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Osmium-Promoted Oxidative Dimerization of Aminoarenes to *N*-Aryl-*o*-arenoquinone Diimines (L). Synthesis, Structure, Electrochemistry, and Reactivity of $OsBr_2L_2$

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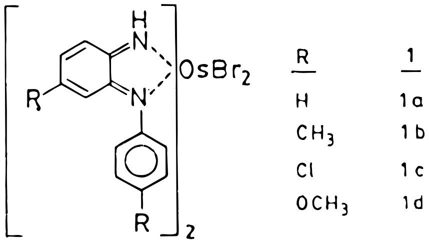
A family of *o*-arenoquinone diimine chelates, $OsBr_2L_2$ (**1**, L = *N*-aryl-*o*-arenoquinone diimine), were isolated from the reaction of $(NH_4)_2OsBr_6$ and primary aromatic amines, Ar−NH_2. These complexes constitute the first examples of osmium compounds of the *o*-benzoquinone diimine family. The above oxidative dimerization reaction of Ar−NH_2 was authenticated by the X-ray structure determination of a representative example. The X-ray structure of $OsBr_2L_2$ (R = H) revealed a cis geometry with respect to two coordinated bromides. The bond length trends within the chelate as well as the aromatic rings are consistent with a diimine character of the ligand bound to osmium in its bivalent oxidation state. The complexes showed multiple transitions in near-IR and visible regions. These are electroactive and undergo multiple electron transfer. Three successive voltammetric responses, two oxidative and one reductive, were observed. The potential range was +1.7 to −0.8 V vs SCE in CH_3CN solution (Pt electrode). The potentials of the above responses for differently substituted compounds depend on the Hammett $\sum\sigma_p$ parameters of the substitution on L. The EPR spectrum of the electrogenerated 1-electron-oxidized complex $\mathbf{1a}^+$ is described. The electrode potentials of **1** are compared with those of related systems. A qualitative correlation between Os−N bond distances and Os(III)/Os(II) formal potentials for the Os(II) compounds of three different N,N donors is noted. The synthesis of a mixed-ligand tris chelate, $[Os(bpy)L_2](ClO_4)_2\cdot H_2O$, is described, involving the reaction of 1 equiv of **1** with 2 equiv of $Ag(bpy)_2^+$. The redox properties of the tris complex are reported. Crystal data for $OsBr_2L_2$ (R = H) are as follows: empirical formula $C_{24}H_{20}Br_2N_4Os$; crystal system triclinic, space group $P\bar{1}$; $a = 10.464(6)$ Å, $b = 11.778(6)$ Å, $c = 12.595(10)$ Å; $\alpha = 103.86(5)°$, $\beta = 112.72(6)°$, $\gamma = 107.79(4)°$; $V = 1245.3(10)$ Å^3; $Z = 2$; $R = 4.46\%$; $R_w = 5.21\%$.

Introduction

The selective transformation of organic functions by a metal is an attractive area of chemical research. In this report, we introduce examples of the Os^{IV}-promoted oxidative dimerization reaction of primary aromatic amines, Ar−NH_2, leading to *N*-aryl-*o*-arenoquinone diimines (L). The resultant compounds, $OsBr_2L_2$ (**1**),belong to the family of complexes[1−5] of *o*-benzoquinone diimine. This class of complexes exhibit many interesting properties not only because of their redox propensities[1,2] but also due to the considerable mixing[6] between metal and ligand orbitals. We note here that our osmium diimine compounds represent the first examples of osmium compounds of the above family. To the best of our knowledge, the only related known[3] osmium compound was an osmium(VIII) dioxo species of composition $OsO_2(opda)_2$ (opda = *o*-phenylenediamine).



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Results and Discussion

A. The Reaction. The reaction procedure consists of heating a mixture of $(NH_4)_2OsBr_6$ (0.2 g) and a large excess of primary aromatic amine, Ar−NH_2 (0.5 g), at 120−130 °C. Chromatographic workup of the reaction mixture afforded $OsBr_2L_2$, **1** (eq i), which was crystallized from a 1:1 dichloromethane−hexane mixture and obtained as dark crystals in ca. 50% yield. The reaction does not take place in a solvent medium (e.g., 2-methoxyethanol) using a stoichiometric amount of Ar−NH_2 (Experimental Section).

$$(NH_4)_2OsBr_6 \xrightarrow[120-130\ °C]{Ar-NH_2} OsBr_2L_2 \qquad \text{(i)}$$

The transformation Ar−NH_2 → **1** involves the transfer of 4 electrons and 4 protons. Therefore, a total of 8 electrons and 8 protons is released for the formation of 2L. In contrast, the metal oxidation levels in starting $OsBr_6^{2-}$ and **1** differ only by 2 units. The mechanism of the formation[7] of **1** in reaction i has not yet been established. However, we wish to note that reaction i does not occur in the absence of O_2 (in N_2 atmos-

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Table 1. Characterization Data

compd	IR,[a] cm^{-1}		^{1}H NMR,[b] ppm		electronic:[c] λ_{max}, nm (ϵ, M^{-1} cm^{-1})
	ν_{N-H}	$\nu_{C=N}$	δ_{Me}	δ_{N-H}	
1a	3200	1590		13.6	1150[d] (650), 900 (780), 605[d] (4312) 500 (20 020), 375 (7290)
1b	3220	1590	2.4	13.3	1199[d] (860), 880 (930), 620[d] (5375) 505 (25 900), 378 (8300)
1c	3180	1585		13.7	1175[d] (1125), 950 (1620), 620[d] (7200) 502 (21 580), 385 (9000)
1d	3240	1595	*e*	*e*	1075[d] (895), 850 (1030), 630[d] (4760) 522 (23 810), 400 (8160)

[a] In Nujol. [b] In CDCl$_3$; aromatic proton resonances occur in the region δ 5−8. [c] In acetonitrile. [d] Shoulder. [e] Not studied.

phere). It is, therefore, proposed that the template synthesis of L from Ar−NH$_2$ presumably occurs via aerial oxidation. It may be noted that ruthenium- and osmium-promoted oxidation of amine to imine by O$_2$ has been documented[8] in the literature.

B. Formulation and Spectral Characterization. All the Os−diimine compounds, **1**, gave satisfactory analyses. These molecular complexes are soluble in common organic solvents and are diamagnetic. Selected spectral data are collected in Table 1. The N−H stretch occurs[2] as a sharp feature of moderate intensity in the range 3250−3150 cm^{-1}. The presence of a strong[9] C=N stretch near 1600 cm^{-1} characterizes the presence of a diimine chromophore in the compound. The ^{1}H NMR spectral features of the complexes consist of sharp methyl resonances (for **1b**) at δ 2−3 and resolved aromatic proton resonances at lower magnetic fields. The N−H resonance was observed[10] as a relatively broad singlet near δ 13.5 (width at half-height 0.06 ppm). Interestingly, each kind of proton of L gave rise to one signal. Thus, the two ligands in **1** are magnetically equivalent—a 2-fold symmetry axis is, therefore, required. Due to the unsymmetric nature of L, there exist[11] five geometric possibilities for OsBr$_2$L$_2$. These complexes are further characterized on the basis of a single-crystal X-ray analysis of a representative complex, viz. **1a**.

The electronic spectral data for the OsBr$_2$L$_2$ complexes are given in Table 1. The lowest energy transition occurring in the near-IR region is weak and broad. It appears that it is a combination of two transitions. By analogy to the assignments made[9,12,13] for the low-energy transitions in OsBr$_2$(tap)$_2$ (tap = 2-(*m*-tolylazo)pyridine), this transition is assigned to the partially allowed singlet−triplet MLCT transitions. The visible-region strongest band at ca. 510 cm^{-1} is systemetically present in the spectra of all four complexes (**1a**−**d**). This band may be assigned[12,13] to an allowed MLCT (singlet−singlet) transition.

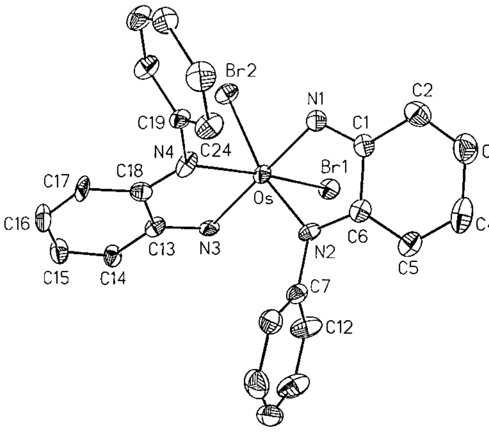

Figure 1. ORTEP plot and labeling scheme for OsBr$_2$L$_2$ with all atoms represented by their 40% probability ellipsoids.

Table 2. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for **1a**

Distances			
Os−Br(1)	2.519(2)	N(1)−C(1)	1.317(19)
Os−Br(2)	2.523(3)	N(2)−C(6)	1.338(19)
Os−N(1)	1.998(11)	N(2)−C(7)	1.417(15)
Os−N(2)	2.000(11)	N(3)−C(13)	1.325(19)
Os−N(3)	1.994(10)	N(4)−C(18)	1.312(20)
Os−N(4)	2.017(11)	N(4)−C(19)	1.458(11)
Angles			
N(1)−Os−N(2)	77.9(4)	N(3)−Os−N(4)	76.6(4)
Os−N(1)−C(1)	116.7(7)	Os−N(3)−C(13)	118.2(6)
Os−N(2)−C(6)	115.5(8)	Os−N(4)−C(18)	117.5(7)
N(1)−C(1)−C(6)	113.6(12)	N(3)−C(13)−C(18)	112.8(12)
N(2)−C(6)−C(1)	114.1(12)	N(4)−C(18)−C(13)	113.8(13)

C. Crystal Structure. The final characterization of the osmium−diimine complex formed from reaction i was made by a structure determination of OsBr$_2$L$_2$. A view of the molecule is shown in Figure 1, and selected bond parameters are collected in Table 2. The coordination sphere involves OsBr$_2$N$_4$. Two bromides are cis to each other and the aryl-substituted imine nitrogens are also in relative cis positions. The imine C−N bond lengths, average 1.323(19) Å, are within the range of values expected[14] for the diimine oxidation state of L. These bonds are much shorter than the two C−N single bonds, viz. C(19)−N(4) and C(7)−N(2), average 1.437(13) Å. Moreover, the C−C bond lengths (average 1.349(26) Å) at positions that would have localized double bonds for the diimine form of the ligands are significantly shorter than the other C−C bond lengths (average 1.418(20) Å) in the same ring. Furthermore, each chelate is a good plane, with no atom deviating by more than 0.07 Å, which further confirms localized diimine character of the ligand L. The Os−Br lengths in our complex compare well[15] with the corresponding Os−Br lengths in OsBr$_2$(C$_2$H$_6$OS)$_4$. The molecule approximates to overall C_2 symmetry. The 2-fold axis bisects the Br(1)−Os−Br(2) angle, as well as the N(2)−Os−N(4) angle.

D. Redox Properties. The redox behavior of the diimine complexes, **1**, were studied by cyclic voltammetry in acetonitrile (0.1 M TEAP), in the potential range +2.0 to −1.8 V, using a platinum working electrode. The potentials are referenced to the saturated calomel electrode (SCE).

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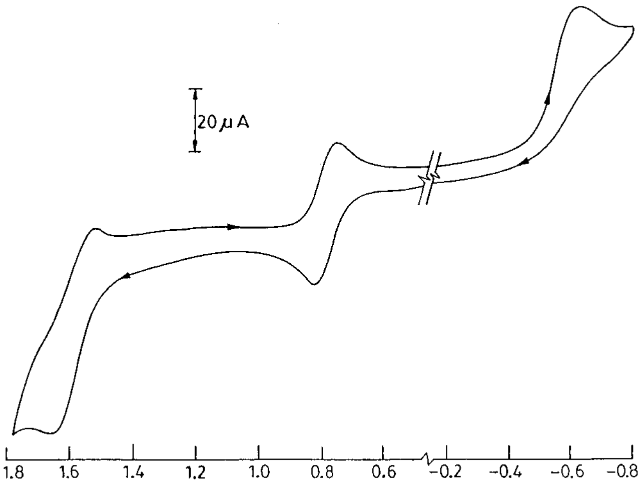

Figure 2. Segmented cyclic voltammogram of $OsBr_2L^1_2$ in CH_3CN (0.1 M TEAP) at a platinum electrode; scan rate 50 mV s^{-1}.

The cyclic voltammogram of a typical $OsBr_2L_2$ complex, displayed in Figure 2, showed three 1-electron redox processes in the above potential range. Two of these are reversible and oxidative in nature, occurring at the positive potential (vs SCE). The third cathodic response is irreversible and occurs at the negative potential (eq ii). There are also two more very weak responses which follow the cathodic response.

$$\mathrm{Os^{IV}Br_2L_2}^{2+} \underset{\mathrm{I}}{\overset{e^-}{\rightleftharpoons}} \mathrm{Os^{III}Br_2L_2}^{+} \underset{\mathrm{II}}{\overset{e^-}{\rightleftharpoons}} \mathrm{Os^{II}Br_2L_2} \xrightarrow[\mathrm{III}]{e^-} \mathrm{Os^{II}L{\cdot}LBr_2}^{-} \rightarrow \text{decomposition} \quad \text{(ii)}$$

The two redox processes, viz. I and II, occurring at the positive potential (vs SCE) correspond[9] to the successive oxidation of the metal center. The process occurring at the negative potential formally corresponds[12] to the ligand reduction. Similar irreversible ligand reductions have been noted[9] for osmium(II)−dihalo complexes. The potentials of the above couples all depend linearly[16] on the Hammett $\sum\sigma_p$ parameter (Supporting Information) of the substitution on L. Indeed there is a quite large change in the donor character of ligand L over the above series of substituents (**1a**−**d**). There is an anodic shift as the electron-withdrawing ability of the substituent increases (Table 2). This shift is quite large. For example, couple II shifts from 0.57 V in **1d** to 0.94 V in **1c**. The observed potential, 0.94 V, for the **1c**$^+$/**1c** couple is notably high—a value which is similar to the highest potential reported[9] for an Os(III)/Os(II) couple in OsX_2(bidentate)$_2$ (X = Cl, Br) systems. In particular, the formal potential value of **1c** is nearly 1 V more positive than the corresponding value[17] of $OsCl_2(bpy)_2$. The values of the reaction constants for the above redox processes are as follows: I, 0.13 V; II, 0.18 V; III, 0.16 V.

One-electron coulometric oxidation of **1a** at 0.9 V afforded a brown solution which displayed three voltammetric responses (two reductions and one oxidation), coinciding with those of $OsBr_2L_2$ (R = H). One-electron reduction of the oxidized solution at 0.5 V regenerated **1a**. Evidently **1a**$^+$ retains the gross structure of the parent complex. It has not been possible to isolate **1a**$^+$ as a pure salt, but its EPR has been studied in acetonitrile−toluene glass at 77 K. The electrogenerated complex displays a rhombic EPR spectrum with three distinct resonances at $g = 2.693$, 2.401, and 1.638, which characterize[18] the trivalent oxidation state of osmium (d^5) in **1a**$^+$. The trivalent complex **1a**$^+$ also can be generated by the chemical oxidation of **1a** by Br_2.

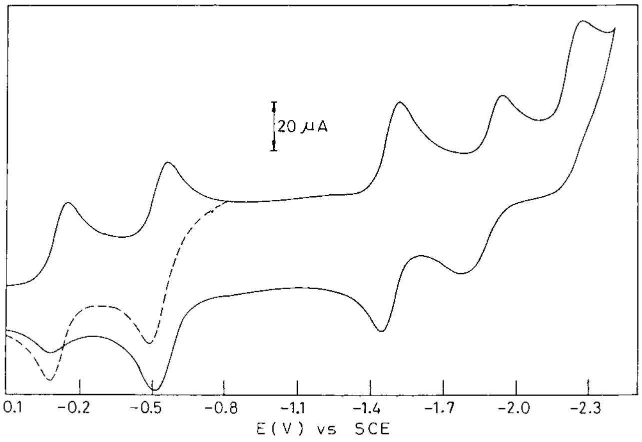

Figure 3. Segmented cyclic voltammogram of $[Os(bpy)L_2](ClO_4)_2{\cdot}H_2O$ in CH_3CN (0.1 M TEAP) at a platinum electrode; scan rate 50 mV s^{-1}. The broken line (- - -) indicates that the scan was reversed at −0.8 V.

It is worthwhile to note that a qualitative correlation between Os−N bond distance and Os(III)/Os(II) formal potential exists in a group of complexes of the type $OsX_2(NN)_2$ (X = Cl, Br) where the NN ligand is bpy, tap, or L. The Os−N bond distance in *cis*-$OsBr_2(bpy)_2$ is not known, but it is reasonable to assume a value of ca. 2.064 Å as in $[Os(bpy)_3](PF_6)_2$.[19] Clearly, the Os−N distances in **1a** are comparable to those in[12] $OsCl_2(tap)_2$ and are shorter than the Os−N distance in $OsBr_2(bpy)_2$. With increasing π-interactions, the Os−N distance is expected to decrease. Thus, the stronger the Os−N bond, the higher the potential required for oxidation of the metal. Therefore, it may be suggested that a short Os−N bond distance in **1a** is responsible for relatively high $E°_{298}$ values.

E. Reactivity. In this section, we describe the reaction of **1a** with $Ag(bpy)_2^+$. This type of reaction has been shown to be particularly useful[20] for the synthesis of mixed-ligand tris complexes, which were, otherwise, not obtainable. It may be noted that the electrochemistry and photochemistry of tris-chelated osmium diimines are of interest.[21] Reaction iii occurs

$$\mathrm{OsBr_2L_2} + 2\mathrm{Ag(bpy)_2}^{+} \rightarrow \mathrm{Os(bpy)L_2}^{2+} + 2\mathrm{AgBr} + 3\mathrm{bpy} \quad \text{(iii)}$$

smoothly to yield the mixed tris chelate $Os(bpy)L_2^{2+}$, which was isolated as its perchlorate salt from the reaction mixture in a high yield (76%). Interestingly, the compound undergoes five reversible to quasireversible reductive responses in the potential range 0 to −2.3 V: −0.11, −0.53, −1.48, −1.86, and −2.23 V (Figure 3). These reductions are attributed to successive ligand reductions. Both, diimines and bpy are known to undergo[1b] two electron reductions. Therefore, a total of six electron reductions of the mixed ligand complex was expected. We believe that the sixth response in this case occurs beyond our accessible potential range. The oxidation of the above complex occurs at a relatively high potential, 1.28 V. We wish to note that examples of such a redox series are scarce.[12]

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Table 3. Crystallographic Data for **1a**

empirical formula	$C_{24}H_{20}Br_2N_4Os$	V, Å^3	1245.3(10)
fw	712.2	Z	2
space group	$P\bar{1}$	T, K	295
a, Å	10.464(6)	λ(Mo Kα), Å	0.710 73
b, Å	11.778(6)	ρ_{calcd}, g cm^{-3}	1.991
c, Å	12.595(10)	transm coeff[a]	0.3006−1.0000
α, deg	103.86(5)	R,[b] %	4.46
β, deg	112.72(6)	R_w,[c] %	5.21
γ, deg	107.79(4)	GOF[d]	1.30

[a] Maximum value normalized to 1. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. $w^{-1} = \sigma^2(|F_o|) + g|F_o|^2$; $g = 0.0004$ for **1a**. [d] The goodness of fit is defined as $[w(|F_o| - |F_c|)^2/(n_o - n_v)]^{1/2}$ where n_o and n_v denote the number of data and variables, respectively.

Table 4. Electrochemical Data

	cyclic voltammetric data:[a] $E_{1/2}$, V (ΔE_p, mV)[b]		
compd	$\mathbf{1}^{2+} \rightleftharpoons \mathbf{1}^{+}$	$\mathbf{1}^{+} \rightleftharpoons \mathbf{1}$	$\mathbf{1} \rightarrow \mathbf{1}^{-}$
1a[c]	1.58 (100)	0.80 (70)	−0.63
1b	1.52 (120)	0.70 (70)	−0.69
1c	1.69 (110)	0.94 (80)	−0.42
1d	1.42 (90)	0.57 (70)	−0.76

[a] Conditions: solvent, acetonitrile; supporting electrolyte, TEAP (0.1 M); working electrode, platinum; reference electrode, SCE; solute concentration, ca. 10^{-3} M. [b] $E_{1/2}$ is calculated as the average of anodic (E_{pa}) and cathodic (E_{pc}) peak potentials; $\Delta E_p = E_{pa} - E_{pc}$. [c] $n = 0.98$; $n = Q/Q'$, where Q' is the calculated coulomb count for the transfer of 1 electron and Q is the observed coulomb count after exhaustive electrolysis; oxidation was performed at 1.0 V vs SCE in CH_3CN (0.1 M $(NEt_4)(ClO_4)$).

Table 5. Bond Distances and $E°_{298}$ Values

compd	Os^{II}−N, Å	$E°_{298}$(Os(III)/Os(II)), V
$OsCl_2(bpy)_2$	2.064[a]	−0.04[e]
$OsCl_2(tap)_2$	1.974,[b] 2.065[c]	0.96[f]
$OsBr_2L_2$ (R = H)	2.002[d]	0.80[d]

[a] Os−N in $OsCl_2(bpy)_2$ is assumed to be similar to that in $[Os(bpy)_3](PF_6)_2$, ref 18. [b] Os−N(azo), ref 12. [c] Os−N(py), ref 12. [d] This work. [e] Reference 17. [f] Reference 9.

F. Conclusions. A series of $Os^{II}Br_2L_2$ complexes have been isolated from the reaction of $(NH_4)_2OsBr_6$ and Ar−NH_2. This template synthesis of L represents an example of unusual oxidative ortho-dimerization of an aromatic amine leading to an *N*-aryl-*o*-arenoquinone diimine which is mediated by Os(IV). The $OsBr_2L_2$ complexes represent the first examples of osmium complexes of the benzoquinone diimine family. Strong π-interaction has been noted in the complexes, which is reflected in the short Os−N distance and high osmium(III)−osmium(II) formal potentials. Silver(I)-assisted substitution of the two cis bromides in **1a** by bpy has resulted in a mixed tris chelate which showed successive 5-electron transfer, presumably at the ligand center. Ongoing studies in this area indicate that the prospect is bright for generalization of the metal-catalyzed oxidation of aromatic amines leading to a wide variety of redox-noninnocent benzoquinone diimine and related complexes.

Experimental Section

Materials. Ammonium hexabromoosmate(IV) was prepared by a reported method,[22] as was the silver complex $[Ag(bpy)_2](NO_3)\cdot 2H_2O$.[23] Solvents and chemicals used for syntheses were of analytical grade. Supporting electrolyte (tetraethylammonium perchlorate, TEAP) and solvents for electrochemical work were obtained as before.[24]

Physical Measurements. A Hitachi 330 spectrophotometer was used to record electronic spectra. IR spectra was recorded with a Perkin-Elmer 783 IR spectrophotometer. A Varian E-109C spectrometer fitted with a quartz dewar was used for EPR studies. DPPH ($g = 2.0037$) was used to calibrate the spectra. ^1H NMR spectra were recorded in $CDCl_3$ with a Varian VXR 300S spectrometer. TMS was used as an internal standard. A Perkin-Elmer 240C elemental analyzer was used to collect microanalytical data (CHN). Electrochemical measurements were obtained under a nitrogen atmosphere on a PAR Model 370-4 electrochemistry system as described earlier.[25] All potentials reported in this work are referenced to the saturated calomel electrode (SCE) and are uncorrected for junction contribution.

Syntheses of Complexes. The complexes were synthesized by a general method. Details are given for one representative compound.

Dibromobis(*N*-phenyl-*o*-benzoquinone diimine)osmium(II), $OsBr_2L^1_2$ (1a). A sample of $(NH_4)_2OsBr_6$ (0.2 g, 0.28 mmol) was added to 0.5 mL of aniline, and the mixture was heated on an oil bath at 120−130 °C for 45 min. The initial blue color gradually changed to violet. The mass was extracted with chloroform, and ether was added. The crude product, thus obtained, was purified on a silica gel column (diameter 1 cm; height 12 cm). A violet band was eluted with a 9:1 chloroform−acetonitrile mixture. Another brown-violet band remained uneluted at the top of the column. On evaporation of the solvent and subsequent crystallization from dichloromethane−hexane (1:1) solution, shiny green crystals were obtained. Yield: 0.1 g, 50%. Anal. Calcd for $C_{24}H_{20}Br_2N_4Os$: C, 40.44; H, 2.81; N, 7.88. Found: C, 40.60; H, 2.93; N, 7.89.

A similar reaction using a stoichiometric amount of aniline in a high-boiling solvent, 2-methoxyethanol, failed to afford **1a**. A mixture of $(NH_4)_2OsBr_6$ and aniline in a 1:4 molar proportion did react to form **1a**, but the yield was very poor (10−12%). Most of $(NH_4)_2OsBr_6$ remained unreacted.

Other substituted compounds were synthesized similarly. The yields and the analytical data of the respective compounds are as follows. **1b**: yield 0.098 g, 45%. Anal. Calcd for $C_{28}H_{30}Br_2N_4Os$: C, 43.62; H, 3.89; N, 7.27. Found: C, 43.54; H, 3.90; N, 7.22. **1c**: yield 0.12 g, 50%. Anal. Calcd for $C_{24}H_{18}Br_2Cl_4N_4Os$: C, 33.79; H, 2.11; N, 6.57. Found: C, 33.67; H, 2.10; N, 6.60. **1d**: yield 0.11 g, 47%. Anal. Calcd for $C_{28}H_{30}O_4Br_2N_4Os$: C, 40.28; H, 3.59; N, 6.71. Found: C, 40.34; H, 3.41; N, 6.80.

(2,2′-Bipyridine)bis(*N*-phenyl-*o*-benzoquinone diimine)osmium(II) Perchlorate Hydrate, $[Os(bpy)L_2](ClO_4)_2\cdot H_2O$. To a suspension of **1a** (1 mmol) in methanol (20 cm^3) was added a solution of $[Ag(bpy)_2](NO_3)\cdot 2H_2O$ (2 mmol) in methanol (20 cm^3), and the resulting mixture was heated to reflux for 2 h. It was then cooled and filtered through a G-4 sintered-glass funnel to remove insoluble AgCl. Then the solution was concentrated to 10 cm^3 and was layered over an aqueous solution of $NaClO_4$. The deep brown crystals were collected by filtration and dried in vacuo. Yield: 76%. Anal. Calcd for $C_{34}H_{30}O_9Cl_2N_6Os$: C, 44.00; H, 3.24; N, 9.06. Found: C, 44.10; H, 3.21; N, 9.14.

X-ray Structure Determination. X-ray-quality crystals (0.4 × 0.3 × 0.25 mm^3) of **1a** were obtained by slow diffusion of a dichloromethane solution of the complex into hexane. Cell parameters were obtained by least-squares fits of 30 machine-centered reflections. Systematic absences afforded the space group $P\bar{1}$. Data were collected ($3° \leqslant 2\theta \leqslant 43°$) on a Nicolet R3m/V diffractometer (295 K) with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Two check reflections measured after every 198 reflections showed no significant changes in intensity over 25 h exposure to X-rays. Data were corrected for Lorentz−polarization effects and for absorption (azimuthal scan).[26] Of the 2953 reflections collected, 2858 were unique, and 2386 reflections satisfying the criterion $I > 3\sigma(I)$ were used for structure solution by the Patterson heavy-atom method

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employing the SHELXTL-PLUS program[27] package on a MicroVax II computer. Refinement was done by the full-matrix least-squares method. All non-hydrogen atoms were made anisotropic. Hydrogen atoms were added at calculated positions with fixed $U = 0.08$ Å^2 and refined. Significant crystal data are listed in Table 3. Atomic coordinates and isotropic thermal parameters have been deposited as Supporting Information.

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Supporting Information Available: Atomic coordinates and equivalent isotropic displacement coefficients (Table S1), complete bond lengths (Table S2), bond angles (Table S3), anisotropic displacement coefficients (Table S4), and hydrogen atom positional parameters (Table S5) for **1a**, the electronic spectrum of **1a** (Figure S1), and a Hammett correlation diagram for $OsBr_2L_2$ (**1a**−**d**) (Figure S2) (7 pages). Ordering information is given on any current masthead page.

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