Mercaptide Complexes of Osmium Porphyrins. Structure of $Os(TTP)(SC_6F_4H)_2$†

James P. Collman,*,‡ D. Scott Bohle,‡,§ and Anne K. Powell‖

Department of Chemistry, Stanford University, Stanford, California 94305, and School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, United Kingdom

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Aryl mercaptans RSH (R = *p*-tolyl, C_6F_4H, C_6F_5, 2,6–$Me_2C_6H_3$) react with dioxoosmium(VI) porphyrins [porphyrin = *meso*-tetra-*p*-tolylporphyrin (TTP), octaethylporphyrin (OEP)] to give diamagnetic osmium(IV) derivatives which contain two mercaptide ligands. When sterically encumbered mercaptans and porphyrins are utilized, an Os(III) mercaptide complex results. Osmium(III) porphyrin mercaptide complexes can also be prepared either by pyridine-promoted reductive elimination of disulfide from $Os(TTP)(SR)_2$ or by treating the metal–metal-bonded dimer $[Os_2(TTP)_2]^{2+}$ with mercaptan/pyridine mixtures. The bis(mercaptido)osmium(IV) complex $Os(TTP)(SC_6F_4H)_2$ has been structurally characterized by X-ray diffraction [monoclinic $C2/c$, a = 23.750(5) Å, b = 16.625(4) Å, c = 15.049(3) Å, β = 92.05(2)°, Z = 4] and exhibits short metal–sulfur bond lengths.

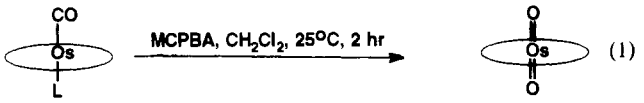
Introduction

Although many biomimetic models for the reactivity of the cytochrome P-450 family of monooxygenases have been developed, structural models for the reactive intermediate and its immediate precursor have eluded isolation.[1] In part, this stems from the extraordinarily high reactivity of the putative ferryl intermediate, formulated at either the iron(V) species **A** or its valence tautomer **B**, which is capable of stereo- and regioselective alkane hydroxylation and olefin epoxidation under biological conditions. Equally critical to the isolation of a structural model is the difficulty of preparing stable mercaptide complexes of iron porphyrins that do not undergo the reductive elimination of disulfide on exposure to oxygen or Lewis bases.[2] The enzyme's polypeptide backbone is able to prevent this pervasive side reaction in model compounds. Of particular interest is the possible role of the mercaptide in promoting a heterolytic cleavage of the oxygen–oxygen bond in the coordinated peroxide intermediate.[3]

A **B**

This paper concerns our attempts to prepare a heavier congener analogue of **A** or **B**. It is widely recognized that high-oxidation-state complexes of the second- and third-row transition metals are more stable than their first-row transition metal analogues. The distribution and stabilities of the known oxidation states of the iron and osmium porphyrin complexes illustrate this phenomenon well; whereas there are only a handful of spectroscopically characterized iron(IV) porphyrin complexes,[1a,4] several osmium(VI) porphyrins, including $Os(OEP)(O)_2$ and Os(OEP)(≡N)(OMe), were reported in Buchler's pioneering work on the metalloporphyrin complexes of the heavier transition metals.[5] In contrast with this well-precedented synthetic, structural, and reaction chemistry of Os(VI), there is only a single report describing the spectroelectrochemical characterization of the Os(V) species generated from the one-electron oxidation of $Os(por)(OEt)_2$.[6]

Since dioxoosmium(VI) porphyrins are readily prepared in a single step by treating the initial porphyrin metalation product, Os(por)(CO)(L), with *m*-chloroperbenzoic acid, MCPBA (eq 1), this material is an ideal starting point for the synthesis of



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middle-valent osmium metalloporphyrins. Early and concomitant work has established that the osmyl fragment is readily reduced to give symmetric complexes of Os(IV) (eq 2).[5b,c,7] In order to prepare an osmium analogue of **A** or **B**, we have prepared complexes of sterically encumbered porphyrins and investigated

† Abbreviations used in this article: TTP = *meso*-tetra-*p*-tolylporphyrinato; OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinato; C_n-PBP = *n*-methylene-strapped picnic basket porphyrinato (see structure in eq 3); TMP = *meso*-tetramesitylporphyrinato; MCPBA = *m*-chloroperbenzoic acid; X^- = monoanionic ligand.

‡ Stanford University.

§ Current address: Department of Chemistry, University of Wyoming, Laramie, WY 82071-3838.

‖ University of East Anglia.

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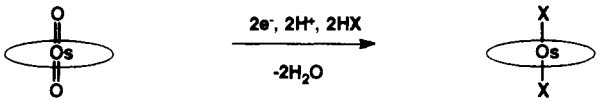
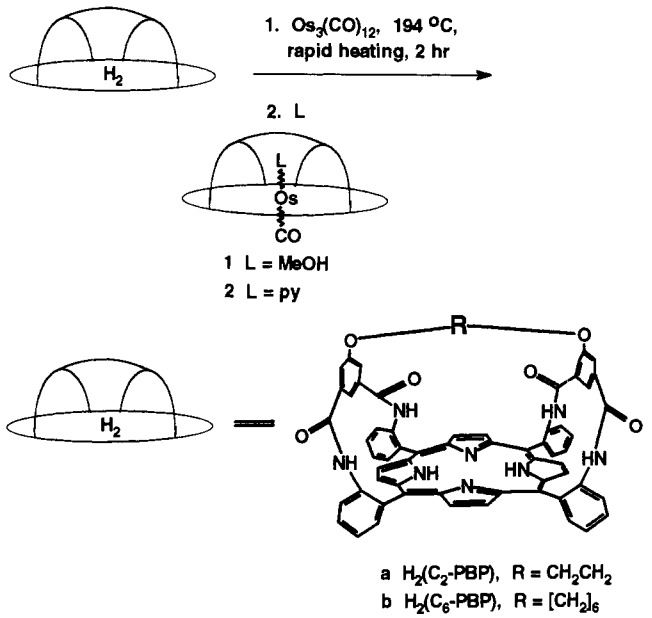


(2)

their reactions with mercaptans. Herein we report (1) the synthesis of new dioxoosmium(VI) complexes of cavity-capped porphyrins, (2) the reactions of these and related osmium tetraarylporphyrin complexes with mercaptans to give Os^{IV}(por)-$(SR)_2$ or Os^{III}(por)(SR)(L) depending upon the porphyrin and mercaptan, and (3) the structure of $Os(TTP)(SC_6F_4H)_2$. Together these results demonstrate the potential of dioxoosmium(VI) porphyrins as precursors for the facile access to middle-oxidation-state osmium porphyrin complexes.

Results

Preparation of Starting Materials. An improved metalation procedure was devised in order to circumvent the relatively prolonged reaction times required in published methods.[5,8] Important details of this method, which is described in the Experimental Section, include the rapid heating of a porphyrin solution in 2-(2-methoxyethoxy)ethanol with a slight excess of $Os_3(CO)_{12}$ (eq 3). Although these conditions were initially



(3)

developed to metalate the functionalized tetraamide cavity-capped porphyrins, C_n-$PBPH_2$, to give **1a**, **1b**, **2a**, and **2b**, they have also been successfully applied to the metalation of $TTPH_2$ by osmium. The regiochemistry of ligation within these cavities is determined by the steric effects of the cavity superstructure and closely parallels the known coordination chemistry of the ruthenium analogues.[9] For example, although pyridine can coordinate within the hexamethylene-strapped cavity to give **2b**, $Os(C_6\text{-PBP})(CO)_{out}(py)_{in}$, for the smaller cavity (n = 2), which cannot accommodate pyridine within the cavity, the sole product is $Os(C_2\text{-PBP})(CO)_{in}(py)_{out}$.

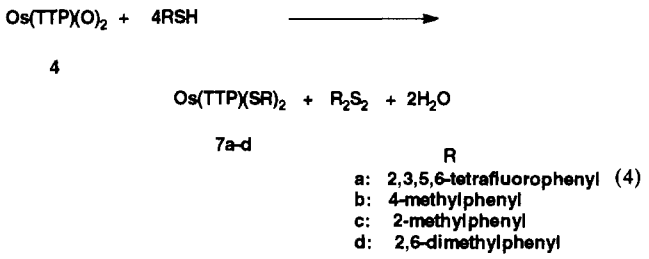
The *trans*-dioxo (osmyl) complexes Os^{VI}(porphyrin)$(O)_2$ [**3a,b** porphyrin = C_n-PBP (**a**, n = 2; **b**, n = 6); **4** porphyrin = TTP] are readily prepared by treating Os(porphyrin)(CO)(MeOH) with *m*-chloroperbenzoic acid in dichloromethane at room temperature (eq 1). These diamagnetic air-stable products are then purified by column chromatography on silica. The NMR, UV–vis, and IR spectroscopic properties are similar to those of previously reported examples.[5,10]

Reactions of Dioxoosmium(VI) Porphyrins. Acid mediates the isotopic exchange of the oxo ligands when either **4** or $Os(OEP)(O)_2$ is treated with $^{18}OH_2$ in predried dichloromethane for 24 h in the presence of a trace (3×10^{-6} L) of trifluoroacetic acid. The isotopic substitution products have UV–vis spectra and chromatographic properties similar to those of the starting materials; however, the IR spectra have bands for the asymmetric stretch ν_{asym}(O═Os═O) shifted from 845 to 800 cm^{-1} for **4** and from 846 to 799 cm^{-1} for $Os(OEP)(O_2)$. Similar shifts have been reported by Groves for $Ru(TMP)(^{18}O)_2$, which was prepared by treating Ru(TMP)(CO)(MeOH) with [^{18}O]iodosobenzene.[11] For the cavity-capped porphyrin $Os(C_2\text{-PBP})(O)_2$, exchange under these conditions was incomplete, required longer acid contact periods, and returned impure products.

The reductive substitution reactions shown in eq 2, originally developed by Buchler and Smith,[5b] utilized ascorbic acid/alcohol mixtures as the reductant and axial ligand source. We have found that catechol or mecaptans are able to provide both the reducing equivalents and the axial ligand in the Os(IV) product. In the case of catechol, the product is $Os(TTP)(\eta^1\text{-}OC_6H_4\text{-}2\text{-}OH)_2$ (**5**), which contains the relatively unusual η^1-catecholate ligand.[12]

Addition of trifluoroacetic acid to $Os(TTP)(OR)_2$ leads to the rapid release of alcohol and the formation of $Os(TTP)(O_2CCF_3)_2$ (**6**), which was characterized by ^{1}H-NMR and UV–vis spectroscopies and elemental analysis. The expected increase in lability of the trifluoroacetate ligand is demonstrated in the synthesis of $Os(TTP)(S\text{-}p\text{-tolyl})_2$ by treating **6** with mercaptide anions (see below).

Excess aryl mercaptans RSH [R = 2,3,5,6–tetrafluorophenyl (**a**), *p*-tolyl (**b**), *o*-tolyl (**c**), 2,6-dimethylphenyl (**d**)] react rapidly at room temperature with $Os(TTP)(O)_2$ (**4**) to yield $Os(TTP)(SR)_2$ (**7a–d**) and the corresponding disulfides. These moderately air-stable diamagnetic products are readily purified by column chromatography. The stoichiometry of eq 4 has been confirmed



(4)

by following the reaction with ^{1}H-NMR with an internal standard. However, when **4** is treated with exactly 4 equiv of *p*-tolyl-SH, a second product, which is formulated as $[(p\text{-tolyl-S})Os(TTP)]_2O$ on the basis of its ^{1}H-NMR and UV–vis spectra, is formed in 5% yield. In contrast with these facile reactions, the alkyl mercaptan *t*-BuSH reacts with **4** to give a mixture of at least four products in poor yield, none of which conform to the expected product, $Os(TTP)(S\text{-}t\text{-Bu})_2$, by ^{1}H-NMR. A similar result was found for the reaction of $Os(OEP)(O)_2$ with *t*-BuSH. However when $Os(OEP)(O_2CCF_3)_2$ was treated with excess NaS-*t*-Bu (5 days, inert atmosphere, $CDCl_3$), a symmetric disubstituted diamagnetic product consistent with $Os(OEP)(S\text{-}t\text{-Bu})_2$ is formed in 61% yield.

The product of the reaction of an aryl mercaptan with a cavity-capped porphyrin depends upon the steric requirements of the aryl mercaptan substituent and the size of the porphyrin cavity. Two important examples illustrate these effects.

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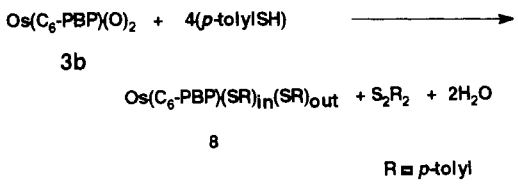
When $Os(C_6\text{-}PBP)(O)_2$ (**3b**) is treated with excess *p*-tolyl-SH under the same conditions outlined in eq 4, the diamagnetic product has spectroscopic properties consistent with the formulation **8** in eq 5. The ^{1}H-NMR is especially informative and

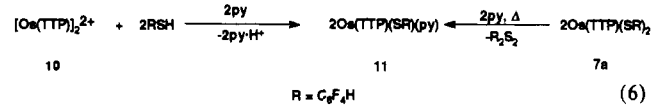


(5)

indicates that the three sets of geminal methylene protons in the hexamethylene strap are no longer magnetically equivalent and are now strongly coupled to one another. Furthermore, the signals of the pyrrolic β protons, two singlets in **3b**, are split into two distinct singlets, one for the pyrrole unit directly under the mercaptide ligand the other for the pyrrole across from this ligand. The remaining two pyrrole units are symmetry related by a mirror plane defined by the metal and thiolate ligands and have inequivalent strongly coupled pyrrolic β protons which have an AB quartet pattern in the ^{1}H-NMR.

On the other hand, when $Os(C_2\text{-}PBP)(O)_2$ (**3a**) is treated with 2,3,5,6-tetrafluorothiophenol, the product is critically dependent upon the stoichiometry of the reactants. Although a disulfide byproduct is observed, the main product is not diamagnetic as in compounds **7a–d** and **8**. For example, when **3a** is treated with 4 equiv of 2,3,5,6-tetrafluorothiophenol in $CDCl_3$ and hexamethylbenzene is added as an internal standard, there is a three-half conversion of mercaptan to disulfide within 4 h. Since there is no remaining free mercaptan present at this point, the missing mercaptan must be coordinated to the metal in a paramagnetic complex, $Os(C_2\text{-}PBP)(SR)_{out}$ (**C**). Isolation of **C** as an air-sensitive product is accomplished by column chromatography. The solution paramagnetism has been confirmed by Evans method[13] and corresponds to $\mu_{eff} = 1.65 \pm 0.08\ \mu_B$. Furthermore, when this product is treated with $[Cp_2Fe][PF_6]$ in methanol, there is a rapid formation of a single product which we formulate as $Os(C_2\text{-}PBP)(OMe)_{in}(SR)_{out}$ (**9**) on the basis of the single set of porphyrin resonances, the distinctive resonance at 5.5 ppm (tt), and the singlet at 16.1 ppm in the ^{1}H-NMR spectrum. We attribute the last two resonances to the protons in the SC_6F_4H and methoxide ligands, respectively. Related downfield shifts have been observed for methoxide-containing Os(IV) porphyrins.[6] This experiment demonstrates that there is a mercaptide ligand in **C** and that the osmium oxidation state is probably +3.

Related (Mercaptido)Osmium(III) Porphyrins. Due to the paucity of data for Os(III) porphyrin complexes and their presence in the products described above, we have examined the synthesis and reactions of these species. We have demonstrated in prior work that metal–metal-bonded dimeric dications $[M_2(porphyrin)_2]^{2+}$ (**10**), are readily cleaved by the addition of strong nucleophiles such as Grignard and lithium reagents, to give M^{III}-(Porp)(R) M = Ru, Os.[14] When $[Ru(OEP)]_2^{2+}$ is treated with an excess of mercaptan, there is rapid formation of a new complex that has only broad contact-shifted bands in the ^{1}H-NMR spectrum and has UV–vis characteristics of a mononuclear complex, *i.e.* a single Soret band at 300 nm. On addition of pyridine to this sample, there is quantitative formation of di-*p*-tolyl disulfide and $Ru(OEP)(py)_2$. For the related osmium species $[Os(TTP)]_2^{2+}$, the reaction with 2,3,5,6-tetrafluorothiophenol requires the addition of noncoordinating base (NEt_3) and results in the formation of equal amounts of $Os(TTP)\text{-}(SC_6F_4H)_2$ (**7a**) and $[OsTTP]_2^+$, which were identified spectroscopically. This result illustrates that although coordination of RSH cannot cleave the Os–Os triple bond in **10**, RS^- can. Furthermore, $Os(TTP)\text{-}(SC_6F_4H)$, the anticipated initial product from the reaction of mercaptan with **10**, must undergo a rapid electron transfer and ligand association reaction to give **7a** as the ultimate product. If a coordinating base (pyridine) is used in high concentration (neat), then a new product, $Os(TTP)(SC_6F_4H)(py)$ (**11**; eq 6), forms in



(6)

high yield (>72%). The same product (**11**) is also formed by treating $Os(TTP)(SR)_2$ with pyridine in toluene at reflux (eq 6). When **11** is thermolyzed as a lyophilized powder (195 °C, 2×10^{-5} Torr), the product undergoes reductive elimination of disulfide and loss of pyridine and has a ^{1}H-NMR spectrum consistent with $[Os(TTP)]_2$.[14] 1,5-Diphenylimidizole also leads to the reductive elimination of disulfide from **7a**, to give $Os(TTP)(SR)(1,5\text{-}Ph_2\text{-}Im)$. If weaker Lewis bases, such as neat THF or acetonitrile, are used, there is no reaction even for prolonged periods at reflux.

^{1}H NMR Properties. Table I lists the observed shifts and assignments for new compounds prepared in the course of this work. In general, these results fall into two categories: (A) diamagnetic derivatives of Os(II), Os(VI), and Os(IV), that is **1–4**, **7**, and **8**; (B) paramagnetic contact-shifted derivatives of Os(IV), *i.e.* **5**, **6**, and **9**. There is little dependence of the chemical shifts observed for the Os(IV) species as a function of temperature. For example, in the spectrum of $Os(OEP)(SC_6F_4H)_2$ the largest change between +22 and −91 °C is the methylene resonance of the ethyl substituents which shifts by 0.25 ± 0.02 ppm (supplementary Table I). Also, in the strongly contact-sifted compound $Os(OEP)(O_2CCF_3)_2$, with $\delta(C\text{–}H_{meso}) = 22.22$ ppm, there is again only a slight variation in the chemical shift of this resonance between −15 and +54 °C. Similar results have also been observed by Che.[6]

Electrochemistry. Formal potentials for the mercaptide-containing compounds **7**, **8**, and **11** are listed in Table II. For the Os(IV) derivatives in dichloromethane, reversible reductions and oxidations are observed for scan rates between 50 and 250 mV/s. Since the potentials are markedly ligand dependent for these compounds, they have been assigned as metal-based redox processes.

Structure of $Os(TTP)(SC_6F_4H)_2$ (7a). In order to further characterize the $Os^{IV}(porphyrin)(SR)_2$ complexes, we have structurally characterized **7a** by X-ray diffraction. As depicted in the ORTEP view in Figure 1, the molecule has a crystallographically imposed center of symmetry at osmium. The metrical data for the porphyrin ring (largest deviation from the best fit plane is 0.035 Å for C(5)) are shown in Figure 2. Selected bond lengths, angles, and positional parameters are collected in Tables III–V, respectively. Complete crystal structure collection data, thermal parameters, and calculated hydrogen positions have been deposited as supplementary Tables II–IV.

Discussion

Porphyrin metalation by the heavier platinum group metals remains a mechanistically obscure process that requires a careful match of conditions with suitable metal precursors. The procedure described herein represents a useful improvement of established procedures.[5,8]

Overall, the dioxoosmium(VI) porphyrin complexes employed in this paper as starting materials provide a facile route to the Os(IV) and Os(III) species. Synthetically these materials are attractive because they are obtained in a single high-yield step from the original *and only known* initial metalation product for osmium, Os(porphyrin)(CO)L. Furthermore, the synthetic approach described herein avoids the preparation of oxygen-sensitive materials that are difficult to purify by chromatography.

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Table I. ^{1}H NMR Data for the New Complexes[a]

no.	complex	solvent	proton signals: porphyrinato ring	proton signals: axial ligand
1a	$Os(C_2\text{-}PBP)(CO)_{in}(MeOH)_{out}$	$CDCl_3$	pyrrolic β 9.00 (s), 8.55 (s); *o*-aminophenyl 8.40 (d), 8.26 (d), 7.82 (t), 7.66 (t), N*H* 6.39 (s); isophthaloyl C*H* 5.96 (s), 5.79 (s), CH_2 3.34 (s)	
1b	$Os(C_6\text{-}PBP)(CO)_{out}(CH_3OH)_{in}$	$CDCl_3$	pyrrolic β 8.74 (s), 8.36 (s); *o*-aminophenyl 8.47 (d), 8.38 (d), 7.81 (t), 7.73 (t), N*H* 7.50 (s); isophthaloyl C*H* 6.44 (s), 5.84 (s), CH_2 3.36 (t), 1.28 (m), 0.86 (m)	
2a	$Os(C_2\text{-}PBP)(CO)_{in}(py)_{out}$	$CDCl_3$	pyrrolic β 8.74 (s), 8.34 (s); *o*-aminophenyl 8.46 (d), 8.45 (d), 7.78 (t), 7.62 (t), N*H* 6.39 (s); isophthaloyl C*H* 6.38 (d), 6.05 (t), CH_2 3.63 (s)	*p*-C*H* 5.49 (t), *m*-C*H* 4.33 (t), *o*-C*H* 2.15 (d)
2b	$Os(C_6\text{-}PBP)(CO)_{out}(py)_{in}$	$CDCl_3$	pyrrolic β 8.72 (s), 8.44 (s); *o*-aminophenyl 8.51 (d), 8.48 (d), 7.79 (t), 7.67 (t), N*H* 6.71 (s); isophthaloyl C*H* 6.57 (s), 5.62 (s), CH_2 3.53 (t), 1.23 (m), 0.86 (m)	*p*-C*H* 4.70 (t), *m*-C*H* 4.18 (t), *o*-C*H* 0.74 (d)
3a	$Os(C_2\text{-}PBP)(O)_2$	$CDCl_3$	pyrrolic β 9.39 (s), 9.00 (s); *o*-aminophenyl 8.75 (d), 8.41 (d), 7.94 (t), 7.82 (t), N*H* 5.86 (s); isophthaloyl C*H* 6.15 (d), 5.62 (t), CH_2 3.5 (s)	
		C_6D_6	pyrrolic β 8.90 (s), 8.67 (s); *o*-aminophenyl 8.85 (d), 8.25 (d), 7.61 (t), 7.38 (t), N*H* 5.75 (s); isophthaloyl C*H* 6.14 (d), 5.07 (t), CH_2 2.57 (s)	
3b	$Os(C_6\text{-}PBP)(O)_2$	$CDCl_3$	pyrrolic β 9.45 (s), 8.99 (s); *o*-aminophenyl 8.67 (d), 8.65 (d), 7.95 (t), 7.78 (t), N*H* 6.84 (s); isophthaloyl C*H* 6.63 (d), 5.90 (t), CH_2 3.41 (t), 1.28 (m), 0.74 (m)	
		C_6D_6	pyrrolic β 8.99 (s), 8.91 (s); *o*-aminophenyl 9.17 (d), 8.21 (d), 7.59 (t), 7.37 (t), N*H* 6.45 (s); isophthaloyl C*H* 6.33 (d), 5.55 (t), CH_2 2.73 (t), 0.92 (m), 0.90 (m)	
5	$Os(TTP)\{O_2C_6H_4(OH)\}_2$	$CDCl_3$	pyrrolic β −1.00 (s); *p*-tolyl C*H* 10.17 (d), 8.39 (s), CH_3 3.22 (s)	O(HO)C_6H_4 9.09 (t), 8.41 (d), −1.50 (t), −6.06 (d), *H*O −8.78 (s)
6	$Os(TTP)(O_2CCF_3)_2$	$CDCl_3$	pyrrolic β −7.88 (s); *p*-tolyl C*H* 10.65 (d), 8.60 (s), CH_3 3.36 (s)	
7a	$Os(TTP)(SC_6F_4H)_2$	$CDCl_3$	pyrrolic β 7.10 (s); *p*-tolyl C*H* 8.12 (d), 7.64 (s), CH_3 2.72 (s)	C_6F_4H 6.01 (tt)
		C_6D_6	pyrrolic β 6.91 (s); *p*-tolyl C*H* 7.96 (d), 7.09 (s), CH_3 2.17 (s)	C_6F_4H 5.21 (tt)
7b	Os(TTP)(S-*p*-tolyl)$_2$	$CDCl_3$	pyrrolic β 7.79 (s); *p*-tolyl C*H* 7.84 (d), 7.45 (s), CH_3 2.65 (s)	C*H* 6.32 (d), 3.86 (d), CH_3 2.13 (s)
		C_6D_6	pyrrolic β 8.14 (s); *p*-tolyl C*H* 7.92 (d), 7.24 (s), CH_3 2.33 (s)	C*H* 6.27 (d), 4.33 (d), CH_3 1.91 (s)
7c	Os(TTP)(*S*-*o*-tolyl)$_2$	CD_2Cl_2	pyrrolic β 7.79 (s); *p*-tolyl C*H* 7.86 (d), 7.43 (s), CH_3 2.67 (s)	C*H* 6.68 (t), 6.33 (m), 3.34 (t), CH_3 0.23 (s)
7d	Os(TTP)(S-2,6$C_6Me_2H_3$)$_2$	$CDCl_3$	pyrrolic β 7.62 (s); *p*-tolyl C*H* 7.92 (d), 7.51 (s), CH_3 2.67 (s)	C*H* 6.51 (d), 6.26 (t), CH_3 0.05 (s)
8	$Os(C_6\text{-}PBP)$(S-*p*-tolyl)$_2$	$CDCl_3$	pyrrolic β 7.96 (d), 7.76 (d), 7.80 (s), 7.51 (s); *o*-aminophenyl 9.31 (d), 9.03 (d), 8.24 (d), 8.18 (d), 7.61 (t), 7.51 (t), 7.33 (t), 7.31 (t), N*H* 6.73 (s), 6.68 (s); isophthaloyl C*H* 6.46, 6.42, 5.49, CH_2 2.88 (m), 2.65 (m), 0.90 (m), 0.60 (m)	*p*-tolyl C*H* 6.7 (d), 5.70 (d), 4.27 (d), 2.1 (d), CH_3 2.10 (s), 1.35 (s)
	O[Os(TTP)(S-*p*-tolyl)]$_2$	C_6D_6	pyrrolic β 8.64 (s); *p*-tolyl C*H* 9.01 (d), 7.64 (s), 7.28 (d), 7.16 (d); CH_3 2.65 (s)	C*H* 5.38 (d), 2.36 (d), CH_3 1.60 (s)
	$Os(OEP)(O_2CCF_3)_2$	$CDCl_3$	H_{meso} 22.11 (s), CH_2 20.91 (q), CH_3 4.26 (t)	

[a] All NMR data measured at 20 °C at 300 MHz with chemical shifts given in δ and referenced to tetramethylsilane (=0.0 ppm). [b] Proton in thiolate ligand not observed in this experiment due to low solubility.

The rate of oxo transfer from MCPBA to Os(porphyrin)(CO)L is markedly dependent upon the lability of L. When L is the relatively inert pyridine ligand, long reaction times (>24 h) are required to obtain an impure product in diminished yield (≈15%). On the other hand, when the axial ligand is the more labile methanol or tetrahydrofuran, reaction times are less than 3 h and there is a corresponding increase in yield to >65%. These observations pertain to both the cavity-capped porphyrins and $TTPH_2$.

The reductive substitution of oxo ligands in the reaction of the osmyl unit is well precedented[7] and represents a synthetically useful approach for the preparation of a diverse range of Os(IV) products. Often a reductant, *i.e.* ascorbic acid, is used in these transformations, although neat mercaptans and catechol, as shown in eq 2, can be employed. The bis(mercaptide) complexes **7a–d** can also be prepared by treating Os(porphyrin)$(O_2CCF_3)_2$ with mercaptide anion but not by treating this material with mercaptan. Although complexes **7a–d** can be handled briefly in the open air, and purified by column chromatography, **7a** decomposes slowly in open air, even as a solid.

The formation of the μ_2-oxo osmium(IV) complex [(*p*-tolyl-S)Os(TTP)]$_2$O as a side product of the stoichiometric reaction

Table II. Formal Potentials for Os(IV) and Os(III) Mercaptide-Containing Porphyrin Complexes:[a] E_f (V) vs $Cp_2Fe^{+/0}$

		Os(III)/Os(IV)	Os(IV)/Os(V)
7a	$Os(TTP)(SC_6F_4H)_2$	−0.48	0.68
7b	$Os(TTP)(S\text{-}p\text{-}C_6H_4Me)_2$	−0.96	0.35

		Os(II)/ Os(III)	Os(III)/ Os(IV)		
11	$Os(TTP)(SC_6F_4H)(py)$	−1.19	0.04	1.02	1.41
	$Os(TTP)(SC_6F_4H)(1,5\text{-}Ph_2Im)$	−1.23	−0.05	0.94	
	$Os(TTP)(S\text{-}p\text{-}C_6H_4Me)(py)$	−1.24	−0.18		

[a] Determined in dichloromethane solution with 0.2 M tetra-*n*-butylammonium hexafluorophosphate on a platinum disk working electrode and referenced to $Cp_2Fe^{+/0}$, which has $E^\circ = -0.3$ V (vs SCE).

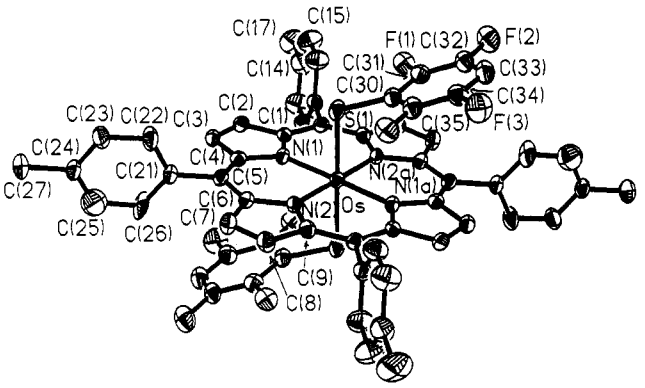

Figure 1. ORETP view of a molecule of $Os(TTP)(SC_6F_4H)_2$ (**7a**) with 30% probability thermal ellipsoids.

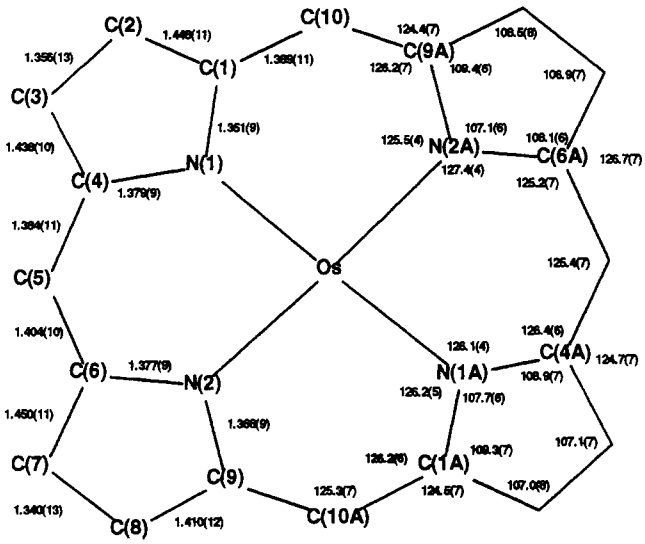

Figure 2. Bond lengths (on left) and bond angles (on right) of the porphyrin ring of **7a**.

Table III. Selected Bond Lengths (Å) for **7a**

Os–S(1)	2.294(3)	Os–N(1)	2.057(6)
Os–N(2)	2.041(6)	S(1)–C(30)	1.749(9)
C(31)–C(32)	1.363(13)	C(31)–C(30)	1.396(13)
C(34)–C(35)	1.371(16)	C(32)–C(33)	1.371(14)
C(35)–C(30)	1.380(14)	C(33)–C(34)	1.351(16)
C(31)–F(1)	1.339(11)	C(34)–F(3)	1.326(14)
C(32)–F(2)	1.368(11)	C(35)–F(4)	1.322(11)

of mercaptan and $Os(TTP)(O)_2$ is unique in light of the general paucity of examples of this class of compounds for osmium. The formulation of this product is based upon the similarity of the UV–vis and ^{1}H-NMR shifts of the four porphyrin tolyl substituents to those of the related ruthenium species. The only reported related complex, $[(RO)(OEP)Os]_2O$ (R = CH_3, H), serendipitously results from the reaction of Os(OEP)(CO)(MeOH), oxygen and 2,3-dimethylindole.[15] It is worth noting that when the conditions used to prepare $Os(porphyrin)(O)_2$ are applied to Ru(porphyrin)(CO)(MeOH), $[(MeO)Ru(porphyrin)]_2O$ is the main product,[12] although Che *et al.* recently reported that the use of high concentrations of MCPBA and Ru(porphyrin)(CO)(ROH) in ethanol leads to the reactive ruthenium(VI) products $Ru(porphyrin)(O)_2$ (porphyrin = OEP, TPP).[17]

The η^1-catecholate complex, **5**, has ^{1}H-NMR spectroscopic properties similar to those observed for other porphyrin complexes.[12] A unique common feature of these complexes is that η^2-catecholate coordination is prevented by the lack of cis coordinate sites. η^2-Catecholate coordination to a metalloporphyrin has been demonstrated in $Ti(TPP)(\eta^2\text{-}O_2C_6H_4)$, whose spectroscopic properties are consistent with the titanium being drawn out of the porphyrin plane.[18]

The contrasting reactions of mercaptides with the cavity-capped porphyrins **3a** and **3b**, which contain markedly differently sized cavities, once again illustrate the importance of steric effects in determining the outcome of the reaction. Thus bulky mercaptans, either 2,3,5,6-tetrafluorothiophenol (**a**) or (2,6-dimethylphenyl)-thiophenol (**d**), cannot bind to the osmium in the small cavity in **3a**, while both faces of the larger cavity-capped porphyrin **3b** bind *p*-tolyl mercaptide to give the bis(mercaptide) complex **8**.

The formulation of $Os^{III}(C_2\text{-}PBP)(L)_{in}(SR)_{out}$ as **C**, the initial product of the reaction of **3a** with 2,3,5,6-tetrafluorothiophenol, is based upon the observed ratio of the disulfide product to osmium complex starting material, 1.5:1, indicating a net three-electron change, or formal reduction of Os(VI) to Os(III). Although there is no spectroscopic evidence for its presence, the sixth coordination site inside the cavity may be occupied by the other byproduct, water. Further support for this formulation stems from the outer-sphere one-electron oxidation of this product in methanol to give **9**. In **9** the observed downfield contact shift is comparable to those found for related $Os^{IV}(porphyrin)(OMe)_2$ complexes.[6]

When **3a** is treated with 2 equiv of mercaptan, a mixture of starting material, disulfide, and **C** is formed. Complete conversion of **3a** to **C** is accomplished by addition of a further 2 equiv of mercaptan. If Os(IV) or Os(V) oxo-containing complexes are the initial product of the reaction, the subsequent reaction with the cavity-side oxo ligand must have a faster rate than the first reaction between **3a** and RSH.

In order to further characterize the Os(III) mercaptide complexes, we have developed other systematic synthetic routes to representative complexes of this class. For example, addition of mercaptan, in the case of $[Ru_2(OEP)_2]^{2+}$, and mercaptan/pyridine, in the case of $[Os_2(TTP)_2]^{2+}$, yields Ru(OEP)(SR) and Os(TTP)(SR)(L) (**11**). These metal(III) mercaptide complexes behave differently in the presence of pyridine, with the ruthenium complex undergoing a facile reductive elimination of disulfide to give $Ru(OEP)(py)_2$, as identified by the ^{1}H-NMR spectrum. However, the related osmium complex **11** is stable even at elevated temperatures and in the presence of concentrated Lewis bases, *i.e.* neat pyridine at reflux. Reductive elimination of disulfide from **11** has only been accomplished by vaccum pyrolysis, conditions which result in concomitant loss of pyridine, and results in the formation of $[Os(TTP)]_2$, as identified by ^{1}H-NMR and UV–vis spectroscopies.

The origin of the contact shift in the ^{1}H-NMR spectra of osmium(IV) porphyrins is residual temperature independent paramagnetism. In terms of simple ligand field theory, the ligand dependence of the contact shift can be attributed to different electronic ground states, that is, the ordering of the degenerate d_{xz}, d_{yz} levels with respect to the d_{z^2} level.

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Table IV. Selected Bond Angles (deg) for **7a**

		At Osmium			
S(1)–Os–N(1)	85.0(2)	S(1)–Os–N(2)	89.2(2)	N(1)–Os–N(2)	89.5(2)
S(1)–Os–S(1A)	180.0(1)	N(1)–Os–S(1A)	95.0(2)	N(2)–Os–S(1A)	90.8(2)
S(1)–Os–N(1A)	95.0(2)	N(1)–Os–N(1A)	180.0(1)	N(2)–Os–N(1A)	90.5(2)
S(1A)–Os–N(1A)	85.0(2)	S(1)–Os–N(2A)	90.8(2)	N(1)–Os–N(2A)	90.5(2)
N(2)–Os–N(2A)	180.0(1)	S(1A)–Os–N(2A)	89.2(2)	N(1A)–Os–N(2A)	89.5(2)
		In Mercaptide Ligand			
Os–S(1)–C(30)	107.8(3)	S(1)–C(30)–C(31)	121.7(7)	S(1)–C(30)–C(35)	122.8(7)
C(32)–C(31)–C(30)	121.0(8)	C(32)–C(31)–F(1)	120.1(9)	C(30)–C(31)–F(1)	118.9(8)
C(31)–C(32)–C(33)	122.0(9)	C(31)–C(32)–F(2)	117.3(8)	C(33)–C(32)–F(2)	120.7(9)
C(32)–C(33)–C(34)	118.0(9)	C(33)–C(34)–C(35)	120.6(10)	C(33)–C(34)–F(3)	118.6(10)
C(35)–C(34)–F(3)	120.7(10)	C(34)–C(35)–C(30)	122.9(9)	C(34)–C(35)–F(4)	117.0(10)
C(30)–C(35)–F(4)	120.1(10)	C(31)–C(30)–C(35)	115.5(8)		

Table V. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients for **7a**

	x/a	*y/b*	*z/c*	*U*(eq)[a]
Os	0.0000	0.0000	0.0000	0.050(1)
S(1)	–0.0537(1)	–0.0115(1)	0.1231(2)	0.083(1)
C(31)	–0.1284(4)	–0.1354(6)	0.0901(6)	0.076(3)
C(32)	–0.1802(4)	–0.1662(6)	0.0676(6)	0.082(3)
C(33)	–0.2245(4)	–0.1181(7)	0.0408(7)	0.092(4)
C(34)	–0.2162(5)	–0.0377(7)	0.0400(7)	0.082(4)
C(35)	–0.1643(5)	–0.0059(5)	0.0621(8)	0.080(4)
C(30)	–0.1187(3)	–0.0525(5)	0.0888(5)	0.066(3)
F(1)	–0.0863(2)	–0.1844(3)	0.1163(4)	0.095(2)
F(2)	–0.1863(3)	–0.2479(4)	0.0715(5)	0.124(3)
F(3)	–0.2583(4)	0.0093(4)	0.0121(8)	0.137(4)
F(4)	–0.1599(3)	0.0734(4)	0.0612(4)	0.105(3)
N(1)	0.0675(3)	–0.0119(3)	0.0885(4)	0.052(2)
N(2)	0.0024(2)	0.1216(4)	0.0184(3)	0.050(2)
C(1)	0.0922(3)	–0.0817(5)	0.1144(5)	0.050(2)
C(2)	0.1375(4)	–0.0647(6)	0.1786(5)	0.065(3)
C(3)	0.1384(3)	0.0160(5)	0.1912(5)	0.058(3)
C(4)	0.0942(3)	0.0496(5)	0.1348(5)	0.052(2)
C(5)	0.0806(3)	0.1304(5)	0.1304(4)	0.056(2)
C(6)	0.0380(3)	0.1642(4)	0.0752(5)	0.056(2)
C(7)	0.0243(4)	0.2489(5)	0.0663(6)	0.072(3)
C(8)	–0.0185(4)	0.2543(5)	0.0062(6)	0.072(3)
C(9)	–0.0328(3)	0.1761(5)	–0.0231(5)	0.055(2)
C(10)	0.0769(3)	–0.1583(5)	0.0857(5)	0.059(3)
C(11)	0.1099(3)	–0.2274(4)	0.1231(5)	0.065(3)
C(12)	0.1606(4)	–0.2505(6)	0.0894(7)	0.095(4)
C(13)	0.1917(5)	–0.3097(7)	0.1247(9)	0.123(6)
C(14)	0.1734(5)	–0.3509(7)	0.1955(10)	0.116(5)
C(15)	0.1235(5)	–0.3303(7)	0.2328(8)	0.120(6)
C(16)	0.0917(5)	–0.2678(7)	0.1963(7)	0.105(5)
C(17)	0.2078(6)	–0.4204(8)	0.2395(9)	0.175(8)
C(21)	0.1121(3)	0.1883(5)	0.1906(5)	0.062(3)
C(22)	0.0948(4)	0.2058(7)	0.2729(7)	0.105(4)
C(23)	0.1238(4)	0.2638(7)	0.3268(7)	0.103(4)
C(24)	0.1708(3)	0.2998(5)	0.3015(5)	0.070(3)
C(25)	0.1893(5)	0.2784(9)	0.2244(7)	0.148(7)
C(26)	0.1622(5)	0.2225(9)	0.1674(7)	0.141(6)
C(27)	0.2008(4)	0.3592(6)	0.3620(7)	0.105(4)
C(60)	0.0275(54)	0.4873(44)	0.0393(80)	0.202(48)
C(61)	0.0950(36)	0.4608(55)	0.0148(54)	0.215(31)
C(62)	0.0115(44)	0.4585(51)	0.2014(55)	0.247(37)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor (Å^2).

The structural data available for metalloporphyrin mercaptide complexes are relatively sparse, although the available data for iron porphyrin containing examples indicate weak mercaptide binding with long iron–sulfur bond lengths (Fe–S = 2.34 ± 0.02 Å). Furthermore, relatively few structural data are available for the high-valent osmium porphyrins or osmium mercaptide complexes (Table VI).[19] The contrast in the structural data for **7a** with the other available results indicates that it contains a strong metal–sulfur interaction with a very compact Os–S–C angle at sulfur. In formal terms the Os(IV) center is only a 16-electron species, and there is the possibility of π donation of sulfur electrons. Although a strong case for π bonding in terminal mercaptide complexes has not been made, the structural dichotomy associated with the closely related phosphido–phosphenium duality[20] suggests that strong π bonding is associated with shorter metal–ligand bonding and increased metal–sulfur–carbon bond angles. Clearly, the structural features for the mercaptide bonding in **7a** do not fit into this pattern. Perhaps the most discernible trend in Table VI is the dependence of the Os–S bond length and Os–S–C bond angle on the nature of the *trans ligand* and the oxidation state of the metal. Recent structural results for the diethoxy-, bis(propanolato)-, and diphenoxyosmium(IV) porphyrins provide for an interesting contrast with the structure of **7a**.[21] Although the trends in Os–O and Os–S bond lengths are similar (that is, they are shorter than in comparable complexes), the Os–S–C bond angle is 20° less than the corresponding Os–O–C bond angles [127.0(3)–128.2(5)°]. The structural and NMR results for these osmium(IV) complexes suggest that the electronic structures of these derivatives are very sensitive to the donor ligand. Studies directed toward further defining the magnetochemistry of these compounds will be described in future reports.

Table VI. Structural Data for Osmium Mercaptide Complexes

complex	Os–S (Å)	Os–S–C (deg)	ref
$Os(TTP)(SC_6F_4H)_2$	2.294(3)	107.8(3)	this work
$Os(salen)(SPh)_2$	2.298(2)	112.1(2)	25
	2.343(2)	112.4(2)	
$Os[(BA)_2en](SCH_2Ph)_2$[a]	2.298(3)	107.8(4)	26
	2.315(3)	102.5(4)	
	2.308(3)	106.8(4)	
	2.323(3)	104.3(4)	
$Os(SC_6F_5)_2(O_2CPh)(PMe_2Ph)_2$[b]	2.329(1)	107.6(1)	26
	2.335(1)	107.0(1)	
$Os(SC_6F_5)_3(PMe_2Ph)_2$[c]	2.201(1)	114.4(1)	27
	2.196(1)	133.4(1)	
	2.195(1)	112.9(1)	
$Os(SC_6F_5)_2(CO)_2(PMe_2Ph)_2$[d]	2.477(1)	114.3(2)	28
$OsCl(SC_6F_5)(N_2)(PMe_2Ph)_3$[e]	2.507(1)	123.9(2)	29

[a] BA_2en = bis(benzoylacetone) ethylenediimine dianion. Two independent molecules per asymmetric unit. [b] Mutually *trans* mercaptide ligands. [c] Trigonal bipyramid geometry with the three mercaptide ligands in the equatorial plane. [d] Trans,trans,trans structure, with an inversion center of symmetry located at the metal. [e] Tertiary phosphine ligands are meridonally arranged with the mercaptide ligand *trans* to the middle one.

Experimental Section

Materials. C_n-$PBPH_2$ and $TTPH_2$ were prepared by literature methods.[9,22] Triosmium dodecacarbonyl (Aldrich) was used without further purification. Mercaptans (Aldrich) were distilled or sublimed

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under nitrogen prior to use. Ferrocenium hexafluorophosphate, $[Cp_2Fe][PF_6]$, was prepared by literature methods.[23] The mercaptide complexes of osmium(IV) were prepared and purified by standard Schlenk techniques and stored in an inert-atmosphere box. The air-sensitive mercaptide complexes of osmium(III) were handled exclusively in an inert-atmosphere box. Physical measurements and general inert-atmosphere techniques were identical to those employed elsewhere.[24]

$Os(C_2$-PBP$)(CO)_{in}(py)_{out}$ (1b). Triosmium dodecacarbonyl, 0.090 g (9.96×10^{-5} mol), 0.066 g of C_2-$PBPH_2$ (6.65×10^{-5} mol), and 20 mL of 2-(2-methoxyethoxy)ethanol were added to a three-necked flask equipped with a gas inlet and a reflux condenser, and the mixture was sonicated at room temperature to dissolve the solids. The solution was then thoroughly degassed with nitrogen, and the reaction vessel was plunged into an oil bath preheated to 220 °C. The reaction was monitored by UV–vis spectroscopy by determining the quantity of unmetalated porphyrin upon treatment of the sample with trifluoroactic acid. Additional quantities of 10 mg of triosmium dodecacarbonyl were added at 3 and 6 h, and the mixture was heated at reflux for 7 h total. After cooling, 5 mL of pyridine was added, the mixture was stirred for 5 min, and the volume of solvent was reduced to less than 1 mL in vacuo. Saturated sodium chloride solution *ca.* 100 mL, was then added to precipitate the porphyrin product, which was allowed to stand overnight. Filtration of this material through Celite followed by washing with copious quantities of water, drying, and then dissolving the precipitate with dichloromethane afforded the crude product. Chromatography on TLC grade silica, with 7:3 dichloromethane/ether, returned 72 mg, 84% yield, of product. UV–vis (CH_2Cl_2): λ_{max} 414 (Soret), 532, 562 nm. IR (CH_2Cl_2): ν(CO) 1927 cm^{-1}. Anal. Calcd for $C_{67}H_{41}N_9O_7Os$: C, 63.39; H, 3.37; N, 9.78. Found: C, 63.58; H, 4.02; N, 9.56.

$Os(C_2$-PBP$)(CO)_{in}(CH_3OH)_{out}$ (1a). This was prepared in 82% yield as for **1** but with methanol added to the reaction mixture instead of pyridine.

$Os(C_6$-PBP$)(CO)_{out}(py)_{in}$ (2b). This was prepared in 93% yield as for **2a** but with pyridine added to the reaction mixture instead of methanol. Anal. Calcd for $C_{72}H_{51}N_9O_7Os$: C, 64.31; H, 3.83; N, 9.38. Found: C, 64.08; H, 3.37; N, 8.97.

$Os(C_6$-PBP$)(CO)_{out}(CH_3OH)_{in}$ (2a). Triosmium dodecacarbonyl, 0.048 g (5.33×10^{-5} mol), 0.055 g of C_6-$PBPH_2$ (5.2×10^{-5} mol), and 20 mL of 2-(2-methoxyethoxy)ethanol were treated as described above for **1** except that methanol was used instead of pyridine and the metalation required only 4 h to reach completion. Chromatographic workup with 9:1 dichloromethane/ether with one drop of methanol afforded 65 mg of brick-red product in 96% yield. UV–vis (CH_2Cl_2): λ_{max} 412 (Soret), 530, 580 nm. IR (CH_2Cl_2): ν(CO) 1928 cm^{-1}.

$Os(C_2$-PBP$)(O)_2$ (3a). $Os(C_2$-PBP$)(CO)_{in}(CH_3OH)_{out}$ (**1a**), 48 mg, and 5 equiv of *m*-chloroperbenzoic acid, 34 mg, were stirred together in 20 mL of dry dichloromethane for 7 h. Chromatographic workup with 2:1 dichloromethane/ether afforded 39 mg (83%) of black-red product after recrystallization from dichloromethane/heptane. UV–vis (CH_2Cl_2): λ_{max} 394 (Soret), 582 nm. IR (Nujol): $\nu(OsO_2)$ 840 cm^{-1}. Anal. Calcd for $C_{62}H_{38}N_8O_8Os \cdot {}^1/_4CH_2Cl_2$: C, 60.56; H, 3.15; N, 9.07. Found: C, 60.64; H, 3.59; N, 8.63.

$Os(C_6$-PBP$)(O)_2$ (3b). $Os(C_6$-PBP$)(CO)_{out}(CH_3OH)_{in}$ (**2a**), 31 mg, and 5 equiv of *m*-chloroperbenzoic acid, 23 mg, were stirred together in 20 mL of dry dichloromethane for 2 h. Chromatographic workup with 8:1 dichloromethane/ether afforded the 20 mg, 67% yield, of black-red product after recrystallization from dichlormethane/heptane. UV–vis (CH_2Cl_2): λ_{max} 394 (Soret), 460 nm. IR (Nujol): $\nu(OsO_2)$ 839 cm^{-1}. Anal. Calcd for $C_{66}H_{46}N_8O_8Os$: C, 62.44; H, 3.66; N, 8.83. Found: C, 62.01; H, 3.29; N, 8.93.

$Os(TTP)(OC_6H_4$-2-$OH)_2$ (5). $Os(TTP)(O)_2$, 5.4 mg (6.1×10^{-6} mol), and 45 mg of catechol (4.1×10^{-4} mol) were thoroughly mixed in a 50-mL flask and then heated on an oil bath at 85 °C for 20 min. During this period, the catechol melted and sublimed, leaving the product as a fine powder. Purification by column chromatography (silica gel/dichloromethane) and recrystallization from dichloromethane/hexane returned 6 mg (92% yield) of fine red crystals of **5**. UV–vis (CH_2Cl_2): λ_{max} 394 (Soret), 504 (shoulder), 588 nm. Anal. Calcd for $C_{64}H_{46}N_4O_4Os$: C, 68.31; H, 4.12; N, 4.98. Found: C, 68.17; H, 3.88; N, 5.23.

$Os(TTP)(O_2CCF_3)_2$ (6). $Os(TTP)(OMe)_2$,[5] 20 mg (2.2×10^{-5} mol), was dissolved in 2 mL of dichloromethane, and 1 mL of trifluoroacetic acid was then added. This mixture was allowed to stir at room temperature for 5 days and was then stripped of all volatile components *in vacuo*. The resulting material was recrystallized from dichloromethane/hexane to return 21 mg (86% yield) of fine red crystals of **6**. UV–vis (CH_2Cl_2): λ_{max} 390 (Soret), 560 (shoulder), 603 nm. Anal. Calcd for $C_{52}H_{36}F_6N_4O_4Os \cdot CH_2Cl_2$: C, 54.40; H, 3.28; N, 4.79. Found: C, 54.78; H, 2.86; N, 4.89.

Preparation of $Os(TTP)(SR)_2$ (7a–d). $Os(TTP)(SC_6F_4H)_2$ (7a). $Os(TTP)(O)_2$, 20 mg (2.3×10^{-5} mol) in 10 mL of dichloromethane was treated with 2,3,5,6-tetrafluorothiophenol, 0.1 mL (6 equiv), at room temperature. Within 10 min, this solution became deep red; after 40 min, it was concentrated *in vacuo*. Chromatography of the red residue on silica with a dichloromethane eluant returned 23 mg (81%) of **5a** after recrystallization from dichloromethane/heptane. UV–vis (CH_2Cl_2): λ_{max} (log ϵ) 409 (4.94) (Soret), 527 (4.11), 571 (shoulder) nm. Anal. Calcd for $C_{60}H_{38}N_4F_8S_2Os$: C, 59.00; H, 3.14; N, 4.59. Found: C, 59.07; H, 2.64; N, 4.33. Larger scale preparations can be purified by repeated recrystallization from dichloromethane/heptane.

7a from $Os(TTP)(O_2CCF_3)_2$ (6). $Os(TTP)(O_2CCF_3)_2$, 2 mg (1.8×10^{-6} mol), in 2 mL of dichloromethane was treated with 0.05 mL of 2,3,5,6-tetrafluorothiophenol and 0.01 mL of triethylamine at room temperature in the open air. After 3 h, the contents of the flask was concentrated *in vacuo* and the residue was passed through a silica plug, eluted with dichloromethane, and then recrystallized from dichloromethane/hexane. The reaction product was identified by spectroscopic characterization and comparison with an authentic sample.

$Os(TTP)(S$-*p*-tolyl$)_2$ (7b). $Os(TTP)(O)_2$, 20 mg (2.3×10^{-5} mol), in 10 mL of dichloromethane was treated with 4-methylthiophenol, 40 mg (3.5 equiv). The resulting red mixture was stirred for 35 min and then stripped to dryness of volatile components. A sublimation cold-finger was then fitted to the flask, and the excess mercaptan was sublimed out of the reaction mixture with gentle heat. The resulting residue was recrystallized twice from dichloromethane/heptane to afford 21 mg of **5b** (83%). UV–vis (CH_2Cl_2): λ_{max} (log ϵ) 411 (4.71) (Soret), 519 (4.19), 583 (4.0) nm. Anal. Calcd for $C_{62}H_{50}N_4OsS_2$: C, 67.29; H, 4.56; N, 5.06. Found: C, 67.00; H, 4.79; N, 5.12.

$Os(TTP)(S$-*o*-tolyl$)_2$ (7c) and $Os(TTP)(S$-2,6-dimethylphenyl$)_2$ (7d). **7c** and **7d** were prepared in a manner analogous to that for **7a,b**. Relevant spectroscopic data for these species are included in Table I.

$Os(C_6$-PBP$)(S$-*p*-tolyl$)_{in}(S$-*p*-tolyl$)_{out}$ (8). $Os(C_6$-PBP$)(O)_2$ (**3b**), 3.2 mg (2.2×10^{-6}), and 3 equiv of *p*-tolylthiophenol (1.2 mg) were dissolved in C_6D_6, and the course of the reaction was monitored with ^{1}H-NMR spectroscopy. After 2 h, the reaction mixture was washed onto a 2-cm silica column, and the residual mercaptan and disulfide byproduct were eluted with dichloromethane. After all sulfur-containing species had been eluted, the product was eluted with 1:1 dichloromethane/acetone and dried; yield 2.5 mg (77%). This compound was characterized by ^{1}H-NMR and UV–vis spectroscopies (CH_2Cl_2): λ_{max} 419 (Soret), 522, 671 nm.

Reaction of $Os(C_2$-PBP$)(O)_2$ (3a) with 2,6-Dimethylthiophenol and with 2,3,5,6-Tetrafluorothiophenol and Standard. $Os(C_2$-PBP$)(O)_2$, 2.4 mg (2×10^{-6} mol), was treated with 12 equiv fo with 2,6-dimethylthiophenol (3.3 mg) in C_6D_6, and the reaction was monitored by ^{1}H-NMR. Within 4 h, no further disulfide formation was observed and the solution was concentrated *in vacuo* and chromatographed on silica. Benzene was used to elute the disulfide byproduct and 1:1 benzene/acetone was then used to elute a red fraction, which was recrystallized from dichloromethane/octane to give 2.7 mg of brown-red product. UV–vis (CH_2Cl_2): λ_{max} 410 (Soret), 512, 572 nm. $\mu = 1.62\ \mu_B$ in $CDCl_3$ at 25 °C. The reaction between **3a**, 2.3 mg, and 2,3,5,6-tetrafluorothiophenol, 1.0 mg (3 equiv), was performed in the presence of hexamethylbenzene in deuteriobenzene as internal standard. Within 6 h and 40 min at room temperature, the reaction was complete with 19% residual porphyrinic starting material and 72% of the original mercaptan present as the

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disulfide. The reaction was brought to completion by the addition of 0.7 mg of additional mercaptan and allowing the mixture to stand a further 3 h. UV–vis (THF): λ_{max} (Soret), 516 nm. This product was further characterized by treating it with ferrocenium hexafluorophosphate, 0.63 mg, in 5 mL of methanol for 1 h and then dried *in vacuo*. The resulting red solid, dissolved in dichloromethane, was loaded onto a small silica column. Ferrocene was eluted with dichloromethane, and the product, $Os(C_2\text{-PBP})(OMe)_{in}(SC_6F_4H)_{out}$, eluted with 5:1 CH_2Cl_2/acetone. UV–vis (CH_2Cl_2): λ_{max} 418 (Soret), 520 nm.

Os(TTP)(SC_6F_4H)(py) (11). From Os(TTP)(SC_6F_4H)$_2$ (7a). **7a**, 26.1 mg, was heated at reflux in 10 mL of benzene and 0.5 mL of pyridine for 3 h. The resulting red-brown mixture was cooled and concentrated to a powder *in vacuo*. This solid was purified by column chromatography on silica, eluted first with *n*-hexane to remove the disulfide byproduct and then with dichloromethane to elute **11**. Recrystallization from dichloromethane/hexane, returned 19 mg (81% yield) of **11**. UV–vis (CH_2Cl_2): λ_{max} (log ϵ) 411 (4.71) (Soret), 519 (4.19), 583 (4.0) nm. Anal. Calcd for $C_{59}H_{42}F_4N_5OsS$: C, 63.31; H, 3.79; N, 6.26. Found: C, 63.78; H, 3.58; N, 6.19.

From [Os(TTP)]$_2$BF$_4$. The starting material, 7 mg (3.7×10^{-6} mol), in 1 mL of pyridine was treated with 2,3,5,6-tetrafluorothiophenol, 1.4 mg (7.5×10^{-6} mol). The resulting red-brown mixture was stirred for 25 min and then stripped to dryness of volatile components. Chromatographic purification, as outlined in the preparation from **7a**, returned 6.0 mg (72% yield) of red-brown powder after recrystallization from dichloromethane/hexane. This material is spectroscopically identical to samples prepared by treating **7a** with pyridine.

X-ray Diffraction Study of Os(TTP)(SC_6F_4H)$_2$ (7a). Black prisms of this compound were grown by vapor-phase diffusion of *n*-hexane into a dichloromethane solution of **7a**. A Siemens R3m/V diffractometer was used to collect 25 reflections in the range $20° < \theta < 24°$ which were least-squares-fit to the unit cell parameters listed in Table VII. Systematic absences observed were as follows: hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$. This indicates that the crystal belongs to either $C2/c$ or C_c; the space group $C2/c$ was confirmed by subsequent successful structural solution and refinement. The position of the osmium atom was determined by Patterson methods, and the remaining atoms were found from successive difference Fourier maps. In the final stages of refinement, the presence of a hexane solvate was determined and independently confirmed by ^{1}H-NMR spectroscopy of other crystals from the same recrystallization. Anisotropic thermal parameters were refined for all atoms except the solvate carbons and the hydrogen atoms. Bond distances, angles, and final positional parameters are given in Tables III–V, respectively, with complete crystal structure collection data, anisotropic coefficients, and H atom coordinates given in supplementary Tables II–IV, respectively. Further details are available from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

Table VII. Crystallographic Data for Os(TTP)(SC_6F_4H)$_2$ (**7a**)

empirical formula $C_{60}H_{38}F_8N_4OsS_2 \cdot C_6H_{14}$	fw 1239.3
a = 23.750(5) Å	space group monoclinic, $C2/c$
b = 16.625(4) Å	temp 293 K
c = 15.049(3) Å	λ = 0.710 73 Å
β = 92.05(2)°	ρ_{calcd} = 1.386 g cm^{-3}
V = 5938(2) Å^3	μ = 0.2279 cm^{-1}
Z = 4	$R(F_o^2)^a$ = 3.80%
	$R_w(F_o^2)^b$ = 6.77%

$^a R = \sum||F_o| - |F_c||$. $^b R_w = \sum w(|F_o| - |F_c|)^2$; $w^{-1} = \sigma^2(F) + 0.0057F^2$.

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Supplementary Material Available: Table SI, giving the variable-temperature ^{1}H-NMR data for Os(OEP)(SC_6F_4H)$_2$, and Tables SII–SIV, listing crystal structure collection data, thermal parameters, and calculated H atom positions for Os(TTP)(SC_6F_4H)$_2$ (5 pages). Ordering information is given on any current masthead page.