



PERGAMON

[www.elsevier.nl/locate/poly](http://www.elsevier.nl/locate/poly)

Polyhedron 19 (2000) 1227–1232



POLYHEDRON

# Chemistry of 2-(phenylazo)pyridine complexes of osmium: synthesis, characterization and reactivities

Anindya Das<sup>a</sup>, Shie-Ming Peng<sup>b</sup>, Samaresh Bhattacharya<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Inorganic Chemistry Section, Jadavpur University, Calcutta 700032, India

<sup>b</sup> Department of Chemistry, National Taiwan University, Taipei, Taiwan, ROC

Received 5 January 2000; accepted 24 February 2000

## Abstract

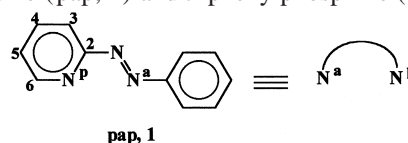
Reaction of 2-(phenylazo)pyridine (pap) with  $[\text{Os}(\text{PPh}_3)_3\text{Br}_2]$  afforded a mixed ligand complex of the type  $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$ . The structure of this complex was determined by X-ray crystallography. The  $\text{PPh}_3$  ligands are *trans* and the bromides are in *cis* positions. The pap ligand is coordinated to osmium as a bidentate N,N-donor forming a five-membered chelate ring. The complex is diamagnetic (low-spin  $d^6$ ,  $S=0$ ) and in dichloromethane solution shows intense MLCT transitions in the visible region. The two bromides were replaced from the coordination sphere of  $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$  under mild conditions by a series of anionic ligands L (where L = quinolin-8-olate (q), picolinate (pic), oxalate (Hox), 1-nitroso-2-naphtholate (nn) and acetyl acetonate (acac)) to afford complexes of the type  $[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{L})]^+$ , which were isolated and characterized as the perchlorate salt. The structure of the  $[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{acac})]\text{ClO}_4$  complex was determined by X-ray crystallography. The  $\text{PPh}_3$  ligands occupy *trans* positions and the acetylacetonate anion is coordinated to osmium as a bidentate O,O-donor forming a six-membered chelate ring. The  $[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{L})]^+$  complexes are diamagnetic and show multiple MLCT transitions in the visible region.  $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$  shows an osmium(II)–osmium(III) oxidation at 0.49 V versus SCE. The same oxidation is displayed by the  $[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{L})]^+$  complexes within 0.69 to 0.96 V versus SCE. Two successive one-electron reductions of the coordinated pap ligand are also observed in all the complexes below  $-0.90$  V versus SCE. ©2000 Elsevier Science Ltd All rights reserved.

**Keywords:** Osmium; Triphenylphosphine; 2-(Phenylazo)pyridine; Synthesis; Structures; Reactivities

## 1. Introduction

The chemistry of osmium has been receiving considerable attention [1–18], largely because of the variety of reactivities exhibited by its complexes. Most of these reactions require direct contact of the reactant with the metal center. As osmium is usually coordinatively saturated in its complexes, such direct links can only be established via dissociation of relatively weak metal–ligand bonds. Osmium complexes having potentially labile ligands are of particular importance in this regard. In the present work, which has emerged from our interest in the chemistry of osmium in different coordination environments [19–23], we have chosen an  $\text{OsBr}_2$  moiety as the reactive fragment, because the Os–Br bonds are known to undergo dissociation under rather mild conditions [24,25]. To satisfy the remaining four coordination sites of osmium

in this  $\text{OsBr}_2$  moiety, two  $\pi$ -acid ligands, i.e. 2-(phenylazo)pyridine (pap, **1**) and triphenylphosphine ( $\text{PPh}_3$ ), have



been utilized. 2-(Phenylazo)pyridine is well known for its strong  $\pi$ -acidity [26–28], by virtue of which it stabilizes the lower oxidation states of a metal. Triphenylphosphine also favors the lower oxidation states of a metal via  $d\pi$ – $d\pi$  interaction. Coordination by these  $\pi$ -acid ligands has been planned in order to stabilize the bivalent state of osmium, which in turn is expected to favor dissociation of the Os–Br bonds. The targeted complex,  $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$ , has been synthesized and the reactivity of the  $\text{OsBr}_2$  fragment towards displacement by a group of bidentate ligands (L) of different types has been studied. An account of the chemistry of  $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$  and  $[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{L})]^+$  complexes is reported here with special reference to synthesis, structure and redox properties.

\* Corresponding author. Tel.: +91-33-483-8393; fax: +91-33-473-4266; e-mail: samaresh\_b@hotmail.com

## 2. Experimental

### 2.1. Materials

Osmium tetroxide was purchased from Arora Matthey, Calcutta, India and was converted into  $[\text{NH}_4]_2[\text{OsBr}_6]$  by reduction with HBr [29].  $[\text{Os}(\text{PPh}_3)_3\text{Br}_2]$  was synthesized from  $[\text{NH}_4]_2[\text{OsBr}_6]$  using a literature method [30]. Triphenylphosphine, acetylacetonone (Hacac), oxalic acid ( $\text{H}_2\text{ox}$ ) and 1-nitroso-2-naphthol (Hnn) were purchased from Loba Chemie, Mumbai, India. Picolinic acid (Hpic) and quinoline-8-ol (Hq) were purchased from E. Merck (India). 2-(Phenylazo) pyridine was prepared by following a literature procedure [31]. All other chemicals and solvents were reagent grade commercial materials and were used as received. Purification of acetonitrile and dichloromethane, and preparation of tetrabutylammonium perchlorate (TBAP) for electrochemical work were performed as reported in the literature [32,33].

### 2.2. Preparation of the complexes

#### 2.2.1. $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$

To a mixture of  $[\text{Os}(\text{PPh}_3)_3\text{Br}_2]$  (100 mg, 0.09 mmol) and 2-(phenylazo)pyridine (16 mg, 0.09 mmol), 2-methoxyethanol (30  $\text{cm}^3$ ) was added. The resulting mixture was refluxed for 2 h. A red crystalline precipitate started to separate during reflux. After cooling the solution to room temperature, the precipitate was collected by filtration, washed thoroughly with ethanol and dried in air. The yield was 52 mg (56%).

#### 2.2.2. $[\text{Os}^{\text{II}}(\text{PPh}_3)_2(\text{pap})(\text{L})]\text{ClO}_4$ (L = pic, q, Hox, nn, acac) complexes

The  $[\text{Os}^{\text{II}}(\text{PPh}_3)_2(\text{pap})(\text{L})]\text{ClO}_4$  (L = pic, q, Hox, nn, acac) complexes were synthesized using a general procedure. Yields varied in the range of 60–65%. Specific details are given for one complex.

$[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{acac})]\text{ClO}_4$ .  $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$  (100 mg, 0.10 mmol) was dissolved in dichloromethane (20  $\text{cm}^3$ ) and to this solution was added acetylacetonone (10 mg, 0.10 mmol) followed by ethanol (30  $\text{cm}^3$ ) and triethylamine (10 mg, 0.10 mmol). The solution was boiled for a few minutes in air to remove dichloromethane as much as possible and then it was heated at reflux for 48 h. After being cooled to room temperature, a saturated aqueous solution of  $\text{NaClO}_4$  (0.5  $\text{cm}^3$ ) was added to it.  $[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{acac})]\text{ClO}_4$  precipitated as a red solid and was collected by filtration, washed with ice-cold water and dried in vacuo over  $\text{P}_4\text{O}_{10}$ . Purification of the product was done by thin layer chromatography on a silica-gel plate, using 1:1 benzene–acetonitrile as the eluant. A red band separated and was extracted with acetonitrile. On evaporation of the acetonitrile solution,  $[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{acac})]\text{ClO}_4$  was obtained as a red microcrystalline solid. The yield was 64 mg (61%).

In the case of HL = Hq and Hnn, 2-methoxyethanol was used as solvent instead of ethanol and triethanolamine was used as base instead of triethylamine.

### 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 Shimadzu UV 1601 spectrophotometer. Magnetic susceptibilities were measured using a PAR 155 vibrating sample magnetometer fitted with a Walker Scientific L75FBAL magnet.  $^1\text{H}$  NMR spectra were obtained on a Bruker AC-200 NMR spectrometer using TMS as the internal standard. Solution electrical conductivities were measured using a Philips PR 9500 bridge with a solute concentration of  $10^{-3}$  M. Electrochemical measurements were made using a PAR model 273 potentiostat. A platinum disk or graphite working electrode, a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in a three-electrode configuration. A RE 0089 X-Y recorder was used to trace the voltammograms. Dinitrogen gas was purified by successively bubbling it through alkaline dithionite and concentrated sulfuric acid and all electrochemical measurements were performed under this dinitrogen atmosphere. All electrochemical data were collected at 298 K and are uncorrected for junction potentials.

### 2.4. Crystallography

Single crystals of  $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$  were obtained directly from the synthetic reaction carried out in 2-methoxyethanol. Selected crystal data and data collection parameters are given in Table 1. Data were collected on a Siemens Smart CCD diffractometer using graphite-monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073$  Å) by frame using  $\omega$  scans within the angular range  $1.48^\circ < \theta < 26.37^\circ$ . X-ray data reduction and structure solution and refinement were done using the SHELXTL package. The structure was solved by direct methods.

Single crystals of  $[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{acac})]\text{ClO}_4$  were grown by slow diffusion of hexane into a dichloromethane solution of the complex. Selected crystal data and data collection parameters are given in Table 1. Data were collected on a Siemens Smart CCD diffractometer using graphite-monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073$  Å) by frame using  $\omega$  scans within the angular range  $1.57^\circ < \theta < 26.37^\circ$ . X-ray data reduction and structure solution and refinement were done using the SHELXTL package. The structure was solved by direct methods.

Table 1  
Crystallographic data for  $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$  and  $[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{acac})]\text{ClO}_4$

Formula	$\text{C}_{47}\text{H}_{39}\text{Br}_2\text{N}_3\text{P}_2\text{Os}$	$\text{C}_{52}\text{H}_{46}\text{ClN}_3\text{O}_6\text{P}_2\text{Os}$
FW	1057.77	1096.51
Space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/n$
$a$ (Å)	10.1561(2)	14.3739(1)
$b$ (Å)	17.3501(2)	15.2881(1)
$c$ (Å)	22.8526(3)	22.2380(1)
$\alpha$ (°)	90	90
$\beta$ (°)	97.624(1)	99.894(1)
$\gamma$ (°)	90	90
$V$ (Å <sup>3</sup> )	3991.24(11)	4814.11(5)
$Z$	4	4
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.760	1.513
$\lambda$ (Å)	0.71073	0.71073
Crystal size (mm)	0.18 × 0.08 × 0.03	0.80 × 0.12 × 0.10
$T$ (K)	295(2)	295(2)
$\mu$ (mm <sup>-1</sup> )	5.316	2.823
$R_1^a$	0.0503	0.0322
$wR_2^b$	0.0793	0.0664
GOF on $F^2$ <sup>c</sup>	1.078	1.093

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ .

<sup>b</sup>  $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ .

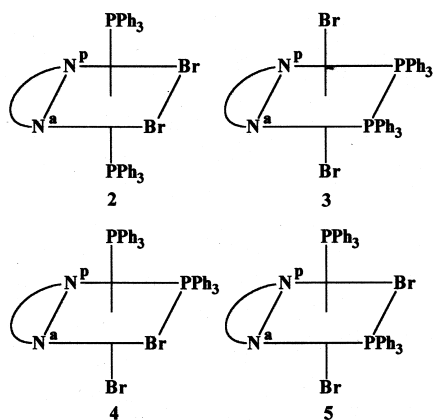
<sup>c</sup> GOF =  $[\sum [w(F_o^2 - F_c^2)^2] / (M - N)]^{1/2}$ , where  $M$  is the number of reflections and  $N$  is the number of parameters refined.

### 3. Results and discussion

#### 3.1. Synthesis and characterization

##### 3.1.1. $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$

Smooth displacement of one  $\text{PPh}_3$  from  $[\text{Os}(\text{PPh}_3)_3\text{Br}_2]$  by 2-(phenylazo)pyridine in refluxing 2-methoxyethanol affords the  $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$  complex in decent yield. The composition of the complex was confirmed by its elemental (C, H, N) analytical data (Table 2). The complex is diamagnetic, which corresponds to the +2 oxidation state of osmium (low-spin  $d^6$ ,  $S=0$ ) in this complex. As 2-(phenylazo)pyridine is an unsymmetrical bidentate ligand, this  $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$  complex may, in principle, exist in four geometrical isomeric forms (2–5). To find out



the actual stereochemistry of  $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$ , its structure was determined by X-ray crystallography. The

Table 2

Characterization data of the  $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$  and  $[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{L})]\text{ClO}_4$  complexes

Compound	Yield (%)	Analytical data <sup>a</sup>			$\lambda_{\text{max}}$ (nm) ( $\epsilon$ (M <sup>-1</sup> cm <sup>-1</sup> ))	Electronic spectral data		Cyclic voltammetric data <sup>e</sup>	
		C (%)	H (%)	N (%)		$E_{1/2}$ (V vs. SCE) ( $\Delta E_p$ (mV))	$E_{1/2}$ (V vs. SCE) ( $\Delta E_p$ (mV))		
$[\text{Os}(\text{PPh}_3)_2(\text{pap})]\text{Br}_2$ <sup>d</sup>	56	53.36 (53.36)	3.71 (3.69)	3.99 (3.97)	504 (4600), 408 <sup>b</sup> (7000), 340 <sup>b</sup> (4300), 252 <sup>b</sup> (12900), 228 (42200)	0.49 (80), -0.98 (100), -1.35 (100)			
$[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{q})]\text{ClO}_4$ <sup>e</sup>	64	58.94 (58.92)	3.99 (3.95)	4.93 (4.91)	538 (5800), 337 <sup>b</sup> (10300), 250 <sup>b</sup> (34200), 219 (61500)	1.01 (80), -0.92 (110), -1.29 (110)			
$[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{pic})]\text{ClO}_4$ <sup>e</sup>	60	56.87 (56.86)	3.86 (3.84)	5.03 (5.01)	480 (1700), 312 (6800), 260 <sup>b</sup> (10200), 220 (56900), 208 <sup>b</sup> (51500)	0.83 (80), -1.03 (120), -1.36 (120)			
$[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{Hox})]\text{ClO}_4$ <sup>e</sup>	65	49.67 (49.66)	3.31 (3.29)	3.57 (3.55)	484 (4600), 328 (14800), 252 <sup>b</sup> (35000), 216 (59000)	0.69 (80), -1.12 (110), -1.53 (120)			
$[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{nn})]\text{ClO}_4$ <sup>e</sup>	62	59.56 (59.54)	3.87 (3.85)	4.78 (4.79)	508 (5300), 335 <sup>b</sup> (11300), 223 (56900)	0.84 (70), -1.28 (130), -1.63 (140)			
$[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{acac})]\text{ClO}_4$ <sup>e</sup>	61	56.96 (56.91)	4.21 (4.20)	3.85 (3.83)	602 <sup>b</sup> (500), 501 (5000), 319 <sup>b</sup> (15900), 260 <sup>b</sup> (26500), 227 <sup>b</sup> (4700), 216 (53900)	0.92 (70), -0.91 (100), -1.33 (110)			

<sup>a</sup> Calculated values are in parentheses.

<sup>b</sup> Shoulder.

<sup>c</sup> Supporting electrolyte, TEAP; scan rate, 50 mV s<sup>-1</sup>;  $E_{1/2} = 0.5(E_{\text{pa}} + E_{\text{pc}})$ , where  $E_{\text{pa}}$  and  $E_{\text{pc}}$  are anodic and cathodic peak potentials respectively;  $\Delta E_p = E_{\text{pa}} - E_{\text{pc}}$ .

<sup>d</sup> Solvent, dichloromethane.

<sup>e</sup> Solvent, acetonitrile.

structure is shown in Fig. 1 and selected bond parameters are listed in Table 3. The pap ligand is coordinated to osmium in the usual manner with a bite angle of  $76.6(2)^\circ$ . The two  $\text{PPh}_3$  ligands are mutually *trans*, while the two bromides occupy mutually *cis* positions. The structure determination thus shows that  $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$  has stereochemistry 2. The  $\text{N}_2\text{P}_2\text{Br}_2$  coordination sphere around osmium is distorted from ideal octahedral geometry, as reflected in the bond parameters centering osmium. The Os–P and Os–Br bond distances are quite normal, as observed in other complexes containing these bonds [23,24]. While the Os–N1 length is also normal [24], the Os–N3 bond is noticeably short and the azo N2–N3 distance is longer than the uncoordinated azo distance [34,35]. The short Os–N3 distance and increase in N2–N3 bond order reflect the considerable  $\pi$ -interaction between osmium(II) and the azo function.

The  $^1\text{H}$  NMR spectrum of  $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$  was recorded in  $\text{CDCl}_3$  solution. The spectrum is rather complex in nature owing to overlapping of signals and hence assignment of all the signals in this region to specific protons has not been possible. However, two doublets (1H each) observed at 8.22 and 7.87 ppm are assigned to the two pyridine-protons of pap at positions 6 and 3, respectively (see 1). The other resonances appear within 6.7 to 7.5 ppm and intensity measurement of these signals corresponds to the remaining number (37) of protons present in the complex. The IR spectrum of  $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$  shows many vibrations in the  $1600\text{--}400\text{ cm}^{-1}$  region. Strong vibrations observed at 740, 690, and  $522\text{ cm}^{-1}$  indicate the presence of the  $\text{Os}(\text{PPh}_3)_2$  moiety [36]. A sharp and strong vibration at  $1310\text{ cm}^{-1}$  is assigned to the  $\nu_{\text{N}=\text{N}}$  stretch [37]. The  $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$  complex is poorly soluble in solvents such as acetonitrile, acetone, ethanol, etc. and moderately soluble in solvents such as dichloromethane, chloroform, *N,N*-dimethylformamide, etc., producing intense red solution. The electronic spectrum of the complex has been recorded in dichloromethane solution. The complex shows intense absorptions in the visible and UV region (Table 2).

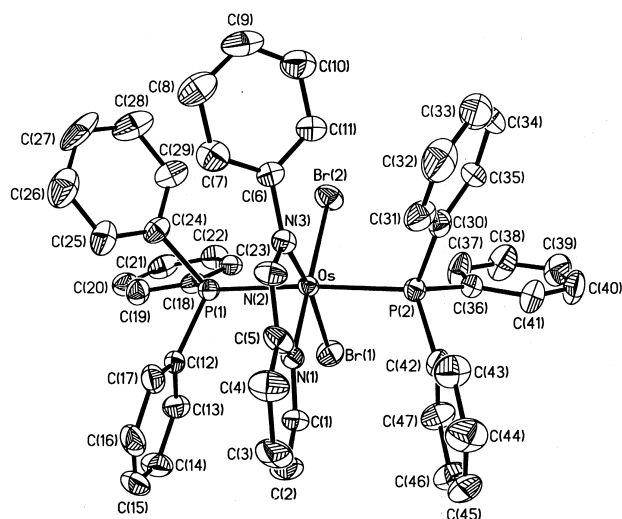


Fig. 1. Structure of  $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$ .

Table 3

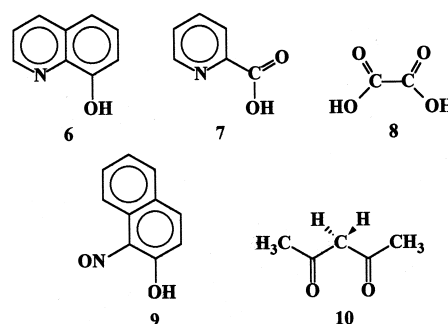
Selected bond distances and bond angles for  $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$  and  $[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{acac})]\text{ClO}_4$

$[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$		$[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{acac})]\text{ClO}_4$	
Os–P1	2.417(2)	Os–P1	2.4485(10)
Os–P2	2.430(2)	Os–P2	2.4740(9)
Os–N1	2.031(5)	Os–O1	2.082(2)
Os–N3	1.978(5)	Os–O2	2.096(2)
Os–Br1	2.5872(7)	Os–N1	2.033(3)
Os–Br2	2.5602(7)	Os–N3	1.977(3)
N2–N3	1.314(7)	O1–C13	1.297(5)
		O2–C15	1.280(4)
		N2–N3	1.329(4)
N1–Os–N3	76.6(2)	N3–Os–N1	76.29(12)
N1–Os–Br1	170.5(2)	N3–Os–O1	171.77(11)
N3–Os–Br2	175.05(14)	N1–Os–O2	175.89(10)
P1–Os–P2	175.10(6)	P1–Os–P2	172.77(3)
		O1–Os–O2	87.89(10)

The absorptions in the UV region are attributable to transitions within the ligand orbitals, whereas the absorptions in the visible region are probably due to allowed metal-to-ligand charge-transfer transitions.

### 3.1.2. $[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{L})]\text{ClO}_4$

One major objective of undertaking this present work has been to scrutinize the reactivity of the  $\text{OsBr}_2$  fragment of  $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$  towards displacement by ligands of different types. This was carried out by reacting  $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$  with five selected acidic ligands, i.e. quinoline-8-ol (**6**), picolinic acid (**7**), oxalic acid ( $\text{H}_2\text{ox}$ , **8**), 1-nitroso-2-naphthol (**9**) and acetylacetonate (**10**). The reactions proceed smoothly in



ethanol/2-methoxyethanol medium (a little dichloromethane was necessary initially to take  $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$  into alcoholic medium) in the presence of a base to afford the expected complexes of the type  $[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{L})]^+$  ( $\text{L} = \text{q, pic, Hox, nn}$  and  $\text{acac}$ ). It is interesting to note here that during the reaction with oxalic acid, only one proton is lost and the monoanionic oxalate ion ( $\text{Hox}$ ) coordinates to osmium. The complex cations were isolated as perchlorate salts in the solid state. Microanalytical data of these five complexes agree well with their compositions (Table 2). These complexes are diamagnetic which shows that the +2 state of osmium is retained in them. Several geometric iso-

mers are possible for these complexes. The structure of  $[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{acac})]\text{ClO}_4$  was determined by X-ray crystallography. The structure is shown in Fig. 2 and selected bond distances and angles are presented in Table 3. The coordination sphere around osmium is  $\text{N}_2\text{O}_2\text{P}_2$  which is slightly distorted octahedral in nature, as reflected in all the bond angles with osmium as the central atom. The acetylacetonate anion is coordinated to osmium as a O,O-donor with a bite angle of  $87.89^\circ$ . The two  $\text{PPh}_3$  ligands are mutually *trans* as observed in the parent  $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$  complex. Distances within the  $\text{Os}(\text{PPh}_3)_2(\text{pap})$  fragment are comparable to those observed in the  $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$  complex [23]. The bond lengths in the  $\text{Os}(\text{acac})$  fragment are also normal [21,38]. The other four  $[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{L})]^+$  complexes have the same  $\text{Os}(\text{PPh}_3)_2(\text{pap})$  fragment and hence they are assumed to have similar structures with the  $\text{PPh}_3$  ligands in mutually *trans* positions. Synthesis of the  $[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{L})]^+$  complexes from  $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$  is therefore stereoretentive.

$^1\text{H}$  NMR spectra of the  $[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{L})]\text{ClO}_4$  complexes, recorded in  $\text{CDCl}_3$  solution, show many signals in the aromatic region and the spectra are complex in nature. In the  $[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{acac})]\text{ClO}_4$  complex, two sharp methyl resonances are observed at 1.67 and 1.58 ppm due to the coordinated acac, and the central C–H proton signal of the same ligand appears at 5.09 ppm. Infrared spectra of the  $[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{L})]\text{ClO}_4$  complexes are mostly similar to the spectrum of the parent  $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$  complex. Some additional vibrations are observed in all the  $[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{L})]\text{ClO}_4$  complexes, of which the two intense ones observed near  $1100$  and  $625\text{ cm}^{-1}$  indicate the presence of perchlorate ion. The  $\nu_{\text{CO}(\text{carboxylate})}$  vibration is observed at  $1700\text{ cm}^{-1}$  in the  $\text{L} = \text{pic}$  complex and at  $1650\text{ cm}^{-1}$  in the  $\text{L} = \text{Hox}$  complex. In the  $\text{L} = \text{nn}$  complex the  $\nu_{\text{NO}}$  vibration is observed at  $1256\text{ cm}^{-1}$ . The  $[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{L})]\text{ClO}_4$  complexes are soluble in acetonitrile solution, producing brown solutions. Conductivity measurements in acetonitrile solution show that all these complexes behave as 1:1 electrolytes ( $\Lambda_{\text{M}} = 145\text{--}160\ \Omega^{-1}\text{ cm}^2\ \text{M}^{-1}$ ), as expected. Electronic spectra of the  $[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{L})]\text{ClO}_4$  complexes, recorded in acetonitrile solution (Table 2), show several intense absorptions in the visible and UV region as before.

### 3.2. Cyclic voltammetric properties

Electrochemical properties of all the complexes were studied by cyclic voltammetry. Voltammetric data are given in Table 2 and selected voltammograms are shown in Fig. 3. Cyclic voltammetry on  $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$  in dichloromethane solution shows a reversible oxidative response at  $0.49\text{ V}$  (all potentials are referenced to SCE) and two quasi-reversible reductive responses at  $-1.03$  and  $-1.40\text{ V}$ . The oxidation is assigned to osmium(II)–osmium(III) oxidation. The one-electron nature of this oxidation was established by comparing its current heights with those of standard ferro-

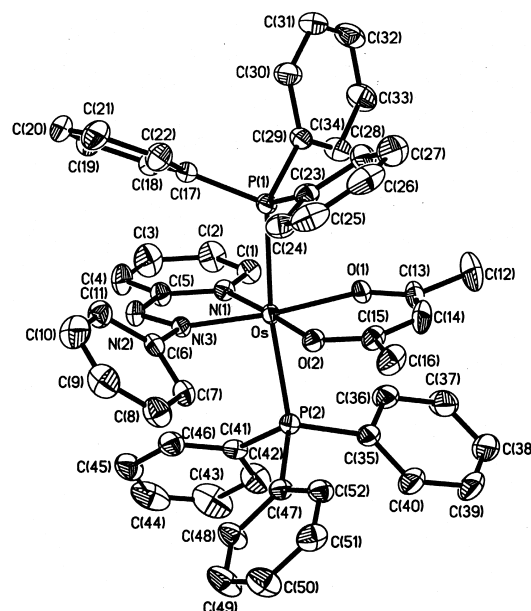


Fig. 2. Structure of  $[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{acac})]\text{ClO}_4$ .

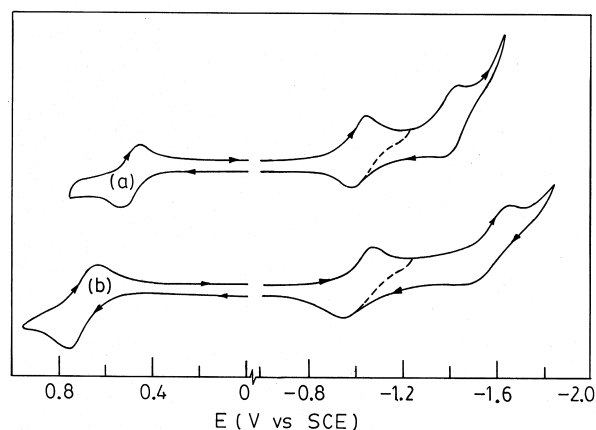


Fig. 3. Cyclic voltammograms of (a)  $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$  in dichloromethane solution (0.1 M TBAP) and (b)  $[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{Hox})]\text{ClO}_4$  in acetonitrile solution (0.1 M TBAP) at a scan rate of  $50\text{ mV s}^{-1}$ .

cene–ferrocenium couple under identical experiment. The reductions are assigned to reductions of the coordinated 2-(phenylazo)pyridine ligand. The 2-(phenylazo)pyridine ligand is known to accept successively two electrons in its lowest unoccupied molecular orbital which is largely azo in nature [39]. Both of these reductions are indeed observed in  $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$ . Cyclic voltammetry on the  $[\text{Os}(\text{PPh}_3)_2(\text{pap})(\text{L})]^+$  complexes in acetonitrile solution also shows a reversible osmium(II)–osmium(III) oxidation and two reductions of the coordinated pap (Table 2, Fig. 3). The potential of the osmium(II)–osmium(III) oxidation varies significantly ( $0.69\text{--}1.01\text{ V}$ ) as L is varied. Reductions of the coordinated pap are observed below  $-0.9\text{ V}$ .

## 4. Conclusion

The Os–Br bonds in the  $[\text{Os}(\text{PPh}_3)_2(\text{pap})\text{Br}_2]$  complex are found to be displaceable by bidentate chelating ligands

under relatively mild conditions. Hence this complex appears to be suitable as a building unit for the preparation of complexes of higher nuclearity and such possibilities are currently being explored.

### Supplementary data

Supplementary data are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@cdc.cam.ac.uk), on request quoting the deposition numbers CCDC 137568 and CCDC 137569.

### Acknowledgements

Financial assistance received from the Department of Science and Technology, New Delhi (Grant No. SP/S1/F33/98) is gratefully acknowledged. Thanks are also due to the Third World Academy of Sciences for financial support enabling the purchase of an electrochemical cell system.

### References

- [1] K.R. Seddon, *Coord. Chem. Rev.* 41 (1982) 159.
- [2] D.S. Moore, *Coord. Chem. Rev.* 44 (1982) 127.
- [3] D.J. Gulliver, W. Levason, *Coord. Chem. Rev.* 46 (1982) 1.
- [4] E.A. Seddon, *Coord. Chem. Rev.* 67 (1985) 243.
- [5] M.O. Albers, D.J. Robinson, E. Singleton, *Coord. Chem. Rev.* 79 (1987) 1.
- [6] N.C. Thomas, *Coord. Chem. Rev.* 93 (1989) 225.
- [7] D. Rong, H.G. Hong, Y.I. Kim, J.S. Krueger, J.E. Mayer, T.E. Mallouk, *Coord. Chem. Rev.* 97 (1990) 237.
- [8] V.W.W. Yam, C.M. Che, *Coord. Chem. Rev.* 97 (1990) 93.
- [9] R. Hage, *Coord. Chem. Rev.* 111 (1991) 161.
- [10] J.P. Collin, S. Guillerez, J.P. Sauvage, F. Barigelletti, L. Flamigni, L.D. Cola, V. Balzani, *Coord. Chem. Rev.* 111 (1991) 291.
- [11] L.D. Cola, F. Barigelletti, V. Balzani, P. Belser, A.V. Zelewsky, C. Seel, M. Frank, F. Vogtle, *Coord. Chem. Rev.* 111 (1991) 255.
- [12] E.C. Constable, C.E. Housecroft, *Coord. Chem. Rev.* 124 (1993) 183.
- [13] M.D. Ward, *Coord. Chem. Rev.* 127 (1993) 1.
- [14] M. Furue, K. Maruyama, Y. Kanematsu, T. Kushida, M. Kamachi, *Coord. Chem. Rev.* 132 (1994) 201.
- [15] F. Barigelletti, L. Flamigni, V. Balzani, J.P. Collin, J.P. Sauvage, A. Sour, E.C. Constable, A.M.W.C. Thompson, *Coord. Chem. Rev.* 132 (1994) 209.
- [16] K. Kalyansundaram, S.M. Zakeeruddin, M.K. Nazeeruddin, *Coord. Chem. Rev.* 132 (1994) 259.
- [17] M.G. Richmond, *Coord. Chem. Rev.* 141 (1995) 63.
- [18] M.D. Ward, *Coord. Chem. Rev.* 146 (1995) 99.
- [19] F. Basuli, S.M. Peng, S. Bhattacharya, *Inorg. Chem.* 36 (1997) 5645.
- [20] F. Basuli, S.M. Peng, S. Bhattacharya, *Polyhedron* 17 (1998) 2191.
- [21] F. Basuli, S.M. Peng, S. Bhattacharya, *Polyhedron* 18 (1998) 391.
- [22] F. Basuli, M. Ruf, C.G. Pierpont, S. Bhattacharya, *Inorg. Chem.* 37 (1998) 6113.
- [23] A. Das, F. Basuli, S.M. Peng, S. Bhattacharya, *Polyhedron* 18 (1999) 2729.
- [24] B.K. Ghosh, A. Mukhopadhyay, S. Goswami, S. Ray, A. Chakravorty, *Inorg. Chem.* 23 (1984) 4633.
- [25] E.M. Kober, J.V. Casper, B.P. Sullivan, T.J. Meyer, *Inorg. Chem.* 27 (1988) 4587.
- [26] R.A. Krause, K. Krause, *Inorg. Chem.* 19 (1980) 2600.
- [27] S. Goswami, A.R. Chakravarty, A. Chakravorty, *Inorg. Chem.* 20 (1981) 2246.
- [28] R.A. Krause, K. Krause, *Inorg. Chem.* 21 (1982) 1714.
- [29] F.P. Dwyer, J.W. Hogarth, *Inorg. Synth.* 5 (1957) 204.
- [30] P.R. Hoffman, K.G. Caulton, *J. Am. Chem. Soc.* 97 (1975) 4221.
- [31] N. Campbell, A.W. Henderson, D. Taylor, *J. Chem. Soc.* (1953) 1281.
- [32] D.T. Sawyer, J.L. Roberts Jr., *Experimental Electrochemistry for Chemists*, Wiley, New York, 1974, pp. 167–215.
- [33] M. Walter, L. Ramaley, *Anal. Chem.* 45 (1973) 165.
- [34] A. Seal, S. Ray, *Acta Crystallogr., Sect. C* 40 (1984) 929.
- [35] P. Majumdar, S.M. Peng, S. Goswami, *J. Chem. Soc., Dalton Trans.* (1998) 1569.
- [36] S. Bhattacharya, C.G. Pierpont, *Inorg. Chem.* 30 (1991) 2906.
- [37] B.K. Ghosh, S. Goswami, A. Chakravorty, *Inorg. Chem.* 22 (1983) 3358.
- [38] K. Sui, S.M. Peng, S. Bhattacharya, *Polyhedron* 18 (1999) 631.
- [39] S. Goswami, R.N. Mukherjee, A. Chakravorty, *Inorg. Chem.* 22 (1983) 2825.