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Chemically Induced Cyclometalation of 2-(Arylazo)phenols. Synthesis, Characterization, and Redox Properties of a Family of Organoosmium Complexes

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Reaction of 2-(arylazo)phenols (H_2ap-R; R = OCH_3, CH_3, H, Cl, and NO_2) with $[Os(PPh_3)_2(CO)_2(HCOO)_2]$ affords a family of organometallic complexes of osmium(II) of type $[Os(PPh_3)_2(CO)(ap\text{-}R)]$ where the 2-(arylazo)phenolate ligand is coordinated to the metal center as a tridentate C,N,O-donor. Structure of the $[Os(PPh_3)_2(CO)(ap\text{-}H)]$ complex has been determined by X-ray crystallography. All the $[Os(PPh_3)_2(CO)(ap\text{-}R)]$ complexes are diamagnetic and show characteristic ^1H NMR signals and intense MLCT transitions in the visible region. They also show emission in the visible region at ambient temperature. Cyclic voltammetry on the $[Os(PPh_3)_2(CO)(ap\text{-}R)]$ complexes shows a reversible Os(II)–Os(III) oxidation within 0.39–0.73 V vs SCE, followed by a reversible Os(III)–Os(IV) oxidation within 1.06–1.61 V vs SCE. Coulometric oxidation of the $[Os(PPh_3)_2(CO)(ap\text{-}R)]$ complexes generates the $[Os^{III}(PPh_3)_2(CO)(ap\text{-}R)]^+$ complexes, which have been isolated as the hexafluorophosphate salts. The $[Os^{III}(PPh_3)_2(CO)(ap\text{-}R)]PF_6$ complexes are one-electron paramagnetic and show axial ESR spectra. In solution they behave as 1:1 electrolytes and show intense LMCT transitions in the visible region. The $[Os^{III}(PPh_3)_2(CO)(ap\text{-}R)]PF_6$ complexes have been observed to serve as mild one-electron oxidants in a nonaqueous medium.

Introduction

There has been considerable current interest in the utilization of transition metal complexes for bringing about interesting chemical transformations of organic substrates.[2] Such reactions often proceed via a C−H activation of the organic substrate,[3] leading to the formation of reactive organometallic complexes, which finally yields the desired product. Thus, there has been a constant demand for transition metal complexes that have the potential for inducing C−H activation of organic molecules and the present work has originated from our search for such complex molecules. We have recently synthesized an osmium complex, viz. $[Os(PPh_3)_2(CO)_2(HCOO)_2]$, which upon reaction with different bidentate acidic ligands (H-LL′) affords complexes of type $[Os(PPh_3)_2(CO)(LL')(H)]$, in which the Os(CO)(LL′)(H) fragment constitutes the equatorial plane and the PPh_3 ligands occupy mutual trans positions (**1**).[4] The disposition of the Os−H bond in the equatorial plane of **1** suggests that if a phenyl ring can be incorporated in the bidentate ligand by linking it to the donor atom, which is cis to the hydride, via one intervening atom X (**2**), then C−H activation may be possible at the ortho position of the pendant phenyl ring, leading to cyclometalation of the modified ligand (**3**) via elimination of molecular hydrogen. With this simple strategy of activating phenyl C−H bond in mind, a group of 2-(arylazo)phenols (**4**) have been chosen

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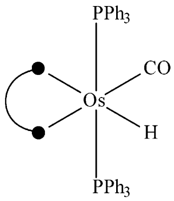

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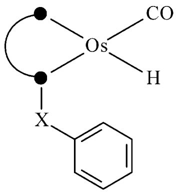

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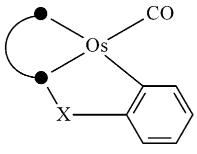

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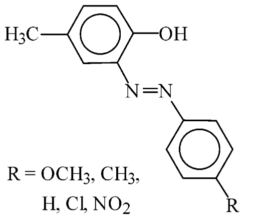
as the target ligands for the present study. Though these ligands (**4**) are known to bind to metal ions usually as bidentate N,O-donors forming a six-membered chelate ring (**5**),[5] we have also observed them to bind to metal ions as bidentate N,O-donors forming a five-membered ring (**6**).[6] It is this latter coordination mode (**6**) of the 2-(arylazo)-phenolate ligands that is of relevance to this present study. Because in this particular coordination mode (**6**) the phenyl ring of the 2-(arylazo)phenolate ligand remains pendant as shown in **2**, it appears perfectly suitable for undergoing orthometalation (**7**) upon reaction with $[Os(PPh_3)_2(CO)_2(HCOO)_2]$, affording organoosmium complexes. This strategy has indeed worked well and reaction of the 2-(arylazo)-phenols with $[Os(PPh_3)_2(CO)_2(HCOO)_2]$ truly afforded a group of organometallic complexes of the expected type, viz. $[Os(PPh_3)_2(CO)(ap\text{-}R)]$, where ap-R refers to the coordinated 2-(arylazo)phenolate ligand in **7**. An account of the chemistry of these complexes is presented here with special reference to their synthesis, characterization, and redox properties.



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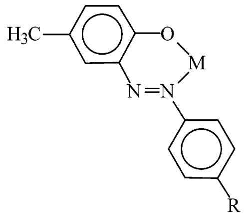

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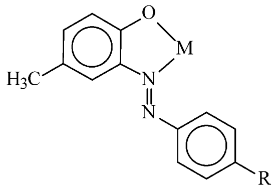

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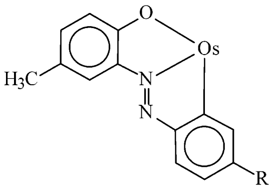

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Experimental Section

Materials. Commercial osmium tetroxide was purchased from Arora Matthey, Kolkata, India, and was converted to $[NH_4]_2[OsBr_6]$ by reduction with hydrobromic acid.[7] $[Os(PPh_3)_3Br_2]$ was synthesized, starting from $[NH_4]_2[OsBr_6]$, by following a reported procedure.[8] $[Os(PPh_3)_2(CO)_2(HCOO)_2]$ was then prepared starting from $[Os(PPh_3)_3Br_2]$ as before.[4a] The 2-(arylazo)phenol ligands were prepared by coupling diazotized para-substituted anilines with *p*-cresol. Purification of dichloromethane and acetonitrile and preparation of tetrabutylammonium perchlorate (TBAP) for electrochemical work were performed as reported in the literature.[9] All other chemicals and solvents were reagent-grade commercial materials and were used as received.

Preparations of Complexes

The $[Os(PPh_3)_2(CO)(ap\text{-}R)]$ complexes were synthesized by following a general procedure. Specific details are given below for one complex.

$[Os(PPh_3)_2(CO)(ap\text{-}H)]$. To a solution of $H_2ap\text{-}H$ (25 mg, 0.11 mmol) in 2-methoxyethanol (40 mL) was added $[Os(PPh_3)_2(CO)_2(HCOO)_2]$ (100 mg, 0.11 mmol). The resulting solution was heated at reflux for 24 h to produce a deep green solution. The solvent was then evaporated on a water bath to give a green residue, which was purified by thin-layer chromatography on a silica plate. When 1:1 hexane−benzene was used as the eluant, a green band separated, which was extracted with dichloromethane. Evaporation of this extract afforded $[Os(PPh_3)_2(CO)(ap\text{-}H)]$ as a green crystalline solid. Yield: 60%.

All the$[Os(PPh_3)_2(CO)(ap\text{-}R)]PF_6$ complexes were synthesized by following a general procedure. Specific details are given below for one complex.

$[Os(PPh_3)_2(CO)(ap\text{-}H)]PF_6$. A solution of $[Os(PPh_3)_2(CO)(ap\text{-}H)]$ (50 mg, 0.05 mmol) in 50 mL of 1:9 dichloromethane−acetonitrile (0.1 M NH_4PF_6) was coulometrically oxidized at 0.9 V vs SCE. Color of the solution gradually changed from bright green to olive green during the oxidation. After the electrolysis was complete ($Q_{observed} = 5.07$ C, $Q_{calculated} = 5.06$ C), the solution containing the oxidized complex was evaporated to dryness under reduced pressure. The dry residue was washed thoroughly with ice-cold water to remove excess NH_4PF_6, leaving the $[Os(PPh_3)_2(CO)(ap\text{-}H)]PF_6$ complex as an olive-green microcrystalline solid, which was dried under vacuo over P_4O_{10}. The yield was quantitative.

Physical Measurements

Microanalyses (C, H, N) were performed using a Heraeus Carlo Erba 1108 elemental analyzer. IR spectra were obtained on a Perkin-Elmer 783 spectrometer with samples prepared as KBr pellets. Solution electrical conductivities were measured using a Phillips PR 9500 bridge with a solute concentration of 10^{-3} M. Electronic spectra were recorded on a JASCO V-570 spectrophotometer. Emission spectra were recorded on a Spex Flurolog spectrometer. 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 Bruker Avance DPX 300 NMR spectrometer using TMS as the internal standard. ESR spectra were recorded with a Varian E-109C X-band spectrometer fitted with a quartz Dewar for measurements at 77 K (liquid

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Table 1. Crystallographic Data for [Os(PPh$_3$)$_2$(CO)(ap-H)]

empirical formula	$C_{50}H_{40}N_2O_2OsP_2$
fw	952.58
space group	monoclinic, $P2_1/c$
a, Å	12.262(3)
b, Å	19.353(5)
c, Å	18.410(4)
β, deg	108.136(16)
V, Å^3	4151.9(16)
Z	4
λ, Å	0.71073
cryst size, mm	0.23 × 0.73 × 0.29
T, K	296(2)
μ, mm^{-1}	3.191
R1^a	0.0354
wR2^b	0.0745
GOF^c	1.020

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

dinitrogen). All spectra were calibrated with the aid of DPPH (g = 2.0037). Electrochemical measurements were made using a CH Instruments model 600A electrochemical analyzer. A platinum disk working electrode, a platinum wire auxiliary electrode, and an aqueous saturated calomel reference electrode (SCE) were used in the cyclic voltammetry experiments. A platinum-wire gauge working electrode was used in the coulometric experiments. All electrochemical experiments were performed under a dinitrogen atmosphere. All electrochemical data were collected at 298 K and are uncorrected for junction potentials.

Oxidation of *N*,*N*-dimethylaniline, 1,2-naphthaquinone-1-oxime, and [Os^{II}(bpy)$_2$Br$_2$] was carried out with all the [Os^{III}(PPh$_3$)$_2$(CO)-(ap-R)]PF$_6$ complexes. Experimental details for the reaction of each reductant with one representative complex are given below.

(i) To a solution of [Os^{III}(PPh$_3$)$_2$(CO)(ap-H)]PF$_6$ (11 mg, 0.01 mmol) in acetonitrile (10 mL) was added TBAP (0.34 g, 0.10 mol) followed by *N*,*N*-dimethylaniline (2.4 mg, 0.02 mmol). An instant color change from olive green to bright green took place and the solution was studied by cyclic voltammetry.

(ii) To a solution of [Os^{III}(PPh$_3$)$_2$(CO)(ap-H)]PF$_6$ (11 mg, 0.01 mmol) in acetonitrile (10 mL) was added 1,2-naphthaquinone-1-oxime (3.2 mg, 0.02 mmol). The color of the solution immediately changed from olive green to bright green. Toluene (10 mL) was then added to the solution and the ESR spectrum of the resultant solution was recorded.

(iii) [Os^{III}(PPh$_3$)$_2$(CO)(ap-H)]PF$_6$ (11 mg, 0.01 mmol) and [Os^{II}(bpy)$_2$Br$_2$] (6.6 mg, 0.01 mmol) were taken together in acetonitrile (20 mL). To the solution TBAP (0.68 g, 0.20 mol) was added and the resultant solution was studied by cyclic voltammetry.

Crystallography of [Os(PPh$_3$)$_2$(CO)(ap-H)]. Single crystals of [Os(PPh$_3$)$_2$(CO)(ap-H)] were obtained 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 Bruker P4 diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) by $2\theta-\omega$ scans within the θ range of 2.41−27.50°. X-ray data reduction, structure solution, and refinement were done using SHELXS-97 and SHELXL-97 programs.[10] The structure was solved by the direct methods.

Results and Discussion

Reaction of the 2-(arylazo)phenol ligands (**4**) with [Os(PPh$_3$)$_2$(CO)$_2$(HCOO)$_2$] proceeds smoothly in refluxing 2-methoxyethanol to afford a group of green complexes of type [Os(PPh$_3$)$_2$(CO)(ap-R)] in decent yields. The observed elemental (C, H, N) analytical data of these complexes agree well with their compositions (Table S1 in the Supporting Information). To find out the coordination mode of the 2-(arylazo)phenolate ligands in these complexes as well as the stereochemistry of the complexes, the structure of one complex of this family, viz. [Os(PPh$_3$)$_2$(CO)(ap-H)], has been determined by X-ray crystallography. The structure is shown in Figure 1 and selected bond parameters are listed in Table 2.

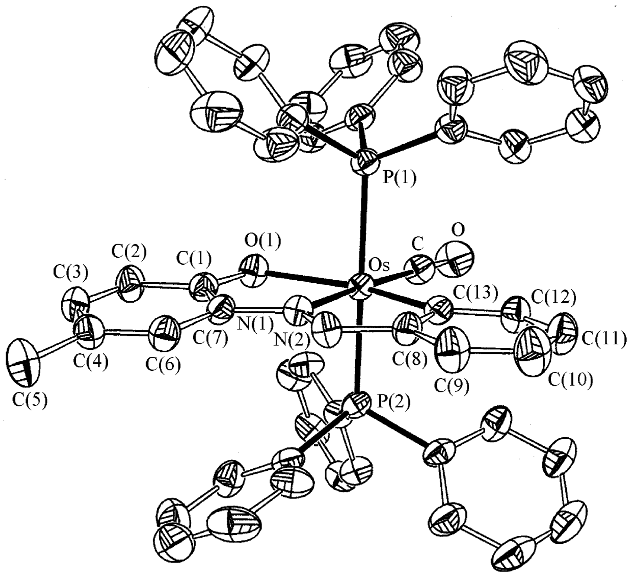

Figure 1. View of the [Os(PPh$_3$)$_2$(CO)(ap-H)] complex.

Table 2. Selected Bond Distances and Bond Angles for [Os(PPh$_3$)$_2$(CO)(ap-H)]

	Bond Distances (Å)		
Os−C	1.863(4)	C−O	1.144(5)
Os−C(13)	2.042(4)	C(1)−O(1)	1.324(5)
Os−N(1)	2.054(3)	N(1)−N(2)	1.282(5)
Os−O(1)	2.186(3)	C(7)−N(1)	1.402(5)
Os−P(1)	2.3714(13)	C(8)−N(2)	1.410(5)
Os−P(2)	2.3623(12)		
	Bond Angles (deg)		
P(1)−Os−P(2)	174.53(4)	C(13)−Os−N(1)	76.55(16)
C−Os−N(1)	175.37(16)	N(1)−Os−O(1)	77.79(13)
C(13)−Os−O(1)	154.30(14)	Os−C−O	178.4

The structure shows that the 2-(arylazo)phenolate ligand is coordinated to osmium in the expected tridentate fashion (**7**). Though relatively less common, this particular coordination mode of the 2-(arylazo)phenols was observed before in their complexes of some heavier transition metal ions.[11] Two triphenylphosphines and a carbonyl are also coordinated to osmium. Osmium is therefore sitting in a $C_2N_1O_1P_2$ coordination environment, which is distorted octahedral in nature as reflected in all the bond parameters around osmium. The coordinated ap-H ligand and the carbonyl have constituted one equatorial plane with the metal at the center, while the PPh$_3$ ligands have occupied the axial positions and hence they are mutually trans. The Os−P and Os−C(carbonyl) and C−O(carbonyl) distances are all quite normal.[12] Within the Os(ap-H) fragment, the Os−C, Os−N, and Os−O distances are also quite normal.[13,6] However, they are slightly longer than those observed in the similar fragment of the [Os(PPh$_3$)$_2$-

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Table 3. ^{1}H NMR Data of the Complexes

compound	chemical shift in ppm[a] PPh$_3$	CH$_3$	aromatic protons	R
[Os(PPh$_3$)$_2$(CO)(ap-OCH$_3$)]	7.12−7.40	1.63	5.80(s),[b] 6.15(d, 8.4),[b] 6.30(s),[b] 7.03 (d, 8.7)[b]	3.50
[Os(PPh$_3$)$_2$(CO)(ap-CH$_3$)]	7.14−7.45	1.68	5.81(s),[b] 6.18(d, 8.4),[b] 6.32(s),[b] 7.09(d, 8.8)[b]	2.04
[Os(PPh$_3$)$_2$(CO)(ap-H)]	7.18−7.50	1.75	5.82−5.87(s + d),[c] 6.42−6.47(d + t),[c] 7.00(d, 7.5),[b] 7.11(d, 7.8)[b]	6.45 (t, 7.5)
[Os(PPh$_3$)$_2$(CO)(ap-Cl)]	7.18−7.55	1.76	5.92(s),[b] 6.16(d, 8.4),[b] 6.33(s),[b] 7.13(d, 8.7)[b]	—
[Os(PPh$_3$)$_2$(CO)(ap-NO$_2$)]	7.20−7.60	1.78	6.01(s),[b] 6.20(d, 8.3),[b] 6.40(s)[b]	—

[a] Multiplicity (s = singlet, d = doublet, t = triplet) of the signal and the coupling constant (in Hz) are given in parentheses. [b] Integration = 1H. [c] Integration = 2H.

Table 4. Electronic Spectral and Cyclic Voltammetric Data

compound	electronic spectral data (absorption) λ_{max}/nm (ϵ/M^{-1} cm^{-1})[a]	electronic spectral data (emission)[b] λ_{max}/nm excitation	emission	quantum yield (ϕ)	cyclic voltammetric data[a,c] $E_{1/2}$[e],V (ΔE_p[f], mV)
[Os(PPh$_3$)$_2$(CO)(ap-OCH$_3$)]	718(3800), 396(7600), 352(10000), 330[d](9000), 258[d](23000)	352	400	1.76×10^{-3}	0.39(70), 1.06(80)
[Os(PPh$_3$)$_2$(CO)(ap-CH$_3$)]	730(4200), 432(5400), 390[d](7200), 356(14200), 256[d](19000)	356	420	0.98×10^{-3}	0.47(70), 1.15(78)
[Os(PPh$_3$)$_2$(CO)(ap-H)]	738(4200), 434(5000), 356(15000), 264[d](32000)	356	420	1.83×10^{-3}	0.51(70), 1.25(82)
[Os(PPh$_3$)$_2$(CO)(ap-Cl)]	738(4000), 428[d](4000), 396[d](6200), 358(14100), 276[d](26000)	358	412	1.12×10^{-3}	0.54(70), 1.29(80)
[Os(PPh$_3$)$_2$(CO)(ap-NO$_2$)]	706(3200), 428(6400), 338(6200), 258[d](15500)	338	375	1.84×10^{-3}	0.73(70), 1.61(85)

[a] In dichloromethane. [b] 1:9 dichloromethane−ethanol. [c] Supporting electrolyte, TBAP, reference electrode SCE; scan rate 50 mV s^{-1}. [d] Shoulder. [e] $E_{1/2} = 0.5(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are anodic peak potential and cathodic peak potential respectively. [f] $\Delta E_p = (E_{pa} - E_{pc})$.

(ap-Cl)Br] complex[11a] and this difference in bond lengths is attributable to the difference in oxidation state of osmium in the two types of complexes. As all the [Os(PPh$_3$)$_2$(CO)(ap-R)] complexes have been synthesized similarly and they show similar properties (vide infra), the other four [Os(PPh$_3$)$_2$(CO)(ap-R)] (R ≠ H) complexes are assumed to have structure similar to the [Os(PPh$_3$)$_2$(CO)(ap-H)] complex. It may be noted here that, though cyclometalated osmium(III) complexes of the 2-(arylazo)phenols of type [Os(PPh$_3$)$_2$(ap-R)Br] were synthesized before in our laboratory,[11a] there is no precedence in the literature of similar cyclometalated complexes of osmium(II).

Magnetic susceptibility measurements show that the [Os(PPh$_3$)$_2$(CO)(ap-R)] complexes are diamagnetic, which corresponds to the +2 oxidation state of osmium (low spin d^6, $S = 0$) in these complexes. ^{1}H NMR spectra of the [Os(PPh$_3$)$_2$(CO)(ap-R)] complexes have been recorded in CDCl$_3$ solution. Spectral data are given in Table 3, and a representative spectrum is shown in Figure S1 in the Supporting Information. Each complex shows broad signals within 7.1−7.5 ppm for the presence of coordinated PPh$_3$ ligands. The methyl signal of the ap-R ligand is uniformly observed as a distinct peak near 1.6 ppm. Among the expected aromatic proton signals for the coordinated ap-R ligand, most have been clearly observed while a few could not be detected due to their overlap with the PPh$_3$ signals. In the infrared spectrum each [Os(PPh$_3$)$_2$(CO)(ap-R)] complex shows a strong band near 1900 cm^{-1} (Table S1 in the Supporting Information) due to the coordinated carbon monoxide[14] and three strong bands near 520, 695, and 745 cm^{-1}, indicating the presence of coordinated PPh$_3$ ligands.[15] Sharp bands are also observed near 1210, 1540, and 1580 cm^{-1}, which were absent in the [Os(PPh$_3$)$_2$(CO)$_2$(HCOO)$_2$] complex, and hence these are attributed to the coordinated 2-(arylazo)phenolate ligand. The ^{1}H NMR and infrared spectral data of the [Os(PPh$_3$)$_2$(CO)(ap-R)] complexes are therefore consistent with their compositions.

The [Os(PPh$_3$)$_2$(CO)(ap-R)] complexes are soluble in acetone, dichloromethane, and chloroform, producing bright green solutions. Electronic spectra of the complexes have been recorded in dichloromethane solution. Spectral data are presented in Table 4, and a selected spectrum is shown in Figure S2 in the Supporting Information. All the [Os(PPh$_3$)$_2$(CO)(ap-R)] complexes show several intense absorptions in the visible and ultraviolet regions. The absorptions in the ultraviolet region are attributable to transitions within the ligand orbitals and those in the visible region are probably due to metal-to-ligand charge-transfer transitions. Multiple charge-transfer transitions in such mixed-ligand complexes may result from the lower symmetry splitting of the metal level, the presence of different acceptor orbitals, and the mixing of singlet and triplet configurations in the excited state through spin−orbit coupling.[16] To have better insight into the nature of the absorptions in the visible region, qualitative EHMO calculations have been performed[17] on

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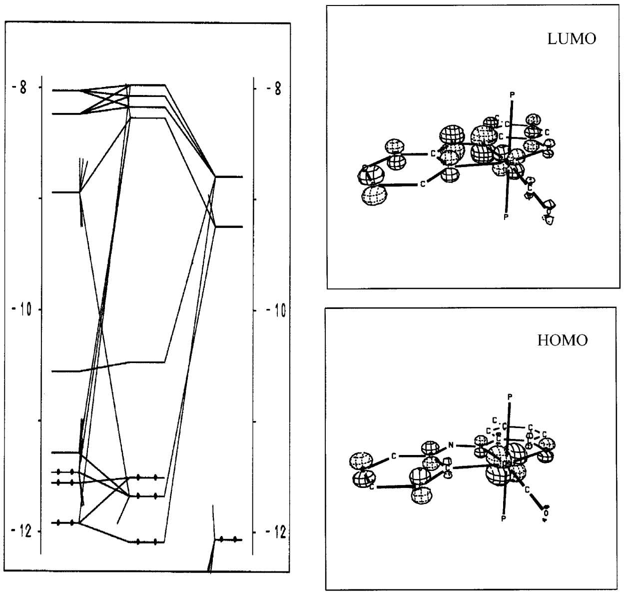

Figure 2. Partial molecular orbital diagram of [Os(PPh_3)$_2$(CO)(ap-H)].

computer-generated models of the [Os(PPh_3)$_2$(CO)(ap-R)] complexes. The results obtained are similar for all the complexes. A partial MO diagram for a representative complex is shown in Figure 2, and composition of selected molecular orbitals is given in Table S2 in the Supporting Information. The highest occupied molecular orbital (HOMO) and the next two filled orbitals (HOMO-1 and HOMO-2) have major (>50%) contributions from the osmium d_{xy}, d_{yz}, and d_{zx} orbitals. These three occupied orbitals may therefore be regarded as the osmium t_2 orbitals. The lowest unoccupied molecular orbital (LUMO), which is rather isolated, has more than 80% contribution from the 2-(arylazo)phenolate ligand and is concentrated heavily on the azo (N=N) fragment. Among the next few vacant orbitals (LUMO+1, LUMO+2, LUMO+3, etc.), LUMO+1 is primarily centered on the carbonyl ligand, while LUMO+2 and LUMO+3 are delocalized over the metalated phenyl ring and the *p*-cresol ring, respectively. The intense and rather isolated absorption in the 700−740-nm region may therefore be assigned to the charge-transfer transition taking place from the highest filled osmium t_2 orbital (HOMO) to the vacant π^*(N=N) orbital of the 2-(arylazo)phenolate ligand (LUMO). The other intense absorptions at higher energies may be assigned to charge-transfer transitions from the osmium t_2 orbitals to the higher energy vacant orbitals. As osmium(II) complexes of ligands containing strong chromophoric groups often show, in addition to intense MLCT transitions, interesting luminescence properties,[18] such properties have also been explored in the [Os(PPh_3)$_2$(CO)(ap-R)] complexes. The luminescence studies were carried out in 1:9 dichloromethane−ethanol solution at ambient temperature (298 K). When an excitation wavelength corresponding to the lowest energy absorption (~700 nm) was used, no emission was observed. However, when an excitation wavelength of ~350 nm was used, all the [Os(PPh_3)$_2$(CO)(ap-R)] complexes showed strong emission (Table 4; Figure S2 in the Supporting Information) within 375−420 nm. This indicates that transition of a metal electron to LUMO+2 (or LUMO+3) leads to a photochemically excited state, which is much more stable compared to excitation of a metal electron to LUMO (π^* of N=N) or LUMO+1 (π^* of CO). The higher stability of the photochemically excited state involving LUMO+2 (or LUMO+3) may be attributed to the possible delocalization of the excited electron over the metalated phenyl ring (or *p*-cresol ring). Quantum yields (ϕ) of these emissions, evaluated with reference to [Ru(bpy)$_3$](ClO_4)$_2$,[19] indicate that these complexes are relatively poor emitters.

Electrochemical properties of all the [Os(PPh_3)$_2$(CO)(ap-R)] complexes have been studied by cyclic voltammetry in dichloromethane solution (0.1 M TBAP). Voltammetric data are given in Table 4, and a selected cyclic voltammogram is shown in Figure S3 in the Supporting Information. Each complex shows an oxidative response within 0.39−0.73 V vs SCE, which is assigned to the osmium(II)−osmium(III) oxidation. This oxidation is reversible, characterized by a peak-to-peak separation (ΔE_p) of 70 mV, which remains unchanged upon changing the scan rate, and the anodic peak current (i_{pa}) is almost equal to the cathodic peak current (i_{pc}), as expected for a reversible electron-transfer process. Comparison of the potential of the osmium(II)−osmium(III) couple in the [Os^{III}(PPh_3)$_2$(ap-R)Br][11a] and [Os^{II}(PPh_3)$_2$(CO)-(ap-R)] complexes shows that the bivalent state of osmium is much more stabilized (more than 1.1 V) in the present group of complexes, which may be attributed to the presence of carbon monoxide in the coordination sphere instead of the bromide. CO being a strong π-acid ligand stabilizes the +2 oxidation state of osmium through effective π-interaction. The [Os(PPh_3)$_2$(CO)(ap-R)] complexes show a second oxidative response within 1.06−1.61 V vs SCE, which is also reversible in nature ($\Delta E_p \sim 80$ mV; $i_{pa} \sim i_{pc}$) and is assigned to the osmium(III)−osmium(IV) oxidation. The one-electron nature of both the oxidations has been verified by comparing their current heights (i_{pa}) with that of the standard ferrocene/ferrocenium couple under identical experimental conditions. The potential of both the osmium(II)−osmium(III) and osmium(III)−osmium(IV) oxidations has been observed to be sensitive to the nature of the substituent R in the 2-(arylazo)phenolate ligand. The potential ($E_{1/2}$) increases with increasing electron-withdrawing character of the substituent R. The plot of $E_{1/2}$ versus σ [σ = Hammett constant of R;[20] $OCH_3 = -0.27$, $CH_3 = -0.17$, H = 0.00, Cl = 0.23,

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Table 5. ESR *g* Values[a] and Electronic Spectral Values of Osmium(III) Complexes

compound	$g_\perp$	$g_\parallel$	electronic spectral data (absorption) λ_{max}/nm (ϵ/M^{-1} cm^{-1})[b]
$[Os(PPh_3)_2(CO)(ap\text{-}OCH_3)]PF_6$	2.100	1.989	1220[c](800), 944[c](1300), 746(3100), 420(5100), 378(5400), 344[c](4500)
$[Os(PPh_3)_2(CO)(ap\text{-}CH_3)]PF_6$	2.125	1.981	1220[c](800), 988(1100), 742(2200), 466[c](2400), 376(5900), 342[c](4800)
$[Os(PPh_3)_2(CO)(ap\text{-}H)]PF_6$	2.138	1.974	1210[c](800), 994(1300), 738(2200), 468[c](2100), 374(6000), 342[c](5500)
$[Os(PPh_3)_2(CO)(ap\text{-}Cl)]PF_6$	2.117	1.985	1220[c](900), 980(1200), 746(2400), 466[c](2300), 376(7000), 346(6300)
$[Os(PPh_3)_2(CO)(ap\text{-}NO_2)]PF_6$	2.078	1.992	1220[c](1700), 944[c](2500), 738(3600), 474(5400), 360(4600)

[a] In 1:1 dichloromethane−toluene at 77 K. [b] In dichloromethane solution. [c] Shoulder.

and NO_2 = 0.78] is linear for both the oxidations (Figure S3 in the Supporting Information) with a slope (ρ) of 0.30 and 0.49 V, respectively (ρ = reaction constant of this couple[21]). This linear correlation of $E_{1/2}$ versus σ with reasonable slopes (ρ) clearly shows that a single substituent on the 2-(arylazo)phenolate ligand can influence the metal-centered oxidation potential in these complexes in a predictable manner.

The electrochemical reversibility of the osmium(II)−osmium(III) couple indicate that the $[Os^{III}(PPh_3)_2(CO)(ap\text{-}R)]^+$ complexes are stable on a cyclic voltammetric time scale. The relatively low positive potential of this oxidation suggests that the oxidized complexes should also be stable on a much longer time scale. To investigate this, all the $[Os(PPh_3)_2(CO)(ap\text{-}R)]$ complexes have been coulometrically oxidized at appropriate potential in dichloromethane solution (0.1 M TBAP). The oxidations have been smooth and quantitative, associated with a color change of bright green to olive green. The solutions containing the oxidized complexes show identical cyclic voltammetric responses such as their respective precursors, except that the couple near 0.4 V now appears as a reductive response. The olive-green solutions of $[Os^{III}(PPh_3)_2(CO)(ap\text{-}R)]^+$ have been quantitatively converted back, upon coulometric reduction at 0.2 V, to the bright green solutions of $[Os^{II}(PPh_3)_2(CO)(ap\text{-}R)]$, identified by their characteristic electronic spectra. This shows that in these $[Os(PPh_3)_2(CO)(ap\text{-}R)]^{n+}$ (n = 0, 1) complexes, interconversion between the +2 and +3 states of osmium takes place without any gross change in stereochemistry.

Encouraged by the observed stability of the oxidized complexes, they have been generated in a much larger scale by coulometric oxidation of the $[Os^{II}(PPh_3)_2(CO)(ap\text{-}R)]$ complexes in 1:9 dichloromethane−acetonitrile solution using NH_4PF_6 as the supporting electrolyte and the cationic $[Os^{III}(PPh_3)_2(CO)(ap\text{-}R)]^+$ complexes have been isolated as the hexafluorophosphate salt in quantitative yield. The $[Os^{III}(PPh_3)_2(CO)(ap\text{-}R)]PF_6$ complexes show satisfactory microanalytical data (Table S1 in the Supporting Information). Magnetic susceptibility measurements show that these $[Os(PPh_3)_2(CO)(ap\text{-}R)]PF_6$ complexes are one-electron paramagnetic (μ_{eff} = 1.89−1.97 μ_B), which corresponds to the +3 state of osmium (low-spin d^5, $S = {}^1/_2$) in these complexes. All the $[Os(PPh_3)_2(CO)(ap\text{-}R)]PF_6$ complexes show axial ESR spectra in 1:1 dichloromethane−toluene solution at 77 K with distinct $g_\perp$ and $g_\parallel$ signals. A selected spectrum is shown in Figure 3 and the spectral data are given in Table 5. Infrared spectrum of each $[Os^{III}(PPh_3)_2(CO)(ap\text{-}R)]PF_6$ complex is mostly similar to that of its $[Os^{II}(PPh_3)_2(CO)(ap\text{-}R)]$ precursor. The ν_{CO} stretch is, however, shifted to ca. 1960 cm^{-1} (Table S1 in the Supporting Information). A strong band near 840 cm^{-1} is displayed by all the $[Os^{III}(PPh_3)_2(CO)(ap\text{-}R)]PF_6$ complexes, which was absent in the $[Os^{II}(PPh_3)_2(CO)(ap\text{-}R)]$ complexes, indicating the presence of the hexafluorophosphate anion. The $[Os(PPh_3)_2(CO)(ap\text{-}R)]PF_6$ complexes are soluble in acetonitrile, acetone, dichloromethane, and chloroform, producing olive-green solutions. Conductivity studies in acetonitrile solution shows that these complexes behave as 1:1 electrolytes (Λ_M = 145−160 Ω^{-1} cm^2 M^{-1}), as expected. Electronic spectra of these complexes have been recorded in acetonitrile solution. Each complex shows six[22] absorptions, two in the near-IR region, two in the visible region, and two[22] in the ultraviolet region (Table 5; Figure S4 in the Supporting Information). The two absorptions displayed by all the complexes within 1300−

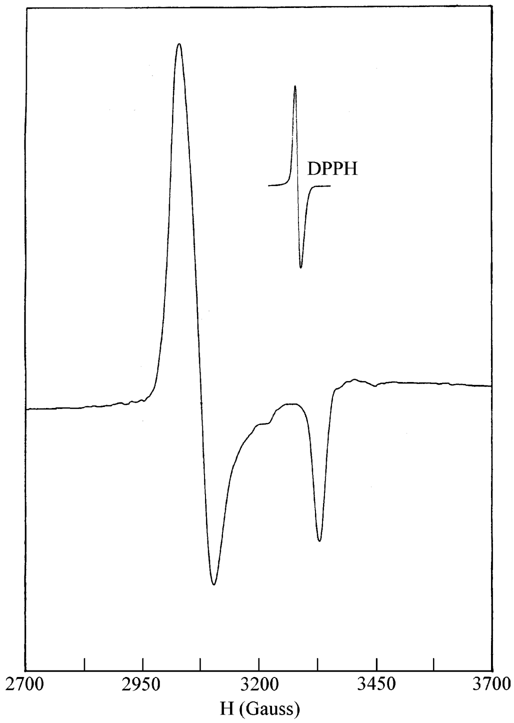

Figure 3. ESR spectrum of $[Os^{III}(PPh_3)_2(CO)(ap\text{-}H)]PF_6$ in 1:1 dichloromethane−toluene solution at 77 K.

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(22) In the $[Os^{III}(PPh_3)_2(CO)(ap\text{-}NO_2)]PF_6$ complex a total of five absorptions was observed (two in the near-IR, two in the visible, and one in the UV region).

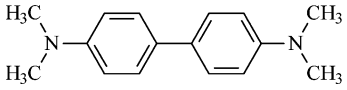
900 nm are relatively much weaker in intensity and these are assigned to transitions within the split components of the osmium t_2 orbitals. The two intense absorptions in the visible region are believed to be due to ligand-to-metal charge-transfer transitions, and those in the ultraviolet region are attributable, as before, to intraligand transitions.

The stability of the $[Os^{III}(PPh_3)_2(CO)(ap\text{-}R)]^+$ complexes and their reduction potential suggest that they might serve as mild one-electron oxidants. To check this, reaction of all the $[Os^{III}(PPh_3)_2(CO)(ap\text{-}R)]^+$ complexes was first carried out with *N*,*N*-dimethylaniline (DMA). Upon addition of DMA to a solution of any $[Os^{III}(PPh_3)_2(CO)(ap\text{-}R)]^+$ complex in acetonitrile (0.1 M TBAP), an instant color change from olive green to bright green takes place and cyclic voltammetry on the resultant solution shows a new response at 0.34 V, which is characteristic of *N*,*N*,*N*′,*N*′-tetramethylbenzidine (TMB, **8**).[23] Evidently, TMB has been produced by one-electron oxidation of DMA, followed by a coupling reaction (eq 1).

$$2DMA + 2[Os^{III}(PPh_3)_2(CO)(ap\text{-}R)]^+ \rightarrow TMB + 2\,[Os^{II}(PPh_3)_2(CO)(ap\text{-}R)] + 2H^+ \quad (1)$$

Conversion of $[Os^{III}(PPh_3)_2(CO)(ap\text{-}R)]^+$ to $[Os^{II}(PPh_3)_2(CO)(ap\text{-}R)]$ has been confirmed by their spectra in the visible region. It appears from the current height measurement of the TMB response that about 45% of the oxidant has been utilized in the coupling reaction. The remainder has probably been wasted in the side reactions.[24] Another organic compound, viz. 1,2-naphthaquinone-1-oxime (Hnqo, **9**), was tried as the next reductant. Addition of Hnqo to an acetonitrile solution of any $[Os^{III}(PPh_3)_2(CO)(ap\text{-}R)]^+$ complex also causes the expected color change as before and the ESR spectrum recorded on the resultant solution at ambient temperature shows an intense signal at $g = 2.006$ with three nitrogen hyperfine lines (Figure S5 in the Supporting Information), characteristic of the iminoxy radical ($nqo^\bullet$).[25] This shows that $[Os^{III}(PPh_3)_2(CO)(ap\text{-}R)]^+$ truly oxidizes Hnqo to generate the $nqo^\bullet$ radical (eq 2).

$$Hnqo + [Os^{III}(PPh_3)_2(CO)(ap\text{-}R)]^+ \rightarrow nqo^\bullet + [Os^{II}(PPh_3)_2(CO)(ap\text{-}R)] + H^+ \quad (2)$$



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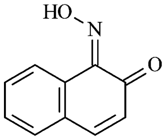

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An easily oxidizable transition metal complex, viz. $[Os^{II}(bpy)_2Br_2]$, has also been used as the reductant. Equimolar quantities of $[Os^{II}(bpy)_2Br_2]$ and any $[Os^{III}(PPh_3)_2(CO)(ap\text{-}R)]^+$ complex were taken together in acetonitrile (0.1 M TBAP) and cyclic voltammetry on the resultant solution confirms that the expected redox reaction (eq 3) has indeed taken place.

$$[Os^{II}(bpy)_2Br_2] + [Os^{III}(PPh_3)_2(CO)(ap\text{-}R)]^+ \rightarrow [Os^{III}(bpy)_2Br_2]^+ + [Os^{II}(PPh_3)_2(CO)(ap\text{-}R)] \quad (3)$$

A reversible one-electron reduction at 0.01 V, characteristic of $[Os^{III}(bpy)_2Br_2]^+$,[26] is observed together with the reversible one-electron oxidation of $[Os^{II}(PPh_3)_2(CO)(ap\text{-}R)]$ within 0.39−0.73 V. These redox reactions show that the $[Os^{III}(PPh_3)_2(CO)(ap\text{-}R)]^+$ complexes can indeed function as efficient one-electron oxidants in a nonaqueous medium.

Conclusions

The present study shows that C−H activation of selective organic substrates may be easily achieved by their reaction with $[Os(PPh_3)_2(CO)_2(HCOO)_2]$, leading to the formation of interesting organoosmium complexes. Such possibilities are currently under exploration.

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Supporting Information Available: ^1H NMR spectrum of $[Os(PPh_3)_2(CO)(ap\text{-}OCH_3)]$ (Figure S1), absorption and emission spectra of $[Os(PPh_3)_2(CO)(ap\text{-}CH_3)]$ (Figure S2), cyclic voltammogram of $[Os(PPh_3)_2(CO)(ap\text{-}OCH_3)]$ and least-squares plot of $E_{1/2}$ values of Os(II)−Os(III) and Os(III)−Os(IV) couples versus σ (Figure S3), absorption spectrum of $[Os(PPh_3)_2(CO)(ap\text{-}H)]PF_6$ (Figure S4), and ESR spectrum of the iminoxy radical ($nqo^\bullet$) (Figure S5), and tables containing microanalytical and ν_{CO} data of the $[Os(PPh_3)_2(CO)(ap\text{-}R)]$ and $[Os(PPh_3)_2(CO)(ap\text{-}R)]PF_6$ complexes (Table S1) and composition of selected molecular orbitals of the $[Os(PPh_3)_2(CO)(ap\text{-}R)]$ complexes (Table S2). X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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