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Chemistry of osmium in $N_2P_2Br_2$ coordination sphere Synthesis, structure and reactivities

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Abstract

A family of three mixed-ligand osmium complexes of type $[Os(PPh_3)_2(N\text{-}N)Br_2]$, where N-N=2,2′-bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy) and 1,10-phenanthroline (phen), have been synthesized and characterized. The complexes are diamagnetic (low-spin d^6, S=0) and in dichloromethane solution they show intense MLCT transitions in the visible region. The two bromide ligands have been replaced from the coordination sphere of $[Os(PPh_3)_2(phen)Br_2]$ under mild conditions by a series of anionic ligands L (where L=quinolin-8-olate (q), picolinate (pic), oxalate (Hox) and 1-nitroso-2-naphtholate (nn)) to afford complexes of type $[Os(PPh_3)_2(phen)(L)]^+$, which have been isolated and characterized as the perchlorate salt. The structure of the $[Os(PPh_3)_2(phen)(pic)]ClO_4$ complex has been determined by X-ray crystallography. The PPh_3 ligands occupy *trans* positions and the picolinate anion is coordinated to osmium as a bidentate N,O-donor forming a five-membered chelate ring. The $[Os(PPh_3)_2(phen)(L)]^+$ complexes are diamagnetic and show multiple MLCT transitions in the visible region. The $[Os(PPh_3)_2(N\text{-}N)Br_2]$ complexes show an osmium(II)–osmium(III) oxidation (−0.02 to 0.12 V vs. SCE) followed by an osmium(III)–osmium(IV) oxidation (1.31 to 1.43 V vs. SCE). The $[Os(PPh_3)_2(phen)(L)]^+$ complexes display the osmium (II)–osmium (III) oxidation (0.26 to 0.84 V vs. SCE) and one reduction of phen (−1.50 to −1.79 V vs. SCE). The osmium (III)–osmium (IV) oxidation has been observed only for the L=q and L=Hox complexes at 1.38 V vs. SCE and 1.42 V vs. SCE respectively. The osmium(III) species, viz. $[Os^{III}(PPh_3)_2(N\text{-}N)Br_2]^+$ and $[Os^{III}(PPh_3)_2(phen)(L)]^{2+}$, have been generated both chemically and electrochemically and characterized in solution by electronic spectroscopy and cyclic voltammetry.

Keywords: Osmium; Triphenylphosphine; Diimine; Synthesis; Structure; Reactivities

1. Introduction

The chemistry of osmium has been of much current interest [1–18] largely because of the variety of reactions exhibited by its complexes. Reactivity of osmium complexes is directed by the coordination environment around osmium. Hence variation of the coordination sphere brings about corresponding variation in the reactivities of the complexes. The reactions displayed by transition metal complexes can be broadly classified into two categories: (i) reactions where no metal–ligand bond breaking is involved [e.g. stereoisomerization, outer-sphere electron-transfer reaction, etc.] and (ii) reactions occurring via metal–ligand bond dissociation [e.g. displacement reactions, insertion (into the metal–ligand bond) reactions]. For the reactions of type (ii) to occur, the complexes must contain one or more labile metal–ligand bond(s). Osmium complexes with Os–X (X=Cl, Br) bonds are of particular attraction in this context because the Os–X bonds are known to be potentially labile. However, the degree of lability and hence reactivities arising therefrom, is a function of the oxidation state of osmium and nature of ligands occupying the other coordination positions. In the present study, which is part of our recent activities in osmium chemistry [19–23], we have chosen a *cis*-$OsBr_2$ moiety as the reactive fragment. To satisfy the remaining four coordination sites of osmium, triphenylphosphine (PPh_3) and some N–N donor ligands (viz. 2,2′-bipyridine (bpy,1); 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy, **2**) and 1,10-phenanthroline (phen, **3**)) have been used.

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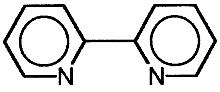

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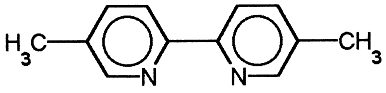

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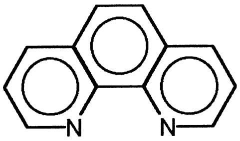

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All these ligands belong to the diimine family and they have recognized π-acid character. Hence their coordination is expected to stabilize the bivalent state of osmium, which is a lower oxidation state of this metal and thus it is expected to favour dissociation of the Os–Br bonds. Herein we wish to report the synthesis and characterization of a family of osmium complexes of type $[Os(PPh_3)_2(N\text{-}N)Br_2]$ and their spectroscopic and electron-transfer properties with special reference to their reactions involving the Os–Br bond cleavage.

2. Experimental

2.1. Materials

Osmium tetroxide was purchased from Arora Matthey, Calcutta, India and was converted into $[NH_4]_2[OsBr_6]$ by reduction with HBr [24]. $[Os(PPh_3)_3Br_2]$ was synthesized from $[NH_4]_2[OsBr_6]$ using a previously published literature method [25]. Triphenylphosphine, 2,2′-bipyridine, oxalic acid (H_2ox) and 1-nitroso-2-naphthol (Hnn) were purchased from Loba Chemie, Mumbai, India. 1,10-Phenanthroline, picolinic acid (Hpic) and quinoline-8-ol (Hq) were purchased from E. Merck (India) Pvt. Ltd., Mumbai. 4,4′-Dimethyl-2,2′-bipyridine was purchased from Aldrich. All other chemicals and solvents were reagent grade commercial materials and were used as received. Purification of acetonitrile and dichloromethane, and preparation of tetraethylammonium perchlorate (TEAP) for electrochemical work were performed as reported in the literature [26,27].

2.2. Preparation of complexes

The $[Os^{II}(PPh_3)_2(N\text{-}N)Br_2]$ (N-N = bpy, Me_2bpy, phen) complexes were synthesized by using a general procedure. Yields varied in the range of 70–75%. Specific details are given below for one complex.

2.2.1. $[Os(PPh_3)_2(phen)Br_2]$

To a mixture of $[Os(PPh_3)_3Br_2]$ (100 mg, 0.09 mmol) and 1,10-phenanthroline (18 mg, 0.09 mmol) was added 2-methoxyethanol (40 cm^3). The resulting mixture was refluxed for 2 h. Upon cooling $[Os(PPh_3)_2(phen)Br_2]$ started to separate out as a greenish-brown solid. The deposited solid was collected by filtration, washed thoroughly with 2-methoxyethanol and dried in vacuo over P_4O_{10}. Recrystallization from dichloromethane–hexane solution gave the pure product as a microcrystalline solid. The yield was 68 mg (73%).

The $[Os^{II}(PPh_3)_2(phen)(L)]ClO_4$ (L = pic, q, Hox, nn) complexes were synthesized by using a general procedure. Yields varied in the range of 60–70%. Specific details are given below for one complex.

2.2.2. $[Os^{II}(PPh_3)_2(phen)(pic)](ClO_4)$

$[Os(PPh_3)_2(phen)Br_2]$ (100 mg, 0.10 mmol) and picolinic acid (12 mg, 0.10 mmol) were dissolved together in dichloromethane (30 cm^3) and triethylamine (10 mg, 0.10 mmol) was added to it followed by ethanol (40 cm^3). The solution was boiled for few minutes in air to remove dichloromethane as much as possible and it was heated at reflux for 6 h. After being cooled to room temperature, a saturated aqueous solution of $NaClO_4$ (0.5 cm^3) was added to it. $[Os(PPh_3)_2(phen)(pic)]ClO_4$ precipitated as a brown solid which was collected by filtration, washed with ice-cold water and dried in vacuo over P_4O_{10}. Purification of the product was done by recrystallization from dichloromethane–hexane solution. The yield was 70 mg (66%).

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 Shimadzu UV 1601 and Hitachi U 3501 spectrophotometers. Magnetic susceptibilities were measured using a PAR 155 vibrating sample magnetometer fitted with a Walker Scientific L75FBAL magnet. ^1H NMR spectra were obtained on a Brucker 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 disc 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 platinum wire gauze working electrode was used in the coulometric experiments. A RE 0074 X–Y recorder was used to trace the voltammograms. Dinitrogen gas was purified by successively bubbling it through alkaline dithionite and concentrated sulphuric acid. Electrochemical measurements were performed under a dinitrogen atmosphere. All electrochemical data were collected at 298 K and are uncorrected for junction potentials.

Table 1
Crystallographic data for $[Os(PPh_3)_2(phen)(pic)]ClO_4 \cdot 3C_6H_6$

Formula	$C_{72}H_{6}0N_{3}O_{6}ClP_{2}Os$
f_w	1350.87
Space group	Monoclinic, $P2_1/n$
a (Å)	14.815(6)
b (Å)	19.575(3)
c (Å)	20.939(4)
β (°)	91.58(3)
V (Å^3)	6070(3)
Z	4
Crystal size (mm)	0.25×0.25×0.20
T (K)	298
μ (cm^{-1})	22.527
R_f [a]	0.043
R_w [b]	0.040
GOF	1.34

[a] $R_f = \Sigma \, \lVert F_o| - |F_c \rVert / \Sigma \, |F_o|$.
[b] $R_w = [\Sigma \, w(|F_o| - |F_c|)^2 / \Sigma \, w(F_o)^2]^{1/2}$.

2.4. Crystallography

Single crystals of $[Os(PPh_3)_2(phen)(pic)]ClO_4.3C_6H_6$ were grown by slow diffusion of benzene into a dichloromethane solution of the complex. Selected crystal data and data collection parameters are given in Table 1. The unit cell dimensions were determined by a least-squares fit of 25 machine-centred reflections ($14.90 < 2\theta < 22.10°$). Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated MoKα radiation ($\lambda = 0.7107$ Å) by $\theta - 2\theta$ scans with a maximum 2θ angle of 45°. Three standard reflections, measured every 3600 s of X-ray exposure, showed no significant intensity variation over the course of data collection. X-ray data reduction and structure solution and refinement were carried out using the NRCVAX package. The structure was solved by the Patterson method.

3. Results and discussion

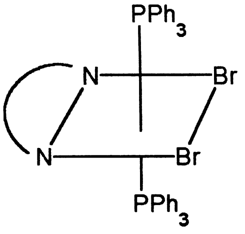
The $[Os(PPh_3)_2(N\text{-}N)Br_2]$ (N-N = bpy, Me_2bpy, phen) complexes were synthesized in decent yields by the smooth displacement of one PPh_3 from $[Os(PPh_3)_3Br_2]$ with the nitrogen donor ligands in refluxing 2-methoxyethanol. Composition of the complexes were confirmed by their elemental (C, H, N) analytical data (Table 2). All three complexes are diamagnetic, which is in accordance with the +2 state of osmium (low-spin d^6, S = 0) in these

Table 2
Characterization data of the $[Os(PPh_3)_2(N\text{-}N)Br_2]$ and $[Os(PPh_3)_2(phen)(L)]ClO_4$ complexes

Compound	Yield	Analytical data[a]			Electronic spectral data	Cyclic voltammetric data[c]
	%	%C	%H	%N	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	$E_{1/2}$, V vs. SCE (ΔE_p, mV)
$[Os(PPh_3)_2(bpy)Br_2]$[d]	70	53.39 (53.59)	3.65 (3.69)	2.66 (2.72)	492[b](2100), 452[b](2200), 348(4300), 296(12900), 248[b](18800), 224(22700)	0.11(60), 1.43(70)
$[Os(PPh_3)_2(Me_2bpy)Br_2]$[d]	68	54.22 (54.43)	3.90 (3.97)	2.61 (2.65)	492(3800), 464[b](3800), 344(7600), 292(26600), 248[b](35900), 224(53100)	−0.02(70), 1.31(80)
$[Os(PPh_3)_2(phen)Br_2]$[d]	73	54.58 (54.65)	3.60 (3.61)	2.67 (2.66)	684[b](800), 480[b](5100), 448(5900), 288[b](13200), 252(33600), 224(45400)	0.12(70), 1.42(70)
$[Os(PPh_3)_2(phen)(q)]ClO_4$[e]	62	60.19 (60.12)	3.79 (3.87)	3.66 (3.69)	660[b](1100), 520[b](2600), 456(4200), 356(3700), 260[b](21400), 240[b](27900), 212(44200)	0.39(70),1.38(160), −1.66(120)
$[Os(PPh_3)_2(phen)(pic)]ClO_4$[e]	66	58.07 (58.08)	3.74 (3.76)	3.71 (3.76)	596[b](1000), 416(6500), 260[b](30900), 244[b](39600), 208(66900)	0.71(80), −1.55(60)
$[Os(PPh_3)_2(phen)(Hox)]ClO_4$[e]	67	55.52 (55.47)	3.46 (3.51)	2.57 (2.59)	676[b](800), 456[b](5900), 436(6400), 312[b](8300), 276[b](19400), 260[b](28500), 244[b](34700), 208(71500)	0.26(70), 1.42(150), −1.79(90)
$[Os(PPh_3)_2(phen)(nn)]ClO_4$[e]	63	59.76 (59.70)	3.81 (3.77)	3.58 (3.60)	516[b](11700), 484(16200), 392[b](6300), 360(8100), 260[b](35200), 244[b](44200), 212(78500)	0.84(70), −1.50(150)

[a] Calculated values are in parentheses.
[b] Shoulder.
[c] Supporting electrolyte, TEAP; scan rate, 50 mVs^{-1}; $E_{1/2} = 0.5(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are anodic and cathodic peak potentials respectively; $\Delta E_p = E_{pa} - E_{pc}$.
[d] Solvent, dichloromethane.
[e] Solvent, acetonitrile.

complexes. As all the N–N ligands are symmetrical bidentate ligands, these [Os$(PPh_3)_2$(N-N)Br_2] complexes may, in principle, exist in three geometrical isomeric forms (**4**–**6**). Structures **4** and **5** have a C_2 axis, and hence only seven ^{1}H NMR signals (three signals from PPh_3 and four from N–N ligands) may be expected for these isomers, provided no overlap of signals occurs. As structure **6** does not have any C_2 symmetry, it is expected to show 14 resonances. ^{1}H NMR spectrum recorded on the [Os$(PPh_3)_2$(Me_2bpy)Br_2] complex showed only one sharp methyl resonance at 1.24 ppm.



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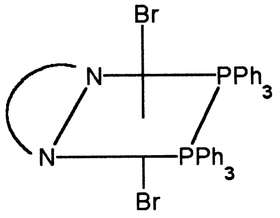

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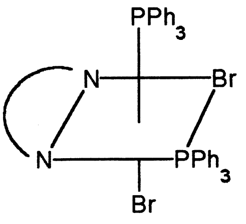

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In the aromatic region four intense and broad signals have been observed at 5.52, 6.10, 6.41 and 6.67 ppm, which indicate fluxional character of these complexes. However, intensity measurements agree with the number of aromatic protons present in the complex molecule. ^{1}H NMR spectral data clearly indicate that the complex molecule has a C_2 symmetry and thus exclude structure **6**. It has not been possible to further distinguish between structures **4** and **5** on the basis of ^{1}H NMR spectra. However, we assume structure **4** for all the three complexes where the bulky PPh_3 ligands are *trans* to each other and hence sterically would be more stable. This structure seems likely also from the π-bonding view point. The N–N ligands are well known for their strong π-acidity and PPh_3 is also an efficient π-acceptor by virtue of the dπ–dπ interaction. In structure **5**, the PPh_3 ligands are mutually *cis* but *trans* to the pyridine nitrogens. Hence each P and N *trans* to it would be competing for the same t_{2g} orbital for π-interaction, hence structure **5** is unfavourable. Structure **4** also seems probable for these [Os$(PPh_3)_2$(N-N)Br_2] complexes in view of the crystal structure of [Os$(PPh_3)_2$(phen)(pic)$]^+$ (vide infra), which has been prepared by replacing the two bromides of [Os$(PPh_3)_2$(phen)Br_2] with a picolinate ligand.

Infrared spectra of the [Os$(PPh_3)_2$(N-N)Br_2] complexes are very similar. Each complex shows many vibrations below 1600 cm^{-1}, some of which (e.g. strong vibrations near 1470, 1420, 1085, 835, 740, 690, 495 and 400 cm^{-1}) are also observed in the spectrum of [Os$(PPh_3)_3Br_2$] while some others (e.g. sharp vibrations near 1400, 1280 and 1240 cm^{-1}) are new and may be attributed to the coordinated N–N ligands. The [Os$(PPh_3)_2$(N-N)Br_2] complexes are moderately soluble in dichloromethane, chloroform and much less soluble in acetonitrile, acetone and ethanol. The solutions are brown in colour. Electronic spectra of the complexes have been recorded in dichloromethane solution. Spectral data are presented in Table 2. All three complexes show several intense absorptions in the visible region and some very intense absorptions in the UV region. 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. Multiple charge-transfer transitions in such mixed-ligand complexes may result from lower symmetry splitting of the metal level, the presence of different acceptor orbitals and from the mixing of singlet and triplet configurations in the excited state through spin-orbit coupling [28–31]. To have a better insight into the nature of these observed electronic transitions, qualitative EHMO calculations have been performed [32,33] on a model of the [Os$(PPh_3)_2$(N-N)Br_2] complexes which was computer generated from [Os$(PPh_3)_2$(bpy)Br_2] by replacing the phenyl groups of the two *trans* PPh_3 by H and imposing a C_2 symmetry. Partial MO diagram is shown in Fig. 1. The highest occupied molecular orbital (HOMO) and the next two occupied orbitals (HOMO-1 and HOMO-2) are predominantly osmium in character (with minor contribution from the bromides) and attributable to the components of osmium t_2 level. The lowest unoccupied molecular orbital (LUMO) and the next two unoccupied orbitals (LUMO+1 and LUMO+2) are basically π* orbitals of bpy. According to this model, several electronic transitions are therefore possible within these orbitals which are indeed experimentally observed. Hence the observed absorptions in the visible region may be assigned to charge-transfer transitions occurring from the filled metal t_2 orbitals to empty π* orbitals of the diimine ligands.

Reactivity studies on the [Os$(PPh_3)_2$(N-N)Br_2] complexes involving dissociation of the Os–Br bonds was restricted only to the N-N = phen complex because of its better solubility. Reactions of [Os$(PPh_3)_2$(phen)Br_2] were studied with four selected acidic ligands, viz. quinolin-8-ol (Hq, **7**), picolinic acid (Hpic, **8**), oxalic acid (H_2ox, **9**) and 1-nitroso-2-naphthol (Hnn, **10**). The reactions proceeded smoothly in ethanol medium (a little dichloromethane was necessary initially to take [Os$(PPh_3)_2$(phen)Br_2] into ethanolic medium) in the presence of a base to afford the expected complexes of type [Os$(PPh_3)_2$(phen)(L)$]^+$ (L = q, pic, Hox and nn). It is interesting to note here that during the reaction with oxalic acid, only one proton is lost from H_2ox and the monoanionic oxalate ion (Hox) coordinates

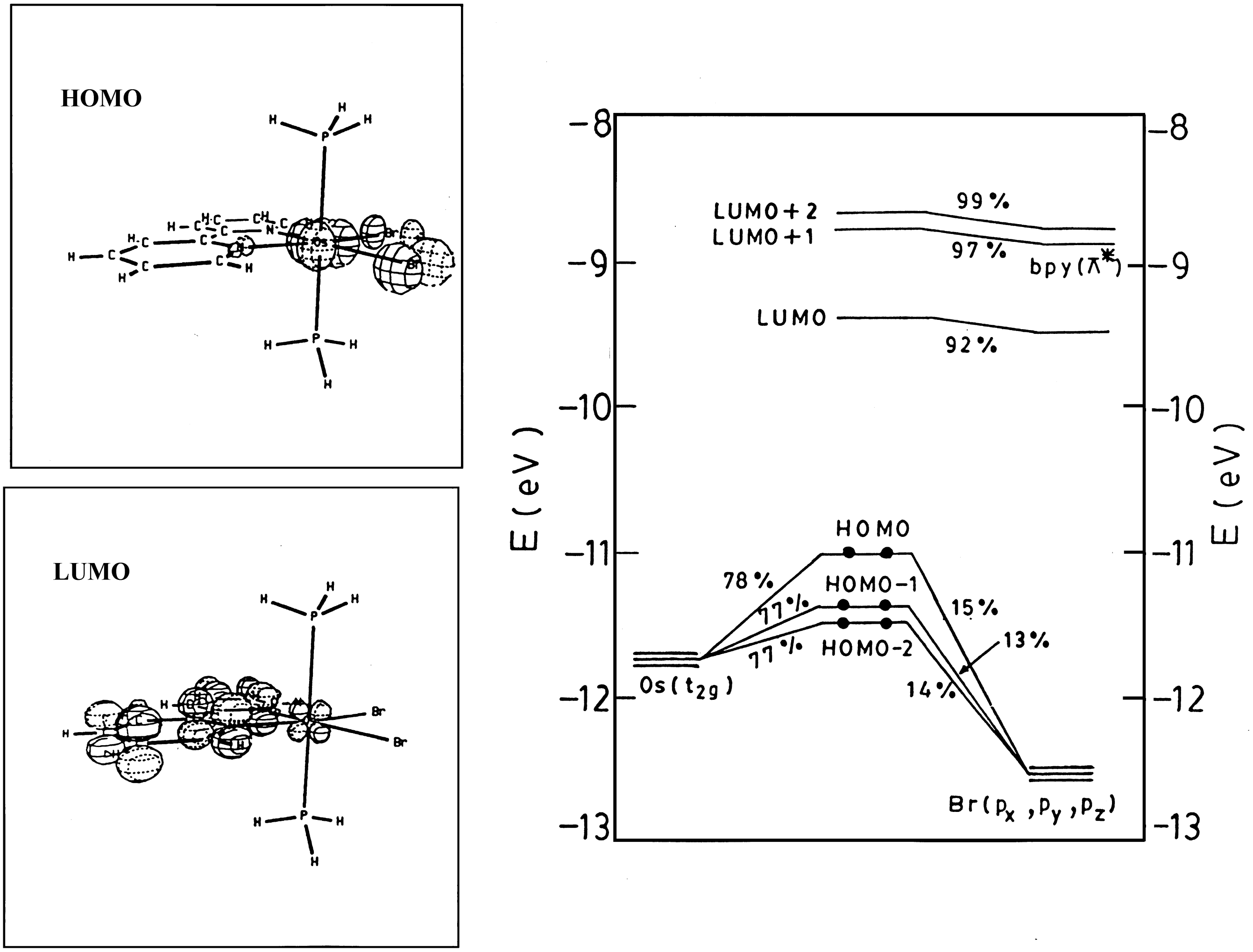
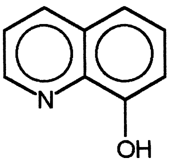


Fig. 1. Qualitative molecular orbital diagram of $[Os(PPh_3)_2(bpy)Br_2]$.

to osmium. The complex cations were isolated as perchlorate salts in the solid state. Microanalytical data of these four complexes agreed well with their compositions (Table 2). These complexes are diamagnetic which shows that the +2 state of osmium is retained in them. Molecular structure of $[Os(PPh_3)_2(phen)(pic)]ClO_4 \cdot 3C_6H_6$ 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 $N_3O_1P_2$ which is slightly distorted octahedral in nature as reflected in all the bond angles with osmium as the central atom. Picolinic acid is coordinated as a N,O-donor with a bite angle of 76°. The two PPh_3 ligands are *trans* as assumed in the parent $[Os(PPh_3)_2(phen)Br_2]$ complex (see structure **4**). The Os–N(phen), Os–N(pic), Os–O and Os–P distances are quite normal [19–23]. The synthesis of the $[Os(PPh_3)_2(phen)(L)]^+$ from $[Os(PPh_3)_2(phen)Br_2]$ is therefore stereoretentive. The other three $[Os(PPh_3)_2(phen)(L)]^+$ complexes, presented in this paper, have the same $[Os(PPh_3)_2(phen)]$ fragment and hence they are assumed to have similar structures with the PPh_3 ligands in *trans* positions.



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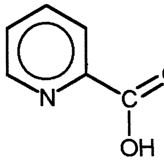

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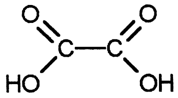

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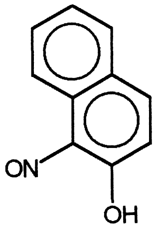

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Infrared spectra of the $[Os(PPh_3)_2(phen)(L)]ClO_4$ complexes are largely similar to the spectrum of the parent $[Os(PPh_3)_2(phen)Br_2]$ complex. Some additional vibra-

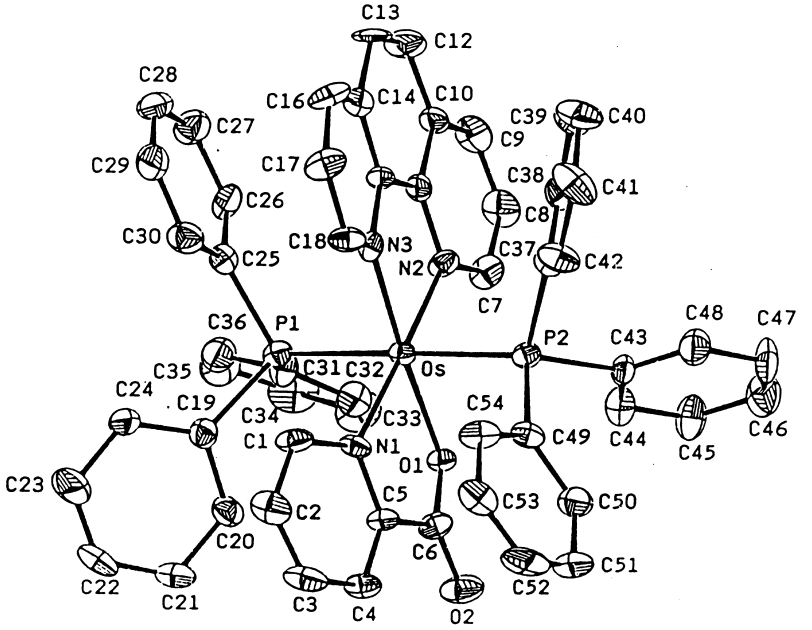

Fig. 2. Structure of the $[Os(PPh_3)_2(phen)(pic)]^+$ complex.

tions are observed in all the $[Os(PPh_3)_2(phen)(L)]ClO_4$ complexes, of which the two intense ones observed near 1100 and 625 cm^{-1} indicate the presence of perchlorate ion. The $\nu_{CO(carboxylate)}$ vibration is observed at 1640 cm^{-1} in the L = pic complex and at 1650 cm^{-1} in the L = Hox complex. In the L = nn complex the ν_{NO} vibration is observed at 1500 cm^{-1}. The $[Os(PPh_3)_2(phen)(L)]ClO_4$ complexes are soluble in acetonitrile solution producing brown solutions. Conductivity measurements in acetonitrile solution shows that these complexes behave as 1:1 eletrolytes ($\Lambda_M = 150–160\ \Omega^{-1}\ cm^2\ M^{-1}$). Electronic spectra of the $[Os(PPh_3)_2(N\text{-}N)(L)]ClO_4$ complexes, recorded in acetonitrile solution (Table 2), show several intense absorptions (due to metal-to-ligand charge-transfer transitions) in the visible region together with very intense absorptions in the UV region (due to transitions within the ligand orbitals).

Cyclic voltammetry on the $[Os(PPh_3)_2(N\text{-}N)Br_2]$ complexes show two reversible oxidations (Table 2, Fig. 3)

Table 3
Selected bond distances and bond angles for $[Os(PPh_3)_2(phen)(pic)]ClO_4 \cdot 3C_6H_6$

Bond distances (Å)			
Os–P1	2.381(3)	Os–N2	2.102(7)
Os–P2	2.387(3)	Os–N3	2.088(8)
Os–O1	2.138(6)	O1–C6	1.273(12)
Os–N1	2.091(7)	O2–C6	1.211(13)
Bond angles (°)			
P1–Os–P2	178.40(12)		
O1–Os–N3	176.5(3)		
N1–Os–N2	174.9(3)		
P1–Os–O1	91.07(19)	P2–Os–N2	93.70(22)
P1–Os–N1	89.19(24)	P2–Os–N3	89.92(23)
P1–Os–N2	86.50(22)	O1–Os–N1	76.0(3)
P1–Os–N3	91.67(23)	O1–Os–N2	101.4(3)
P2–Os–O1	87.34(19)	N1–Os–N3	106.2(3)
P2–Os–N1	90.54(24)	N2–Os–N3	76.6(3)

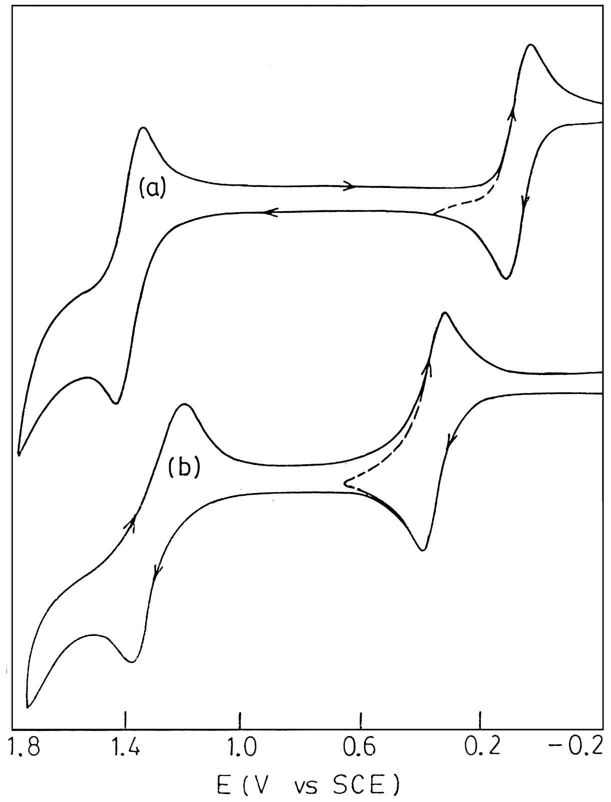

Fig. 3. Cyclic voltammograms of (a) $[Os(PPh_3)_2(phen)Br_2]$ in dichloromethane solution (0.1 M TEAP) and (b) $[Os(PPh_3)_2(phen)(q)]^+$ in acetonitrile solution (0.1 M TEAP) at a scan rate of 50 m Vs^{-1}.

within −0.02 to 0.12 V (all potentials are referenced to SCE) and 1.31 to 1.43 V, respectively. The first oxidation is assigned to the osmium(II)–osmium(III) oxidation and the second one to osmium(III)–osmium(IV) oxidation. The osmium(II)–osmium(III) oxidation potential in the $[Os(PPh_3)_2(Me_2bpy)Br_2]$ complex is 130 mV more negative than that in the $[Os(PPh_3)_2(bpy)Br_2]$ complex, which may be attributed to the electron-donating character of the methyl groups of the Me_2bpy ligand. It is interesting to note that the osmium(II)–osmium(III) oxidation potential in the $[Os(PPh_3)_2(N\text{-}N)Br_2]$ complexes is about 150 mV more positive than that in the corresponding $[Os(N\text{-}N)_2Br_2]$ complexes [34], which indicates that replacement of one N–N ligand by two PPh_3 has stabilized the bivalent state of osmium.

Cyclic voltammetry on the $[Os(PPh_3)_2(phen)(L)]^+$ complexes show a reversible osmium(II)–osmium(III) oxidation, whose potential varies significantly (0.26–0.84 V) as L is varied. A second quasi-reversible oxidation, assumed to be the osmium(III)–osmium(IV) oxidation, has been observed only for the L = q and L = Hox complexes at 1.38 V and 1.42 V, respectively. A reversible/quasi-reversible reduction has been displayed by all four $[Os(PPh_3)_2(phen)(L)]^+$ complexes below −1.5 V which is assigned to reduction of the coordinated phen ligand. These N–N ligands are known to undergo two successive one-electron reductions [35,36], the first of which has been experimentally observed while the second reduction could not be observed due to solvent cut-off. In the $[Os(PPh_3)_2(N\text{-}N)Br_2]$ complexes, even the first reduction of the N–N ligand could not be observed due to the smaller voltage window of dichloromethane.

The reversible nature of the osmium(II)–osmium(III) oxidation in $[Os(PPh_3)_2(N\text{-}N)Br_2]$ complexes indicates that the oxidized species, viz. $[Os^{III}(PPh_3)_2(N\text{-}N)Br_2]^+$, are stable, at least on the cyclic voltammetric time-scale. The low oxidation potentials further indicate that the oxidized complexes could be air-stable for a much longer time. To investigate the stability of these oxidized species, the $[Os(PPh_3)_2(N\text{-}N)Br_2]$ complexes have been coulometrically oxidized in dichloromethane solution at 0.4 V. The oxidations have been smooth and quantitative with $n \sim 1$ [n(number of electron-transfer) $= Q_f/Q_c$, where Q_f = observed coulomb count and Q_c = calculated coulomb count]. Solutions of the oxidized complexes are green in colour and display identical voltammograms as their respective $[Os^{II}(PPh_3)_2(N\text{-}N)Br_2]$ precursors (except that the osmium(II)–osmium(III) couple now appears as a reductive response). This indicates that the osmium(II)–osmium(III) oxidation takes place without any gross change in stereochemistry. Coulometric reduction of the green solution at −0.2 V quantitatively afforded back brown solutions of the respective $[Os^{II}(PPh_3)_2(N\text{-}N)Br_2]$ complexes, which have been identified by their characteristic electronic spectrum. The $[Os^{III}(PPh_3)_2(N\text{-}N)Br_2]^+$ complexes were also generated by chemical oxidation of the $[Os^{II}(PPh_3)_2(N\text{-}N)Br_2]$ complexes by bromine. Electronic spectra of the green $[Os^{III}(PPh_3)_2(N\text{-}N)Br_2]^+$ complexes in acetonitrile solution show several intense absorptions in the visible region (probably ligand-to-metal charge-transfer transitions) together with very intense transitions in the UV region (Table 4). Chemical reduction of the oxidized green solutions gives back brown solutions of the osmium(II) complexes. The $[Os^{II}(PPh_3)_2(phen)(L)]^+$ complexes have also been oxidised in acetonitrile solution by bromine to afford solutions of respective $[Os^{III}(PPh_3)_2(phen)(L)]^{2+}$ complexes. Electronic spectra of these solutions (Table 4) show intense absorptions in the visible and UV region. Addition of hydrazine to these oxidized solutions immediately brings about reduction to the brown osmium(II) complexes. This indicates that the osmium(II)–osmium(III) oxidation is chemically reversible. However, stability of the $[Os^{III}(PPh_3)_2(phen)(L)]^{2+}$ complexes (towards prolonged

Table 4
Electronic spectral data of the $[Os^{III}(PPh_3)_2(N\text{-}N)Br_2]^+$ and $[Os^{III}(PPh_3)_2(phen)(L)]^{2+}$ complexes in dichloromethane solution

Compound	λ_{max}, nm (ϵ, M^{-1} cm^{-1})
$[Os^{III}(PPh_3)_2(bpy)Br_2]^+$	232(29200), 264^{a}(13400), 296^{a}(7700), 409(2400), 475(1800), 608^{a}(770)
$[Os^{III}(PPh_3)_2(Me_2bpy)Br_2]^+$	229(99800), 295(23000), 426(4900), 433^{a}(4000), 588^{a}(2300), 608(4200), 782^{a}(2700), 895^{a}(1800), 1003^{a}(1200)
$[Os^{III}(PPh_3)_2(phen)Br_2]^+$	262(72500), 325(15600), 375(5500), 405^{a}(5000), 476(3400), 609(2800), 852^{a}(2200)
$[Os^{III}(PPh_3)_2(phen)(q)]^{2+}$	267(29200), 386(4600), 488(4400), 549^{a}(2200), 676^{a}(1100)
$[Os^{III}(PPh_3)_2(phen)(pic)]^{2+}$	254(30900), 275^{a}(21200), 300^{a}(9600), 443(5300), 600(800)
$[Os^{III}(PPh_3)_2(phen)(Hox)]^{2+}$	263(52400), 277^{a}(35600), 298^{a}(15000), 403(5100), 619(900)
$[Os^{III}(PPh_3)_2(phen)(nn)]^{2+}$	217(138500), 268(202600), 401^{a}(7900), 490(15900), 635^{a}(870), 718(930), 939(830)

[a] Shoulder.

exposure to air) is less than that of the $[Os^{III}(PPh_3)_2(N\text{-}N)Br_2]^+$ complexes.

4. Supplementary data

Supplementary data are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, on request, quoting the deposition number CCDC 112233.

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