One-Pot Synthesis of Dihalo(porphyrinato)osmium(IV) Complexes. Evidence for Monohalo(carbonyl)osmium(III) Intermediates[†]

Zeev Gross* and Atif Mahammed

Department of Chemistry, Technion—Israel Institute of Technology, Haifa 32000, Israel

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trans-Dichloro-, *trans*-dibromo-, and *trans*-diiodoosmium(IV) tetraarylporphyrins were obtained by extremely facile synthetic routes directly from the reactions of the corresponding (carbonyl)osmium(II) complexes with CCl_4, CBr_4, and CI_4, respectively. At short reaction times, appreciable amounts of intermediates—one for each reaction—were observed by spectroscopic investigations. These intermediates were shown to be (carbonyl)(halo)(porphyrinato)osmium(III) complexes by independent preparation of an authentic (carbonyl)(bromo)(porphyrinato)osmium(III) complex, which was identical to the reaction intermediate in the reaction of CBr_4 and very similar to those of the other reactions. This provided strong evidence for the reaction mechanism, two stepwise one-electron oxidations of the metal ion. The relatively strong binding of carbon monoxide to osmium(III) is proposed to be an important factor in avoiding dimerization of the reaction intermediates.

Introduction

Ongoing interest in the chemistry of ruthenium(IV) and osmium(IV) porphyrins derives from their rich coordination chemistry,[1−5] including very interesting organometallic complexes.[3,4a] The most important precursors of organoruthenium and organoosmium porphyrins are *trans*-dihalometal(IV) complexes, $[M^{IV}(por)X_2]$, with M = Ru, Os, and X = halide anion. It was also recently proposed that $[Ru^{IV}(por)X_2]$ complexes are important intermediates in the highly efficient oxygenation of hydrocarbons by aromatic *N*-oxides under catalysis of ruthenium porphyrins in the presence of mineral acids.[6] Practically all ruthenium and osmium porphyrin complexes are prepared from the corresponding metal carbonyls, $[M^{II}(por)(CO)]$. The carbonyl group in these complexes is considered chemically inert, and most existing synthetic routes for preparation of more reactive derivatives rely on its removal by either oxidative or photochemical methods. The full series of dihalo(porphyrinato)ruthenium complexes—$[Ru^{IV}(por)X_2]$, with X = F, Cl, Br, I—can be prepared from [Ru(por)(CO)] in three distinct steps. The first two steps, leading to the dinuclear complexes $[Ru(por)]_2$, require however photochemical, high temperatures, and ultrahigh-vacuum procedures.[3] Such lengthy and experimentally demanding procedures were avoided in the recently reported two-step syntheses of the first two dihalo(porphyrinato)osmium(IV) complexes by three independent groups. In all three cases, the carbonyl complexes [Os(por)(CO)] were first oxidized to the corresponding *trans*-dioxoosmium(VI) porphyrins. Subsequent reduction of $[Os^{VI}(oep)(O)_2]$ with Br_2 afforded $[Os^{IV}(oep)Br_2]$ in 40% yield,[2c] and $[Os^{IV}(ttp)Cl_2]$ was obtained in yields of 80% and 51% from the reaction of $[Os^{VI}(ttp)(O)_2]$ with $SOCl_2$ or $SnCl_2$, respectively.[4]

In line with the desire for simple methods for the preparation of $[M^{IV}(por)X_2]$ derivatives, we have very recently discovered an extremely simple alternative one-pot synthetic route to $[Ru^{IV}(por)X_2]$ complexes. Thus, $[Ru^{IV}(tdmpp)Cl_2]$ and $[Ru^{IV}(tdmpp)Br_2]$ were prepared directly from [Ru(tdmpp)(CO)] in > 80% yields by simply heating it with CCl_4 or CBr_4.[5] For non sterically hindered porphyrins, such as [Ru(ttp)(CO)], dimeric derivatives were however formed. We now report our investigation of that reaction for osmium porphyrins, which shows that it has even a larger scope for Os than for Ru. Thus, the dichloro-, dibromo-, and diiodoosmium(IV) complexes of both ttp and tmp were prepared in very simple one-pot procedures directly from the corresponding (carbonyl)osmium(II) porphyrins (Scheme 1). The *in situ* observation of $[Os^{III}(por)(CO)(X)]$ intermediates during these reactions—identified by comparison to the independently prepared and fully characterized $[Os^{III}(por)(CO)(Br)]$ complex—clearly suggest that the transformations of $[Os^{II}(por)(CO)]$ to $[Os^{IV}(por)X_2]$ proceed by two distinct one-electron oxidation steps. In addition, the characterization of the intermediates as (carbonyl)osmium(III) complexes also provided a clue about the different reaction pathways of [Os(por)(CO)] and [Ru(por)(CO)].

Results and Discussion

The reactions were investigated for two porphyrin derivatives, one which can form dimeric products—[Os(ttp)(CO)]—and one which cannot—[Os(tmp)(CO)]. In the reactions with CCl_4 the reagent served as solvent as well and the reactions with CBr_4 and CI_4 were performed in benzene at reflux. Since CI_4 releases I_2 very easily, the last reactions were also studied with I_2. The yields were very high for both CI_4 and I_2, and accordingly the syntheses were much more conveniently performed with I_2. The

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[†] Abbreviations used: por = unspecified porphyrin dianion; oep = 2,3,7,8,12,13,17,18-octaethylporphyrin dianion; tpp = 5,10,15,20-tetraphenylporphyrin dianion; ttp =5,10,15,20-tetra-*p*-tolylporphyrin dianion; tmp = 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphyrin dianion; tdmpp = 5,10,15,20-tetrakis(2,6-dimethylphenyl)porphyrin dianion.

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(1) Groves, J. T.; Scott, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 5594. Cheng, S. Y. S.; Rajapakse, N.; Rettig, S. J.; James, B. R. *J. Chem. Soc., Chem. Commun.* **1994**, 2669. Huang, J.-S.; Che, C.-M.; Li, Z.-Y.; Poon, C.-K. *Inorg. Chem.* **1992**, *31*, 1313.

(2) (a) Collman, J. P.; Bohle, D. S.; Powell, A. K. *Inorg. Chem.* **1993**, *32*, 4004. (b) Che, C. M.; Huang, J. S.; Li, Z. Y.; Poon, C. K.; Tong, W. F.; Lai, T. F.; Cheng, M. C.; Wang, C. C.; Wang, Y. *Inorg. Chem.* **1992**, *31*, 5220. (c) Che, C. M.; Leung, W. H.; Chung, W. C. *Inorg. Chem.* **1990**, *29*, 1841. (d) Masuda, H.; Taga, T.; Osaki, K.; Sugimoto, H.; Mori, M. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2345.

(3) (a) Collman,J. P. ; Rose, E.; Venburg, G. D. *J. Chem. Soc., Chem. Commun.* **1994**, 11. (b) Ke, M.; Sishta, C.; James, B. R.; Dolphin, D.; Sparapany, J. W.; Ibers, J. A. *Inorg. Chem.* **1991**, *30*, 4766.

(4) (a) Leung, W. H.; Hun, T. S. M.; Wong, K. Y.; Wong, W. T. *J. Chem. Soc., Dalton Trans.* **1994**, 2713. (b) Smieja, J. A.; Ormberg, K. M.; Busuego, L. N.; Breneman, G. L. *Polyhedron* **1994**, *13*, 339.

(5) Gross, Z.; Barzilay, C. M. *J. Chem. Soc., Chem. Commun.* **1995**, 1287.

(6) Ohtake, H.; Higuchi, T.; Hirobe, M. *Heterocycles* **1995**, *40*, 867.

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Table 1. 200 MHz ^{1}H NMR Data for the [Os^{IV}(tmp)X$_2$] Complexes at Various Temperatures in CDCl$_3$

	chem shift (δ)											
	[Os^{IV}(tmp)Cl$_2$]				[Os^{IV}(tmp)Br$_2$]				[Os^{IV}(tmp)I$_2$]			
T (K)	*m*-H	*p*-CH$_3$	*o*-CH$_3$	*pyr*-H	*m*-H	*p*-CH$_3$	*o*-CH$_3$	*pyr*-H	*m*-H	*p*-CH$_3$	*o*-CH$_3$	*pyr*-H
215	8.21	3.32	2.67	−5.68	8.22	3.29	2.67	−5.05	8.27	3.25	2.75	−4.17
235	8.22	3.32	2.67	−5.59	8.21	3.28	2.68	−4.93	8.26	3.25	2.76	−3.91
250	8.21	3.31	2.67	−5.41	8.21	3.28	2.69	−4.75	8.25	3.25	2.78	−3.57
295	8.20	3.31	2.68	−5.10	8.20	3.28	2.70	−4.42	8.25	3.24	2.80	−3.16

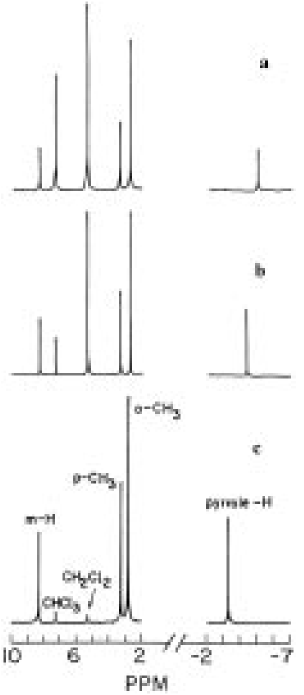


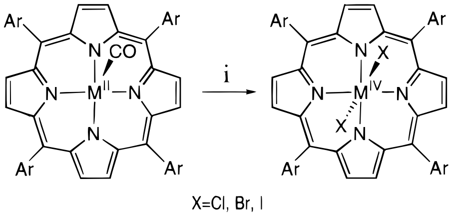
Figure 1. 200 MHz ^{1}H NMR spectra of [(Os^{IV}(tmp)(X)$_2$] in CDCl$_3$ at room temperature: (a) X = Cl; (b) X = Br; (c) X = I.

dibromo derivatives could also be prepared by reaction with Br$_2$/benzene at reflux, but the yields were lower than with CBr$_4$ and many byproducts were formed. In all cases the *trans*-dihaloosmium(IV) derivatives were obtained free of dimeric products. The yields for the various products were as follows: [Os^{IV}(ttp)Cl$_2$], 48%; [Os^{IV}(ttp)Br$_2$], 56%; [Os^{IV}(ttp)I$_2$], 94%; [Os^{IV}(tmp)Cl$_2$], 45%; [Os^{IV}(tmp)Br$_2$], 71%; [Os^{IV}(tmp)I$_2$], 96%. These moderate to excellent yields are not only higher than the existing methods for the only previously reported complex of this type—[Os^{IV}(ttp)Cl$_2$], obtained in 30−64% from [Os(ttp)(CO)]—but the synthetic procedure is much simpler and is of broader scope.

All five new complexes were identified by routine methods and by comparison of their ^{1}H NMR data to that of previously characterized [Os^{IV}(ttp)Cl$_2$].[4] In particular, the high symmetry of the complexes is apparent by the observation of only one signal for each of the *meta* H and the *ortho* H (ttp) or *ortho* CH$_3$ (tmp) of the phenyl groups (Figure 1). The chemical shifts of the pyrrole H of the six complexes were located at high field—between −5.23 and −3.16 ppm—in accord with their paramagnetism. Only the pyrrole H chemical shifts were temperature-dependent, as can be seen from the data collected in Table 1 for the [Os^{IV}(tmp)X$_2$] complexes.

We have also examined the effect of light, O$_2$, and MeOH on the reactions with CCl$_4$ and CBr$_4$. Ambient laboratory light had no effect, MeOH (17% v/v) inhibited the reactions completely, and reactions performed aerobically were much slower (24 h for full consumption of starting material) than those under N$_2$ or Ar (2 h), although the final yields were not affected. The last result was found by examining small aliquots of reaction mixtures by ^{1}H NMR at given times, which also led to a very meaningful observation. In all investigations we noticed that at early stages up to 65% of a complex was formed that is neither the starting material nor the product. The position of its proton resonances (i.e., pyrrole H at 4.13 ppm for the reaction of [Os(tmp)(CO)] with CBr$_4$) pointed toward a paramagnetic complex, while the observation of two sets of resonances for each of the phenyl's *meta* H and *ortho* H (ttp) or *ortho* CH$_3$ (tmp) indicated a complex of low symmetry. Furthermore, at longer reaction times these complexes disappeared in favor of the final products, strongly indicating that the reactions proceed in two discrete steps. Attempts to isolate intermediates by column chromatography disclosed curious behavior. Reaction mixtures, which according to NMR contained only traces of [Os(por)(CO)] and about equimolar amounts of [Os^{IV}(por)X$_2$] and the intermediate, were eluted on silica with CHCl$_3$. First [Os^{IV}(por)X$_2$] came out, followed by unreacted [Os(por)(CO)]. The rest of the material remained at the top of the column and could only be liberated with acetone. But, to our surprise, what came out was [Os(por)(CO)]. We thus concluded that the intermediates were decomposed on the column back to the starting material, which also implies that they still carry a metal-bound carbonyl. A reasonable structure to account with all of these observations is [Os^{III}(por)(X)(CO)], since it is also in accord with the earlier mentioned paramagnetism and low symmetry.

Scheme 1[a]



[a] Reagents and conditions: i, reflux of 10−30 mg of [M(por)(CO)] in 20 mL of CCl$_4$ or with 10 equiv of either CBr$_4$, CI$_4$, or I$_2$ in 20 mL of benzene for 2−24 h. Key: (a) M = Ru, Ar = 2,6-dimethylphenyl; (b) M = Os, Ar = 2,4,6-trimethylphenyl; (c) M = Os, Ar = 4-methylphenyl.

Supporting evidence for the above mentioned structural proposal was provided by the reaction of [Os(tmp)(CO)] with 0.5 equiv of Br$_2$ in benzene at room temperature. Fortunately, this reaction was very clean and required no chromatographic treatment, which when attempted gave results similar to the earlier mentioned observations—reduction to the starting material. The reaction product was identified as [Os^{III}(tmp)(Br)(CO)] by elemental analysis and a combination of spectroscopic methods. In particular, a CO stretch at 1933 cm^{-1} was observed in its IR spectrum, which is shifted in the expected position relative to the value of 1920 cm^{-1} in the lower valent [Os^{II}(tmp)(CO)] complex. Most important, the ^{1}H NMR spectrum of [Os^{III}(tmp)(Br)(CO)], which is shown in Figure 2, was identical to that of the *in situ* observed intermediate in the reaction of [Os(tmp)(CO)] with CBr$_4$. Furthermore, heating of the independently prepared [Os^{III}(tmp)(Br)(CO)] with CBr$_4$ in benzene

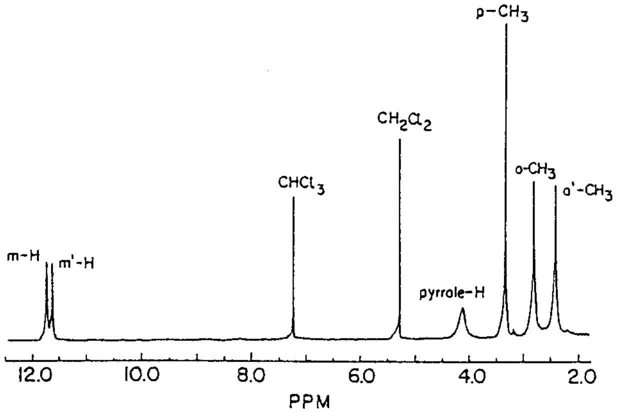
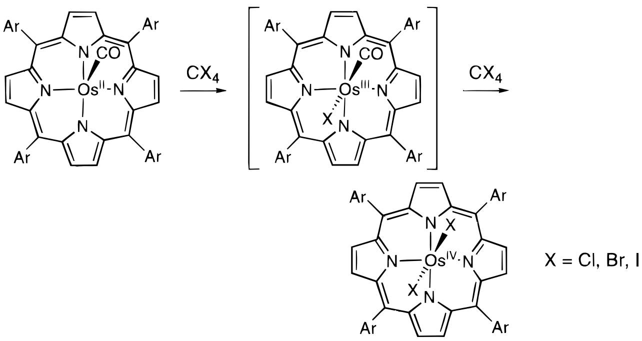


Figure 2. 200 MHz ^{1}H NMR spectrum of [(Os(tmp)(CO)(Br)] in CDCl$_3$ at room temperature.

Scheme 2



resulted in its transformation to [Os^{IV}(tmp)Br$_2$]. Thus, we may safely conclude that the reactions of [Os(por)(CO)] with CX$_4$ proceed according to Scheme 2, one-electron oxidation to [Os^{III}(por)(X)(CO)], followed by a second one-electron oxidation to [Os^{IV}(por)(X)$_2$].

The presence of the carbonyl group in [Os^{III}(por)(X)(CO)] constitutes a quite rare case of a high-valent metal carbonyl.[7] The strong binding of CO to Os is actually already reflected in the +2 oxidation state, as the comparison of a series of [M(ttp)-(CO)(pyr)] complexes clearly shows, i.e., $\nu_{CO} = 1977$, 1943, and 1920 cm^{-1} for M = Fe, Ru, and Os, respectively.[8] Furthermore, assuming a similar mechanism for the reactions of [Os(por)(CO)] and [Ru(por)(CO)] with CX$_4$, the stronger binding of CO to the former can account for the different reaction products in the two cases. Monomeric [M(por)(X)$_2$] are obtained for both [Os(tmp)(CO)] and [Os(ttp)(CO)], regardless of porphyrin structure, and also for [Ru(tdmpp)CO]. For [Ru(ttp)(CO)] however, in which no steric protection against dimerization is provided by the porphyrin, dimeric products are formed.[5] We propose that dimerization is avoided in the reactions of (carbonyl)(porphyrinato)osmium(II) with CX$_4$, because the intermediate [Os^{III}(por)(X)(CO)] complexes are hexacoordinated. The ν_{CO} of a putative [Ru^{III}(por)(X)(CO)] complex is however expected at 1955 cm^{-1} (1942 cm^{-1} of [Ru^{II}(ttp)(CO)] + 13 cm^{-1} for the increased positive charge), a value well above 1935 ± 5 cm^{-1}, which is considered the upper limit for irreversible binding of CO to metalloporphyrins.[9] Thus, [Ru^{III}(por)(X)(CO)] intermediates can be expected to lose their CO spontaneously, providing the required empty coordination site for dimerization.

In conclusion, in this paper we introduce an extremely easy one-pot synthetic procedure for superior preparation of dihalo-(porphyrinato)osmium(IV) derivatives, utilized for one recently reported complex and five new complexes. In addition, we have characterized an intermediate reaction product which shines some light on the mechanism of this reaction and on the difference between Os and Ru porphyrins. Crystallographic characterization of the Os(IV) derivatives, as well as their utilizations as precursors for new organoosmium complexes are currently under investigation.

Experimental Section

Solvents and Reagents. Dichloromethane (Lab-Scan, HPLC grade) was dried by distillation over CaH$_2$. Thiophene-free benzene (Biolab Ltd.) was repeatedly washed with concentrated H$_2$SO$_4$ until colorless, followed by washing with water, drying with CaCl$_2$ and final distillation over CaH$_2$. Analytical grade CCl$_4$ (Frutarom), CBr$_4$ (Merck, >98%), CDCl$_3$ (Aldrich), and Os$_3$(CO)$_{12}$ (Strem Chemicals, 99%) were used as received. 5,10,15,20-tetra-*p*-tolylporphyrin and 5,10,15,20-tetrakis-(2,4,6-trimethylphenyl)porphyrin were prepared by literature methods.[10] [Os(ttp)(CO)] and [Os(tmp)(CO)] were synthesized from the corresponding porphyrins in 70% and 63% yields, respectively, by metalation with Os$_3$(CO)$_{12}$ in diethylene glycol monomethyl ether, as previously described.[11]

Spectroscopic Measurements. The ^{1}H NMR spectra were recorded on a Brucker AM 200 instrument, operating at 200 MHz. Chemical shifts are reported relative to residual hydrogens in the deuterated solvent, 7.24 ppm for CHCl$_3$. Electronic spectra were recorded on a HP 8452A diode array spectrophotometer, and infrared spectra on a FT-IR Nicolet Impact 400 spectrometer. Elemental analyses were performed by the microanalysis service at the Hebrew University, Jerusalem.

Preparation of the Dihalo(porphyrinato)osmium(IV) Complexes [Os(por)X$_2$], X = Cl, Br. The appropriate [Os(por)(CO)] (22−25 mg, 25 μmol) was dissolved in 20 mL of CCl$_4$ or in 20 mL of benzene containing 8.3 mg (250 μmol) of CBr$_4$ and heated under Ar at reflux temperatures for 2−3 h. After evaporation of the solvents, column chromatography (silica/CHCl$_3$), solvent evaporation, and recrystallization from CH$_2$Cl$_2$/hexane, [Os(ttp)(Cl)$_2$], [Os(ttp)(Br)$_2$], [Os(tmp)-(Cl)$_2$], and [Os(tmp)(Br)$_2$], were obtained as dark violet crystals in 48, 56, 45, and 71% yields, respectively.

[Os(ttp)(Cl)$_2$]. MS (DCI, isobutane, negative ion): cluster around *m/z* 930.3 (M$^-$, 100%, correct isotopic pattern for C$_{48}$H$_{36}$Cl$_2$N$_4$Os). ^{1}H NMR (δ, CDCl$_3$, room temperature): 10.89 (8H, d, J = 7.2 Hz, H$_o$), 8.68 (8H, d, J = 7.2 Hz, H$_m$), 3.41 (12H, s, *p*-CH$_3$), −5.23 (8H, s, pyrrole H). UV−vis (CH$_2$Cl$_2$), λ_{max}/nm (log ϵ, M^{-1} cm^{-1}): 394 (5.29), 504 (3.88), 530 (3.81), 612 (3.62).

[Os(ttp)(Br)$_2$]. MS (FAB$^-$, Magic Bullet): cluster around *m/z* 1018.2 (M$^-$, 100%, correct isotopic pattern for C$_{48}$H$_{36}$Br$_2$N$_4$Os). ^{1}H NMR (δ, CDCl$_3$, room temperature): 10.65 ((8H, d, J = 7.4 Hz, H$_o$) 8.64 (8H, d, J = 7.4 Hz, H$_m$), 3.39 (12 H, s, *p*-CH$_3$), −4.42 (8H, s, pyrrole H). UV−vis (CH$_2$Cl$_2$): λ_{max}/nm (log ϵ, M^{-1} cm^{-1}) 398 (5.34), 508 (4.13), 534 (4.06), 618 (3.80).

[Os(tmp)(Cl)$_2$]. MS (DCI, isobutane, negative ion): cluster around *m/z* 1042.4 (M$^-$, 100%, correct isotopic pattern for C$_{56}$H$_{52}$Cl$_2$N$_4$Os); ^{1}H NMR (δ, CDCl$_3$, room temperature): 8.21 (8H, s, H$_m$), 3.31 (12H, s, *p*-CH$_3$), 2.68 (24H, s, *o*-CH$_3$), −5.13 (8H, s, pyrrole H). UV−vis (CH$_2$Cl$_2$), λ_{max}/nm (log ϵ, M^{-1} cm^{-1}): 394 (5.14), 508 (3.82), 612 (3.55).

[Os(tmp)(Br)$_2$]. Anal. Calcd. for C$_{56}$H$_{52}$Br$_2$N$_4$Os·CH$_2$Cl$_2$: C, 56.30; H, 4.48; N, 4.61. Found: C, 56.32; H, 4.73; N, 4.25; MS (FAB$^-$): cluster around *m/z* 1132.5 (M$^-$, 100%, correct isotopic pattern for C$_{56}$H$_{52}$Br$_2$N$_4$Os). ^{1}H NMR (δ, CDCl$_3$, room temperature): 8.21 (8H,

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(7) Hill, A. F. in *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier: Oxford, England, 1995; Vol. 7 (Shriver, D. F., Bruce, M. I., Eds.), p 319.

(8) Buchler, J. W.; Kokish, W.; Smith, P. D. *Struct. Bonding (Berlin)* **1978**, *34*, 121.

(9) Buchler, J. W. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978; Vol. I, p 463.

(10) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476. Lindsey, J. S.; Wagner, R. J. *J. Org. Chem.* **1989**, *54*, 828.

(11) Che, C. M.; Chung, W. C.; Lai, T. F. *Inorg. Chem.* **1988**, *27*, 2801. Che, C. M.; Poon, C. K.; Chung, W. C.; Gray, H. B. *Inorg. Chem.* **1985**, *24*, 1277.

s, H_m), 3.28 (12H, s, p-CH_3), 2.70 (24H, s, o-CH_3), −4.44 (8H, s, pyrrole H). UV−vis (CH_2Cl_2), λ_{max}/nm (log ϵ, M^{-1} cm^{-1}): 398 (5.28), 508 (3.95), 534 (3.81), 616 (3.57).

Preparation of the Diiodo(porphyrinato)osmium(IV) complexes, [Os(por)I_2]. A 10 mg sample of [Os(ttp)CO] or [Os(tmp)CO] (11.3 and 10.0 μmol, respectively) and 25 mg (98.5 μmol) of I_2 were dissolved in 20 mL of benzene and heated for 30 min. After evaporation of the solvent at reduced pressure and recrystallization from CH_2Cl_2/hexane, dark violet crystals were obtained in quantitative yields: isolated yields of 94% and 96% for [Os(ttp)I_2] and [Os(tmp)I_2], respectively.

[Os(ttp)I_2]. MS (DCI, isobutane, negative ion): cluster around m/z 1113.7 (M^-, 100%, correct isotopic pattern for $C_{48}H_{36}I_2N_4Os$); ^{1}H NMR (δ, $CDCl_3$, room temperature): 10.30 (8H, d, J = 7.4 Hz, H_o), 8.58 (8H, d, J = 7.4 Hz, H_m), 3.37 (12H, s, p-CH_3), −2.88 (8H, s, pyrrole H). UV−vis (CH_2Cl_2), λ_{max}/nm (log ϵ, M^{-1} cm^{-1}): 358 (4.43), 408 (4.76), 520 (3.75), 630 (3.81).

[Os(tmp)I_2]: Anal. Calcd. for $C_{56}H_{52}I_2N_4Os\cdot 4CH_2Cl_2$: C, 46.05; H, 3.86; N, 3.58. Found: C, 46.40; H, 4.10; N, 3.60. MS (DCI, isobutane, negative ion): cluster around m/z 1225.8 (M^-, 100%, correct isotopic pattern for $C_{56}H_{52}I_2N_4Os$). ^{1}H NMR (δ, $CDCl_3$, room temperature): 8.25 (8H, s, H_m), 3.24 (12H, s, p-CH_3), 2.80 (24H, s, o-CH_3), −3.16 (8H, s, pyrrole H). UV−vis (CH_2Cl_2), λ_{max}/nm (log ϵ, M^{-1} cm^{-1}): 366 (4.48), 410 (4.81), 526 (3.20), 630 (3.32).

Preparation of [Os(tmp)(CO)(Br)]. A solution of [Os(tmp)CO] (10 mg, 10 μmol) in 20 mL benzene was treated with 0.5 equiv Br_2 (0.8 mg, 5 μmol). Evaporation of the solvent and recrystallization from CH_2Cl_2/hexane afforded [Os(tmp)(CO)(Br)] as a dark violet solid (9.4 mg, 87%). Anal. Calcd. for $C_{57}H_{52}BrON_4Os\cdot 2H_2O$: C, 61.39; H, 5.06; N, 5.02. Found: C, 61.84; H, 5.05; N, 4.79. MS (FAB$^+$): clusters around m/z 1079 (M^+, 24%), 1050 (M^+ − CO, 32%), 1000 (M^+ − Br, 80%), 971 (M^+ − Br − CO, 100%). ^{1}H NMR (δ, $CDCl_3$, room temperature): 11.74 (4H, s, H_m), 11.64 (4H, s, H_m), 4.11 (8H, br s, pyrrole H), 3.32 (12H, s, p-CH_3), 2.80 (12H, s, o-CH_3), 2.41 (12H, s, o-CH_3). UV−vis (CH_2Cl_2), λ_{max}/nm (log ϵ, M^{-1} cm^{-1}): 410 (5.06), 518 (4.20). IR (KBr): 1933 cm^{-1} (CO).

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