



# Olefin epoxidation catalyzed by $[\text{Ru}^{\text{III}}(\text{TDL})(\text{tmeda})\text{H}_2\text{O}]$ complexes (TDL = tridentate Schiff-base ligand; tmeda = tetramethylethylenediamine)

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## ABSTRACT

Mixed-chelate complexes of ruthenium have been synthesized using tridentate Schiff-base ligands (TDLs) derived from condensation of 2-aminophenol or 2-aminobenzoic acid with aldehydes (salicylaldehyde, 2-pyridinecarboxaldehyde), and tmeda (tetramethylethylenediamine).  $[\text{Ru}^{\text{III}}(\text{hpsd})(\text{tmeda})(\text{H}_2\text{O})]^+$  (**1**),  $[\text{Ru}^{\text{III}}(\text{hppc})(\text{tmeda})(\text{H}_2\text{O})]^{2+}$  (**2**),  $[\text{Ru}^{\text{III}}(\text{cpsd})(\text{tmeda})(\text{H}_2\text{O})]^+$  (**3**) and  $[\text{Ru}^{\text{III}}(\text{cppc})(\text{tmeda})(\text{H}_2\text{O})]^{2+}$  (**4**) complexes (where  $\text{hpsd}^{2-} = \text{N}-(2\text{-hydroxyphenyl})\text{salicylaldiminato}$ ;  $\text{hppc}^- = \text{N}-(2\text{-hydroxyphenyl})\text{pyridine-2-carboxaldiminato}$ ;  $\text{cpsd}^{2-} = \text{N}-(2\text{-carboxyphenyl})\text{salicylaldiminato}$ ;  $\text{cppc}^- = \text{N}-(2\text{-carboxyphenyl})\text{pyridine-2-carboxaldiminato}$ ) were characterized by microanalysis, spectral (IR and UV-vis), conductance, magnetic moment and electrochemical studies. Complexes **1–4** catalyzed the epoxidation of cyclohexene, styrene, 4-chlorostyrene, 4-methylstyrene, 4-methoxystyrene, 4-nitrostyrene, *cis*- and *trans*-stilbenes effectively at ambient temperature using *tert*-butylhydroperoxide (*t*-BuOOH) as terminal oxidant. On the basis of Hammett correlation ( $\log k_{\text{rel}}$  vs.  $\sigma^+$ ) and product analysis, a mechanism involving intermediacy of a  $[\text{Ru}-\text{O}-\text{O}(\text{Bu})]^*$  radicaloid species is proposed for the catalytic epoxidation process.

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## 1. Introduction

The significance of ruthenium complexes for promoting studies towards development of oxo-transfer catalysts has been well established in the literature [1–4]. In this regard  $[\text{Ru}(\text{TDL})(\text{XY})(\text{H}_2\text{O})]$  type mixed-chelate complexes (where ‘TDL’ symbolizes tridentate ligands; ‘XY’ stands for bidentate ligands) have constituted an important class of catalysts for oxo-functionalization of organic substrate [3,5]. The following benefits are accrued in  $[\text{Ru}(\text{TDL})(\text{XY})(\text{Z})]$  type of complexes. First, the TDLs provide sites that can undergo stereogenic as well as chiral substitution, thus affording potential chiral controlling shapes for asymmetric catalysis. Secondly, the electrophilicity of the ruthenium center in the catalyst complex could be tuned by changing the ancillary ligand (XY). A strong  $\pi$ -accepting ligand would make the ruthenium center electrophilic, while a strong  $\sigma$ -donating ligand could enhance the electron density on the metal center of a transfer catalyst.

Our abiding research interests import a new family of  $[\text{Ru}(\text{TDL})(\text{XY})(\text{H}_2\text{O})]$  complexes (TDL =  $\text{hpsd}^{2-}$ ,  $\text{hppc}^-$ ,  $\text{cpsd}^{2-}$  and  $\text{cppc}^-$ ; XY = bipy,  $\text{pic}^-$ ) and their catalytic properties towards hydrocarbon oxidations [6–13]. Structural representations of the above ligands (‘TDL’ and ‘XY’) are shown in Fig. 1. Catalytic ability of such  $[\text{Ru}^{\text{III}}(\text{TDL})(\text{XY})\text{H}_2\text{O}]$  complexes examined earlier, and it was found

that the  $[\text{Ru}^{\text{III}}(\text{TDL})(\text{XY})\text{H}_2\text{O}]/t\text{-BuOOH}$  catalytic system is selective towards C–H bond activation. In the present investigation, we have undertaken a new series of  $[\text{Ru}^{\text{III}}(\text{TDL})(\text{XY})(\text{H}_2\text{O})]$  complexes where the bidentate ligand, ‘XY’ (bipy/ $\text{pic}^-$ ) is changed to ‘tmeda’ (tetramethylethylenediamine) as shown in Fig. 1. As far as the choice of ‘tmeda’ is concerned, the use of ammine donors, which are strong  $\sigma$ -donating ligand as compared to ‘bipy’ or ‘ $\text{pic}^-$ ’, could enhance the electron density on the metal center in  $[\text{Ru}^{\text{III}}(\text{TDL})(\text{XY})(\text{H}_2\text{O})]$  catalyst complexes. As a consequence, the tendency of ruthenium center to undergo reduction via outer-sphere electron transfer is reduced, thus facilitating them to act as epoxidation catalysts instead of hydroxylating agents. We report herein, the syntheses, characterization and the catalytic ability of a new series of ruthenium(III) complexes towards hydrocarbon oxidations. We also illustrate the mechanistic details of oxidation process and scrutinize the efficacy of the various  $[\text{Ru}(\text{TDL})(\text{XY})(\text{H}_2\text{O})]$  type complexes towards achieving hydrocarbon oxidation in terms of product yield and selectivity.

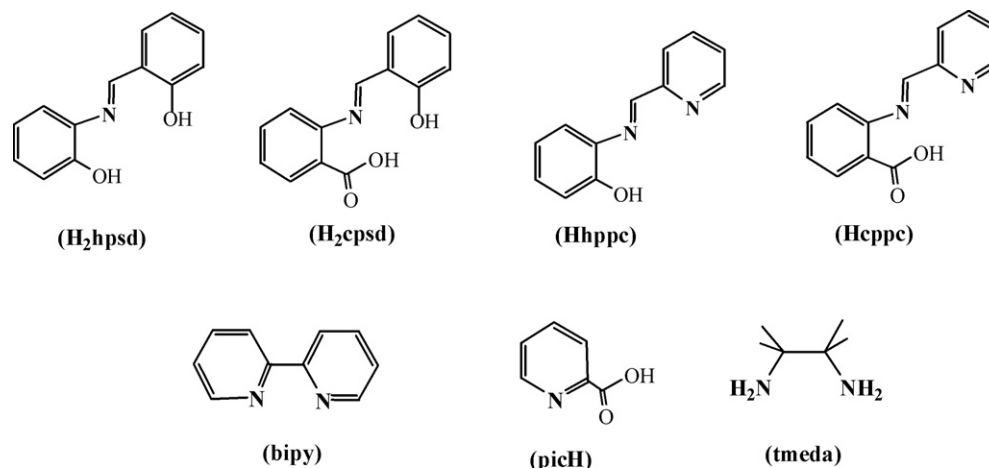
## 2. Experimental

### 2.1. Materials

Preparation of tridentate Schiff-base ligand,  $\text{H}_2\text{cpsd}$  [10],  $\text{Hcppc}$  [10],  $\text{Hhppc}$  [12] and  $\text{H}_2\text{hpsd}$  [13] were reported earlier. All the  $[\text{Ru}(\text{TDL})(\text{tmeda})(\text{H}_2\text{O})]$  complexes employed in the present studies were prepared by following the procedure somewhat similar to

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TDL: **a** = N-(2-hydroxyphenyl)salicylaldiminato (hpsd<sup>2-</sup>)  
**b** = N-(2-carboxyphenyl)salicylaldiminato (cpsd<sup>2-</sup>)  
**c** = N-(2-hydroxyphenyl)pyridine-2-carboxaldiminato (hppc<sup>-</sup>)  
**d** = N-(2-carboxyphenyl)pyridine-2-carboxaldiminato (cppc<sup>-</sup>)

XY: bipy = 2,2'-bipyridyl  
pic = picolinate  
tmeda = tetramethylethylenediamine

**Fig. 1.** Structural representations of 'TDL' and 'XY' ligands.

that reported [10–13] earlier for other pertinent ruthenium complexes. All chemicals used were of reagent grade, obtained from the Aldrich Chemical Company and, were appropriately degassed before use.

### 2.1.1. Synthesis of aquotetramethylethylenediamine(2-hydroxyphenyl-2-salicylaldiminato) ruthenium(III)chloride (**1**)

Synthesis of [Ru<sup>III</sup>(hpsd)(tmeda)H<sub>2</sub>O]Cl complex (**1**) was carried out by following the method as outlined below. To a methanolic solution (15 ml) of H<sub>2</sub>hpsd (0.213 g, 1 mmol) was added tmeda (0.116 g, 1 mmol). On the addition of RuCl<sub>3</sub>·3H<sub>2</sub>O (0.261 g, 1 mmol) to this solution, the orange colour changed to dark brown. The mixture was refluxed for 8 h. A dark solid separated, which was filtered, washed with water and little methanol, and finally dried in desiccator over CaCl<sub>2</sub>. Yield (80%). Anal. Calculated for C<sub>19</sub>H<sub>27</sub>N<sub>3</sub>O<sub>3</sub>RuCl: Calc. C, 47.3; H, 5.61; N, 8.72. Found. C, 48.0; H, 5.93; N, 8.55.  $\Lambda_M$  ( $\Omega^{-1} M^{-1} cm^2$ ) in H<sub>2</sub>O = 93. UV–vis in H<sub>2</sub>O:  $\lambda_{max}$  ( $\epsilon_{max}$ )/nm ( $mol^{-1} dm^3 cm^{-1}$ ): 438 (2190), 307 (7540), 233 (11,374). IR:  $\nu_{C=N}$  = 1587  $cm^{-1}$ .  $\mu_{eff}$  = 1.89 B.M.  $E_{1/2}$  (Ru<sup>III</sup>/Ru<sup>II</sup>) = 0.27 V (vs. SCE) in CH<sub>3</sub>CN.

### 2.1.2. Synthesis of aquotetramethylethylenediamine(2-hydroxyphenyl-2-pyridylcarboxaldiminato) ruthenium(III)chloride (**2**)

Synthesis of [Ru<sup>III</sup>(hppc)(tmeda)H<sub>2</sub>O]Cl<sub>2</sub> (**2**) was prepared by following the similar manner as adopted for **1**, except H<sub>2</sub>hpsd was replaced by Hhppc. Yield (78%). Anal. Calculated for C<sub>18</sub>H<sub>27</sub>N<sub>6</sub>O<sub>2</sub>RuCl<sub>2</sub>: Calc. C, 42.9; H, 5.38; N, 11.1. Found. C, 43.1; H, 5.51; N, 10.9.  $\Lambda_M$  ( $\Omega^{-1} M^{-1} cm^2$ ) in H<sub>2</sub>O = 135.6. UV–vis in H<sub>2</sub>O:  $\lambda_{max}$  ( $\epsilon_{max}$ )/nm ( $mol^{-1} dm^3 cm^{-1}$ ): 465 (2668), 263 (10,640). IR:  $\nu_{C=N}$  = 1598  $cm^{-1}$ .  $\mu_{eff}$  = 1.87 B.M.  $E_{1/2}$  (Ru<sup>III</sup>/Ru<sup>II</sup>) = 0.29 V (vs. SCE) in CH<sub>3</sub>CN.

### 2.1.3. Synthesis of aquotetramethylethylenediamine

#### {N-(2-carboxyphenyl)salicylalimine} ruthenium(III)chloride (**3**)

Synthesis of [Ru<sup>III</sup>(cpsd)(tmeda)H<sub>2</sub>O]Cl (**3**) was achieved in an analogous manner as adopted for **1**, however, H<sub>2</sub>hpsd was used in place of H<sub>2</sub>hpsd. Yield (75%). Anal. Calculated (found), for RuC<sub>20</sub>H<sub>27</sub>N<sub>3</sub>O<sub>4</sub>Cl. C, 47.1; H, 5.3; N, 8.24. Found. C, 47.7; H, 5.11; N, 8.52. UV–vis in H<sub>2</sub>O:  $\lambda_{max}$  ( $\epsilon_{max}$ )/nm ( $mol^{-1} dm^3 cm^{-1}$ ) 435 (1230) nm, 248 (11,223), IR (KBr):  $\nu_{C=N}$  = 1585  $cm^{-1}$  (s).  $\Lambda_M$  in H<sub>2</sub>O, 148  $\Omega^{-1} mol^{-1} cm^2$  at 25 °C.  $\mu$  (B.M.), 1.98.  $E_{1/2}$  (Ru<sup>III</sup>/Ru<sup>II</sup>) = 0.34 V (vs. SCE) in CH<sub>3</sub>CN.

### 2.1.4. Synthesis of aquotetramethylethylenediamine-

#### {N-(2-carboxyphenyl)pyridine-2-carboxaldiminato}ruthenium(III)chloride (**4**)

A similar procedure that adopted for synthesis of **2** was employed for synthesis of [Ru<sup>III</sup>(cppc)(tmeda)H<sub>2</sub>O]Cl<sub>2</sub> (**4**). 'Hcppc' was used in place of 'Hhppc'. Yield (70%). Anal. Calculated for C<sub>57</sub>H<sub>61</sub>NO<sub>6</sub>P<sub>2</sub>RuCl (M.W. = 1053.5): Calc. C, 42.9; H, 5.1; N, 10.5. Found. C, 43.3; H, 5.5; N, 10.1.  $\Lambda_M$  in H<sub>2</sub>O, 148  $\Omega^{-1} mol^{-1} cm^2$  at 25 °C. UV–vis in H<sub>2</sub>O:  $\lambda_{max}$  ( $\epsilon_{max}$ )/nm ( $mol^{-1} dm^3 cm^{-1}$ ): 455 (1475), 350 (4776). IR:  $\nu_{C=N}$  1610  $cm^{-1}$ .  $\mu_{eff}$  = 1.81 B.M.  $E_{1/2}$  (Ru<sup>III</sup>/Ru<sup>II</sup>) = 0.36 V (vs. SCE) in CH<sub>3</sub>CN.

## 2.2. Instrumentation

The UV–vis and IR spectra were collected on a PerkinElmer (Model Lambda 35) spectrophotometer and a PerkinElmer (Model 783) spectrometer using KBr pellets, respectively. Cyclic voltammetric experiments were carried out in a glass cell equipped with a platinum working electrode, a platinum-wire auxiliary electrode and a standard calomel electrode (SCE) as reference electrode. A CH Electrochemical Instruments (CHI-660B) was used for this purpose.

Cyclic voltammetric studies of **1–4** were performed in acetonitrile using tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. NMR studies were performed on a Bruker 300AC NMR spectrometer in CD<sub>3</sub>OD. Magnetic susceptibility was measured by using a PAR-155 vibrating sample magnetometer. A PerkinElmer 240C elemental analyzer was used to collect microanalytical (C, H, N) data.

### 2.3. Catalysis studies and product identification

Catalytic activity of ruthenium(III)-complexes (**1–4**) was generally assessed at room temperature. In a typical experiment 0.01 mmol of catalyst, 1.0 mmol of terminal oxidant and 1.0 mmol of substrate in 5 ml of CH<sub>2</sub>Cl<sub>2</sub> were rapidly magnetically stirred at room temperature (25 °C). Water (5 ml) was added, the mixture was stirred for 10 min and aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (5 ml × 3). The organic phase was dried over MgSO<sub>4</sub>, filtered and concentrated. Flash chromatography (SiO<sub>2</sub>, 95% pet ether/5% EtOAc) of the concentrated liquid mass afforded the desired product. Identification and quantification of reaction products were carried out gas chromatographically (GC). GC analysis was performed with a Trace GC Ultra Series (Thermoelectron Corporation) on a fused silica capillary column (SE-52; i.d. = 0.25 μm) fitted with FID. GC parameters were quantified with authentic samples of product prior to the analysis. Reaction products were further confirmed by GC–MS analysis performed on a GC–MS–MS equipment (Thermoelectron Corporation) equipped with PolarisQ mass detector. The relative reactivity ( $k_{rel}$ ) were determined by the following equation:

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

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.

### 3. Results and discussion

Microanalysis (C, H, N), spectral (UV–vis, IR), molar conductance and magnetic susceptibility data (see Section 2.1) are in well agreement to the proposed structure (tentative) of the catalyst complexes (**1–4**) as represented in Fig. 2. As shown typically in Fig. 3 the UV–vis spectra of **1–4** are characterized by charge-transfer bands.

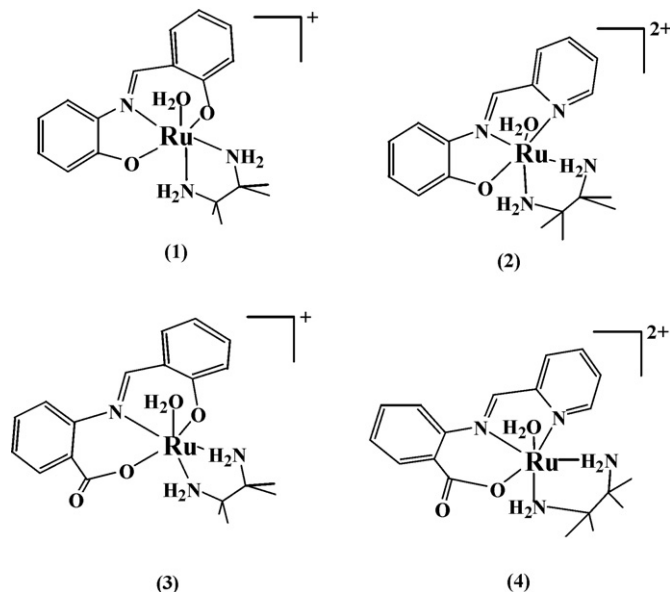


Fig. 2. Structural representations of complexes **1–4**.

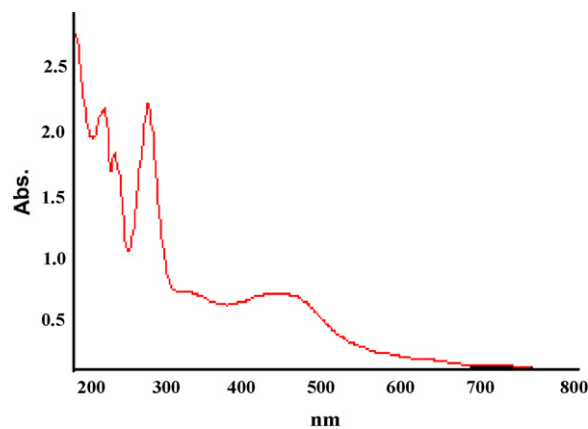


Fig. 3. Absorption spectrum of **2** in H<sub>2</sub>O.

The bands in the UV region are characteristics of intra-ligand charge transition, whereas, bands in the visible region are ascribed to the ligand to metal charge transitions. The IR spectra of the complexes showed bands characteristics of coordinated Schiff-base and other ancillary ligands.

Cyclic voltammogram of **1–4** in acetonitrile displayed quasi-reversible waves a peak-to-peak separation ( $\Delta E_p$ ) values lying in the range 90–130 mV, which are assigned to Ru<sup>III</sup>/Ru<sup>II</sup> redox couples. Representative cyclic voltammogram is displayed in Fig. 4. The  $E_{1/2}$  values of **1** (0.27 V) and **2** (0.29 V) are more cathodic than that of **3** (0.34 V) and **4** (0.36 V). The oxygen donors in the ‘hdsd<sup>2-</sup>/hdpc<sup>-</sup>’ ligand system are phenolic oxygen, whereas, in ‘cpsd<sup>2-</sup>/cppc<sup>-</sup>’ are either carboxylate oxygen or combination of both carboxylate and phenolate oxygen. Presence of carboxylate donors in ‘TDL’ which are less  $\sigma$ -donating than phenolate donors, would make ruthenium center more electrophilic as revealed by the anodic shift of  $E_{1/2}$  values in **3** and **4**. Small anodic shift in  $E_{1/2}$  values observed for **2/4** as compared to **1/3** is in agreement with the fact that pyridyl-N donor is more electron-withdrawing than phenolato oxygen donors of the Schiff-base ligands coordinated to the ruthenium center. Coordination of pyridyl-N donor atoms would make metal center more electrophilic, and shift the oxidation potential towards a more positive value as observed for both **2** and **4** as compared to **1** and **3** in the present case.

The catalytic activity of complexes **1–4** was examined under a standard set of conditions (see Section 2 for reaction conditions). Preliminary experiments ascertained the necessity of each component (catalyst, oxidant and substrates) to observe the resulting

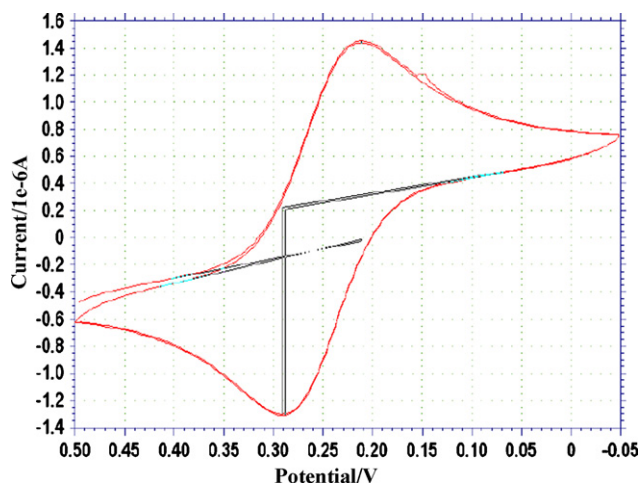


Fig. 4. Cyclic voltammogram of **1** in CH<sub>3</sub>CN. Scan rate = 100 mV s<sup>-1</sup>.

**Table 1**  
Results of complexes **1–4** catalyzed alkene epoxidation with *t*-BuOOH<sup>a</sup>.

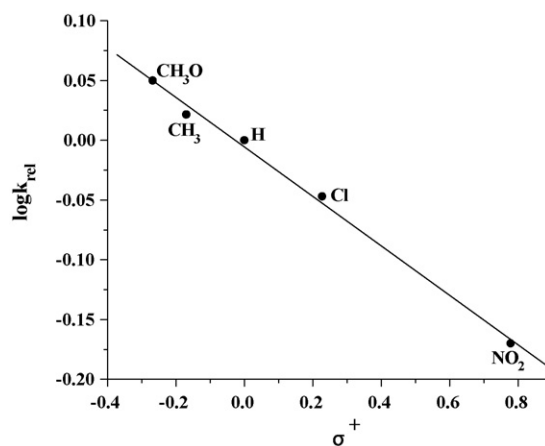
Substrate	Product	(% Yield)			
		1	2	3	4
Cyclohexene	Cyclohexene-1-ol	11	13	12	15
	Cyclohexene epoxide	42	38	34	30
Styrene (Run 1)	Styrene oxide	58	56	51	49
	Benzaldehyde	5	5	8	7
Styrene (Run 2)	Styrene oxide	47	44	41	39
	Benzaldehyde	4	3	5	4
Styrene (Run 3)	Styrene oxide	35	31	35	31
	Benzaldehyde	2	1	5	5
Styrene (Run 4)	Styrene oxide	29	27	27	24
	Benzaldehyde	1	Trace	3	2
4-Methylstyrene	4-Methylstyrene oxide	54	51	49	47
	4-Methylbenzaldehyde	7	8	7	6
4-Chlorostyrene	4-Chlorostyrene oxide	62	59	54	52
	4-Chlorobenzaldehyde	3	6	7	8
4-Nitrostyrene	4-Nitrostyrene oxide	67	63	57	57
	4-Nitrobenzaldehyde	8	5	11	12
4-Methoxystyrene	4-Methoxystyrene oxide	48	50	47	45
	4-Methoxybenzaldehyde	11	7	8	6
<i>cis</i> -Stilbene	<i>cis</i> -Stilbeneoxide	6	7	5	8
	<i>trans</i> -Stilbeneoxide	51	48	46	45
	Benzaldehyde	9	11	13	18
<i>trans</i> -Stilbene	<i>cis</i> -Stilbeneoxide	–	–	–	–
	<i>trans</i> -Stilbeneoxide	64	62	56	49
	Benzaldehyde	11	12	14	16

<sup>a</sup> **1–4** = 0.01 mmol, *t*-BuOOH = 1 mmol, substrate = 1 mmol. Reaction was carried out in CH<sub>2</sub>Cl<sub>2</sub> at RT.

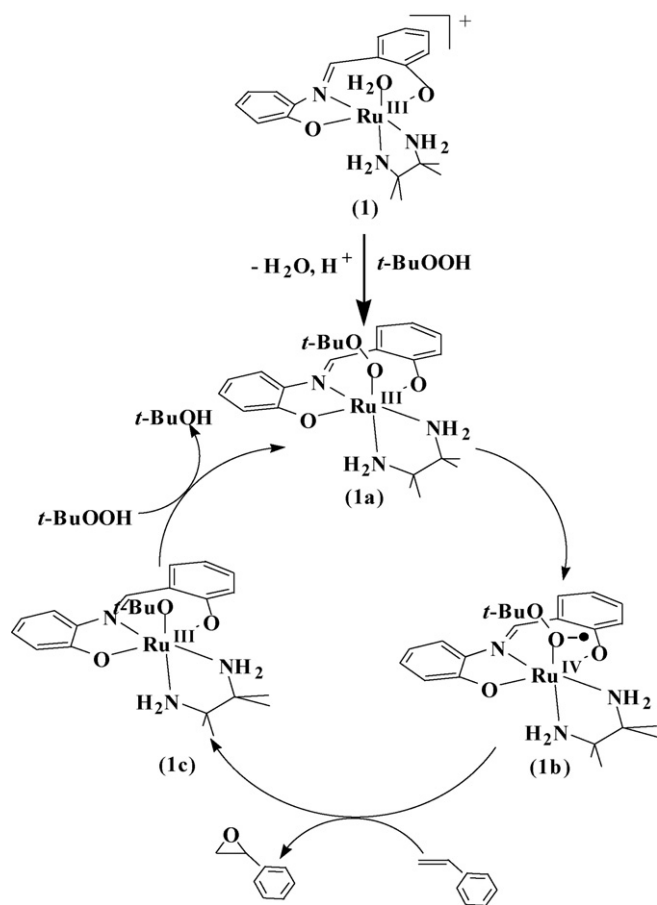
catalytic activity. It was demonstrated earlier [10–13] that CH<sub>2</sub>Cl<sub>2</sub> and *t*-BuOOH were the optimal solvent and oxidant, respectively, for the hydrocarbon oxidation catalyzed by [Ru<sup>III</sup>(TDL)(XY)(H<sub>2</sub>O)] (XY = bipy, pic<sup>−</sup>). Therefore, in the present study, catalytic ability of **1–4** towards hydrocarbon oxidation was evaluated in CH<sub>2</sub>Cl<sub>2</sub> using *t*-BuOOH as the precursor oxidant. It has been found that **1–4** catalyzed the conversion of cyclohexene to cyclohexene epoxide (Table 1) in the presence of *t*-BuOOH. This is in contrast to our earlier findings [10–13] wherein, cyclohexene-1-ol was found to be the major product in [Ru<sup>III</sup>(TDL)(XY)(H<sub>2</sub>O)] (XY = bipy, pic<sup>−</sup>) catalyzed oxidation of cyclohexene with *t*-BuOOH. The catalytic ability of **1–4** towards alkene epoxidation was further examined using a range of alkenes including styrene, *para*-substituted styrenes, and *cis*- and *trans*-stilbenes. In each case epoxides were noticeably the major products, however, minor amounts of benzaldehyde (or corresponding substituted benzaldehydes) were also noticed (Table 1). With styrene as substrate, catalytic activity of **1–4** was further evaluated through a sequence of four successive reactions. The results of successive reactions by sequential adding of fresh styrene (1.0 mmol) and *t*-BuOOH (1.0 mmol) to the catalytic mixture at an interval of 4 h for a period of 16 h are summarized in Table 1. As seen in Table 1, the catalytic activity of **1–4** in respect to styrene conversion decreases with successive runs. The terminal oxidant *t*-BuOOH is converted into *t*-BuOH during epoxidation reaction. In 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 (**1–4**) presumably resulting in the observed decrease in the efficacy of the catalytic process. The insignificant substrate conversion (<3% conversion) observed when *t*-BuOH was used as solvent is evidently supportive of the above argument. However, no significant change in the spectral features of the catalyst complexes (**1–4**) at the end of the four catalytic runs essentially suggests that they are reasonably stable under the specified turnover conditions.

In our earlier studies [10–13] intermediacy of Ru(V)–oxo species was proposed in the [Ru<sup>III</sup>(TDL)(XY)(H<sub>2</sub>O)] (TDL = hpsd<sup>2−</sup>, cpsd<sup>2−</sup>, hppc<sup>−</sup>, cppc<sup>−</sup>; XY = bipy, pic<sup>−</sup>) catalyzed hydrocarbon oxidation with *t*-BuOOH. In the present case, attempts to isolate the [Ru<sup>V</sup>(TDL)(tmeda)O] species by interacting precursor complexes **1–4** with *t*-BuOOH were unsuccessful. Moreover, absorption spectra of the resultant reaction mixture that obtained from the reaction of precursor catalyst complex (**1–4**) and *t*-BuOOH did not exhibit any spectral features in the wave length range 390–450 nm which is characteristic of  $d_{xy} \rightarrow d_{\pi^*}$  charge transition band of Ru(V)–oxo species [14–17]. Nevertheless, reaction of **1** and **2** with *m*-CPBA (*m*-chloroperbenzoic acid) followed by evaporation of the resultant reaction mixture yielded solid product complexes. IR spectra of the solid products were somewhat similar to that of **1/2** which is suggestive of the fact that the coordinated 'TDL' and 'XY' ligands in the product complexes thus obtained remain intact at the end of the oxidation of **1/2** by *m*-CPBA. However, IR spectrum of the product complex derived from **1** exhibited a strong band at 867 cm<sup>−1</sup>. A similar band at 878 cm<sup>−1</sup> was observed in the IR spectrum of the product that obtained from **2**. These bands are assigned to the Ru<sup>V</sup>=O stretch [14–17]. This band was absent in the IR spectra of precursor complexes, **1** and **2**. Based on the above experimental facts, these product complexes obtained by oxidizing **1** and **2** with *m*-CPBA could be recognized as [Ru<sup>V</sup>(hpsd)(tmeda)O]<sup>+</sup> (**5**) and [Ru<sup>V</sup>(hppd)(tmeda)O]<sup>2+</sup> (**6**), respectively. It is noteworthy here that stoichiometric reaction of cyclohexene (1 mmol) with **5** (1 mmol) carried out in CH<sub>2</sub>Cl<sub>2</sub> for 4 h at room temperature, revealed the formation of cyclohexene-1-ol (36%) and cyclohexene-1-one (6%), but no epoxide was noticed by gas chromatographic analysis of the reaction mixture. Similarly, cyclohexene-1-ol (34%) and cyclohexene-1-one (4%) were also detected in the stoichiometric oxidation of cyclohexene with **6**. Moreover, benzaldehyde appears to be the dominant product for the reaction of styrene with both **5** and **6**. It is worth mentioning here that a stable Ru(V)–oxo intermediate species selectively hydroxylates C–H bond and effect oxidative cleavage of the C=C bond of arenes [14,16].

The effect of electron-withdrawing or electron-donating *para*-substituents in **1–4** catalyzed epoxidation of styrenes is not much pronounced (Table 1). In Fig. 5 typically shown is the relationship between relative reactivity ( $k_{rel}$ ) and substituent constant ( $\sigma^+$ ) of *para*-substituted styrenes for **1** catalyzed epoxidation of styrenes. Though Fig. 5 depicts a linear Hammett relationship, the value of  $\rho^+$  (estimated from the slope of the plot),  $-0.2$  ( $R = -0.997$ ) is small enough as compared to the values reported for other reactive metal-oxo systems [18–22] where a linear free energy relationship for the oxidation is usually observed.



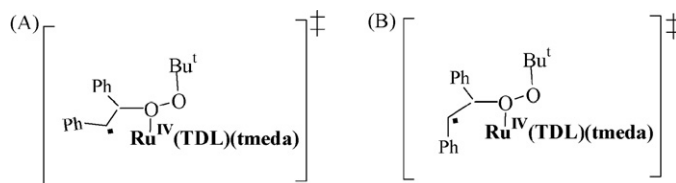
**Fig. 5.** Hammett plot for the oxidation of *para*-substituted styrenes with *t*-BuOOH catalyzed by **1**.



**Scheme 1.** Mechanism of  $[\text{Ru}^{\text{III}}(\text{hdsd})(\text{temda})(\text{H}_2\text{O})]^+$  catalyzed styrene epoxidation with *t*-BuOOH.

Based on the above facts, it appears that the  $\text{Ru}^{\text{V}}=\text{O}$  intermediate is not the plausibly operative in the  $[\text{Ru}^{\text{III}}(\text{TDL})(\text{temda})(\text{H}_2\text{O})]$  catalyzed epoxidation of selected hydrocarbons with *t*-BuOOH. Considering the use of alkylperoxometal complexes in alkene epoxidation has precedent in the literature [23–25] the results of the above investigation may be explicable in terms of the catalytic scheme (Scheme 1) involving the intermediacy of a  $[\text{Ru}-\text{O}-\text{OBu}^t]^\bullet$  radicaloid species.

In the first step of Scheme 1  $[\text{Ru}^{\text{III}}(\text{TDL})(\text{temda})(\text{H}_2\text{O})]$  reacts with *t*-BuOOH to form an intermediate  $[\text{Ru}^{\text{III}}(\text{TDL})(\text{temda})(\text{OO}^t\text{Bu})]$  (**1a**) species in a aquo-substitution step. Coordinated *t*-BuOO<sup>−</sup> in **1a** oxidizes the metal center to form the radicaloid intermediate (**1b**) through an inner-sphere electron transfer pathway. Interaction between **1b** and alkene seems to be the plausible route for the catalytic epoxidation of unsaturated hydrocarbons studied in the present work. The catalytic cycle is further repeated by the generation of **1a** in the reaction between  $[\text{Ru}^{\text{III}}(\text{TDL})(\text{temda})(\text{OBu}^t)]$  (**1c**) and another molecule of *t*-BuOOH as shown in Scheme 1. No appreciable substrates conversion (<1%) after 10 h of reaction in presence of benzoquinone (radical trapping agent) reinforce the arguments in favor of the formation of such radicaloid type intermediate (**1b**). The ammine donor of bidentate 'temda', which is a strong  $\sigma$ -donor as compared to 'bipy' or 'pic', could enhance the electron density on the ruthenium center of complexes **1–4**. As a consequence, tendency of the inner-sphere electron transfer from Ru to *t*-BuOO<sup>−</sup> to form a radicaloid intermediate (**1b**) is increased, thus leading to the epoxidation reaction. The oxygenation of C=C bond of alkenes by  $\text{Ru}^{\text{IV}}$ -intermediate species (**1b**) possibly takes place in a concerted manner involving pre-association of **1b** and alkene followed



**Fig. 6.** Transition states of the epoxidation of (A) *cis*-stilbene and (B) *trans*-stilbene.

by charge transfer resulting in reduction of  $\text{Ru}^{\text{IV}}$  to  $\text{Ru}^{\text{III}}$  accompanied by epoxide formation.

It was reported earlier [26–28] that the evidence of radical character of the pathway in the epoxidation of stilbenes is that the *trans*-stilbene is epoxidized with retention of stereochemistry and *cis*-stilbene produces mixture of *cis*-oxide and *trans*-oxide with a predominance of *trans*-oxide. In this pathway rotation of C–C single bond is allowed in the intermediate. Steric repulsions of the phenyl rings favor rotation into less-strained *trans*-arrangement. In order to look at the stereoselectivity and the nature of intermediate that governs the catalytic process, epoxidation of both *cis*-stilbene and *trans*-stilbene was performed using **1–4**/*t*-BuOOH under specified conditions. Identification and quantification of epoxides of stilbenes were carried out by following an earlier report on the <sup>1</sup>H NMR analysis of stilbene epoxides [14], wherein, the peaks at 3.90 and 4.31 ppm were assigned to *trans*-stilbene oxide and *cis*-stilbene oxide, respectively. A mixture of *cis*- and *trans*-epoxides was produced (Table 1) during epoxidation of *cis*-stilbene. The loss of stereoselectivity necessarily indicates that the intermediate species formed during catalytic process allowed a limited amount of rotation through C–C bond prior to the epoxide formation. Under identical conditions, epoxidation of *trans*-stilbene yielded only *trans*-epoxide product (Table 1). Based on the above experimental facts, plausible transition states of the epoxidation *cis*- and *trans*-stilbenes are drawn in Fig. 6.

It is currently believed that in most of the hydrocarbon oxidations catalyzed by  $\text{Ru}^{\text{III}}$ -complexes using *t*-BuOOH proceed by the heterolytic *t*-BuOOH cleavage, forming  $\text{Ru}^{\text{V}}=\text{O}$  species with the avoidance of *t*-butoxy (*t*-BuO<sup>•</sup>) radicals. It is worth mentioning here that in  $\text{Fe}^{\text{III}}$ -promoted hydrocarbon oxidations, as demonstrated recently [29] the electron density on the O–O bond must be optimized (i.e. it should not be too small but also not too large) for heterolytic cleavage of O–O bond to form  $(\text{PorY}^{\bullet+})\text{Fe}^{\text{IV}}=\text{O}$  species. Although the effect of changing donors (by changing 'TDL' or 'XY') at ruthenium center is complicated [30], it emerges that the formation of radical intermediate  $[(\text{TDL})(\text{XY})\text{Ru}^{\text{IV}}(\text{OOBu}^t)]^\bullet$  is optimum when XY = 'temda'.

#### 4. Conclusions

A new series of ruthenium(III)-complexes (**1–4**) have been synthesized and characterized. The results of present studies demonstrate the catalytic ability of **1–4** for effecting alkene epoxidation in presence of *t*-BuOOH. Epoxide yields appear to be little sensitive to the variation of the *para*-substituents of styrene. In absence of any clear evidence in favor of the intermediacy of  $\text{Ru}^{\text{V}}=\text{O}$  species, a  $[\text{Ru}^{\text{IV}}-\text{O}(\text{tBu})-\text{O}^\bullet]$  radicaloid species, is proposed as the catalytically active intermediate in the present case. Oxygen insertion from  $[\text{Ru}^{\text{IV}}-\text{O}(\text{tBu})-\text{O}^\bullet]$  radicaloid species into C=C bond probably takes place through a pathway mainly radical in character involving a loosely bound charge-transfer complex.

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