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Novel Osmium(IV) and -(V) Porphyrins. Synthesis, Spectroscopy, and Electrochemistry

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Reduction of $[Os^{VI}(P)(O)_2]$ (P = porphyrin dianion) with PPh_3, ascorbic acid, or $N_2H_4 \cdot H_2O$ in the presence of ROH and RSH yielded $[Os^{IV}(P)(OR)_2]$ and $[Os^{IV}(P)(SR)_2]$, respectively. $[Os^{IV}(OEP)Br_2]$ (H_2OEP = octaethylporphyrin) was prepared from $[Os^{VI}(OEP)(O)_2]$ and Br_2. The dialkoxyosmium(IV) and dibromoosmium(IV) porphyrin complexes are paramagnetic with measured μ_{eff} values of 2.27–2.79 μ_B, which are close to the spin-only values for two unpaired electrons and independent of temperature from −30 to 30 °C. The $[Os^{IV}(P)(SR)_2]$ species are diamagnetic, suggesting that the RS^- ligand is a poor π-donor. The ^1H NMR spectral data for the paramagnetic $[Os^{IV}(P)(OR)_2]$ and $[Os^{IV}(P)Br_2]$ complexes are discussed. For the $[Os^{IV}(p\text{-X-TPP})(OEt)_2]$ system [$H_2(p\text{-X-TPP})$ = para-substituted tetraphenylporphyrin], the relative isotopic shifts of the phenyl protons are mainly due to dipolar interactions. A large ring current effect on the methine C–H and pyrrolic methylene protons of $[Os^{IV}(OEP)X_2]$ has been found. Except for $[Os^{IV}(P)(SR)_2]$, the osmium(IV) porphyrins exhibit reversible Os(IV/III) and Os(V/IV) couples. For $[Os^{IV}(P)X_2]$, the redox potentials of Os(IV/III) couples decrease in the order of X = Br > PhO > PhS > MeO, EtO > *i*-PrO. $[Os^{IV}(OEP)(OEt)_2]$ can be oxidized to $[Os^{V}(OEP)(OEt)_2]^+$ at a potential of 0.13 V vs $Cp_2Fe^{+/0}$. For the $[Os^{IV}(p\text{-X-TPP})(OEt)_2]$ system, the redox potentials of Os(V/IV) couples, which lie between 0.27 and 0.37 V, show a linear free energy relationship with the 4σ constants of the para substituents on the four phenyl rings. Oxidation of $[Os^{IV}(OEP)(OEt)_2]$ and $[Os^{IV}(TPP)(OEt)_2]$ gave the respective $[Os^{V}(OEP)(OEt)_2]^+$ and $[Os^{V}(TPP)(OEt)_2]^+$, characterized by UV–vis spectroscopy.

Introduction

The oxidation chemistry of cytochrome P-450 and its biomimetic models has been an active area of research.[1] In the P-450 reactions, the reactive intermediate is suggested to be a high-valent oxoiron porphyrin complex, which is responsible for the hydroxylation of C–H bonds. Studies on this putative iron–oxo species, however, are difficult, and efforts have been directed to synthetic iron porphyrins as models for the heme system.[2] In several reports,[2] the existence of the unstable $[Fe^{IV}(P^{\bullet +})(O)]$ and $[Fe^{IV}(P)O]$ complexes (P = porphyrin dianion) has been established by ^1H NMR spectroscopy at low temperature.

We have been interested in the oxidation chemistry of ruthenium and osmium porphyrins because of their periodic relationship with the iron system and the stability of their high oxidation state derivatives.[3-5] Our interest in the osmium system also arouses as a result of a previous study that an osmoglobin modified by attachment of $Ru(NH_3)_5$ units on surface histidines had been found to catalyze aerobic oxidation of ascorbate.[6] This modified osmoglobin shows resemblance to cytochrome P-450 in a way that both systems catalyze the four-electron reduction of oxygen to water. In an attempt to elucidate the mechanism of its oxidative reactions, we believe that knowledge on the redox chemistry of high-valent osmium porphyrins is essential. However, the studies in this area are rather sparse.[4,5] We describe here the results of a detailed study on the syntheses, spectroscopic properties, and redox chemistry of osmium(IV) and -(V) porphyrins. The $[Os^{V}(P)(OR)_2]^+$ complexes have been characterized by ^1H NMR and UV–vis spectroscopy.

Experimental Section

Materials. Octaethylporphyrin (H_2OEP) and dodecacarbonyltriosmium $[Os_3(CO)_{12}]$ were purchased from Strem Co. Ltd. Mesoporphyrin IX dimethyl ester ($H_2MIX\text{-DME}$) was obtained from Sigma Co. Ltd. All solvents and chemicals in the syntheses were analytical grade. Para-substituted tetraphenylporphyrins, $H_2(p\text{-X-TPP})$ (X = MeO, Me, H, Cl) and $[Os^{VI}(p\text{-X-TPP})(O)_2]$ were prepared by literature methods.[5]

$[Os^{IV}(P)(OR)_2]$ (P = OEP, MIX-DME, *p*-X-TPP; R = Me, Et, *i*-Pr). A mixture of $[Os^{VI}(P)(O)_2]$ (100 mg) and *L*-(+)-ascorbic acid (200 mg) was stirred in a CH_2Cl_2/ROH (3:2, 50 mL) solution at room temperature for 2 h. The reaction was monitored by following the optical spectral changes of the solution. When the 580-nm band of $[Os^{VI}(P)(O)_2]$ had completely disappeared, the solution was filtered through a Celite pad, which was then washed with CH_2Cl_2. The washing and filtrate were combined and reduced to 5 mL. Chromatography of the resulting solution on a silica gel column with CH_2Cl_2/C_2H_5OH solution (9:1) as the eluent yielded $[Os^{IV}(P)(OR)_2]$, which was eluted as an orange band. After evaporation of the solvent, the product was recrystallized from hot alcohol to give needle-shaped crystals (yield ≈ 70%). Anal. Calcd for $[Os^{IV}(OEP)(OEt)_2]$: C, 59.1; H, 6.6; N, 6.9. Found: C, 59.4; H, 6.8; N, 6.7. Calcd for $[Os^{IV}(TPP)(OMe)_2]$: C, 62.9; H, 4.3; N, 6.3. Found: C, 63.3; H, 3.9; N, 6.0. Calcd for $[Os^{IV}(TPP)(OEt)_2]$: C, 64.6; H, 4.3; N, 6.3. Found: C, 64.6; H, 4.0; N, 6.6. Calcd for $[Os^{IV}(TPP)(O\text{-}i\text{-}Pr)_2]$: C, 65.2; H, 4.6; N, 6.1. Found: C, 65.1; H, 4.5; N, 6.2. Calcd for $[Os^{IV}(p\text{-Cl-TPP})(OEt)_2]$: C, 55.9; H, 3.3; N, 5.4; Cl, 13.8. Found: C, 55.6; H, 3.2; N, 5.3; Cl, 13.5. Calcd for $[Os^{IV}(p\text{-Me-TPP})(OEt)_2]$: C, 65.8; H, 4.8; N, 5.9. Found: C, 65.5; H, 4.9; N, 5.7. Calcd for $[Os^{IV}(p\text{-MeO-TPP})(OEt)_2]$: C, 61.6; H, 4.5; N, 5.5. Found: C, 61.8; H, 4.6; N, 5.4. Calcd for $[Os^{IV}(MIX\text{-DME})(OEt)_2]$: C, 54.9; H, 6.1; N, 6.1. Found: C, 54.5; H, 6.4; N, 6.0.

$[Os^{IV}(P)(OPh)_2]$ (P = OEP, TPP). A mixture of $[Os^{VI}(P)(O)_2]$ (0.1 g) and L-(+)-ascorbic acid (0.2 g) in molten phenol (5 g) was heated at 100 °C for 5 min and then cooled to room temperature. Water (100 mL) was added to dissolve the unreacted phenol and ascorbic acid. The solid residue was dissolved in $CHCl_3$ (50 mL) and washed with water (2 × 50 mL). The solution was then evaporated to 2 mL and loaded on a silica gel column. The desired product was eluted with $CHCl_3$ and recrys-

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tallized from CH_2Cl_2/CH_3CN (1:1) solution (yield ≈ 60%). Anal. Calcd for $[Os^{IV}(OEP)(OPh)_2]$: C, 63.4; H, 6.0; N, 6.2. Found: C, 63.5; H, 6.2; N, 6.2. Calcd for $[Os^{IV}(TPP)(OPh)_2]$: C, 68.0; H, 3.8; N, 5.6. Found: C, 67.8; H, 4.0; N, 5.7.

$[Os^{IV}(P)(SPh)_2]$ (P = OEP, TPP). $[Os^{VI}(P)(O)_2]$ (0.1 g) and PhSH (1 mL) in CH_2Cl_2 (50 mL) were stirred in CH_2Cl_2 (50 mL) at room temperature for 2 h. The solvent was reduced to 2 mL at room temperature. Excess *n*-hexane (50 mL) was added to precipitate the product, which was filtered on a Celite pad and chromatographed on a silica gel column. Upon elution with $CHCl_3$, a violet-red band first came out, which was evaporated to dryness. The crude $[Os^{IV}(P)(SPh)_2]$ product was recrystallized from $CHCl_3/CH_3CN$ (1:1) solution (yield ≈ 80%). Anal. Calcd for $[Os^{IV}(OEP)(SPh)_2]$: C, 61.2; H, 5.8; N, 6.0. Found: C, 61.3; H, 5.6; N, 5.8. Calcd for $[Os^{IV}(TPP)(SPh)_2]$: C, 60.0; H, 3.4; N, 4.9. Found: C, 60.2; H, 3.5; N, 5.0.

$[Os^{IV}(OEP)Br_2]$. $[Os^{IV}(OEP)(O)_2]$ (0.1 g) and bromine (0.5 mL) were stirred in CH_2Cl_2 (40 mL) at room temperature for 5 min. Excess bromine was removed by shaking the reaction mixture with an aqueous solution of sodium thiosulfate (2 M, 50 mL). The organic solution was washed with water (50 mL) and then evaporated to dryness. The crude solid was loaded on a silica gel column. The $[Os^{IV}(OEP)Br_2]$ product was eluted as a brown band with $CHCl_3$ and was recrystallized from CH_2Cl_2/CH_3CN (1:1) solution (yield 40%). Anal. Calcd: C, 49.0; H, 5.0; N, 6.4; Br, 18.2. Found: C, 48.8; H, 4.8; N, 6.1; Br, 18.4.

Physical Measurements. UV-visible spectra were obtained on a Shimadzu UV-250 spectrophotometer. ^1H NMR spectra were run on a JEOL Model FX-90Q spectrometer (90 MHz). Chemical shifts (ppm) were reported relative to tetramethylsilane (TMS). Magnetic susceptiblity was determined at room temperature by using Evans' method with chloroform as solvent. Elemental analyses of newly prepared complexes were performed by the Australian National Laboratory.

Electrochemistry. Cyclic voltammetry was performed with a Princeton Applied Research (PAR) Model 175 universal programmer, Model 173 potentiostat, and Model 179 digital coulometer. Cyclic voltammograms were recorded with a Houston 2000 X-Y recorder at scan rate 50 mV s^{-1}. The $E°$ is taken to be $(E_{pa} + E_{pc})/2$ for a reversible redox couple. The electrolytic cell is a conventional two-compartment cell. $Ag/AgNO_3$ (0.1 M in CH_3CN) was used as the reference electrode. The ferrocenium/ferrocene couple ($Cp_2Fe^{+/0}$) was used as the internal standard to which the reported potentials are referenced. The working electrode was a platinum disk electrode. Controlled-potential coulometry was performed by using a PAR Model 377A coulometric cell system.

Results and Discussion

Although oxidation state IV is not uncommon in osmium chemistry, there are few studies on osmium(IV) porphyrins.[4b,c,5a,7,8] In this work, reduction of $[Os^{VI}(P)(O)_2]$ with mild reductants in the presence of ROH or RSH offers a general synthetic route for $[Os^{IV}(P)(OR)_2]$ and $[Os^{IV}(P)(SR)_2]$. $N_2H_4{\cdot}H_2O$, PPh_3, and ascorbic acid are effective reductants. The $[Os^{IV}(P)(X)_2]$ (X = Cl, Br) complexes were first reported to be the products formed upon broad-band irradiation of osmium(II) porphyrins in halocarbons.[7] In the present study, it has been found that the reaction of $[Os^{VI}(OEP)(O)_2]$ with Br_2 in CH_2Cl_2 also gave $[Os^{IV}(OEP)Br_2]$ with reasonable yield; however, the mechanism of this reaction is not clear. Throughout this work, we observed that osmium porphyrins are very stable with respect to the formation of oxo-bridged Os–O–Os complexes. In fact, attempts to synthesize $[Os^{IV}(TPP)(OH)]_2O$ following Ogoshi's procedure[8] for $[Os^{IV}(OEP)(OCH_3)]_2O$ were unsuccessful despite many trials. Both reduction of $[Os^{VI}(OEP)(O)_2]$ by ascorbic acid and oxidation of $[Os^{II}(OEP)(CO)]$ by 3-chloroperoxybenzoic acid in CH_2Cl_2 were found to give $[Os^{IV}(OEP)(OH)_2]$[5b] whereas similar reactions of $[Ru^{VI}(OEP)(O)_2]$[9] and $[Ru^{II}(OEP)(CO)]$[8-10] will lead to the immediate formation of $[Ru^{IV}(OEP)(OH)_2]O$.

The newly prepared osmium complexes have satisfactory elemental analyses and are stable in fluid solutions. Except for $[Os^{IV}(OEP)(SPh)_2]$, which is diamagnetic ($\mu_{eff} = 0\ \mu_B$), the osmium(IV) porphyrins are paramagnetic. Magnetic susceptibility measurements established the respective room-temperature μ_{eff} values for $[Os^{IV}(TPP)(OMe)_2]$, $[Os^{IV}(TPP)(OEt)_2]$, $[Os^{IV}(OEP)(OPh)_2]$, and $[Os^{IV}(OEP)Br_2]$ to be 2.27, 2.31, 2.60, and 2.79 μ_B. These values are independent of temperature from −30 to 30 °C and close to the spin-only value of 2.83 μ_B for two unpaired electrons. Previous works on iron(IV)[2] and ruthenium(IV)[3] porphyrins also indicated that their μ_{eff} values are close to 2.83 μ_B. For d^4 dialkoxy- and dihalogenometalloporphyrin systems where the axial ligands are good donors, the d_{xz} and d_{yz} orbitals are destabilized relative to d_{xy} as result of p_π and d_π bonding interaction (the *z* axis is RO–M–OR/X–M–X). Hence, a triplet ground with the $(d_{xy})^2(d_{xz})^1(d_{yz})^1$ electronic configuration is expected for $[Os^{IV}(P)(X)_2]$ (X = OR, OPh, Br).

Table I. UV–Vis Spectral Data for Osmium(IV) Porphyrins

complex	λ_{max}/nm (log ε)
$[Os^{IV}(OEP)(OEt)_2]$	527 (3.70), 495 (3.74), 340 (4.72), 279 (4.04)
$[Os^{IV}(OEP)(OPh)_2]$	530 sh (3.82), 494 (3.96), 476 (3.97), 378 (4.97), 265 sh (4.32)
$[Os^{IV}(OEP)(SPh)_2]$	585 sh (3.83), 531 (3.98), 507 sh (3.91), 394 (4.58), 364 sh (4.36)
$[Os^{IV}(OEP)Br_2]$	665 (3.46), 548 (3.60), 506 sh (4.19), 496 (4.22), 439 (4.34), 389 (5.18), 254 (4.50)
$[Os^{IV}(TPP)(OMe)_2]$	508 (4.07), 408 (5.02), 274 (4.35)
$[Os^{IV}(TPP)(O\text{-}i\text{-}Pr)_2]$	506 (4.24), 409 (5.04), 278 (4.58)
$[Os^{IV}(TPP)(OEt)_2]$	507 (4.03), 405 (4.98), 270 (4.35)
$[Os^{IV}(p\text{-}MeO\text{-}TPP)(OEt)_2]$	504 (4.18), 409 (5.14), 273 (4.49)
$[Os^{IV}(p\text{-}Me\text{-}TPP)(OEt)_2]$	505 (4.18), 405 (4.07), 273 (4.50)
$[Os^{IV}(p\text{-}Cl\text{-}TPP)(OEt)_2]$	506 (4.18), 408 (5.10), 279 (4.57)
$[Os^{IV}(TPP)(OPh)_2]$	565 (3.79), 504 (4.08), 396 (4.99), 266 (4.45)
$[Os^{IV}(TPP)(SPh)_2]$	570 sh (4.09), 518 (4.24), 408 (5.02), 252 (4.69)

In previous work by Antipas et al.,[11] a temperature-independent μ_{eff} value of 1.11 μ_B was reported for $[Os^{IV}(OEP)(OCH_3)_2]$, which is different from our results. We offer no explanation for this discrepancy. In their report, Antipas et al.[11] explained their finding by assuming a low-energy triplet excited state due to the bending of the CH_3O–Os–OCH_3 axis. However, the X-ray structures of $[Os^{IV}(OEP)(OEt)_2]$, $[Os^{IV}(TPP)(O\text{-}i\text{-}Pr)_2]$, and $[Os^{IV}(TPP)(OPh)_2]$, which will be reported later, provide no evidence for this suggestion.[12]

For the $[Os^{IV}(P)(X)_2]$ complexes, their μ_{eff} values decrease in the order of X = Br > OPh > OEt, OMe ≫ SPh. The observed highest μ_{eff} value for $[Os^{IV}(OEP)Br_2]$ may suggest that Br^- is even a better π-donor than RO^-. The observed diamagnetism of $[Os^{IV}(OEP)(SPh)_2]$ is not unexpected since PhS^- is a poor π-donor. Previous work on $[Os^{IV}(salen)(SPh)_2]$ also showed no significant d_π (Os) and p_π (SPh) π-bonding interaction, as evidenced by the very normal Os–S distances in this molecule.[13]

The UV–vis spectral data of the osmium complexes are set in Table I. Typical optical spectra are shown in Figure 1. In each case, the soret band is broad in accordance with previous studies that osmium(IV) complexes have hyper absorption spectra due to the low-energy state of (π, d_{π^*}) character.[11] The visible absorptions of $[Os^{IV}(OEP)Br_2]$ are red-shifted from $[Os^{IV}(OEP)(SPh)_2]$, which in turn are of lower energy than $[Os^{IV}(OEP)(OEt)_2]$. This indicates that the electronic transitions involved have substantial ligand-to-metal charge-transfer character.

^1H NMR Spectra. All osmium(IV) porphyrins show well-resolved ^1H NMR spectra; the spectral data are summarized in Table II. Unlike those in the Fe(IV) and Ru(IV) systems, the proton signals, in particular those of porphyrinato rings, show very little dependence on temperature from −30 to 30 °C. Variable-temperature ^1H NMR spectral data of $[Os^{IV}(TPP)(OEt)_2]$ are

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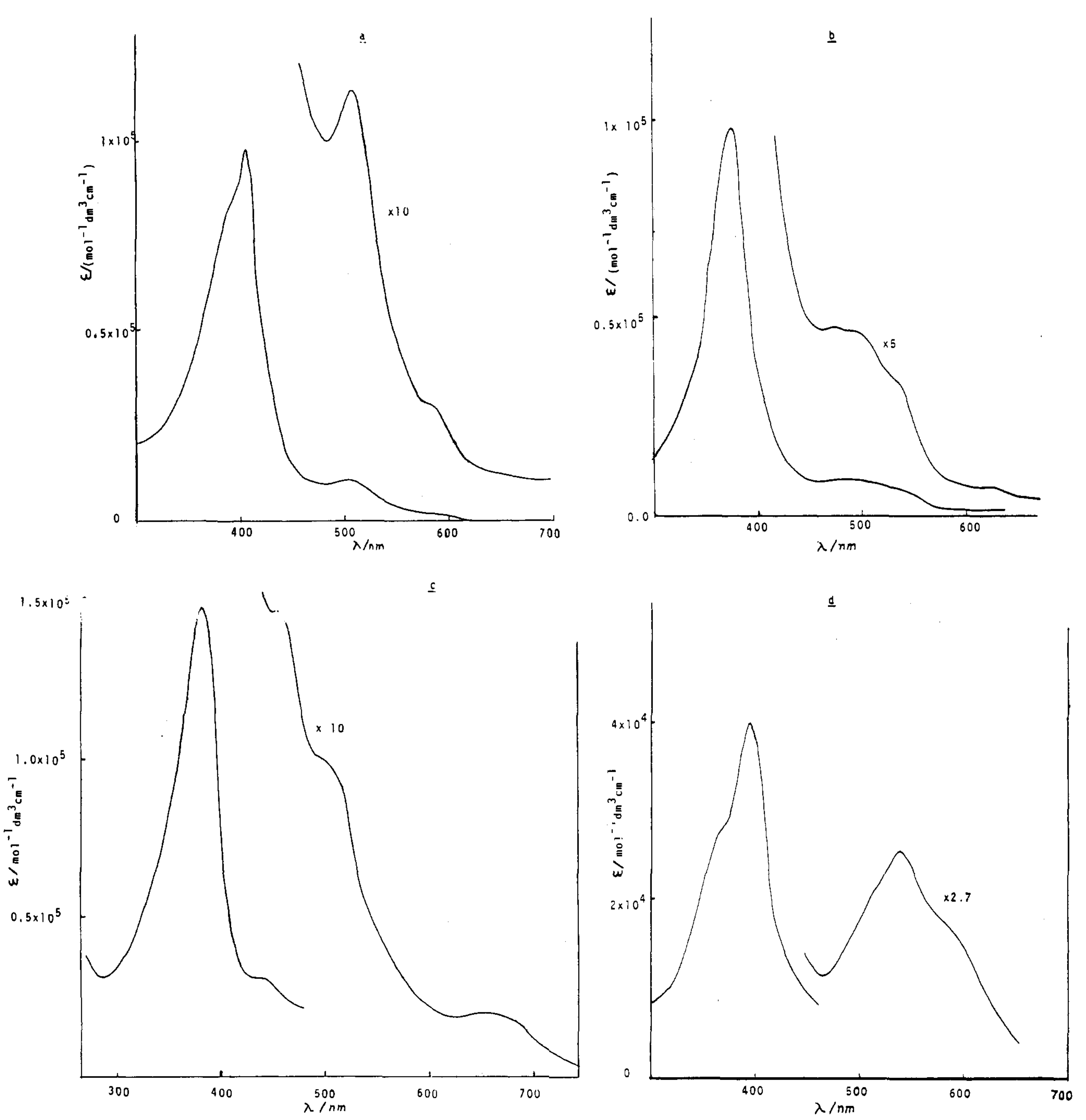

Figure 1. UV–vis spectra of (a) [Os^{IV}(TPP)(OMe)$_2$], (b) [Os^{IV}(OEP)(OPh)$_2$], (c) [Os^{IV}(OEP)Br$_2$], and (d) [Os^{IV}(OEP)(SPh)$_2$] in dichloromethane.

set in Table S1 (supplementary material). This finding is in accordance with the temperature-independent paramagnetism of the metal complexes described in an earlier section. For [Os^{IV}(*p*-X-TPP)(OEt)$_2$], the pyrrolic protons show large isotropic upfield shift whereas the *meso*-phenyl protons are downfield shifted from those in the corresponding diamagnetic [Os^{VI}(*p*-X-TPP)(O)$_2$]. A detailed analysis of the ^{1}H NMR spectra is prohibited at this stage due to the low resolution of the employed NMR spectrometer, which does not allow resolution of the meta and para protons of TPP ring. Nevertheless, the relative isotropic shifts of the phenyl protons in [Os^{IV}(TPP)(OEt)$_2$] and [Os^{IV}(*p*-Me-TPP)(OEt)$_2$] (Table S1) are similar to those values found in [Fe^{III}(*p*-Me-TPP)(Im)$_2$]$^+$ (Im = imidazole),[14] suggesting that the shifts are mainly due to dipolar interactions. Previous work by Buchler and co-workers[4b,c] suggested that the pyrrolic and –OCH$_3$ protons in [Os^{IV}(TPP)(OCH$_3$)$_2$] are at 35.25 and 4.79 ppm, respectively. In this work, the [Os^{IV}(P)(OEt)$_2$] complexes exhibit well-resolved quartet and triplet signals at 25 to 29 and –4 to –6 ppm, respectively (Table II), as illustrated in Figure 2. These signals are logically due to the methylene (–CH$_2$–) and methyl (–CH$_3$) protons of the axial –OC$_2$H$_5$ ligands. As the chemical shifts for the –OCH$_3$ protons in [Os^{IV}(TPP)(OCH$_3$)$_2$] and methylene protons of –OC$_2$H$_5$ in [Os^{IV}(TPP)(OC$_2$H$_5$)$_2$] should be similar, the previous assignment by Buchler and co-workers[4] needs revision. The 4.79 and 35.25 ppm signals in [Os^{IV}(*p*-Me-TPP)(OCH$_3$)$_2$] are thus reassigned to be the pyrrolic and –OCH$_3$ protons, respectively.

For [Os^{IV}(OEP)(SPh)$_2$], the chemical shifts of the methine C–H and pyrrolic –CH$_2$ and –CH$_3$ protons are virtually the same as those values in [Os^{VI}(OEP)(O)$_2$]. This is not unexpected given the fact that the metal complex is diamagnetic. The other paramagnetic [Os^{IV}(OEP)(X)$_2$] complexes (X = Br, OPh, OEt) show large ring current effects on the methine C–H and pyrrolic –CH$_2$ protons, which are substantially downfield shifted from that in [Os^{VI}(OEP)(O)$_2$].

Electrochemistry and Osmium(V) Porphyrins. The osmium(IV) porphyrins exhibit reversible electrochemistry in most cases; the

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Table II. ^{1}H NMR Data (90 MHz)[a] for Osmium(IV) Porphyrin Complexes in $CDCl_3$ Solutions

complex	proton signals of porphyrinato ring	proton signals of axial ligands
$[\mathrm{Os^{IV}(MIX\text{-}DME)(OEt)_2}]$	$\mathrm{CH_2}\mathit{CH}_3$ (t), 2.75; $\mathrm{CH_2}\mathit{CH}_2\mathrm{CO_2}$ (t), 4.00; $\mathrm{CH_3}$ (s), 10.13, 10.50, 10.63; $\mathrm{CO_2}\mathit{CH}_3$ (s), 3.69; $\mathit{CH}_2\mathrm{CH_3}$ (q), 8.11; $\mathit{CH}_2\mathrm{CH_2CO_2}$ (t), 8.47; methine CH (s), 14.95, 15.11	$\mathit{CH}_3\mathrm{CH_2O}$ (t), −5.43; $\mathrm{CH_3}\mathit{CH}_2\mathrm{O}$ (q), 27.29
$[\mathrm{Os^{IV}(MIX\text{-}DME)(SPh)_2}]$	$\mathrm{CH_2CH_3}$ (t), 2.00; $\mathrm{CH_2}\mathit{CH}_2\mathrm{CO_2}$ (t), 3.57; CH_3 (s), 5.03, 5.18, 5.21; $\mathrm{CO_2}\mathit{CH}_3$ (s), 3.76; $\mathit{CH}_2\mathrm{CH_3}$ (q), 3.31; $\mathit{CH}_2\mathrm{CH_2CO_2}$ (t), 4.87; methine CH (s), 10.53, 10.55, 10.64	*o*-H (dm), 3.54; *m*-H (tm), 6.54; *p*-H (m), 6.17
$[\mathrm{Os^{IV}(OEP)(OEt)_2}]$	$\mathrm{CH_2}\mathit{CH}_3$ (t), 2.82; $\mathrm{CH_3}\mathit{CH}_2$ (q), 8.23; methine CH (s), 15.22	$\mathit{CH}_3\mathrm{CH_2O}$ (t), −5.15; $\mathrm{O}\mathit{CH}_2\mathrm{CH_3}$ (q), 25.34
$[\mathrm{Os^{IV}(OEP)(OPh)_2}]$	$\mathrm{CH_2}\mathit{CH}_3$ (t), 3.45; $\mathrm{CH_3}\mathit{CH}_2$ (q), 12.40; methine CH (s), 19.17	*o*-H (dm), 5.07; *p*-H and *m*-H (m), 7.94
$[\mathrm{Os^{IV}(OEP)(SPh)_2}]$	$\mathrm{CH_2}\mathit{CH}_3$ (t), 2.03; $\mathrm{CH_3}\mathit{CH}_2$ (q), 4.89; methine CH (s), 10.65	*o*-H (dm), 3.51; *p*-H (m), 6.09; *m*-H (tm), 6.51
$[\mathrm{Os^{IV}(OEP)Br_2}]$	$\mathrm{CH_2}\mathit{CH}_3$ (t), 4.33; $\mathrm{CH_3}\mathit{CH}_2$ (q), 19.29; methine CH (s), 21.96	
$[\mathrm{Os^{IV}(TPP)(OMe)_2}]$	pyrrolic C–H (s), 4.76; *o*-H (m), 9.21; *m*-H and *p*-H (m), 8.17	$o\text{-}\mathit{CH}_3$ (s), 34.13
$[\mathrm{Os^{IV}(TPP)(OEt)_2}]$	pyrrolic C–H (s), 4.81; *o*-H (m), 9.21; *m*-H and *p*-H (m), 8.13	$\mathit{CH}_2\mathrm{CH_3}$ (q), 28.54; $\mathrm{CH_2}\mathit{CH}_3$ (t), −4.70
$[\mathrm{Os^{IV}}(p\text{-}\mathrm{MeO\text{-}TPP)(OEt)_2}]$	pyrrolic C–H (s), 4.61; *o*-H (m), 9.20; *m*-H (m), 7.70; $p\text{-}\mathit{CH}_3\mathrm{O}$ (s), 4.33	$\mathit{CH}_2\mathrm{CH_3}$ (q), 29.56; $\mathrm{CH_2}\mathit{CH}_3$ (t), −5.03
$[\mathrm{Os^{IV}}(p\text{-}\mathrm{Me\text{-}TPP)(OEt)_2}]$	pyrrolic C–H (s), 4.75; *o*-H (m), 9.14; *m*-H (m), 7.95; $p\text{-}\mathit{CH}_3$ (s), 2.93	$\mathit{CH}_2\mathrm{CH_3}$ (q), 28.65; $\mathrm{CH_2}\mathit{CH}_3$ (t), −4.79
$[\mathrm{Os^{IV}}(p\text{-}\mathrm{Cl\text{-}TPP)(OEt)_2}]$	pyrrolic C–H (s), 4.93; *o*-H (m), 9.09; *m*-H (m), 8.11	$\mathit{CH}_2\mathrm{CH_3}$ (q), 28.57; $\mathrm{CH_2}\mathit{CH}_3$ (t), −4.69
$[\mathrm{Os^{IV}(TPP)(O\text{-}}i\text{-}\mathrm{Pr)_2}]$	pyrrolic C–H (s), 4.95; *o*-H (m), 9.14; *m*-H and *p*-H (m), 8.11	$(\mathit{CH}_3)_2\mathrm{CHO}$ (d), −3.69; $\mathrm{O}\text{-}\mathit{CH}(\mathrm{CH_3})_2$ (sep), 12.08
$[\mathrm{Os^{IV}(TPP)(OPh)_2}]$	pyrrolic C–H (s), 0.94; *o*-H (m), 10.06; *m*-H and *p*-H (m), 8.53	*o*-H (dm), −5.26; *m*-H and *p*-H (m), 8.84
$[\mathrm{Os^{IV}(TPP)(SPh)_2}]$	pyrrolic C–H (s), 7.79; *o*-H (m), 8.07; *m*-H and *p*-H (m), 7.72	*o*-H (dd), 3.96; *p*-H (tm), 6.48; *m*-H (tm), 6.63

[a] Chemical shifts are in ppm referenced to Me_4Si in $CDCl_3$. Abbreviations: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; sep = septet.

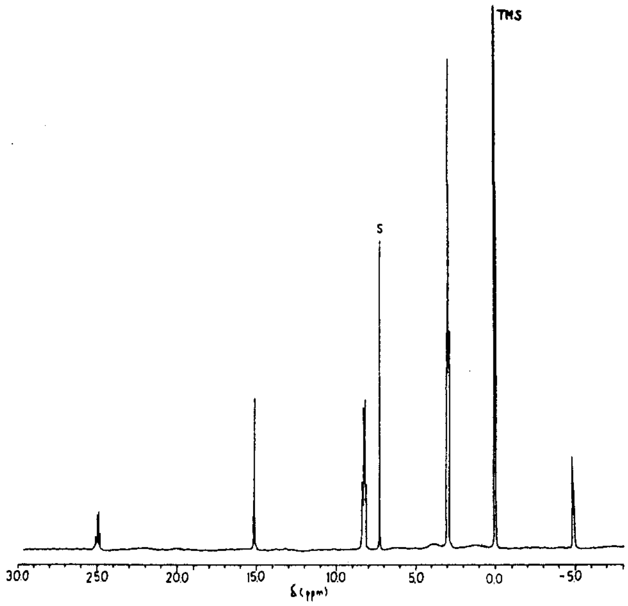

Figure 2. ^{1}H NMR spectrum of $[Os^{IV}(OEP)(OEt)_2]$ in $CDCl_3$. S = residual solvent protons.

results on redox potentials ($E°$) of $[Os^{IV}(P)X_2]$ in CH_2Cl_2 are set in Table III. Figure 3 shows the cyclic voltammogram of $[Os^{IV}(OEP)(OEt)_2]$ in CH_2Cl_2. Two reversible/quasi-reversible couples at +0.13 and −1.37 V (vs $Cp_2Fe^{+/0}$) corresponding to the oxidation and reduction of the osmium complex are found. Since the respective current ratios (i_{pa}/i_{pc}) and peak-to-peak separation (ΔE_p) are close to unity and 60–70 mV and are independent of scan rates from 20 to 200 mV s^{-1}, the electrochemical reactions are reversible one-electron-transfer processes. As the $E°$ of the oxidative wave is lower than that required for the oxidation of the OEP ring, the electrode reaction is metal-centered, as represented by eq 1. Although the $[Os^V(OEP)(OEt)_2]^+$ complex

$$[Os^{IV}(OEP)(OEt)_2] - e^- \rightarrow [Os^V(OEP)(OEt)_2]^+ \qquad (1)$$

is stable in the cyclic voltammetric time scale, it is not stable in fluid solutions. Although bulk electrolysis of $[Os^{IV}(OEP)(OEt)_2]$ at 0.35 V established $n = 0.98$, the cyclic voltammogram of the solution after electrolysis was different from that of the beginning, indicating that a new osmium complex or complexes from a secondary reaction or reactions of $[Os^V(OEP)(OEt)_2]^+$ were formed. Attempts have been made to investigate the stability and properties of $[Os^V(OEP)(OEt)_2]^+$. The Os(V) complex was generated through chemical oxidation. Figure 4 shows the optical spectrum immediately measured after the addition of $[NH_4][Ce^{IV}(NO_3)_6]$ to a solution of $[Os^{IV}(OEP)(OEt)_2]$ in CH_2Cl_2/EtOH mixture (2:3). The immediate product formed, which has absorption peaks at 374 and 483 nm, can be immediately reduced back to the starting $[Os^{IV}(OEP)(OEt)_2]$ with over 95% recovery with $N_2H_4 \cdot H_2O$ or ascorbic acid. The lack of broad absorption in the 600–700-nm region and the increase in the intensity of the

Table III. Summary of the Formal Potentials of $[Os^{IV}PX_2]$ Complexes in CH_2Cl_2 with 0.1 M Tetra-*n*-butylammonium Tetrafluoroborate as Supporting Electrolyte (Working Electrode; Platinum Disk)

complex	$E_f(\mathrm{Os(IV/OsV)})/\mathrm{V}$ vs $Cp_2Fe^{+/0}$			4σ
$[\mathrm{Os(MIX\text{-}DME)(OEt)_2}]$		−1.34	0.15	1.04
$[\mathrm{Os(OEP)(OEt)_2}]$		−1.37	0.13	1.06
$[\mathrm{Os(TPP)(OMe)_2}]$		−1.09	0.37	
$[\mathrm{Os(TPP)(O\text{-}}i\text{-}\mathrm{Pr)_2}]$		−1.23	0.27	
$[\mathrm{Os}(p\text{-}\mathrm{MeO\text{-}TPP)(OEt)_2}]$		−1.21	0.27	−1.072
$[\mathrm{Os}(p\text{-}\mathrm{Me\text{-}TPP)(OEt)_2}]$		−1.15	0.29	−0.860
$[\mathrm{Os(TPP)(OEt)_2}]$		−1.13	0.32	0.000
$[\mathrm{Os}(p\text{-}\mathrm{Cl\text{-}TPP)(OEt)_2}]$		−1.05	0.37	0.908
$[\mathrm{Os(OEP)(OPh)_2}]$	−2.02	−1.05	0.39	
$[\mathrm{Os(TPP)(OPh)_2}]$	−1.79	−0.88	0.57	
$[\mathrm{Os(OEP)(SPh)_2}]$		−1.05	0.31[a]	
$[\mathrm{Os(TPP)(SPh)_2}]$		−1.00	0.56[a]	
$[\mathrm{Os(OEP)Br_2}]$	−1.77	−0.50	0.69	

[a] Only oxidation part of the couple observed. The $Cp_2Fe^{+/0}$ couple was 0.16 V versus the $Ag/AgNO_3$ (0.1 M in CH_3CN) reference electrode.

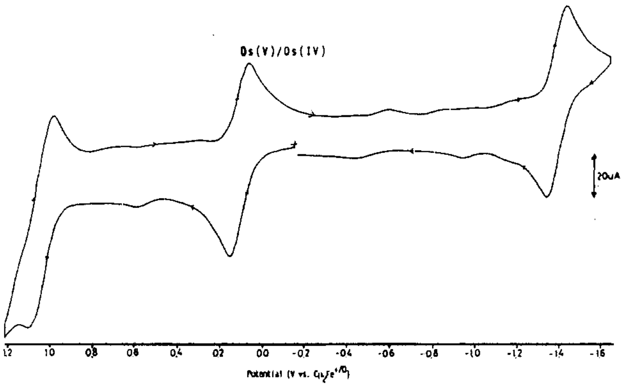

Figure 3. Cyclic voltammogram of $[Os^{IV}(OEP)(OEt)_2]$ in dichloromethane with 0.1 M $[Bu_4N]BF_4$ as supporting electrolyte (working electrode, Pt; scan rate 100 mV s^{-1}).

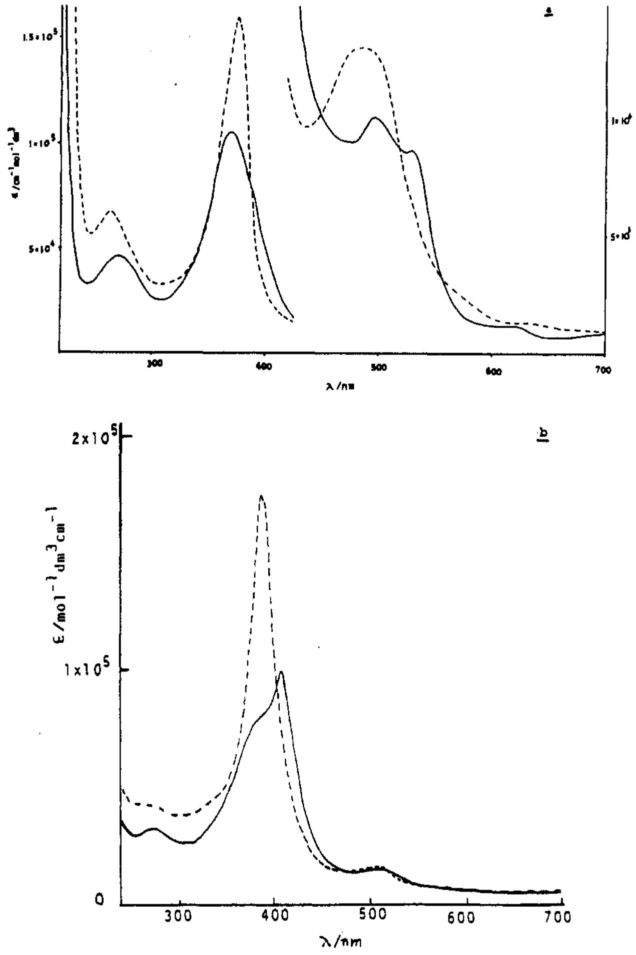

Figure 4. Optical spectra of $[\mathrm{Os^{IV}(P)(OEt)_2}]$ (—) and $[\mathrm{Os^{V}(P)(OEt)_2}]^+$ (---) in $\mathrm{CH_2Cl_2/EtOH}$ (2:3) solution: (a) P = OEP; (b) P = TPP.

Soret band argue that the oxidized species is not the π cation radical. We tentatively assign this species to be $[\mathrm{Os^V(OEP)(OEt)_2}]^+$. The $[\mathrm{Os^V(OEP)(OEt)_2}]^+$ complex was found to be unstable and gradually transform to $[\mathrm{Os^{VI}(OEP)(O)_2}]$ (major) within $^1/_2$ h together with some unknown species (minor). Oxidation of $[\mathrm{Os^{IV}(OEP)(OEt)_2}]$ with $\mathrm{Ag(CF_3SO_3)}$ in $\mathrm{CH_2Cl_2}$ also gave $[\mathrm{Os^{VI}(OEP)(O)_2}]$ after work up. If bromine was the oxidant, $[\mathrm{Os^{IV}(OEP)Br_2}]$ was found as the major product, identified by its optical absorptions at 665, 548, 496, and 389 nm.

Other $[\mathrm{Os^{IV}(P)(OR)_2}]$ complexes also exhibit reversible Os(V)/Os(IV) couples at potentials less than that required for the oxidation of the porphyrinato ring. Interestingly, the $E°$ values for the Os(V)/Os(IV) couples show linear free energy relationship with the 4σ constants of the para substituents on the four phenyl rings, illustrated by the plot in Figure 5a. The calculated Hammett reactivity parameter (P) of 0.048 V is substantially lower than that found for the oxidation of the porphyrinato ring but close to the value of 0.054 V for the reduction of $[\mathrm{Mn^{III}}(p\text{-X-TPP})\mathrm{Cl}]$ to $[\mathrm{Mn^{III}}(p\text{-X-TPP})\mathrm{Cl}]^-$[15] in $\mathrm{CH_2Cl_2}$ under similar reaction conditions. Thus, the electrode reaction is

$$[\mathrm{Os}(p\text{-X-TPP})(\mathrm{OR})_2] - e^- \rightarrow [\mathrm{Os^V}(p\text{-X-TPP})(\mathrm{OR})_2]^+ \qquad (2)$$

The optical spectrum of oxidized product immediately measured after addition of Ce(IV) to a $\mathrm{CH_2Cl_2/EtOH}$ (2:3) solution of $[\mathrm{Os^{IV}(TPP)(OEt)_2}]$ is shown in Figure 4. We tentatively assign this species to be $[\mathrm{Os^V(TPP)(OEt)_2}]^+$.

$[\mathrm{Os^{IV}(OEP)Br_2}]$ also displays a reversible oxidative couple but at potential similar to the $E°$ value of the $[\mathrm{Os^{VI}(OEP^{\bullet+})(O)_2}]/[\mathrm{Os^{VI}(OEP)(O)_2}]$ couple $[\mathrm{OEP^{\bullet+}}$ = octaethyl porphyrin cation radical].[16] Accordingly, the electrochemical oxidation of $[\mathrm{Os^{IV}(OEP)Br_2}]$ occurs at the OEP ring. Figure 6 shows the cyclic voltammogram of $[\mathrm{Os^{IV}(OEP)(SPh)_2}]$ in 0.1 M $[\mathrm{Bu_4N}]\mathrm{BF_4}$ $\mathrm{CH_2Cl_2}$ solution. The oxidation wave for $[\mathrm{Os^{IV}(OEP)(SPh)_2}]$ at 0.3 V is irreversible. Presumably, the electrogenerated $[\mathrm{Os^V(OEP)(SPh)_2}]^+$ complex is unstable and undergoes secondary chemical reaction(s) with breakage of the Os–S bond. A similar result for $[\mathrm{Os^{IV}(TPP)(SPh)_2}]$ has also been found.

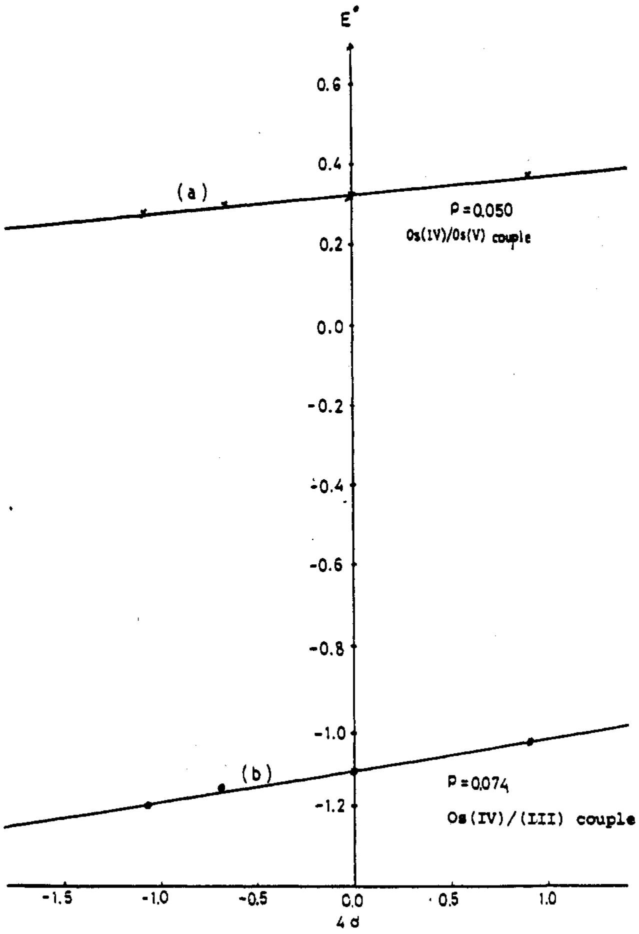

Figure 5. Hammett plot of $E°$ (V vs $\mathrm{Cp_2Fe^{+/0}}$) against 4σ for $[\mathrm{Os^{IV}}(p\text{-X-TPP})(\mathrm{OEt})_2]$.

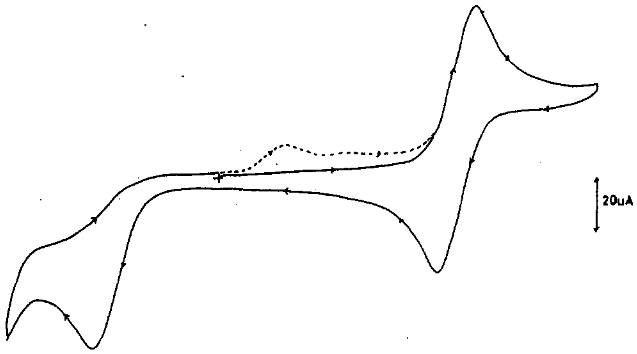

Figure 6. Cyclic voltammogram of $[\mathrm{Os^{IV}(OEP)(SPh)_2}]$ in $\mathrm{CH_2Cl_2}$ with 0.1 M $[\mathrm{Bu_4N}]\mathrm{BF_4}$ as supporting electrolyte (working electrode, Pt; scan rate 100 mV $\mathrm{s^{-1}}$).

The electrochemical reduction of osmium(IV) porphyrins is reversible/quasi-reversible with an i_{pa}/i_{pc} of 1 and a ΔE_p of 60–70 mV, which are independent of scan rates from 50 to 200 mV $\mathrm{s^{-1}}$. For the $[\mathrm{Os^{IV}(OEP)(X)_2}]$ system, there is a large dependence of the $E°$ values on the axial ligands, suggesting that the electro-

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chemical reduction is metal-centered in nature, as represented by eq 3. For $[Os^{IV}(p\text{-X-TPP})(X)_2]$, the situation is less clear-cut.

$$[Os^{IV}(OEP)(X)_2] + e^- \rightarrow [Os^{III}(OEP)(X)_2]^- \qquad (3)$$

Their $E°$ values are close to those for the $[In(TPP)R]/[In(TPP)R]^-$ and $[Ga(TPP)Cl]/[Ga(TPP)Cl]^-$ couples,[17] where the corresponding electrochemical reductions are ligand-centered in nature. Furthermore, the effect of axial ligands on redox potentials is not as large as in the OEP case. For example, the difference in the redox potentials for the reduction of $[Os^{IV}(OEP)(SPh)_2]$ and $[Os^{IV}(OEP)(OEt)_2]$ is 0.32 V; the corresponding difference is just 0.13 V in the TPP system. Figure 5b shows the Hammett linear free energy plot ($E°$ versus 4σ) for the electrochemical reduction of $[Os^{IV}(p\text{-X-TPP})(OEt)_2]$. The calculated Hammett reactivity parameter of 0.070 V is essentially the same as those values found for the authentic porphyrin ring reduction under the same conditions.[18] We believe that further studies are required to identify the site of reduction. From Table III, it can be seen that the $E°$ values for both Os(V/IV) and Os(IV/III) couples decrease in the order of X = Br > PhO > PhS > MeO, EtO > *i*-PrO, which parallels the order of donor strength of the ligands. The fact that replacing bromide by alkoxide would significantly reduce the redox potentials of Os(IV) and Os(V) porphyrins reflects that alkoxide is a better ligand for high-valent osmium complexes.

General Comments

There are not many examples of high-valent metalloporphyrins of the d^4 system. Although numerous studies by various workers showed that iron(IV) porphyrins with coordinated oxo, alkyl, and fluoro ligands can be generated under suitable conditions,[2] these species are very unstable and rapidly reconvert back to iron(III) at room temperature. There are several reports on ruthenium(IV) porphyrins;[3] however, their redox chemistry has not been investigated.

The results described here clearly demonstrate the remarkable stabilities of high-valent osmium porphyrins, in contrast to its iron analogue. Electrochemical works by Groves and others showed that the $E°$ values for Fe(IV/III) couples of $[Fe^{III}(TPP)(OMe)]$[2d] and $[Fe^{III}(TMP)(OH)]$[2f] (H_2TMP = tetramesitylporphyrin) are 1.11 and 1.0 V vs SCE, respectively, which are at least 800 mV higher than those for the analogous dialkoxyosmium(IV) complexes. Such a dramatic lowering in redox potentials from iron to osmium possibly explains why Os(IV), instead of Os(III), is formed upon aerobic oxidation of $[Os^{II}(P)(ROH)_2]$ in alcoholic solution.[16]

We have previously communicated that osmium(III) porphyrins can catalyze epoxidation of olefins with PhIO under mild conditions.[19] As with another metalloporphyrin system,[20] an osmium(V)–oxo intermediate was postulated for the catalytic reactions. In this work we find that dialkoxyosmium(V) porphyrins although not very stable can be generated by chemical or electrochemical oxidation of Os(IV). In fact, osmium(V) compounds are rare, only a few halo-substituted derivatives being known.[21] The $E°$ values for Os(V/IV) couples of $[Os^{IV}(P)(OR)_2]$ are found to be less than 0.4 V vs $Cp_2Fe^{+/0}$ in most cases, which are even lower than the redox potentials of Fe(IV) porphyrins.[2d,f] Thus, from the view point of redox potentials, oxidation of osmium(III) by PhIO to give oxoosmium(V) is not out of expectation. As the donor strength of an oxo group could be comparable to two alkoxides, monoxoosmium(V) porphyrin, if it exists, should have its $E°$ close to that of its dialkoxy analogue. Thus, one would expect the redox potential of the hypothetical $[Os^V(OEP)O(ROH)]^+$ complex to be around 0.13 V vs $Cp_2Fe^{+/0}$. If one further assumes that changing the central metal from osmium to iron would lead to an increase in redox potential by 800 mV as in the case with dialkoxyosmium(III) and -iron(III), the hypothetical $[Fe^V(OEP)O(ROH)]^+$ species should have its $E°$ value around 0.93 V vs $Cp_2Fe^{+/0}$. This is a very high redox potential and would be very difficult to be reached by oxidation of iron(III) with O_2.

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Supplementary Material Available: Table S1, containing variable-temperature ^1H NMR spectral data for $[Os^{IV}(TPP)(OEt)_2]$ (1 page). Ordering information is given on any current masthead page.

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