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Asymmetric epoxidation catalyzed by Cr(III)-binaphthyl Schiff base complexes

Zheng-Kai Li [a], Lei Liang [a], Li Yang [a,b], Hua Chen [a], Xiang-Ge Zhou [a,c,*]

[a] *College of Chemistry, Sichuan University, Wangjiang Road 29, Chengdu 610064, China*
[b] *Experimental Center, Yibin University, Yibin 644000, China*
[c] *State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, China*

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Abstract

A series of chromic complexes with binaphthyl Schiff base as ligands are synthesized. Their catalytic abilities in asymmetric epoxidation and the effects of reaction conditions such as temperature, solvent and additive have also been studied, leading to the highest ee of 65% for 4-chlorostyrene; the reaction seems to involve a Cr(V)-oxo active species.

Keywords: Chromic complex; Binaphthyl Schiff base; Asymmetric epoxidation

1. Introduction

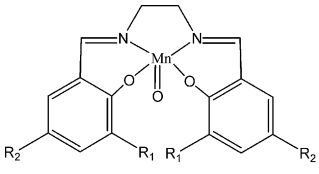
Chiral epoxides are valuable intermediates for the stereocontrolled synthesis of complex organic compounds, and their utilities have expanded dramatically with the advance in practical asymmetric catalytic methods [1]. Among the different synthetic methods, metalloporphyrin complexes, which were stimulated by the attempts to model the reactivity of hemoproteins, such as cytochrome P-450, have drawn much attention due to its high chiral induction as well as extremely large turnover numbers obtained.

However, besides oxidative degradation of porphyrinato ligands, laborious procedure involved in the porphyrin synthesis, which results in a high cost of the metalloporphyrin catalysts, retards their use in industrial process. Owing to these problems, non-porphyrin type chelating multianionic ligands have recently received considerable attention [2].

The breakthrough in asymmetric epoxidation of unfunctionated alkenes catalyzed by non-porphyrin complexes was reported by Jacobsen and co-workers [3] and subsequently Katsuki and co-workers [4], etc., by using homochiral manganese(III) salen complexes.

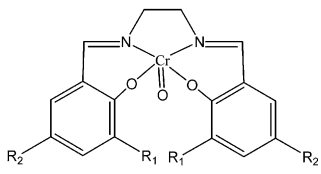
Besides high enantioselectivities obtained, another advantage of the metal–salen system is the lower cost and easy availability compared with chiral porphyrins [5]. Furthermore, the easy preparation of a large variety of chiral salen complexes allows systematic study by the method of variation of the steric and electronic environments.

Besides manganese, chromium was another metal which was studied in detail by Kochi and co-workers for kinetics and mechanism of epoxidation by using achiral salen complex [6], and they observed that both of the active species were probably the metal–oxo salen complexes (**I** and **II**).



Mn-oxo-salen

I



Cr-oxo-salen

II

* Corresponding author. Tel.: +86 2885407986; fax: +86 2885412026.
E-mail address: zhouxiangge@hotmail.com (X.-G. Zhou).

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On the other hand, the successful chiral sources for the preparation of salens for epoxidation were 1,2-diaminocyclohexane and 1,2-diphenylethylenediamine. The complexes with these salens resemble porphyrin complexes: the four coordination atoms are co-planar, and the chiral environment is produced by the chiral center adjacent to the coordination atoms.

The binaphthyl moiety, which has been effectively employed in other asymmetric reactions [7], has rarely been incorporated into Schiff base ligand for mediating asymmetric catalysis except the recent epoxidation and silylcyanation catalyzed by manganese(III), palladium(II) and titanium(IV) complexes reported by Che and us [8].

Herein is described the asymmetric epoxidation of styrenes catalyzed by Cr(III)-binaphthyl Schiff base, of which the structure is different from that of the above-mentioned co-planar metallosalens or porphyrinato complexes. In the free ligand state, the four coordination atoms of binaphthyl Schiff base are not in the same plane with a dihedral angle of 120° between the two napthyl units due to the steric hindrance, which might cause more rigid chiral induction. Another important feature is that the carbon atoms adjacent to the coordination atoms of binaphthyl Schiff base complex are sp^2-hybridized like the porphyrinato ligand, while there are two sp^3 carbon atoms in a co-planar salen ligand.

2. Experimental

2.1. Physical measurements

UV–vis spectra were recorded on a Perkin-Elmer Lambda 19 spectrophotometer or a HP 8453 spectrometer. Infrared spectra were obtained on a Shimadzu-470 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Jeol 270 FT-NMR spectrometer and Brucker DPX-300 FT-NMR spectrometer, respectively. Chemical shifts (δ, ppm) were reported relative to tetramethylsilane. Mass spectra were recorded on a Finnigan MAT 95 Mass spectrometer. Elemental analyses were performed by Butterworth Laboratories Ltd., or by Institute of Chemistry, Chinese Academy of Sciences. GC analyses were done on a HP model 5890 series II Chromatograph equipped with a flame ionization detector.

2.2. Materials

All chemicals were purchased from Aldrich or Lancaster and used as received unless otherwise noted. Solvents were purified by standard procedures. Iodosylbenzene was prepared by hydrolysis of the corresponding diacetate with aqueous potassium hydroxide and stored at refrigerator [9]. *m*-Chloroperoxybenzoic acid was purchased from Fluka. 2,6-Dichloropyridine-*N*-oxide was prepared by oxidation of 2,6-dichloropyridine with hydrogen peroxide [10]. Anhydrous TBHP in toluene was prepared by the method of Sharpless and co-workers [11]. *cis*-β-Methylstyrene was prepared by hydrogenation of 1-phenyl-1-propyne [12]. Triphenyl phosphine oxide was prepared with the method of Dunbar and Haefner [13].

2.3. General preparation of complexes [14]

The chromium catalysts were prepared from $CrCl_2$ and corresponding Schiff base ligands. In a typical procedure: chromium dichloride (1.1 mmol) and binaphthyl Schiff base (1 mmol) were added to dry and degased THF (20 mL) in a Schlenk flask under argon. The color of the solution turned from brown to green. After 3 h reaction at room temperature, the mixture was exposed to the air; chromium(II) was then oxidized to chromium(III). After another 3 h reaction, solvent was removed and the desirable product could be obtained as green solid by recrystallization from dichloromethane and hexane.

The results of spectroscopic characterization of chromium binaphthyl Schiff base complexes are as follows (abbreviated as Cr-ligand; Cr-**VI** shows the same spectra as Cr-**V** except for the opposite optical rotation):

Cr-**III**: (353.6 mg, 61%) IR (KBr, cm^{-1}): 3436, 1607, 1560, 1507, 1442, 1300, 1189, 1152, 1080, 840, 756, 614. MS (FAB): 577 ($M^{+\bullet}$), 542 ($M-Cl$). Anal. Calcd for $C_{34}H_{22}N_2O_2CrCl{\cdot}3H_2O$: C, 64.61; H, 4.43; N, 4.43. Found: C, 64.63; H, 4.25; N, 4.58.

Cr-**IV**: (522.2 mg, 72%) IR (KBr, cm^{-1}): 3442, 1605, 1507, 1430, 1302, 1207, 1178, 830, 752, 613. MS (FAB): 716 ($M^{+\bullet}$), 715 ($M-1$), 680 ($M-Cl$). Anal. Calcd for $C_{34}H_{18}N_2O_2C_{l4}CrCl{\cdot}0.5H_2O$: C, 56.33; H, 3.04; N, 4.30. Found: C, 56.31; H, 2.99; N, 4.26.

Cr-**V**: (706.1 mg, 78%) IR (KBr, cm^{-1}): 3443, 1603, 1507, 1430, 1302, 1207, 1160, 1072, 820, 751, 715, 688, 539. MS (FAB): 893 ($M^{+\bullet}$), 858 ($M-Cl$). Anal. Calcd for $C_{34}H_{18}N_2O_2Br_4CrCl{\cdot}2H_2O$: C, 43.89; H, 2.37; N, 3.01. Found: C, 43.71; H, 2.58; N, 3.21.

Cr-**VII**: (218.8 mg, 27%) IR (KBr, cm^{-1}): 3438, 1608, 1547, 1390, 1372, 1278, 1198, 835, 752. MS (FAB): 801 ($M^{+\bullet}$), 766 ($M-Cl$). Anal. Calcd for $C_{50}H_{54}N_2O_2CrCl{\cdot}2H_2O$: C, 71.68; H, 6.93; N, 3.34. Found: C, 71.21; H, 7.26; N, 3.07.

Cr-**VIII**: (471.6 mg, 60%) IR (KBr, cm^{-1}): 3440, 1610, 1530, 1405, 1309, 1168, 964, 834, 800, 773, 747. MS (FAB): 759 ($M^{+\bullet}$), 722($M-Cl$). Anal. Calcd for $C_{42}H_{36}N_2O_2Cl_2CrCl{\cdot}1.5H_2O$: C, 58.91; H, 4.40; N, 3.16. Found: C, 58.56; H, 4.68; N, 3.17.

Cr-**IX**: (253.8 mg, 36%) IR (KBr, cm^{-1}): 3442, 1603, 1546, 1507, 1420, 1384, 1208, 1072, 865, 830, 750. MS (FAB): 633 ($M^{+\bullet}$), 598 ($M-Cl$). Anal. Calcd for $C_{38}H_{30}N_2O_2CrCl{\cdot}4H_2O$: C, 64.59; H, 5.38; N, 3.97. Found: C, 64.88; H, 4.89; N, 3.77.

Cr-**X**: (498.5 mg, 62%) IR (KBr, cm^{-1}): 3420, 1616, 1522, 1435, 1304, 1204, 1175, 869, 766. MS (FAB): 723 ($M^{+\bullet}$), 688 ($M-Cl$). Anal. Calcd for $C_{34}H_{26}N_2O_2Cl_4CrCl{\cdot}4.5H_2O$: C, 50.68; H, 4.35; N, 3.48. Found: C, 50.15; H, 3.89; N, 2.99.

Cr-**XI**: (611.2 mg, 64%) IR (KBr, cm^{-1}): 3433, 1610, 1508, 1431, 1304, 1206, 1160, 712. MS (FAB): 901 ($M^{+\bullet}$), 866 ($M-Cl$). Anal. Calcd for $C_{34}H_{26}N_2O_2Br_4CrCl{\cdot}3H_2O$: C, 42.67; H, 3.34; N, 2.93. Found: C, 42.58; H, 3.19; N, 2.93.

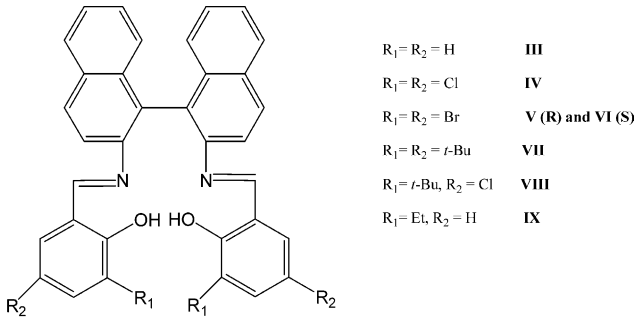
2.4. General procedure for asymmetric epoxidation

In a dry Schlenk tube was placed chromium binaphthyl Schiff base complex (0.0156 mmol) and freshly distilled toluene (2.5 mL). The mixture was then cooled down to 0 °C. To this solution was added excess alkene (7.8 mmol) through a syringe. Then the resulting solution was stirred for 10 min, and the oxidant PhIO (1.56 mmol) was added. The whole mixture was stirred for 12–14 h at this temperature. After the reaction was complete, the mixture was separated by column chromatography on silica gel to give oil or solid products. The enantioselectivity and chemical yield could be obtained by GC or NMR analysis.

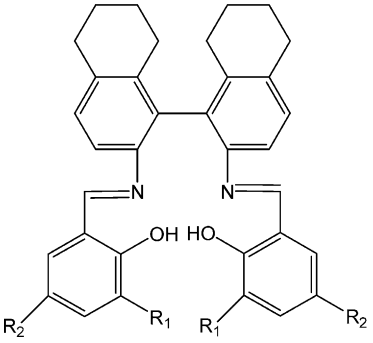
3. Results and discussion

3.1. Preparation of ligands and complexes

All the chiral binaphthyl Schiff base ligands were prepared by the condensation of diamine with corresponding salicylaldehydes. Except **VI** in *S* configuration, all were in *R*.



$R_1 = R_2 = H$ **III**
$R_1 = R_2 = Cl$ **IV**
$R_1 = R_2 = Br$ **V (R) and VI (S)**
$R_1 = R_2 = t\text{-Bu}$ **VII**
$R_1 = t\text{-Bu}, R_2 = Cl$ **VIII**
$R_1 = Et, R_2 = H$ **IX**



$R_1 = R_2 = Cl$ **X**
$R_1 = R_2 = Br$ **XI**

The chromium catalysts were prepared as shown in Scheme 1 and described in Section 2.

3.2. Characterization of complexes

All these new chromium binaphthyl Schiff base complexes were characterized by MS(FAB), IR, UV–vis and elemental analyses. Owing to the paramagnetic nature of the complexes, NMR spectra of good quality were not obtained.

UV–vis spectra show the differences between free ligand and its chromium complex. After coordinated with chromium, the peaks of ligand almost disappeared or were much weakened; there appeared a new peak around 420 nm which indicated the formation of complex. Meanwhile, the above mentioned coplanar chromium complex has a peak around 400 nm [6]. Unfortunately, suitable X-ray quality crystals of these complexes were not obtained despite numerous attempts.

3.3. Epoxidation of alkenes

All these chiral chromium binaphthyl Schiff base complexes were used for the asymmetric epoxidation of 4-chlorostyrene. The influences of solvent and temperature were also investigated and the results are listed in Table 1.

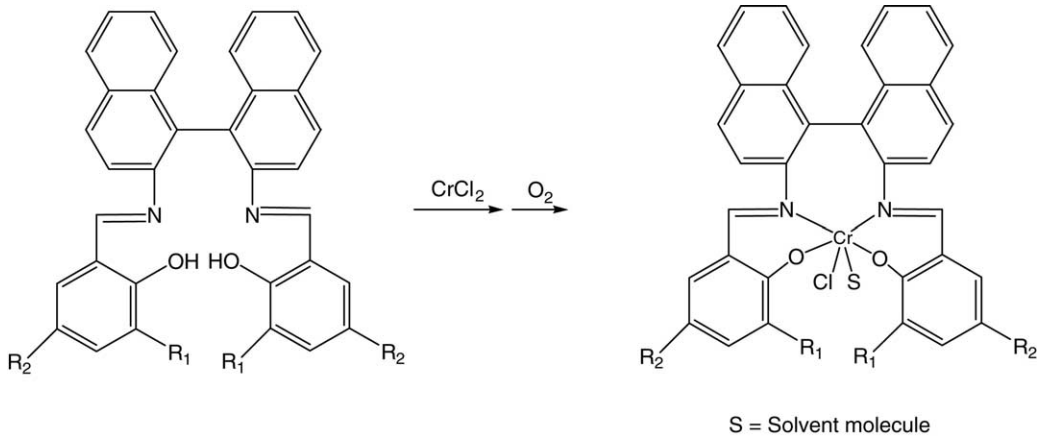
In general, during the whole process of reaction, the enantioselectivity was rather stable, although the chemical yield increased considerably in the first 3–5 h according to the reaction temperature. Besides epoxide, an oxidative-cleavage product, namely benzaldehyde and rearrangement byproduct, namely phenylacetaldehyde were also generally formed in the epoxidation of styrenes.

As shown in Table 1, the results are strongly influenced by the structure of the ligands and reaction temperature. In contrast, solvent only slightly affected the enantioselectivity, but considerably the yield. Among the solvents examined, aromatic solvents were suitable for the reaction. Toluene was then selected for further study because of less toxicity and lower melting point than benzene.

Table 1
Asymmetric epoxidation of 4-Cl-styrene catalyzed by chromium-binaphthyl Schiff bases with PhIO as oxidant[a]

Entry	Catalyst	ee[b] (%)	Cy[c] (%)	Condition
1	Cr-**III**	12	8	20 °C, CH_3CN
2	Cr-**IV**	48	19	
3	Cr-**V**	50	14	
4	Cr-**VII**	4	3	
5	Cr-**VIII**	17	5	
6	Cr-**IX**	24	4	
7	Cr-**V**	48	58	20 °C, benzene
8	Cr-**V**	49	54	20 °C, toluene
9	Cr-**V**	61	63	0 °C, toluene
10	Cr-**V**	65	68	−20 °C, toluene
11	Cr-**VI**	62[d]	60	0 °C, toluene
12	Cr-**X**	55	52	0 °C, toluene
13	Cr-**XI**	59	57	0 °C, toluene
14	Cr-**IV**	52	67	0 °C, toluene
15	Cr-**V**	45	32	20 °C, CH_2Cl_2

[a] 20% catalyst was used.
[b] Determined by GC with a chiral β-cyclodextrin column. All the products were in *R* configuration compared with standard optically pure epoxides.
[c] Determined by GC based on the PhI formed.
[d] The configuration of the product is in *S* configuration, which is contrary to that by using Cr-**V**.



Scheme 1.

Reaction temperature, on the other hand, exhibited great influence on the results. Low temperature was essential for higher ee as expected, and also beneficial to the chemical yield. As shown in Table 1 (entries 8–10), when Cr-**V** was used as catalyst and temperature dropped from 20 to 0 °C and −20 °C, the enantioselectivity increased from 49% to 61% and 65%, respectively, and the yield also increased from 54% to 68%. Low temperature retarded or prevented some side reactions, resulting in the increase in chemical yield. On the other hand, lower temperature diminished the activity of the catalyst, and longer reaction time was required for the completion of reaction: thus, 2, 5–7 h and 2 days were needed for the reaction respectively. Reaction temperature as low as −78 °C was also tried, but there was only trace of the product to be detected by GC even after 2 days' reaction. Thus, the reaction temperature of 0 °C was selected for the further studies.

The ligand structure is, as usual, a dominant factor in determining the activity and selectivity of the catalyst. Groups (R_1 and R_2) which are *ortho* and *para* to the OH group have large effects on the reaction. The best enantioselectivity, 65%, was obtained when both R_1 and R_2 were Br atoms (entry 10), which are electron-withdrawing groups with proper steric hindrance [15]. When the substituents were strong electron-donating groups such as *t*-butyl, only 4% ee was observed (entry 4).

Partially reduced ligands **X** and **XI** were also applied to this reaction with similar results to those of **IV** and **V** due to almost the same steric effect (entries 9, 14, 12, and 13). As expected, the same results could be obtained by using **VI** instead of **V** except for the opposite configuration product.

Bousquet and Gilheany [16] reported that some additives were beneficial to the reaction. In our study, however, ee and yield decreased by adding either ordinary achiral additives or chiral phosphine oxide additives (See Table 2).

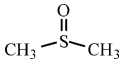
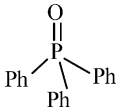
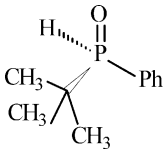
Effects of the amount of catalyst were also studied for 4-Cl-styrene epoxidation catalyzed by Cr-**V**. The ee's and yields remained unchanged while the reaction time needed to be extended from 7, 9 to 14 h when 20% catalyst, 5% catalyst, or 1% catalyst was used, and the TON turned from 3.2, 12 to 61, respectively.

Two other oxidants, 2,6-dichloropyridine-*N*-oxide and TBHP, gave rise to only 18% and 16% ee, respectively.

At last, Cr-**V** complex was selected as catalyst for other substrates under the optimum reaction conditions: 1 mol% catalyst, 0 °C and toluene. The results are listed in Table 3.

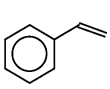
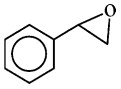
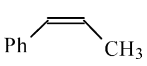
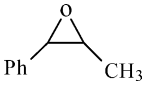
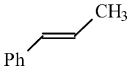
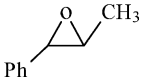
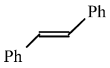
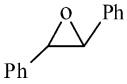
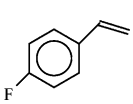
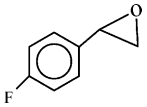
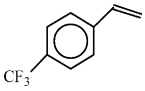
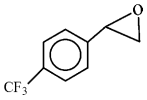
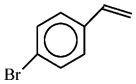
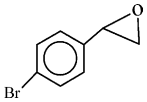
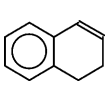
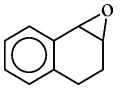
In general, styrenes with electron withdrawing substituents are epoxidized with higher enantiomeric excesses and yields than those with electron donating groups. As usual, *cis* configuration styrenes were epoxidized with better results than *trans* substrate. The best enantioselectivity of 62% could be obtained with *cis*-β-methyl styrene as substrate, while only 7% was obtained for *trans*-β-methyl styrene. For the more bulky *trans*-configuration substrate, *trans*-stilbene, almost racemic product (3% ee) was obtained with only 10% yield.

Table 2
Effects of additives on the reaction[a]

Additive	Substrate	ee (%)	Cy (%)
		43	35
		37	50
	4-Cl-styrene	23	44
		56	33
		47	27

[a] The reactions were carried out by using 20 mol% Cr-V, 0 °C, toluene as solvent and one equiv. additive was added.

Table 3
Epoxidation of other styrenes catalyzed by Cr(III)-**V**

Substrate	Product	ee (%)	Cy (%)
		50	55
		62	52[a]
		7	12
		3	10
		57	65
		60	89
		21	34
		44	21

[a] Including *cis* and *trans* product (*cis*:*trans* = 91:9), when the reaction was performed at room temperature, 43% ee and 54% yield could be obtained while the ratio between *cis* and *trans* was 66:34.

3.4. Mechanistic study

It is reported that the active species in the epoxidation catalyzed by co-planar Cr(III)–salen complexes is a Cr(V)–oxo complex. In our study, ESIMS observations on the in situ reaction between Cr-**V** and PhIO are consistent with the presence of Cr(V)=O ($m/z = 874$). The existence of 5+ oxidation state of the chromium ion is further confirmed by the ESR spectrum (See also supporting material) showing a signal at $g = 1.97$, virtually identical with that reported for complex **II** [17]. Thus, a similar chromium(V)–oxo complex might be expected to be the active species for the epoxidation reactions although it would be more bulky than the former one.

4. Concluding remarks

Several variables that affect the enantioselective epoxidation of unfunctionalized styrenes by chromium-binaphthyl Schiff base complexes were investigated. Low temperature, nonpoalr aromatic solvents such as toluene are found to be suitable for the reaction. The best ee of 65% was obtained with 4-chlorostyrene as substrate. The oxochromium complex seems to be the active species during the reaction.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at 10.1016/j.molcata.2005.04.002.

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