$(CN)_6]^{4-}$ and $[Co(CN)_6]^{3-}$ to polyammonium macrocycles of different sizes, show the absence of any selectivity and are consistent with strong interactions, mainly Coulombic in nature, between the anion and the protonated second-sphere ligand. The crystal structure of one of these "supercomplexes" proves that (i) the anionic species $[Co(CN)_6]^{3-}$ does not go inside the macrocyclic cavity, (ii) the rigid conformation of the macrocyclic ring is essentially determined by electrostatic repulsions and very likely maintained in solution, and (iii) electrostatic interactions and hydrogen bonds between the cationic and anionic species have a synergistic effect in the supercomplex formation.

Acknowledgment. We thank the Generalitat of Valencia for a grant to E.G.-E.

Registry No. L1, 57970-53-3; L2, 862-28-2; L3, 60464-68-8; $Co(CN)_6^{3-}$, 14897-04-2; $Fe(CN)_6^{4-}$, 13408-63-4; $[H_8L2][Co(CN)_6]_2Cl_2\cdot 10H_2O$, 110433-16-4.

Supplementary Material Available: Table of thermal parameters (2 pages); table of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, University of Hong Kong, Hong Kong,
and Contribution No. 7597 from the Arthur Amos Noyes Laboratory, California Institute of Technology, Pasadena, California 91125

Triphenylphosphine Reduction of Dioxoosmium(VI) Porphyrins. Crystal Structures of Bis(triphenylphosphine oxide)(octaethylporphinato)osmium(II) and Bis(triphenylphosphine)(*meso*-tetraphenylporphinato)osmium(II)

Chi-Ming Che,*[1a] Ting-Fong Lai,[1a,c] Wai-Cheung Chung,[1a] William P. Schaefer,[1b] and Harry B. Gray[1b]

Received September 18, 1986

The reactions of $Os^{VI}(OEP)O_2$ and $Os^{VI}(TPP)O_2$ (H_2OEP = octaethylporphyrin; H_2TPP = *meso*-tetraphenylporphyrin) with PPh_3 in CH_2Cl_2 yield $Os^{II}(OEP)(OPPh_3)_2$ (**1**) and $Os^{II}(TPP)(PPh_3)_2$ (**2**), respectively. The crystal structures of complexes **1** and **2** have been determined: **1**·$3H_2O$, monoclinic, space group $P2_1/c$, a = 13.020 (2) Å, b = 14.474 (2) Å, c = 17.988 (3) Å, β = 103.36 (1)°, Z = 2; **2**, triclinic, space group $P\bar{1}$, a = 11.536 (1) Å, b = 13.445 (1) Å, c = 21.237 (2) Å, α = 85.25 (1)°, β = 75.77 (1)°, γ = 69.55 (1)°, Z = 2. The Os–porphinato unit in **1** is planar within 0.07 Å, with Os–N = 2.029 (8) Å and Os–O($OPPh_3$) = 2.036 (7) Å. The structure of **2** shows two independent, centrosymmetric molecules with Os–N = 2.044 (3) Å and Os–P = 2.148 (6) Å; the Os–porphinato groups are somewhat puckered, with out-of-plane deviations up to 0.12 Å. The Os–P distances in **2** are substantially longer than normal, reflecting the strong trans influence of PPh_3.

Introduction

We have begun a program of investigating oxygen atom transfer reactions of *trans*-dioxoosmium(VI) complexes.[2,3] The reactions of $Os^{VI}(OEP)O_2$ (H_2OEP = octaethylporphyrin) with PPh_3 in ROH (R = CH_3 or C_2H_5) were found to produce $Os(OEP)(OR)_2$.[2] In CH_2Cl_2, PPh_3 reduction of $Os(OEP)O_2$ gives $Os(OEP)(OPPh_3)_2$ (**1**) and PPh_3 reduction of $Os(TPP)O_2$ yields $Os(TPP)(PPh_3)_2$ (**2**) (H_2TPP = *meso*-tetraphenylporphyrin). The formation of $Os(OEP)(OPPh_3)_2$ from the reaction of $Os(OEP)O_2$ and PPh_3 implies that both $Os(OEP)(O_2)$ and the presumed $Os^{IV}(OEP)O(OPPh_3)$ intermediate are able to transfer an oxygen atom to PPh_3.[6] In this paper we describe the X-ray crystal structure characterization of these two new compounds. As far as we are aware, there are only two other structures reported for osmium porphyrins.[4,5]

Experimental Section

Octaethylporphyrin (H_2OEP), *meso*-tetraphenylporphyrin (H_2TPP), and $Os_3(CO)_{12}$ were obtained from Strem Chemicals. $Os(OEP)O_2$ and $Os(TPP)O_2$ were prepared as described previously.[2,6,7] All solvents and reagents were of analytical grade and used without further purification. UV–vis spectra were recorded on a Beckman Acta CIII spectrophotometer. Elemental analyses were performed by the Australian National Laboratory.

Bis(triphenylphosphine oxide)(octaethylporphinato)osmium(II), $Os(OEP)(OPPh_3)_2$ (1). Method 1. $Os(OEP)O_2$ (100 mg, 0.13 mmol) and PPh_3 (200 mg, 0.76 mmol) were stirred in CH_2Cl_2 (50 mL) for 3 h. When all the dioxoosmium(VI) complex had reacted, as monitored by following the uV–vis spectral changes of the solution, the solvent was evaporated to ~2 mL at room temperature. The reaction product was purified by column chromatography on a silica column with $CHCl_3$ as eluant. The first orange-red band was $Os(OEP)(PPh_3)_2$ contaminated with some PPh_3. With acetone as the eluting solvent, a brown species was washed out. The desired product $Os(OEP)(OPPh_3)_2$ was finally eluted by methanol. The solvent was evaporated at room temperature, and the crude product was recrystallized as dark, air-stable plates from a CH_2Cl_2–cyclohexane mixture (1:1); yield 50%.

Method 2. $Os(OEP)O_2$ (50 mg, 0.07 mmol) and PPh_3 (60 mg, 0.22 mmol) in CH_2Cl_2 (200 mL) were irradiated with a 450-W high-pressure Hg short-arc lamp for 4 h.[8] The solvent was then evaporated, and the crude product was purified as described in method 1. UV–vis spectrum (CH_2Cl_2, λ_{max}/nm): 391, 454, 496, 506 sh, 536.

Bis(triphenylphosphine)(*meso*-tetraphenylporphinato)osmium(II), $Os(TPP)(PPh_3)_2$ (2). *trans*-$[Os(TPP)O_2]$ (0.3 g, 0.36 mmol) and PPh_3 (1 g, 3.81 mmol) were stirred in a CH_2Cl_2–CH_3CN (1:1, 50 mL) mixture for 2 h. Violet, air-stable crystals of $Os(TPP)(PPh_3)_2$ gradually depositing upon standing; yield about 40%. Anal. Calcd for $OsC_{80}H_{58}N_4P_2$: C, 72.4; H, 4.4; N, 4.2; P, 4.7. Found: C, 72.3; H, 4.1; N, 4.2; P, 4.8. A $\sim 10^{-6}$ M CH_2Cl_2 solution of $Os(TPP)(PPh_3)_2$ exhibits an intense Soret band at 408 nm.

Bis(triphenylphosphine)(octaethylporphinato)osmium(II). Reaction between $Os(OEP)O_2$ (0.1 g, 0.13 mmol) and PPh_3 (1 g, 3.81 mmol) in benzene (30 mL) at 50 °C for 2 h yielded $Os(OEP)(PPh_3)_2$. The UV–vis spectrum in benzene is similar to that of the well-characterized $Os(OEP)(PBu_3)_2$[9] (λ_{max}/nm): 492, 516. Attempts to isolate an analytically pure sample of this compound were unsuccessful.

Crystal Structure Determination of $Os(OEP)(OPPh_3)_2\cdot 3H_2O$ (1·3H_2O). Crystal Data: $C_{72}H_{80}O_5N_4P_2Os$, crystal size 0.22 × 0.34 × 0.08 mm, M_r = 1333.61, space group $P2_1/c$, a = 13.020 (2) Å, b = 14.474 (2) Å, c = 17.988 (3) Å, β = 103.36 (1)°, V = 3298.1 (15) $Å^3$ (21 °C),

---

* To whom correspondence should be addressed.

(1) (a) University of Hong Kong. (b) California Institute of Technology. (c) On sabbatical leave at the California Institute of Technology.

(2) Che, C.-M.; Poon, C.-K.; Chung, W.-C.; Gray, H. B. *Inorg. Chem.* **1985**, *24*, 1277.

(3) Che, C.-M.; Cheng, W. K.; Mak, T. C. W. *Inorg. Chem.* **1986**, *25*, 703.

(4) Buchler, J. W.; Lam Lay, K.; Smith, P. D.; Scheidt, W. R.; Rupprecht, G. A.; Kenny, J. E. *J. Organomet. Chem.* **1976**, *110*, 109.

(5) Masuda, H.; Taga, T.; Osaki, K.; Sugimoto, H.; Mori, M. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2345.

(6) Recent work by Groves and co-workers suggests that $Ru^{IV}(TMP)O$ (H_2TMP = tetramesitylporphyrin) disproportionates into Ru(II) and Ru(IV) in fluid solution: Groves, J. T.; Quinn, R. *J. Am. Chem. Soc.* **1985**, *107*, 5790.

(7) Buchler, J. W.; Smith, P. D. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 341.

(8) Further information about the photochemical reactions of $Os(OEP)O_2$ with PPh_3 will be given later: Tang, W.-T.; Che, C.-M., manuscript in preparation.

(9) (a) Che, C.-M.; Chung, W.-C. *J. Chem. Soc., Chem. Commun.* **1986**, 386. (b) Buchler, J. W.; Smith, P. D. *Chem. Ber.* **1976**, *109*, 1465.

0020-1669/87/1326-3907$01.50/0

$Z = 2$, $d_{\text{X-ray}} = 1.343$ (6) g cm^{-3}, $F(000) = 1372$, μ(Mo Kα) = 21.53 cm^{-1}.

Two crystals grown from a $CH_3C{\equiv}N/CH_2Cl_2$ mixture by evaporation were used in the data collection after oscillation and Weissenberg photographs showed them to be single. A monoclinic cell was found, and cell dimensions were obtained from the setting angles of 25 reflections in the range $19° < 2\theta < 31°$ on a Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα (0.71073 Å) radiation. Altogether 9315 reflections were scanned at room temperature in a θ–2θ mode at 2° min^{-1} (2θ) in the octants $\pm h,\pm k,l$, with $2° < 2\theta < 45°$, including three check reflections measured every 10000 s of X-ray exposure. The check reflections showed no fluctuations greater than those expected from counting statistics. Backgrounds were measured at each end of each scan; an average background as a function of 2θ was calculated and was used to correct the measured scan counts. Systematic absences of $h0l$ with l odd and $0k0$ with k odd indicated space group $P2_1/c$ (No. 14). After space group absences were deleted and equivalent reflections were merged (the goodness of fit for merging was 1.39), 4283 independent reflections remained, of which 3560 had $F_o^2 > 0$ and 2714 had $F_o^2 > 3\sigma(F_o^2)$. The intensities were corrected for Lorentz and polarization factors but not for absorption. The value of $\mu r_{\max}$ is 0.41, and neglect of the absorption correction could have caused a maximum error of 20% in an F value. Variances of the averaged intensities were assigned on the basis of counting statistics plus an additional term, $0.014I^2$; variances for the merged reflections were determined by standard propagation of error plus another additional term, $0.014I^2$.

Structure Solution and Refinement. The position of the osmium atom at the origin was obvious from the zero-level Weissenberg photograph, and subsequent structure factor–Fourier cycles confirmed this and revealed the remaining non-hydrogen atoms. Refinement was carried out by full-matrix least squares. The quantity minimized was $\sum w(F_o^2 - F_c^2)^2$, with weight $w = 1/\sigma^2(F_o^2)$. The ethyl groups on one of the pyrrole rings were disordered. We represented them and the carbon atoms they are bonded to by two partially populated groups. The occupancy factors were refined to 0.634 (9) and 1 − 0.634. For these disordered groups, the coordinates of the ring carbons were refined by least squares, the methylene carbon atoms were placed at calculated positions 1.54 Å from the ring atoms, and the terminal methyl carbon atoms were positioned from difference maps calculated in the planes where they were expected. The Os, P, O, and N atoms were refined anisotropically, as were the 2 terminal carbon atoms on the other 2 ethyl groups and 8 of the 18 carbon atoms in the triphenylphosphine oxide group; the remaining carbon atoms were isotropic. Hydrogen atoms were introduced at calculated positions, with C–H distances of 0.95 Å and staggered geometry being assumed, on carbon atoms with full occupancy. They were assigned isotropic thermal parameters equal to those of the carbon atom to which they are bonded. Their parameters were not refined, but they were repositioned four times during the refinement. The final R index for all reflections with $F_o^2 > 0$ is 0.076; for those with $F_o^2 > 3\sigma(F_o^2)$ it is 0.056. The goodness of fit for 4283 data and 238 parameters is 2.84 ($R = \sum||F_o| - |F_c||/\sum|F_o|$; GOF $= [\sum w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$. The final difference Fourier map showed excursions of ±0.80 e Å^{-3} near the osmium atom; the rest of the map was flat, except near the disordered ethyl groups, where peaks as high as 1.7 e A^{-3} indicated that our model was not perfect. The peaks, however, gave no clear indication for improving the model; since the details of the rest of the structure are not affected by small changes in this area, we have left it as described. Two regions of the cell show peaks that we have modeled as solvent (water), one site fully populated and the other half-populated. The compound was crystallized from a $CH_3C{\equiv}N/CH_2Cl_2$ mixture, but neither of these molecules fits the difference map at all. All calculations were done on a VAX 11/750 computer using programs of the CRYRM system.[10] Form factors for neutral atoms were taken from ref 11; anomalous dispersion corrections of −1.816 e for osmium and +0.09 e for phosphorus were applied.[12] Final atomic parameters for the non-hydrogen atoms are listed in Table I and selected distances and angles in Table II. The observed and calculated structure factors, anisotropic thermal parameters, hydrogen parameters, and other distances and angles are in the supplementary material.

Table I. Heavy-Atom Parameters for **1**[a]

atom	x	y	z	U_{eq}[b] or B, Å^2	POP[c]
Os	0	0	0	622 (2)	2
N1	−357 (6)	346 (5)	−1125 (4)	678 (26)	
N2	1207 (6)	919 (6)	219 (5)	695 (27)	
C1	183 (9)	1101 (8)	−1453 (7)	6.8 (3)	
C2	1064 (9)	1498 (8)	−1068 (7)	6.8 (3)	
C3	1555 (9)	1460 (8)	−312 (7)	6.2 (3)	
C4	2428 (9)	2007 (8)	76 (7)	6.3 (3)	
C5	2614 (8)	1805 (7)	805 (6)	5.4 (2)	
C6	1864 (8)	1116 (7)	902 (6)	4.9 (2)	
C7	1816 (9)	717 (8)	1576 (7)	6.4 (3)	
C8	1155 (8)	12 (9)	1691 (6)	6.2 (2)	
C9A	1237 (14)	−587 (14)	2385 (10)	5.6 (4)	2.54 (4)
C9B	906 (23)	−109 (26)	2474 (16)	5.9 (7)	1.46
C10A	447 (15)	−1212 (14)	2258 (11)	6.3 (5)	2.54 (4)
C10B	125 (24)	−747 (23)	2332 (17)	5.3 (7)	1.46
C11	3043 (11)	2620 (9)	−349 (8)	8.7 (4)	
C12	3838 (13)	2112 (11)	−650 (10)	1616 (62)	
C13	3444 (9)	2203 (9)	1443 (7)	7.6 (3)	
C14	3127 (12)	2954 (13)	1876 (11)	1911 (74)	
C15A	2108	−518	3116	7.0	2.54 (4)
C15B	1444	349	3230	6.5	1.46
C16A	1852	305	3591	12.2	2.54 (4)
C16B	2531	−68	3521	12.2	1.46
C17A	278	−1979	2814	7.3	2.54 (4)
C17B	−409	−1183	2931	5.4	1.46
C18A	−547	−1627	3243	12.2	2.54 (4)
C18B	−250	−2225	2967	12.2	1.46
O1	976 (5)	−997 (5)	−242 (4)	811 (24)	
P	1988 (3)	−1508 (2)	−122 (2)	702 (9)	
C21	2429 (9)	−1461 (8)	−994 (7)	5.7 (3)	
C22	3239 (10)	−2014 (8)	−1124 (8)	7.6 (3)	
C23	3519 (11)	−1965 (10)	−1821 (9)	8.4 (4)	
C24	3063 (14)	−1394 (11)	−2347 (9)	1205 (53)	
C25	2257 (16)	−861 (13)	−2235 (9)	1516 (70)	
C26	1900 (11)	−899 (11)	−1554 (8)	1245 (51)	
C27	3026 (8)	−1054 (7)	606 (6)	5.0 (2)	
C28	3685 (9)	−366 (7)	422 (7)	6.4 (3)	
C29	4497 (8)	−5 (9)	999 (6)	6.9 (2)	
C30	4633 (9)	−314 (8)	1716 (7)	7.3 (3)	
C31	3998 (10)	−969 (8)	1922 (7)	7.8 (3)	
C32	3161 (9)	−1346 (8)	1353 (7)	6.8 (3)	
C33	1778 (9)	−2659 (8)	131 (6)	5.9 (3)	
C34	2560 (10)	−3307 (10)	312 (8)	8.3 (3)	
C35	2367 (17)	−4234 (10)	519 (9)	1368 (72)	
C36	1393 (23)	−4446 (18)	550 (14)	1723 (99)	
C37	601 (20)	−3820 (17)	394 (14)	1646 (90)	
C38	786 (11)	−2924 (10)	185 (8)	1118 (46)	
O2	5139 (6)	4253 (7)	599 (7)	1621 (42)	
O3	4846 (17)	925 (15)	3473 (13)	14.0 (7)	

[a] x, y, z, and U_{eq} have been multiplied by 10^4. [b] $U_{\text{eq}} = {}^1/_3\sum_i\sum_j[U_{ij}(a^*_ia^*_j)a_i\cdot a_j]$; $\sigma(U_{\text{eq}}) = (1/6^{1/2})\langle(\sigma U_{ii})/U_{ii}\rangle U_{\text{eq}}$. [c] POP is the number of atoms in the unit cell; if blank, 4 is understood.

Table II. Selected Distances (Å) and Angles (deg) for **1**

Os–N1	2.031 (8)	Os–O1	2.036 (7)
Os–N2	2.027 (8)	O1–P	1.483 (8)
N1–Os–N2	91.2 (3)	N2–Os–O1	90.7 (3)
N1–Os–O1	88.4 (3)	Os–O1–P	154.2 (5)

Crystal Structure Determination of Os(TPP)(PPh$_3$)$_2$ (2). Crystal Data: $C_{80}H_{58}N_4P_2Os$, $M_r = 1327.52$, triclinic, space group $P\bar{1}$, $a = 11.536$ (1) Å, $b = 13.445$ (1) Å, $c = 21.237$ (2) Å, $\alpha = 85.25$ (1)°, $\beta = 75.77$ (1)°, $\gamma = 69.55$ (1)°, $V = 2991.7$ Å^3, $Z = 2$, $d_{\text{X-ray}} = 1.474$ g cm^{-3}, $F(000) = 1344$, μ(Mo Kα) = 23.68 cm^{-1}.

Intensity data were collected and handled as described for Os(OEP)(OPPh$_3$)$_2$; the dimensions of the crystal were 0.14 × 0.18 × 0.28 mm. Reflections within one hemisphere of reciprocal space out to $2\theta = 50°$ were measured. A total of 10433 independent reflections was obtained, of which 9223 had net intensity (I) greater than zero. An absorption correction was applied by the method of Busing and Levy.[13]

Structure Determination and Refinement. The positions of the osmium and phosphorus atoms were determined from a Patterson synthesis, and the rest of the non-hydrogen atoms were located on subsequent Fourier maps. Refinement was carried out as described for **1**. Atomic scattering

---

(10) Duchamp, D. J. *Abstracts of Papers*, National Meeting of the American Crystallographic Association, Bozeman, MT, 1964; Abstract No. B19, p 29.

(11) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1962; Vol. III, p 202.

(12) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, p 149.

(13) Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1957**, *10*, 180.

Table III. Heavy-Atom Parameters for **2**[a]

atom	x	y	z	U_{eq} or B, Å^2	atom	x	y	z	U_{eq} or B, Å^2
Molecule A									
Os	0	0	0	225 (1)	C20	1151 (7)	1121 (6)	−3683 (4)	5.1 (2)
N1	579 (4)	390 (3)	748 (2)	2.1 (1)	C21	−14 (8)	1581 (7)	−3330 (4)	7.0 (2)
N2	722 (4)	1031 (3)	−589 (2)	2.3 (1)	C22	−314 (7)	1426 (6)	−2648 (4)	5.9 (2)
C1	380 (5)	24 (4)	1379 (3)	2.4 (1)	P	−2012 (1)	1444 (1)	288 (1)	282 (3)
C2	901 (5)	525 (4)	1764 (3)	3.0 (1)	CP1	−2597 (5)	2057 (4)	−435 (3)	2.5 (1)
C3	1367 (5)	1195 (4)	1368 (3)	2.9 (1)	CP2	−1979 (5)	2703 (4)	−816 (3)	3.0 (1)
C4	1164 (5)	1133 (4)	737 (3)	2.3 (1)	CP3	−2414 (6)	3225 (5)	−1347 (3)	3.8 (1)
C5	1376 (5)	1799 (4)	213 (3)	2.5 (1)	CP4	−3446 (6)	3116 (5)	−1502 (3)	4.5 (1)
C6	1187 (5)	1741 (4)	−403 (3)	2.3 (1)	CP5	−4045 (7)	2480 (5)	−1135 (3)	4.7 (2)
C7	1565 (5)	2339 (4)	−966 (3)	2.9 (1)	CP6	−3622 (6)	1951 (5)	−600 (3)	3.4 (1)
C8	1358 (5)	1965 (4)	−1482 (3)	3.0 (1)	CP7	−2193 (5)	2636 (4)	726 (3)	2.5 (1)
C9	798 (5)	1152 (4)	−1253 (3)	2.4 (1)	CP8	−1670 (6)	2525 (5)	1265 (3)	3.3 (1)
C10	312 (5)	649 (4)	−1616 (3)	2.5 (1)	CP9	−1849 (6)	3396 (5)	1626 (3)	4.1 (1)
C11	1860 (5)	2657 (4)	327 (3)	2.5 (1)	CP10	−2544 (7)	4373 (5)	1465 (3)	4.7 (2)
C12	3077 (6)	2425 (4)	397 (3)	3.3 (1)	CP11	−3130 (7)	4510 (5)	961 (3)	4.6 (2)
C13	3497 (6)	3236 (5)	520 (3)	3.9 (1)	CP12	−2952 (6)	3641 (5)	590 (3)	3.8 (1)
C14	2702 (6)	4261 (5)	557 (3)	3.8 (1)	CP13	−3333 (5)	1073 (4)	799 (3)	2.7 (1)
C15	1503 (6)	4499 (5)	489 (3)	4.3 (2)	CP14	−3655 (6)	273 (5)	600 (3)	3.5 (1)
C16	1055 (6)	3704 (5)	375 (3)	3.5 (1)	CP15	−4650 (6)	−22 (5)	989 (3)	4.3 (1)
C17	581 (5)	836 (4)	−2338 (3)	2.8 (1)	CP16	−5285 (7)	463 (5)	1560 (4)	4.9 (2)
C18	1788 (7)	360 (5)	−2704 (4)	5.1 (2)	CP17	−4992 (7)	1239 (6)	1782 (4)	5.4 (2)
C19	2066 (7)	512 (6)	−3388 (4)	6.0 (2)	CP18	−3989 (7)	1553 (5)	1400 (3)	4.0 (1)
Molecule B									
Os	5000	5000	5000	232 (1)	C20	3325 (6)	366 (5)	4031 (3)	4.0 (1)
N1	6555 (4)	5473 (3)	4730 (2)	2.1 (1)	C21	3303 (6)	1168 (5)	3599 (3)	4.5 (1)
N2	5841 (4)	3817 (3)	4318 (2)	2.3 (1)	C22	3556 (6)	2057 (5)	3758 (3)	3.9 (1)
C1	6734 (5)	6293 (4)	4999 (3)	2.5 (1)	P	3896 (1)	6122 (1)	4233 (1)	302 (3)
C2	7954 (5)	6354 (4)	4671 (3)	3.0 (1)	CP1	2382 (5)	7067 (4)	4659 (3)	2.6 (1)
C3	8472 (5)	5623 (4)	4194 (3)	3.0 (1)	CP2	1259 (6)	6821 (5)	4895 (3)	3.6 (1)
C4	7594 (5)	5070 (4)	4218 (3)	2.3 (1)	CP3	184 (6)	7599 (5)	5237 (3)	4.5 (1)
C5	7769 (5)	4254 (4)	3808 (3)	2.5 (1)	CP4	206 (7)	8554 (6)	5370 (4)	5.0 (2)
C6	6997 (5)	3636 (4)	3869 (3)	2.4 (1)	CP5	1308 (7)	8787 (5)	5174 (4)	5.1 (2)
C7	7229 (5)	2738 (4)	3470 (3)	3.0 (1)	CP6	2382 (6)	8044 (5)	4814 (3)	3.8 (1)
C8	6235 (5)	2384 (4)	3687 (3)	3.1 (1)	CP7	4519 (5)	7026 (4)	3663 (3)	2.8 (1)
C9	5350 (5)	3068 (4)	4207 (3)	2.3 (1)	CP8	3865 (6)	7540 (5)	3199 (3)	4.5 (1)
C10	4162 (5)	3019 (4)	4520 (3)	2.4 (1)	CP9	4303 (7)	8222 (5)	2747 (4)	5.0 (2)
C11	8878 (5)	4055 (4)	3229 (3)	2.7 (1)	CP10	5412 (7)	8339 (6)	2746 (4)	5.2 (2)
C12	9890 (6)	3122 (5)	3140 (3)	3.6 (1)	CP11	6080 (7)	7860 (6)	3199 (4)	5.5 (2)
C13	10902 (6)	2974 (5)	2593 (3)	4.2 (1)	CP12	5609 (6)	7204 (5)	3666 (3)	4.1 (1)
C14	10873 (6)	3764 (5)	2145 (3)	4.4 (1)	CP13	3580 (5)	5430 (4)	3618 (3)	2.8 (1)
C15	9900 (6)	4692 (5)	2223 (3)	4.2 (1)	CP14	4620 (6)	4885 (5)	3140 (3)	3.7 (1)
C16	8873 (6)	4858 (5)	2774 (3)	3.5 (1)	CP15	4499 (6)	4378 (5)	2632 (3)	4.0 (1)
C17	3833 (5)	2108 (4)	4340 (3)	2.6 (1)	CP16	3339 (6)	4400 (5)	2593 (3)	4.2 (1)
C18	3806 (6)	1285 (5)	4784 (3)	3.9 (1)	CP17	2294 (7)	4937 (6)	3046 (4)	5.8 (2)
C19	3549 (6)	416 (5)	4622 (3)	4.3 (1)	CP18	2402 (7)	5453 (5)	3567 (3)	4.9 (2)

[a] x, y, z, and U_{eq} have been multiplied by 10^4.

factors, with anomalous dispersion corrections applied to those for osmium and phosphorus, were obtained from ref 10 and 11.

For the final refinement stages, all hydrogen atoms were included at their calculated positions with assigned isotropic thermal parameters. Altogether 368 parameters were adjusted: coordinates of the phosphorus, nitrogen, and carbon atoms, anisotropic thermal parameters of the osmium and phosphorus atoms, isotropic thermal parameters of the nitrogen and carbon atoms, a scale factor, and a secondary extinction factor. The final R value is 0.054 for 9223 reflections with $F_o^2 > 0$ and 0.039 for 7254 reflections with $F_o^2 > 3\sigma(F_o^2)$. The goodness of fit is 2.13 for 10433 measurements and 368 parameters. The final value of the secondary extinction parameter was $(0.10 \pm 0.02) \times 10^{-6}$.

Final atomic parameters of the non-hydrogen atoms are listed in Table III. Bond distances and angles are given in Table IV. Tables of hydrogen atomic parameters and structure factors are available as supplementary material.

Results and Discussion

The formation of $Os(OEP)(OPPh_3)_2$ in the PPh_3 reduction of $Os(OEP)O_2$ suggests that the reaction involves two sequential oxo-transfer steps with an $Os^{IV}{=}O$ intermediate:

$$Os^{VI}(OEP)O_2 + PPh_3 \rightarrow Os^{IV}(OEP)(O)(OPPh_3) \quad (1)$$

$$Os^{IV}(OEP)(O)(OPPh_3) + PPh_3 \rightarrow Os^{II}(OEP)(OPPh_3)_2 \quad (2)$$

Figure 1 shows the optical spectrum of $Os(OEP)(OPPh_3)_2$ in CH_2Cl_2. For the analogous reaction of $Os(TPP)O_2$ with PPh_3, $Os(TPP)(PPh_3)_2$ rather than $Os(TPP)(OPPh_3)_2$ is the isolable product. We presume that $Os(TPP)(O)(OPPh_3)$ or $Os(TPP)(OPPh_3)_2$ forms first; the $OPPh_3$ moiety is labile for steric reasons, and excess PPh_3 gives the product $Os(TPP)(PPh_3)_2$. The $Os(OEP)(OPPh_3)_2$ intermediate, on the other hand, is less crowded and therefore can be isolated. Heating $Os(OEP)O_2$ with excess PPh_3 in benzene converts the phosphine oxide to $Os(OEP)(PPh_3)_2$.

Table IV. Selected Distances (Å) and Angles (deg) for **2**

	molecule A	molecule B
Os–N1	2.037 (4)	2.045 (4)
Os–N2	2.047 (4)	2.045 (4)
Os–P	2.425 (1)	2.412 (2)
N1–Os–N2	89.7 (2)	90.0 (2)
N1–Os–P	90.7 (1)	94.9 (1)
N2–Os–P	88.4 (1)	89.5 (1)

Structures of $Os(OEP)(OPPh_3)_2$ and $Os(TPP)(PPh_3)_2$. The structure of $Os(OEP)(OPPh_3)_2$ is the first example of an Os(II) complex with two axial $OPPh_3$ ligands. Figure 2 shows an ORTEP drawing of the $Os(OEP)(OPPh_3)_2$ molecule; Figure 3 shows the OEP moiety and the atomic numbering scheme. The triphenylphosphine oxide group includes atom O1 and carbon atoms C21–26, C27–32, and C33–38; atoms O2 and O3 are solvent, and atoms C9B,10B and C15B–18B are the alternate locations of the

Table V. Average Bond Lengths (Å) in the Porphyrin Skeleton of Osmium and Ruthenium Porphyrin Complexes[a,b]

complex	M-N	N-C_q	C_q-C_p	C_q-C_m	C_p-C_p
Os(OEP)$(OPPh_3)_2$[c]	2.029 (8)	1.378 (16)	1.431 (16) [1.526 (20)][d]	1.374 (17)	1.310 (16) [1.351 (27)][d]
Os(TPP)$(PPh_3)_2$[c]	2.044 (2)	1.381 (8)	1.443 (9)	1.393 (8)	1.345 (8)
$[Os(OEP)(OMe)]_2O$[e]	2.033 (77)	1.374 (73)	1.470 (45)	1.392 (73)	1.366 (85)
$[Os(Me_2OEP)(CO)(py)]$[f]	2.067 (3)	1.337 (5) 1.398 (4)	1.430 (5)	1.384 (5) 1.500 (7)	1.375 (6)
Ru(OEP)$(py)_2$[g]	2.047	1.367	1.45	1.40	1.32
Ru(OEP)$(PPh_3)_2$[h]	2.051 (9)	1.376 (5)	1.455 (5)	1.385 (5)	1.354 (14)

[a] The number in parentheses is the standard deviation of an individual measurement from the mean value. [b] The notation M, C_q, C_p, and C_m is that of Hoard: Hamor, T. A.; Caughey, W. S.; Hoard, J. L. *J. Am. Chem. Soc.* **1965**, *87*, 2305. [c] This work. [d] Disordered. [e] Reference 5. [f] Reference 4. [g] Reference 15. Neither coordinates nor distances were published. These were taken from the drawing, which appears incomplete. [h] Reference 20.

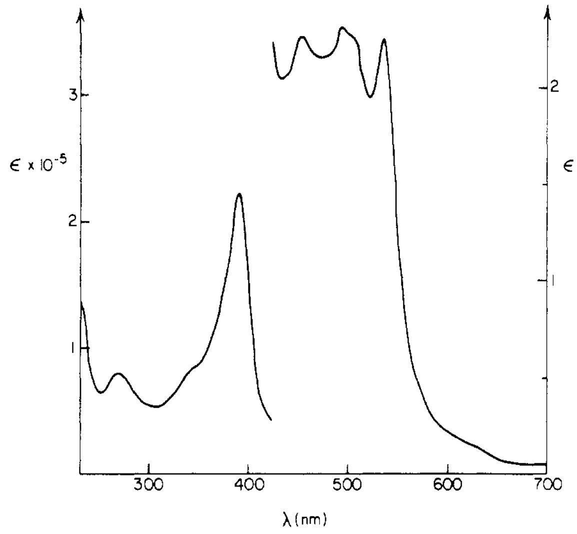

Figure 1. Optical spectrum of Os(OEP)$(OPPh_3)_2$ in CH_2Cl_2.

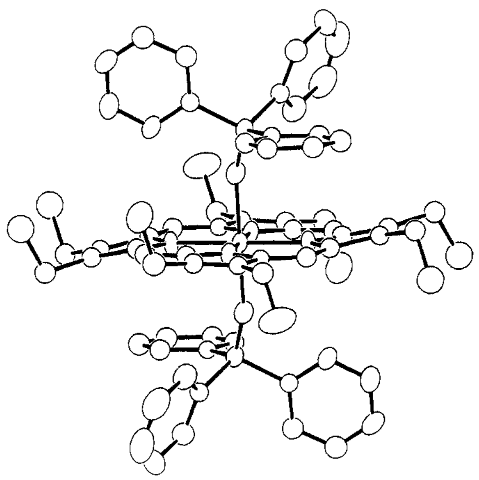

Figure 2. ORTEP drawing of the Os(OEP)$(OPPh_3)_2$ molecule with 20% probability ellipsoids.

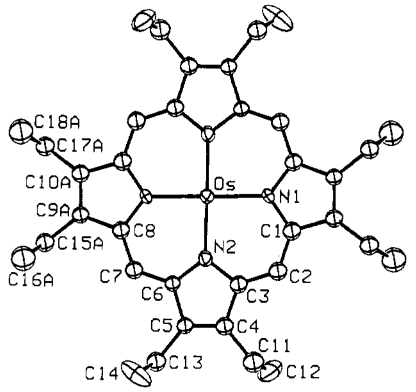

Figure 3. ORTEP drawing of the porphyrin portion of Os(OEP)$(OPPh_3)_2$, with 20% probability ellipsoids, showing the numbering system.

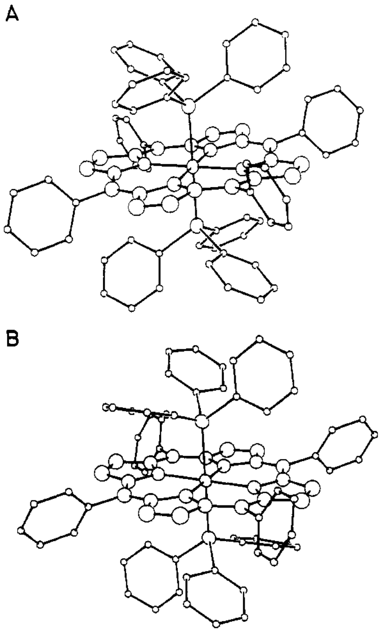

Figure 4. ORTEP drawing of the two Os(TPP)$(PPh_3)_2$ molecules viewed in the same orientation with 20% probability ellipsoids. Carbon atoms of the PPh_3 groups were given arbitrary, small thermal parameters.

corresponding "A" atoms. The osmium-porphyrin complex is planar: except for the ethyl groups and the disordered carbon atoms, all the atoms are within 0.07 Å of their least-squares plane. This is in agreement with the structure of an iron(II) octaethylporphyrin complex, Fe(OEP)(CS).[14] We found the same conformation of ethyl groups in the Os(II) porphyrin as in the iron compound; this depends on the molecular packing within the crystal, as has been noted before.[15] The two axial $OPPh_3$ ligands complete the octahedral coordination about the osmium atom with N1-Os-O1 and N2-Os-O1 angles of 88.4 (3) and 90.7 (3)°, respectively. The Os-O distance of 2.036 (7) Å is slightly longer than that found in $K_2[Os^{IV}(\eta^4\text{-chba-Et}(OPPh_3)]_2O$ (H_4(chba-Et) = 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane) (1.971 Å),[16a] in agreement with the smaller atomic radius of Os(IV). The measured Os-O1-P angle of 154.2 (5)° is comparable to the 153° found in $K_2[Os^{IV}(\eta^4\text{-chba-Et})(OPPH_3)]_2O$.[16b] The Os-N bonds are longer than the Fe-N bonds (2.029 (8) vs 1.982 (5) Å) in

---

(14) Scheidt, W. R.; Geiger, D. K. *Inorg. Chem.* **1982**, *21*, 1208.

(15) See, for example: Hopf, F. R.; O'Brien, T. P.; Scheidt, W. R.; Whitten, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 277.

(16) (a) Christe, J. A.; Collins, T. J.; Krafft, T. E.; Santarsiero, B. D.; Spies, G. H. *J. Chem. Soc., Chem. Commun.* **1984**, 198. (b) Metal-O-P angles in triphenylphosphine oxide complexes range from around 140° to almost 180°.

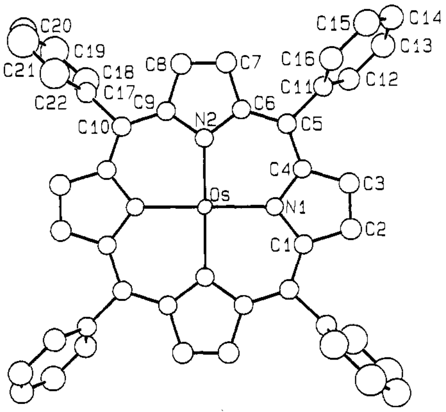

Figure 5. ORTEP drawing of the porphyrin portion of Os(TPP)(PPh$_3$)$_2$ showing the numbering system.

Fe(OEP)(CS), but the ring cavity appears not to be distorted by this.[14] The average bond distances and angles for the octaethylporphinato ligand agree with those found in other metalloporphyrins.[14,15,17] Distances and angles in the triphenylphosphine oxide ligand are as expected.[16] There are no short ($<$3.2 Å) contacts the solvent molecules and the complex molecules.

For Os(TPP)(PPh$_3$)$_2$, there are two independent centrosymmetric molecules in the unit cell, designated A and B. The osmium atoms are located at the crystallographic centers of symmetry (0, 0, 0) and $^1/_2$, $^1/_2$, $^1/_2$); the asymmetric unit contains half of molecule A and half of molecule B. Figure 4 shows an ORTEP drawing of molecules A and B viewed in the same orientation; Figure 5 shows the TPP moiety and the atomic numbering scheme. The porphyrin skeletons in both A and B are slightly puckered. Deviations from the least-squares plane of 24 core atoms vary from 0.008 to 0.115 Å (rms displacement 0.056 Å) for A and from 0.010 to 0.121 Å (rms displacement 0.079 Å) for B. The phenyl rings are essentially planar, and the mean C–C distance (1.377 ± 0.003 Å) is normal. The dihedral angles between the two peripheral phenyl rings and the porphyrin core are 75.6 (2) and 103.7 (2)° for A and 65.0 (2) and 68.5 (2)° for B. The geometry of the TPP moiety is very similar to that found in Ru(TPP)(dmp)$_2$.[18] The average Os–P distance of 2.148 Å is typical for trans P atoms on Os(II),[19] and the mean P–C distance of 1.839 ± 0.002 Å is also normal. The long Os–P distance suggests that the coordinated PPh$_3$ may be labile.[20]

A direct comparison of the distances and angles in the porphyrin skeltons of four osmium compounds and two related ruthenium complexes is given in Table V. Interestingly, the Os–N distances in Os(OEP)(OPPh$_3$)$_2$ (2.029 (8) Å) and Os(TPP)(PPh$_3$)$_2$ (2.044 (2) Å) are nearly the same and are comparable to those found in [Os(OEP)(OMe)]$_2$O[5] (2.033 (28) Å) and Os(Me$_2$OEP)(CO)(py)[4] (2.067 (2) Å), despite the variations in the oxidation state of the osmium atom and the nature of the porphinato ligand.

Acknowledgment. We thank Terry Collins for helpful discussions. This research was supported by the Committee on Research and Conference Grants of the University of Hong Kong (C.-M.C.), in part by the National Institute of General Medical Sciences, USPHS, Grant No. GM-16966 to Richard E. Marsh (T.-F.L.), and in part by the National Science Foundation (Grant No. CHE85-18793 to H.B.G.).

Registry No. 1·3H$_2$O, 110589-20-3; **2**, 110589-21-4; Os(OEP)O$_2$, 51349-77-0; Os(TPP)O$_2$, 110589-22-5; PPh$_3$, 603-35-0.

Supplementary Material Available: Tables of anisotropic thermal parameters, bond lengths and angles, and hydrogen atom coordinates and temperature factors for Os(OEP)(OPPh$_3$)$_2$ and Os(TPP)(PPh$_3$)$_2$ (8 pages); tables of calculated and observed structure factors for the two compounds (67 pages). Ordering information is given on any current masthead page.

---

(17) Structure of [Fe(OEP)]ClO$_4$: Masuda, H.; Taga, T.; Osaki, K.; Sugimoto, H.; Yoshida, Z. I.; Ogoshi, H. *Inorg. Chem.* **1980**, *19*, 950.

(18) Ball, R. G.; Domazetis, G.; Dolphin, D.; James, B. R.; Trotter, J. *Inorg. Chem.* **1981**, *20*, 1556.

(19) (a) Wilson, R. D.; Ibers, J. A. *Inorg. Chem.* **1979**, *18*, 336. (b) Brown, K. C.; Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 503.

(20) The substitutional chemistry of the isoelectronic Ru(TPP)(PPh$_3$)$_2$ has previously been reported: Ariel, S.; Dolphin, D.; Domazetis, G.; James, B. R.; Leung, T. W.; Rettig, S. J.; Trotter, J.; Williams, G. M. *Can. J. Chem.* **1984**, *62*, 755.