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Mn(III) complexes of chiral 'salen' type ligands derived from carbohydrates in the asymmetric epoxidation of styrenes

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Abstract—A strategy for the synthesis of new chiral salen type ligands derived from α-D-glucose and α-D-mannose is described. The compounds were obtained by introducing appropriate functions at the C2 and C3 positions of the sugar ring. The efficiency of the complexes in the epoxidation of styrenes was also examined and shown to give good results, for example, *cis*-β-methylstyrene was functionalised with ee's of up to 86%.

1. Introduction

Salicylethylenediamine (salen, **I** in Fig. 1) can be considered as the prototype for *N*,*N*′,*O*,*O*′ tetradentate Schiff base ligands.[1] Its complexes with transition metals are well known, as is their ability to catalyse several transformations of organic molecules. Recent studies[2] have emphasised the remarkable skill of this old fashion ligand, as several chiral versions of salen (e.g., **II** and **III** in Fig. 1) have successfully been used in enantioselective oxidations of alkenes to epoxides promoted by transition metals. A number of theoretical and experimental investigations[2] have been undertaken to help understand the factors, which govern the selectivity of the reaction. All of these acknowledge that a chiral pocket of C_2 symmetry created by the ligand around the metal is one of the main steric features accounting for the observed high enantiomeric excesses of the products.

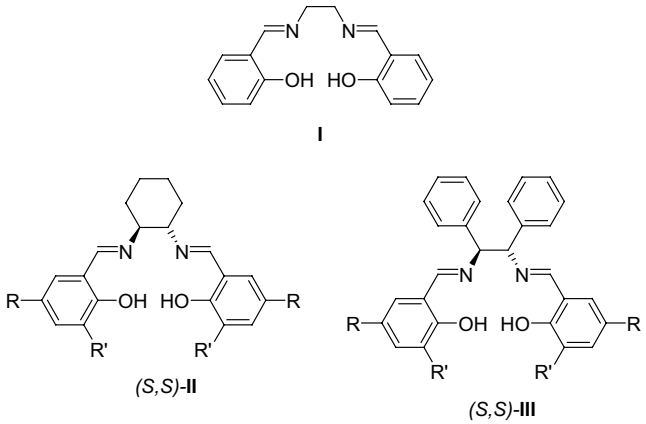

Figure 1. General formula of ligands **I**, (*S*,*S*)-**II** and (*S*,*S*)-**III**.

Recently, we became interested[3] in the design of new chiral nitrogen ligands derived from common and inexpensive carbohydrates[4,5] with the assumption that sugars can be a very convenient source of chiral auxiliaries. Inter alia, we have described new diimines and diamines (e.g., **1** and **2** in Fig. 2) derived from α-D-glucose **G** and α-D-mannose **M** obtained by introducing nitrogen functions at positions 2 and 3 of the sugar ring. The new ligands were employed in the Cu(I)-catalysed styrene cyclopropanation[3b] and the Rh(I)-catalysed hydrogenation of ketones[3a] with promising results. We extended this strategy to the synthesis of new chiral salen type ligands $\mathbf{H_2}$-**G** and $\mathbf{H_2}$-**M** (Fig. 3) containing a

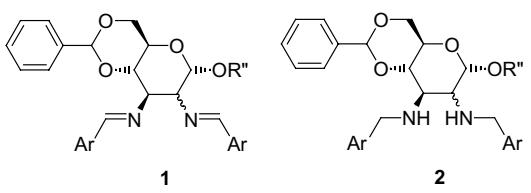

Figure 2. General formula of ligands of types **1** and **2**.

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carbohydrate core. Herein we report new ligands, the corresponding complexes of manganese(III) and their use in the asymmetric epoxidation of styrenes.

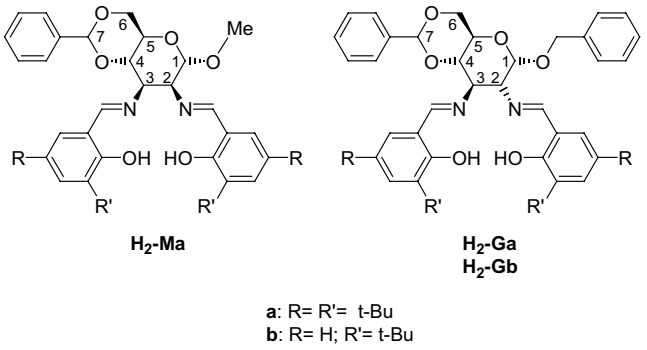


Figure 3. General formula of ligands of type $\mathbf{H_2}$-**M** and $\mathbf{H_2}$-**G**. The ligands are indicated by a letter (G = glucose and M = mannose) followed by specification of the hydroxyaryl moiety.

2. Results and discussion

2.1. Synthesis and characterisation of the ligands

Ligands of type $\mathbf{H_2}$-**G** and $\mathbf{H_2}$-**M** are pictured in Figure 3 (the labels **a** and **b** define the hydroxoaryl moieties). Commercial materials are *N*-acetyl-α-D-glucosamine and methyl-α-D-glucopyranoside for glucose and mannose derivatives, respectively. Known procedures[6] allow their transformation into 2,3-*gluco*- and 2,3-*manno*-diamines **3G** and **3M**, which can be converted into $\mathbf{H_2}$-**G** and $\mathbf{H_2}$-**M** species by condensation with two equivalents of the appropriate 2-hydroxybenzaldehyde (Scheme 1). The reactions were carried out in toluene with the products recovered in high yields as yellow microcrystalline powders. These were soluble in chlorinated solvents and in aromatic hydrocarbons, but did not appreciably dissolve in alcohols or paraffins. Deuteriobenzene was used as the solvent for NMR measurements, in order to inhibit hydrolysis of the imino functionalities, which occurs more easily in acidic chlorinated solvents. As expected, the CH=N protons resonate at high frequency with the signals of the corresponding carbon atoms found to be in the range 150–160 ppm in the ^{13}C spectra. The –OH signals were detectable between 14 and 16 ppm, while the complete assignment of the sugar moieties was accomplished through 2D spectroscopy due to crowding of the corresponding region. The absorptions at ca. 1630 cm^{-1} in the IR spectra recorded in nujol mull are attributed to the C=N stretchings.

2.2. Synthesis and characterisation of the Mn(III) complexes

Five manganese(III) complexes (Fig. 4) were prepared from $Mn(AcO)_2$ by adapting established procedures.[7] Three of them were cations with the formulae $[Mn(\mathbf{Ga})]^+(PF_6^-)$, $[Mn(\mathbf{Gb})]^+(PF_6^-)$ and $[Mn(\mathbf{Ma})]^+(PF_6^-)$, where **G** and **M** indicate the doubly deprotonated form of ligands $\mathbf{H_2}$-**G** and $\mathbf{H_2}$-**M**, respectively, for example:

$$2[Mn(AcO)_2] + 1/2O_2 + 2\mathbf{H_2}\text{-}\mathbf{Ga} + 2KPF_6 = 2[Mn(\mathbf{Ga})]PF_6 + 2KOAc + 2HOAc + H_2O$$

In two cases, neutral complexes were prepared, namely [Mn(**Ga**)(OH)] and [Mn(**Ma**)(OH)] (Fig. 4), for example:

$$2[Mn(AcO)_2] + 1/2O_2 + 2\mathbf{H_2}\text{-}\mathbf{Ga} + H_2O = 2[Mn(\mathbf{Ga})(OH)] + 4HOAc$$

The dark brown compounds were soluble in chlorinated solvents, acetone, aromatic hydrocarbons. The molar conductivity of the cationic species in dichloromethane was within the range 20–25 $S^{-1}\,cm^2\,mol^{-1}$, which confirmed that they were 1/1 electrolytes.[8] On the other

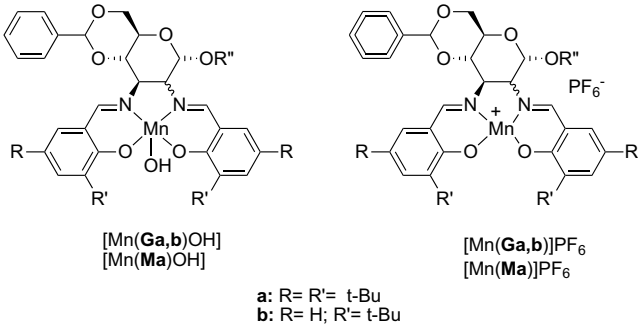
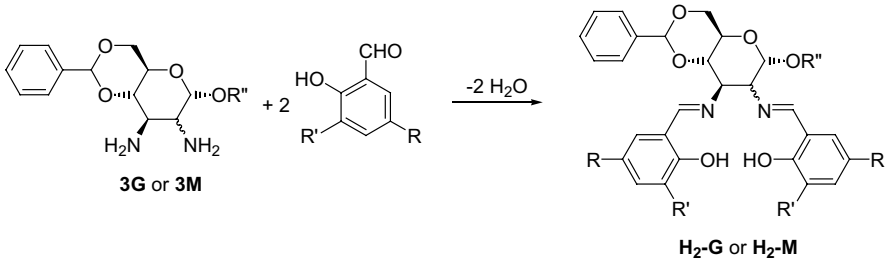


Figure 4. General formula of Mn(III) complexes.



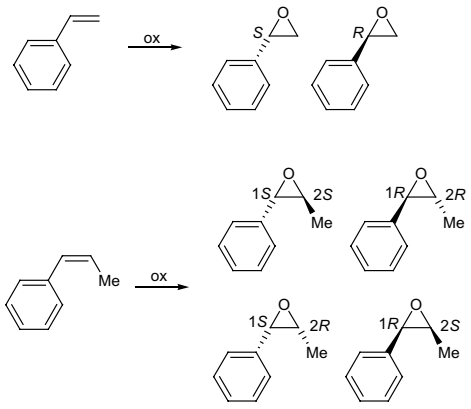
Scheme 1. Syntheses of ligands of types $\mathbf{H_2}$-**M** and $\mathbf{H_2}$-**G**.

hand, the neutral hydroxospecies did not appreciably conduct in the same solvent.

In the IR spectra, the CH=N stretchings shift to lower frequencies with respect to those observed for the parent ligands. The PF_6^- anion gives rise to a broad bond at ca. 850 cm^{-1}, while the spectra of the hydroxospecies display O–H stretchings[9] at 3570 cm^{-1}.

2.3. Epoxidation reactions

The asymmetric epoxidation of styrenes promoted by Mn(III) complexes is of great interest because the resulting optically active epoxides are valuable intermediates for a wide variety of pharmaceutically relevant compounds. Thus, we examined the ability of the new sugar based Mn complexes to promote the asymmetric epoxidation of styrene and *cis*-β-methylstyrene (Scheme 2). The reactions were performed in the conditions described by Jacobsen et al.,[10] that is, in dichloromethane at −78 °C, using *m*-chloroperbenzoic acid as the oxidant in the presence of *N*-methylmorpholine-*N*-oxide, with a catalyst/substrate ratio of 1/25. The results are summarised in Table 1. Concerning the epoxidation of *cis*-β-methylstyrene, all glucose based complexes (entries 1–3) afforded the *cis*-epoxide (*cis*/*trans* 95/5) as the major product, with high conversions (up to 99% within 30 min) and good ee's (86%).[11] On the other hand, use of [Mn(**Ma**)OH] and [Mn(**Ma**)]PF_6 as catalysts (entries 4 and 5) gave low conversion yields (36% and 59% within 180 min, respectively), a reduced *cis*/*trans* ratio (80/20) and poor enantioselectivity (0% and 50% ee's). Furthermore, the mannose ligands induced opposite selectivity with respect to the corresponding glucose ligands. These differences were not unexpected, since it has been suggested[2] that the presence of a chiral diimine bridge with C_2 symmetry is necessary for inducing enantioselectivity during the oxidation step. This condition is fulfilled in D-glucose based complexes, where the nitrogen atoms are both placed in equatorial positions (as sketched in Fig. 5a), thus mimicking the C_2 symmetry of the Jacobsen catalysts derived from 1,2-(*S*,*S*)-cyclohexanediamine (*S*,*S*)-**II** (Fig. 1).[12] Accordingly, the main product is attained in the same configuration (1*S*,2*R*) with nearly identical ee to that obtained



Scheme 2. Epoxidation of styrene and *cis*-β-methylstyrene.

Table 1. Results of the manganese-catalysed epoxidation of styrene and *cis*-β-methylstyrene

Entry	Catalyst	Substrate	Time (min)	Conversion (%)[a]	Selectivity (*cis*/*trans*)	Ee (%)[b,c]
1	[Mn(**Ga**)]PF_6	*cis*-β-Methylstyrene	30	99	95/5	86 (1*S*,2*R*)
2	[Mn(**Ga**)(OH)]	*cis*-β-Methylstyrene	180	84	94/6	86 (1*S*,2*R*)
3	[Mn(**Gb**)]PF_6	*cis*-β-Methylstyrene	30	99	94/6	86 (1*S*,2*R*)
4	[Mn(**Ma**)]PF_6	*cis*-β-Methylstyrene	180	59	80/20	50 (1*R*,2*S*)
5	[Mn(**Ma**)(OH)]	*cis*-β-Methylstyrene	180	36	80/20	0
6	[Mn(**Ga**)]PF_6	Styrene	30	99	—	45 (*S*)
7	[Mn(**Ga**)(OH)]	Styrene	30	99	—	50 (*S*)
8	[Mn(**Gb**)]PF_6	Styrene	30	99	—	54 (*S*)
9	[Mn(**Ma**)]PF_6	Styrene	180	97	—	32 (*R*)
10	[Mn(**Ma**)(OH)]	Styrene	30	99	—	30 (*R*)

[a] The conversion has been calculated by integration of suitable peaks in NMR spectrum.
[b] The determination of ee's was carried out by ^1H NMR analysis in $CDCl_3$ in the presence of Eu(hfc)$_3$ as shift reagent.
[c] For the epoxidations of *cis*-β-methylstyrene the ee's refer to the *cis*-epoxide.

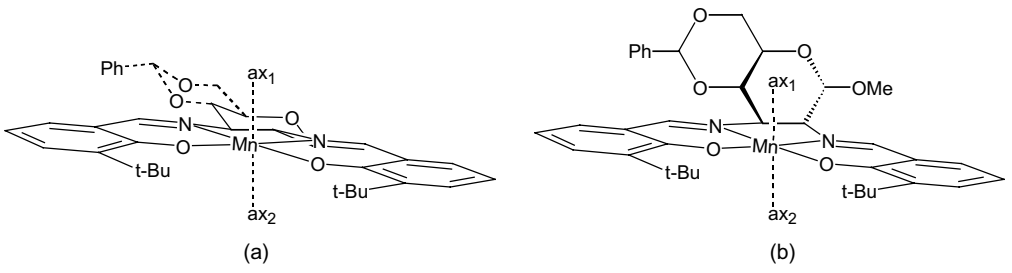


Figure 5. Schematic view of glucose (a) and mannose (b) Mn(III) complexes. The labels ax_1 and ax_2 indicates the axial positions. The benzyl group at position 1 of the glucose has been omitted for the sake of clarity.

using the Jacobsen catalyst with (*S*,*S*)-**II** containing the same substituents on the aryl rings.[10] In the case of D-mannose, the inversion of configuration at C(2) provided a different local geometry (Fig. 5b), which is apparently less well suited to promote asymmetry in the reaction. The behaviour of glucose and mannose also exhibited another notable difference. In fact, the cationic complex [Mn(**Ma**)]PF_6 displayed a moderate selectivity (entry 4), while the neutral [Mn(**Ma**)OH] afforded only racemic product (entry 5). On the other hand, no such difference was found amongst the corresponding glucose complexes (entries 1 and 2). Also these findings may be a consequence of the different local symmetry generated by the two sugars around the metal. In the pseudo-C_2 symmetry created by glucose, the active axial sites (ax_1 and ax_2 in Fig. 5a) become nearly equivalent and, hence, the enantioselectivity did not change if one apical position was occupied by the OH^- ligand. This did not hold true in complexes containing mannose ligands, because the absence of a local C_2 symmetry generated a substantial difference between the axial positions. In this case, the low enantioselectivity observed when using [Mn(**Ma**)(OH)] may be due to the preferential coordination of the OH^- ligand to the apical site where chiral discrimination is more effective.

The epoxidation of styrene (entries 6–10) gave in all cases high conversions (99%). The highest ee [54% of (*S*)-enantiomer] can be achieved by using [Mn(**Gb**)]PF_6, while with [Mn(**Ga**)OH] and [Mn(**Ga**)]PF_6 the enantioselectivity was slightly lower (ee's 50% and 45%, respectively). As expected on the grounds of the above results, the mannose complexes were less selective, and induced the preferential formation of the other enantiomer (ee 30% and 32%, respectively, for [Mn(**Ga**)OH] and [Mn(**Ga**)]PF_6). These findings are in agreement with the literature,[2] because the oxidation of terminal olefins promoted by Mn salen complexes is known to afford only moderate ee's. For instance, under the same experimental conditions, the Jacobsen catalyst with (*S*,*S*)-**II** (R = R′ = *t*-Bu) promotes the epoxidation of styrene in 56% ee.[10,13] In any case, the results described herein largely update those obtained[14] with the recently described Mn(III) salen complex derived from a carbohydrate, that is, by suitable modification of β-L-idofuranose. In that study, styrene was oxidised in 13% ee and 75% yield.

3. Conclusion

We have shown that with the appropriate modification of common carbohydrates we can afford ligands useful for asymmetric synthesis. More precisely, Mn(III) catalysts with salen ligands derived from 2,3-D-glucosediamine have been found to be as active as those based on 1,2-cyclohexanediamine. These promising results deserve further investigation with the aim of exploiting the presence of other functional groups naturally present on the carbohydrate skeleton. For instance, –OH groups not involved in metal coordination (C1, C4 and C6), may be used for other purposes, such as anchoring to a polymeric matrix or improving the solubility in alternative solvents.

4. Experimental

4.1. General methods

NMR spectra were recorded in C_6D_6 with a 200 or a 300 MHz spectrometer (Varian Model Gemini). The following abbreviations were used for describing the NMR multiplicities: s, singlet; d, doublet; t, triplet; dd, double doublet; m, multiplet. Benzyl-4,6-*O*-2,3-diamino-2,3-dideoxy-α-D-glucoside[6a] and methyl-4,6-*O*-benzylidene-2,3-diamino-2,3-dideoxy-α-D-mannoside[6b] were prepared according to literature methods.

4.2. Synthesis of ligands H_2-G and H_2-M

The appropriate aldehyde (2 mmol) was added to a stirred solution of the 2,3-hexapyranosediamine **3** (1 mmol) in 4 mL of dry toluene under nitrogen. After stirring for 1 h at 60 °C, the solvent was removed under vacuum. The addition of methanol to the crude reaction yielded a yellow microcrystalline solid, which was separated, washed with methanol and dried under vacuum (yield >75%). **H_2-Ga**: Selected ^{1}H NMR data (200 MHz, δ, C_6D_6): δ 14.30 (s, 1H, OH), 13.90 (s, 1H, OH), 8.15 (s, 1H, N=CH), 7.75 (s, 1H, N=CH), 5.30 (s, 1H, H7), 4.82 (d, 1H, H1, $^3J_{H1-H2} = 3.6$ Hz), 4.75 (d, 1H, C*H*HPh, $^3J_{gem} = 12.2$ Hz), 4.45 (d, 1H, CH*H*Ph), 4.35 (m, 2H, H5 and H6eq, $^3J_{H5-H4} = 9.3$ Hz, $^3J_{H5-H6ax} = {}^3J_{H6eq-H6ax} = 11.8$ Hz), 3.90 (t, 1H, H3, $^3J_{H3-H2} = {}^3J_{H3-H4} = 9.3$ Hz), 3.60 (m, 2H, H4 and H6ax), 3.45 (dd, 1H, H2) ppm. Selected ^{13}C NMR data (75.5 MHz, δ, C_6D_6): δ 170.8, 169.2, 159.1–118.3 (20C, aromatics), 101.7, 98.2, 79.9, 71.6, 69.9, 69.3, 67.8, 63.9 ppm. IR (Nujol, KBr): ν 1628 cm^{-1}. Anal. Calcd for $C_{50}H_{64}N_2O_6$: C, 76.11; H, 8.18; N, 3.55. Found: C, 75.87; H, 8.33; N, 3.56. **H_2-Gb**: Selected ^{1}H NMR data (200 MHz, δ, C_6D_6): δ 14.55 (s, 1H, OH), 14.05 (s, 1H, OH), 8.05 (s, 1H, N=CH), 7.75 (s, 1H, N=CH), 5.03 (s, 1H, H7), 4.75 (d, 1H, H1, $^3J_{H1-H2} = 3.6$ Hz), 4.70 (d, 1H, C*H*HPh, $^3J_{gem} = 12.2$ Hz), 4.45 (d, 1H, CH*H*Ph), 4.30 (m, 2H, H5 and H6eq, $^3J_{H5-H4} = 9.4$, $^3J_{H5-H6ax} = {}^3J_{H6eq-H6ax} = 11.2$ Hz), 3.95 (t, 1H, H3, $^3J_{H3-H2} = {}^3J_{H3-H4} = 9.8$ Hz), 3.65 (m, 2H, H4 and H6ax), 3.40 (dd, 1H, H2) ppm. Selected ^{13}C NMR data (75.5 MHz, δ, C_6D_6): δ 170.2, 168.7, 161.3–118.4 (20C, aromatics), 101.7, 98.1, 79.8, 71.5, 69.9, 69.3, 67.8, 63.7 ppm. IR (Nujol, KBr): ν 1629 (C=N) cm^{-1}. Anal. Calcd for $C_{42}H_{48}N_2O_6$: C, 74.53; H, 7.15; N, 4.14. Found: C, 74.71; H, 7.04; N, 4.29. **H_2-Ma**: Selected ^{1}H NMR data (300 MHz, δ, C_6D_6): δ 14.05 (s, 1H, OH), 13.73 (s, 1H, OH), 8.09 (s, 1H, N=CH), 8.08 (s, 1H, N=CH), 4.97 (s, 1H, H7), 4.51 (d, 1H, H1), 4.16 (m, 4H, H3, H5, H6ax and H6eq, $^3J_{H3-H2} = 4.0$ Hz, $^3J_{H3-H4} = {}^3J_{H5-H4} = 9.4$ Hz), 3.65 (t, 1H, H4), 3.48 (dd, 1H, H2) ppm. Selected ^{13}C NMR data (75.5 MHz, δ, C_6D_6): δ 169.7, 169.3, 158.9–118.5 (16C, aromatics), 101.4, 77.3, 72.0, 69.0, 67.2, 65.2, 59.8, 54.7 ppm. IR (Nujol, KBr): ν 1628 (C=N) cm^{-1}.

Anal. Calcd for $C_{44}H_{60}N_2O_6$: C, 74.12; H, 8.48; N, 3.93. Found: C, 74.54; H, 8.60; N, 3.78.

4.3. Synthesis of the complexes [Mn(Ga)]PF_6, [Mn(Gb)]PF_6 and [Mn(Ma)]PF_6

Manganese(II) acetate tetrahydrate (1.0 mmol) was added to a solution of the appropriate ligand (0.50 mmol) in hot ethanol (5 mL) and the mixture was refluxed for 90 min. Solid KPF_6 was added (1.5 mmol) and air was allowed to pass through the reaction mixture for 30 min under reflux. Then the mixture was cooled in an ice bath, water (5 mL) was added and a dark-brown precipitate was obtained. The mixture was extracted with dichloromethane (3×5 mL) and the organic phases were dried over Na_2SO_4, filtered and dried in vacuo. The resulting crude product was crystallised from dichloromethane/hexane (yields: 50–54%). [Mn(**Ga**)]PF_6: IR (Nujol, KBr): ν 1609 (C=N), 843 (PF_6^-) cm^{-1}. MS (electrospray) m/z: 841.4 $[M-PF_6]^+$. Anal. Calcd for $C_{50}H_{62}F_6MnN_2O_6P$: C, 60.85; H, 6.33; N, 2.84; Mn, 5.57. Found: C, 60.69; H, 6.18; N, 2.90; Mn, 5.43. [Mn(**Gb**)]PF_6: IR (Nujol, KBr): ν 1610 (C=N), 843 (PF_6^-) cm^{-1}. MS (electrospray) m/z: 729.4 $[M-PF_6]^+$. Anal. Calcd for $C_{42}H_{46}F_6MnN_2O_6P$: C, 57.67; H, 5.30; N, 3.20; Mn, 6.28. Found: C, 57.72; H, 5.47; N, 3.21; Mn, 6.02. [Mn(**Ma**)]PF_6: IR (Nujol, KBr): ν 1601 (C=N), 841 (PF_6^-) cm^{-1}. MS (electrospray) m/z: 765.5 $[M-PF_6]^+$. Anal. Calcd for $C_{44}H_{58}F_6MnN_2O_6P$: C, 58.02; H, 6.42; N, 3.08; Mn 6.03. Found: C, 57.84; H, 6.45; N, 3.22; Mn, 6.26.

4.4. Synthesis of the complexes [Mn(Ga)OH] and [Mn(Ma)OH]

To a solution of the appropriate ligand (0.5 mmol) in 3 mL of DMF was added manganese(II) acetate tetrahydrate (1.0 mmol). The stirred solution was heated at 100 °C for 60 min, after which air was allowed to pass through the reaction mixture for a further 60 min. The solution was then cooled in an ice bath, whereupon the addition of 3 mL of water afforded a brown precipitate. This was collected by vacuum filtration, washed with water and dried under vacuum. The solid was recrystallised from dichloromethane/hexane (yield: 50–60%). [Mn(**Ga**)OH]: IR (Nujol, KBr): ν 3570 (OH), 1618(C=N) cm^{-1}. MS (electrospray) m/z: 842.0 $[M-OH]^+$. Anal. Calcd for $C_{50}H_{63}MnN_2O_7$: C, 69.91; H, 7.39; N, 3.26; Mn, 6.40. Found: C, 69.55; H, 7.58; N, 3.19; Mn, 6.77. [Mn(**Ma**)OH]: IR (Nujol, KBr): ν 3570 (OH), 1609 (C=N) cm^{-1}. MS (electrospray) m/z: 765.9 $[M-OH]^+$. Anal. Calcd for $C_{44}H_{59}MnN_2O_7$: C, 67.50; H, 7.60; N, 3.58; Mn, 7.02. Found: C, 67.88; H, 7.49; N, 3.45; Mn, 6.89.

4.5. Epoxidation reactions

The olefin substrate (0.96 mmol) and *N*-methylmorpholine-*N*-oxide (4.8 mmol) were added to a solution of the appropriate Mn complex (0.038 mmol) in 8 mL of dry dichloromethane. The mixture was cooled at −78 °C after which *m*-chloroperbenzoic acid (1.92 mmol) was added as a solid over a 2 min period. The reaction was monitored throughout by TLC (10/1 petroleum ether/ethyl acetate). After an established period of time, 10 mL of 1 M NaOH were added, and the organic phase separated, washed with brine (1×10 mL) and dried over Na_2SO_4. The solvent was removed in vacuo and the resulting residue purified by filtration through a small pad of silica gel. The filtrate was concentrated and analysed by ^1H NMR.

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12. Actually, it should be noted that according to the stereochemical rules, the configurations at C2 and C3 are (*R*,*R*) and (*S*,*R*) for 2,3-D-*gluco*-diamines and 2,3-D-*manno*-diamines, respectively.
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