at room temperature under an argon atmosphere unless specified. In a typical run the alkene (100 mg), catalyst (5 mg) and PhIO (50 mg) were stirred in the appropriate solvent (5 cm^3) until all PhIO had dissolved. The epoxide product and iodobenzene formed were quantified by GC using the internal standard method and the epoxide yield for the PhIO epoxidation was based on the amount of iodobenzene formed.

Results and Discussion

Previous studies by Meunier and co-workers[5] demonstrated that Schiff bases can readily form complexes with transition-metal ions in alcohol. Despite this, we found that the catalytically inactive $[Mn^{III}{}_2L^1{}_2(OMe)_2]$ dimer was afforded by refluxing the binaphthyl Schiff base with $Mn(O_2CMe)_3$ in methanol.[4]

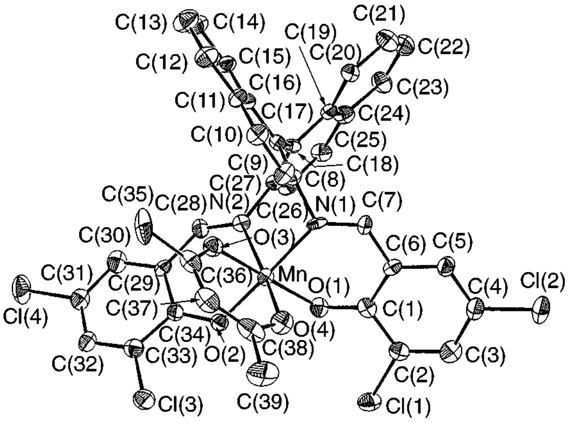

Fig. 1 Perspective view of one enantiomer of complex **3**·CH_2Cl_2 (30% probability ellipsoids, solvent molecule omitted)

Subsequently, by using acetonitrile as solvent and hence removing the methoxide ions, we have been able to prepare monomeric binaphthyl Schiff-base complexes. Hence treatment of $Mn(O_2CMe)_3$ with H_2L^1 and H_2L^2 in acetonitrile yielded $[Mn^{III}L^1(O_2CMe)]$ **1** and $[Mn^{III}L^2(O_2CMe)]$ **2** as dark green solids respectively. In solution, complexes **1** and **2** are stable for 2 h at room temperature, but slow decomposition is observed over longer periods. By comparison, reaction of $[Mn(acac)_3]$ and $[Fe(acac)_3]$ with H_2L^1 in acetonitrile afforded $[Mn^{III}L^1(acac)]$ **3** and $[Fe^{III}L^1(acac)]$ **4** respectively, which are stable in solution for over 24 h. This difference may be attributed to the strained nature of the four-membered ring formed between the metal ion and the bidentate acetato group in **1** and **2**, while by analogy a six-membered ring is present in **3** and **4**. The UV/VIS spectra of **1** and **3** are comparable indicating that the complexes are structurally related.

Crystal structures of binaphthyl Schiff-base complexes

The different chiral modes of ligation by the tetradentate ligand in an octahedral complex are shown in Fig. 3. The remaining sites are *cis*, while α and β denotes *trans*- and *cis*-aryloxide groups respectively; Δ chirality at the metal atom arises from co-ordination by an (*R*)-ligand, and the Λ form is generated upon complexation by an (*S*)-ligand.

Molecular structures of the racemic complexes **3**·CH_2Cl_2 and **4**·$2H_2O$ have been established by X-ray crystallography. The geometry around the manganese atom in **3**·CH_2Cl_2 (Fig. 1) is octahedral with the Schiff-base ligand bound to the metal centre in a *cis*-β configuration. The acac ligand occupies the remaining co-ordination sites with Mn–O(3) and Mn–O(4) distances of 1.915(7) and 2.124(7) Å respectively. The dihedral angle of 85.5(3)° between the two naphthalene rings is similar to those of 75.5(1) and 87.59(5)° in $[Cu^{II}L^1]$[4] and 2,2′-bis(pyridine-2-carboxamido)-1,1′-binaphthyl.[14] As expected, the (*S*)-binaphthyl Schiff-base ligand induces a chiral centre (Λ) at the manganese atom while the (*R*) form affords Δ chirality at the metal. Complex **4**·$2H_2O$ (Fig. 2) is isostructural to **3**·CH_2Cl_2 hence the corresponding dihedral angle of 72.1(1)° is comparable. All metal–ligand bond lengths are slightly longer due to the greater radius of the iron(III) ion.

Catalytic epoxidation of alkenes using PhIO

We have previously demonstrated that the *in situ* Mn^{III} + (*S*)-H_2L system can catalyse asymmetric epoxidation of alkenes using PhIO with moderate e.e.[4] However, there are potential problems associated with *in situ* catalysis: complexation is not well defined and may be incomplete, greater than one active species may be present and the choice of solvents is limited to

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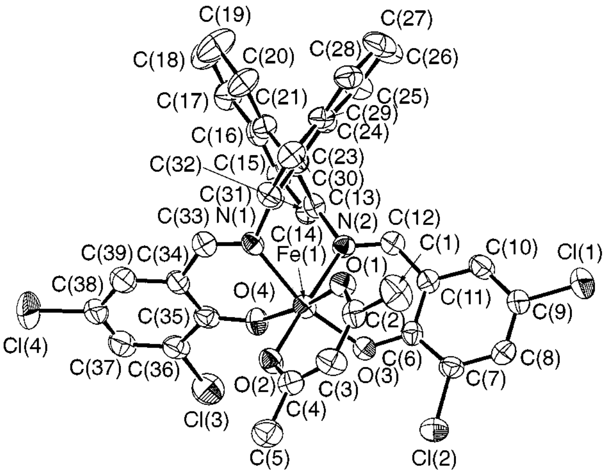

Fig. 2 Perspective view of one enantiomer of complex **4**·$2H_2O$ [Molecule A, 40% probability ellipsoids, solvent molecules omitted, C(22) is obscured by C(30)]

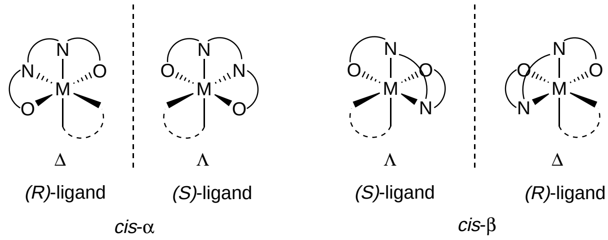

Fig. 3 Chiral centres in binaphthyl Schiff-base complexes

those which can solubilise the reactants. We therefore investigated the catalytic reactivity of the isolated chiral Schiff-base manganese complexes using an analogous procedure and found that they are also active towards asymmetric alkene epoxidation by PhIO. The reactivity of (*R*)-**1** and (*R*)-**2** and their respective yields and e.e. for the epoxidation of styrene are very similar to those for the corresponding *in situ* systems under identical conditions, which implies that the catalytic cycle of the latter proceeds by generating the monomeric species isolated in this work.

For the present study attention was focused on complex (*R*)-**2** since the *in situ* system bearing the same ethyl/nitro substituents gave the highest e.e. of 58% and *cis*:*trans* ratio of 10:1 for the epoxidation of *cis*-β-methylstyrene.[4] Results are summarised in Table 4: significantly, the enantioselectivity is enhanced by using a low-polarity solvent, *e.g.* benzene and toluene and at lower temperatures. This also suppresses the *cis/trans* isomerisation of *cis*-disubstituted alkenes. The effect of solvents upon e.e. has recently been observed for epoxidation catalysts based on ruthenium porphyrins.[15] Hence the epoxidation of *cis*-β-methylstyrene in toluene gave e.e. of 63% at 25 °C and 76% at −20 °C. A *cis*:*trans* ratio of 14:1 was obtained at 25 °C, while only a trace amount of the *trans* product was afforded at −20 °C. Lowering the reaction temperature to −20 °C did not affect the yield markedly, although at −60 °C virtually no epoxidation reaction was observed.

The acac derivative (*R*)-**3** is also active towards the epoxidation of alkenes, although slightly lower yields and e.e. were detected compared to (*R*)-**1**. For example, an e.e./yield of 43%/72% for (*R*)-**3** and 54%/80% for (*R*)-**1** were obtained using *cis*-β-methylstyrene. The active species for the epoxidation reaction may be an oxo-intermediate,[2] or a PhIO adduct in accordance with the study by Hill and co-workers[16] on the Mn(tpp) system (H_2tpp = 5,10,15,20-tetraphenylporphyrin) and work by Valentine and co-workers.[17] Nevertheless, since there is no direct evidence for the formation of such species and their

Table 1 Crystal data for complexes **3**·CH_2Cl_2 and **4**·$2H_2O$

	3·CH_2Cl_2	**4**·$2H_2O$
Formula	$C_{39}H_{25}Cl_4MnN_2O_4\cdot CH_2Cl_2$	$C_{39}H_{25}Cl_4FeN_2O_4\cdot 2H_2O$
M	867.32	819.33
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$ (no. 2)
a/Å	13.974(6)	11.664(2)
b/Å	18.036(8)	17.550(4)
c/Å	15.5367(17)	20.876(4)
α/°		66.00(2)
β/°	100.193(24)	80.09(1)
γ/°		84.87(2)
U/Å³	3854.1(24)	3503(1)
Z	4	4
D_c/g cm⁻³	1.495	1.415
μ/cm⁻¹	70.9	7.17
F(000)	1760	1676
R,*R*′	0.077, 0.087	0.045, 0.050

$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

Table 2 Selected bond distances (Å) and angles(°) for complex **3**·CH_2Cl_2

Mn−O(1)	1.896(7)	Mn−N(2)	2.277(7)
Mn−O(2)	1.887(6)	N(1)−C(7)	1.276(12)
Mn−O(3)	1.915(7)	N(1)−C(8)	1.444(12)
Mn−O(4)	2.124(7)	N(2)−C(27)	1.447(12)
Mn−N(1)	2.056(8)	N(2)−C(28)	1.275(12)
O(1)−Mn−O(2)	90.9(3)	O(2)−Mn−N(2)	86.9(3)
O(1)−Mn−O(3)	178.2(3)	O(3)−Mn−O(4)	87.5(3)
O(1)−Mn−O(4)	91.0(3)	O(3)−Mn−N(1)	92.0(3)
O(1)−Mn−N(1)	87.0(3)	O(3)−Mn−N(2)	84.9(3)
O(1)−Mn−N(2)	96.5(3)	O(4)−Mn−N(1)	93.3(3)
O(2)−Mn−O(3)	90.3(3)	O(4)−Mn−N(2)	172.3(3)
O(2)−Mn−O(4)	94.7(3)	N(1)−Mn−N(2)	85.5(3)
O(2)−Mn−N(1)	171.8(3)		

Table 3 Selected bond distances (Å) and angles (°) for molecule A of complex **4**·$2H_2O$; parameters for molecule B in square brackets

Fe(1)−O(1)	2.015(4) [2.017(5)]	Fe(1)−N(2)	2.149(5) [2.144(5)]
Fe(1)−O(2)	2.001(4) [1.993(5)]	N(1)−C(32)	1.442(7) [1.442(7)]
Fe(1)−O(3)	1.941(4) [1.947(4)]	N(1)−C(33)	1.278(7) [1.277(7)]
Fe(1)−O(4)	1.918(4) [1.912(4)]	N(2)−C(12)	1.276(7) [1.276(7)]
Fe(1)−N(1)	2.166(5) [2.170(5)]	N(2)−C(13)	1.442(7) [1.446(8)]
O(1)−Fe(1)−O(2)	86.5(2) [86.9(2)]	O(2)−Fe(1)−N(2)	175.8(2) [174.4(2)]
O(1)−Fe(1)−O(3)	88.2(2) [88.6(2)]	O(3)−Fe(1)−O(4)	103.1(2) [101.8(2)]
O(1)−Fe(1)−O(4)	168.3(2) [169.4(2)]	O(3)−Fe(1)−N(1)	165.2(2) [165.6(2)]
O(1)−Fe(1)−N(1)	84.3(2) [85.5(2)]	O(3)−Fe(1)−N(2)	84.2(2) [84.0(2)]
O(1)−Fe(1)−N(2)	89.3(2) [88.4(2)]	O(4)−Fe(1)−N(1)	85.2(2) [84.8(2)]
O(2)−Fe(1)−O(3)	95.7(2) [98.8(2)]	O(4)−Fe(1)−N(2)	94.5(2) [94.6(2)]
O(2)−Fe(1)−O(4)	89.6(2) [89.5(2)]	N(1)−Fe(1)−N(2)	82.9(2) [82.7(2)]
O(2)−Fe(1)−N(1)	96.6(2) [94.0(2)]		

Table 4 Alkene epoxidation catalysed by complex (*R*)-**2** using PhIO

		e.e.[a] (%)			
		Benzene	Toluene		
Substrate	Product	25 °C[b]	25[b]	0[c]	−20 °C[d]
Styrene	Styrene oxide[e,f]	38 (82)	34 (68)	42 (62)	46 (68)
4-Chlorostyrene	4-Chlorostyrene oxide[e,g]	38 (91)	36 (65)	43 (63)	46 (64)
cis-β-Methylstyrene	*cis*-β-Methylstyrene oxide[h]	64 (70)	63 (59)	71 (67)	76 (63)

[a] Based on amount of PhI formed; yields (%) in parentheses. [b] Reaction for 0.5–1 h. [c] Reaction for 1–1.5 h. [d] Reaction for 3 h. [e] *R* configuration. [f] Benzaldehyde (2%) was detected after each run. [g] 4-Chlorobenzaldehyde (trace, except toluene, 25 °C: 4%) was detected after each run. [h] 1*R*, 2*S* Configuration. *trans*-β-Methylstyrene oxide (benzene: 6%; toluene, 25 °C: 7%; 0 °C and −20 °C: trace) was detected after each run.

isolation has so far been unsuccessful, the active species in this system remains a point of contention.

Unlike the manganese(III) catalysts, epoxidation of alkenes was not observed using the iron(III) complex (*R*)-**4**. Addition of PhIO to a solution of (*R*)-**4** led to rapid decomposition of the metal species.

Conclusion

New monomeric chiral binaphthyl Schiff-base complexes of manganese and iron have been prepared using acetonitrile as solvent. The manganese(III) derivatives (*R*)-**1** to **3** mediate the catalytic asymmetric epoxidation of alkenes by PhIO and the highest e.e. in this system so far has been achieved at −20 °C in low-polarity toluene. In contrast to the planar structures observed for Jacobsen-type catalysts,[18] the crystal structures of the racemic complexes **3**·CH_2Cl_2 and **4**·$2H_2O$ depict non-planar molecules. This fundamental difference may be responsible for the higher e.e. obtained by Jacobsen, since in our system the environment for metal–alkene interaction is evidently more open, and this may ultimately lead to different reaction patterns.

Acknowledgements

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