

Chemistry of ruthenium in $N_2P_2X_2$ ($X = Cl, Br$) coordination sphere: Synthesis, characterization and reactivities

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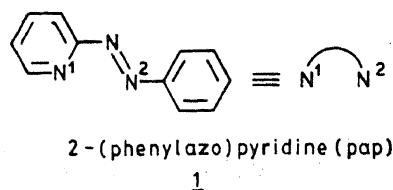
Abstract. Reaction of 2-(phenylazo)pyridine (pap) with $[Ru(PPh_3)_3X_2]$ ($X = Cl, Br$) in dichloromethane solution affords $[Ru(PPh_3)_2(pap)X_2]$. These diamagnetic complexes exhibit a weak $d-d$ transition and two intense MLCT transitions in the visible region. In dichloromethane solution they display a one-electron reduction of pap near -0.90 V vs SCE and a reversible ruthenium(II)-ruthenium(III) oxidation near 0.70 V vs SCE. The $[Ru^{III}(PPh_3)_2(pap)Cl_2]^+$ complex cation, generated by coulometric oxidation of $[Ru(PPh_3)_2(pap)Cl_2]$, shows two intense LMCT transitions in the visible region. It oxidizes *N,N*-dimethylaniline and $[Ru^{II}(bpy)_2Cl_2]$ (*bpy* = 2,2'-bipyridine) to produce *N,N,N',N'*-tetramethylbenzidine and $[Ru^{III}(bpy)_2Cl_2]^+$ respectively. Reaction of $[Ru(PPh_3)_2(pap)X_2]$ with Ag^+ in ethanol produces $[Ru(PPh_3)_2(pap)(EtOH)_2]^{2+}$ which upon further reaction with *L* (*L* = pap, *bpy*, acetylacetonate ion (*acac*[−]) and oxalate ion (*ox*^{2−})) gives complexes of type $[Ru(PPh_3)_2(pap)(L)]^{n+}$ ($n = 0, 1, 2$). All these diamagnetic complexes show a weak $d-d$ transition and several intense MLCT transitions in the visible region. The ruthenium(II)-ruthenium(III) oxidation potential decreases in the order (of *L*): pap > *bpy* > *acac*[−] > *ox*^{2−}. Reductions of the coordinated pap and *bpy* are also observed.

Keywords. Ruthenium; $N_2P_2X_2$ ($X = Cl, Br$) coordination sphere; reactivities.

1. Introduction

The chemistry of ruthenium has been receiving increasing attention (Seddon 1981, 1982, 1985; Kalyansundaram 1982; Seddon and Seddon 1984; Ghosh and Chakravorty 1989; Wong 1994), much of which is due to the interesting redox properties exhibited by the complexes of this metal. Ruthenium offers a wide range of oxidation states which are stabilized by different coordination spheres. Study of the chemistry of ruthenium in various coordination environments has thus been of special importance. In the present work, which originated from our interest in the chemistry of ruthenium (Bhattacharya 1993, 1994; Chakravarty and Bhattacharya 1994; Ghatak and Bhattacharya 1994; Ghatak *et al* 1994), we have created a $N_2P_2X_2$ ($X = Cl, Br$) coordination sphere around ruthenium where 2-(phenylazo)pyridine (pap, **1**) has been used as the *N,N*-donor ligand and triphenylphosphine (PPh_3) as the *P*-donor ligand. The 2-(arylo)pyridine ligands have strong π -acid character and are good stabilizers of the lower oxidation states of ruthenium (Krause and Krause 1980, 1982; Goswami *et al* 1981) and the Ru-pap complexes usually display interesting redox reactions (Lahiri *et al* 1990). Herein we report the synthesis and characterization of new Ru-pap complexes and

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their reactivities with special reference to electron-transfer and ligand-displacement reactions.

2. Experimental

2.1 Materials

Commercial ruthenium trichloride was purchased from Arora Matthey, Calcutta, India and was converted to $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ by repeated evaporation to dryness with concentrated hydrochloric acid. Triphenylphosphine and 2,2'-bipyridine (bpy) were obtained from Loba Chemie, Bombay, India. Acetylacetone (Hacac), oxalic acid (H_2ox) and triethylamine (NEt_3) were bought from S.D. Fine-Chem, Bombay, India. Preparation of $[\text{Ru}(\text{PPh}_3)_3\text{X}_2]$ and 2-(phenylazo)pyridine were done by following reported procedures (Stephenson and Wilkinson 1966; Goswami *et al* 1981). Purification of acetonitrile and dichloromethane, and preparation of tetraethylammonium perchlorate (TEAP) for electrochemical work were performed as reported in the literature (Sawyer and Roberts 1974; Walter and Ramalay 1973). All other chemicals and solvents were reagent grade commercial materials and were used as received.

2.2 Preparation of complexes

$[\text{Ru}(\text{PPh}_3)_2(\text{pap})\text{Cl}_2]$ – To a mixture of $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]$ (500 mg, 0.52 mmol) and pap (100 mg, 0.55 mmol) was added dichloromethane (50 ml). The resulting red-violet solution was stirred for 1 h. Hexane (100 ml) was layered over this red-violet solution. Upon slow diffusion of the solvents $[\text{Ru}(\text{PPh}_3)_2(\text{pap})\text{Cl}_2]$ deposited as shining needle-shaped crystals, which were collected by filtration, washed thoroughly with hexane and dried in air. The yield was 87%.

$[\text{Ru}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$ – This complex was synthesized by following the above procedure, using $[\text{Ru}(\text{PPh}_3)_3\text{Br}_2]$ (550 mg, 0.53 mmol) instead of $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]$. The yield was 90%.

$[\text{Ru}(\text{PPh}_3)_2(\text{pap})_2]$ (Method A) – To a suspension of $[\text{Ru}(\text{PPh}_3)_3\text{X}_2]$ (0.20 mmol) in ethanol (40 ml) was added pap (100 mg, 0.55 mmol) and the mixture was refluxed for 2 h. The resulting blue-violet solution was cooled to room temperature and a saturated aqueous solution of NaClO_4 (10 ml) was added to it. Dark crystalline precipitate of $[\text{Ru}(\text{PPh}_3)_2(\text{pap})_2](\text{ClO}_4)_2$ separated, which was collected by filtration, washed with cold water and dried *in vacuo* over P_4O_{10} . The yield was 75%.

$[\text{Ru}(\text{PPh}_3)_2(\text{pap})_2](\text{ClO}_4)_2$ (Method B) – $[\text{Ru}(\text{PPh}_3)_2(\text{pap})\text{X}_2]$ (0.20 mmol) was taken in ethanol (40 ml) and AgNO_3 (70 mg, 0.41 mmol) was added to it. The mixture was stirred for 30 min and the deposited AgX was separated by filtration. To the filtrate was added pap (40 mg, 0.22 mmol) and the solution was refluxed for 1 h. The resulting

blue-violet solution was cooled to room temperature and a saturated aqueous solution of $NaClO_4$ (10 ml) was added to it. $[Ru(PPh_3)_2(pap)_2](ClO_4)_2$ precipitated as a dark crystalline solid, which was collected by filtration, washed with cold water and dried *in vacuo* over P_4O_{10} . The yield was 70%.

$[Ru(PPh_3)_2(pap)(bpy)](ClO_4)_2$ – This complex was synthesized by following the method B, described above, using bpy (35 mg, 0.22 mmol) instead of pap. The yield was 70%.

$[Ru(PPh_3)_2(pap)(acac)]ClO_4$ – This complex was synthesized by following the method B, described above, using a mixture of Hacac (25 mg, 0.25 mmol) and NEt_3 (25 mg, 0.25 mmol) instead of pap. The yield was 75%.

$[Ru(PPh_3)_2(pap)(ox)]$ – A mixture of $[Ru(PPh_3)_2(pap)X_2]$ (0.20 mmol) and $AgNO_3$ (70 mg, 0.41 mmol) was stirred in ethanol (40 ml) for 30 min. The deposited AgX was removed by filtration and to the filtrate was added oxalic acid (30 mg, 0.24 mmol) and NEt_3 (50 mg, 0.50 mmol). The solution was refluxed for 1 h and then partially evaporated to give $[Ru(PPh_3)_2(pap)(ox)]$ as a deep red crystalline solid. This was collected by filtration, washed with hexane and water, and dried *in vacuo* over P_4O_{10} . The yield was 65%.

2.3 Physical measurements

Microanalyses (C, H, N) were performed using a Perkin–Elmer 240C elemental analyzer. Infrared spectra were obtained on a Perkin–Elmer 783 spectrometer with samples prepared as KBr pellets. Electronic spectra were recorded on a Hitachi U-3400 spectrophotometer. Magnetic susceptibility measurements were done by using a PAR 155 vibrating sample magnetometer. Solution electrical conductivities were measured using a Philips PR 9500 bridge with a solute concentration of about 10^{-3} M. Electrochemical measurements were made using the PAR model 370-4 electrochemical system incorporating the following components: 174A polarographic analyzer, 175 universal programmer, RE 0074 X-Y recorder, 173 potentiostat, 179 digital coulometer and 377 cell system. All electrochemical experiments were performed under a dinitrogen atmosphere. A planar Beckman 39273 platinum-inlay working electrode, a platinum-wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in a three electrode configuration. A platinum-wire gauge working electrode was used in the coulometric experiments. All electrochemical data were collected at 298 K and are uncorrected for junction potentials.

3. Results and discussion

3.1 Synthesis and characterization

$[Ru(PPh_3)_2(pap)X_2]$ ($X = Cl, Br$) complexes have been synthesized in good yields by the smooth displacement of one PPh_3 from $[Ru(PPh_3)_3X_2]$ by pap in dichloromethane solution at ambient temperature. The compositions of the complexes have been confirmed by elemental analytical data (table 1). The complexes are diamagnetic which corresponds to the +2 oxidation state of ruthenium (low-spin d^6 , $S = 0$). The infrared spectra of these complexes contain many bands and are complex in nature. Assignment of each individual band has not been attempted. However, characteristic bands showing the presence of all three types of ligands could be

Table 1. Microanalytical, molar conductivity, electronic spectral and cyclic voltammetric data

Compound	Analytical data ^a				Λ^b ($\Omega^{-1} \text{ cm}^2 \text{ M}^{-1}$)	λ_{max} , nm ($\epsilon^c, \text{ M}^{-1} \text{ cm}^{-1}$)	Ru ^{II/III}	$E_{298}^o, V(\Delta E_p, \text{ mV})^d$	
	%C	%H	%N					Ligand	reduction
[Ru(PPh ₃) ₂ (pap)Cl ₂]	64.1 (64.2)	4.3 (4.5)	4.9 (4.8)	—	—	^e 765(140), 525 (3400), 350(8700)	0.68(70) ^e	—	0.93(120) ^e
[Ru(PPh ₃) ₂ (pap)Br ₂]	58.1 (58.3)	4.0 (4.1)	4.4 (4.4)	—	—	^e 762(150), 530 (3700), 352(9300)	0.67(70) ^e	—	0.92(120) ^e
[Ru(PPh ₃) ₂ (pap) ₂] (ClO ₄) ₂	58.7 (58.5)	4.2 (4.1)	7.0 (7.1)	238	—	^b 750 ^f (280), 540 (4100), 475 ^f (3000), 310 ^f (14700)	1.65(70) ^b	—	0.23(100), — 0.79(120), — 1.23(120) ^b
[Ru(PPh ₃) ₂ (pap)(bpy)] (ClO ₄) ₂	59.0 (58.8)	4.0 (4.0)	6.2 (6.0)	244	—	^b 725 ^f (145), 500 (2300), 350 ^f (3600)	1.50(70) ^b	—	0.42(100), — 1.36(120), — 1.52(120) ^b
[Ru(PPh ₃) ₂ (pap)(acac)] ClO ₄	61.7 (62.0)	4.8 (4.8)	4.1 (4.2)	142	—	^b 750 ^f (320), 525 (4700), 300(13600)	1.17(70) ^b	—	0.32(100), — 1.31(120) ^b
[Ru(PPh ₃) ₂ (pap)(ox)]	65.3 (65.6)	4.5 (4.6)	4.8 (4.7)	—	—	^e 700(180), 510 (3500), 330(9300)	0.32(70) ^e	—	0.43(100), — 1.38(120) ^e

^a Calculated values are in parentheses; ^b in acetonitrile solution; ^c extinction coefficient; ^d reference electrode, SCE; supporting electrolyte, TEAP; solute concentration, $\sim 10^{-3} \text{ M}$; $E_{298}^o = 0.5(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are anodic and cathodic peak potentials; $\Delta E_p = E_{pa} - E_{pc}$; scan rate = 50 mV s^{-1} ; ^e in dichloromethane solution; ^f shoulder.

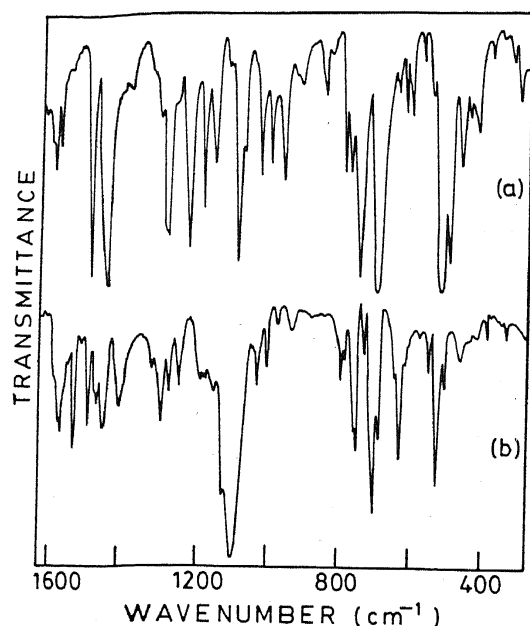


Figure 1. Infrared spectra of (a) $[Ru(PPh_3)_2(pap)Cl_2]$ and (b) $[Ru(PPh_3)_2(pap)(acac)]ClO_4$.

identified. A selected spectrum is shown in figure 1. $[Ru(PPh_3)_2(pap)Cl_2]$ exhibits a sharp band of medium intensity at 305 cm^{-1} , which is absent in $[Ru(PPh_3)_2(pap)Br_2]$. Hence this band is assigned to the $\nu(Ru-Cl)$ stretching mode (Chowdhury *et al* 1992). The $\nu(Ru-Br)$ stretch in the bromo complex could not be observed because it probably occurs beyond our experimentally accessible range. Comparison of the spectra of $[Ru(PPh_3)_2(pap)X_2]$ with those of corresponding $[Ru(PPh_3)_3X_2]$ shows that some vibrations are common to both spectra (e.g. intense bands at 495, 520, 695, 745, 1090, 1160, 1190, 1435 and 1482 cm^{-1}), which is due to the common $Ru(PPh_3)_2$ fragment in both complexes. Many additional bands are present in the spectra of $[Ru(PPh_3)_2(pap)X_2]$ (e.g. intense bands at 965, 1232, 1291 and 1450 cm^{-1}), which are obviously due to the coordinated pap. The band at 1450 cm^{-1} is assigned to the $\nu(N=N)$ stretching vibration (Goswami *et al* 1981). Therefore the infrared spectral data are in good agreement with the composition of these complexes.

Four geometrical isomers are possible for the $[Ru(PPh_3)_2(pap)X_2]$ complexes. Assignment of any particular stereochemistry to these complexes has not been possible due to lack of structural evidence. The complexes are readily soluble in dichloromethane and less soluble in acetonitrile producing red-violet solutions. Conductivity measurements show that these complexes are non-electrolytes in solution, which indicates that the halide ligands do not dissociate in solution. Electronic spectra recorded in dichloromethane solution show three absorptions in the visible region (figure 2, table 1). The low-intensity band near 760 nm is assigned to the $d-d$ ($^1A_1 \rightarrow ^1T_1$) transition (Mercer and Buckley 1965; El-Hendawy *et al* 1993). The other probable $d-d$ ($^1A_1 \rightarrow ^1T_2$) transition (Mercer and Buckley 1965) could not be identified due to intense absorptions at higher energies. The two intense absorptions near 525 nm and 350 nm are assigned to the metal-to-ligand charge-transfer transitions (Dose and Wilson 1978).

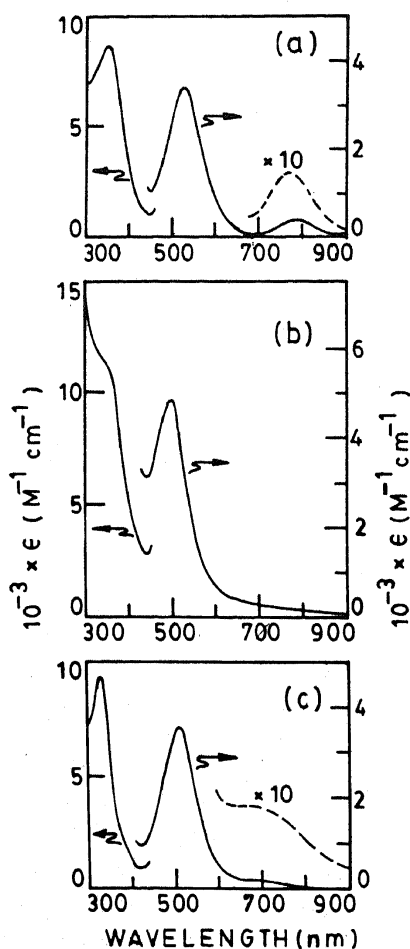
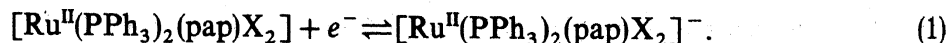


Figure 2. Electronic spectra in dichloromethane solution of (a) $[\text{Ru}(\text{PPh}_3)_2(\text{pap})\text{Cl}_2]$, (b) $[\text{Ru}^{\text{III}}(\text{PPh}_3)_2(\text{pap})\text{Cl}_2]^+$ and (c) $[\text{Ru}(\text{PPh}_3)_2(\text{pap})(\text{ox})]$.

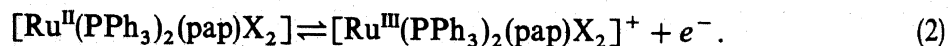
3.2 Electron-transfer reactions

Cyclic voltammetric studies on the $[\text{Ru}(\text{PPh}_3)_2(\text{pap})\text{X}_2]$ complexes in dichloromethane solution show a one-electron reduction of the coordinated pap and an oxidation of the metal. Voltammetric data are given in table 1 and voltammograms are shown in figure 3. Each 2-(aryloxy)pyridine ligand is known to accept electrons in its lowest unoccupied molecular orbital which is largely azo in nature (Goswami *et al* 1983). Hence two one-electron reductions are expected in these complexes of which only the first (see (1)) is observed near -0.90 V (all potentials are referenced to SCE),



The second reduction, which usually occurs at a much lower potential (Goswami *et al* 1981, 1983), is not observed due to solvent cut-off.

The ruthenium(II)–ruthenium(III) oxidation takes place reversibly near 0.70 V



The ΔE_p value is 70 mV and the anodic and cathodic peak currents are almost equal, as expected for reversible couples. The reversible nature of this ruthenium (II)–ruthenium(III) oxidation and its potential indicate that $[\text{Ru}^{\text{III}}(\text{PPh}_3)_2(\text{pap})\text{X}_2]^+$ may

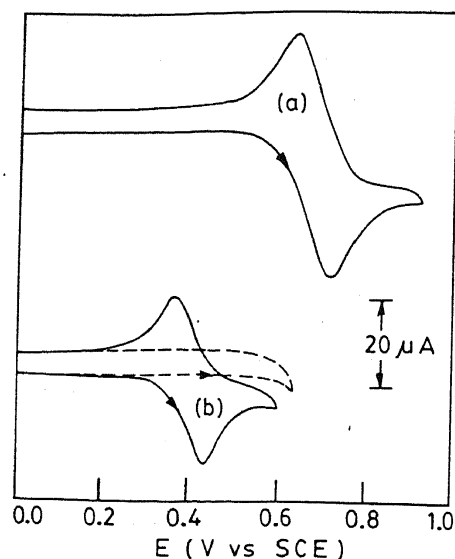
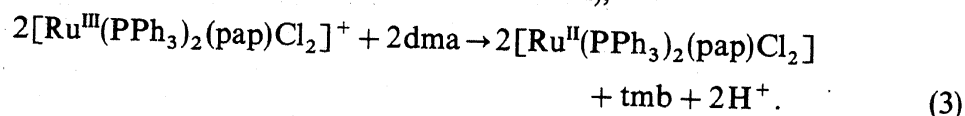


Figure 3. Segmented cyclic voltammograms in dichloromethane solution (0.1 M TEAP) of (a) $[Ru(PPh_3)_2(pap)Cl_2]$ and (b) free dma (---) and dma mixed with an equimolar quantity of $[Ru^{III}(PPh_3)_2(pap)Cl_2]^+$ at a scan rate of 50 mVs^{-1} .

function as a moderately strong one-electron oxidation. To explore this possibility, $[Ru^{III}(PPh_3)_2(pap)Cl_2]^+$ has been generated by coulometric oxidation of $[Ru^{II}(PPh_3)_2(pap)Cl_2]$ in dichloromethane solution (0.1 M TEAP) at 0.95 V. The orange solution of $[Ru^{III}(PPh_3)_2(pap)Cl_2]^+$ displays the same voltammogram as its precursor, indicating that no gross change in stereochemistry has taken place during the oxidation. The solution of $[Ru^{III}(PPh_3)_2(pap)Cl_2]^+$ shows two intense absorptions in the visible region at 500 nm ($\epsilon = 5400 \text{ M}^{-1} \text{ cm}^{-1}$) and 350 nm (shoulder, $\epsilon = 11500 \text{ M}^{-1} \text{ cm}^{-1}$) (figure 2) which are probably due to ligand-to-metal charge-transfer transitions. No attempt has been made to isolate this complex-cation as a salt. The efficiency of $[Ru^{III}(PPh_3)_2(pap)Cl_2]^+$ as an oxidant has been tested by the following two reactions.

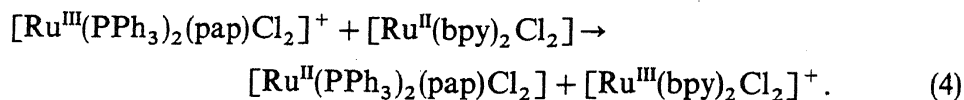
Oxidation of *N,N*-dimethylaniline – Addition of *N,N*-dimethylaniline (dma, 1 mmol) to a solution of $[Ru^{III}(PPh_3)_2(pap)Cl_2]^+$ (1 mmol) in dichloromethane brings about a colour change from orange to red-violet, indicating the conversion of the ruthenium(III)-complex to $[Ru^{II}(PPh_3)_2(pap)Cl_2]$. Cyclic voltammetry of the resultant solution shows a new response near 0.40 V (figure 3), which is characteristic of *N,N,N',N'*-tetramethylbenzidine (tmb) (Mizoguchi and Adams 1962),



Evidently dma, the reductant, undergoes a simultaneous one-electron oxidation followed by a coupling reaction to produce tmb, (3) (Lahiri *et al* 1990). The current height measurement of the tmb-response shows that about 40% of the oxidant has been utilized in the coupling reaction. The first of it has probably been used in the side reactions (Galus and Adams 1962; Galus *et al* 1962).

Oxidation of a ruthenium(II)-complex – $[Ru(bpy)_2Cl_2]$ is known to undergo a one-electron metal-centred oxidation near 0.30 V (Johnson *et al* 1978) and hence it may be

expected to reduce $[\text{Ru}^{\text{III}}(\text{PPh}_3)_2(\text{pap})\text{Cl}_2]^+$. To test the feasibility of this reaction, a solution of $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ (1 mmol) in dichloromethane has been added to a solution of $[\text{Ru}^{\text{III}}(\text{PPh}_3)_2(\text{pap})\text{Cl}_2]^+$ (1 mmol) in the same solvent,

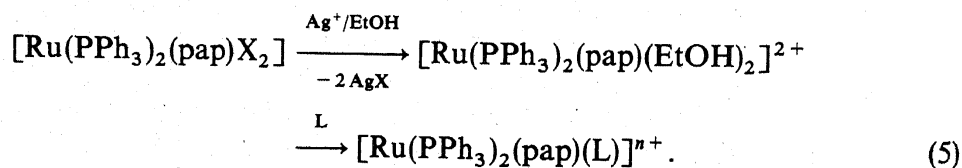


Cyclic voltammetry on the resultant solution shows that the expected redox reaction, (4), has indeed taken place. A reversible one-electron reduction near 0.30 V characteristic of $[\text{Ru}^{\text{III}}(\text{bpy})_2\text{Cl}_2]^+$ (Johnson *et al* 1978), is observed together with the reversible one-electron oxidation of $[\text{Ru}^{\text{II}}(\text{PPh}_3)_2(\text{pap})\text{Cl}_2]$ at 0.68 V.

The above two reactions prove that $[\text{Ru}^{\text{III}}(\text{PPh}_3)_2(\text{pap})\text{Cl}_2]^+$ can function as a good one-electron oxidant to oxidize both organic molecules and transition-metal complexes in non-aqueous media.

3.3 Reactions involving dissociation of the Ru-X bonds

The halide ligands of the $[\text{Ru}(\text{PPh}_3)_2(\text{pap})\text{X}_2]$ complexes, though not dissociating in solution, can be displaced by reacting these complexes with silver ion in ethanol. $[\text{Ru}(\text{PPh}_3)_2(\text{pap})(\text{EtOH})_2]^{2+}$, thus produced, reacts smoothly with a group of bidentate chelating ligands (L) to afford complexes of type $[\text{Ru}(\text{PPh}_3)_2(\text{pap})(\text{L})]^n+$ in decent yields,



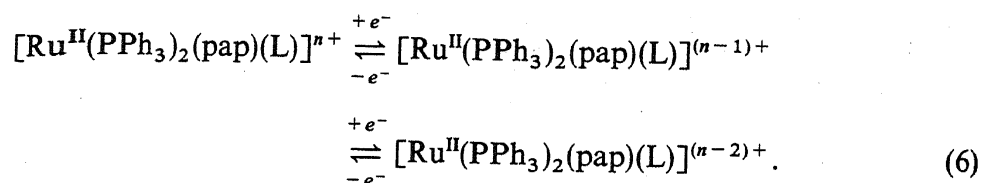
Three types of L [neutral (pap, bpy), monoanionic (acac⁻) and dianionic (ox²⁻)] have been used and the net charge of the complex varies ($n = 2, 1, 0$) accordingly. The $[\text{Ru}(\text{PPh}_3)_2(\text{pap})_2]^{2+}$ complex (i.e. L = pap) has also been prepared by the direct reaction of $[\text{Ru}(\text{PPh}_3)_3\text{X}_2]$ with pap in refluxing ethanol. Elemental analytical data (table 1) agree well with the compositions of the complexes. Magnetic susceptibility measurements show that the complexes are diamagnetic as expected for complexes of ruthenium(II). As pap is an unsymmetrical bidentate ligand, several geometrical isomers are possible for these $[\text{Ru}(\text{PPh}_3)_2(\text{pap})(\text{L})]^n+$ complexes. Lack of structural evidence has prevented us from assigning any stereochemistry to these complexes.

Infrared spectra of the $[\text{Ru}(\text{PPh}_3)_2(\text{pap})(\text{L})]^n+$ complexes show many vibrations due to the presence of PPh_3 , pap and L (also ClO_4^- ; for $n = 1, 2$), and are therefore very complex in nature. A selected spectrum is shown in figure 1. However, useful information is obtained on comparing the spectra of these complexes with the spectrum of $[\text{Ru}(\text{PPh}_3)_2(\text{pap})\text{Cl}_2]$. For example, the $\nu(\text{Ru-Cl})$ stretch at 305 cm^{-1} is absent in these complexes, as expected. For the ionic ($n = 1, 2$) complexes, a very intense vibration near 1100 cm^{-1} and another strong band near 620 cm^{-1} are observed, which indicate the presence of ClO_4^- . Additional vibrations, due to the coordinated L, are observed in $[\text{Ru}(\text{PPh}_3)_2(\text{pap})(\text{L})]^n+$.

The $[\text{Ru}(\text{PPh}_3)_2(\text{pap})(\text{L})]^n+$ complexes are soluble in both acetonitrile and dichloromethane, the ionic ($n = 1, 2$) complexes are more soluble in acetonitrile and the neutral ($n = 0$) complex in dichloromethane. Conductivity measurements show (table 1) that in acetonitrile solution the L = pap, bpy complexes behave as 1:2

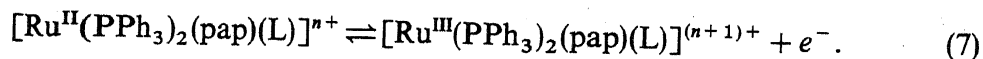
electrolytes, the $L = acac^-$ complex as 1:1 electrolyte, while the $L = ox^{2-}$ complex is a nonelectrolyte, as expected. Electronic spectra of these complexes show several absorptions in the visible region (table 1, figure 2). The low-intensity band in the 700–750 nm region is assigned (*vide supra*) to the $d-d(^1A_1 \rightarrow ^1T_1)$ transition. The other intense absorptions are probably due to metal-to-ligand charge-transfer transitions.

Cyclic voltammetry on the $[Ru(PPh_3)_2(pap)(L)]^{n+}$ complexes shows both metal-oxidation and ligand (pap, bpy)-reductions. Voltammetric data are given in table 1. All four complexes show two quasi-reversible reductions of the pap,



In the *bis*-pap complex ($L = pap$) the first two reductions at -0.23 and -0.79 V are assigned to the first reductions of the two pap ligands. The third reduction at -1.23 V is due to the second reduction of one pap, the second reduction of the other pap is not observed due to solvent cut-off. In the $L = bpy$ complex, a third reduction at -1.52 V is observed which is assigned to the first reduction of bpy (Tokel-Takvorian *et al* 1973). The second reduction of bpy has not been observed because the solvent reduction precedes it.

A reversible ruthenium(II)-ruthenium(III) oxidation is displayed by all four $[Ru(PPh_3)_2(pap)(L)]^{n+}$ complexes,



The nature of L is observed to have considerable influence on this oxidation potential. The potential decreases in the order (of L): pap bpy $acac^-$ ox^{2-} , as expected (Bhattacharya 1993; Chakravarty and Bhattacharya 1994). Therefore the potential of this couple can be shifted in any desired direction by varying the nature of L .

4. Conclusions

New and stable 2-(phenylazo)pyridine (pap) complexes of ruthenium of type $[Ru^{II}(PPh_3)_2(pap)X_2]$ ($X = Cl, Br$), have been synthesized and characterized. The oxidized complexes, $[Ru^{III}(PPh_3)_2(pap)X_2]^+$, are good oxidants and can oxidize both organic molecules and metal-complexes in non-aqueous medium. The Ru-X bonds in the $[Ru(PPh_3)_2(pap)X_2]$ complexes are dissociable under mild conditions and hence they can be used as starting materials to prepare complexes of the type $[Ru(PPh_3)_2(pap)(L)]^{n+}$ ($L =$ chelating bidentate ligand).

Acknowledgements

Financial support received from the Jadavpur University, Calcutta, is gratefully acknowledged. Thanks are due to the Council of Scientific and Industrial Research, New Delhi, for awarding a fellowship to Joydip Chakravarty. The authors thank Professor Ramgopal Bhattacharyya of the Jadavpur University, and Dr Sreebrata Goswami of the Indian Association for the Cultivation of Science for their help.

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