



Synthesis, characterization and catalytic activity of chiral binaphthyl Schiff-base manganese complexes for the epoxidation of styrene



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ABSTRACT

Chiral binaphthyl Schiff base ligands were prepared by condensation of 2,2'-diamino-1,1'-binaphthalene with various salicylaldehydes. Ligands were coordinated with Mn(III) as catalysts. The catalytic efficiency of the complexes was tested on the epoxidation of styrene. The influences of the parameters such as reaction time, position of substituents with various oxidants on the epoxidation reactions were investigated.

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1. Introduction

In recent years, chiral metal complexes containing binaphthyl rings have attracted many researchers about synthesizing enantioselective organics. In particular, binaphthyl-derived Schiff base ligands that have C₂ symmetry are used in chiral catalytic processes [1–3]. Due to the widespread use of modern coordination chemistry, the resulting synthesised products are claimed as potential materials in medical and agricultural areas [4]. Binaphthyl chiral Schiff base ligands are highly valuable structures in various metal-based catalytic reactions [5,6]. Specifically, the use of chiral metal complexes as epoxidation catalysts has become one of the most important research fields lately [7–13].

The development of the salen Mn catalyzed epoxidation reactions, especially as a procedure for asymmetric epoxidation of styrene, has provided a useful tool for the formation of chiral centers with carbon–oxygen bonds. One of the most important oxidation reactions is the oxidation of alkenes. Manganese(III) complexes with salen type ligands have been shown to be highly effective chemoselective and stereoselective catalysts for this reaction, and when chiral ligands are used, they can also be highly enantioselective [13–18]. Moreover, it is generally recognized that manganese complexes are less environmentally damaging than other transition metal complexes and that such complexes have received considerable attention as oxidation catalysts [16].

In order to improve the activity and enantioselectivity of chiral manganese Schiff base complexes in the epoxidation of terminal olefins, we have developed a new type of ligands and metal complexes based on optically active binaphthyl motif. These compounds were obtained by condensation of 1,1'-binaphthyl-2,2'-diamine with various substituted salicylaldehydes and following metalation with manganese(III) (see Scheme 2.1).

In this article, two different ligands (Scheme 2.1) were synthesized. Afterwards, they were coordinated with Mn(III) to achieve different Schiff base complex as catalysts (Scheme 2.2). Finally, it has been reported that the epoxidation of styrene by H₂O₂ and ditertiary butyl peroxide with two readily available oxygen atom donors was catalyzed by chiral manganese(III) Schiff base complexes (Scheme 2.3).

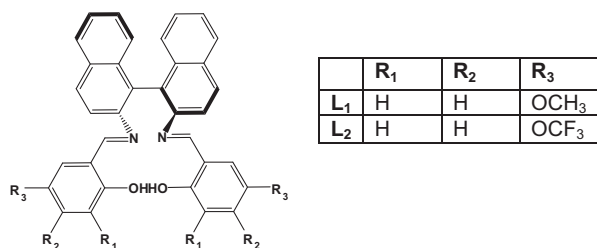
2. Experimental

2.1. Materials and methods

¹H NMR spectra were recorded with a DPX 400 Bruker-Advance spectrometer operating at 400 MHz. IR spectra were obtained on a Perkin Elmer Mattson 1000 FT-IR spectrometer. Melting points were determined on a Perkin-Elmer Pyris Diamond DSC analyzer. High-performance liquid chromatography coupled with tandem mass spectra were performed on a Agilent 1100 MSD instrument. Elemental analysis was performed on a CHNS-932 (LECO) instrument. The asymmetric epoxidation products were analyzed on a Agilent Gas Chromatograph equipped with Beta DEXTM 120 capillary column (30 m * 0,25 mm * 0,25 μm) using an FID detector.

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Scheme 2.1. Synthesized ligands.

Styrene, ditertbutylperoxide, and hydrogen peroxide were purchased from Merck. The other chemicals were obtained from local suppliers or prepared in our laboratory. All solvents used were purified by standard procedures.

2.2. Synthesis of Schiff-base ligands

2.2.1. 2,2'-Bis(2-hydroxy-5-methoxy benzylideneamino)-1,1'-naphthyl (L1)

A solution of 2-hydroxy-5-methoxybenzaldehyde (0.241 g, 1.58 mmol) in 10 ml of absolute ethanol was added dropwise into the solution of binaphthyl amine (0.2 g, 0.7 mmol) in 20 ml of warm absolute ethanol while stirring. The mixture was refluxed for 3 h until the reaction was completed. After 3 h, the solvent was removed and the reaction mixture cooled at room temperature. Then 1 ml of water was added. The resulting orange precipitate was filtered, dried and re-crystallized in dichloromethane/hexane to obtain pure orange crystal ligand L1 with a yield of 89%. M.p.: 222 °C. Elemental Anal. (C, H and N, wt.%) Calc. for C₃₆H₂₈N₂O₄ (L4): C, 78.29; H, 5.50; N, 4.93. Found: C, 77.94; H, 5.14; N, 4.94%. IR (KBr, cm⁻¹): 3500–3200, OH; 3054, Ar–H; 2933, 2829, C–H(O–CH₃); 1607, 1593, C–H(imine); 1572–1564, C=C(Ar). ¹H NMR (400 MHz, CDCl₃, δ: ppm): 11.63 (s, 2H, OH), 8.63 (s, 2H, CH=N), 8.13 (d, J = 9 Hz, 2H, Ph–H), 8.01 (d, J = 8 Hz, 2H, Ph–H), 7.50 (d, J = 1 Hz, 4H, naphthyl-H), 7.3 (m, 2H, Ph–H, 2H, naphthyl-H), 7.66 (d, J = 9 Hz, 2H, naphthyl-H), 6.86 (d, J = 3 Hz, 2H, naphthyl-H), 6.83 (d, J = 3 Hz, 2H, naphthyl-H), 6.67–6.71 (m, 4H, naphthyl-H), 3.74 (s, 6H, O–CH₃). [α]_D²⁰: –120 deg cm² g⁻¹.

2.2.2. 2,2'-Bis(2-hydroxy-5-trifluoromethoxy benzylideneamino)-1,1'-naphthyl (L2)

The experimental procedure for the synthesis of L2 was carried out as described in the synthesis of [L1]. Pure yellow crystal ligand

was obtained with a yield of 93%. M.p.: 212 °C. Elemental Anal. (C, H and N, wt.%) Calc. for C₃₆H₂₂F₆N₂O₄ (L5): C, 65.46; H, 3.36; N, 4.24. Found: C, 64.84; H, 3.41; N, 4.19%. IR (KBr, cm⁻¹): 3500–3200, –OH; 3060, Ar–H; 1609, 1623, C–H(imine); 1574, C=C(Ar). ¹H NMR (400 MHz, CDCl₃, δ: ppm) 12.34 (s, 2H, OH), 8.74 (s, 2H, CH=N), 8.23 (d, J = 9 Hz, 2H, Ph–H), 8.08 (d, J = 8 Hz, 2H, Ph–H), 7.76 (d, J = 9 Hz, 2H, naphthyl-H), 7.57 (t, J = 15 Hz, 2H, naphthyl-H), 7.41 (m, 4H, naphthyl-H), 7.21 (s, 2H, Ph–H), 7.19 (d, J = 10 Hz, naphthyl-H), 6.78 (d, J = 9 Hz, 2H, naphthyl-H).

2.3. Synthesis of salen–Mn(III) complexes

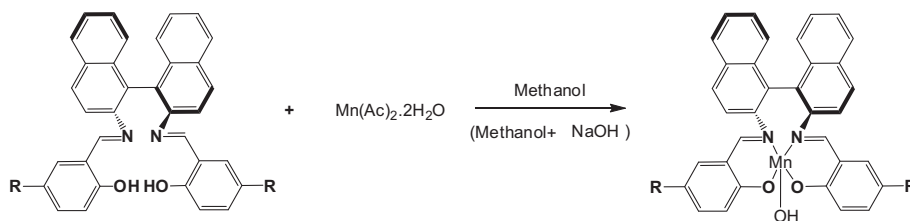
The general preparation of all complexes, began by dissolving an appropriate amount of Schiff base ligands (0.41 mmol) in 20 ml of absolute methanol. Then 1.5 ml of sodium methoxide and Mn(Ac)₂·2.5H₂O (140 mg, 0.81 mmol) was added. The resulting mixture was refluxed for 3 h. At the same time, air was pumped into the reaction via an aquarium air pump for 10–15 s every 5 min until the reaction of the complex was completed (checked by TLC). After the procedure, the amount of methanol was decreased by 10 ml and cooled to room temperature. The dark brown precipitate was filtered and then dried under vacuum.

2.3.1. 2,2'-Bis(2-hydroxy-5-methoxy benzylideneamino)-1,1'-naphthyl (III) complex (L1Mn)

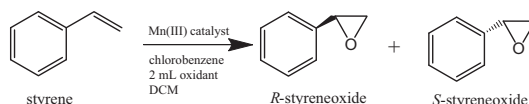
Complex L1Mn (C₃₆H₂₇MnN₂O₅), was prepared as described in the above procedure. Yield% 86, m.p.: 372 °C. Elemental Anal. Calc. (C, H and N, wt.%) C, 69.45; H, 4.37; N, 4.50. Found: C, 57.93; H, 4.28; N, 3.41%. IR (KBr, ν = cm⁻¹): 3418 –OH; 3050 Ar–H, 2925 C–H, 1618, 1603 C=N; 1571, 1550 C=C (Ar). LC/MS (Agilent 1100 MSD) (m/s): 622.00 (M⁺), 605.10 (M⁺–OH), 553.20 (M⁺–OH, Mn), 419.20 (73.8), 285.10 (100), 143.10 (22.8). UV–Vis: λ, nm, CH₂Cl₂: 295.0 (max); ε₂₉₅: 2.85 × 10⁵.

2.3.2. 2,2'-Bis(2-hydroxy-5-trifluoro methoxy benzylideneamino)-1,1'-naphthyl Mn(III) complex (L2Mn)

Complex L2Mn (C₃₆H₂₁F₆MnN₂O₅), was prepared as described in the above procedure. Yield% 82, m.p.: 418 °C. Elemental Anal. Calc. (C, H and N, wt.%) C, 59.19; H, 2.90; N, 3.83; Found: C, 59.45; H, 3.30; N, 3.81%. IR (KBr, ν = cm⁻¹): 3061 Ar–H; 1617, 1602 C=N; 1540 C=C (Ar). LC/MS (Agilent 1100 MSD) (m/s): 729.00 (M⁺), 713.00 (M⁺–OH), 661.10 (M⁺–OH, Mn), 473.10. UV–Vis: λ, nm, CH₂Cl₂: 293.58(max), 425.07; ε₂₉₃: 1.3 × 10⁴.



Scheme 2.2. Synthesis reaction of Mn(III) complexes.



Scheme 2.3. Conversion of styrene to R-styreneoxide and S-styreneoxide.

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