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Racemic and chiral expanded salen-type complexes derived from biphenol and binaphthol: Salbip and salbin

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Abstract

The reaction of 2-fluoronitrobenzene with 2,2′-biphenol or (*R*)-binaphthol, followed by reduction and subsequent reaction of the resulting diamine with two equivalents of a salicylaldehyde, affords expanded salen-type ligands having backbones based on biphenol or binaphthol: salbipH_2, (*R*)-salbinH_2 and (*R*)-salbin(*t*-Bu)$_4H_2$. Deprotonation of these ligands with sodium methoxide or potassium hydride, followed by metallation with M(OAc)$_2$ (M = Mn, Co, Ni, or Cu), affords the corresponding metal complexes in good yield (61–85%). The species containing Mn, Co, and Ni all have distorted octahedral geometry, as determined by X-ray crystallography. The ethereal oxygen atoms occupy two coordination sites with metal–oxygen distances ranging from 2.19 to 2.36 Å. The imine nitrogen atoms are *trans* to each other in the solid state, an impossible geometry in traditional salen-type complexes. The species containing Cu are distorted square planar and show much longer metal–ethereal oxygen distances ranging from 2.79 to 3.22 Å. The manganese complexes are competent catalysts for the epoxidation of olefins.

Keywords: Salen; Catalytic epoxidation; *R*-binaphthol; 2,2′-Biphenol; Chiral

1. Introduction

The salen ligand is a versatile, widely used ligand for homogeneous transition metal mediated catalysis [1–11]. The simple salen ligand is synthesized by the condensation of two equivalents of salicylaldehyde with one equivalent of ethylene diamine (Scheme 1) [12]. Transition metal complexes of salen have been known since at least 1931 [12–15], but the most intense investigations have occurred since chiral variants were first applied to asymmetric catalysis in the early 1990s [16,17]. Modified salen complexes have served as catalysts in varied reactions such as asymmetric epoxidation [2], copolymerization of carbon dioxide with epoxides [5,6], and hydrolytic kinetic resolution of racemic epoxides [18,19], depending on the metal employed.

Jacobsen and coworkers [17,20,21] reported the synthesis of a very successful chiral variant of the salen ligand (Scheme 1). The corresponding manganese (III)-based catalyst is useful for the epoxidation of *cis*-disubstituted olefins in the presence of commercial bleach [2]. Overall the asymmetric epoxidation of *cis*-olefins with Jacobsen's catalyst is effective but the optimized conditions rely on a large catalyst loading (6 mol%) and the use of 4-phenylpyridine-*N*-oxide as an additive in order to obtain high enantiomeric excesses (*ee*'s). Gilheany and coworkers [22–25] reported the synthesis of a series of chiral chromium–salen complexes capable of epoxidizing *trans*-disubstituted olefins with poor to good *ee*'s, but the system suffers from limited substrate tolerance and requires high catalyst loading (10 mol%). Furthermore, it requires an expensive additive and an expensive oxidant (PhIO). The *ee*'s obtained by Gilheany range from 10% to 92% depending on the catalyst, the conditions, and the substrate, and the isolated yields

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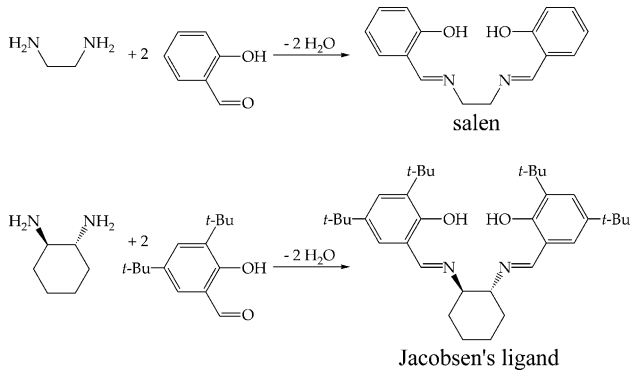
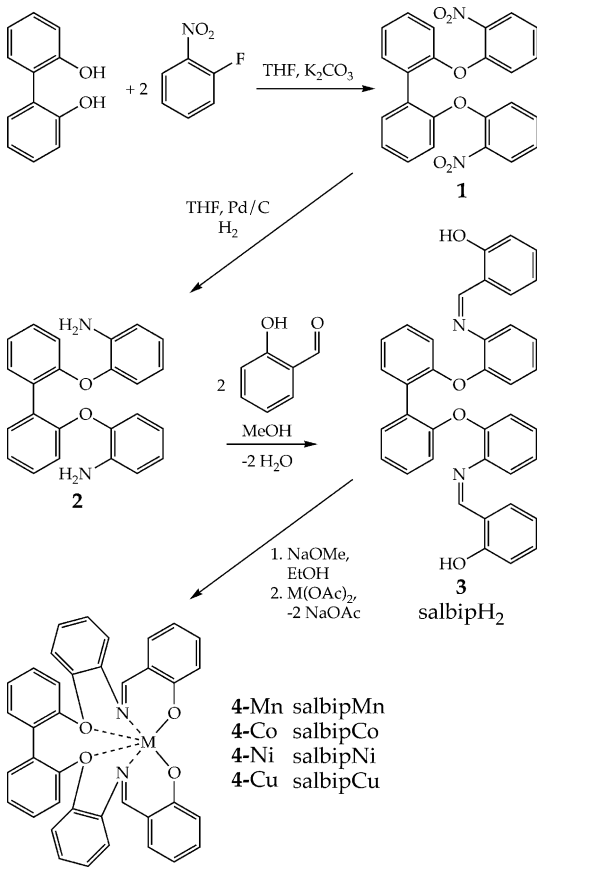


Scheme 1. Synthesis of the original salen ligand and Jacobsen's ligand.

in most cases are 40% or less. The need for new catalysts that are more efficient, less expensive, and more selective is evident.

We have general goals of designing and synthesizing new chiral ligands in an efficient and economical manner on large scale. In this work, we exploit an underutilized nucleophilic aromatic substitution reaction for the synthesis of a novel class of racemic and chiral expanded salen-type ligands derived from 2,2′-biphenol and *R*-binaphthol. These new ligands are readily coordinated to manganese, cobalt, nickel, and copper. The X-ray crystal structures of six of these complexes are reported and interpreted. The catalytic abilities of these species are briefly investigated and compared to those of existing systems.



Scheme 2. Synthesis of an expanded salen-type ligand (**3**, salbipH_2) and its coordination to metals.

2. Results and discussion

2.1. Complex synthesis and X-ray crystallography

2-fluoronitrobenzene reacts readily with a variety of mildly nucleophilic species, such as alcohols or amines, to generate a new carbon-nucleophile bond and hydrofluoric acid [26]. In order to synthesize new salen-type ligands, we took advantage of this facile nucleophilic aromatic substitution reaction (Scheme 2). 2,2′-biphenol reacts readily with 2-fluoronitrobenzene in refluxing THF to give the doubly arylated product **1**. Reduction of **1** with hydrogen using a palladium on carbon catalyst gives the previously unknown diamine **2** in excellent overall yield (97%).

Reaction of **2** with two equivalents of salicylaldehyde gives the corresponding dialdimine, **3** (Scheme 2). This ligand is an "expanded salen ligand" because it has the usual chelating atoms of salen (two imines, two aryloxides) plus two additional neutral donor atoms (ethers). However, since it is derived from *sal*icylaldehyde and *bip*henol, the moniker salbipH_2 is applied. Facile deprotonation of **3** (salbipH_2) is accomplished with sodium methoxide in ethanol; subsequent exposure to transition metal acetates affords salbipM coordination complexes (Scheme 2).

The X-ray structures of **4**-Mn, **4**-Co, **4**-Ni and **4**-Cu were obtained (Fig. 1). Crystallographic data are given in Table 1 and selected bond lengths and angles are given in Table 2. The complexes containing Mn, Co, and Ni have distorted octahedral geometries with *trans* nitrogen atoms. The observation of *trans* nitrogen chelation is quite unusual because in conventional salen complexes, *trans* coordination of the nitrogen atoms is geometrically impossible. The N–M–N angle increases with increasing atomic number (Mn, 159.9°; Co, 167.2°; Ni, 167.6°) as a consequence of the decreasing ionic radius of the metal. In **4**-Mn, **4**-Co, and **4**-Ni, the ethereal oxygen atoms are coordinated to the metal in the solid state. The increase in the N–M–N angle is accompanied by a decrease in average metal–ethereal oxygen distances, which are 2.36, 2.23 and 2.19 Å, respectively. The copper complex **4**-Cu has distorted square planar geometry and its ethereal oxygen atoms are apparently less strongly bound to the metal compared to the Mn, Co, and Ni species. The average metal–ethereal oxygen distance is quite large (2.79 Å) and a N–M–N angle of only 164.6° is observed.

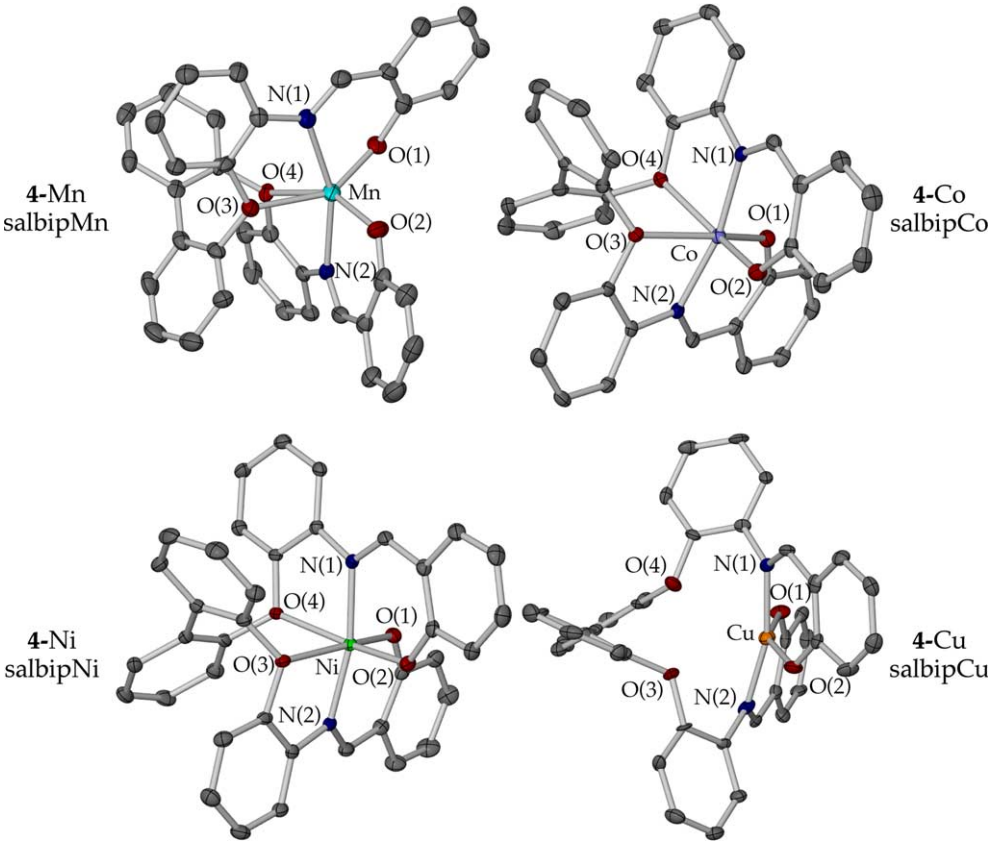


Fig. 1. X-ray structures of **4**-Mn, **4**-Co, **4**-Ni, and **4**-Cu with thermal ellipsoids drawn at 50% probability and hydrogen atoms omitted for clarity. O(3) and O(4) are the ethereal oxygen atoms.

Given the facility of the salbipH_2 ligand synthesis, we sought to synthesize a chiral version of our expanded salen ligand using (*R*)-binaphthol. Unfortunately (*R*)-binaphthol reacts very slowly with 2-fluoronitrobenzene in refluxing THF, taking up to two weeks for complete reaction. However, the reaction proceeds quite rapidly in DMF, affording the expected product **5** in high yield after several hours (Scheme 3). Reduction of **5** in THF with hydrogen using a palladium on carbon catalyst gives the previously unknown chiral diamine **6** in excellent overall yield (90.1%). Reaction of **6** with two equivalents of salicylaldehyde or a substituted salicylaldehyde affords the expected chiral expanded salen ligand **7a** or **7b** (Scheme 3). These are termed salbinH_2 and salbin (t-Bu)$_4H_2$ because they are derived from *sal*icylaldehyde and *bin*aphthol.

Ligands **7a** and **7b** are readily deprotonated in THF with potassium hydride and coordinated to transition metals (Scheme 3). The complexes are very difficult to crystallize and in many cases crystals suitable for X-ray diffraction could not be grown. Nonetheless, we were able to obtain crystals of **8**-Co (Fig. 2). Its structure is similar to that of **4**-Co (Fig. 1) with minor differences. For example, the N–Co–N angle is 164.8° in **8**-Co, compared to the N–Co–N angle of 167.2° in **4**-Co. Also, the ethereal oxygen atoms in **8**-Co are 2.31 and 2.25 Å from the cobalt atom. This compares well to distances of 2.23 and 2.24 Å in **4**-Co. Fig. 3 shows the similarities in the core structures of **4**-Co and **8**-Co. Additionally, X-ray quality crystals of **8**-Cu were obtained (Fig. 2). Its structure is similar to that of **4**-Cu (Fig. 1) with minor differences. The N–Cu–N angle in **8**-Cu is 160.5°, whereas the N–Cu–N angle in **4**-Cu is 164.6°. Also, the ethereal oxygen atoms in **8**-Cu are 3.22 and 2.76 Å from the copper atom. This contrasts with the nearly identical copper-ethereal oxygen distances of 2.80 and 2.79 Å in **4**-Cu. Fig. 4 shows the similarities in the core structures of **4**-Cu and **8**-Cu.

2.2. Catalytic epoxidation of olefins

Using commercially available Mn(III) Jacobsen's catalyst, it is possible to obtain high *ee*'s for the epoxidation of many *cis* olefins. However, a pyridine-*N*-oxide derivative (or other additive) is required, usually with a 25 mol% loading relative to the olefin substrate. Jacobsen asserts that this additive acts as an axial ligand to the manganese center [1,2]. Our initial hope that the ethereal oxygens of **4** or **8** may supplant this

Table 1
Crystallographic data

Compound	**4**-Mn	**4**-Co	**4**-Ni	**4**-Cu	**8**-Co	**8**-Cu
Empirical formula	$C_{38}H_{26}MnN_2O_4$	$C_{38}H_{26}CoN_2O_4 \cdot 2(CH_2Cl_2)$	$C_{38}H_{26}NiN_2O_4 \cdot 2(CH_2Cl_2)$	$C_{38}H_{26}CuN_2O_4 \cdot (CH_2Cl_2)$	$C_{46}H_{30}CoN_2O_4 \cdot 0.67(C_4H_8O_2)$	$C_{46}H_{30}CuN_2O_4 \cdot (C_4H_8O_2)$
Formula weight	629.55	803.39	803.17	723.07	792.39	826.36
Temperature (K)	110(2)	110(2)	110(2)	110(2)	110(2)	110(2)
Wavelength (Å)	1.54184	1.54178	0.71069	1.54178	1.54184	1.54178
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Tetragonal	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P4_12_12$	P_1
a (Å)	10.040(2)	12.151(5)	12.062(5)	10.1638(14)	15.439(2)	9.6049(2)
b (Å)	10.464(2)	12.226(5)	12.119(5)	10.7654(15)	15.439(2)	20.1868(4)
c (Å)	15.633(3)	12.890(5)	12.858(5)	14.831(2)	56.434(12)	10.4445(2)
α(°)	84.865(11)	77.837(5)	78.888(5)	86.426(8) 53 + (8)	90	90
β(°)	79.931(11)	88.325(5)	88.475(5)	79.784(8)	90	95.9610(10)
γ(°)	66.126(11)	73.528(5)	74.846(5)	80.540(8)	90	90
Volume (Å^3)	1478.4(5)	1794.1(13)	1779.6(12)	1574.4(4)	13452(4)	2014.16(7)
Z	2	2	2	2	12	2
Density (calc., gcm^{-3})	1.414	1.487	1.499	1.525	1.174	1.363
μ (mm^{-1})	4.004	6.860	0.891	2.926	3.369	1.207
Crystal size (mm^3)	$0.10 \times 0.10 \times 0.10$	$0.30 \times 0.10 \times 0.05$	$0.30 \times 0.30 \times 0.10$	$0.10 \times 0.10 \times 0.30$	$0.20 \times 0.10 \times 0.10$	$0.10 \times 0.10 \times 0.05$
Reflections	13845	10841	19921	8824	107481	00807
Independent reflections	4035	4868	7993	4175	9364	4955
Data/restraints/parameters	4035/0/404	4868/0/461	7993/4/476	4175/0/433	9364/604/766	4955/1/534
GOF (F^2)	1.068	1.059	1.079	1.006	1.003	1.009
$R_1[I > 2\sigma(I)]$	0.0475	0.0427	0.0452	0.0521	0.1038	0.315
$wR_2[I > 2\sigma(I)]$	0.0646	0.0991	0.1179	0.1068	0.2095	0.0798
R_1 (all data)	0.1017	0.0556	0.0574	0.1074	0.1783	0.0347
wR_2 (all data)	0.0725	0.1047	0.1323	0.1240	0.2477	0.0816
Largest difference in peak, hole (e Å^{-3})	0.339, 0.428	0.811, −0.586	1.114, −0.530	0.527, −0.449	0.455, −0.365	0.335, −0.297

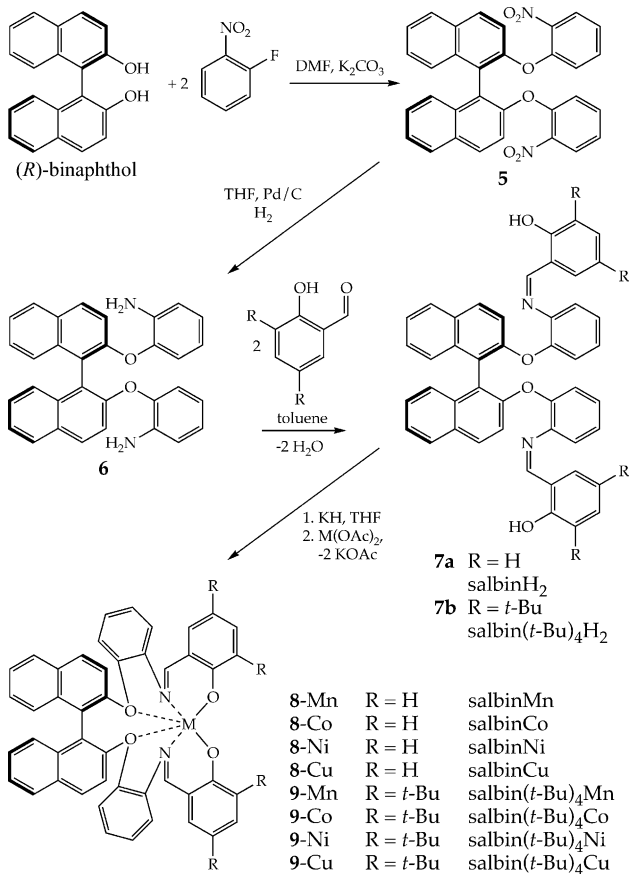
Table 2
Selected bond lengths (Å) and angles (°)

	4-Mn	4-Co	4-Ni	4-Cu	8-Co	8-Cu
M–O(1)	2.02	1.97	1.96	1.91	1.96	1.90
M–O(2)	2.02	1.97	1.96	1.91	1.95	1.89
M–O(3)	2.37	2.23	2.18	2.80	2.31	3.22
M–O(4)	2.35	2.24	2.20	2.79	2.25	2.76
M–N(1)	2.22	2.08	2.01	1.97	2.07	1.98
M–N(2)	2.22	2.07	2.01	1.98	2.10	1.99
N(1)–M–N(2)	159.9	167.2	167.6	164.6	164.8	160.5
O(1)–M–O(2)	109.5	110.5	103.5	149.3	106.1	156.9
O(1)–M–O(3)	152.1	159.2	165.2	127.4	161.5	125.6
O(1)–M–O(4)	90.9	88.8	89.2	82.3	87.4	84.5
O(2)–M–O(3)	94.7	88.1	89.5	81.9	87.0	74.4
O(2)–M–O(4)	149.2	158.0	165.2	126.6	81.7	117.6
O(3)–M–O(4)	74.2	75.0	79.0	57.4	64.3	61.6

additive was not realized; an additive is indeed required to obtain reasonable catalytic activity. The ether oxygen atom, along with its persistence by chelation, does not mimic the net electronic effects of the pyridine-*N*-oxide additive.

The octahedral manganese complex **4**-Mn catalyzes the epoxidation of various olefins under the standard conditions used by Jacobsen [2] with 5 mol% catalyst loading (Scheme 4). The results are listed in Table 3. Overall, the performance of the achiral catalyst **4**-Mn is comparable to other salen–manganese complexes with regard to turnover numbers and rates [1,2,22].

Encouraged by the results with racemic **4**-Mn, we sought to employ our chiral manganese complexes to obtain enantiomerically enriched epoxides (also under the standard conditions outlined in Scheme 4). (*R*)-binaphthol-based complex **8**-Mn is capable of epoxidizing olefins with an activity comparable to that of **4**-Mn. Unfortunately, the *ee* for the epoxidation of styrene is quite low at 11%. Thus, we turned to the *tert*-butylated complex **9**-Mn in the pursuit of higher *ee*'s. Complex **9**-Mn is capable of epoxidizing olefins; however, the activity is lower. In order to obtain complete conversion of styrene to styrene oxide, 10 mol% catalyst loading was



Scheme 3. Synthesis of an expanded chiral salen-type ligand (**7a**, salbinH_2; **7b**, salbin(*t*-Bu)$_4H_2$) and its coordination to metals.

required. Furthermore, the addition of *tert*-butyl groups to the catalyst only increased the *ee* in the case of styrene oxide to 22%. In the epoxidation of *trans*-stilbene, the reaction does not reach completion even with 10% catalyst loading. The GC yield of epoxide is only 15% and the *ee* is only 18%.

Finally, the initial testing of **4**-Co, **8**-Co, and **9**-Co for the hydrolytic kinetic resolution of racemic epoxides [18] was unfruitful. This is not wholly unexpected because

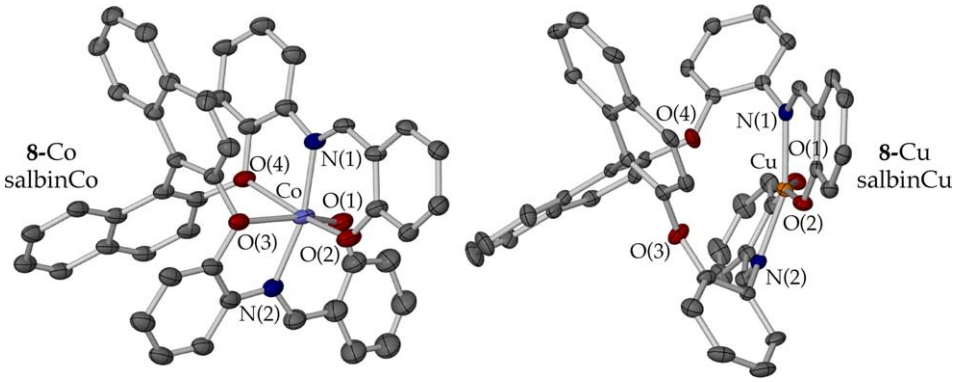


Fig. 2. X-ray structures of **8**-Co and **8**-Cu with thermal ellipsoids drawn at 50% probability and hydrogen atoms omitted for clarity. O(3) and O(4) are the ethereal oxygen atoms.

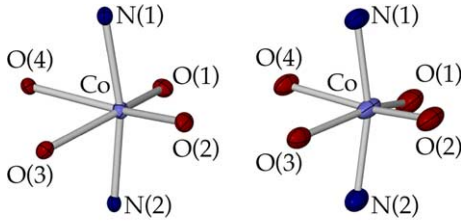


Fig. 3. Coordination sphere of **4**-Co and **8**-Co with thermal ellipsoids drawn at 50% probability.

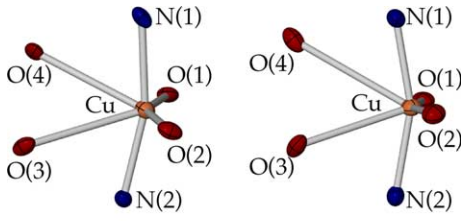
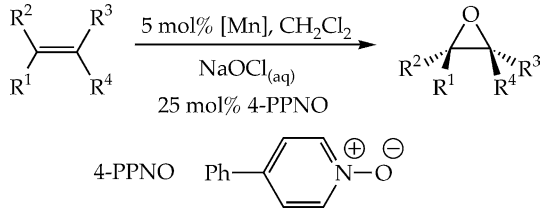


Fig. 4. Coordination sphere of **4**-Cu and **8**-Cu with thermal ellipsoids drawn at 50% probability.



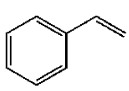
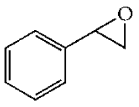
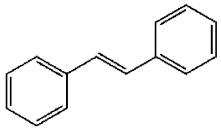
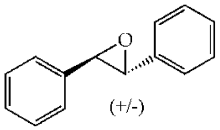
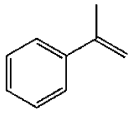
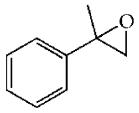
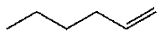
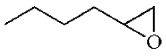
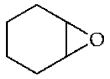
Scheme 4. Catalytic epoxidation of olefins with [Mn] = **4**-Mn, **8**-Mn, or **9**-Mn.

the ethereal oxygen atoms (Figs. 1, 2, O(3) and O(4)) seemingly prevent the creation of an open coordination site, a prerequisite for coordination and activation of the epoxide substrate.

3. Conclusions

Novel racemic and chiral expanded salen ligands were synthesized and readily coordinated to Mn, Co, Ni, and Cu to yield complexes with unique structural motifs. Catalytically, the manganese-based complexes generally behaved comparably to their salen analogues for the epoxidation of olefins. While asymmetric induction was minimal with **8**-Mn and **9**-Mn, a variety of other asymmetric catalytic reactions will be explored using these readily synthesized and inexpensive transition metal complexes derived from chiral binaphthol.

Table 3
Substrates, epoxidation products, and isolated yields for catalyst **4**-Mn

Olefin	Epoxide	Yield (%)
		83%
	 (+/-)	56%
		78%
		85%
		77%

4. Experimental

4.1. General remarks

All air sensitive procedures were conducted under a purified atmosphere of nitrogen in a glove box or using standard Schlenk line techniques. Solvents were distilled under nitrogen using standard techniques. Manganese (II) acetate tetrahydrate (Acros, 99+%), cobalt (II) acetate tetrahydrate (Acros, 99+%), nickel (II) acetate tetrahydrate (Acros, 99+%), and copper (II) acetate tetrahydrate (Acros, 99+%), were each dehydrated by heating under dynamic vacuum at 150 °C for 3 h. The anhydrous materials were stored in a dry box under nitrogen. (*R*)-binaphthol was obtained from ABCR Chemical and 3,5-di-*tert*-butyl salicylaldehyde was obtained from Advanced Asymmetrics. All other reagents were used as received. All NMR chemical shifts are given in ppm and were recorded on a Mercury-300BB spectrometer (^{1}H, 299.91 MHz; ^{13}C {^{1}H} 75.41 MHz) using the solvent as an internal standard ($CDCl_3$ (or residual $CHCl_3$): ^{1}H 7.27 ppm; ^{13}C 77.0 ppm). Chiral phase gas chromatography was performed on an Agilent 6850 gas chromatograph with a 30-m 3-*o*-trichloracetyl-2,6-di-*o*-pentyl β-cyclodextrin column. X-ray crystallographic data were obtained using a Bruker SMART 1000 three-circle diffractometer operating at 50 kV and 40 mA, Mo Kα (λ = 0.71073 Å) with a graphite monochromator and a CCD-PXL-KAF2 detector or a Bruker GADPS instrument operating at 40 kV and 40 mA, Cu Kα (λ = 1.54578 Å) with a graphite monochromator and a CCD-PXL-KAF2 detector.

4.2. Synthesis of 2,2′-bis-(2-nitrophenoxy)-biphenyl (**1**)

2,2′-biphenol (10.00 g, 53.7 mmol) and potassium carbonate (16.33 g, 118.2 mmol) were added to a 500 mL round bottom flask with THF (200 mL). The reaction was refluxed for 72 h. Removal of the insoluble potassium salts by filtration, followed by removal of the THF by rotary evaporation and high vacuum gave the product as a white solid: 22.36 g (97.2%). Note: THF removal is not necessary as it is a suitable solvent for the next reaction. ^{1}H NMR ($CDCl_3$): δ 6.85 (d, $J = 8.4$ Hz, 2H, Ar*H*), 6.97 (d, $J = 9.3$ Hz, 2H, Ar*H*), 7.05 (t, $J = 6.3$ Hz, 2H, Ar*H*), 7.19 (t, $J = 6.9$ Hz, 2H, Ar*H*), 7.26–7.39 (m, 4H, Ar*H*), 7.45 (d, $J = 6.8$ Hz, 2H, Ar*H*), 7.80 (d, $J = 4.1$ Hz, 2H, Ar*H*). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 119.8, 122.7, 125.0, 125.8, 129.3, 129.8, 132.7, 135.4, 137.5, 140.7, 151.8, 152.7. TOF MS/ESI: *m*/*z* 429 $(M + H)^+$.

4.3. Synthesis of 2,2′-bis-(2-aminophenoxy)-biphenyl (**2**)

A solution of **1** (10.00 g, 23.3 mmol) in THF (200 mL) was placed into a hydrogenation vessel with 10% Pd/C (0.25 g) and one drop of concentrated sulfuric acid. The vessel was purged for several minutes with hydrogen and then pressurized to 40 psi. The slurry was stirred for 8 h at room temperature. The pressure was released and the solution was then filtered to remove the palladium catalyst. Removal of the solvent by rotary evaporation and high vacuum gave the product as an off-white solid which was sufficiently pure for characterization and further use: 8.55 g (99.6%) ^{1}H NMR ($CDCl_3$): δ 3.749 (broad, 4H, N*H*), 6.66 (t, $J = 7.2$ Hz, 2H, Ar*H*), 6.75 (m, 4H, Ar*H*), 6.87 (d, $J = 7.8$ Hz, 2H, Ar*H*), 6.95 (t, $J = 7.8$ Hz, 2H, Ar*H*), 7.12 (t, $J = 7.5$ Hz, 2H, Ar*H*), 7.25 (t, $J = 7.5$ Hz, 2H, Ar*H*), 7.40 (d, $J = 7.2$ Hz, Ar*H*). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 115.5, 116.6, 118.8, 121.4, 122.6, 125.4, 128.6, 129.2, 132.0, 139.3, 142.7, 155.3. TOF MS/ESI: *m*/*z* 369 $(M + H)^+$.

4.4. Synthesis of salbipH_2 (**3**)

A quantity of **2** (10.00 g, 25.9 mmol) was added to a round bottom flask with methanol (250 mL). Salicylaldehyde (6.32 g, 51.8 mmol) was added to the flask. A yellow precipitate formed almost instantly. The slurry was stirred for 3 h to ensure reaction completion. The slurry was then cooled in an ice bath. The solid was collected by filtration and washed with cold methanol (3×100 mL). The yellow power was dried by vacuum: 14.1 g (91.6%). ^{1}H NMR ($CDCl_3$): δ −1.95 (s, 2H, O*H*), 6.78 (d, $J = 9.6$ Hz, 2H, Ar*H*), 6.85–6.94 (m, 6H, Ar*H*), 7.00–7.13 (m, 8H, Ar*H*), 7.20–7.35 (m, 6H, Ar*H*), 7.45 (d, $J = 7.8$ Hz, 2H, Ar*H*), 8.47 (s, 2H, Ar–N=C*H*–Ar). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 117.5, 118.0, 118.9, 119.5, 120.2, 121.4, 123.5, 124.0, 127.7, 129.1, 129.2, 132.5, 132.6, 133.2, 139.8, 149.8, 154.4, 161.5, 164.1. TOF MS/ESI: *m*/*z* 577 $(M + H)^+$.

4.5. Typical procedure for the metallation of ligand 3 (**4**-Mn, **4**-Co, **4**-Ni, **4**-Cu)

A quantity of **3** (1.00 g, 1.7 mmol) and sodium methoxide (0.18 g, 3.3 mmol) were placed into a swivel frit. The vessel was evacuated and dry, degassed ethanol (~40 mL) was vacuum transferred into the frit. The solution was warmed to 50 °C for 4 h. All solvent was removed by vacuum. The frit was brought into the glove box and anhydrous $M(OAc)_2$ (1.8 mmol) was added. Ethanol (~30 mL) was vacuum transferred into the frit. The reaction was heated to 50 °C for 4 h during which time a precipitate formed. This precipitate was filtered, washed with ethanol and dried under vacuum.

4.5.1. Synthesis of salbipMn (**4**-Mn)

M = Mn: red-orange micro crystals, 0.87 g (79.9%). Crystals (needles) for X-ray diffraction were grown by cooling a saturated dichloromethane solution to −35 °C.

4.5.2. Synthesis of salbipCo (**4**-Co)

M = Co: red micro crystals, 0.94 g (85.8%). Crystals (needles) for X-ray diffraction were grown by cooling a saturated dichloromethane solution to −35 °C.

4.5.3. Synthesis of salbipNi (**4**-Ni)

M = Ni: yellow powder, 0.62 g (56.6%). Crystals (needles) for X-ray diffraction were grown by cooling a saturated dichloromethane solution to −35 °C.

4.5.4. Synthesis of salbipCu (**4**-Cu)

M = Cu: green-brown micro crystals, 0.79 g (71.8%). Crystals (needles) for X-ray diffraction were grown by cooling a saturated dichloromethane solution to −35 °C.

4.6. Synthesis of (*R*)-2,2′-bis-(2-nitrophenoxy)-[1,1′]binaphthalenyl (**5**)

R-binaphthol (10.00 g, 34.9 mmol) and potassium carbonate (10.14 g, 73.3 mmol) were dissolved in DMF (120 mL). 2-fluoronitrobenzene (9.85 g, 69.8 mmol) was added to the solution. The obtained solution was stirred at 80 °C for 6 h and then poured over ice water (250 mL). A white precipitate formed immediately. The white precipitate was collected by filtration, washed with hot water (3×50 mL) and dried under vacuum: 18.0 g (97.8%) ^{1}H NMR ($CDCl_3$): δ 7.00–7.04 (m, 4H, Ar*H*), 7.23 (d, $J = 9.0$ Hz, 2H, Ar*H*), 7.21–7.37 (m, 6H, Ar*H*), 7.44 (t, $J = 6.2$ Hz, 2H, Ar*H*), 7.72 (d, $J = 8.4$ Hz, 2H, Ar*H*), 7.89 (d, $J = 8.1$ Hz, 2H, Ar*H*), 7.941 (d, $J = 9.0$ Hz, 2H, Ar*H*). ^{13}C {^{1}H} NMR ($CDCl_3$) δ 119.1, 120.7, 122.4, 122.9, 125.5, 125.8, 126.1, 127.3, 128.3,

130.8, 131.1, 134.1, 134.3, 141.0, 150.8, 151.2. TOF MS/ESI: *m/z* 529 $(M + H)^+$.

4.7. Synthesis of (R)-2,2′-bis-(2-aminophenoxy)-[1,1′]binaphthalenyl (6)

A quantity of **5** (10.00 g, 18.9 mmol) was dissolved in THF (200 mL) and the solution was added to a hydrogenation vessel containing 10% Pd/C (0.25 g). One drop of concentrated sulfuric acid was added. The vessel was flushed for several minutes with hydrogen and then pressurized to 40 psi. The slurry was stirred for 8 h at room temperature. The pressure was released and the solution was then filtered to remove the palladium catalyst. Removal of the solvent by rotary evaporation and high vacuum gave the product was an off-white solid, which was sufficiently pure for characterization and further use (14.83 g, 90.6%): ^{1}H NMR ($CDCl_3$): δ 3.55 (broad, 4H, N*H*), 6.61 (t, J = 8.7 Hz, 2H, Ar*H*), 6.66 (d, J = 6.6 Hz, 2H, Ar*H*), 6.82 (d, J = 7.8 Hz, 2H, Ar*H*), 6.90 (t, J = 7.5 Hz, 2H, Ar*H*), 7.20 (d, J = 9.0 Hz, 2H, Ar*H*), 7.31–7.43 (m, 6H, Ar*H*), 7.87–7.91 (m, 4H, Ar*H*). ^{13}C $\{^1H\}$ NMR ($CDCl_3$) δ 116.4, 117.5, 118.7, 120.6, 120.7, 124.7, 124.9, 125.6, 127.0, 128.5, 130.0, 130.5, 134.4, 138.9, 143.5, 153.0. TOF MS/ESI: *m/z* 469 $(M + H)^+$.

4.8. Synthesis of salbinH_2 (7a)

A quantity of **6** (10.00 g, 21.3 mmol) was dissolved in toluene (200 mL) in a round bottom flask with a few crystals of *p*-toluenesulfonic acid (0.05 g). Salicylaldehyde (5.21 g, 42.7 mmol) was added and a Dean–Stark trap was attached. The solution was refluxed for 3 h during which time approximately 0.75 mL of water were collected. The toluene was then removed by rotary evaporation followed by high vacuum to give a yellow glass: 13.69 g (98.4%). This glass was sufficiently pure for characterization and further use. A powder could be obtained by adding 100 mL of methanol to the glass and stirring the slurry for 2 h. ^{1}H NMR ($CDCl_3$): δ −2.24 (s, 2H, O*H*), 6.706–6.821 (m, 6H, Ar*H*), 6.890–7.11 (m, 10H, Ar*H*), 7.19–7.35 (m, 8H, Ar*H*), 7.85–7.95 (m, 4H, Ar*H*), 8.17 (s, 2H, Ar–N=C*H*–Ar). ^{13}C $\{^1H\}$ NMR ($CDCl_3$) δ 117.2, 118.3, 118.8, 119.4, 120.3, 123.0, 124.1, 124.9, 125.8, 125.9, 127.1, 127.3, 128.2, 130.1, 130.5, 132.7, 133.1, 134.4, 140.0, 149.2, 152.1, 161.2, 165.4. TOF MS/ESI: *m/z* 677 $(M + H)^+$.

4.9. Synthesis of salbin(t-Bu)$_4H_2$ (7b)

A quantity of **6** (10.00 g, 21.3 mmol) was dissolved in toluene (200 mL) in a round bottom flask with a few crystals of *p*-toluenesulfonic acid (0.05 g). 3,5-di-*tert*-butyl salicylaldehyde (10.00 g, 42.7 mmol) was added and a Dean–Stark trap was attached. The solution was refluxed for 3 h during which time approximately 0.75 mL of water were collected. The toluene was then removed by rotary evaporation followed by high vacuum to give a yellow glass: 27.32 g (93.5%). This glass was sufficiently pure for characterization and further use. A powder could be obtained by adding 100 mL of methanol to the glass and stirring the slurry for 2 h. ^{1}H NMR ($CDCl_3$): δ–1.99 (s, 2H, O*H*), 1.26 (s, 18H, Ar–C(CH_3)$_3$), 1.32 (s, 18H, Ar–C(CH_3)$_3$), 6.74 (t, J = 6.9 Hz, 2H, Ar*H*), 6.82 (d, J = 8.1 Hz, 2H, Ar*H*), 6.89–6.99 (m, 6H, Ar*H*), 7.17–7.28 (m, 6H, Ar*H*), 7.39 (d, J = 2.7 Hz, 2H, Ar*H*), 7.80 (d, J = 8.1 Hz, 2H, Ar*H*), 7.88 (d, J = 9.0 Hz, 2H, Ar*H*), 8.25 (s, 2H, Ar–N=C*H*–Ar). ^{13}C $\{^1H\}$ NMR ($CDCl_3$) δ 29.5, 31.8, 34.4, 35.2, 118.6, 120.3, 121.6, 122.0, 123.9, 124.6, 126.1, 126.6, 127.0, 127.2, 127.9, 128.0, 128.5, 129.9, 130.6, 134.4, 137.1, 140.3, 140.5, 149.6, 152.5, 158.3, 165.5. TOF MS/ESI: *m/z* 901 $(M + H)^+$.

4.10. Typical procedure for the metallation of ligand (7a) or (7b)

The ligand **7a** or **7b** (2.2 mmol) was placed into a swivel frit with potassium hydride (0.18 g, 4.4 mmol) under an atmosphere of nitrogen. THF (∼40 mL) was transferred into the swivel frit. The reaction was stirred for 2 h at room temperature open to a bubbler during which time the color changed from yellow to red-orange. The THF was removed under high vacuum. The frit was brought into the glove box and anhydrous $M(OAc)_2$ (2.3 mmol) was added. THF (∼40 mL) was transferred into the swivel frit. The reaction was stirred at 50 °C for 6 h. The THF was removed by vacuum and toluene (∼40 mL) was transferred into the frit. The solution was filtered to remove the potassium acetate salt. The salt cake was washed several times with toluene to extract the product. The volume of toluene was reduced to 10 mL and the solution was allowed to stand until precipitate formed. The precipitate was collected by filtration and dried under high vacuum.

4.10.1. Synthesis of salbinMn (8-Mn)

M = Mn: red-orange powder, 1.78 g (82.5%).

4.10.2. Synthesis of salbinCo (8-Co)

M = Co: red powder, 1.24 g (77.1%). Crystals (needles) for X-ray diffraction were grown by cooling a saturated ethyl acetate solution to −35 °C.

4.10.3. Synthesis of salbinNi (8-Ni)

M = Ni: yellow powder, 1.41 g (87.2%).

4.10.4. Synthesis of salbinCu (8-Cu)

M = Cu: green-brown micro crystals, 1.90 g (87.1%). Crystals (needles) for X-ray diffraction were grown by cooling a saturated dichloromethane solution to −35 °C.

*4.10.5. Synthesis of salbin(t-Bu)$_4$Mn (**9**-Mn)*

M = Mn: red-orange powder, 1.83 g (84.0%).

*4.10.6. Synthesis of salbin(t-Bu)$_4$Co (**9**-Co)*

M = Co: red powder, 1.33 g (62.1%).

*4.10.7. Synthesis of salbin(t-Bu)$_4$Ni (**9**-Ni)*

M = Ni: yellow powder, 1.98 g (90.9%).

*4.10.8. Synthesis of salbin(t-Bu)$_4$Cu (**9**-Cu)*

M = Cu: green-brown micro crystals, 1.49 g (68.4%). Crystals (needles) for X-ray diffraction were grown by cooling a saturated dichloromethane solution to −35 °C.

*4.11. Typical procedure for epoxidation of olefins with **4**-Mn, **8**-Mn, or **9**-Mn*

An olefin (9.6 mmol), **4**-phenylpyridine-*N*-oxide (0.41 g, 2.4 mmol), the manganese catalyst **4**-Mn, **8**-Mn, or **9**-Mn (0.48 mmol), and dichloromethane (30 mL) were placed into a round bottom flask. This solution was cooled to 0 °C in an ice bath. Commercial bleach (*circa* 5% aqueous NaOCl, 100 mL) was cooled to 0 °C in an ice bath and added in one portion to the flask. The reaction was stirred for 3 h at 0 °C and then allowed to stir for 3 h at room temperature. The reaction was transferred into a separatory funnel with 100 mL of diethyl ether. The organic layer was removed and set aside. The aqueous layer was extracted with diethyl ether (2×50 mL). The combined organic extracts were washed with water (2×20 mL) and brine (10 mL). The organic layer was then dried over anhydrous magnesium sulfate and filtered. Removal of the ether by rotary evaporation gave the crude product. The product was purified by fractional distillation. Isolated yields for catalyst **4**-Mn are given in Table 3. When applicable, the enantiomeric excess of the epoxide was determined by chiral phase GC.

5. Supplementary material

Crystallographic data for **4**-Mn (CCDC 264655), **4**-Co (CCDC 264656), **4**-Ni (CCDC 264658), **4**-Cu (CCDC 264657), **8**-Co (CCDC 264660), and **8**-Cu (CCDC 264659) have been deposited with the Cambridge Crystallographic Data Centre. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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