

# Synthesis and Characterization of New Chiral Schiff Base Complexes with Diiminobinaphthyl or Diiminocyclohexyl Moieties as Potential Enantioselective Epoxidation Catalysts

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New chiral Schiff base complexes have been obtained by condensation of 2,2'-diamino-1,1'-binaphthalene or 1,2-diaminocyclohexane and various salicylaldehydes and by subsequent metalation with manganese, iron, cobalt, nickel, copper, or zinc. The complete <sup>1</sup>H and <sup>13</sup>C NMR characterization of the ligands is reported, as are the X-ray crystal structures of (1*R*,2*R*)-(–)-*N,N'*-bis[3-(*N,N*-dimethylamino)salicylidene]-*trans*-1,2-cyclohexanediimine and [(1*R*,2*R*)-(–)-*N,N'*-bis(salicylidene)-*trans*-1,2-cyclohexanediiminato]copper(II). The new chiral manganese complexes have been evaluated in the oxygenation of prochiral olefins and sulfides using sodium hypochlorite, hydrogen peroxide, or *N*-methylmorpholine *N*-oxide/*m*-chloroperbenzoic acid as oxidant.

## Introduction

Enantiomerically pure epoxides play an eminent role as intermediates and building blocks in the synthesis of optically active compounds. Cytochrome P-450 enzymes represent a versatile class of biological oxidation catalysts<sup>1</sup> able to perform enantioselective epoxidation of prochiral olefins.<sup>2,3</sup> Due to the high efficiency of catalytic epoxidation systems using a synthetic metalloporphyrin and a single oxygen atom donor,<sup>4,5</sup> work has concentrated on the synthesis and catalytic activities of metalloporphyrins bearing chiral motifs.<sup>6–14</sup> In recent years, efficient enantioselective C–O bond formation has been performed by Sharpless *et al.* in the case of allylic alcohol epoxidation<sup>15,16</sup> and olefin dihydroxylation.<sup>17,18</sup>

Chiral Schiff base manganese complexes based on optically active 1,2-diamines (mainly 1,2-diaminocyclohexane) have been

used in the epoxidation of *cis*-disubstituted olefins,<sup>19,20a</sup> cyclic dienes,<sup>20b</sup> or polyenes.<sup>20c</sup> This family of catalysts was also recently found to be efficient for the enantioselective epoxidation of styrene<sup>21</sup> and hydroxylation at the allylic position of 1,2-dihydronaphthalene 1,2-oxide.<sup>22</sup> Katsuki *et al.* reported that the epoxidation of *cis*-disubstituted olefins or styrene derivatives was catalyzed by the manganese complexes of chiral Schiff bases containing four chiral centers.<sup>23</sup>

In order to improve the activity and the enantioselectivity of chiral manganese Schiff base complexes in the epoxidation of terminal olefins,<sup>24</sup> we have developed a new series of ligands<sup>25</sup> and metal complexes based on the optically active binaphthyl

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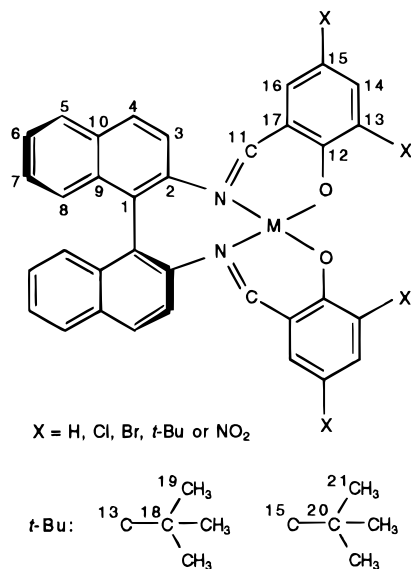
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## Free ligands:

<b>1-H<sub>2</sub></b> , H <sub>2</sub> Salbinapht	M = H <sub>2</sub>	X = H
<b>2-H<sub>2</sub></b> , H <sub>2</sub> Cl <sub>4</sub> Salbinapht	M = H <sub>2</sub>	X = Cl
<b>3-H<sub>2</sub></b> , H <sub>2</sub> Br <sub>4</sub> Salbinapht	M = H <sub>2</sub>	X = Br
<b>4-H<sub>2</sub></b> , H <sub>2</sub> <i>t</i> Bu <sub>4</sub> Salbinapht	M = H <sub>2</sub>	X = <i>t</i> -Bu
<b>5-H<sub>2</sub></b> , H <sub>2</sub> (NO <sub>2</sub> ) <sub>4</sub> Salbinapht	M = H <sub>2</sub>	X = NO <sub>2</sub>

## Metal complexes:

**1-Mn**, M = Mn, X = H; **2-Mn**, M = Mn, X = Cl; **3-Mn**, M = Mn, X = Br; **4-Mn**, M = Mn, X = *t*-Bu; **2-Ni**, M = Ni, X = Cl; **3-Ni**, M = Ni, X = Br; **2-Fe**, M = Fe, X = Cl; **2-Co**, M = Co, X = Cl; **2-Zn**, M = Zn, X = Cl; **2-Cu**, M = Cu, X = Cl; **3-Cu**, M = Cu, X = Br.



**Figure 1.** Structure of ligands and complexes based on binaphthyl as the chiral residue.

motif. These compounds were obtained by condensation of 1,1'-binaphthyl-2,2'-diamine with various substituted salicylaldehydes and consecutive metalation. In order to enlarge the availability of chiral binaphthyl-based complexes, the corresponding Mn, Fe, Co, Ni, Cu, and Zn compounds have been prepared.

In addition, we synthesized a new potential catalyst by condensation of 1,2-diaminocyclohexane with 4-(dimethylamino)-2-hydroxybenzaldehyde and subsequent metalation. By alkylation of the dimethylamino groups, the corresponding dicationic complexes could be used as oxidation catalysts either in an aqueous medium or in a heterogeneous medium after adsorption of the ammonium residues on an appropriate support.

In this article, the oxidation of 1,2-dihydronaphthalene, 4-chlorostyrene, and sulfides by H<sub>2</sub>O<sub>2</sub> and NaOCl, two readily available oxygen atom donors, catalyzed by several chiral manganese Schiff base complexes is reported.

## Experimental Section

**Synthesis of (S)-(+)-Schiff Base Ligands Based on a Binaphthyl Moiety.** The synthesis of ligands **1-H<sub>2</sub>**, **2-H<sub>2</sub>**, **3-H<sub>2</sub>**, and **4-H<sub>2</sub>** (for structures, see Figure 1) bearing a binaphthyl residue as a chiral motif was recently described in a preliminary communication.<sup>25</sup> **5-H<sub>2</sub>** was obtained as follows: To a stirred solution of 3,5-dinitrosalicylaldehyde (138 mg, 0.65 mmol) in 20 mL of absolute ethanol were added *S*-(-)-1,1'-binaphthyl-2,2'-diamine (92 mg, 0.32 mmol) and a large excess of sodium sulfate (50–70 mmol). The resulting suspension was heated at reflux for 24 h, and the solvent was evaporated *in vacuo*. The crude mixture was dissolved in dichloromethane, sodium sulfate was removed by filtration, and the pure deep orange ligand was obtained by evaporation to dryness (207 mg, 95% yield). [ $\alpha$ ]<sub>D</sub> = +1100 × 10<sup>-1</sup> deg cm<sup>2</sup> g<sup>-1</sup> (*c* = 0.95 × 10<sup>-3</sup>, acetone). Anal. Calcd for C<sub>34</sub>H<sub>20</sub>N<sub>6</sub>O<sub>10</sub>·0.2CH<sub>2</sub>Cl<sub>2</sub>: C, 59.57; H, 2.98; N, 12.19. Found: C, 59.52; H, 3.16; N, 12.08. MS (DCI/NH<sub>3</sub>) *m/z*: 673 (MH<sup>+</sup>, 100), 674 (44), 675 (11). IR (KBr):  $\nu_{C=N}$  = 1626 cm<sup>-1</sup>. UV-vis (dichloromethane): 234, 256, 324, 458 nm. The product was characterized by complete assignment of <sup>1</sup>H and <sup>13</sup>C NMR signals (see Table 1).

**Metalation of (S)-(+)-H<sub>2</sub>Cl<sub>4</sub>Salbinapht, 2-H<sub>2</sub>, and (S)-(+)-H<sub>2</sub>Br<sub>4</sub>Salbinapht, 3-H<sub>2</sub>.** **General Method.** To a solution of ligand **2-H<sub>2</sub>** or **3-H<sub>2</sub>** (0.20 mmol) with sodium methoxide (54 mg, 1 mmol) under nitrogen in absolute ethanol (20 mL) was added the appropriate metal(II) salt MX<sub>2</sub> (1.2–5 equiv), and the resulting solution was heated at reflux for 6 h. After cooling, water was added to precipitate the complex, which was washed with further water and ethanol. The resulting solid was dried *in vacuo* or recrystallized as indicated.

**2-Mn, (S)-(+)-Mn<sup>III</sup>(OH)Cl<sub>4</sub>Salbinapht.** MX<sub>2</sub> used for metalation = Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O. Product recrystallized from dichloromethane/hexane (106 mg, 76% yield). [ $\alpha$ ]<sub>D</sub> = +510 × 10<sup>-1</sup> deg cm<sup>2</sup> g<sup>-1</sup> (*c* = 0.10 × 10<sup>-3</sup>, acetone). Anal. Calcd for C<sub>34</sub>H<sub>18</sub>Cl<sub>4</sub>N<sub>2</sub>O<sub>2</sub>Mn(OH): C, 58.32; H, 2.73; N, 4.00. Found: C, 60.43; H, 3.19; N, 4.06. MS (DCI/NH<sub>3</sub>) *m/z*: 699 (75), 700 (33), 701 (MH<sup>+</sup>, 100), 702 (41), 603 (50), 704 (19), 705 (13). IR (KBr):  $\nu_{C=N}$  = 1609 cm<sup>-1</sup>. UV-vis (dichloromethane): 232, 276, 326, 380 nm.

**Table 1.** <sup>1</sup>H and <sup>13</sup>C NMR Data for Binaphthyl-Based Ligands and a Zinc Complex<sup>a</sup>

	<sup>1</sup> H chemical shifts						<sup>13</sup> C chemical shifts					
	<b>1-H<sub>2</sub></b>	<b>2-H<sub>2</sub></b>	<b>3-H<sub>2</sub></b>	<b>4-H<sub>2</sub></b>	<b>5-H<sub>2</sub></b>	<b>2-Zn</b>	<b>1-H<sub>2</sub></b>	<b>2-H<sub>2</sub></b>	<b>3-H<sub>2</sub></b>	<b>4-H<sub>2</sub><sup>c</sup></b>	<b>5-H<sub>2</sub></b>	<b>2-Zn</b>
1 <sup>b</sup>							129.93	130.22	130.10	129.53	127.39	125.61
2							144.09	143.04	143.08	144.47	137.92	145.30
3	7.91	7.97	7.96	7.88	8.27	7.61	117.44	117.24	117.38	117.82	116.65	122.11
4	8.22	8.28	8.26	8.20	8.47	8.18	130.25	130.70	130.70	130.11	132.28	130.93
5	8.06	8.10	8.10	8.04	8.18	8.02	128.60	128.74	128.73	128.56	129.14	128.72
6	7.49	7.54	7.53	7.44	7.63	7.48	126.13	126.73	126.71	125.90	127.93	126.09
7	7.32	7.36	7.35	7.30	7.43	7.29	127.15	127.53	127.52	127.09	128.54	127.35
8	7.19	7.17	7.16	7.28	7.21	6.95	126.28	126.35	126.35	126.48	126.29	126.37
9							133.45	133.30	133.30	133.63	133.00	133.42
10							133.03	133.38	133.37	132.99	133.99	132.48
11	8.98	9.08	9.04	8.97	9.63	8.64	163.05	161.95	161.91	164.20	162.16	170.43
12							161.09	155.74	157.08	158.34	165.97	164.55
13	6.60						116.77	121.97	111.31	140.25	139.83	127.68
14	7.22	7.41	7.67	7.36	8.65	7.41	133.14	132.32	137.76	127.68	125.85	133.78
15	6.81						118.87	122.85	109.77	136.33	135.01	116.76
16	7.42	7.52	7.69	7.28	8.70	7.26	132.86	130.70	134.39	127.35	134.54	133.59
OH	12.18	13.08	13.21	13.04	15.86							
17							119.65	121.08	121.54	118.80	119.13	120.01

<sup>a</sup> Chemical shifts (ppm) vs TMS. Solvent: acetone-*d*<sub>6</sub>. <sup>b</sup> For the labeling of C and H positions, see Figure 1. <sup>c</sup>  $\delta$ : 131.86 [18-C(CH<sub>3</sub>)<sub>3</sub>], 29.12 (19-CH<sub>3</sub>), 128.80 [20-C(CH<sub>3</sub>)<sub>3</sub>], 31.19 (21-CH<sub>3</sub>).

**2-Fe, S(-)-Fe<sup>III</sup>(OH)Cl<sub>4</sub>Salbinaphth.** MX<sub>2</sub> = (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O. Precipitate dried *in vacuo* (119 mg, 85% yield). [α]<sub>D</sub><sup>25</sup> = -1078 × 10<sup>-1</sup> deg cm<sup>2</sup> g<sup>-1</sup> (c = 0.09 × 10<sup>-3</sup>, acetone). Anal. Calcd for C<sub>34</sub>H<sub>18</sub>Cl<sub>4</sub>N<sub>2</sub>O<sub>2</sub>Fe(OH): C, 58.24; H, 2.73; N, 4.00. Found: C, 59.59; H, 2.97; N, 4.00. MS (DCI/NH<sub>3</sub>) m/z: 700 (73), 701 (33), 702 (MH<sup>+</sup>, 100), 703 (41), 704 (48), 705 (20), 706 (13). IR (KBr): ν<sub>C=N</sub> = 1605 cm<sup>-1</sup>. UV-vis (dichloromethane): 234, 270, 358 nm.

**2-Co, (S)-(+)-Co<sup>III</sup>Cl<sub>4</sub>Salbinaphth.** MX<sub>2</sub> = Co(OAc)<sub>2</sub>·4H<sub>2</sub>O. Precipitate dried *in vacuo* (113 mg, 82% yield). [α]<sub>D</sub><sup>25</sup> = +93 × 10<sup>-1</sup> deg cm<sup>2</sup> g<sup>-1</sup> (c = 0.13 × 10<sup>-3</sup>, acetone). Anal. Calcd for C<sub>34</sub>H<sub>18</sub>Cl<sub>4</sub>N<sub>2</sub>O<sub>2</sub>Co: C, 59.42; H, 2.64; N, 4.08. Found: C, 59.57; H, 2.63; N, 4.15. MS (DCI/NH<sub>3</sub>) m/z: 703 (74), 704 (30), 705 (MNH<sub>4</sub><sup>+</sup>, 100), 706 (38), 707 (74), 708 (30), 709 (13). IR (KBr): ν<sub>C=N</sub> = 1602 cm<sup>-1</sup>. UV-vis (dichloromethane): 234, 280, 390 nm.

**2-Ni, (S)-(+)-Ni<sup>II</sup>Cl<sub>4</sub>Salbinaphth.** MX<sub>2</sub> = Ni(OAc)<sub>2</sub>·2H<sub>2</sub>O. Product recrystallized from dichloromethane/hexane (84 mg, 62% yield). [α]<sub>D</sub><sup>25</sup> = +74 × 10<sup>-1</sup> deg cm<sup>2</sup> g<sup>-1</sup> (1.21 × 10<sup>-3</sup>, acetone). Anal. Calcd for C<sub>34</sub>H<sub>18</sub>Cl<sub>4</sub>N<sub>2</sub>O<sub>2</sub>Ni·0.5 H<sub>2</sub>O: C, 58.67; H, 2.75; N, 4.03. Found: C, 58.37; H, 3.13; N, 3.93. MS (DCI/NH<sub>3</sub>) m/z: 685 (63), 686 (30), 687 (MH<sup>+</sup>, 100), 688 (40), 689 (85), 690 (33), 691 (36), 692 (13), 693 (9). IR (KBr): ν<sub>C=N</sub> = 1607 cm<sup>-1</sup>. UV-vis (dichloromethane): 278, 326 nm. <sup>1</sup>H NMR (acetone-d<sub>6</sub>, 400 MHz): δ 31.05, 20.2, 13.8, 12.33, 10.91, 3.70, 2.7, 0.24, -1.3 (9 × 1H).

**2-Zn, (S)-(+)-Zn<sup>II</sup>Cl<sub>4</sub>Salbinaphth.** MX<sub>2</sub> = Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O. Precipitate dried *in vacuo* (104 mg, 76% yield). [α]<sub>D</sub><sup>25</sup> = +627 × 10<sup>-1</sup> deg cm<sup>2</sup> g<sup>-1</sup> (c = 0.14 × 10<sup>-3</sup>, acetone). Anal. Calcd for C<sub>34</sub>H<sub>18</sub>Cl<sub>4</sub>N<sub>2</sub>O<sub>2</sub>Zn·0.5 H<sub>2</sub>O: C, 58.11; H, 2.73; N, 3.99. Found: C, 58.00; H, 2.96; N, 4.18. MS (DCI/NH<sub>3</sub>) m/z: 691 (51), 692 (31), 693 (MH<sup>+</sup>, 100), 694 (54), 695 (100), 696 (49), 697 (61), 698 (27), 699 (22), 700 (9). IR (KBr): ν<sub>C=N</sub> = 1607 cm<sup>-1</sup>. UV-vis (dichloromethane): 236, 282, 332, 398 nm. For <sup>1</sup>H and <sup>13</sup>C NMR analysis, see Table 1.

**2-Cu, S(-)-Cu<sup>II</sup>Cl<sub>4</sub>Salbinaphth.** MX<sub>2</sub> = CuCl<sub>2</sub>. Product was recrystallized from dichloromethane/hexane (32 mg, 25% yield). [α]<sub>D</sub><sup>25</sup> = -111 × 10<sup>-1</sup> deg cm<sup>2</sup> g<sup>-1</sup> (c = 45 × 10<sup>-3</sup>, acetone). Anal. Calcd for C<sub>34</sub>H<sub>18</sub>Cl<sub>4</sub>N<sub>2</sub>O<sub>2</sub>Cu: C, 59.02; H, 2.62; N, 4.05. Found: C, 59.03; H, 2.62; N, 4.05. MS (DCI/NH<sub>3</sub>) m/z: 692 (MH<sup>+</sup>). IR (KBr): ν<sub>C=N</sub> = 1605 cm<sup>-1</sup>. UV-vis (dichloromethane): 280, 314, 328, 374, 398, 440 nm.

**3-Mn, (S)-(+)-Mn<sup>III</sup>(OH)Br<sub>4</sub>Salbinaphth.** MX<sub>2</sub> = Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O. Product recrystallized from dichloromethane/hexane (136 mg, 75% yield). [α]<sub>D</sub><sup>25</sup> = +477 × 10<sup>-1</sup> deg cm<sup>2</sup> g<sup>-1</sup> (c = 0.10 × 10<sup>-3</sup>, acetone). Anal. Calcd for C<sub>34</sub>H<sub>18</sub>Br<sub>4</sub>N<sub>2</sub>O<sub>2</sub>Mn(OH): C, 46.51; H, 2.18; N, 3.19. Found: C, 46.52; H, 2.30; N, 3.05. MS (DCI/NH<sub>3</sub>) m/z: 877 (38), 878 (15), 879 (MH<sup>+</sup>, 59), 880 (26), 881 (42), 882 (14). IR (KBr): ν<sub>C=N</sub> = 1605 cm<sup>-1</sup>. UV-vis (dichloromethane): 234, 280 nm.

**3-Ni, (S)-(+)-Ni<sup>II</sup>Br<sub>4</sub>Salbinaphth.** MX<sub>2</sub> = Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O. Product recrystallized from dichloromethane/hexane mixture (160 mg, 93% yield). [α]<sub>D</sub><sup>25</sup> = +45 × 10<sup>-1</sup> deg cm<sup>2</sup> g<sup>-1</sup> (c = 1.15 × 10<sup>-3</sup>, acetone). Anal. Calcd for C<sub>34</sub>H<sub>18</sub>Br<sub>4</sub>N<sub>2</sub>O<sub>2</sub>Ni·2H<sub>2</sub>O: C, 45.33; H, 2.46; N, 3.11. Found: C, 45.24; H, 2.36; N, 3.07. MS (DCI/NH<sub>3</sub>) m/z: 861 (11), 862 (9), 863 (56), 865 (MH<sup>+</sup>, 100), 866 (44), 867 (88), 868 (37), 869 (42), 870 (15), 871 (11). IR (KBr): ν<sub>C=N</sub> = 1607 cm<sup>-1</sup>. UV-vis (dichloromethane): 230, 270 nm.

**3-Cu, (S)-(+)-Cu<sup>II</sup>Br<sub>4</sub>Salbinaphth.** MX<sub>2</sub> = CuCl<sub>2</sub>. Product was recrystallized from dichloromethane (45 mg, 26% yield). [α]<sub>D</sub><sup>25</sup> = +960 × 10<sup>-1</sup> deg cm<sup>2</sup> g<sup>-1</sup> (c = 50 × 10<sup>-3</sup>, dichloromethane). Anal. Calcd for C<sub>34</sub>H<sub>18</sub>Br<sub>4</sub>N<sub>2</sub>O<sub>2</sub>Cu: C, 46.96; H, 2.09; N, 3.22. Found: C, 46.97; H, 2.07; N, 3.04. MS (DCI/NH<sub>3</sub>) m/z: 807 (62), 808 (25), 809 (M<sup>+</sup> - Cu, 82), 810 (32), 811 (59), 812 (24), 810 (MH<sup>+</sup>, 26), 872 (24), 887 (MNH<sub>4</sub><sup>+</sup>, 30), 889 (25). IR (KBr): ν<sub>C=N</sub> = 1630 cm<sup>-1</sup>. UV-vis (dichloromethane): 280, 324, 378, 444 nm.

**Metalation of (S)-(+)-H<sub>2</sub>Salbinaphth, 1-H<sub>2</sub>, by Manganese.** To a stirred solution of the free-base ligand (400 mg, 0.81 mmol) under nitrogen in the presence of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN, 5 equiv) in dry dimethylformamide (30 mL) at 120 °C was added dimanganese decacarbonyl (2 equiv). The resulting mixture was stirred for 6 h. After cooling, water was added to precipitate the complex. The solid was filtered off, washed with cold water and ethanol, and dissolved in dichloromethane. The solution was filtered, and the solvent was removed *in vacuo*. The manganese complex S(-)-Mn<sup>III</sup>(OH)-Salbinaphth, **1-Mn**, was recrystallized from a mixture of dichloromethane and hexane (339 mg, 76% yield). [α]<sub>D</sub><sup>25</sup> = -88 × 10<sup>-1</sup> deg cm<sup>2</sup> g<sup>-1</sup> (c =

0.49 × 10<sup>-3</sup>, acetone). Anal. Calcd for C<sub>34</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>Mn(OH)·1.5DMF·0.5CH<sub>2</sub>Cl<sub>2</sub>: C, 65.55; H, 4.87; N, 6.86. Found: C, 65.01; H, 4.77; N, 6.25. MS (DCI/NH<sub>3</sub>) m/z: 546 [(M - OH)H<sup>+</sup>]. IR (KBr): ν<sub>C=N</sub> = 1610 cm<sup>-1</sup>. UV-vis (dichloromethane): 230, 276 nm.

**Metalation of (S)-(+)-H<sub>2</sub>Bu<sub>4</sub>Salbinaphth, 4-H<sub>2</sub>, by Manganese.** To a stirred solution of the free-base ligand (80 mg, 0.11 mmol) under nitrogen in the presence of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN, 5 equiv) in dry dimethylformamide (7 mL) at 120 °C was added dimanganese decacarbonyl (2 equiv). The resulting mixture was stirred for 6 h. After cooling, water was added to precipitate the complex. The solid was filtered off, washed with cold water and ethanol, and dissolved in dichloromethane. The solution was filtered, and the solvent was removed *in vacuo* (84 mg, 99% yield). [α]<sub>D</sub><sup>25</sup> = +462 × 10<sup>-1</sup> deg cm<sup>2</sup> g<sup>-1</sup> (c = 0.11 × 10<sup>-3</sup>, acetone). Anal. Calcd for C<sub>50</sub>H<sub>54</sub>N<sub>2</sub>O<sub>2</sub>Mn(OH)·1.5DMF: C, 73.01; H, 7.36; N, 5.47. Found: C, 73.01; H, 7.86; N, 5.03. MS (DCI/NH<sub>3</sub>) m/z: 770 [(M - OH)H<sup>+</sup>]. IR (KBr): ν<sub>C=N</sub> = 1610 cm<sup>-1</sup>. UV-vis (dichloromethane): 232, 278 nm.

**Synthesis of (1R,2R)-(-)-H<sub>2</sub>NMe<sub>2</sub>C<sub>6</sub>Salen, 6-H<sub>2</sub>.** To a stirred solution of 4-(dimethylamino)-2-hydroxybenzaldehyde (obtained by addition of Vilsmeier reagent to 3-(dimethylamino)phenol<sup>26</sup>) (730 mg, 4.42 mmol) in ethanol (8 mL) was added (1R,2R)-(-)-trans-1,2-diaminocyclohexane (250 mg, 2.19 mmol), and the resulting solution was heated at reflux for 4 h. The reaction was stopped by addition of water (5 mL), resulting in the precipitation of a pale brown solid. The precipitate was filtered off, washed with water (10 mL) and hexane (10 mL), dissolved in dichloromethane (15 mL), dried with anhydrous sodium sulfate, filtered off, and then recrystallized over 48 h by addition of hexane (20 mL) to the dichloromethane solution to yield yellow rhombic crystals of the title compound (404 mg, 45% yield); mp 171–171.8 °C. [α]<sub>D</sub><sup>25</sup> = -1237 × 10<sup>-1</sup> deg cm<sup>2</sup> g<sup>-1</sup> (c = 135 × 10<sup>-3</sup>, dichloromethane). Anal. Calcd for C<sub>24</sub>H<sub>32</sub>N<sub>4</sub>O<sub>2</sub>: C, 70.56; H, 7.90; N, 13.71. Found: C, 70.66; H, 8.20; N, 13.71. MS (DCI/NH<sub>3</sub>) m/z: 409 (MH<sup>+</sup>). IR (KBr): 1645, 1622 cm<sup>-1</sup>. UV-vis (acetonitrile): 328, 338 nm. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz): δ 1.4–1.95 (8H, 4 × m, cycl-CH<sub>2</sub>), 2.93 (12H, s, 2 × N(CH<sub>3</sub>)<sub>2</sub>), 3.15 (2H, ddd, J = 9.8, 2.2 and 1.4 Hz, 1-H and 2-H), 6.03 (2H, d, J = 2.5 Hz, 9-H), 6.08 (2H, dd, J = 8.6 and 2.5 Hz, 11-H), 6.89 (2H, d, J = 8.6 Hz, 12-H), 7.95 (2H, s, 7-H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 62.8 MHz): δ 24.5 (4-C and 5-C), 33.3 (3-C and 6-C), 39.9 (14-C and 15-C), 71.6 (1-C and 2-C), 98.5 (9-C), 103.3 (11-C), 108.9 (13-C), 132.4 (12-C), 153.6 (8-C), 163.3 (7-C), 164.1 (10-C).

**Metalation of (1R,2R)-(-)-H<sub>2</sub>NMe<sub>2</sub>C<sub>6</sub>Salen, 6-H<sub>2</sub>. General Method.** To a solution of **6-H<sub>2</sub>** (108 mg, 0.26 mmol for metalation with Mn; 54 mg, 0.13 mmol in other cases) in dimethylformamide (3 mL) was added the appropriate metal(II) salt MX<sub>2</sub> (0.52 mmol for M = Mn; 0.26 mmol for M = Ni, Fe, Cu), and the resulting solution was heated at reflux for 3 h. Water (5 mL) was added to precipitate the complex, which was washed with further water (2 × 15 mL) and hexane (2 × 15 mL). The precipitate was dissolved in dichloromethane and dried. The title compound was recovered by evaporation of the solvent *in vacuo* or recrystallization as indicated.

**6-Mn, (1R,2R)-(-)-Mn<sup>III</sup>(Cl)NMe<sub>2</sub>C<sub>6</sub>Salen.** MX<sub>2</sub> = MnCl<sub>2</sub>·4H<sub>2</sub>O. Product dried *in vacuo* (45 mg, 30% yield). [α]<sub>D</sub><sup>25</sup> = -2666 × 10<sup>-1</sup> deg cm<sup>2</sup> g<sup>-1</sup> (c = 12 × 10<sup>-3</sup>, dichloromethane). Anal. Calcd for C<sub>24</sub>H<sub>30</sub>N<sub>4</sub>O<sub>2</sub>Mn(Cl)·CH<sub>2</sub>Cl<sub>2</sub>: C, 51.61; H, 5.54; N, 9.63. Found: C, 52.06; H, 5.36; N, 10.08. MS (FAB) m/z: 461 [(M - Cl)<sup>+</sup>]. IR (KBr): 1618, 1581, 1307, 1154 cm<sup>-1</sup>. UV-vis (acetonitrile): 322 nm.

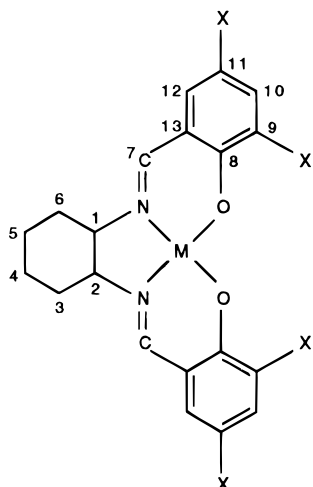
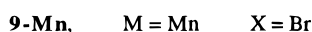
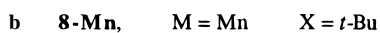
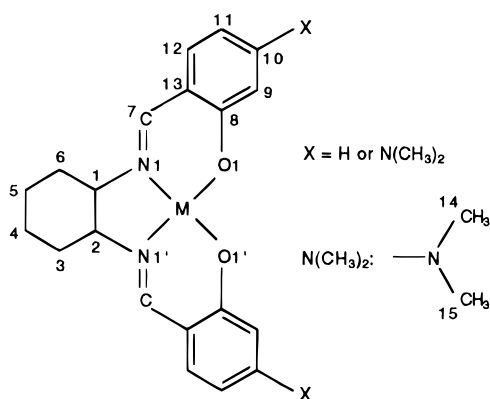
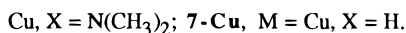
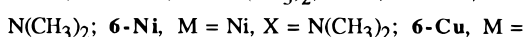
**6-Ni, (1R,2R)-(-)-Ni<sup>II</sup>NMe<sub>2</sub>C<sub>6</sub>Salen.** MX<sub>2</sub> = Ni(OAc)<sub>2</sub>·2H<sub>2</sub>O. Product recrystallized from dichloromethane (48 mg, 76% yield). [α]<sub>D</sub><sup>25</sup> = -760 × 10<sup>-1</sup> deg cm<sup>2</sup> g<sup>-1</sup> (c = 4.6 × 10<sup>-3</sup>, dichloromethane). Anal. Calcd for C<sub>24</sub>H<sub>30</sub>N<sub>4</sub>O<sub>2</sub>Ni·0.5CH<sub>2</sub>Cl<sub>2</sub>: C, 57.96; H, 6.15; N, 11.04. Found: C, 58.34; H, 6.14; N, 11.13. MS (DCI/NH<sub>3</sub>) m/z: 465 (MH<sup>+</sup>, 100), 466 (29), 467 (41). IR (KBr): 1599, 1517, 1366, 1154 cm<sup>-1</sup>. UV-vis (acetonitrile): 258, 316, 352, 394 nm. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz): δ 1.28 (4H, m, cycl-CH<sub>2</sub> axials), 1.85 (2H, m, 4-CH<sub>2</sub> and 5-CH<sub>2</sub> equatorials), 2.38 (2H, m, 3-CH<sub>2</sub> and 6-CH<sub>2</sub> equatorials), 2.96 (12H, s, 2 × N(CH<sub>3</sub>)<sub>2</sub>), 2.93 (2H, m, 1-H and 2-H), 6.05 (2H, d, J = 2.5 Hz, 9-H), 6.09 (2H, dd, J = 8.2 and 2.5 Hz, 11-H), 6.96 (2H, d, J = 8.2 Hz, 12-H), 7.18 (2H, s, 7-H). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100

(26) *Reagents for Organic Synthesis*; Fieser, L. F., Fieser, M., Eds.; John Wiley: New York, 1967; Vol. 1, p 284.

## a Free ligand:



Metal complexes:



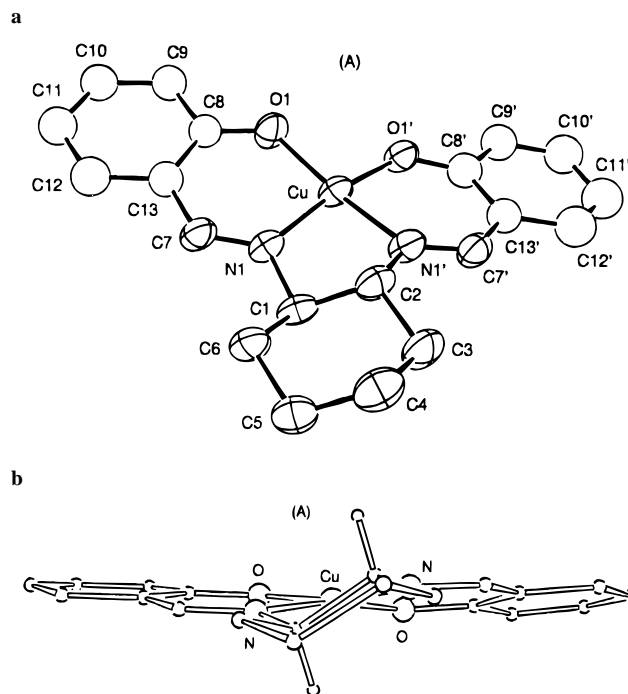
**Figure 2.** (a) Structure of ligands and complexes based on cyclohexyl as the chiral residue. (b) The two manganese catalysts used in comparative epoxidation studies.

MHz):  $\delta$  23.9 (4-C and 5-C), 28.0 (3-C and 6-C), 39.2 (14-C and 15-C), 69.1 (1-C and 2-C), 99.4 (9-C), 101.9 (11-C), 111.0 (13-C), 132.9 (12-C), 154.1 (10-C), 154.2 (7-C), 165.0 (8-C).

**6-Fe**, (1*R*,2*R*)-(-)-Fe<sup>III</sup>(OH)NMe<sub>2</sub>C<sub>6</sub>Salen. MX<sub>2</sub> = (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O. Product dried *in vacuo* from dichloromethane solution (25 mg, 38% yield).  $[\alpha]_D^{25} = -408 \times 10^{-1} \text{ deg cm}^2 \text{ g}^{-1}$  ( $c = 12 \times 10^{-3}$ , dichloromethane). Anal. Calcd for C<sub>24</sub>H<sub>30</sub>N<sub>4</sub>O<sub>2</sub>Fe(OH)·0.5CH<sub>2</sub>Cl<sub>2</sub>·0.5C<sub>6</sub>H<sub>14</sub>: C, 58.47; H, 6.96; N, 9.92. Found: C, 58.53; H, 6.23; N, 9.44. MS (FAB)  $m/z$ : 461 (31), 462 [(M - OH)<sup>+</sup>, 100], 463 (31). IR (KBr): 1638, 1602, 1523 cm<sup>-1</sup>. UV-vis (acetonitrile): 340 nm.

**6-Cu**, (1*R*,2*R*)-(-)-Cu<sup>II</sup>NMe<sub>2</sub>C<sub>6</sub>Salen. MX<sub>2</sub> = Cu(OTf)<sub>2</sub>·6H<sub>2</sub>O. Product recrystallized from dichloromethane (25 mg, 35% yield).  $[\alpha]_D^{25} = -667 \times 10^{-1} \text{ deg cm}^2 \text{ g}^{-1}$  ( $c = 2 \times 10^{-3}$ , dichloromethane). Anal. Calcd for C<sub>24</sub>H<sub>30</sub>N<sub>4</sub>O<sub>2</sub>Cu·CH<sub>2</sub>Cl<sub>2</sub>: C, 54.10; H, 5.81; N, 10.09. Found: C, 54.02; H, 5.91; N, 10.45. MS (FAB)  $m/z$ : 468 (42), 469 (63), 470 (MH<sup>+</sup>, 100), 471 (51), 472 (40). IR (KBr):  $\nu_{\text{C=N}} = 1596 \text{ cm}^{-1}$ . UV-vis (acetonitrile): 278, 346, 376<sub>sh</sub> nm.

**Synthesis of (1*R*,2*R*)-(-)-Cu<sup>II</sup>C<sub>6</sub>Salen, 7-Cu.** To a stirred solution of salicylaldehyde (122 mg, 1 mmol) in ethanol (10 mL) at 60 °C were sequentially added copper chloride (67 mg, 0.5 mmol) and (1*R*,2*R*)-(-)-*trans*-1,2-diaminocyclohexane (62 mg, 0.5 mmol). The resulting



**Figure 3.** (a) ORTEP plot of molecule A of the chiral Schiff base complex (1*R*,2*R*)-(-)-7-Cu. (b) Near-planar geometry of the chiral Schiff base complex (1*R*,2*R*)-(-)-7-Cu (molecule A).

mixture was stirred for 10 min, and then 1 M NaOH in water (1 mL) was added, resulting in the precipitation of a fibrous purple solid. The solid was filtered off, washed with water (2 × 10 mL) and hexane (2 × 10 mL), and dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The solution was filtered, and the solvent was removed *in vacuo*. Recrystallization of the complex from CH<sub>2</sub>Cl<sub>2</sub> over 3 days resulted in dark purple crystals (76 mg, 40% yield).  $[\alpha]_D^{25} = -612 \times 10^{-1} \text{ deg cm}^2 \text{ g}^{-1}$  ( $c = 2.5 \times 10^{-3}$ , dichloromethane). Anal. Calcd for C<sub>20</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>Cu·0.1CH<sub>2</sub>Cl<sub>2</sub>: C, 61.52; H, 5.19; N, 7.14. Found: C, 61.37; H, 5.18; N, 7.07. MS (DCI/NH<sub>3</sub>)  $m/z$ : 384 (MH<sup>+</sup>, 100), 385 (27), 386 (50), 387 (12), 401 (MNH<sub>4</sub><sup>+</sup>, 16). IR (KBr): 1631, 1601, 1537, 1446, 1323, 1148 cm<sup>-1</sup>. UV-vis (acetonitrile): 272, 358 nm.

**Collection and Reduction of X-ray Data for 7-Cu and 6-H<sub>2</sub>.** A dark purple crystal of CuC<sub>6</sub>Salen, 7-Cu (0.50 × 0.30 × 0.20 mm), was glued on a glass fiber. A yellow crystal of H<sub>2</sub>NMe<sub>2</sub>C<sub>6</sub>Salen, 6-H<sub>2</sub> (0.40 × 0.40 × 0.30 mm), was mounted in a similar way. The crystals were then transferred to a CAD4 diffractometer. Lattice parameters of the two compounds were obtained from a least-squares analysis of 25 carefully centered reflections with 12° < θ < 18°. The data were collected at ambient temperature using the ω-2θ scan technique at variable rates: 7495 unique reflections were collected for 7-Cu up to 27° ( $h$  -14, 14;  $k$  -16, 16;  $l$  0, 15) and 6814 reflections for 6-H<sub>2</sub> up to 23° ( $h$  -25, 25;  $k$  -10, 10;  $l$  0, 12) of which 6444 were unique ( $R_{\text{av}} = 0.010$  on  $I$ ).

Decay corrections were based on the measured intensities of three reflections monitored periodically throughout the course of the data collections; a slight linear decay of 5.9% was observed for 6-H<sub>2</sub>. The data were corrected for Lorentz and polarization effects using the MolEN package.<sup>27</sup> Empirical absorption corrections<sup>28</sup> were applied to 7-Cu using  $\psi$ -scan data ( $T_{\text{min,max}} = 0.790, 1.000$ ).

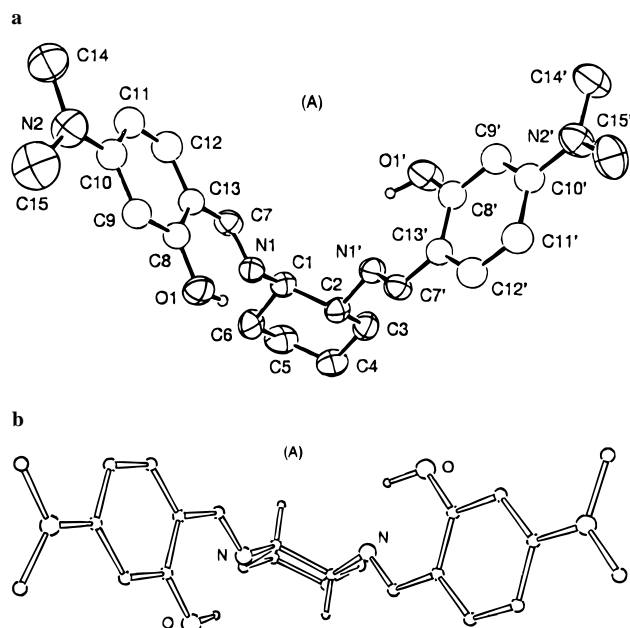
**Structure Solution and Refinement.** The structures were solved by direct methods with SHELXS-86<sup>29</sup> and refined on  $F_o^2$  with SHELXL-93<sup>30</sup> programs. The atomic scattering factors, including

(27) Fair, C. K. *MolEN. Structure Solution Procedures*; Enraf-Nonius: Delft, The Netherlands, 1990.

(28) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *A21*, 351-359.

(29) Sheldrick, G. M. *SHELXS-86. Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1986.

(30) Sheldrick, G. M. *SHELXL-93. Program for the Refinement of Crystal Structures from Diffraction Data*; University of Göttingen: Göttingen, Germany, 1993.



**Figure 4.** (a) ORTEP plot of molecule A of the chiral Schiff base complex (1*R*,2*R*)-(-)-**6-H<sub>2</sub>**. (b) Open-armed geometry of the chiral Schiff base complex (1*R*,2*R*)-(-)-**6-H<sub>2</sub>** (molecule A).

**Table 2.** Crystallographic Data for CuC<sub>6</sub>Salen, **7-Cu**, and H<sub>2</sub>NMe<sub>2</sub>Salen, **6-H<sub>2</sub>**

	<b>7-Cu</b>	<b>6-H<sub>2</sub></b>
empirical formula	C <sub>20</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> Cu	C <sub>24</sub> H <sub>32</sub> N <sub>4</sub> O <sub>2</sub>
fw	383.92	408.54
temp, °C	20	20
space group	<i>P</i> 2 <sub>1</sub> (No. 4)	<i>P</i> 2 <sub>1</sub> (No. 4)
<i>a</i> , Å	11.066(1)	22.747(3)
<i>b</i> , Å	12.650(2)	9.476(1)
<i>c</i> , Å	12.350(2)	10.943(1)
$\beta$ , deg	95.81(1)	99.46(1)
<i>V</i> , Å <sup>3</sup>	1719.9(5)	2326.7(5)
<i>Z</i>	4	4
$\lambda$ (Mo K $\alpha$ ), Å	0.710 73	0.710 73
$\rho_{\text{calc}}$ , g cm <sup>-3</sup>	1.483	1.166
$\mu$ , mm <sup>-1</sup>	1.285	0.07
<i>R</i> <sup>a</sup> (obs, all)	0.038, 0.089	0.040, 0.076
<i>R<sub>w</sub></i> <sup>b</sup> (obs, all)	0.085, 0.095	0.104, 0.115

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum w(F_o^2 - F_c^2)^2 - \sum w(F_o^2)^2]^{1/2}.$$

anomalous dispersion, were taken from a standard compilation.<sup>31</sup> Both structures crystallized in space group *P*2<sub>1</sub> with two independent molecules in the asymmetric unit. All non-hydrogen atoms, except phenyl C atoms, were refined anisotropically. Hydrogen atoms were placed in idealized generated positions with isotropic thermal parameters kept fixed. Final *R* values for **7-Cu** were *R* = 0.038, *R<sub>w</sub>* = 0.085 with 4948 observed reflections having  $F_o^2 > 2\sigma(F_o^2)$ , 331 variable parameters,  $w = [\sigma^2(F_o^2) + (0.0562P)^2]^{-1}$  where  $P = (F_o^2 + 2F_c^2)/3$ , *S* = 1.023 (for all reflections *R* = 0.089, *R<sub>w</sub>* = 0.095, *S* = 0.922),  $(\Delta/\sigma)_{\text{max}}$  = 0.042 (*y* of C(3A) atom), and  $(\Delta/\sigma)_{\text{mean}}$  = 0.006. Absolute configuration was determined unambiguously: Flack<sup>32</sup> value = 0.005-(12). There are not significant differences between molecules A and B; one of them (i.e. molecule A) is shown in Figure 3a with atom numbering. Final *R* values for **6-H<sub>2</sub>** were *R* = 0.040, *R<sub>w</sub>* = 0.104 with 4674 observed reflections having  $F_o^2 > 2\sigma(F_o^2)$ , 424 variable parameters,  $w = [\sigma^2(F_o^2) + (0.0654P)^2 + 0.3934P]^{-1}$  where  $P = (F_o^2 + 2F_c^2)/3$ , *S* = 1.008 (for all reflections *R* = 0.076, *R<sub>w</sub>* = 0.115, *S* = 1.085),  $(\Delta/\sigma)_{\text{max}}$  = 0.126 (*U*<sub>22</sub> of O(1'B) atom), and  $(\Delta/\sigma)_{\text{mean}}$  = 0.019. Absolute configuration could not be determined reliably. As for **7-Cu**,

(31) *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C, Tables 4.2.6.8 and 6.1.1.4.

(32) Flack, H. D. *Acta Crystallogr., Sect. A* **1983**, A39, 876–881.

**Table 3.** Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å<sup>2</sup> × 10<sup>3</sup>) for CuC<sub>6</sub>Salen, **7-Cu**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) <sup>a</sup>
Cu(A)	0.48897(4)	0.50000(3)	0.78983(4)	5.07(2)*
O(1A)	0.6585(2)	0.4754(3)	0.8142(2)	6.21(9)*
O(1'A)	0.4867(2)	0.5271(3)	0.9410(2)	5.67(8)*
N(1A)	0.4748(3)	0.4486(3)	0.6422(2)	4.99(8)*
N(1'A)	0.3235(3)	0.5475(3)	0.7545(3)	5.63(9)*
C(1A)	0.3494(3)	0.4533(3)	0.5890(3)	5.2(1)*
C(2A)	0.2922(3)	0.5507(3)	0.6352(3)	5.4(1)*
C(3A)	0.1587(4)	0.5601(4)	0.5945(3)	7.0(1)*
C(4A)	0.1425(4)	0.5595(4)	0.4723(4)	8.2(2)*
C(5A)	0.2015(4)	0.4657(4)	0.4245(3)	7.3(1)*
C(6A)	0.3356(4)	0.4556(4)	0.4660(3)	5.9(1)*
C(7A)	0.5625(4)	0.4118(4)	0.5937(3)	5.6(1)*
C(8A)	0.7282(4)	0.4353(3)	0.7458(3)	5.1(1)
C(9A)	0.8534(4)	0.4251(3)	0.7792(3)	6.0(1)
C(10A)	0.9307(4)	0.3781(3)	0.7136(3)	6.3(1)
C(11A)	0.8907(4)	0.3474(4)	0.6089(3)	6.7(1)
C(12A)	0.7691(4)	0.3564(4)	0.5732(4)	6.7(1)
C(13A)	0.6868(4)	0.4017(4)	0.6388(3)	5.5(1)
C(7'A)	0.2507(4)	0.5783(4)	0.8226(4)	5.7(1)*
C(8'A)	0.3966(4)	0.5584(4)	0.9914(3)	5.9(1)
C(9'A)	0.4123(4)	0.5710(4)	1.1038(3)	6.7(1)
C(10'A)	0.3209(5)	0.6047(4)	1.1624(4)	7.7(1)
C(11'A)	0.2049(5)	0.6233(4)	1.1113(5)	8.1(2)
C(12'A)	0.1865(5)	0.6178(4)	1.0023(5)	7.7(2)
C(13'A)	0.2781(4)	0.5829(3)	0.9383(3)	5.5(1)
Cu(B)	0.48959(4)	0.26248(3)	0.27311(3)	4.92(1)*
O(1B)	0.4894(3)	0.2167(3)	0.4198(2)	5.79(8)*
O(1'B)	0.6549(3)	0.3026(3)	0.3048(2)	6.43(9)*
N(1B)	0.3144(3)	0.2444(3)	0.2406(2)	4.83(8)*
N(1'B)	0.4892(3)	0.2834(3)	0.1187(2)	4.65(8)*
C(1B)	0.2719(3)	0.2772(3)	0.1277(3)	5.03(9)*
C(2B)	0.3742(3)	0.2471(3)	0.0586(3)	4.67(8)*
C(3B)	0.3477(3)	0.2820(4)	-0.0584(3)	5.3(1)*
C(4B)	0.2258(3)	0.2380(4)	-0.1069(3)	6.4(1)*
C(5B)	0.1235(4)	0.2684(5)	-0.0375(3)	7.6(1)*
C(6B)	0.1514(4)	0.2329(4)	0.0799(3)	6.3(1)*
C(7B)	0.2435(4)	0.2088(4)	0.3056(3)	5.7(1)*
C(8B)	0.3952(4)	0.1858(4)	0.4682(3)	5.2(1)
C(9B)	0.4151(4)	0.1584(3)	0.5789(3)	6.2(1)
C(10B)	0.3214(5)	0.1255(4)	0.6337(4)	7.3(1)
C(11B)	0.2055(5)	0.1165(4)	0.5852(4)	8.0(2)
C(12B)	0.1830(5)	0.1458(4)	0.4805(4)	7.5(1)
C(13B)	0.2767(4)	0.1777(4)	0.4164(3)	5.6(1)
C(7'B)	0.5753(4)	0.3256(3)	0.0718(3)	5.0(1)*
C(8'B)	0.7252(4)	0.3441(3)	0.2369(3)	4.88(9)
C(9'B)	0.8450(4)	0.3716(3)	0.2765(3)	6.0(1)
C(10'B)	0.9210(4)	0.4186(3)	0.2101(3)	6.2(1)
C(11'B)	0.8859(4)	0.4385(4)	0.1043(3)	6.9(1)
C(12'B)	0.7714(4)	0.4060(4)	0.0602(4)	6.4(1)
C(13'B)	0.6897(4)	0.3593(3)	0.1259(3)	4.95(9)

<sup>a</sup> *U*(eq) is defined as one-third of the trace of the orthogonalized *U<sub>ij</sub>* tensor. Asterisks indicate anisotropic refinement.

there are not significant differences between molecules A and B. Figure 4a shows molecule A of **6-H<sub>2</sub>** with atom numbering.

Final difference Fourier maps were featureless for the two compounds. Crystal data are given in Table 2. Atomic coordinates and equivalent isotropic thermal parameters for **7-Cu** and **6-H<sub>2</sub>** are presented in Tables 3 and 4, respectively. Relevant bond distances and angles are presented in Tables 5 and 6, respectively. All calculations were performed on a MicroVax 3400 computer. Crystallographic drawings were made by using the ORTEP program.<sup>33</sup> Complete crystallographic data are given in the Supporting Information.

**Experimental Conditions for Olefin Epoxidations. General Method Used for Epoxidation Catalyzed by 1-Mn, 2-Mn, 3-Mn, or 4-Mn with H<sub>2</sub>O<sub>2</sub> as Oxidant.**<sup>34</sup> To a solution of catalyst (0.06 mmol, 12 mol %), 1,2-dihydronaphthalene (65 μL, 0.50 mmol), 1,4-dibromobenzene (33 mg, 0.14 mmol), and imidazole (17 mg, 0.25 mmol)

(33) Johnson, C. K. ORTEP. Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

(34) Pietikäinen, P. *Tetrahedron Lett.* **1994**, 35, 941–944.

**Table 4.** Atomic Coordinates and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for  $\text{H}_2\text{NMe}_2\text{C}_6\text{Salen}$ , **6-H<sub>2</sub>**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) <sup>a</sup>
O(1A)	0.4700(1)	0.50000(0)	1.1030(2)	6.47(6)*
O(1'A)	0.3307(1)	0.6415(3)	0.5678(2)	7.59(7)*
N(1A)	0.4714(1)	0.4154(3)	0.8767(2)	5.15(6)*
N(1'A)	0.4416(1)	0.6214(3)	0.6777(2)	5.23(6)*
C(1A)	0.4958(1)	0.4070(4)	0.7601(3)	5.42(8)*
C(2A)	0.5003(1)	0.5538(4)	0.7070(3)	5.18(7)*
C(3A)	0.5279(1)	0.5450(4)	0.5891(3)	6.54(9)*
C(4A)	0.5887(1)	0.4729(4)	0.6141(3)	6.95(9)*
C(5A)	0.5844(2)	0.3284(5)	0.6686(4)	8.1(1)*
C(6A)	0.5568(1)	0.3373(4)	0.7863(3)	6.77(9)*
C(7A)	0.4310(1)	0.3287(4)	0.8934(3)	5.59(7)*
C(8A)	0.4259(1)	0.4065(4)	1.1057(3)	4.73(7)
C(9A)	0.4010(1)	0.3974(4)	1.2130(3)	5.55(7)
C(10A)	0.3545(1)	0.3038(4)	1.2218(3)	5.75(8)
C(11A)	0.3346(1)	0.2155(4)	1.1207(3)	6.26(8)
C(12A)	0.3599(1)	0.2255(4)	1.0159(3)	6.60(9)
C(13A)	0.4058(1)	0.3194(4)	1.0035(3)	4.80(7)
N(2A)	0.3285(1)	0.2947(4)	1.3264(3)	7.38(8)*
C(14A)	0.2765(2)	0.2063(5)	1.3301(4)	9.0(1)*
C(15A)	0.3555(2)	0.3565(6)	1.4413(3)	10.0(1)*
C(7'A)	0.4360(1)	0.7468(4)	0.7140(3)	5.34(7)*
C(8'A)	0.3307(1)	0.7733(4)	0.6128(3)	5.44(7)
C(9'A)	0.2796(1)	0.8539(4)	0.5833(3)	5.89(8)
C(10'A)	0.2772(1)	0.9914(4)	0.6254(3)	5.17(7)
C(11'A)	0.3280(1)	1.0470(4)	0.6970(3)	5.81(8)
C(12'A)	0.3789(1)	0.9672(4)	0.7252(3)	5.97(8)
C(13'A)	0.3818(1)	0.8281(4)	0.6850(3)	4.83(7)
N(2'A)	0.2261(1)	1.0717(4)	0.5980(2)	6.65(7)*
C(14'A)	0.1746(2)	1.0189(5)	0.5170(3)	8.2(1)*
C(15'A)	0.2217(2)	1.2069(4)	0.6545(3)	7.8(1)*
O(1B)	0.8753(1)	1.0048(4)	0.3970(2)	8.07(7)*
O(1'B)	0.91576(9)	0.3703(3)	0.2702(2)	7.76(7)*
N(1B)	0.9646(1)	0.8478(4)	0.3693(3)	6.53(7)*
N(1'B)	0.9405(1)	0.6216(3)	0.1880(2)	5.91(7)*
C(1B)	1.0088(1)	0.7984(4)	0.2972(3)	6.35(8)*
C(2B)	0.9780(1)	0.7432(4)	0.1721(3)	6.27(8)*
C(3B)	1.0228(2)	0.7012(4)	0.0911(4)	7.7(1)*
C(4B)	1.0660(2)	0.8199(5)	0.0746(4)	9.5(1)*
C(5B)	1.0955(2)	0.8752(6)	0.1967(5)	10.6(1)*
C(6B)	1.0497(2)	0.9200(5)	0.2755(4)	8.6(1)*
C(7B)	0.9683(1)	0.8123(4)	0.4825(3)	6.05(8)*
C(8B)	0.8822(1)	0.9610(4)	0.5160(3)	5.89(8)
C(9B)	0.8434(2)	1.0092(4)	0.5893(3)	6.72(9)
C(10B)	0.8481(2)	0.9669(4)	0.7127(3)	6.59(9)
C(11B)	0.8938(1)	0.8717(4)	0.7579(3)	7.34(9)
C(12B)	0.9324(2)	0.8233(4)	0.6831(3)	6.89(9)
C(13B)	0.9278(1)	0.8652(4)	0.5601(3)	5.78(8)
N(2B)	0.8098(2)	1.0181(4)	0.7867(3)	8.75(9)*
C(14B)	0.8167(2)	0.9810(6)	0.9155(4)	11.0(2)*
C(15B)	0.7628(2)	1.1162(5)	0.7426(4)	9.8(1)*
C(7'B)	0.8883(1)	0.6181(4)	0.1253(3)	5.94(8)*
C(8'B)	0.8623(1)	0.3824(4)	0.1958(3)	5.24(7)
C(9'B)	0.8232(1)	0.2709(4)	0.1954(3)	5.82(8)
C(10'B)	0.7666(1)	0.2744(4)	0.1206(3)	5.31(7)
C(11'B)	0.7522(2)	0.3946(4)	0.0467(3)	6.62(9)
C(12'B)	0.7925(1)	0.5033(4)	0.0502(3)	6.65(9)
C(13'B)	0.8482(1)	0.5013(4)	0.1248(3)	5.16(7)
N(2'B)	0.7279(1)	0.1648(4)	0.1172(3)	6.79(7)*
C(14'B)	0.7419(2)	0.0413(5)	0.1918(4)	8.3(1)*
C(15'B)	0.6681(1)	0.1753(5)	0.0455(4)	8.1(1)*

<sup>a</sup> *U*(eq) is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor. Asterisks indicate anisotropic refinement.

in a mixture of dichloromethane and methanol (1/1 v/v, 1 mL) was added 30% aqueous hydrogen peroxide (0.14 mL, 1.1 mmol, 2 equiv) in four portions during 45 min. The mixture was stirred at room temperature and the reaction followed by GC on a 25 m Cydex-B (SGE) capillary column (column temperature 140 °C, N<sub>2</sub> pressure 0.8 bar). The blank experiment (same reaction mixture, but without the manganese complex) produced 6% olefin conversion in 1 h. With all the manganese complexes assayed, the conversion of the substrate within 1 h under these conditions was not significantly different from that observed in the blank experiment. Under similar conditions but

**Table 5.** Selected Bond Lengths (Å) and Angles (deg) for **7-Cu**

	molecule A	molecule B
Cu—O(1)	1.896(3)	1.902(3)
Cu—O(1')	1.901(2)	1.901(3)
Cu—N(1)	1.927(3)	1.953(3)
Cu—N(1')	1.935(3)	1.925(3)
N(1)—C(1)	1.475(5)	1.485(4)
N(1')—C(2)	1.479(5)	1.480(4)
O(1)—Cu—O(1')	89.1(1)	88.8(1)
O(1)—Cu—N(1)	94.6(1)	93.6(1)
O(1)—Cu—N(1')	170.3(2)	170.2(1)
O(1')—Cu—N(1)	169.2(1)	171.2(2)
O(1')—Cu—N(1')	93.4(1)	94.2(1)
N(1)—Cu—N(1')	84.6(1)	84.8(1)
N(1)—C(1)—C(2)	105.9(3)	105.7(3)
N(1)—C(1)—C(6)	116.3(3)	116.5(3)
N(1')—C(2)—C(1)	106.7(3)	106.8(3)
N(1')—C(2)—C(3)	117.0(3)	117.6(3)
C(1)—N(1)—C(7)	122.0(3)	122.6(3)
C(2)—N(1')—C(7')	123.1(3)	122.9(3)
N(1)···N(1')	2.599(5)	2.616(4)
N(1)···O(1)	2.808(4)	2.811(4)
N(1')···O(1')	2.792(4)	2.802(4)

**Table 6.** Selected Bond Lengths (Å) and Angles (deg) for **6-H<sub>2</sub>**

	molecule A	molecule B
N(1)—C(1)	1.474(4)	1.455(4)
N(1')—C(2)	1.469(4)	1.461(5)
N(1)—C(1)—C(2)	109.9(3)	109.9(2)
N(1)—C(1)—C(6)	108.8(2)	109.6(3)
N(1')—C(2)—C(1)	111.5(2)	110.8(3)
N(1')—C(2)—C(3)	108.9(2)	109.0(3)
C(1)—N(1)—C(7)	118.3(3)	120.2(3)
C(2)—N(1')—C(7')	118.4(2)	117.9(3)
Intramolecular Hydrogen Bond Parameters (O—H = 0.82 Å)		
O(1)···N(1)	2.607(3)	2.575(4)
H(O1)···N(1)	1.88(2)	1.84(2)
O(1)—H(O1)···N(1)	147(2)	149(1)
O(1')···N(1')	2.617(3)	2.639(4)
H(O1')···N(1')	1.99(2)	1.91(2)
O(1')—H(O1')···N(1')	133(1)	147(2)
N(1)···N(1')	2.921(4)	2.912(4)

using **8-Mn** as catalyst (2 mol %), the conversion of 1,2-dihydronaphthalene was complete in 1 h and the enantiomeric excess of the obtained epoxide was 61%.

**General Method for Epoxidation Catalyzed by 1-Mn, 2-Mn, 3-Mn, or 4-Mn with NaOCl as Oxidant.** To a solution of catalyst (0.06 mmol, 10 mol %), 1,2-dihydronaphthalene (79 μL, 0.60 mmol), 1,4-dibromobenzene (116 mg, 0.49 mmol), and 4-methylpyridine (62 μL, 0.64 mmol) in dichloromethane (0.6 mL) at room temperature was added NaOCl (2.3 mL, 1.2 mmol, 2 equiv), and the reaction was followed by GC on a 25 m Cydex-B (SGE) capillary column (column temperature 140 °C, N<sub>2</sub> pressure 0.8 bar). The blank experiment (same reaction mixture, but without the manganese complex) produced less than 2% olefin conversion within 1 h.

**General Method Used for Epoxidations Catalyzed by 6-Mn with NaOCl as Oxidant.** A standard solution of the substrate (0.1 mmol) and 1,4-dibromobenzene (23.5 mg, 0.1 mmol) in MeCN (1 mL) was prepared; 100 μL aliquots of this solution were taken and dissolved in an acetonitrile/water mixture (MeCN/H<sub>2</sub>O, v/v, 1/1.2 mL) along with **6-Mn** (5 mg in 1 mL of MeCN; 100 μL aliquot, 0.0009 mmol, 9 mol %). After 2–3 min of stirring, NaOCl (38 μL, 0.02 mmol, 2 equiv) was added, and the reaction was followed over 24 h by GC on either a 25 m Cydex-B (SGE) or a 30 m Chiraldex G-TA (Alltech) capillary column (final concentration of substrate 4.45 mM, catalyst 0.4 mM). Substrates assayed: 1,2-dihydronaphthalene, *cis*-stilbene, 1-methylcyclohexene, 1-phenylcyclohexene, 4-chlorostyrene, (±)-limonene, 4-vinylcyclohexene, thiophenol, thioanisole. In all cases, no conversion of the substrate was observed under these conditions.

**Epoxidation of Styrene Catalyzed by 6-Mn, Using Jacobsen's Method.**<sup>21</sup> To a solution of **6-Mn** (5.4 mg, 10 mol %), styrene (10

$\mu\text{L}$ , 0.086 mmol), 1,4-dibromobenzene (12.0 mg, 0.089 mmol), and *N*-methylmorpholine *N*-oxide (8 mg, 6 equiv) in  $\text{CH}_2\text{Cl}_2$  (1 mL) at  $-78^\circ\text{C}$  was slowly added *m*-chloroperbenzoic acid (3.4 mg, 2 equiv). The reaction was followed by GC on a 25 m Cydex-B (SGE) capillary column (column temperature  $115^\circ\text{C}$ ,  $\text{N}_2$  pressure 0.4 bar). As already pointed out, no epoxidation was observed using *N*-methylmorpholine *N*-oxide in the absence of *m*-chloroperbenzoic acid.<sup>21</sup> Furthermore the blank experiment (complete reaction mixture, but without the manganese complex) produced no conversion of styrene: the "MCPBA-complex" does not react with a terminal olefin (styrene or substituted styrene) without a catalyst; therefore there is no achiral leakage in the asymmetric reaction.

## Results

**Synthesis of New Chiral Schiff Base Complexes.** We recently reported the synthesis of new chiral Schiff base ligands based on 1,1'-binaphthyl-2,2'-diamine and substituted salicylaldehydes  $\text{H}_2\text{X}_4\text{Salbinaph}$  ( $\text{X} = \text{H, Cl, Br, tert-butyl}$ ),<sup>25</sup> **1-H<sub>2</sub>** to **4-H<sub>2</sub>**, respectively (see Figure 1 for the structures of these ligands and their metal complexes). A drying agent should be used during the condensation reaction to obtain the nitro-substituted **5-H<sub>2</sub>** ligand. A series of transition metal complexes could be obtained from these ligands: The chloro-derivative **2-H<sub>2</sub>** was metalated with manganese, iron, cobalt, nickel, copper, and zinc. The bromo derivative **3-H<sub>2</sub>** was metalated by manganese, nickel, and copper. These metalations were typically performed in absolute ethanol, in the presence of a strong base (sodium methoxide) and an appropriate metal(II) salt. Using these conditions, the metalation of **1-H<sub>2</sub>** and **4-H<sub>2</sub>** with manganese was unsuccessful. The complexes **1-Mn** and **4-Mn** were obtained by metalation of the corresponding free ligands with  $\text{Mn}_2(\text{CO})_{10}$  under nitrogen in DMF, in presence of DBN as a base.

The metalations were monitored by UV-vis spectroscopy of a diluted aliquot (in  $\text{CH}_2\text{Cl}_2$ ) of the reaction mixture. The free ligands exhibit characteristic absorption bands at 326 and 378 nm assigned to the  $\pi \rightarrow \pi^*$  transitions of the intramolecularly hydrogen-bonded salicylideneamino chromophore.<sup>35</sup> The metalation reactions lead to a strong decrease of these absorption bands. A new absorption was evidenced at 398 nm by metalation with zinc.

NMR characterizations of free ligands **1-H<sub>2</sub>** to **5-H<sub>2</sub>**, diamagnetic complex **2-Zn** (with complete assignment of signals), and paramagnetic **2-Ni** are reported. From ligand **2-H<sub>2</sub>**, monocrystals suitable for X-ray structure determination could be obtained by slow evaporation of a dichloromethane/hexane solution.<sup>25</sup>

The copper complex of  $\text{H}_2\text{C}_6\text{Salen}$ , **7-Cu** (see Figure 2a for the structure), was obtained by one-pot reaction of (1*R*,2*R*)-(-)-*trans*-diaminocyclohexane with salicylaldehyde in the presence of copper chloride. Monocrystals suitable for X-ray diffraction studies were obtained from a dichloromethane solution. The X-ray structure analysis is reported here.

In order to prepare chiral Schiff base complexes capable of being soluble in water or fixed onto a support, the synthesis of a derivative bearing dimethylamino groups on the salicylidene moiety has been performed by condensation of (1*R*,2*R*)-(-)-*trans*-diaminocyclohexane with 4-(dimethylamino)-2-hydroxybenzaldehyde. This ligand was metalated with manganese, nickel, iron, and copper to give complexes **6-Mn**, **6-Ni**, **6-Fe**, and **6-Cu**, respectively. The X-ray structure analysis of compound **6-H<sub>2</sub>** is reported here.

**NMR Spectra of the Schiff Base Ligands and the Zinc Complex with a Binaphthyl Moiety, 1-H<sub>2</sub> to 5-H<sub>2</sub> and 2-Zn.** The  $^1\text{H}$  and  $^{13}\text{C}$  spectra were recorded at 400.13 and 100.62

MHz, respectively, in deuterated acetone, with TMS as external standard. The assignments are based on  $\delta_{^1\text{H}}-\delta_{^1\text{H}}$  GE-COSY,  $\delta_{^1\text{H}}-\delta_{^{13}\text{C}}$  GE-HMQC ( $^1J$ ), and long-range proton-carbon ( $^3J$ ) correlations. Results are reported in Table 1 (for the labeling of protons and carbon atoms, see Figure 1).

It can be noticed that, except for the case of ligand **5-H<sub>2</sub>**, the influence of substitution on the chemical shifts of the binaphthyl moiety is weak. When two nitro groups are present on each salicylidene residue, a significant deshielding of the proton signals can be observed, due to the strong withdrawing effect of these substituents.

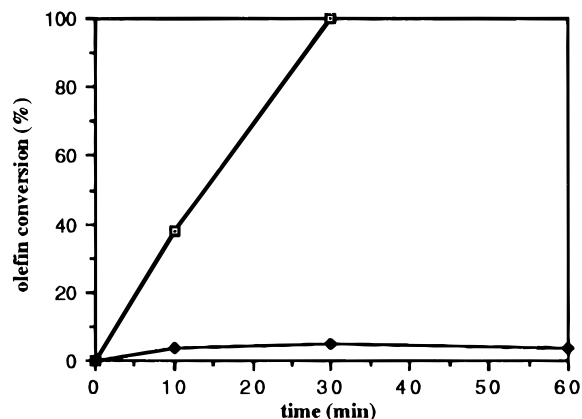
When a ligand is metalated by zinc (comparison of **2-H<sub>2</sub>** and **2-Zn**), the NMR signals due to protons which are close to the coordination site are shifted to low-field frequency ( $\Delta\delta = -0.36, -0.44,$  and  $-0.26$  for 11-H (imine), 3-H, and 16-H respectively). The carbon atoms which are the most affected by the zinc coordination are 11-C (imine), 12-C (C-O), and 13-C ( $\Delta\delta = +8.48, +8.81,$  and  $+5.71$ , respectively). These features confirm the complexation of zinc by the imino nitrogen and phenolate oxygen atoms.

**X-ray Analyses.** The X-ray structures of  $\text{CuC}_6\text{Salen}$ , **7-Cu** (Figure 3a), and  $\text{H}_2\text{NMe}_2\text{C}_6\text{Salen}$ , **6-H<sub>2</sub>** (Figure 4a), contain two independent molecules, called A and B, differing by slight conformational changes in the cyclohexyl cycle and, in the case of **6-H<sub>2</sub>**, in the OH positioning. In **7-Cu**, the copper atom sits in a pseudo-square-planar coordination site. Selected bond lengths and angles are reported in Table 5. The Cu-N(1, 1') and Cu-O(1, 1') bond lengths are 1.927(3), 1.935(3) and 1.896(3), 1.901(2) Å, respectively. The dihedral angle between the two aromatic cycles is  $15.2(3)^\circ$  in motif A and  $10.4(4)^\circ$  in motif B, presenting an almost planar structure (Figure 3b). Selected bond lengths and angles for **6-H<sub>2</sub>** are reported in Table 6. The structure is best described as "open armed", the imine-aromatic ring moieties diverging outward from the cyclohexyl ring (Figure 4b). The dihedral angle between the two aromatic rings ( $75.8(1)^\circ$  in motif A and  $76.0(1)^\circ$  in motif B) indicates that these cycles are far away from coplanar geometry. This is a significant difference from the geometry of the metal complex **7-Cu**. A  $\text{C}_2$  axis is maintained by one hydroxyl sitting below and the other above the plane of the cyclohexyl ring, and short O-H...N intramolecular hydrogen bonds (see Table 6) indicate a strong hydrogen bonding of these groups to the imine N.

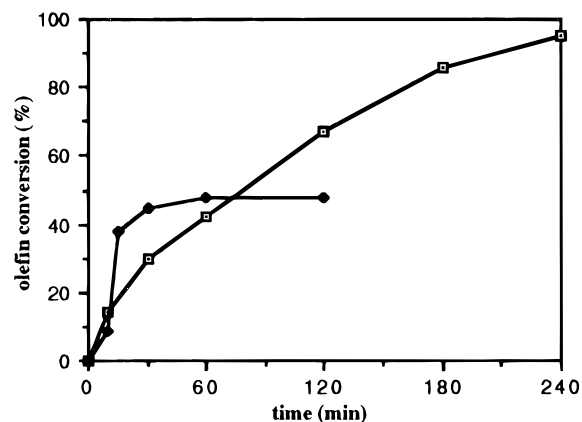
**Epoxidation of 1,2-Dihydronaphthalene by 1-Mn, 2-Mn, 3-Mn, or 4-Mn with NaOCl as Oxidant.** With **1-Mn**, after 60 min, 10% conversion of the substrate was observed with 15% enantiomeric excess for the epoxide product. With **4-Mn**, a conversion of the substrate as low as 4-5% was observed under these conditions (10 mol % of catalyst). Under similar conditions, but with **8-Mn** as catalyst (2 mol %), the conversion of 1,2-dihydronaphthalene was complete within 30 min and the epoxide enantiomeric excess was 58%. The comparison of the reactivity of these two catalysts based on cyclohexyl (**8-Mn**) and binaphthyl (**4-Mn**) chiral moieties is illustrated by Figure 5.

With **2-Mn** and **3-Mn**, after 60 min, 31% and 50% conversions were respectively obtained with the same enantiomeric excess (13%). These results can be compared with the catalytic activity of the manganese complex of a Schiff base obtained by condensation of 1,2-diaminocyclohexane and 3,5-dibromo-2-hydroxybenzaldehyde, **9-Mn**.<sup>24</sup> In the latter case, nearly complete conversion could be obtained in 4 h (2 mol % of catalyst) with 13% of enantiomeric excess.

With **2-Mn** and **3-Mn**, addition of further NaOCl (2.3 mL, 1.2 mmol) and catalyst (0.06 mmol) fractions increased the



**Figure 5.** Conversion of 1,2-dihydronaphthalene by NaOCl catalyzed by the manganese complexes of di-*tert*-butylsalicylidene Schiff bases bearing cyclohexyl (**8-Mn**, □) or binaphthyl (**4-Mn**, ●) as the chiral moiety.



**Figure 6.** Conversion of 1,2-dihydronaphthalene by NaOCl catalyzed by the manganese complexes of dibromosalicylidene Schiff bases bearing cyclohexyl (**9-Mn**, □) or binaphthyl (**3-Mn**, ●) as the chiral moiety.

conversion of the substrate to 100%, but the enantiomeric excess remained unchanged (13%).

**Epoxidation of Olefins by 6-Mn.** The epoxidation of several olefins (1,2-dihydronaphthalene, *cis*-stilbene, 1-methylcyclohexene, 1-phenylcyclohexene, 4-chlorostyrene, ( $\pm$ )-limonene, 4-vinylcyclohexene) and the sulfoxidation of thiophenol and thioanisole were attempted in a homogeneous reaction mixture of water/acetonitrile, using sodium hypochlorite as oxidant. Under these conditions, no conversion of substrate was observed over a 24 h period.

Using the Jacobsen method<sup>21</sup> (*N*-methylmorpholine *N*-oxide/*m*-chloroperbenzoic acid as reaction mixture, in dichloromethane,  $-78$  °C), the epoxidation of styrene could be achieved. After 90 min, 40% conversion to styrene oxide was observed with 35% enantiomeric excess. Addition of further *m*-chloroperbenzoic acid (3.4 mg, 2 equiv) increased the conversion to 60%, but the enantiomeric excess remained unchanged. Under similar conditions, the racemic catalyst led to a 37% conversion to styrene oxide in 90 min, but with 0% enantiomeric excess.

## Discussion

**Synthesis of New Chiral Ligands and Complexes.** In this article, the synthesis of a wide family of chiral diimine ligands and their transition metal complexes is reported.

Chiral manganese(III) Schiff base complexes based on 1,2-diphenyl-1,2-diaminoethane and 1,2-diaminocyclohexane have

been used by Jacobsen to catalyze the enantioselective epoxidation of olefins. This method gives high enantiomeric excesses when the substrate is a *cis*-disubstituted olefin, but it is much less efficient in standard conditions for the epoxidation of terminal olefins.<sup>19</sup> Mn Schiff base complexes with binaphthylidene residues in place of salicylidene were also synthesized and shown to be highly efficient for asymmetric epoxidation of conjugated *cis* olefins.<sup>23,36</sup> But once more, the enantiomeric excesses were moderate to low with *trans* or terminal olefins.

One of the most successful chiral diphosphine ligands (BINAP) in asymmetric catalytic hydrogenation is based on a binaphthyl motif.<sup>37</sup> A copper Salbinapht catalyst gave 66% ee in the cyclopropanation of prochiral olefins<sup>38</sup> and 38% ee in the styrene oxidation to 1-phenylethanol.<sup>39</sup> The highest stereoselectivities reported in the epoxidation of olefins (including styrene derivatives) and hydroxylation of alkanes by chiral metalloporphyrins were obtained with manganese complexes bearing binaphthyl residues on one or both faces of the tetrapyrrolic unit.

We attempted to improve the enantioselectivity and the scope of activity of the Schiff base catalysts using 1,1'-binaphthyl-2,2'-diamine as the chiral backbone in the complexes. Complexes bearing different electron-withdrawing or -attracting ligands at the *ortho* and *para* positions of the salicylidene moieties were also synthesized. Such substituents are able to produce different electronic and steric effects and to tune the catalytic efficiency of metalloporphyrin complexes.<sup>5a</sup> In the case of Schiff base complexes, it has been pointed out that the presence of electron-withdrawing groups such as nitro enhanced the catalytic activity of the manganese(III) Salen complex in the epoxidation of olefins.<sup>40</sup> We therefore prepared several transition metal complexes (including iron and manganese) of the Salbinapht ligand bearing Cl, Br, H, and *tert*-butyl substituents. The ligand with four nitro groups at the *ortho* and *para* positions of the salicylidene has also been prepared. Unfortunately, until now we have not succeeded in the metalation of this new chiral ligand with manganese.

The utilization of Schiff base complexes in catalysis, especially for oxidation reactions, should not be limited to complexes only soluble in organic solvents. When activated with a single oxygen atom donor, water-soluble iron and manganese porphyrins are highly efficient catalysts in aqueous medium for lignin model oxidation,<sup>41</sup> trichlorophenol oxidation,<sup>42</sup> olefin epoxidation<sup>43</sup> or DNA hydroxylation.<sup>44</sup> A manganese(III) Salen complex has been immobilized on a clay<sup>45</sup> for catalytic epoxidation with *tert*-butyl hydroperoxide. This supported

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catalyst was 3 times more active than its soluble analogue. On this basis and by analogy with the metalloporphyrin properties, the synthesis of the chiral ligand **6-H<sub>2</sub>** has been performed. The dimethylamino groups of this ligand can be easily quaternarized by reaction with methyl iodide. After metalation, the resulting complex bearing two positive charges can be solubilized in water or adsorbed onto a support.

**X-ray Structure Analyses.** The near-planar structure of CuC<sub>6</sub>Salen, **7-Cu**, differs from similar structures that have been observed in the literature. The influence of the cyclohexyl ring may be seen in the comparison of this structure with the ethylenediamine-based copper complex CuC<sub>2</sub>Salen.<sup>46</sup> The average Cu–N (1.93 Å) bond length in the present structure is shorter than the 1.98 Å observed in many Cu–N<sub>2</sub>O<sub>2</sub> complexes,<sup>47</sup> and comparison with CuC<sub>2</sub>Salen shows that both the Cu–N and Cu–O bonds are slightly longer in the latter, inferring both stronger coordinate and ionic bonding in the present structure. The dihedral angle between the two salicylidene residues of the C<sub>6</sub> complex is 15.2(3) or 10.4(4)°, depending on the motif chosen, whereas the “stepped” C<sub>2</sub> complex shows a distinctly “bent” shape. In the C<sub>2</sub> complex, the copper sits in a “tetragonally distorted square-planar conformation”, and deformation of a symmetrical N<sub>2</sub>O<sub>2</sub> coordination is seen, with Cu–O distances of 1.945 and 1.911 Å (both Cu–N distances are the same: 1.958 and 1.959 Å) and O–Cu–N angles of 170.4 and 171.3°. In the C<sub>6</sub> complex, the Cu–O distances are both shorter and are effectively the same (1.901(2) and 1.896(3) Å); the Cu–N distances are shorter (1.927(3), 1.935(3) Å), and the O–Cu–N angles are remarkably similar to those of the C<sub>2</sub> complex at 170.3(2) and 169.2(1)°. This would suggest that the cyclohexyl group is responsible for the near-planarity of the present copper complex, and its influence is stronger than the “stepped” distortion observed in the C<sub>2</sub> copper complex and in chloroiron(III) Salen complexes.<sup>48</sup>

Comparison of this structure with the only other reported X-ray structure of a metalated chiral Schiff base complex based on a cyclohexyl motif<sup>49</sup> leads to several surprising observations. The chloromanganese(III) complex of C<sub>6</sub>H<sub>4</sub>Bu<sub>2</sub>Me<sub>2</sub>Salen is observed to have a conformation very similar to that of CuC<sub>6</sub>Salen, **7-Cu**—a planar structure, with a dihedral angle of 169.0(3)° and a slight twist between the two aromatic rings. It would appear, then, that the bulky *tert*-butyl group *ortho* to the phenoxy function has little steric effect on the structure adopted in the solid state. Feringa *et al.* were surprised by the complex structure, especially as the cyclohexyl backbone shows very little steric effect, despite the efficiency of asymmetric induction observed with this catalyst. They suggested that, in the active high-valent Mn=O form, there was a pronounced change in geometry, greatly increasing the cyclohexyl participation in the steric environment of the Jacobsen complex. In the C<sub>6</sub> copper complex, the axial hydrogens of the cyclohexyl ring are more prominent; though this arises from the inherent planarity of the unsubstituted complex.

The structure of the H<sub>2</sub>C<sub>6</sub>NMe<sub>2</sub>Salen compound, **6-H<sub>2</sub>**, is remarkably similar to the reported<sup>25</sup> X-ray structure of the H<sub>2</sub>-Cl<sub>4</sub>Salbinapht ligand. Whereas it would be imagined that the almost perpendicular binaphthyl motif was responsible for the “open-armed” structure observed, the structure reported here

would indicate that this arises from more than just steric considerations and electronic effects play an important role in the conformation of these types of compounds.

Comparison of the H<sub>2</sub>C<sub>6</sub>NMe<sub>2</sub>Salen, **6-H<sub>2</sub>**, and CuC<sub>6</sub>Salen, **7-Cu** structures<sup>50</sup> shows that, in metal complexation, there is not only an inwards turn of the two aromatic rings but also an increase in strain energy of the molecule. The mean value for molecules A and B of angles N(1)–C(1)–C(6) and N(1')–C(2)–C(3) changes from 109.1° in the free Schiff base ligand, **6-H<sub>2</sub>**, to 116.9° in the copper complex, **7-Cu**, and the mean value of C(1)–N(1)–C(7) and C(2)–N(1')–C(7') changes from 118.7 to 122.7°. Comparison of the interatomic distances between the two structures suggests that, after complexation, the N(1)–O(1) (and N(1')–O(1')) distance increases from 2.610 to 2.803 Å and the N–N distance shortens from 2.917 to 2.608 Å.

#### Epoxidation Assay of 1-Mn, 2-Mn, 3-Mn, and 4-Mn.

Several explanations can be proposed for the unexpected poor reactivity of the binaphthyl-based manganese complexes as oxygenation catalysts. The geometry of the binaphthyl moiety should induce a severe distortion around the metal, far from the square-planar geometry (the nickel complex **2-Ni** was found to be paramagnetic, due to a tetrahedral environment of the metal ion). The manganese–oxo species, if it is formed, could therefore be hidden at the bottom of a well which is too narrow for the access of the organic substrate. For instance, with the **4-Mn** complex associated to H<sub>2</sub>O<sub>2</sub> as oxidant, rapid gas evolution was observed in the reaction mixture. This feature evidenced the catalytic dismutation of H<sub>2</sub>O<sub>2</sub> by the manganese complex: after formation of the active metal–oxo species, the steric hindrance around the metal site could be such that the access of a second molecule of H<sub>2</sub>O<sub>2</sub> (leading to the catalase-like activity) is more favorable than the access of a large organic substrate (leading to the oxygenase activity). In the case of nonhindered Schiff base complexes, it has been possible to fully determine by X-ray diffraction the structures of bis( $\mu$ -oxo) dimers generated by H<sub>2</sub>O<sub>2</sub> oxidation of the corresponding manganese(III) monomers.<sup>51</sup> However, no catalase activity was reported for these nonhindered Schiff base complexes.

In several other cases, especially with chloro- or bromo-substituted salicylidene moieties, demetalation of the manganese complex occurred under oxidation conditions. In fact, full olefin conversion was never observed, even with 10% catalyst, indicating that these binaphthyl-based catalysts are unable to effect 10 catalytic cycles.

It should be noted that, in the series of manganese Schiff base complexes based on the diaminocyclohexyl moiety, the compound bearing *tert*-butyl substituents (**8-Mn**) is more reactive for the epoxidation of olefins than the chloro- and bromo-substituted catalysts (**9-Mn** with X = Br; for previous data concerning the catalytic activity with *t*-Bu, Br, and Cl substituents, see ref 24). On the other hand, in the “binaphthyl series”, the epoxidation of 1,2-dihydronaphthalene by sodium hypochlorite could be achieved only when chloro or bromo substituents were present on the salicylidene (catalysts **2-Mn** and **3-Mn**, respectively), even though the observed enantioselectivity was rather low (10–15%). The *tert*-butyl-substituted complex **4-Mn**, in this “binaphthyl series”, was completely inactive as an epoxidation catalyst (either with NaOCl or H<sub>2</sub>O<sub>2</sub> as oxidant) under conditions where its cyclohexyl-based ana-

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(50) Since *o-tert*-butyl- and H-substituted salicylidene complexes have similar structures, it might be inferred that there will only be minor differences between a metal complex of C<sub>6</sub>NMe<sub>2</sub>Salen **6-H<sub>2</sub>** and the structural motifs seen in CuC<sub>6</sub>Salen, **7-Cu**.

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logue gave the best results. Two opposite factors might explain this contradiction. In metalloporphyrin-catalyzed oxidations, halogen substituents are expected to increase the catalytic activity. Such a favorable electronic effect is observed in the binaphthyl series (**2-Mn** and **3-Mn**) but not in the cyclohexyl series (**9-Mn**). In this case, without bulky substituents on the salicylidene residues, the catalytic activity is probably lost because of intermolecular bleaching of the catalyst molecules.

**Epoxidation Assay of 6-Mn.** The absence of catalytic activity for the **6-Mn** complex in the NaOCl olefin epoxidations in an acetonitrile/water mixture was quite disappointing. The effect of the inclusion of two dimethylamino substituents in the salicylidene motifs was evident though in the increased solubility of the complex in the reaction media.

The catalytic epoxidation of styrene mediated by **6-Mn**, using the *N*-methylmorpholine *N*-oxide/*m*-chloroperbenzoic acid oxidant system of Jacobsen,<sup>21</sup> proved to be more interesting. Primarily it showed that the present complex *could* act as a catalyst (40% conversion in 90 min, 35% ee), and secondly, since the addition of further oxidant led to increased turnover *without* compromising the enantioselectivity (60% conversion, ee unchanged), that the catalyst retains its stereochemical integrity. Under these reaction conditions, but with **8-Mn** as catalyst, Jacobsen obtained a styrene oxide yield of 94% after 30 min of reaction time and ee values up to 59%.<sup>21</sup> The lower conversion and ee's obtained with **6-Mn** could be due either to electronic effects of the N(CH<sub>3</sub>)<sub>2</sub> groups or, more probably, to the lack of steric hindrance in positions 9 and 11 of **6-Mn**. To obtain information about the relative importance of these factors, it should be of interest to synthesize an analog of **6-Mn** bearing *tert*-butyl groups in positions 9 and 11, which unfortunately is not easily accessible.

## Conclusion

This article describes the synthesis and characterization of new optically active Schiff base complexes containing diimi-

nobinaphthyl or diiminocyclohexyl chiral entities. Differently substituted salicylaldehydes (bearing *tert*-butyl, H, Cl, or Br) were used in the synthesis of these complexes in order to tune their catalytic activity *via* the electronic or steric effects of the salicylidene moiety.

The manganese complexes containing the diiminobinaphthyl residue have been tested as catalysts for the epoxidation of a *cis*-disubstituted prochiral olefin, 1,2-dihydronaphthalene. In spite of a chiral manganese environment, the catalytic activity and enantioselectivity of these complexes were found to be poor compared to those of their diiminocyclohexyl analogues. This low activity is probably due to extensive decomposition of the manganese binaphthyl-based complexes under the oxidation reaction conditions. One possible explanation for the instability of these manganese complexes is the highly distorted geometry of the Salbinaphth ligands, more compatible with tetrahedral rather than octahedral or square-pyramidal coordination.

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**Supporting Information Available:** Tables of complete crystal data and experimental details, all atomic positional, thermal, and anisotropic thermal parameters, bond lengths and angles, and least-squares planes with deviations of atoms therefrom and figures showing molecules B and views of the unit cells for compounds **7-Cu** and **6-H<sub>2</sub>** (25 pages). Ordering information is given on any current masthead page.

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