

## Studies on the reactivity of *cis*-RuCl<sub>2</sub> fragment in Ru(PPh<sub>3</sub>)<sub>2</sub>(TaiMe)Cl<sub>2</sub> with N,N'-chelators (TaiMe = 1-methyl-2-(*p*-tolylazo)imidazole). Spectral and electrochemical characterisation of the products

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**Abstract.** Dechlorination of Ru(PPh<sub>3</sub>)<sub>2</sub>(TaiMe)Cl<sub>2</sub> (TaiMe = *p*-Me-C<sub>6</sub>H<sub>4</sub>-N=N-C<sub>3</sub>H<sub>2</sub>NN(1)-Me (**1**), 1-methyl-2-(*p*-tolylazo)imidazole) has been carried out in acetone solution by Ag<sup>+</sup> and reacted with N,N'-chelators to synthesise [Ru(PPh<sub>3</sub>)<sub>2</sub>(TaiMe)(N,N')]<sup>2+</sup>. The complexes have been isolated as their perchlorate salts. The N,N' chelators are 1-alkyl-2-(phenylazo)imidazoles (PaiX, X = Me, Et, CH<sub>2</sub>Ph); 2-(arylo)pyridines, (Raap, *p*-R-C<sub>6</sub>H<sub>4</sub>-N=N-C<sub>5</sub>H<sub>4</sub>N; R = H, Me, Cl); 2-(arylo)pyrimidines (Raapm, *p*-R-C<sub>6</sub>H<sub>4</sub>-N=N-C<sub>3</sub>N<sub>2</sub>H<sub>2</sub>; R = H, Me, Cl); 2,2'-bipyridine (bpy) and 1,10-phenanthroline (*o*-phen). Unsymmetrical N,N' chelators may give two isomers and this is indeed observed. The <sup>1</sup>H NMR spectral data refer to the presence of two isomers in the mixture in different proportions. With consideration of coordination pairs in the order of PPh<sub>3</sub>, PPh<sub>3</sub>; N,N (N refers to N(imidazole)) and N',N (N' refers to N(azo)), the complexes have been characterised as *trans-cis-cis* and *trans-trans-trans* configuration; the former predominates in the mixture. Electrochemical studies exhibit high potential Ru(III)/Ru(II) couple and quasireversible N=N reduction. Electronic spectra show high intensity ( $\epsilon \sim 10^4$ ) MLCT transition in the visible region (520 ± 10) nm along with a shoulder ( $\epsilon \sim 10^3$ ) in the longer wavelength region.

**Keywords.** Ruthenium(II) mixed chelates; arylazoheterocycles; phosphine; MLCT.

### 1. Introduction

This work stems from our interest in the exploration of chemical reactivity of arylazoimidazole complexes of ruthenium(II)<sup>1–5</sup>. The exobidentate behaviour of imidazole has been eliminated by N(1)-alkylation. N(1)-alkyl-2-(arylo)imidazole (RaaiX) are bidentate N,N'-chelators (abbreviation: N(imidazole) is N and N(azo) is N') and form several complexes with ruthenium(II) depending on experimental conditions and the starting compound of ruthenium used. For example, the reaction between RuCl<sub>3</sub> and RaaiX in refluxing ethanol isolates pseudo-octahedral RuCl<sub>2</sub>(RaaiX)<sub>2</sub> in four geometrical isomeric structures<sup>1</sup>. By considering coordinated atoms in three pairs, viz. Cl, Cl, N, N and N', N'; four isomers of configuration *trans-cis-cis*, *cis-trans-cis*, *cis-cis-trans* and *cis-cis-cis*<sup>4,5</sup> have been identified and two of them *tcc*- and *ctc*-RuCl<sub>2</sub>(RaaX)<sub>2</sub>

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have been structurally confirmed by X-ray diffraction study<sup>1</sup>. The reaction<sup>3</sup> between  $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$  and  $\text{RaaiX}$  in dichloromethane isolates  $\text{Ru}(\text{PPh}_3)_2(\text{RaaiX})\text{Cl}_2$  while the reaction<sup>6</sup> in ethanol under reflux gives  $[\text{Ru}(\text{PPh}_3)_2(\text{RaaiX})_2](\text{ClO}_4)_2$ .  $\text{Ru}(\text{PPh}_3)_2(\text{RaaiX})\text{Cl}_2$  may exist in four geometrical isomers, (i)–(iv)<sup>3,7–9</sup>, with considering coordination pairs of  $\text{PPh}_3$ ,  $\text{PPh}_3$  and  $\text{Cl}$ ,  $\text{Cl}$  respectively. The product in isomer (i) has been characterised as having *trans*- $\text{Ru}(\text{PPh}_3)_2$  configuration.

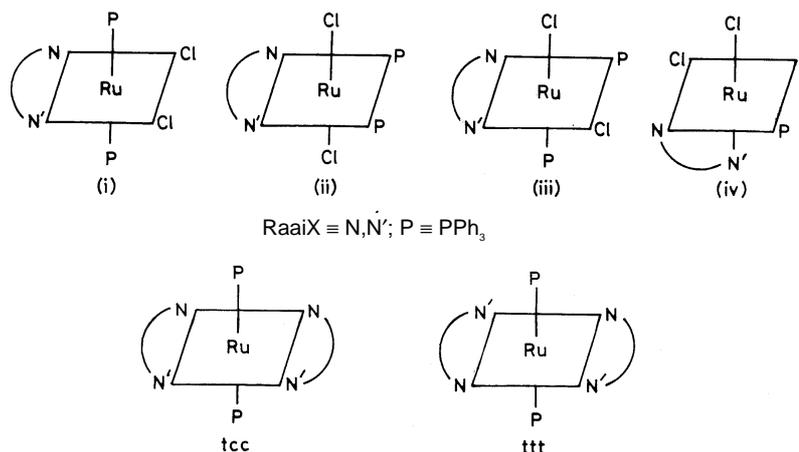


Chart 1.

Ruthenium(II) complexes with *cis*- $\text{RuCl}_2$  configuration undergo  $\text{Cl}$ -substitution reactions that are catalysed by  $\text{Ag}^+$ . In this work we wish to report several complexes of  $\text{RuN}_4\text{P}_2$  configuration synthesised from  $\text{Ru}(\text{PPh}_3)_2(\text{TaiMe})\text{Cl}_2$  ( $\text{TaiMe} = \text{N}(1)\text{-methyl-2-}(p\text{-tolylazo})\text{imidazole}$ , **1**) and symmetrical  $\text{N,N}$  donor ligands or unsymmetrical  $\text{N,N}'$ -donor ligands like  $\text{N}(1)\text{-alkyl-2-}(phenylazo)\text{imidazole}$  ( $\text{PaiX}$ ), arylazopyridines ( $\text{Raap}$ ) and arylazopyrimidines ( $\text{Raapm}$ ).

## 2. Experimental

Commercial  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  was purchased from Arora Matthey, Calcutta, India and was converted into  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  by repeated evaporation to dryness with conc.  $\text{HCl}$ . Triphenylphosphine ( $\text{PPh}_3$ ) was obtained from E Merck.  $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ <sup>3</sup> and  $\text{N}(1)\text{-methyl-2-}(p\text{-tolylazo})\text{imidazole}$ <sup>1</sup> were obtained as described earlier. Tetrabutylammonium perchlorate ( $\text{Bu}_4\text{NClO}_4$ ) and acetonitrile for electrochemical works were purified by the reported procedure<sup>1</sup>. All other chemicals and solvents were reagent grade and were used as received.

Microanalyses (C, H, N) were carried out using a Perkin-Elmer 2400 CHN elemental analyser. Spectroscopic measurements were done using the following instruments; IR spectra, Jasco FT-IR model 420; UV-Vis spectra, Jasco UV-Vis-NIR model V-570 and <sup>1</sup>H-NMR spectra, Bruker 200 and 300 MHz FT-NMR spectrometers. Molar conductances ( $\Lambda_M$ ) were measured in a Systronics conductivitymeter 304 model using  $\sim 10^{-3}$  M solution in MeOH. Electrochemical measurements were made with a computer-controlled PAR (model 270) Versat electrochemical instrument using a glassy carbon disk working electrode. All measurements were made at 298 K and referenced to the

saturated calomel electrode (SCE) in acetonitrile with tetrabutylammonium perchlorate (Bu<sub>4</sub>NClO<sub>4</sub>) as supporting electrolyte. The reported potentials are uncorrected for junction potential.

### 2.1 Preparation of complexes

The complexes were prepared following the general procedure and for one case is detailed below.

2.1a *Bis*-(triphenylphosphine) {*N*(1)-methyl-2-(*p*-tolylazo)imidazole} (2,2'-bipyridine) ruthenium (II) perchlorate, monohydrate. [Ru(PPh<sub>3</sub>)<sub>2</sub>(TaiMe)(bpy)](ClO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O (**5**): To a suspension of Ru(PPh<sub>3</sub>)<sub>2</sub>(TaiMe)Cl<sub>2</sub> (0.04 g, 0.04 mM) in acetone (20 cm<sup>3</sup>) was added AgNO<sub>3</sub> (0.015 g, 0.09 mM) and the mixture stirred for 2 h. The precipitated AgCl was filtered through a G-4 crucible. To the filtrate, 2,2'-bipyridine (0.007 g, 0.04 mM) was added and refluxed for 3 h, when the colour changed from red-violet to brownish-red. The resulting solution was cooled to room temperature and a saturated aqueous solution of NaClO<sub>4</sub> (5 cm<sup>3</sup>) was added. The [Ru(PPh<sub>3</sub>)<sub>2</sub>(TaiMe)(bpy)](ClO<sub>4</sub>)<sub>2</sub> which precipitated as a dark solid was collected by filtration, washed with cold H<sub>2</sub>O and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub>. The dried mass was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (minimum volume) and chromatographed on a silica gel column. The yellow band was eluted by C<sub>7</sub>H<sub>8</sub> and the desired brown-red mass was eluted with CH<sub>3</sub>CN–C<sub>7</sub>H<sub>8</sub> (1:1, *v/v*). The solution was evaporated in air and dried over P<sub>4</sub>O<sub>10</sub>. Yield: 48%; 0.02 g.

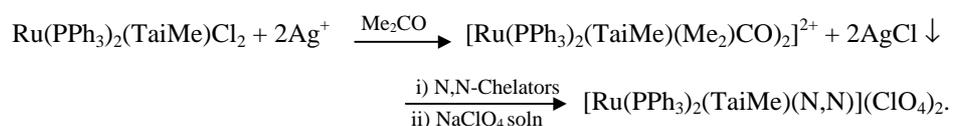
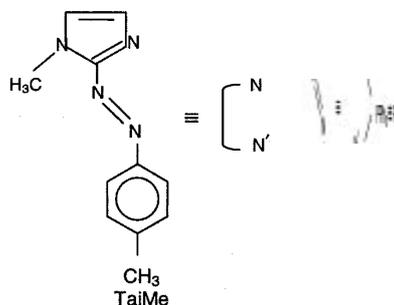
## 3. Results and discussion

Dechlorination of Ru(PPh<sub>3</sub>)<sub>2</sub>(TaiMe)Cl<sub>2</sub> has been achieved by the Ag<sup>+</sup> assisted route in acetone solution (equation (1), scheme 1). Upon addition of *N,N*-chelators to the solution of [Ru(PPh<sub>3</sub>)<sub>2</sub>(TaiMe)(Me<sub>2</sub>CO)<sub>2</sub>]<sup>2+</sup>, [Ru(PPh<sub>3</sub>)<sub>2</sub>(TaiMe)(*N,N*)]<sup>2+</sup> is formed and precipitated as perchlorate salt. Four classes of complexes have been synthesised following this reaction (1), (scheme 1), of structure [Ru(PPh<sub>3</sub>)<sub>2</sub>(TaiMe){*N*(1)-alkyl-(2-phenylazo)imidazole}](ClO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O (**2**), [Ru(PPh<sub>3</sub>)<sub>2</sub>(TaiMe){2-(arylazo)pyridine}](ClO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O (**3**), Ru(PPh<sub>3</sub>)<sub>2</sub>(TaiMe){2-(arylazo)pyrimidine}](ClO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O (**4**); [Ru(PPh<sub>3</sub>)<sub>2</sub>(TaiMe)(*a*-diimine)](ClO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O (*a*-diimine = 2,2'-bipyridine (bpy) (**5**) and 1,10-phenanthroline (*o*-phen, **6**). PaiX, Raap, Raapm are *N,N'*-chelators, two geometrical isomers are possible for [Ru(PPh<sub>3</sub>)<sub>2</sub>(TaiMe)(*N,N'*)]<sup>2+</sup> (**2–4**). In *N,N'*-chelators, *N* refers to *N*(heterocycle) and *N'* refers to *N*(azo) donor centres. For symmetrical *N,N*-chelators, 2,2'-bipyridine (bpy), 1,10-phenanthroline (*o*-phen), one isomer is possible. The isomers have not been separated by chromatography. Two isomers are probable with *trans*-Ru(PPh<sub>3</sub>)<sub>2</sub> configuration: *tcc* (isomer A) and *ttt* (isomer B). The <sup>1</sup>H NMR spectral data are useful in characterising the isomers.

The complexes are soluble in common organic solvents like MeOH, EtOH, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN and develop deep brown colour. Molar conductance measurements (Λ<sub>M</sub>, 120–160 Ω<sup>-1</sup> M<sup>-1</sup>) in CH<sub>3</sub>OH exhibit 1:2 electrolytic behaviour of the complexes.

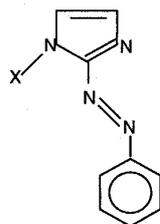
### 3.1 Spectral characterisation

IR spectra of the complexes exhibit broad medium intense bands at 3420–3450 cm<sup>-1</sup> and support the presence of H<sub>2</sub>O in the molecule<sup>10</sup>. An intense band observes at 1085–

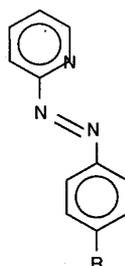


(1)

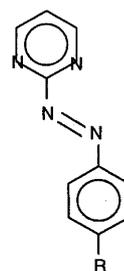
N,N'-Chelators:



PaiX (2)  
X = Me (a), Et (b), PhCH<sub>2</sub> (c)

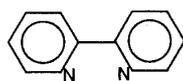


Raap (3)  
R = H (a), Me (b), Cl (c)

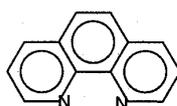


Raapm (4)  
R = H (a), Me (b), Cl (c)

N,N-Chelators:



2,2'-bpy (5)



o-phen (6)

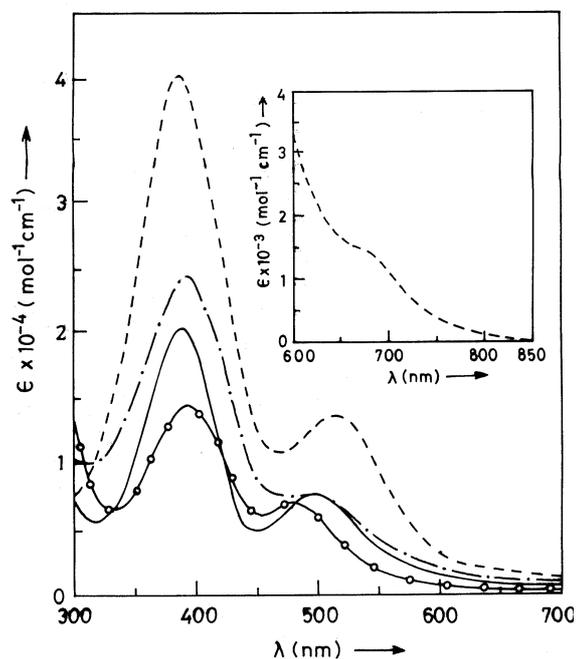
Scheme 1.

1090  $\text{cm}^{-1}$  with a weak band at 625  $\text{cm}^{-1}$  corresponds to  $\nu(\text{ClO}_4)$  vibration<sup>6</sup>. The N=N band appears at 1365–1380  $\text{cm}^{-1}$  in **2–4** while it is shifted to lower frequency at 1345  $\text{cm}^{-1}$  in  $\text{Ru}(\text{PPh}_3)_2(\text{TaiMe})(\text{a-dimine})(\text{ClO}_4)_2$  (**5, 6**). The red shifting of  $\nu(\text{N}=\text{N})$  in the latter complexes may result from better  $\pi$ -backbonding,  $t_2(\text{Ru}) \rightarrow \pi^*(\text{azo})$  in these complexes<sup>1</sup>. All other bands are difficult to assign and are only compared with the IR spectra of  $\text{Ru}(\text{PPh}_3)_2(\text{TaiMe})\text{Cl}_2$  and the corresponding N,N'-donor ligand.

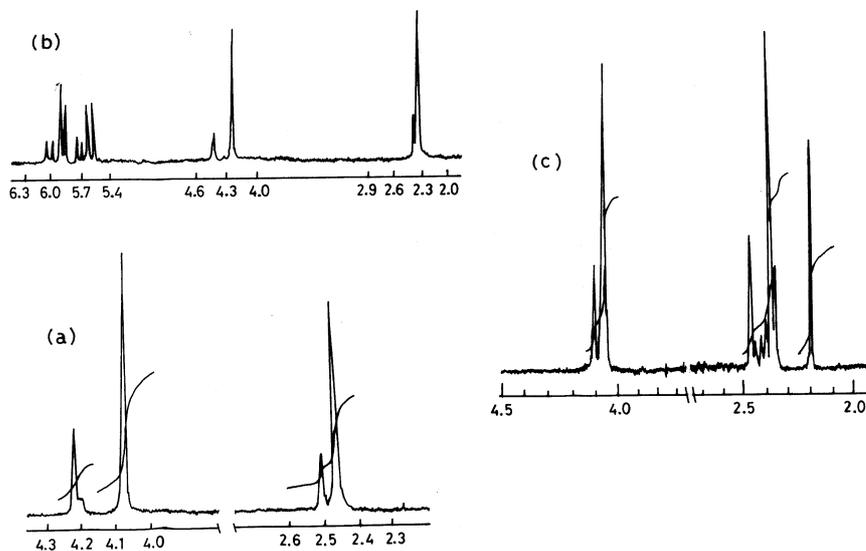
**Table 1.** Microanalytical, UV-Vis<sup>b</sup> and cyclic voltammetric<sup>c</sup> data.

Compounds	Elemental analyses <sup>a</sup>			$\lambda_{\text{max}}$ , (nm) ( $10^{-3} \epsilon, \text{M}^{-1} \text{cm}^{-1}$ )	Cyclic voltammetric data ( $\Delta E_p$ , mV)	
	C (%)	H (%)	N (%)		$^{\circ}E_M^0/V - E^0/V$	$^{\circ}E_M^0/V - E^0/V$
[RuP <sub>2</sub> (TaiMe)(PaiMe)](ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O ( <b>2a</b> )	55.5 (55.7)	4.0 (4.4)	9.4 (9.1)	668 (1.64) <sup>d</sup> , 515 (16.76), 389 (9.84)	1.10 (120) 1.18 (130)	0.79 (70), 1.16 (85), 1.40 (200)
[RuP <sub>2</sub> (TaiMe)(PaiEt)](ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O ( <b>2b</b> )	55.8 (56.0)	4.7 (4.5)	9.3 (9.0)	692 (1.18) <sup>d</sup> , 495 (14.74), 387 (3.60)	1.07 (110) 1.14 (110)	0.75 (90), 1.02 (95), 1.55 (200)
[RuP <sub>2</sub> (TaiMe)(PaiCH <sub>2</sub> Ph)](ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O ( <b>2c</b> )	58.0 (57.9)	4.6 (4.4)	8.5 (8.6)	688 (1.62) <sup>d</sup> , 524 (13.34), 390 (35.56)	1.11 (120) 1.20 (120)	0.76 (90), 1.13 (80), 1.50 (200)
[RuP <sub>2</sub> (TaiMe)(Haap)](ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O ( <b>3a</b> )	57.3 (56.8)	4.0 (4.3)	7.8 (8.0)	648 (0.636) <sup>d</sup> , 494 (4.34), 390 (8.24)	1.13 (110) 1.24 (110)	0.72 (90), 0.92 (110), 1.35 (220)
[RuP <sub>2</sub> (TaiMe)(Meaap)](ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O ( <b>3b</b> )	57.2 (57.1)	4.1 (4.4)	8.0 (7.9)	650 (2.58) <sup>d</sup> , 498 (13.12), 397 (40.340)	1.12 (110) 1.21 (120)	0.70 (90), 0.86 (100), 1.28 (200)
[RuP <sub>2</sub> (TaiMe)(Claap)](ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O ( <b>3c</b> )	55.6 (55.3)	4.0 (4.1)	8.1 (7.8)	656 (0.74) <sup>d</sup> , 493 (5.20), 390 (3.20)	1.14 (120) 1.24 (120)	0.76 (90), 1.00 (90)
[RuP <sub>2</sub> (TaiMe)(Haapm)](ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O ( <b>4a</b> )	56.0 (55.8)	4.0 (4.2)	8.8 (9.1)	608 (1.28) <sup>d</sup> , 509 (3.86), 394 (11.65)	1.13 (100) 1.21 (110)	0.76 (100), 1.13 (130)
[RuP <sub>2</sub> (TaiMe)(Meaapm)](ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O ( <b>4b</b> )	56.3 (56.1)	4.0 (4.3)	8.9 (9.0)	592 (1.83) <sup>d</sup> , 520 (3.15), 401 (10.99)	1.15 (110) 1.24 (120)	0.76 (90), 1.09 (120)
[RuP <sub>2</sub> (TaiMe)(Claapm)](ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O ( <b>4c</b> )	54.1 (54.3)	3.7 (4.0)	8.7 (8.9)	644 (1.30) <sup>d</sup> , 516 (4.53), 394 (2.9)	1.15 (110) 1.26 (110)	0.73 (90), 0.97 (120)
[RuP <sub>2</sub> (TaiMe)(bpy)](ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O ( <b>5</b> )	56.8 (57.1)	4.0 (4.3)	7.6 (7.0)	477 (2.04), 395 (3.40)	1.15 (80)	0.88 (130), 1.51 (120)
[RuP <sub>2</sub> (TaiMe)(ophen)](ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O ( <b>6</b> )	58.0 (57.9)	4.4 (4.2)	7.2 (6.9)	514 (4.61), 392 (3.05)	1.03 (100)	0.90 (130), 1.55 (120)

<sup>a</sup>Calculated values are in parentheses; <sup>b</sup>solvent MeCN; <sup>c</sup>working electrode glassy carbon, reference SCE, supporting electrolyte [Bu<sub>4</sub>N][ClO<sub>4</sub>], solvent MeCN at 300 K, solute concentration  $\sim 10^{-3}$  M, scan rate 0.05 V s<sup>-1</sup>; <sup>d</sup>shoulder; <sup>e</sup> $E_M^0 = 0.5 (E_{pa} + E_{pc})$  and  $\Delta E_p = (E_{pa} - E_{pc})$  mV.



**Figure 1.** Electronic spectra of  $[\text{Ru}(\text{PPh}_3)_2(\text{TaiMe})\text{Cl}_2]$  (—),  $[\text{Ru}(\text{PPh}_3)_2(\text{TaiMe})(\text{PaiMe})(\text{ClO}_4)_2]$  (---),  $[\text{Ru}(\text{PPh}_3)_2(\text{TaiMe})(\text{Meapp})(\text{ClO}_4)_2]$  (- · - · -) and  $[\text{Ru}(\text{PPh}_3)_2(\text{TaiMe})(\text{bpy})(\text{ClO}_4)_2]$  (- ° - ° -).



**Figure 2.** Aliphatic region of  $^1\text{H}$  NMR spectra of (a)  $[\text{Ru}(\text{PPh}_3)_2(\text{TaiMe})(\text{PaiMe})]^{2+}$  (**2a**), (b)  $[\text{Ru}(\text{PPh}_3)_2(\text{TaiMe})(\text{PaiCH}_2\text{Ph})]^{2+}$  (**2b**) and (c)  $[\text{Ru}(\text{PPh}_3)_2(\text{TaiMe})(\text{Meapp})]^{2+}$  (**2c**) in  $\text{CDCl}_3$ .

The absorption spectra of the complexes were taken in  $\text{CH}_3\text{CN}$  solution. The transitions below 400 nm are the intraligand charge transfer transitions<sup>3</sup> and are not considered further. The complexes exhibit multiple transition in the visible region



Table 2. <sup>1</sup>H-NMR spectral data<sup>a</sup> in the aliphatic region of the complexes.

Compound	fcc isomer						ttr isomer			
	N(1)-CH <sub>3</sub>	10-Me	(N(1')-CH <sub>2</sub> )-CH <sub>3</sub>	N(1')-CH <sub>2</sub>	10'-Me	N(1)-CH <sub>3</sub>	10-Me	(N(1')-CH <sub>2</sub> )-CH <sub>3</sub>	N(1')-CH <sub>2</sub>	10'-Me
(2a)	4.08	2.39				4.24	2.43			
(2b)	4.10	2.35	1.42 (7.0)	4.32 (9.0)		4.25	2.41	1.48 (7.0)	4.44 (9.0)	
(2c)	4.22	2.37		5.64 (18.0) <sup>b</sup> 5.92 (18.0) <sup>b</sup>		4.34	2.42		5.73 (18.0) <sup>b</sup> 5.99 (18.0) <sup>b</sup>	
(3a)	4.08	2.23				4.18	2.36			2.47
(3b)	4.06	2.14			2.40	4.14	2.38			
(3c)	4.09	2.28				4.16	2.36			
(4a)	4.10	2.30				4.21	2.32			
(4b)	4.07	2.19			2.39	4.26	2.29			2.45
(4c)	4.11	2.27				4.14	2.38			
(5)	4.19	2.29								
(6)	4.12	2.24								

<sup>a</sup>In CDCl<sub>3</sub>; <sup>b</sup>J = geminal coupling constant for CH<sub>2</sub> protons.

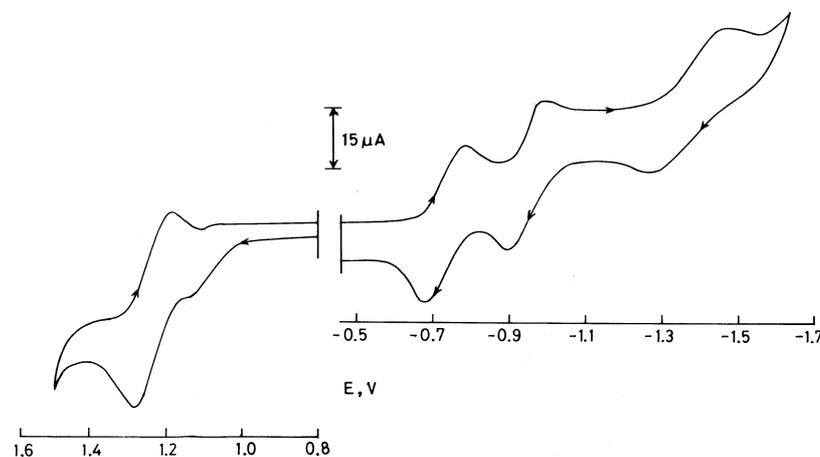
(table 1). High intense transition ( $\epsilon \sim 10^4$ ) is observed around  $520 \pm 20$  nm along with two/three weak bands ( $\epsilon \sim 10^3$ ) at longer wavelengths. The spectral comparison is given in figure 1. The main transition is assigned to  $t_2(\text{Ru}) \rightarrow p^*(\text{L})$  and weak bands may correspond to spin-forbidden singlet–triplet transition. Multiple charge transfer transitions in mixed-ligand complexes may result from the lower symmetry splitting of the metal-dominated molecular orbitals, the presence of different acceptor orbitals and from the mixing of singlet and triplet configurations in the excited state through spin-orbit coupling<sup>11</sup>.

The <sup>1</sup>H NMR spectra of the complexes were compared with the free ligands and Ru(PPh<sub>3</sub>)<sub>2</sub>(TaiMe)Cl<sub>2</sub> (**1**) to establish the structure and stereochemistry of the complexes. Aromatic regions of the spectra are very complex owing to the large number of protons from PPh<sub>3</sub> and aryl rings. The aliphatic region has only been considered to identify the isomers and their population. Representative spectra are given in figure 2 and data are given in table 2. Ru(PPh<sub>3</sub>)<sub>2</sub>(TaiMe)Cl<sub>2</sub> shows two responses corresponding to Ar-Me and N(1)-Me at 2.42 and 3.92 ppm respectively<sup>3</sup>. These signals serve as guides to identify the isomers. [Ru(PPh<sub>3</sub>)<sub>2</sub>(TaiMe)(PaiMe)]<sup>2+</sup> (**2**) shows two N(1)-Me signals in the intensity ratio 1:0.45 and two Ar-Me signals. The appearance of two signals refers to the presence of two isomers in the mixture<sup>12</sup>. Integration of two types of Me signals, N(1)-Me and Ar-Me also shows 2:1 proportion. Two isomers are *tcc* and *ttt*. The *tcc*-configuration is less symmetric than *ttt*. The signal at higher *d* is assigned to the *tcc*-isomer. Thus, the *tcc*-isomer dominates in the mixture. [Ru(PPh<sub>3</sub>)<sub>2</sub>(TaiMe)-(PaiCH<sub>2</sub>CH<sub>3</sub>)]<sup>2+</sup> exhibits AB-type complex multiplet for –CH<sub>2</sub>– group (N(1)-CH<sub>2</sub>(CH<sub>3</sub>)); [Ru(PPh<sub>3</sub>)<sub>2</sub>(TaiMe)(PaiCH<sub>2</sub>Ph)]<sup>2+</sup> shows AB-type quartet and the geminal coupling constant is 18 Hz (figure 2). There are two closely spaced quartets of 1:0.2 intensity ratio. This indicates the presence of two isomers in the same ratio.

Appearance of Ar-Me signals, their number and intensity ratios also supports the population of isomers in the mixture. There are, however, neither neighbouring chiral centres nor any appreciable bond-rotational barriers, though there does exist a distorted coordination around the metal. This overall distortion leads to molecular dissymmetry<sup>1,13</sup>. [Ru(PPh<sub>3</sub>)<sub>2</sub>(TaiMe)(*a*-diimine)]<sup>2+</sup> (*a*-diimine = 2,2' bpy, *o*-phen) exhibit only two signals which correspond to N(1)-Me and Ar-Me of the coordinated TaiMe ligand. This refers to the presence of one component in the product. [Ru(PPh<sub>3</sub>)<sub>2</sub>(TaiMe) (Haap/Haapm)]<sup>2+</sup> exhibit two sets of –Me signals at 4.1–4.2 and 2.2–2.3 ppm assigned to N(1)-Me and Ar-Me responses respectively. The signal patterns and intensity ratios support the presence of two isomers in the mixture in the ratio 1:0.30 and of these, the *tcc*-isomer dominates. [Ru(PPh<sub>3</sub>)<sub>2</sub>(TaiMe)(Meap/Meapm)]<sup>2+</sup> show four Ar-Me signals and two N(1)-Me signals; [Ru(PPh<sub>3</sub>)<sub>2</sub>(TaiMe)(Claap/(Claapm)]<sup>2+</sup> exhibit two Ar-Me signals and two N(1)-Me signals. The observations are corroborated with the presence of two isomers in the mixture. Imidazole 4- and 5-H appear at 7.0–7.1 and 6.7–6.8 ppm respectively. PPh<sub>3</sub> protons appear as broad high intense signals at 7.1–7.2 and 7.4–7.5 ppm<sup>14</sup>. Pyridine/pyrimidine protons in Raap/Raapm appear at most downfield positions, 7.7–8.2 ppm.

### 3.2 Redox studies

The electrochemical activity of the complexes was studied in MeCN solution by cyclic voltammetry as glassy carbon disks using SCE as reference and Pt-wire as auxiliary electrodes. A representative voltammogram is shown in figure 3 and data are given in



**Figure 3.** Cyclic voltammogram of  $[\text{Ru}(\text{PPh}_3)_2(\text{TaiMe})(\text{Haap})](\text{ClO}_4)_2$  in MeCN using GC electrode at a scan rate of  $50 \text{ mV s}^{-1}$ .

table 1. The voltammetric responses positive to SCE are due to the oxidation of metal, (2) below. There are two closely spaced redox couples in the potential range 1.00–1.30 V for the complexes **2–4** while only one couple is observed for **5** and **6**.



The two couples are separated by 70–110 mV. Besides they show different current height ratios in the range 1:0.3 to 1:0.4. The one-electron stoichiometry of the couple is established by comparing the current height of the main couple with that of the standard ferrocene–ferrocenium couple under identical experimental conditions. Current height ratio of the two redox couples at any direction (either  $i_{pa}$  or  $i_{pc}$ ) may correspond to the ratio of isomers present in the solution<sup>4,5</sup>. The estimated concentration ratio of the isomers is 1:0.3 to 1:0.4. This is also supported by <sup>1</sup>H-NMR spectral information (*vide supra*). There are two quasireversible responses negative to SCE along with irreversible responses whose scan reversals do not exhibit anodic responses. These correspond to azo reduction<sup>1</sup>. The azo group can accommodate up to two electrons stepwise at the LUMO.



It is observed that two isomers exist in case of unsymmetrical the  $\text{N},\text{N}'$ -donor system: *tcc* and *ttt*. Two azo functions in the *tcc*-configuration appear in *cis*-form and can compete with two different  $d\mathbf{p}(\text{Ru})$  orbitals during backbonding interaction while transoid geometry of azo functions in *ttt*-configuration has compelled sharing of the same  $d\mathbf{p}(\text{Ru})$  orbital<sup>3</sup>. Thus, backbonding interaction follows the redox potential order as *tcc* > *ttt*-configuration. The main redox couple appears at higher  $E_M^0$  and is assigned to the *tcc*-configuration. The weak couple at lower  $E_M^0$  refers to the *ttt*-configuration.

[Ru(PPh<sub>3</sub>)<sub>2</sub>(TaiMe)(*a*-diimine)](ClO<sub>4</sub>)<sub>2</sub> (**5** and **6**) shows only one redox response and supports the presence of only one isomer.

#### 4. Conclusions

Ag<sup>+</sup>-assisted dechlorination of Ru(PPh<sub>3</sub>)<sub>2</sub>(TaiMe)Cl<sub>2</sub>, followed by the reaction of either unsymmetrical bidentate *N,N'* (from azoimine function) or symmetrical bidentate *N,N* (from *a*-diimine) yields [Ru(PPh<sub>3</sub>)<sub>2</sub>(TaiMe)(*N,N'*)]<sup>2+</sup> or [Ru(PPh<sub>3</sub>)<sub>2</sub>(TaiMe)(*N,N*)]<sup>2+</sup>. The complexes have been isolated as their perchlorate salts. They have been characterised by elemental analyses, UV-Vis, IR and <sup>1</sup>H-NMR data. [Ru(PPh<sub>3</sub>)<sub>2</sub>(TaiMe)(*N,N'*)]<sup>2+</sup> may exist in two isomeric forms. The isomers are assigned, on the basis of order of the coordination pairs of PPh<sub>3</sub>; N(imidazole) and N(azo), as of *tcc*- and *ttt*-configuration. Aliphatic regions of the <sup>1</sup>H-NMR spectra also suggest the existence of two isomers: *tcc* and *ttt*. The *tcc*-isomer exists in major proportion in the mixture. Cyclic voltammetry exhibits Ru(III)/Ru(II) couple ( $E_M^0 > 1.0$  V) along with azo reductions.

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