

# Asymmetric epoxidation of alkenes with aqueous *t*-BuOOH catalyzed by novel chiral complexes of chromium(III) containing tridentate Schiff-base ligands

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## Abstract

The  $[\text{Cr}^{\text{III}}(\alpha\text{-TDL}_1^*)(\text{bipy})(\text{Cl})]$  (**1**) and  $[\text{Cr}^{\text{III}}(\text{TDL}_2^*)(\text{bipy})(\text{Cl})]$  (**2**) complexes (where  $\text{H}_2\text{TDL}_1^* = N\text{-}3,5\text{-di-}(t\text{-butyl})\text{salicylidine-D-glucosamine}$ ,  $\text{H}_2\text{TDL}_2^* = N\text{-}3,5\text{-di-}(t\text{-butyl})\text{salicylidine-L-alanine}$ ,  $\text{bipy} = \text{bipyridyl}$ ) have been synthesized and characterized by analytical, spectral (UV–vis and IR), molar conductivity, magnetic moment and electrochemical studies. Complexes **1** and **2** catalyzed the epoxidation of styrenes, stilbenes, 1-methylcyclohexene and 1,2-dihydronaphthalene using aqueous *tert*-butyl hydroperoxide (*t*-BuOOH) as terminal oxidant. The selected alkenes were converted to their corresponding epoxides exhibiting moderate enantioselectivity at ambient temperature.

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**Keywords:** Chromium complex; Sugar derived Schiff-base ligand; *t*-BuOOH; Alkene epoxidation; Enantioselectivity

## 1. Introduction

Asymmetric epoxidation is an industrially important method for synthesizing epoxides from readily available olefins [1]. In this regard, use of coordination complexes of transition metals as catalysts is of abiding importance [2,3], as it proffers an effective possibility for synthesis of enantiomerically pure compounds. Although there is a wide range of transition metal complexes [2,3] that are known to be capable of catalyzing asymmetric epoxidation of unfunctionalized olefins in presence of terminal oxidants, reports on the use of chiral chromium complexes are sparse in the literature [2b,4–8]. Moreover, studies are mainly limited to epoxidation of *trans*- and *cis*- $\beta$ -methylstyrene [4], and the scope of Cr-salen type complexes for asymmetric alkene epoxidation is still not clear.

We are presently concerned with the use of transition metal complexes containing sugar-based tridentate Schiff-base chiral

ligands (TDL\*) [9–11]. We are attracted to such ligands, since carbohydrates are naturally occurring enantiomerically pure compounds. Furthermore, there are only a few reports on the asymmetric epoxidation of olefins catalyzed by transition metal complexes containing sugar-based ligands in literature [12,13], and no such chromium complex has been reported till date. Very recently we have reported ruthenium [10] and manganese [11] complexes containing a tridentate (O, N, O) chiral ligand, which was derived from the condensation of a saccharide containing an  $\text{NH}_2$  group (D-glucose amine) with 3,5-ditertiarybutylsalicylaldehyde can induce remarkably high enantioselectivity in alkene epoxidation. In order to examine the efficiency of the corresponding chromium complex (Fig. 1) towards asymmetric epoxidation of alkenes we have undertaken the present work. We report herein, the syntheses, characterization and catalytic activity of a mixed-ligand complexes,  $[\text{Cr}^{\text{III}}(\alpha\text{-TDL}_1^*)(\text{bipy})(\text{Cl})]$  (**1**) and  $[\text{Cr}^{\text{III}}(\text{TDL}_2^*)(\text{bipy})(\text{Cl})]$  (**2**) (where  $\text{H}_2\text{TDL}_1^* = N\text{-}3,5\text{-di-}(t\text{-butyl})\text{salicylidine-D-glucosamine}$ ,  $\text{H}_2\text{TDL}_2^* = N\text{-}3,5\text{-di-}(t\text{-butyl})\text{salicylidine-L-alanine}$  and  $\text{bipy} = \text{bipyridyl}$ ) towards epoxidation of styrenes and other alkenes using *t*-BuOOH as terminal oxidant. Complex **2** was included in this study to examine the effect of changes in the parent ( $\text{H}_2\text{TDL}^*$ ) ligands on the efficacy and selectivity of

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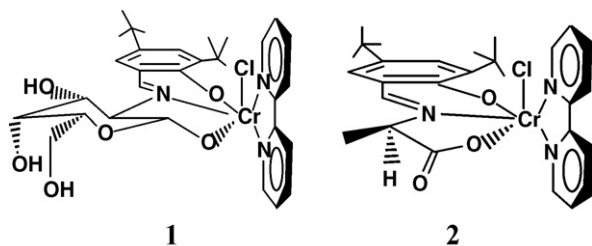


Fig. 1. Pictorial representations of **1** and **2**.

$[\text{Cr}^{\text{III}}(\text{TDL}^*)(\text{XY})\text{Cl}]$  catalyzed alkene epoxidation reaction. Pictorial representation of **1** and **2** is shown in Fig. 1.

## 2. Experimental

### 2.1. Synthesis of $[\text{Cr}^{\text{III}}(\alpha\text{-TDL}_1^*)(\text{bipy})(\text{Cl})]$ (**1**)

Preparation of tridentate Schiff-base chiral ligands, *N*-3,5-di-tertiary-butylsalicylidine-*D*-glucosamine ( $\text{H}_2\text{TDL}_1^*$ ) and *N*-3,5-di-(tertiary-butyl)salicylidine-*L*-alanine ( $\text{H}_2\text{TDL}_2^*$ ) had been reported earlier [8,9]. The chromium catalyst complexes were prepared by interacting  $\text{CrCl}_2$  with appropriate  $\text{H}_2\text{TDL}^*$  and bipy. To an argon purged methanolic solution (30 ml) of the  $\text{H}_2\text{TDL}_1^*$  ligand (1 mmol = 395.5 mg) was added solid anhydrous  $\text{CrCl}_2$  (1 mmol = 122 mg), and the reaction mixture was magnetically stirred for 12 h under argon. The Bipy ligand (1 mmol = 156.19 mg) was added to the brown color solution and stirring was continued for another 12 h at room temperature under argon. The resultant reddish-brown solution was evaporated to dryness and the reddish-brown solid product thus obtained was washed several times with diethyl ether and recrystallized from a dichloromethane–methanol mixture and finally dried in a desiccator over  $\text{CaCl}_2$ . Yield 80%. Anal. calculated for  $\text{C}_{31}\text{H}_{39}\text{N}_3\text{O}_6\text{ClCr}$ : C 58.44, H 6.13, N 6.59; Found: C 58.51, H 6.18, N 6.62. MS (FAB): 601.1 (M–Cl).  $\Delta_M$  ( $\Omega^{-1} \text{M}^{-1} \text{cm}^2$ ) in  $\text{CH}_3\text{OH}$  = 66.4.  $\mu_{\text{eff}}$  = 3.61 B.M. UV–vis in  $\text{CH}_3\text{OH}$ :  $\lambda_{\text{max}}$  ( $\epsilon_{\text{max}}$ )/nm ( $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$ ): 403 (1606), 301 (10,829), 231 (18,447). IR:  $\nu_{\text{C}=\text{N}}$  = 1647  $\text{cm}^{-1}$ ,  $\nu_{\text{C}-\text{O}}$  = 1447  $\text{cm}^{-1}$ .

### 2.2. Synthesis of $[\text{Cr}^{\text{III}}(\text{TDL}_2^*)(\text{bipy})(\text{Cl})]$ (**2**)

The  $[\text{Cr}^{\text{III}}(\text{TDL}_2^*)(\text{bipy})(\text{Cl})]$  (**2**) complex was synthesized in a similar manner to **1** except that  $\text{H}_2\text{TDL}_2^*$  was used in place of  $\text{H}_2\text{TDL}_1^*$ . The reddish-brown solid product was collected, washed with diethyl ether and recrystallized from a dichloromethane–methanol mixture (yield: 75%). Anal. calculated for  $(\text{C}_{28}\text{H}_{33}\text{N}_3\text{O}_3\text{ClCr})$ : C 61.48, H 6.04, N 7.68; Found: C 61.57, H 6.15, N 7.57. MS (FAB): 511.2 (M–Cl).  $\Delta_M$  ( $\Omega^{-1} \text{M}^{-1} \text{cm}^2$ ) in  $\text{CH}_3\text{OH}$  = 35.2.  $\mu_{\text{eff}}$  = 3.54 B.M. UV–vis in  $\text{CH}_3\text{OH}$ :  $\lambda_{\text{max}}$  ( $\epsilon_{\text{max}}$ )/nm ( $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$ ): 421 (3167), 301 (19,345), 231 (35,988). IR:  $\nu_{\text{C}=\text{N}}$  = 1649  $\text{cm}^{-1}$ ,  $\nu_{\text{C}-\text{O}}$  = 1449  $\text{cm}^{-1}$ .

### 2.3. Instrumentation

A Perkin-Elmer 240C elemental analyzer was used to obtain microanalytical (C, H, N) data. The UV–visible spectral mea-

surements were performed on a Perkin-Elmer (Model Lambda 35) spectrophotometer. IR spectra were obtained on a Perkin-Elmer (Model 783) spectrometer. Electrochemical studies were carried out with a CH Instruments (Model CHI-660B). NMR studies were performed on a Bruker 300AC NMR spectrometer in  $\text{CD}_3\text{OD}$ . Magnetic susceptibility was measured by using a PAR-155 vibrating sample magnetometer.

### 2.4. Procedure of catalytic studies

Catalytic activity of **1** and **2** in the epoxidation of the selected alkenes was assessed at room temperature. In a typical experiment 0.01 mmol of catalyst (**1/2**), 1.0 mmol of 70% aqueous *t*-BuOOH and 1.0 mmol of alkene in 5 ml of  $\text{CH}_2\text{Cl}_2$  were rapidly magnetically stirred at room temperature (25 °C). Identification and quantification of reaction products were carried out gas chromatographically (Carlo Erba GC 8000<sup>TOP</sup> series on a Tenax column fitted with FID) using decane as internal standard. GC parameters were quantified with authentic samples of products prior to the analysis. Reaction products were further confirmed by GC–MS (Polaris Q) studies.

The reaction of styrene and substituted styrenes were carried independently. The relative reactivities ( $k_{\text{rel}}$ ) were determined by the following equation:

$$k_{\text{rel}} = \frac{k_Y}{k_H} = \frac{\log(Y_f/Y_i)}{\log(H_f/H_i)}$$

where  $Y_f$  and  $Y_i$  are the final and initial quantities of substituted styrenes;  $H_f$  and  $H_i$  are the final and initial quantities of styrene. The enantiomeric excess (ee) of the epoxide product was determined using a HPLC (Shimadzu SPD-M10A) equipped with diode array detector fitted with a Chiralcel OD-H column (mobile phase = 90% *n*-hexane/10% isopropyl alcohol). In each case, conditions for determination of enantiomeric excess were set up with concerned racemic epoxides.

## 3. Results and discussion

The IR spectra of the complexes **1** and **2** exhibited bands characteristic of coordinated TDL\* ligands (viz. 1640–1650  $\text{cm}^{-1}$  for  $\nu_{\text{C}=\text{N}}$  and 1447–1450  $\text{cm}^{-1}$  for  $\nu_{\text{C}-\text{O}}$  stretches). Conductance data established that both **1** and **2** are non-electrolyte in solution, respectively. Complexes **1** and **2** afforded reddish brown solutions in methanol. A number of bands, charge transfer in nature, were observed in the UV–vis region (see Section 2). Representative example is shown in Fig. 2. The bands that appeared in the UV region are attributed to intra-ligand charge transition, whereas bands in the visible region are of a ligand-to-metal charge transfer type ( $\pi \rightarrow t_{2g}$  origin). The magnetic moments of complexes **1** and **2** conformed to the  $d^3$  configuration. Complexes **1** and **2** were cyclic voltammetrically examined at a platinum-working electrode in acetonitrile solution. Both **1** and **2** exhibited a pair of quasi-reversible anodic and cathodic peaks with a large peak-to-peak separation ( $\Delta E_p = 110$ – $130$  mV), and the  $E_{1/2}$  values corresponding to the  $\text{Cr}^{\text{III}}/\text{Cr}^{\text{II}}$  redox couple for **1** and **2** are 0.32 and 0.35 V (versus  $\text{Ag}/\text{AgCl}$ ), respectively. The  $E_{1/2}$  value of **1** was more

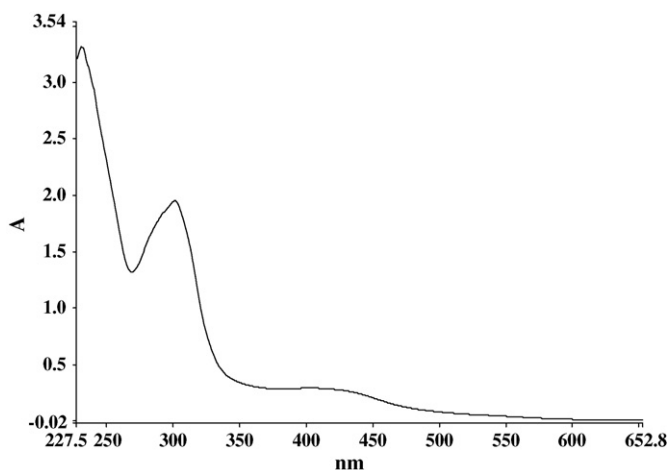


Fig. 2. UV-visible spectrum of **1** in CH<sub>3</sub>OH.

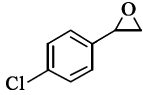
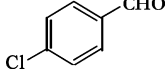
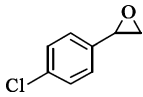
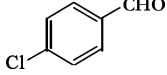
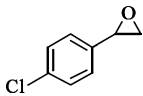
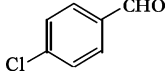
cathodic than that of **2**. This is qualitatively consistent with the fact that coordination of the glycosidic O atom enhances the electron density on the chromium(III) center and shifts the oxidation potential to a more negative as observed for **1** as compared to **2** in the present case.

Preliminary experiments established that all the components, viz. catalyst complex (**1/2**), terminal oxidant and substrate were essential for an effective catalytic transformation, and that the oxidation did not take place under O<sub>2</sub> in the absence of terminal oxidant. Using 4-chlorostyrene as substrate, effect

of various terminal oxidants and solvents in **1/2** catalyzed epoxidation has been examined. Results of catalytic studies using various terminal oxidants, such as *t*-BuOOH, H<sub>2</sub>O<sub>2</sub>, and PhIO (iodosylbenzene), and solvents such as dichloromethane, toluene, acetonitrile, etc., revealed that *t*-BuOOH is the most efficient terminal oxidant for **1/2** catalyzed epoxidation of enlisted olefins (Table 1). Due to a solubility problem the use of H<sub>2</sub>O<sub>2</sub> as precursor oxidant appeared to be inefficient in effecting epoxidation of 4-chlorostyrene either in dichloromethane or in toluene. Use of non-polar and non-coordinating solvents such as dichloromethane and toluene was found to have an advantage over the use of CH<sub>3</sub>CN, because coordination of CH<sub>3</sub>CN to the catalyst complexes (**1/2**) hinders the formation of catalytically active intermediate, thus diminishing the catalytic efficiency. Based on the above preliminary observations *t*-BuOOH was chosen as terminal oxidant for thorough investigations.

The catalytic ability of **1** and **2** towards asymmetric epoxidation of alkenes was evaluated at room temperature. The results of catalytic oxidation of styrenes and other alkenes catalyzed by **1** and **2** using aqueous *t*-BuOOH as a terminal oxidant are summarized in Table 2. Epoxides were noticeably the major products in all cases; however, minor amounts of benzaldehyde (or corresponding substituted benzaldehyde) along with the ‘other reaction products’ (usually diols, phenylacetaldehyde for styrenes and 1,2-dihydronaphthalene, and allylic oxidation products for 1-methylcyclohexene) formed due to side reactions (over-oxidation, rearrangement, etc.) were also noticed. Results

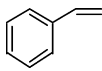
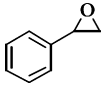
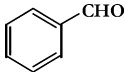
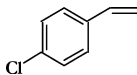
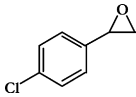
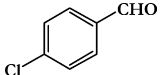
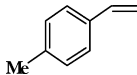
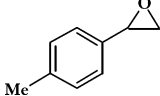
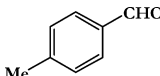
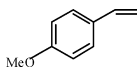
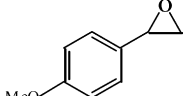
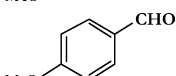


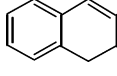
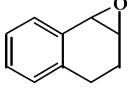
Table 1  
Effect of terminal oxidants and solvents in 4-chlorostyrene epoxidation catalyzed by **1**

Oxidant	Product	CH <sub>2</sub> Cl <sub>2</sub>		C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>		CH <sub>3</sub> CN	
		% yield	% ee	% yield	% ee	% yield	% ee
<i>t</i> -BuOOH		37	45	28	33	13	27
		5		3		1	
	ORP	3		1			
H <sub>2</sub> O <sub>2</sub>		Trace <sup>a</sup>		Trace <sup>a</sup>		6%	n.d.
						Trace	
	ORP						
PhIO		26	29	23	27	11	21
		7		5		2	
	ORP	3		2		Trace	

See Section 2 for reaction conditions.

<sup>a</sup> No reaction without phase transfer agent, n.d. = not determined.

Table 2  
Results of epoxidation of styrenes and other alkenes under ambient conditions

Substrate	1			2			
	Product	% Yield <sup>a,b</sup>	% Selectivity	% ee	% Yield <sup>a,b</sup>	% Selectivity	% ee
		34	79	43	30	81	25
		6	14		4	11	
	ORP <sup>c</sup>	3	7		3	8	
		37	82	45	32	82	23
		5	11		5	13	
	ORP <sup>c</sup>	3	7		2	5	
		38	83	41	33	80	19
		6	13		6	15	
	ORP <sup>c</sup>	2	4		2	5	
		40	82	44	36	77	24
		8	16		8	17	
	ORP <sup>c</sup>	2	2		3	6	
		29	88	39	32	91	21
	ORP <sup>c</sup>	4	12		3	9	
		38	93	43	40	93	24
	ORP <sup>c</sup>	3	7		3	7	

See Section 2 for turn-over conditions.

<sup>a</sup> Based on substrate concentration.

<sup>b</sup> After 16 h.

<sup>c</sup> ORP = other reaction products (usually diols, phenylacetaldehyde for styrenes and 1,2-dihydronaphthalene, and allylic oxidation products for 1-methylcyclohexene).

of repetitive experiments by periodically adding fresh substrate (1.0 mmol) and *t*-BuOOH (1.0 mmol) to the catalytic mixture at an interval of 16 h for a period of 64 h are summarized in Table 3. As seen in Table 3, although the catalytic activity of **1/2** in terms of product yield decreases with successive runs, enantioselectivity as well as product selectivity was found to be unchanged by and large. The terminal oxidant *t*-BuOOH was converted into *t*-BuOH in the catalytic oxo-transfer reaction. During the course of the reaction, *t*-BuOH accumulated

in the catalytic system competes in parallel with *t*-BuOOH for the same coordination site in the catalyst complexes (**1/2**) presumably resulting in the observed decrease in the activity of the catalytic process. The poor yield (7–9% conversion) observed when *t*-BuOH was used as solvent evidently supports the above argument. However, no significant change in the spectral features of the catalyst complexes (**1** and **2**) at the end of the catalytic runs essentially suggests that they are reasonably stable under the specified conditions.

Table 3  
Results of four consecutive runs for the epoxidation of 4-chlorostyrene catalyzed by **1** and **2** under ambient conditions

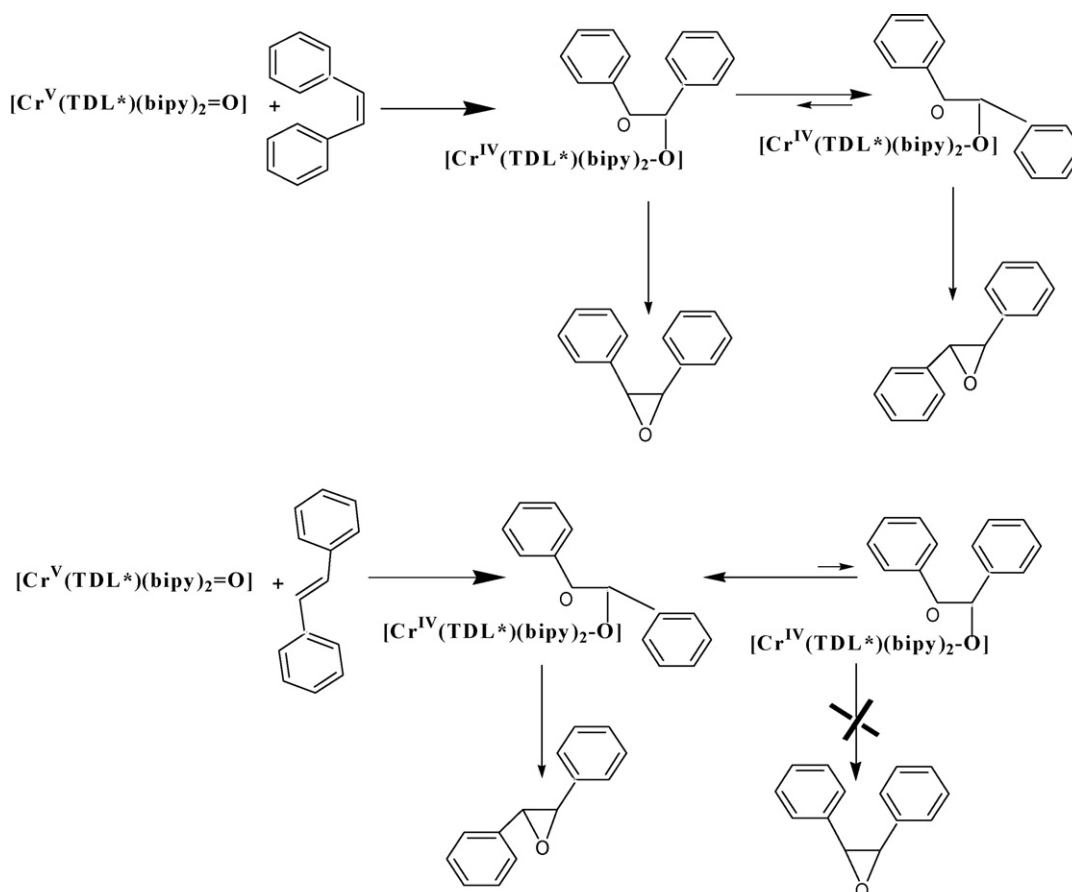
Catalytic run	Reaction time (h)	Catalyst			
		<b>1</b>		<b>2</b>	
		Epoxide yield (%)	ee	Epoxide yield (%)	ee
Run-1	16	37	45	32	23
Run-2	16	31	46	25	22
Run-3	16	26	44	19	21
Run-4	16	21	45	14	22

See Section 2 for reaction conditions.

In order to examine the stereoselectivity and the nature of intermediate that governs the epoxidation process, we have carried out epoxidation of both *cis*-stilbene and *trans*-stilbene under specified conditions. Product analysis for epoxides of stilbenes was carried out using NMR technique [14]. In case of epoxidation of *cis*-stilbene catalyzed by **1**, a mixture of epoxides (11 % of *cis*-epoxide and 26% of *trans*-epoxide) was formed, whereas only *trans*-epoxide (40%) was obtained from the epoxidation of *trans*-stilbene under identical conditions. Similarly, formation of 9% *cis*-stilbene epoxide and 30% *trans*-stilbene was observed using **2** as catalyst in the epoxidation of *cis*-stilbene with *t*-BuOOH. Under identical conditions epoxidation of *trans*-stilbene yielded only *trans*-epoxide (43%). Based on the above results it is reasonable to postulate

that transfer of oxo-atom to olefins could involve a radicaloid intermediate species, which would allow a limited amount of rotation through –C–C– bond prior to the epoxide formation (Scheme 1).

The effect of *para*-substituents **1/2** catalyzed epoxidation of styrenes have been investigated by following the alkene consumption using gas chromatography (see Section 2). The minor effect of electron-withdrawing or electron-donating *para*-substituents on the **1/2**-catalyzed styrene epoxidation seems to be compatible to the fact that there is a small degree of charge transfer in the transition state. Additional support in favor of the argument involving radicaloid intermediate comes from the linear dependence (Fig. 3) of the relative reactivities ( $k_{rel}$ ) on the total substituent effect (TE) parameter [15]. Based on the linear-



Scheme 1. .

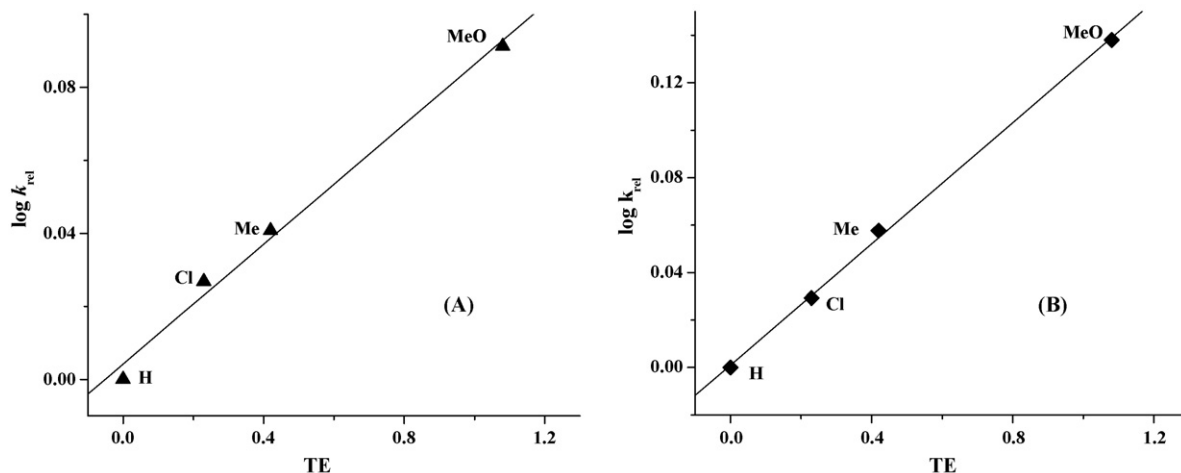


Fig. 3. Plots of  $\log k_{\text{rel}}$  vs. Hammett total substituent constant (TE) in the epoxidation of styrene and *para*-substituted styrenes with *t*-BuOOH catalyzed by (A) **1** and (B) **2**.

ity of such plots, formation of a loosely bound radical type of intermediate was suggested for the stoichiometric epoxidation of *para*-substituted styrenes by chiral Ru-oxo complexes [16,17]. In our case, the loss of stereo-specificity in the epoxidation of *cis*-stilbene and linear relationship between total substituent effect (TE) parameter and relative reactivities ( $k_{\text{rel}}$ ) as depicted in Fig. 3 for the epoxidation of *para*-substituted styrenes are strongly suggestive of the intermediacy of a radical type intermediate in the present epoxidation reaction.

Formation of high-valent Cr(V)-oxo species as an active species in alkene epoxidation catalyzed by Schiff-base complexes of chromium(III) had been proposed earlier [18,19] and confirmed later by several recent studies [2b,20]. On the basis of linear correlation between total substituent effect (TE) parameter and relative reactivities ( $k_{\text{rel}}$ ) of *para*-substituted styrenes an oxo-chromium intermediate is favored in the present case. Further, a similar product distribution pattern observed for two different terminal oxidants, *t*-BuOOH and PhIO (Table 1), also argues for a similar species which acts as a major oxidizing intermediate in both the cases. The sense of chirality induced is governed by the asymmetric center(s) at the sugar or amino acid part of the coordinated TDL\*<sup>2-</sup> ligands. The higher asymmetry-inducing ability of **1** is attributed to the location of asymmetric centers of the sugar moiety of the TDL<sub>1</sub>\*<sup>2-</sup> ligand proximal to the Cr=O bond; they could interact deeply with the incoming alkene and effect high enantioface selection.

#### 4. Conclusion

Syntheses and reactivity of a new family of mixed-ligand octahedral chiral chromium(III)-complexes, **1** and **2**, that run under mild conditions is reported. The results of the catalytic studies reveal that enantioselective epoxidation of various unfunctionalized alkenes is achievable in the presence of either **1** or **2** using *t*-BuOOH as a precursor oxidant, though **2** is comparatively less efficient. Studies concerning further modification

of [Cr<sup>III</sup>(\*TDL)(XY)Cl] and optimization of reaction conditions are in progress for achieving higher enantioselectivity.

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