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Synthesis and characterization of manganese(III) complexes of a chiral disulfonamide ligand based on *trans*-1,2-diaminocyclohexane

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Abstract—The synthesis and characterization of an optically active disulfonamide ligand based on *trans*-1,2-diaminocyclohexane as chiral motif is reported. The corresponding anionic manganese(III) complex has been evaluated as potential catalyst for enantioselective olefin epoxidations, and found to be inactive. © 1997 Elsevier Science Ltd

Keywords: chiral; disulfonamide ligand; manganese(III); epoxidation; *trans*-1,2-diaminocyclohexane.

Recently, many efforts have been made to develop methods for the asymmetric epoxidation of alkenes. Work has concentrated on the synthesis and catalytic activity of metalloporphyrins [1,2] or manganese Schiff base complexes [3] bearing chiral motifs, and the development of Sharpless-type catalysts for the epoxidation of allylic alcohols [4]. Schiff base manganese(III) complexes based on optically active 1,2-diamines (specially on the 1,2-diaminocyclohexane chiral motif) have been used in the epoxidation of *cis*-disubstituted olefins [5], cyclic or conjugated polyenes [6] and of styrene derivatives [7].

These catalysts are active and enantioselective when associated with a powerful oxygen atom donor such as NaOCl, but they are also relatively fragile and turnover numbers higher than 40–50 usually cannot be obtained, due to their oxidative self-degradation. In order to improve the stability and the activity of chiral manganese(III) Schiff base complexes, we developed a new series of Schiff base ligands and complexes bearing chlorine or bromine atoms on the salicylidene moieties, based on the optically active 1,2-diaminocyclohexane [8] or 2,2′-diamino-1,1′-binaphthalene [9,10] motifs. But the corresponding manganese(III) complexes were also quickly degraded in strong oxidizing conditions. We therefore decided to synthesize ligand **1**, and the corresponding manganese complexes **2** and **3**, where the fragile imines were replaced by sulfonamide functions (see Fig. 1 for structures). The synthesis of this ligand was recently reported by Zhang and Guo [11] but without any details on isolation methods or spectroscopic data and was used as a titanium(IV) chelate in the enantioselective addition of diethylzinc to aldehydes.

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EXPERIMENTAL

General methods

Proton and carbon NMR spectra were recorded on a Bruker AMX 400. UV-visible spectra were obtained with a Hewlett-Packard 8452A spectrophotometer, optical rotations with a Perkin-Elmer 241 polarimeter. Mass spectrometry analyses were performed on a Nermag R10-10 instrument.

Abbreviations. **(1-Mn)**$^-$ stands for the anionic moiety of complexes **2** and **3**. BDTAC stands for the benzyldimethyltetradecylammonium chloride and MNBA for *m*-nitrobenzyl alcohol.

Synthesis of ligand **1**. (1*S*,2*S*)-(−)-*N*,*N*′-bis(3,5-dichlorosalicylidene) - *trans* - 1,2 - cyclohexane disulfonamide. Compound **1** was prepared as follows:

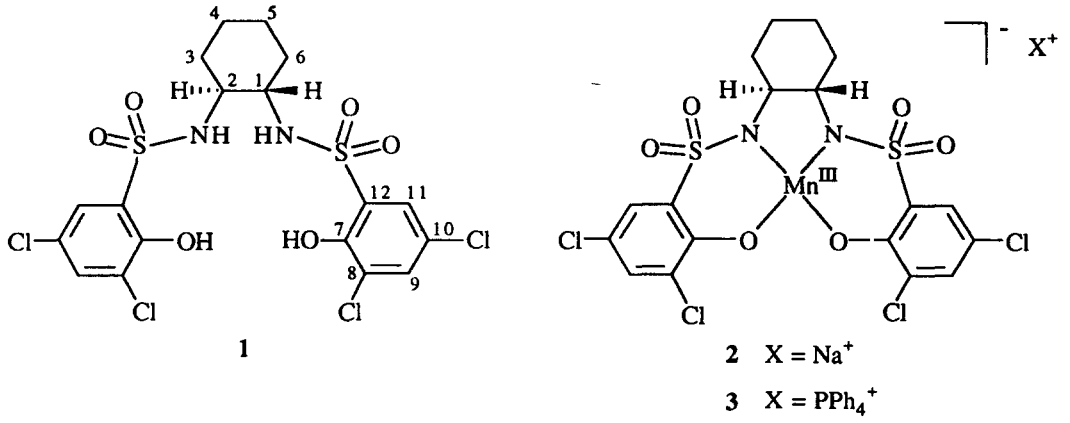

Fig. 1. Structures of the chiral disulfonamide ligand **1** and the corresponding anionic manganese complexes **2** and **3**.

3,5-dichloro-2-hydroxybenzenesulfonyl chloride (521 mg, 2 mmol, Aldrich) was dissolved in 10 cm^3 of dioxane (<0.01% H_2O, kept on molecular sieve, Fluka) under nitrogen, and solid (1*S*,2*S*)-(+)-1,2-diaminocyclohexane (114 mg, 1 mmol) was added and then triethylamine (2.2 cm^3, 15 mmol). The reaction mixture was heated at 100°C for 18 h. After cooling, the crude reaction mixture was acidified with 10^{-2} M aqueous hydrochloric acid (30 cm^3) and the product was extracted twice with ethylacetate. The organic layer was washed twice with 10^{-2} M HCl (2×30 cm^3), dried over sodium sulfate and the solvent was removed *in vacuo*. The pure ligand **1** was obtained by recrystallization in a mixture of CH_2Cl_2/hexane and dried *in vacuo* (478 mg, yield = 85%).

Characterization of **1**. $[\alpha]_{365} = -88$ ($c = 7.55 \times 10^{-3}$ g/cm^3, methanol). Found: C 38.7, H 3.3, N 4.8, S 10.6. Calc. for $C_{18}H_{18}Cl_4N_2O_6S_2$, $0.1C_6H_{14}$: C 38.8, H 3.3, N 4.9, S 11.2%. MS (DCI/NH_3) *m/z* (relative intensity): 580 (72), 581 (19), 582 (100, MNH_4^+), 583 (25), 584 (56), 585 (13), 586 (16), 587 (3), 588 (2). UV-vis (dichloromethane) λ, nm (ε, L mol^{-1} cm^{-1}): 230 (15×10^3), 306 (7×10^3). ^1H NMR (CD_2Cl_2, 400.13 MHz) δ, ppm *vs* external TMS: 1.18, 1.23, 1.63, 1.87 ($4 \times$ m, $4 \times 2H$, H_3, H_4, H_5 and H_6), 2.89 (m, 2H, H_1 and H_2), 5.35 (bs, 2H, NH), 7.60 (d, 2H, H_9 and $H_{9'}$, $^4J_{HH} = 2.5$ Hz), 7.68 (d, 2H, H_{11} and $H_{11'}$, $^4J_{HH} = 2.5$ Hz), 8.10 (bs, 2H, OH). ^{13}C NMR (CD_2Cl_2, 100.62 MHz) δ, ppm *vs* external TMS: 23.5 (C_4 and C_5), 32.7 (C_3 and C_6), 56.6 (C_1 and C_2), 123.2 (C_8 and $C_{8'}$), 124.7 (C_{10} and $C_{10'}$), 125.9 (C_{12} and $C_{12'}$), 126.6 (C_{11} and $C_{11'}$), 133.8 (C_9 and $C_{9'}$), 148.1 (C_7 and $C_{7'}$). NMR assignments were based on $\delta_{^1H} - \delta_{^1H}$ GE-COSY and $\delta_{^1H} - \delta_{^{13}C}$ GE-HMQC (^1J, $D_2 = 3.5$ ms) and long-range (^3J, $D_2 = 50$ ms) proton-carbon correlations.

Preparation of the manganese(III) complex of **1**

The ligand **1** was reacted with manganese(II) acetate in the presence of sodium methylate as follows: **1** (564 mg, 1 mmol) was dissolved in 20 cm^3 of degassed absolute ethanol. $Mn(OAc)_2 \cdot 4H_2O$ (1.23 g, 5 mmol) was added and then sodium methylate as a solid (270 mg, 5 mmol). The solution was refluxed for 24 h under nitrogen. After cooling, water was added and the reaction mixture was concentrated. The product was extracted with ethylacetate. The organic phase was dried with sodium sulfate and solvent was removed *in vacuo*. The resulting sodium salt of the manganese(III) complex **2** was recrystallized with a mixture of ethylacetate/hexane and dried *in vacuo* (427 mg, yield = 67%).

Characterization of the sodium salt of [(1*S*,2*S*)-(+)-*N*,*N*′-bis(3,5-dichlorosalicylidene)-*trans*-1,2-cyclohexane disulfonamidomanganese(III)](1-) **2**. $[\alpha]_{365} = +1570$ ($c = 2 \times 10^{-5}$ g/cm^3, methanol). Found: C 34.6, H 2.6, N 4.5, S 9.6. Calc. for $(C_{18}H_{14}Cl_4MnN_2O_6S_2)^-Na^+$, $0.1C_6H_{14}$: C 34.5, H 2.4, N 4.3, S 9.9%. UV–vis (methanol) λ, nm (ε, L mol^{-1} cm^{-1}): 216 (41×10^3), 254 (15×10^3), 328 (8×10^3). MS (FAB$^+$/MNBA) *m/z* (relative intensity): 585 (33), 587 (47, **1**+Na^+), 638 (80), 639 (27), 640 [100, (**1**-**Mn**)$^-$ + e^- + 2H^+ + Na^+], 641 (31), 642 (57), 662 [54, (**1**-**Mn**)$^-$ + e^- + H^+ + 2Na^+]. It has to be noted that, in these experimental conditions (i) demetallation of complex **2** could occur, (ii) adducts are formed between the manganese complex anion and sodium cations present in the mass spectrometer. Conductivity (1.039×10^{-3} M, methanol) $\Lambda_M = 57$ Ω^{-1} cm^2 mol^{-1}. This result is in agreement with the identification of **2** as a 1 : 1 electrolyte [12].

Exchange of Na^+ counterion. Sodium ion of **2** was exchanged for tetraphenylphosphonium as follows: 50.7 mg (79 μmol) of **2** was dissolved in 5 cm^3 of methanol. A solution of tetraphenylphosphonium chloride (284 mg, 760 μmol) in methanol (3 cm^3) was added, and the resulting solution was stirred at room temperature for 3 h. Complex **3** was precipitated by addition of water, filtered, washed with water, and recrystallized in a mixture of ethylacetate and hexane (49 mg, yield = 58%).

Characterization of the tetraphenylphosphonium salt

of [(1*S*,2*S*)-(+)-*N*,*N*′-bis(3,5-dichlorosalicylidene)-*trans* - 1,2 - cyclohexane disulfonamidomanganese (III)](1-) **3**. $[\alpha]_{365} = +930$ ($c = 2 \times 10^{-5}$ g/cm^3, methanol). Found: C 53.0, H 4.0, N 3.1, S 6.9. Calc. for $(C_{18}H_{14}Cl_4MnN_2O_6S_2)^-[P(C_6H_5)_4]^+$, $0.1C_6H_{14}$: C 53.1, H 3.7, N 2.9, S 6.7%. UV–vis (methanol) λ, nm (ε, L mol^{-1} cm^{-1}): 210 (89×10^3), 254 (20×10^3), 276$_{sh}$ (4×10^3), 328 (9×10^3). MS (FAB$^-$/MNBA) *m/z* (relative intensity): 561 (12), 563 (15, **1**-H$^+$), 565 (9), 614 (77), 615 (32), 616 [100, (**1-Mn**)$^-$ + e$^-$ + H$^+$], 617 (28), 618 (49), 636 (10), 638 [13, (**1-Mn**)$^-$ + e$^-$ + Na$^+$], 640 (7). Conductivity (1.010×10^{-3} M, methanol) $\Lambda_M = 61\ \Omega^{-1}\ cm^2\ mol^{-1}$.

Olefin epoxidation assays using **2** *as potential catalyst*

Complex **2** was used as a possible catalyst in the epoxidation of 2,2-dimethyl-3-chromene (prepared according to [13]) and 1,2-dihydronaphthalene using sodium hypochlorite, hydrogen peroxide, or potassium monopersulfate as primary oxidants in experimental conditions similar to olefin epoxidations performed with manganese Schiff base complexes [8,10].

NaOCl as oxidant. With 2,2-dimethyl-3-chromene as substrate, the reaction mixture was as follows: catalyst (7 μmol), BDTAC (12 μmol), 1,2,4,5-tetrachlorobenzene (internal standard for GC analyses, 30 μmol), 4-methylpyridine (510 μmol), and the olefin (80 μmol) were dissolved in CH_2Cl_2 (0.5 cm^3). After 2 min of stirring at 0°C under an air atmosphere, an aqueous solution of NaOCl (0.5 M, 250×10^{-3} cm^3) was added, and the reaction was followed by GC on a 30 m × 0.25 mm Chiraldex G-TA (Alltech) capillary column (column temperature 120°C, N_2 pressure 0.55 bar). With 1,2-dihydronaphthalene, the reaction mixture was the same as in the case of 2,2-dimethyl-3-chromene, except that 1,4-dibromobenzene (50 μmol) was used as a GC internal standard, instead of 1,2,4,5-tetrachlorobenzene. GC analyses were performed on a 25 m × 0.20 mm Cydex-B (SGE) capillary column (column temperature 130°C, N_2 pressure 0.9 bar).

H_2O_2 as oxidant. A solution of complex **2** (8 μmol or 27 μmol, corresponding to 1.7 mol% or 5.3 mol% respectively *vs* the substrate), 1,4-dibromobenzene (internal standard for GC analyses, 140 μmol), imidazole (250 μmol), and the olefin (500 μmol) were dissolved in a mixture of methanol/CH_2Cl_2 (1/1, v/v, 2.5 cm^3). The solution was cooled at 0°C. A 30 wt% solution of H_2O_2 (140×10^{-3} cm^3 in four portions of 35×10^{-3} cm^3 each 15 min) was then added. The reaction mixture was stirred at 0°C and the reaction was followed by GC analyses on a 25 m × 0.20 mm Cydex-B (SGE) capillary column (column temperature 130°C, N_2 pressure 0.9 bar).

$KHSO_5$ as oxidant. Complex **2** (9 μmol or 36 μmol, corresponding to 1.2 mol% or 5.2 mol% respectively *vs* the substrate), BDTAC (68 μmol), 1,4-dibromobenzene (internal standard for GC analyses, 190 μmol), 4-methylpyridine (1020 μmol) or 4-*t*-butylpyridine (680 μmol), and the olefin (690 μmol) were dissolved in 1 cm^3 of CH_2Cl_2. A solution of $KHSO_5$ (500 μmol) in 5 cm^3 of a 66 mM phosphate buffer pH 5 was then added. The reaction mixture was stirred at room temperature (1.2% of catalyst) or at 0°C (5.2% of catalyst). The reaction was followed by GC analyses on a 25 m × 0.20 mm Cydex-B (SGE) capillary column (column temperature 130°C, N_2 pressure 0.9 bar).

RESULTS AND DISCUSSION

The synthesis of the chiral disulfonamide ligand **1** was performed with high yield by direct condensation of (1*S*,2*S*)-(+)1,2-diaminocyclohexane and 3,5-dichloro-2-hydroxybenzenesulfonyl chloride, in the presence of triethylamine, in dried dioxane. When this ligand was dissolved in ethanol with an excess of sodium methylate, the deprotonation of the two sulfonamide functions occurred, and reaction of **1** with manganese(II) acetate yielded the corresponding manganese(III) complex as a monoanionic species. The presence of counterions sodium or tetraphenylphosphonium allowed the characterization of complexes **2** and **3**, respectively.

Several terminal oxidants (namely NaOCl, H_2O_2, and $KHSO_5$) were used in order to check the possibility to use complex **2** as a catalyst for the epoxidation of 2,2-dimethyl-3-chromene and 1,2-dihydronaphthalene. With sodium hypochlorite as oxidant and 9 mol% of complex **2** *vs* substrate, in the presence of a phase transfer agent and of 4-methylpyridine as co-catalyst [10], no significant conversion of these two olefins was observed after 4 h at 0°C. With H_2O_2 and 5 mol% of complex **2**, in a mixture of methanol and dichloromethane (1/1, v/v) in the presence of imidazole [14], the conversion of 1,2-dihydronaphthalene was below 5% after 1 h at 0°C, and no epoxide was detected. Epoxidation of 1,2-dihydronaphthalene was also attempted using potassium monopersulfate $KHSO_5$ in a biphasic mixture dichloromethane/phosphate buffer pH 5, in the presence of 1 mol% of complex **2** at room temperature, or 5 mol% of complex **2** at 0°C. With 1% of **2**, the olefin conversion was 8% in 3 h, and the enantiomeric excess of the epoxide was 6% (epoxide yield = 3%). Under similar conditions but without complex **2**, the 1,2-dihydronaphthalene conversion was 5%, but no epoxide was detected after 2 h. With 5% of complex **2** at 0°C, 26% of olefin conversion was observed but the epoxide yield was only 10% after 3 h of reaction time. Unfortunately, the epoxide enantiomeric excess was below 2%, indicating that, under these conditions, the epoxidation is probably mainly catalyzed by non-chiral degradation products of the disulfonamide manganese complex.

Despite an expected increased ligand stability with respect to strong oxidizing conditions, this dis-

ulfonamide manganese compound is not an efficient epoxidation catalyst. As a possible explanation, we can assume that this anionic complex might be easily oxidized by a one-electron complex to a manganese(IV) derivative stabilized by the tetraanionic sulfonamide ligand, leading then to an inactive form of the complex unable to be oxidized to a Mn^{VI}=O species *via* an oxygen atom transfer. Such a high-valent metal-oxo entity is required as an active epoxidizing species in a catalytic oxygen transfer from the primary oxidant to the olefin substrate. In metalloporphyrin-catalyzed oxygenations, catalytic cycles involved a Mn^{III}/Mn^{V}=O cycling process [15].

In order to obtain new complexes with potential enantioselective catalytic activities, the preparations of other metal complexes of this chiral disulfonamide ligand **1** are in progress.

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