DALTON
FULL PAPER

Cyclometallation and N=N bond cleavage of 2-(arylazo)phenols by osmium. Synthesis, structure and redox properties†

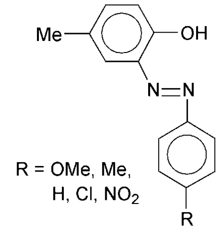
Kanchana Majumder,[a] **Shie-Ming Peng**[b] **and Samaresh Bhattacharya** *[a]

[a] *Department of Chemistry, Inorganic Chemistry Section, Jadavpur University, Calcutta 700 032, India. E-mail: samaresh_b@hotmail.com*
[b] *Department of Chemistry, National Taiwan University, Taipei, Taiwan, Republic of China*

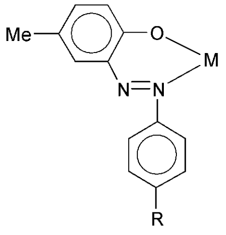
Received 15th September 2000, Accepted 13th November 2000
First published as an Advance Article on the web 11th January 2001

Reaction of 2-arylazo-4-methylphenol, (H_2ap-R, where H_2 indicates the two protons (the phenolic proton and one phenyl proton at the *ortho* position of the arylazo fragment) that undergo dissociation upon complexation) with [Os(PPh$_3$)$_3$Br$_2$] in the presence of a base afford two types of organometallic complexes of osmium(III), *viz.* red [Os(PPh$_3$)$_2$(ap-R)Br] and brownish-green [Os(PPh$_3$)(ap-R)(N–O)] [N–O is an iminosemiquinonate ligand generated from the 2-(arylazo)phenol *via* N=N bond cleavage]. The structures of [Os(PPh$_3$)$_2$(ap-Cl)Br] and [Os(PPh$_3$)(ap-Cl)(N–O)] have been determined by X-ray crystallography. In the [Os(PPh$_3$)$_2$(ap-R)Br] complexes, the ap-R ligand coordinates to osmium as a tridentate C,N,O donor ligand forming two five-membered chelate rings and the two PPh$_3$ ligands are *trans*. In the [Os(PPh$_3$)(ap-R)(N–O)] complexes, osmium is bound to one PPh$_3$, one ap-R ligand coordinated as a tridentate C,N,O donor ligand and one iminosemiquinonate ligand. The [Os(PPh$_3$)$_2$(ap-R)Br] complexes are paramagnetic (low-spin d^5, $S = 1/2$) and show anisotropic EPR spectra at 77 K. The [Os(PPh$_3$)(ap-R)(N–O)] complexes are diamagnetic and show sharp ^{1}H and ^{13}C NMR signals. In acetonitrile solution all the complexes display intense charge-transfer transitions in the visible region. Cyclic voltammetry on these complexes in acetonitrile solution shows an osmium(III)–osmium(IV) oxidation positive to SCE and an osmium(II)–osmium(III) reduction negative to SCE. Two irreversible oxidations are also displayed by all the [Os(PPh$_3$)(ap-R)(N–O)] complexes in the range 1.10–1.76 V *vs.* SCE.

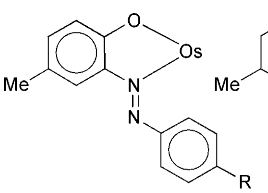
Introduction



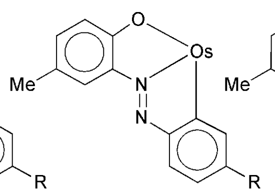
1



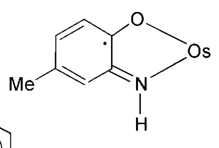
2



3



4



5

The chemistry of osmium has been receiving much current attention[1] primarily because of the interesting properties exhibited by the complexes of this metal. As planned variation in the coordination environment around osmium brings about corresponding variation in the properties of its complexes, coordination of osmium by ligands of different types has been of significant importance. In the present work, which has originated from our interest in the chemistry of osmium in different coordination spheres,[2] we have chosen 2-(arylazo)phenols (**1**) as the principal ligand type. This ligand type is familiar as a bidentate N,O-donor forming six-membered chelate rings (**2**).[3] However, in a series of osmium complexes of type [Os(bpy)$_2$(L)]$^+$ [bpy = 2,2′-bipyridine; L = 2-(arylazo)phenolate], we have recently observed a rather uncommon coordination mode of this ligand type with formation of a five-membered chelate ring (**3**).[2c] The proximity of the phenyl ring, pendant from the uncoordinated azo-nitrogen, to osmium points to the possibility of formation of an Os–C bond at the *ortho* position (**4**). Such orthometallation could not take place in the [Os(bpy)$_2$(L)]$^+$ complexes, probably because of non-availability of a vacant coordination site. However, this study clearly indicated that the necessary prerequisite for the expected C,N,O-coordination to occur, is to choose the right osmium starting material which can provide three vacant coordination sites and which preferably will retain some π-acid ligands, since formation of Os–C bonds is observed to be facile when π-acid co-ligands are present.[4] With this strategy in mind we selected [Os(PPh$_3$)$_3$Br$_2$] as the starting material since in its reaction with ligands containing dissociable protons, it is known to lose one PPh$_3$ and at least one bromide while retaining the two PPh$_3$ ligands[2a,d,5] and thus it provides at least three vacant coordination sites on osmium. This selection indeed turned out to be very successful and two families of organo-osmium complexes (*viz.* red and brownish-green complexes), both containing the 2-(arylazo)phenolate ligand coordinated in the expected fashion (**4**), have been obtained from the reaction of 2-(arylazo)phenols with [Os(PPh$_3$)$_3$Br$_2$]. It may be mentioned here that osmium is in the +3 state in all these complexes and to our knowledge these represent the first[6] group of cyclometallated complexes of osmium(III). In the red complexes, osmium is bound to two PPh$_3$ ligands, one 2-(arylazo)phonolate ligand (as in **4**) and one bromide. In the brownish-green complexes osmium is coordinated to one PPh$_3$, one 2-(arylazo)phenolate ligand (as in **4**) and an iminosemiquinonate ligand (**5**) generated

---

† Electronic supplementary information (ESI) available: microanalytical and EPR data. See http://www.rsc.org/suppdata/dt/b0/b007486l/

DOI: 10.1039/b007486l

from the cleavage of one 2-(arylazo)phenol across the N=N bond. These two groups of complexes appear to be of particular interest because they represent two very interesting reactions: (i) formation of organometallic complexes of trivalent osmium, which is rare[6] and (ii) metal promoted N=N bond cleavage which is also not that common and of much current interest.[7] An account of the chemistry of these organo-osmium complexes is presented here with special reference to synthesis, characterization and electrochemistry.

Experimental

Materials

Osmium tetroxide was purchased from Arora Matthey, Calcutta, India and was converted to $[NH_4]_2[OsBr_6]$ by reduction with hydrobromic acid.[8] $[Os(PPh_3)_3Br_2]$ was synthesized, starting from $[NH_4]_2[OsBr_6]$, by following a reported procedure.[9] The 2-(arylazo)phenol ligands were prepared by reacting the respective diazotized aniline with alkaline *para*-cresol. Purification of acetonitrile and preparation of tetraethylammonium perchlorate (TEAP) for electrochemical work were performed as reported in the literature.[10] All other chemicals and solvents were reagent grade commercial materials and were used as received.

Preparations

Each $[Os(PPh_3)_2(ap\text{-}R)Br]$ complex and the corresponding $[Os(PPh_3)(ap\text{-}R)(N\text{–}O)]$ complex were obtained from a single reaction. Details are given below for a particular case.

$[Os(PPh_3)_2(ap\text{-}H)Br]$ and $[Os(PPh_3)(ap\text{-}H)(N\text{–}O)]$. To a solution of H_2ap-H (43 mg, 0.20 mmol) in 2-methoxyethanol (30 cm^3) was added $[Os(PPh_3)_3Br_2]$ (100 mg, 0.09 mmol) followed by triethanolamine (0.03 cm^3, 0.20 mmol). The mixture was heated at reflux for 6 h. The solvent was then evaporated on a water bath and purification of the crude product thus obtained was achieved by chromatography through a silica gel (60–120 mesh) column. Using a 1 : 1 hexane–benzene mixture as the eluent, a yellow band eluted first and this was rejected. With a 1 : 7 hexane–benzene mixture as the next eluent, a red band was eluted (leaving behind a brownish-green band) which was collected. Evaporation of the eluate gave $[Os(PPh_3)_2(ap\text{-}H)Br]$ as a crystalline solid. The yield was 32%.

After eluting the red band with a 1 : 7 hexane–benzene mixture, the remaining brownish-green band was eluted using benzene as the eluent. Evaporation of the eluate gave $[Os(PPh_3)(ap\text{-}H)(N\text{–}O)]$ as a crystalline solid. The yield was 58%.

Physical measurements

Microanalyses (C, H, N) were performed using a Perkin-Elmer 240C elemental analyzer. Electronic spectra were recorded on Shimadzu UV 1601 and Hitachi 330 spectrophotometers. Magnetic susceptibilities were measured using a PAR 155 Vibrating Sample Magnetometer fitted with a Walker scientific L75FBAL magnet. EPR spectra were recorded with a Varian Model 109C E-line X-band spectrometer fitted with a quartz Dewar for measurements at 77 K (liquid dinitrogen). All spectra were calibrated with the aid of DPPH (diphenylpicrylhydrazyl, $g = 2.0037$). NMR spectra were recorded on a Bruker DRX-500 NMR spectrometer. Electrochemical measurements were performed 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 RE 0089 X–Y recorder was used to trace the voltammograms. Electrochemical measurements were made under a dinitrogen atmosphere. All electrochemical data were collected at 298 K and are uncorrected for junction potentials.

Table 1 Crystallographic data for $[Os(PPh_3)_2(ap\text{-}Cl)Br]$ and $[Os(PPh_3)(ap\text{-}Cl)(N\text{–}O)]$

	$[Os(PPh_3)_2(ap\text{-}Cl)Br]$	$[Os(PPh_3)(ap\text{-}Cl)(N\text{–}O)]$
Empirical formula	$C_{49}H_{39}BrClN_2OsP_2$	$C_{38.50}H_{31.50}Cl_2N_3O_2OsP$
M_w	1039.32	859.23
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$
a/Å	12.2703(2)	40.4327(2)
b/Å	19.1253(1)	10.9195(2)
c/Å	19.2075(3)	17.5688(3)
β/°	107.742(1)	112.731(1)
V/Å^3	4293.1(1)	7154.2(2)
Z	4	8
λ/Å	0.71073	0.71073
Crystal size/mm	0.40 × 0.20 × 0.4	0.30 × 0.22 × 0.02
T/K	295(2)	295(2)
μ/mm^{-1}	4.0776	3.797
R indices	$R1 = 0.0571$[a]	$R1 = 0.0565$[a]
	$wR2 = 0.1494$[b]	$wR = 0.1355$[b]
GOF	1.045[c]	1.022[c]

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)\}]^{1/2}$. [c] $GOF = [\Sigma\{w(F_o^2 - F_c^2)^2)/(M - N)]^{1/2}$, where M is the number of reflections and N is the number of parameters refined.

Crystallography

$[Os(PPh_3)_2(ap\text{-}Cl)Br]$. Single crystals of $[Os(PPh_3)_2(ap\text{-}Cl)Br]$ 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 SMART CCD diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using ω-scans. X-Ray data reduction and structure solution and refinement were performed using the SHELXTL-PLUS package.[11] The structure was solved by direct methods.

$[Os(PPh_3)(ap\text{-}Cl)(N\text{–}O)]$. Single crystals of $[Os(PPh_3)(ap\text{-}Cl)(N\text{–}O)]$ 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 collection and structure solution and refinement were done similarly as above.

CCDC reference number 186/2268.

See http://www.rsc.org/suppdata/dt/b0/b007486l/ for crystallographic files in .cif format.

Results and discussion

Five 2-(arylazo)phenol ligands (**1**) have been used in the present study. The ligands are abbreviated in general as H_2ap-R, where H_2 corresponds to the two protons (one phenolic proton and one phenyl proton at the *ortho* position of the arylazo fragment) which undergo dissociation upon complexation (*vide infra*) and R corresponds to the substituent. Reaction of each of these ligands with $[Os(PPh_3)_3Br_2]$ in 2 : 1 mole ratio proceeds smoothly in refluxing 2-methoxyethanol in the presence of a base to afford two complexes, one red and the other brownish-green, which have been subsequently separated by chromatography. The combined yield of the two complexes was high. These two types of complexes turned out to be significantly different in composition and properties (*vide infra*) and hence they are discussed below under two separate headings.

The red complexes $[Os(PPh_3)_2(ap\text{-}R)Br]$

The molecular structure of a representative member of this family, *viz.* that obtained from the reaction with H_2ap-Cl, has been determined by X-ray crystallography. A view of the complex molecule is shown in Fig. 1 and selected bond parameters are presented in Table 2. In the complex molecule, one ap-Cl ligand, two triphenylphosphines and one bromide are bound to

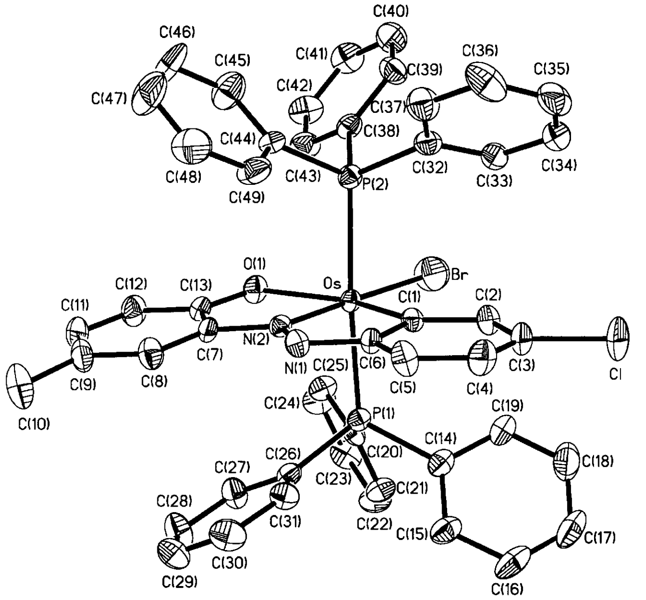


Fig. 1 View of the [Os(PPh_3)$_2$(ap-Cl)Br] molecule.

Table 2 Selected bond distances (Å) and bond angles (°) for [Os(PPh_3)$_2$(ap-Cl)Br]

Os–P(1)	2.400(2)	C(3)–C(4)	1.385(13)
Os–P(2)	2.408(2)	C(4)–C(5)	1.382(13)
Os–C(1)	2.034(8)	C(5)–C(6)	1.386(12)
Os–N(2)	2.005(6)	C(6)–C(1)	1.422(11)
Os–O(1)	2.130(6)	C(6)–N(1)	1.357(10)
Os–Br	2.4686(14)	C(7)–N(2)	1.427(10)
C(1)–C(2)	1.410(11)	C(13)–O(1)	1.329(10)
C(2)–C(3)	1.367(12)	N(1)–N(2)	1.301(9)
P(2)–Os–P(1)	174.08(7)	N(2)–Os–Br	178.3(2)
O(1)–Os–C(1)	153.6(3)		
P(2)–Os–Br	85.79(6)	P(1)–Os–Br	88.29(6)
P(2)–Os–C(1)	91.7(2)	P(1)–Os–C(1)	90.2(2)
P(2)–Os–N(2)	95.7(2)	P(1)–Os–N(2)	90.2(2)
P(2)–Os–O(1)	88.8(2)	P(1)–Os–O(1)	92.1(2)
O(1)–Os–Br	100.9(2)	N(2)–Os–O(1)	78.2(2)
C(1)–Os–Br	105.5(2)	N(2)–Os–C(1)	75.4(3)

osmium indicating the molecular composition to be [Os(PPh_3)$_2$(ap-Cl)Br]. Elemental (C,H,N) analytical data of all the red complexes agree well with the [Os(PPh_3)$_2$(ap-R)Br] composition. The ap-Cl ligand is coordinated in a tridentate fashion (**4**), the two PPh_3 ligands are mutually *trans* and the bromide ligand is *trans* to the coordinated azo-nitrogen. The $CNOP_2Br$ coordination sphere around osmium is distorted octahedral in nature, which is reflected in all the bond parameters around osmium. Valid comparison of the observed Os–C distance with others has not been possible owing to the lack of precedence of such Os^{III}–C bonds. However, the observed Os^{III}–C length is slightly shorter than known Os^{II}–C lengths,[12] which may be attributed to the difference in oxidation states of osmium. The Os–N, Os–O, Os–P and Os–Br distances are all normal, upon comparison with structurally characterized osmium(III) complexes containing these bonds.[13] The spectral and electrochemical properties of all the [Os(PPh_3)$_2$(ap-R)Br] complexes are similar (*vide infra*) and hence they are all assumed to have the same structure as [Os(PPh_3)$_2$(ap-Cl)Br].

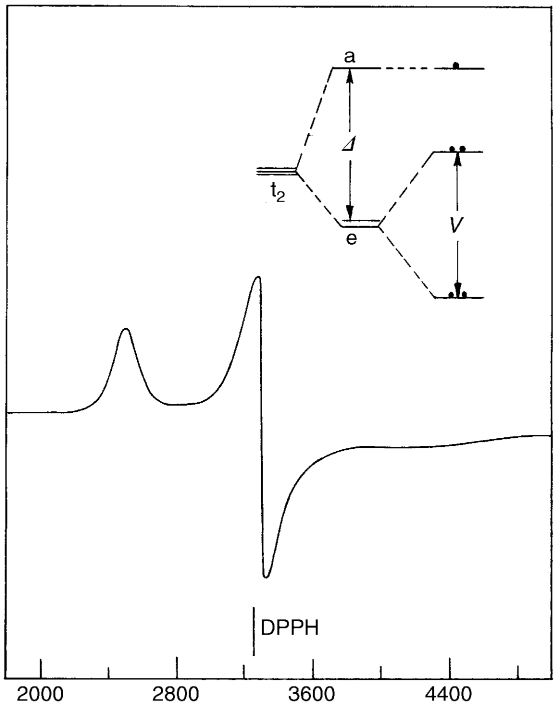


Fig. 2 EPR spectrum and t_2-splitting of [Os(PPh_3)$_2$(ap-H)Br] in 1 : 1 dichloromethane–toluene solution at 77 K.

Magnetic susceptibility measurements show that all the [Os(PPh_3)$_2$(ap-R)Br] complexes are one-electron paramagnetic species ($\mu_{eff} = 1.85$–1.97 μ_B), which corresponds to the +3 state of osmium (low-spin d^5, $S = 1/2$) in these complexes. It may be noted here that osmium has undergone a one-electron oxidation during the course of the synthetic reaction and in view of the osmium(II)–osmium(III) potential (*vide infra*) aerial oxygen appears to be the probable oxidant. Considering the coordination sphere around osmium in the [Os(PPh_3)$_2$(ap-R)Br] complexes, consisting of three non-equivalent P–Os–P, C–Os–O and N–Os–Br axes, rhombic EPR spectra may logically be expected. However, EPR spectra of all these complexes, recorded in 1 : 1 dichloromethane–toluene solution at 77 K, show anisotropic spectra with only two distinct resonances (g_1 and g_2). A representative spectrum is shown in Fig. 2. Though the presence of the third resonance has not been detectable, the observed spectra do show a broad feature near 4200 G, which could be due to the third signal (g_3). Non-appearance of the g_3 signal in its usual shape is quite common in complexes of osmium(III).[14] Electronic spectra of these complexes, recorded in acetonitrile solution, uniformly show two intense absorptions in the visible region together with one weak absorption near 700 nm (Table 3). The intense absorptions in the visible region are probably due to ligand-to-metal charge-transfer transitions. The weak transition near 700 nm may be assigned to one of the two possible transitions within the three split metal orbitals (components of the t_2 orbitals).

Electrochemical properties of the [Os(PPh_3)$_2$(ap-R)Br] complexes have been studied in acetonitrile solution (0.1 M TEAP) by cyclic voltammetry. Each complex shows a reductive response negative to SCE and an oxidative response positive to SCE (Table 3). The oxidative response, observed in the range 0.75–0.91 V (all potentials are referenced to SCE), is irreversible and is assigned to the osmium(III)–osmium(IV) oxidation. The reductive response, observed in the range −0.68 to −0.74 V, is reversible with a peak-to-peak separation(ΔE_p) of 60–70 mV and is assigned to the osmium(III)–osmium(II) reduction. The one-electron stoichiometry of these responses has been established by comparing their current heights with that of the standard ferrocene/ferrocenium couple under identical experimental conditions. The potentials of both the metal-centered oxidation and reduction are found to increase linearly with increasing electron-withdrawing character of substituent R in the 2-(arylazo)phenolate ligand expressed in terms of Hammett substituent constant (σ)[15] [σ values of the substituents are: OMe = −0.27, Me = −0.17, H = 0.00, Cl = 0.23, NO_2 = 0.78]. It is interesting that a single substituent which is four bonds away from the electroactive metal center can influence the metal-centered redox potentials in a predictable manner.

Table 3 Characterization data for the [Os(PPh$_3$)$_2$(ap-R)Br] complexes

Compound	Electronic spectral data[a] λ_{max}/nm (ε/M^{-1} cm^{-1})	Cyclic voltammetric data[a,b] $E_{\frac{1}{2}}$/V (ΔE_p/mV)
[Os(PPh$_3$)$_2$(ap-OMe)Br]	676 (120), 480 (3900), 380 (3500), 328[c] (4800), 312 (6500)	0.75,[d] −0.74 (60)
[Os(PPh$_3$)$_2$(ap-Me)Br]	676 (530), 468 (4800), 400 (5000), 336 (6100), 316 (7400)	0.76,[d] −0.73 (60)
[Os(PPh$_3$)$_2$(ap-H)Br]	688 (380), 460 (3300), 400 (3800), 324[c] (7100), 308 (8600)	0.79,[d] −0.72 (70)
[Os(PPh$_3$)$_2$(ap-Cl)Br]	684 (570), 460 (2300), 404 (2900), 304[c] (5300), 312 (5800)	0.83,[d] −0.71 (60)
[Os(PPh$_3$)$_2$(ap-NO$_2$)Br]	748 (370), 512 (1900), 432 (2300), 368[c] (3700), 312 (5900)	0.91,[d] −0.68 (70)

[a] In acetonitrile solution. [b] Supporting electrolyte TEAP; reference electrode SCE; $E_{\frac{1}{2}} = 0.5(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are anodic and cathodic peak potentials respectively; $\Delta E_p = E_{pa} - E_{pc}$; scan rate 50 mV s^{-1}. [c] Shoulder. [d] E_{pa} value.

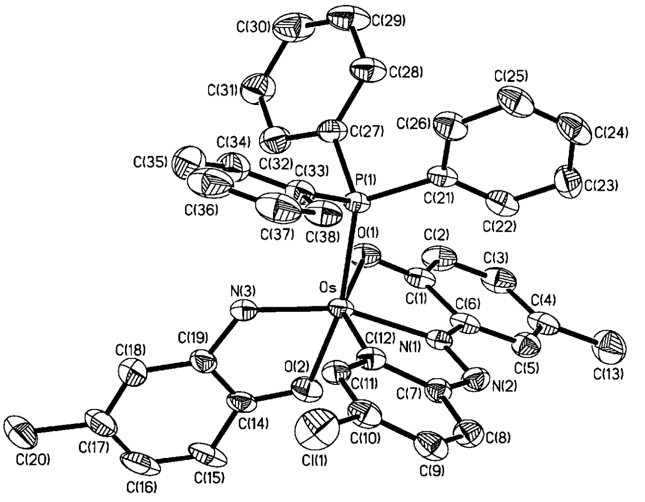


Fig. 3 View of the [Os(PPh$_3$)(ap-Cl)(N–O)] molecule.

Table 4 Selected bond distances (Å) and bond angles (°) for [Os(PPh$_3$)(ap-Cl)(N–O)]·0.5CH$_2$Cl$_2$

Os–P(1)	2.341(2)	C(17)–C(16)	1.42(2)
Os–O(1)	2.075(5)	C(16)–C(15)	1.34(2)
Os–N(1)	2.045(6)	C(15)–C(14)	1.419(11)
Os–C(12)	2.056(7)	C(14)–O(2)	1.303(10)
Os–O(2)	2.074(5)	C(12)–C(7)	1.434(11)
Os–N(3)	1.933(7)	C(7)–N(2)	1.405(10)
C(19)–N(3)	1.414(10)	N(2)–N(1)	1.303(8)
C(19)–C(18)	1.397(12)	C(1)–O(1)	1.315(10)
C(18)–C(17)	1.36(2)	C(6)–N(1)	1.426(10)
P(1)–Os–O(2)	166.2(2)	N(1)–Os–N(3)	161.3(2)
O(1)–Os–C(12)	150.4(3)		
P(1)–Os–O(1)	85.7(2)	P(1)–Os–N(1)	103.3(2)
O(1)–Os–N(1)	77.3(2)	P(1)–Os–C(12)	89.3(2)
N(1)–Os–C(2)	75.5(3)	P(1)–Os–O(2)	166.2(2)
C(12)–Os–O(2)	101.5(3)	P(1)–Os–N(3)	92.0(2)
O(2)–Os–N(3)	78.9(3)	C(19)–N(3)–Os	117.0(6)
N(3)–Os–P(1)	92.0(2)	C(14)–O(2)–Os	113.7(5)

The brownish-green complexes [Os(PPh$_3$)(ap-R)(N–O)]

The identity of these complexes has been revealed by structure determination of a representative member (obtained from reaction with H$_2$ap-Cl) of this family. The structure is shown in Fig. 3 and selected bond parameters are listed in Table 4. The structure shows that two 2-(arylazo)phenol ligands have interacted with the osmium center, but in different fashions. While one 2-(arylazo)phenol ligand is coordinated as a tridentate C,N,O donor ligand forming two five-membered chelate rings (**4**) as above, the second 2-(arylazo)phenol has undergone cleavage across the N=N bond and the iminophenol fragment, thus generated, is coordinated as a bidentate N,O donor ligand forming a five-membered chelate ring (**5**). The sixth coordination site is occupied by one triphenylphosphine ligand. From the bond parameters around osmium, it is clear that the CN$_2$O$_2$P coordination sphere around osmium is distorted octahedral in nature. Bond distances within the Os(C–N–O) chelate compare well with the structure of [Os(PPh$_3$)$_2$(ap-Cl)Br]. In the bidentate iminophenolate fragment, the C(14)–O(2) and C(19)–N(3) distances lie between those expected for localized single and double bonds, while the C(15)–C(16) and C(17)–C(18) bonds are much shorter than the other four C–C bonds within the phenyl ring. All these data clearly indicate that this ligand is coordinated in the iminosemiquinonate form (**5**).[16] All five complexes belonging to this family are therefore formulated as [Os(PPh$_3$)(ap-R)(N–O)], where N–O is the iminosemiquinonate ligand. The observed microanalytical data for all these complexes are consistent with this formulation. As all the [Os(PPh$_3$)(ap-R)(N–O)] complexes display similar properties (*vide infra*), the other four [Os(PPh$_3$)(ap-R)(N–O)] complexes are assumed to have the same structure as [Os(PPh$_3$)(ap-Cl)(N–O)].

The mechanism of the N=N bond cleavage is, as yet, not clear. However, coordination of the 2-(arylazo)phenolate ligand to osmium as a bidentate N,O-donor forming five-membered chelate ring (**3**) seems to be a probable step preceding the N=N bond cleavage. Coordination of 2-(arylazo)phenolate ligands to osmium in this mode has been observed by us.[2c] While cleavage of the N=N bond is a four-electron reduction process, osmium underwent only one-electron oxidation during the course of the synthetic reaction. The solvent (2-methoxyethanol) appears to serve as the source of necessary reducing equivalents. Indirect evidence for the involvement of solvent in the redox reaction comes from the fact that reaction carried out in *tert*-butyl alcohol does not yield the brownish-green product.

From the composition of these [Os(PPh$_3$)(ap-R)(N–O)] complexes it is clear that osmium is in the +3 oxidation state (low-spin d^5, $S = 1/2$). However, magnetic susceptibility measurements show that the [Os(PPh$_3$)(ap-R)(N–O)] complexes are diamagnetic. Antiferromagnetic interaction between the unpaired electron on osmium(III) and that on the iminosemiquinonate radical appears to be responsible for the observed diamagnetism. Such antiferromagnetic interaction is quite common in transition metal complexes of quinones and related ligands.[17] ^{1}H NMR spectra of the [Os(PPh$_3$)(ap-R)(N–O)] complexes have been recorded in CDCl$_3$ solution. All five complexes uniformly display two distinct methyl signals at δ *ca.* 2.3 and 1.2 which are assigned, respectively, to the methyl group in the *p*-cresol fragment of the tridentate ap-R ligand and the methyl group in the iminosemiquinonate ligand. The N–H signal is observed in all the [Os(PPh$_3$)(ap-R)(N–O)] complexes as an isolated resonance at δ *ca.* 12. The aromatic region (δ 5.0–8.0) is rather complex in nature owing to overlap of signals arising from all the three types of ligands. Therefore assignment of these signals to specific protons has not been possible. However, intensity measurement of the signals corresponds well with the total number of aromatic protons present in the respective complexes. ^{13}C NMR spectra of the [Os(PPh$_3$)(ap-R)(N–O)] complexes have also been recorded in CDCl$_3$ solution. The expected number of signals are observed in all the complexes. The two methyl carbons, one in the *p*-cresol fragment of the ap-R ligand and the other in the N–O ligand,

Table 5 Characterization data for the [Os(PPh$_3$)(ap-R)(N–O)] complexes

Compound	Electronic spectral data^a λ_{max}/nm (ε/M^{-1} cm^{-1})	Cyclic voltammetric data^{a,b} $E_{\frac{1}{2}}$/V (ΔE_p/mV)
[Os(PPh$_3$)(ap-OMe)(N–O)]	600 (2700), 393 (9500), 362 (11500)	−0.96 (60), 0.58 (60), 1.10,^{c} 1.60^c
[Os(PPh$_3$)(ap-Me)(N–O)]	600 (3900), 401 (10300), 353 (12900)	−0.95 (60), 0.60 (60), 1.10,^{c} 1.68^c
[Os(PPh$_3$)(ap-H)(N–O)]	585 (3400), 410 (10200), 345 (11600)	−0.92 (60), 0.62 (60), 1.12,^{c} 1.68^c
[Os(PPh$_3$)(ap-Cl)(N–O)]	590 (4800), 406 (12200), 353 (14300)	−0.88 (60), 0.67 (60), 1.12,^{c} 1.70^c
[Os(PPh$_3$)(ap-NO$_2$)(N–O)]	569 (5400), 436 (9700), 366 (10800)	−0.78 (60), 0.78 (60), 1.30,^{c} 1.76^c

^{a} In acetonitrile solution. ^{b} Supporting electrolyte TEAP; reference electrode SCE; $E_{\frac{1}{2}} = 0.5$ (E_{pa} + E_{pc}), where E_{pa} and E_{pc} are anodic and cathodic peak potentials respectively; $\Delta E_p = E_{pa} - E_{pc}$; scan rate 50 mV s^{-1}. ^{c} E_{pa} value.

are respectively observed at δ *ca.* 20.4 and 20.9. The aromatic carbons are observed in the range δ 115–175, of which the most downfield signal (δ *ca.* 174) is assigned to the metallated carbon. Electronic spectra of the [Os(PPh$_3$)(ap-R)(N–O)] complexes have been recorded in acetonitrile solution. Each complex shows intense absorptions in the visible region (Table 5) which are probably due to allowed charge-transfer transitions involving both metal and ligand orbitals.

The electrochemical properties of the [Os(PPh$_3$)(ap-R)(N–O)] complexes have been studied by cyclic voltammetry in acetonitrile solution (0.1 M TEAP). Each complex shows three oxidative responses positive to SCE and a reductive response negative to SCE (Table 5). The first oxidative response, observed in the range 0.58–0.78 V, is reversible in nature ($\Delta E_p = 60$ mV) and is tentatively assigned to the osmium(III)–osmium(IV) oxidation. The reductive response, displayed within −0.96 to −0.78 V, is also reversible ($\Delta E_p = 60$ mV) and is assumed to be an osmium(III)–osmium(II) reduction. The one-electron nature of these couples has been established by comparing their current heights with those of the standard ferrocene/ferrocenium couple under identical experimental conditions. The potential of both the metal-centered oxidation and reduction is found to correlate linearly with the electron-withdrawing character (σ) of the substituent R in the ap-R ligand. Two irreversible oxidations are also displayed by all the [Os(PPh$_3$)(ap-R)(N–O)] complexes in the range 1.10–1.76 V, but the sites of these oxidations are not clear.

Conclusion

The present study shows that 2-(arylazo)phenols (**1**) undergo two types of interesting chemical transformation upon reaction with [Os(PPh$_3$)$_3$Br$_2$], *viz.* osmium(III)–carbon bond formation yielding cyclometallates of osmium (**2**) and N=N bond cleavage affording iminosemiquinonate chelates of osmium (**3**). The organoosmium fragment (**2**) appears suitable for studying reactivities of the Os–C bond and such studies are currently in progress.

Acknowledgements

Financial assistance received from the Council of Scientific and Industrial Research, New Delhi [Grant No. 01(1408)/96/EMR-II] and the Department of Science and Technology, New Delhi [Grant No. SP/S1/F33/98] is gratefully acknowledged. We thank the Third World Academy of Sciences for financial support enabling the purchase of an electrochemical cell system. Thanks are also due to Dr Falguni Basuli for her help.

References

1 R. Hage, *Coord. Chem. Rev.*, 1991, **111**, 161; J. P. Collin, S. Guillerez, J. P. Sauvage, F. Barigelletti, L. Flamigni, L. D. Cola and V. Balzani, *Coord. Chem. Rev.*, 1991, **111**, 291; L. D. Cola, F. Barigelletti, V. Balzani, P. Belser, A. V. Zelewsky, C. Seel, M. Frank and F. Vogtle, *Coord. Chem. Rev.*, 1991, **111**, 255; E. C. Constable and C. E. Housecroft, *Coord. Chem. Rev.*, 1993, **124**, 183; M. D. Ward, *Coord. Chem. Rev.*, 1993, **127**, 1; M. Furue, K. Maruyama, Y. Kanematsu, T. Kushida and M. Kamachi, *Coord. Chem. Rev.*, 1994, **132**, 201; F. Barigelletti, L. Flamigni, V. Balzani, J. P. Collin, J. P. Sauvage, A. Sour, E. C. Constable and A. M. W. C. Thompson, *Coord. Chem. Rev.*, 1994, **132**, 209; K. Kalyansundaram, S. M. Zakeeruddin and M. K. Nazeeruddin, *Coord. Chem. Rev.*, 1994, **132**, 259; M. G. Richmond, *Coord. Chem. Rev.*, 1995, **141**, 63; M. D. Ward, *Coord. Chem. Rev.*, 1995, **146**, 99; M. D. Ward, *Coord. Chem. Rev.*, 1997, **164**, 483; B. R. McGarvey, *Coord. Chem. Rev.*, 1998, **170**, 75.

2 (*a*) F. Basuli, S. M. Peng and S. Bhattacharya, *Inorg. Chem.*, 1997, **36**, 5645; (*b*) F. Basuli, S. M. Peng and S. Bhattacharya, *Polyhedron*, 1998, **17**, 2191; (*c*) F. Basuli, S. M. Peng and S. Bhattacharya, *Polyhedron*, 1998, **18**, 391; (*d*) F. Basuli, M. Ruf, C. G. Pierpont and S. Bhattacharya, *Inorg. Chem.*, 1998, **37**, 6113; (*e*) A. Das, F. Basuli, S. M. Peng and S. Bhattacharya, *Polyhedron*, 1999, **18**, 2729; (*f*) F. Basuli, S. M. Peng and S. Bhattacharya, *Inorg. Chem.*, 2000, **39**, 1120.

3 H. M. Haendur and G. M. P. Smith, *J. Am. Chem. Soc.*, 1940, **62**, 1669; K. Ueno, *J. Am. Chem. Soc.*, 1957, **79**, 3066; J. A. J. Jarvis, *Acta Crystallogr.*, 1961, **14**, 961; R. J. Price, *J. Chem. Soc. A*, 1969, 1296; K. C. Kalia, *Indian J. Chem.*, 1970, **8**, 1035; O. A. Dyachenko, L. O. Atovmyan and S. M. Aldosin, *J. Chem. Soc.*, *Chem. Commun.*, 1975, 105; I. N. Marov, D. G. Gambarov, V. K. Belyaeva, A. G. Guseinov and A. B. Sokolov, *Russ J. Inorg. Chem.*, 1948, **29**, 1452; C. R. Sinha, D. Bandopadhyay and A. Chakravorty, *J. Chem. Soc.*, *Chem. Commun.*, 1988, 468; R. Bhawmik, H. Biswas and P. Bandopadhyay, *J. Org. Met. Chem.*, 1995, **81**, 498.

4 P. J. Desrosiers, R. S. Shinamoto, M. A. Deming and T. C. Flood, *Organometallics*, 1989, **8**, 286; M. A. Esteruelas, F. J. Lahoz, A. M. Lopez, E. Onate and L. A. Oro, *Organometallics*, 1995, **14**, 2496; E. Arcia, D. S. Kolwaite, E. Rosenberg, K. Hardcastle, J. Ciurash, R. Duque, R. Gobetto, L. Milone, D. Osella, M. Botta, W. Dastru, A. Viale and I. Fiedler, *Organometallics*, 1998, **17**, 415.

5 S. Bhattacharya and C. G. Pierpont, *Inorg. Chem.*, 1991, **30**, 2906; A. Pramanik, N. Bag, G. K. Lahiri and A. Chakravorty, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 101.

6 Z. Gross and A. Mohammed, *Inorg. Chem.*, 1996, **35**, 7260.

7 M. A. Lockwood, P. E. Fanwick, O. Eisenstein and I. P. Rothwell, *J. Am. Chem. Soc.*, 1996, **118**, 2762; S. D. Gray, J. L. Thorman, V. A. Adamian, K. M. Kadish and L. K. Woo, *Inorg. Chem.*, 1998, **37**, 1; M. A. Aubart and R. G. Bergman, *Organometallic*s, 1999, **18**, 811; F. Y. Petillon, P. Schollhammer and J. Talarmin, *Inorg. Chem.*, 1999, **38**, 1954; A. Ghosh, P. Majumdar, L. R. Falvello, G. Mostafa and S. Goswami, *Organometallics*, 1999, **18**, 5086.

8 E. P. Dwyer and J. W. Hogarth, *Inorg. Synth.*, 1957, **5**, 204.

9 P. R. Hoffman and K. G. Caulton, *J. Am. Chem. Soc.*, 1975, **97**, 4221.

10 D. T. Sawyer and J. L. Roberts, Jr., *Experimental Electrochemistry for Chemists*, Wiley, New York, 1974, pp. 167–215; M. Walter and L. Ramaley, *Anal. Chem.*, 1973, **45**, 165.

11 G. M. Sheldrick, SHELXTL-PLUS, Program package for structure solution and refinement, version 4.2, Siemens Analytical X-Ray Instruments, Madison, WI, 1990.

12 M. H. Esteruelas, F. J. Lahoz, A. M. Lopez, E. Onate and L. A. Oro, *Organometallics*, 1995, **14**, 415.

13 A. Pramanik, N. Bag, D. Ray, G. K. Lahiri and A. Chakravorty, *Inorg. Chem.*, 1991, **30**, 410; K. Majumder, S. M. Peng and S. Bhattachyarya, unpublished work.

14 R. E. De-Simone and R. S. Drago, *J. Am. Chem. Soc.*, 1970, **92**, 2343; E. M. Kober and T. J. Meyer, *Inorg. Chem.*, 1983, **22**, 1614; G. K. Lahiri, S. Bhattacharya, B. K. Ghosh and A. Chakravorty, *Inorg. Chem.*, 1987, **26**, 4324.

15 L. P. Hammett, *Physical Organic Chemistry*, McGraw Hill, New York, 2nd edn., 1970.

16 C. N. Verani, S. Gallert, E. Bill, T. Weyhermuller, K. Wieghardt and P. Chaudhuri, *Chem. Commun.*, 1999, 410.

17 S. Bhattacharya and C. G. Pierpont, *Inorg. Chem.*, 1991, **30**, 1511; S. Bhattacharya and C. G. Pierpont, *Inorg. Chem.*, 1991, **30**, 2906; S. Bhattacharya and C. G. Pierpont, *Inorg. Chem.*, 1992, **31**, 2020; S. Bhattacharya and C. G. Pierpont, *Inorg. Chem.*, 1994, **33**, 6038.