Nitrosylation of Octaethylporphyrin Osmium Complexes with Alkyl Nitrites and Thionitrites: Molecular Structures of Three Osmium Porphyrin Derivatives

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Received July 9, 1997

(OEP)Os(CO) reacts with *n*-butyl nitrite to give, after workup, the (OEP)Os(NO)(O-*n*-Bu) trans addition product (OEP = octaethylporphyrinato dianion). Similarly, the reaction of (OEP)Os(CO) or $[(OEP)Os]_2$ with isoamyl nitrite gives the corresponding nitrosyl alkoxide, (OEP)Os(NO)(O-*i*-C_5H_{11}). The related reactions of (OEP)Os(CO) or $[(OEP)Os]_2$ with isoamyl thionitrite gives the (OEP)Os(NO)(S-*i*-C_5H_{11}) nitrosyl thiolate. The reaction of the $[(OEP)Os]_2(PF_6)_2$ reagent with isoamyl thionitrite gives the nitrosylation product, $[(OEP)Os(NO)]PF_6$, which undergoes anion hydrolysis to give the isolable difluorophosphate (OEP)Os(NO)(O_2PF_2) derivative. Interestingly, the reaction of $O_2NC_6H_4N{=}NSPh$ with $[(OEP)Os]_2$ gives the $(OEP)Os(SPh)_2$ product with loss of the arylazo fragments. The solid-state structures of (OEP)Os(NO)(O-*n*-Bu), (OEP)Os(NO)(O_2PF_2), and $(OEP)Os(SPh)_2$ have been determined by X-ray crystallography.

Introduction

The heme unit in guanylyl cyclase is a receptor for nitric oxide (NO).[1] Reactions of NO with organic fragments to result in nitrosation reactions in vitro and in vivo are also very important.[2,3] The interaction of NO with hemes and heme models has also commanded renewed interest.[4] It is known that various organic nitroso (and inorganic nitrite) compounds are capable of nitrosylating metal centers, depending on the reaction conditions.[5] We have also demonstrated that organic nitroso compounds such as nitrosamines (*N*-nitroso),[6] Cupferron (*N*-nitroso),[7] nitrosoarenes (*C*-nitroso),[8] thionitrites (*S*-nitroso), and alkyl nitrites (*O*-nitroso)[9] interact with heme models to result in either simple adduct formation or activation of the organic nitroso groups to give metal nitrosyls. Of particular interest was our report that thionitrites and isoamyl nitrite add to the group 8 metalloporphyrins via a formal trans addition process to give nitrosyl thiolates and alkoxides, respectively.[9]

Although a number of ruthenium porphyrin nitrosyls are now known,[6b,9−12] only four osmium porphyrin nitrosyls were reported prior to our studies, namely (OEP)Os(NO)X (X = F, NO, OMe, $OClO_3$; OEP = octaethylporphyrinato dianion),[13] with X-ray structural data on osmium nitrosyl porphyrins being available only for (TTP)Os(NO)(S-*i*-C_5H_{11}) (TTP = tetratolylporphyrinato dianion).[9b] In this present paper, we report on the extension of the reaction chemistry of osmium porphyrins with thionitrites and alkyl nitrites. We also provide new insight on the mode of interaction of RSNO with osmium porphyrins.

(1) (a) Deinum, G.; Stone, J. R.; Babcock, G. T.; Marletta, M. A. *Biochemistry* **1996**, *35*, 1540. (b) Stone, J. R.; Marletta, M. A. *Biochemistry* **1994**, *33*, 5636. (c) Dierks, E. A.; Hu, S.; Vogel, K. M.; Yu, A. E.; Spiro, T. G.; Burstyn, J. N. *J. Am. Chem. Soc.* **1997**, *119*, 7316.

(2) (a) Stamler, J. S.; Jia, L.; Eu, J. P.; McMahon, T. J.; Demchenko, I. T.; Bonaventura, J.; Gernet, K.; Piantadosi, C. A. *Science* **1997**, *276*, 2034 and references therein. (b) Keshive, M.; Singh, S.; Wishnok, J. S.; Tannenbaum, S. R.; Deen, W. M. *Chem. Res. Toxicol.* **1996**, *9*, 988. (c) Park, J.-W. *Biochem. Biophys. Res. Commun.* **1988**, *152*, 916. (d) Stamler, J. S.; Simon, D. I.; Osborne, J. A.; Mullins, M. E.; Jaraki, O.; Michel, T.; Singel, D. J.; Loscalzo, J. *Proc. Natl. Acad. Sci. U.S.A.* **1992**, *89*, 444. (e) Stamler, J. S.; Simon, D. I.; Jaraki, O.; Osborne, J. A.; Francis, S.; Mullins, M.; Singel, D.; Loscalzo, J. *Proc. Natl. Acad. Sci. U.S.A.* **1992**, *89*, 8087. (f) Goldstein, S.; Czapski, G. *J. Am. Chem. Soc.* **1996**, *118*, 3419. (g) Goldstein, S.; Czapski, G. *J. Am. Chem. Soc.* **1996**, *118*, 6806 [erratum]. (h) Jia, L.; Bonaventura, C.; Bonaventura, J.; Stamler, J. S. *Nature* **1996**, *380*, 221. (i) Simon, D. I.; Mullins, M. E.; Jia, L.; Gaston, B.; Singel, D. J.; Stamler, J. S. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 4736.

(3) Williams, D. L. H. *Nitrosation*; Cambridge University Press: Cambridge, U.K., 1988.

(4) (a) Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyls*; Oxford University Press: New York, 1992; Chapter 6. (b) Hoshino, M.; Maeda, M.; Konishi, R.; Seki, H.; Ford, P. C. *J. Am. Chem. Soc.* **1996**, *118*, 5702.

(5) (a) Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyls*; Oxford University Press: New York, 1992; Chapter 2 and references therein. (b) Bladon, P.; Dekker, M.; Knox, G. R.; Willison, D.; Jaffari, G. A.; Doedens, R. J.; Muir, K. W. *Organometallics* **1993**, *12*, 1725. (c) Pandey, D. S.; Khan, M. I.; Agarwala, U. C. *Indian J. Chem.* **1987**, *26A*, 570.

(6) (a) Yi, G.-B.; Khan, M. A.; Richter-Addo, G. B. *J. Am. Chem. Soc.* **1995**, *117*, 7850. (b) Yi, G.-B.; Khan, M. A.; Richter-Addo, G. B. *Inorg. Chem.* **1996**, *35*, 3453.

(7) Yi, G.-B.; Khan, M. A.; Richter-Addo, G. B. *Inorg. Chem.* **1995**, *34*, 5703.

(8) (a) Wang, L.-S.; Chen, L.; Khan, M. A.; Richter-Addo, G. B. *Chem. Commun.* **1996**, 323. (b) We have successfully extended *N*-binding of nitrosoarenes to osmium porphyrins (manuscript in preparation) and *O*-binding to manganese porphyrins: Fox, S. J. S.; Chen, L.; Khan, M. A.; Richter-Addo, G. B. *Inorg. Chem.* **1997**, *36*, 6465.

(9) (a) Yi, G.-B.; Khan, M. A.; Richter-Addo, G. B. *Chem. Commun.* **1996**, 2045. (b) Yi, G.-B.; Chen, L.; Khan, M. A.; Richter-Addo, G. B. *Inorg. Chem.* **1997**, *36*, 3876.

(10) (a) Miranda, K. M.; Bu, X.; Lorkovic, I.; Ford, P. C. *Inorg. Chem.* **1997**, *36*, 4838. (b) Kadish, K. M.; Adamian, V. A.; Van Caemelbecke, E.; Tan, Z.; Tagliatesta, P.; Bianco, P.; Boschi, T.; Yi, G.-B.; Khan, M. A.; Richter-Addo, G. B. *Inorg. Chem.* **1996**, *35*, 1343. (c) Bohle, D. S.; Hung, C.-H.; Powell, A. K.; Smith, B. D.; Wocaldo, S. *Inorg. Chem.* **1997**, *36*, 1992. (d) Srivastava, T. S.; Hoffman, L.; Tsutsui, M. *J. Am. Chem. Soc.* **1972**, *94*, 1385.

(11) (a) Hodge, S. J.; Wang, L.-S.; Khan, M. A.; Young, V. G., Jr.; Richter-Addo, G. B. *Chem. Commun.* **1996**, 2283. (b) Massoudipour, M.; Pandey, K. K. *Inorg. Chim. Acta* **1989**, *160*, 115.

(12) Antipas, A.; Buchler, J. W.; Gouterman, M.; Smith, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 3015.

(13) (a) Antipas, A.; Buchler, J. W.; Gouterman, M.; Smith, P. D. *J. Am. Chem. Soc.* **1980**, *102*, 198. (b) Buchler, J. W.; Smith, P. D. *Chem. Ber.* **1976**, *109*, 1465.

S0020-1669(97)00857-4 CCC: $15.00
Published on Web 01/14/1998

Experimental Section

All reactions were performed under an atmosphere of prepurified nitrogen using standard Schlenk techniques and/or in an Innovative Technology Labmaster 100 Dry Box unless stated otherwise. Solvents were distilled from appropriate drying agents under nitrogen just prior to use: CH_2Cl_2 (CaH_2), benzene (Na), hexane (Na/benzophenone/tetraglyme), and THF (Na/benzophenone).

Chemicals. (OEP)Os(CO)[14] and $[(OEP)Os]_2$[15a] were prepared by literature methods (OEP = octaethylporphyrinato dianion). The known $[(OEP)Os]_2(PF_6)_2$[15b] was prepared by $AgPF_6$ oxidation of $[(OEP)Os]_2$. Isoamyl nitrite (i-$C_5H_{11}ONO$, 97%), and isoamyl thiol (mercaptan, i-$C_5H_{11}SH$, 97%), *n*-butyl nitrite (95%), thiophenol (97%), $AgPF_6$ (98%), and $NOPF_6$ (96%) were purchased from Aldrich Chemical Co. Chloroform-*d* (99.8%) was obtained from Cambridge Isotope Laboratories, subjected to three freeze−pump−thaw cycles, and stored over Linde 4 Å molecular sieves. Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

Instrumentation. Infrared spectra were recorded on a Bio-Rad FT-155 FTIR spectrometer. ^1H NMR spectra were obtained on a Varian XL-300 spectrometer and the signals referenced to the residual signal of the solvent employed. All coupling constants are in Hz. The ^{31}P NMR spectrum was recorded on a Varian 400 MHz spectrometer, and the signals were referenced to external H_3PO_4. The ^{19}F NMR spectrum was also recorded on the same 400 MHz instrument, and the signals referenced to external trifluoroacetic acid (δ at −79.45 ppm). FAB mass spectra were obtained on a VG-ZAB-E mass spectrometer. UV−vis spectra were recorded on a Hewlett-Packard HP8453 Diode Array instrument.

Preparation of Thionitrites. The preparation of thionitrites (i-$C_5H_{11}SNO$ and PhSNO) follows established routes from their precursor thiols.[16] The preparation of PhSNO was performed at low temperature, since this thionitrite decomposes at room temperature in solution.

Preparation of (OEP)Os(NO)(O-*n*-Bu). To a CH_2Cl_2 (20 mL) solution of (OEP)Os(CO) (0.075 g, 0.100 mmol) was added excess *n*-butyl nitrite (0.4 mL, 3 mmol). The color of the solution changed from pink red to bright red immediately. The mixture was left to stir for 40 min. The mixture was taken to dryness, and the residue was redissolved in CH_2Cl_2. The solvent was allowed to evaporate under inert atmosphere to generate a crystalline solid residue. The resulting crystals were washed with hexane to remove a green-colored component, and the remaining solid was redissolved in CH_2Cl_2/hexane (1:2) and filtered over a neutral alumina column in air. The column was washed with more of the solvent mixture and then with CH_2Cl_2 until the washings were colorless. The filtrate was taken to dryness in vacuo, and the residue was dried in vacuo for 5 h to give (OEP)Os(NO)(O-*n*-Bu)·1.4CH_2Cl_2 (0.055 g, 0.058 mmol, 58% yield). Anal. Calcd for $C_{40}H_{53}O_2N_5Os_1$·1.4CH_2Cl_2: C, 52.62; H, 5.95; N, 7.41; Cl, 10.50. Found: C, 52.32; H, 5.83; N, 7.56; Cl, 10.60. IR (CH_2Cl_2, cm^{-1}): υ_{NO} = 1757. IR (KBr, cm^{-1}): υ_{NO} = 1743 s; also 2962 w, 2931 w, 2868 w, 1790 w, 1467 m, 1451 m, 1372 m, 1316 w, 1274 m, 1263 m, 1230 w, 1155 m, 1111 w, 1077 w, 1056 m, 1021 m, 993 m, 963 m, 860 w, 843 m, 764 w, 746 s, 718 w, 705 w, 596 m br. ^1H NMR ($CDCl_3$, δ): 10.32 (s, 4H, *meso*-H of OEP), 5.27 (s, CH_2Cl_2), 4.16 (q, J = 8 Hz, 16H, CH_3CH_2 of OEP), 2.00 (t, J = 8 Hz, 24H, CH_3CH_2 of OEP), −0.55 (t, J = 7 Hz, 3H, $CH_3CH_2CH_2CH_2O$), −1.53 (m (qt), J = 7/8 Hz, 2H, $CH_3CH_2CH_2CH_2O$), −2.73 (t, J = 7 Hz, 2H, $CH_3CH_2CH_2CH_2O$), −3.04 (m (tt), J = 8/7 Hz, 2H, $CH_3CH_2CH_2CH_2O$). Low-resolution mass spectrum (FAB): *m*/*z* 827 [(OEP)Os(NO)(OC_4H_9) + H]$^+$ (17%), 754 [(OEP)Os(NO) + H]$^+$ (100%), 723 [(OEP)Os]$^+$ (23%). UV−vis spectrum (λ (ϵ, mM^{-1} cm^{-1}), 1.31 × 10^{-5} M in CH_2Cl_2): 342 (40), 418 (91), 533 (17), 567 (26) nm.

Preparation of (OEP)Os(NO)(O-*i*-C_5H_{11}). Method I. To a CH_2Cl_2 (20 mL) solution of (OEP)Os(CO) (0.080 g, 0.107 mmol) was added excess isoamyl nitrite (0.20 mL, 1.5 mmol). The color of the solution changed from pink red to bright red immediately. The solution was stirred for another 30 min. The mixture was taken to dryness in vacuo, and the product was redissolved in a CH_2Cl_2/hexane (1:2) mixture and filtered through a neutral alumina column in air. The column was washed with more of the solvent mixture until the washings were colorless. The filtrate was taken to dryness in vacuo, and the product obtained was dried in vacuo for 5 h to give (OEP)Os(NO)(O-*i*-C_5H_{11})·0.85CH_2Cl_2 (0.050 g, 0.055 mmol, 51% yield). Anal. Calcd for $C_{41}H_{55}O_2N_5Os_1$·0.85CH_2Cl_2: C, 55.10; H, 6.26; N, 7.68; Cl, 6.61. Found: C, 54.86; H, 6.23; N, 7.74; Cl, 6.98. IR (CH_2Cl_2, cm^{-1}): υ_{NO} = 1756. IR (KBr, cm^{-1}): υ_{NO} = 1747 s; also 2962 w, 2928 w, 2864 w, 2020 w, 1954 w, 1794 w, 1685 w, 1560 w, 1508 w, 1465 s br, 1372 m, 1316 w, 1272 m, 1230 w, 1200 w, 1153 s, 1111 s, 1077 s, 1056 s, 1020 s, 993 m, 962 m, 856 w, 842 m, 744 s, 738 s, 717 m, 704 w, 642 w, 589 m. ^1H NMR ($CDCl_3$, δ): 10.31 (s, 4H, *meso*-H of OEP), 5.27 (s, CH_2Cl_2), 4.15 (q, J = 8 Hz, 16H, CH_3CH_2 of OEP), 1.99 (t, J = 8 Hz, 24H, CH_3CH_2 of OEP), −0.70 (d, J = 7 Hz, 6H, $(CH_3)_2CHCH_2CH_2O$), −1.19 (m, 1H, $(CH_3)_2CHCH_2CH_2O$), −2.72 (t, J = 8 Hz, 2H, $(CH_3)_2CHCH_2CH_2O$), −3.27 (dt (app q), J = 7/8 Hz, 2H, $(CH_3)_2CHCH_2CH_2O$). Low-resolution mass spectrum (FAB): *m*/*z* 841 [(OEP)Os(NO)(O-*i*-C_5H_{11}) + H]$^+$ (16%), 754 [(OEP)Os(NO) + H]$^+$ (100%), 723 [(OEP)Os]$^+$ (20%). UV−vis spectrum (λ (ϵ, mM^{-1} cm^{-1}), 1.29 × 10^{-5} M in CH_2Cl_2): 341 (41), 418 (102), 533 (19), 567 (30) nm.

Method II. To a CH_2Cl_2 (15 mL) solution of $[(OEP)Os]_2$ (0.030 g, 0.021 mmol) was added excess isoamyl nitrite (0.10 mL, 0.75 mmol). The color of the solution changed from brown to bright red immediately. The mixture was left to stir for another 3 h. The mixture was taken to dryness, and the residue was redissolved in CH_2Cl_2/hexane (1:2) and filtered over a neutral alumina column in air. The column was washed with more of the solvent mixture until the washings were colorless. The filtrate was taken to dryness in vacuo, and the residue was dried in vacuo for 3 h to give (OEP)Os(NO)(O-*i*-C_5H_{11}) in 29% isolated yield.

Preparation of (OEP)Os(NO)(S-*i*-C_5H_{11}). Method I. To a CH_2Cl_2 (20 mL) solution of (OEP)Os(CO) (0.080 g, 0.107 mmol) was added excess isoamyl thionitrite (ca. 1 mmol). The color of the solution changed gradually from pink red to bright red over a period of 1 h. The mixture was left to stir for another 4 h. The mixture was taken to dryness, and the residue was redissolved in CH_2Cl_2/hexane (1:2) and filtered over a neutral alumina column in air. The column was washed with more of the solvent mixture until the washings were colorless. The filtrate was taken to dryness in vacuo, and the residue was dried in vacuo for 5 h to give (OEP)Os(NO)(S-*i*-C_5H_{11})·0.3CH_2Cl_2 (0.031 g, 0.035 mmol, 33% yield). Anal. Calcd for $C_{41}H_{55}O_1S_1N_5Os_1$·0.3$CH_2Cl_2$: C, 56.26; H, 6.36; N, 7.94; Cl, 2.41; S, 3.64. Found: C, 56.12; H, 6.39; N, 7.80; Cl, 2.58; S, 3.55. IR (CH_2Cl_2, cm^{-1}): υ_{NO} 1757. IR (KBr, cm^{-1}): υ_{NO} = 1751 s; also 2964 w, 2932 w, 2870 w, 1467 m, 1450 m, 1373 w, 1316 w, 1271 m, 1229 w, 1154 m, 1110 w, 1057 m, 1020 m, 993 m, 962 m, 843 m, 746 m, 729 m, 717 w. ^1H NMR ($CDCl_3$, δ): 10.29 (s, 4H, *meso*-H of OEP), 5.28 (s, CH_2Cl_2), 4.14 (q br, 16H, CH_3CH_2 of OEP), 1.99 (t, J = 8 Hz, 24H, CH_3CH_2 of OEP), −0.35 (d, J = 6 Hz, 6H, $(CH_3)_2CHCH_2CH_2S$), −0.43 (m, 1H, $(CH_3)_2CHCH_2CH_2S$), −1.92 (dt (app q), J = 6/8 Hz, 2H, $(CH_3)_2CHCH_2CH_2S$), −3.26 (t, J = 8 Hz, 2H, $(CH_3)_2CHCH_2CH_2S$). Low-resolution mass spectrum (FAB): *m*/*z* 856 [(OEP)Os(NO)(S-*i*-C_5H_{11})]$^+$ (2%), 827 [(OEP)Os(S-*i*-C_5H_{11}) + H]$^+$ (7%), 754 [(OEP)Os(NO) + H]$^+$ (96%), 724 [(OEP)Os + H]$^+$ (28%). UV−vis spectrum (λ (ϵ, mM^{-1} cm^{-1}), 1.18 × 10^{-5} M in CH_2Cl_2): 354 (69), 441 (38), 551 (15), 584 (11) nm.

Method II. To a CH_2Cl_2 (15 mL) solution of $[(OEP)Os]_2$ (0.030 g, 0.021 mmol) was added excess isoamyl thionitrite (ca. 0.7 mmol). The color of the solution changed from brown to bright red immediately. The mixture was left to stir for another 5 h. The mixture was taken to dryness, and the residue was redissolved in CH_2Cl_2/hexane (1:2) and filtered over a neutral alumina column in air. The column was washed with more of the solvent mixture until the washings were colorless. The filtrate was taken to dryness in vacuo, and the residue was dried in vacuo for 3 h to give (OEP)Os(NO)(S-*i*-C_5H_{11}) in 33% isolated yield.

(14) Che, C.-M.; Poon, C.-K.; Chung, W.-C.; Gray, H. B. *Inorg. Chem.* **1985**, *24*, 1277.
(15) (a) Collman, J. P.; Barnes, C. E.; Woo, L. K. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 7684. (b) Collman, J. P.; Prodolliet, J. W.; Leidner, C. R. *J. Am. Chem. Soc.* **1986**, *108*, 2916.
(16) (a) Roy, B.; d'Hardemare, A. du M.; Fontecave, M. *J. Org. Chem.* **1994,** *59*, 7019. (b) Oae, S.; Shinhama, K.; Fujimori, K.; Kim, Y. H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 775. (c) Oae, S.; Kim, Y. H.; Fukushima, D.; Shinhama, K. *J. Chem. Soc., Perkin Trans. 1*, **1978**, 913.

Reaction of $[(OEP)Os]_2(PF_6)_2$ with Isoamyl Thionitrite. To a CH_2Cl_2 (20 mL) solution of $[(OEP)Os]_2(PF_6)_2$ (0.040 g, 0.023 mmol) was added excess isoamyl thionitrite (ca. 1.5 mmol). The color of the solution changed from brown to red. A solution IR spectrum of the reaction mixture after 10 min revealed the quantitative conversion of $[(OEP)Os]_2(PF_6)_2$ to $[(OEP)Os(NO)]PF_6$, indicated by the presence of a new band at 1829 cm^{-1} assigned to υ_{NO} and a band at 847 cm^{-1} assigned to υ_{PF_6}. The reaction mixture was stirred for an additional 20 min, and the mixture was taken to dryness. An IR spectrum of the residue (as a KBr pellet) at this stage showed the presence of noticeable bands at 1816 and 1787 cm^{-1} and also at 840 cm^{-1}. Exposure of the solid to air for 30 h resulted in the formation of only one υ_{NO} band at 1808 cm^{-1}. The peak at 840 cm^{-1} assigned to υ_{PF_6} also disappeared. Crystallization by slow solvent evaporation of a CH_2Cl_2 solution of the solid gives $(OEP)Os(NO)(O_2PF_2)$, which was identified by X-ray diffraction (see later).

Alternate Preparation of $(OEP)Os(NO)(O_2PF_2)$. (OEP)Os(CO) (0.060 g, 0.080 mmol) and $NOPF_6$ (0.015 g, 96%, 0.082 mmol) were dissolved in CH_2Cl_2 (20 mL). A solution IR spectrum of the reaction mixture showed the disappearance of the starting (OEP)Os(CO) (υ_{CO} = 1883 cm^{-1}) and the formation of $[(OEP)Os(NO)]PF_6$ (υ_{NO} = 1833 cm^{-1}; υ_{PF_6} = 848 cm^{-1}). The mixture was left to stir for 40 min and then exposed to air for 3 days. The mixture was then filtered through a neutral alumina column in air with CH_2Cl_2 as eluent to remove presumably $[(OEP)Os(NO)(H_2O)]PF_6$. All the solvent was removed from the filtrate thus obtained, and the resulting solid was dried in vacuo overnight to give $(OEP)Os(NO)(O_2PF_2)$ (0.019 g, 0.022 mmol, 28% yield). A sample for elemental analyses was obtained from crystallization of a CH_2Cl_2/hexane solution by slow evaporation of the solvent mixture at room temperature and dried in vacuo for 5 h. Anal. Calcd for $C_{36}H_{44}O_3P_1F_2N_5Os_1$·0.2hexane: C, 51.29; H, 5.41; N, 8.04. Found: C, 51.58; H, 5.41; N, 7.92. IR (CH_2Cl_2, cm^{-1}): υ_{NO} = 1820. IR (KBr, cm^{-1}): υ_{NO} = 1808 s; also 2969 w, 2932 w, 2872 w, 1464 w, 1451 w, 1383 w, 1374 w, 1324 s, 1275 w, 1260 w, 1229 w, 1156 m, 1116 m, 1105 m, 1058 m, 1022 m, 996 m, 964 m, 887 m, 856 m, 847 m. ^1H NMR ($CDCl_3$, δ): 10.47 (s, 4H, *meso*-H of OEP), 4.20 (q, J = 8 Hz, 16H, CH_3CH_2 of OEP), 2.01 (t, J = 8 Hz, 24H, CH_3CH_2 of OEP), 1.25 (hexane). ^{31}P NMR ($CDCl_3$, 400 MHz, δ): −27.85 (t, J_{P-F} = 985). ^{19}F NMR ($CDCl_3$, 400 MHz, δ): −89.49 (d, J_{P-F} = 985). Low-resolution mass spectrum (FAB): m/z 855 $[(OEP)Os(NO)(O_2PF_2) + H]^+$ (11%), 754 $[(OEP)Os(NO) + H]^+$ (13%). UV−vis spectrum (λ (ϵ, mM^{-1} cm^{-1}), 1.66 × 10^{-5} M in benzene): 347 (42), 374 (44), 421 (62), 539 (14), 575 (24) nm.

Preparation of $(OEP)Os(SPh)_2$.[17] To a CH_2Cl_2 (20 mL) solution of $[(OEP)Os]_2$ (0.040 g, 0.028 mmol) was added $O_2NC_6H_4N{=}NSPh$[18] (0.030 g, 0.116 mmol). Effervescence (a white smoke) was seen right after mixing the reagents. The color of the solution changed from brown to purple over a 1 h period. The mixture was left to stir for another 1 h. All the solvent was then removed, the residue was redissolved in a benzene/hexane mixture (1:5), and the product was purified by neutral alumina column chromatography in air. Elution with hexane and then benzene/hexane (1:5) produced a yellow band (presumably unreacted ligand), which was discarded. Further elution with CH_2Cl_2/hexane (1:3) produced a purple band, which was collected. The solvent was removed from the purple solution, and the product was dried in vacuo for 5 h to give the known $(OEP)Os(SPh)_2$ (0.022 g, 0.023 mmol, 41% yield)[17] which was identified by ^1H NMR spectroscopy and by X-ray crystallography. IR (KBr, cm^{-1}): 2964 w, 2931 w, 2865 w, 1725 w, 1576 w, 1536 w, 1470 m, 1447 m, 1436 w, 1372 w, 1316 w, 1266 m, 1226 w, 1149 m, 1111 w, 1084 w, 1056 m, 1020 s, 992 m, 961 m, 924 w, 865 w, 842 m, 740 s, 719 w, 700 w, 686 m.

Preparation of (OEP)Os(NO)(SPh). To a CH_2Cl_2 solution of (OEP)Os(CO) (0.064 g, 0.085 mmol) was added excess freshly prepared PhSNO (ca. 3 mmol), and the reaction was left to stir for 90 min. The mixture was taken to dryness in vacuo, and the residue was redissolved in benzene and purified by chromatography using a neutral alumina column under N_2 with benzene as first eluent. The green elute was discarded. A red fraction was then eluted with CH_2Cl_2. All the solvent was removed from this elute, and the resulting solid was dried in vacuo for 5 h to give (OEP)Os(NO)(SPh)·0.65CH_2Cl_2 (0.035 g, 0.038 mmol, 45% yield). Anal. Calcd for $C_{42}H_{49}N_5O_1S_1Os_1$·0.65$CH_2Cl_2$: C, 55.84; H, 5.53; N, 7.63; Cl, 5.02; S, 3.49. Found: C, 56.49; H, 5.69; N, 7.64; Cl, 5.39; S, 3.47. IR (CH_2Cl_2, cm^{-1}): υ_{NO} = 1766. IR (KBr, cm^{-1}): υ_{NO} = 1749 s; also 2966 w, 2932 w, 2870 w, 1578 w, 1470 m, 1451 m, 1375 w, 1315 w, 1265 m, 1230 vw, 1154 m, 1111 w, 1057 m, 1021 m, 994 m, 963 m, 867 vw, 843 m, 740 m, 702 w, 689 w. ^1H NMR ($CDCl_3$, δ): 10.20 (s, 4H, *meso*-H of OEP), 6.25 (t, J = 7 Hz, 1H, *p*-H of SPh), 5.84 (t, J = 7 Hz, 2H, *m*-H of SPh), 5.28 (s, CH_2Cl_2), 4.12 (q, J = 8 Hz, 16H, CH_3CH_2 of OEP), 2.82 (d, J = 7 Hz, 2H, *o*-H of SPh), 1.99 (t, J = 8 Hz, 24H, CH_3CH_2 of OEP). Low-resolution mass spectrum (FAB): m/z 862 $[(OEP)Os(NO)(SPh)]^+$ (5%), 833 $[(OEP)Os(SPh) + H]^+$ (23%), 754 $[(OEP)Os(NO) + H]^+$ (100%), 724 $[(OEP)Os + H]^+$ (23%). UV−vis spectrum (λ (ϵ, mM^{-1} cm^{-1}), 1.40 × 10^{-5} M in CH_2Cl_2): 363 (58), 451 (25), 555 (12), 589 (8) nm.

Structural Determinations by X-ray Crystallography. All crystal data were collected on a Siemens P4 diffractometer with Mo Kα radiation (λ = 0.710 73 Å). The structures were solved using the SHELXTL (Siemens) system and refined by full-matrix least squares on F^2 using all reflections (SHELXL-93). The data were corrected for Lorentz and polarization effects, and empirical absorption corrections based on ψ scans were applied. Hydrogen atoms were included in the idealized positions. Thermal ellipsoid plots are drawn at 50% probability. Details of crystal data and refinement are given in Table 1, and selected bond lengths and angles are collected in Tables 2 and 3.

(i) (OEP)Os(NO)(O-*n*-Bu). A suitable crystal was grown by slow evaporation of a CH_2Cl_2 solution of the compound. Data suggested the choice of the two space groups *P*2/*n* and *Pn*. The structure solution and refinement was tried in both space groups. Best refinement was obtained in the noncentric space group *Pn* using a model involving racemic twinning. The racemic twinning which affects mainly the axial NO, OBu, and the CH_2Cl_2 solvent molecule results in limiting the accuracy of the positional and displacement parameters of these atoms. Hence, the accuracy of the bond lengths, particularly involving the OBu group, is of poor quality.

(ii) $(OEP)Os(NO)(O_2PF_2)$. A suitable crystal was grown from a saturated solution of $[(OEP)Os]_2(PF_6)_2$ and isoamyl thionitrite in CH_2Cl_2 left under nitrogen for 25 days, followed by slow evaporation of the solution in the dry box for 2 days.

(iii) $(OEP)Os(SPh_2)$. A suitable crystal was obtained by slow evaporation of CH_2Cl_2/toluene solution of the compound at room temperature under inert atmosphere. Hydrogen atoms were included in the idealized positions. The molecule is situated on a crystallographic center of symmetry, with only half of the molecule being unique, and the Os atom is situated at the center of symmetry.

Results and Discussion

We have previously reported that isoamyl nitrite and thionitrites add to metalloporphyrins of the group 8 metals.[9] The reaction of (OEP)Os(CO) with *n*-butyl nitrite in CH_2Cl_2 at room temperature gives, after workup, the (OEP)Os(NO)(O-*n*-C_4H_9) trans addition product in 58% yield (eq 1).

$$\text{(OEP)Os(CO)} + n\text{-}C_4H_9ONO \rightarrow \text{(OEP)Os(NO)(O-}n\text{-}C_4H_9) \quad (1)$$

This red nitrosyl alkoxide product is moderately air-stable, showing no signs of decomposition for at least 8 h in solution and several days in the solid state. The product is freely soluble in CH_2Cl_2 but is only slightly soluble in hexane. The ^1H NMR spectrum of the complex in $CDCl_3$ shows the expected peaks for the OEP and *n*-butyl groups. The IR spectrum of the complex (as a KBr pellet) shows a band at 1743 cm^{-1} assigned to υ_{NO}. The value of υ_{NO} is consistent with this $\{Os(NO)\}^6$ complex having a linear Os−NO linkage according to the

(17) Che, C.-M.; Leung, W.-H.; Chung, W.-C. *Inorg. Chem.* **1990**, *29*, 1841.
(18) Sakla, A. B.; Masoud, N. K.; Sawiris, Z.; Ebaid, W. S. *Helv. Chim. Acta* **1974**, *57*, 481.

Table 1. Crystal Data and Structure Refinement

	(OEP)Os(NO)(O-*n*-Bu)·CH_2Cl_2	(OEP)Os(NO)(O_2PF_2)	(OEP)Os(SPh)$_2$
empirical formula	$C_{41}H_{55}N_5O_2Cl_2Os$	$C_{36}H_{44}N_5O_3F_2POs$	$C_{48}H_{54}N_4S_2Os$
fw	911.00	853.93	941.27
T, K	188(2)	188(2)	188(2)
crystal system	monoclinic	triclinic	monoclinic
space group	*Pn*	$P\bar{1}$	$P2_1/c$
unit cell dimensions	$a = 8.3335(6)$ Å, $\alpha = 90°$ $b = 10.4951(6)$ Å, $\beta = 91.052(5)°$ $c = 22.846(2)$ Å, $\gamma = 90°$	$a = 10.232(2)$ Å, $\alpha = 98.90(2)°$ $b = 10.928(3)$ Å, $\beta = 95.76(2)°$ $c = 15.994(4)$ Å, $\gamma = 97.71(2)°$	$a = 12.572(1)$ Å, $\alpha = 90°$ $b = 8.497(1)$ Å, $\beta = 103.21(3)°$ $c = 19.664(2)$ Å, $\gamma = 90°$
V, *Z*	1997.8(2) Å^3, 2	1737.4(7) Å^3, 2	2045.0(4) Å^3, 2
D(calcd), g/cm^3	1.514	1.632	1.529
absorption coefficient, mm^{-1}	3.366	3.770	3.259
F(000)	924	856	956
crystal size	0.22 × 0.36 × 0.42 mm	0.12 × 0.22 × 0.26 mm	0.09 × 0.23 × 0.28 mm
θ range for data collection	1.78−29.73°	1.91−25.00°	2.13−25.97°
index ranges	$-1 \le h \le 9$, $-14 \le k \le 12$, $-27 \le l \le 27$	$0 \le h \le 12$, $-12 \le k \le 12$, $-19 \le l \le 18$	$0 \le h \le 14$, $0 \le k \le 10$, $-23 \le l \le 23$
no. of reflections collected	7426	6466	3790
no. of independent reflections	3798 [*R*(int) = 0.0371]	6087 [*R*(int) = 0.0349]	3600 [*R*(int) = 0.0284]
no. of data/restraints/parameters	3778/303/462	6073/0/442	3599/0/250
goodness-of-fit on F^2	1.075	1.066	1.043
final *R* indices [$I > 2\sigma(I)$]^{a,b}	R1 = 0.0415, wR2 = 0.1044	R1 = 0.0443, wR2 = 0.1070	R1 = 0.0337, wR2 = 0.0783
R indices (all data)^{a,b}	R1 = 0.0469, wR2 = 0.1251	R1 = 0.0596, wR2 = 0.1223	R1 = 0.0517, wR2 = 0.0881
largest diff. peak and hole	2.665 and −1.392 e Å^{-3}	1.583 and −1.547 e Å^{-3}	1.378 and −1.590 e Å^{-3}

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[wF_o^4]\}^{1/2}$.

Table 2. Structural Parameters (in Å and deg) for Osmium Nitrosyl Complexes^a

	coord. no.	M−N(O)	N−O	M−N−O	ref
(OEP)Os(NO)(O-*n*-Bu)	6	1.833(8)	1.173(11)	172.8(8)	this work
(OEP)Os(NO)(O_2PF_2)	6	1.711(6)	1.179(8)	174.3(6)	this work
(TTP)Os(NO)(S-*i*-C_5H_{11})	6	2.041(7)	1.086(10)	172.0(9)	9b
[(η^5−C_5H_5)Os(NO)(PMe_3)$_2$](PF_6)$_2$	6	1.747(11)	1.17(2)	179.8(15)	22
Os(NO)(η^2-*O,O*-ON═C(O)CF_3)(O_2CCF_3)(PPh_3)$_2$	6	1.726(7)	1.209(9)	176.1(6)	23
Os(NO)(Cl)$_2$(CF_3)(PPh_3)$_2$	6	1.741(9)	1.175(12)	180.0	24
trans-[Os(NO)(tpy)(Cl)$_2$]BF_4	6	1.704(14)	1.188(19)	176.6(10)	25
Os(NO)(Cl)$_2$(η^1−CH═C═CPh_2)(P^iPr_3)$_2$	6	1.733(6)	1.106(8)	174.4(5)	26
[(DMSO)$_2$H][Os(NO)(DMSO)(Cl)$_4$]	6	1.717(8)	1.16(1)	179.2(8)	27
Os(NO){η^2−*C,O*−CH_2CH_2S(O)NSO_2tol}(Cl)(PPh_3)$_2$	6	1.706(9)	1.179	174.7	28a
Os(NO)(═CH_2)(Cl)(PPh_3)$_2$	5	1.93(1)^b	0.915^b	155.4(2)	28b
Os(NO)Br_3(Et_2S)(Et_2SO)	6	1.712(22)	1.148(31)	174.3(29)	29
Os(NO)Cl_2(OCH_2CH_2OMe)($PPhEt_2$)$_2$	6	1.837(10)	1.098(14)	177.3(8)	29
[$MePPh_3$][Os(NO)(Cl)$_4$]	5	1.89(2)	0.90(3)	177(2)	30
[Os(NO)$_2$(OH)(PPh_3)$_2$]PF_6	5	1.63(1)	1.24(2)	178(1)	31
		1.86(1)^b	1.17(2)^b	134(1)	

^{a} All of these complexes appear to contain Os^{II}, with the exception of [(DMSO)$_2$H][Os(NO)(DMSO)(Cl)$_4$] which contains Os^{III}. ^{b} Bent NO.

Enemark−Feltham notation.[19] The related (OEP)Os(NO)(OMe)[13b] (υ_{NO} = 1745 cm^{-1}, KBr) was prepared previously by a different route: via the formation of the dinitrosyl (OEP)Os(NO)$_2$ intermediate obtained from the reaction of (OEP)Os(CO)(py) in CH_2Cl_2 with NO gas, in the presence of methanol.

The linearity of the Os−NO linkage was confirmed by a single-crystal X-ray crystallographic analysis of a suitable crystal of the compound (Figure 1) grown by slow evaporation of a CH_2Cl_2 solution of the complex at room temperature under nitrogen.

The Os−N(O) and N−O bond lengths are 1.833(8) and 1.173(11) Å, respectively, and the Os−N−O bond angle is 172.8(8)°. The average Os−N(porphyrin) bond length is 2.056 Å. These data are compared with those for other structurally characterized Os nitrosyls and porphyrins in Tables 2 and 3. The axial Os−O distance of 1.877(7) Å appears short[20] relative to the 1.909(4)−2.200(7) Å previously observed for Os alkoxides;[21] however, it is longer than that expected for an Os═O bond in porphyrins (Table 3, bottom). The Os−O−C alkoxide bond angle of 130.8(9)° falls within the 123.1(2)−133.8(8)° range seen for other Os alkoxides.[21] The butoxide carbon C37 nearly eclipses a porphyrin nitrogen, with a N2−Os−O2−C37 torsion angle of 18.4°.

The related reaction of (OEP)Os(CO) with isoamyl nitrite gives (OEP)Os(NO)(O-*i*-C_5H_{11}) in 51% isolated yield. To determine whether the presence of the carbonyl ligand in (OEP)Os(CO) was needed for the activation of the organic nitrites (RONO), we employed the non-carbonyl-containing [(OEP)Os]$_2$ as a reagent in this reaction. Interestingly, the same trans-addition product is also obtained from the reaction of

(19) Feltham, R. D.; Enemark, J. H. *Topics Stereochem.* **1981**, *12*, 155.

(20) As indicated in the Experimental Section, the OBu and NO groups are affected by "racemic twinning" (SHELXL-93), which causes the NO and OBu groups to be disordered. This causes a problem in accurately determining the position of the O atom of the OBu group because of its correlation with the N atom of the NO group. Hence, the short Os−O contact should be treated with caution due to the limited accuracy of this bond length.

(21) For structurally characterized Os alkoxides, see: (a) Cheng, W.-K.; Wong, K.-Y.; Tong, W.-F.; Lai, T.-F.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1992**, 91. (b) Masuda, H.; Taga, T.; Osaki, K.; Sugimoto, H.; Mori, M. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2345. (c) Hinckley, C. C.; Ali, I. A.; Robinson, P. D. *Acta Crystallogr.* **1990**, *C46*, 697. (d) Reference 29. (e) Reference 36.

Table 3. Structurally Characterized Monometallic Osmium Porphyrins with *O*- and *S*-Donor Ligands[32]

compound	metal oxidation state	Os−N$_p$ (Å)	Os−X (Å) (axial)	Os−X−Y (°)	ref
nitrosyl					
(OEP)Os(NO)(O-*n*-Bu)	II	1.986(9), 2.078(8) 2.051(7), 2.109(8)	1.877(7)	130.8(9)	this work
(OEP)Os(NO)(O_2PF_2)	II	2.060(6), 2.053(5) 2.065(6), 2.067(6)	2.046(5)	138.7(3)	this work
(TTP)Os(NO)(S-*i*-C_5H_{11})	II	2.035(5), 2.074(8) 2.076(9), 2.049(6)	2.209(3)	111.8(5)	9b
non-nitrosyl					
(OEP)Os($OPPh_3$)$_2$	II	2.031(8), 2.027(8)	2.036(7)	154.2(5)	33
(OEP)Os(PMS)$_2$[a]	II	2.057(5), 2.044(5)	2.352(2)	110.3(3) 110.4(3)	34
[(OEP)Os(PMS)$_2$]PF$_6$[a]	III	2.047(4), 2.044(4)	2.382(2)	109.94(20) 109.81(21)	34
(OEP)Os(SPh)$_2$	IV	2.047(4), 2.050(4)	2.295(1)	110.9(2)	this work
(TTP)Os(SC_6F_4H)$_2$	IV	2.041(6), 2.057(6)	2.294(3)	107.8(3)	35
(TPP)Os(OR)$_2$	IV				36
R = Et		2.046(5), 2.038(5)	1.915(4)	128.2(5)	
R = *i*-Pr		2.042(3), 2.040(3)	1.909(4)	127.0(3)	
R = Ph		2.042(3), 2.038(2)	1.938(2)	127.5(2)	
(OEP)Os(O)$_2$	VI	2.052(6)	1.745(5)		37
(TTP)Os(O)$_2$	VI	2.065(4), 2.067(4)	1.743(3)		38

[a] Data from Supporting Information.

[(OEP)Os]$_2$ with isoamyl nitrite (eq 2).

$$[(OEP)Os]_2 + i\text{-}C_5H_{11}ONO \rightarrow 2(OEP)Os(NO)(O\text{-}i\text{-}C_5H_{11}) \quad (2)$$

The red (OEP)Os(NO)(O-*i*-C_5H_{11}) product has similar solubility properties as the *n*-butyl analogue (eq 1). The υ_{NO} of 1747 cm^{-1} is similar to the *n*-butyl analogue (1743 cm^{-1}) but is 23 cm^{-1} lower than the related and previously reported (TTP)Os(NO)(O-*i*-C_5H_{11}) complex (1770 cm^{-1}).[9b] The UV−vis spectra of (OEP)Os(NO)(O-*n*-C_4H_9) and (OEP)Os(NO)(O-*i*-C_5H_{11}) are almost identical with that of (OEP)Os(NO)(OMe),[12] which has been described as a hypso/hyper type. Importantly, the success of eq 2 implies that the presence of the carbonyl ligand in eq 1 is not required for the activation of the RONO group toward formal trans addition across the metal center.

The red isoamyl thiolate analogue, (OEP)Os(NO)(S-*i*-C_5H_{11}), is also prepared by thionitrite addition to (OEP)Os(CO) or [(OEP)Os]$_2$ in 33% nonoptimized yields (eqs 3 and 4).

$$(OEP)Os(CO) + i\text{-}C_5H_{11}SNO \rightarrow (OEP)Os(NO)(S\text{-}i\text{-}C_5H_{11}) \quad (3)$$

$$[(OEP)Os]_2 + i\text{-}C_5H_{11}SNO \rightarrow 2(OEP)Os(NO)(S\text{-}i\text{-}C_5H_{11}) \quad (4)$$

This nitrosyl thiolate is also freely soluble in CH_2Cl_2 but only slightly soluble in hexane. It also shows no sign of decomposition in air (as judged by ^{1}H NMR and IR spectroscopy) for at least 5 h in solution or after several days in the solid state. The υ_{NO} of 1751 cm^{-1} is only 4 cm^{-1} higher than that of the alkoxide analogue (eq 2), although their υ_{NO}'s in CH_2Cl_2 solution are identical.

We were interested in extending the thionitrite addition chemistry to Os^{III} porphyrins. Interestingly, although isoamyl thionitrite will add trans to Os^{II} to give isolable nitrosyl thiolate products (as shown in eqs 3 and 4), we were only able to isolate nitrosyl adducts from the reaction with Os^{III} with no thiolate or thiol ligands present. For example, the reaction of [(OEP)Os^{III}]$_2$(PF_6)$_2$ with isoamyl thionitrite in CH_2Cl_2 resulted in the

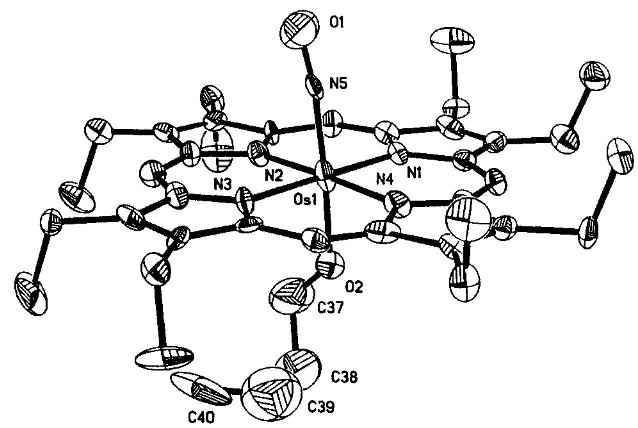


Figure 1. Molecular structure of (OEP)Os(NO)(O-*n*-Bu).

observation (by IR spectroscopy) of the cationic [(OEP)Os(NO)]-PF_6 complex (υ_{NO} = 1829 cm^{-1}, υ_{PF_6} = 847 cm^{-1}), which subsequently underwent anion hydrolysis by adventitious moisture upon attempted crystallization to give the isolable difluorophosphate (OEP)Os(NO)(O_2PF_2) derivative (Scheme 1). Our attempts to isolate [(OEP)Os(NO)]PF_6 have not been successful, although the related [(OEP)Ru(NO)(H_2O)]BF_4 has been prepared and structurally characterized by us previously.[6b]

Scheme 1

$$[(OEP)Os]_2(PF_6)_2 + i\text{-}C_5H_{11}SNO \rightarrow 2[(OEP)Os(NO)]PF_6 \rightarrow 2(OEP)Os(NO)(O_2PF_2)$$

The hydrolysis of the PF_6 anion is a common feature in coordination chemistry[39,40] and is known to occur even in $AgPF_6$

(22) Bruce, M. I.; Tomkins, B.; Wong, F. S.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1982**, 687.
(23) Boyar, E. B.; Dobson, A.; Robinson, S. D.; Haymore, B. L.; Huffman, J. C. *J. Chem. Soc., Dalton Trans.* **1985**, 621.
(24) Clark, G. R.; Greene, T. R.; Roper, W. R. *Aust. J. Chem.* **1986**, *39*, 1315.
(25) Williams, D. S.; Meyer, T. J.; White, P. S. *J. Am. Chem. Soc.* **1995**, *117*, 823.
(26) Werner, H.; Flügel, R.; Windmüller, B.; Michenfelder, A.; Wolf, J. *Organometallics* **1995**, *14*, 612.

(which we used to prepare the $[(OEP)Os^{III}]_2(PF_6)_2$ reagent).[41] In our case, neither the $AgPF_6$ nor the $[(OEP)Os]_2(PF_6)_2$ salts contained the difluorophosphate group (by IR spectroscopy). Indeed, we synthesized $[(OEP)Os(NO)]PF_6$ independently by reacting (OEP)Os(CO) with $NOPF_6$.[42] Exposure of this product in solution to air also transforms it to $(OEP)Os(NO)(O_2PF_2)$.

Not surprisingly, the red $(OEP)Os(NO)(O_2PF_2)$ product is air-stable. The ν_{NO} of 1808 cm^{-1} (KBr) is higher than those displayed by the related osmium nitrosyl alkoxide or thiolate complexes. The IR spectrum also contains bands attributable to a monodentate difluorophosphate group (ν_{PF_2} = 887 (ν_{as}) and 856 (ν_s) cm^{-1}; ν_{PO_2} = 1324 cm^{-1}).[43,44] A porphyrin band at 1156 cm^{-1} probably obscures the expected ν_s (PO_2) A_1 band of the O_2PF_2 anion.[43] The locations of these bands are similar to those for other monodentate difluorophosphate groups in structurally characterized iridium[39] and palladium[41] and other η^1-difluorophosphate complexes.[45,46] The ^{31}P NMR (−27.85 ppm, triplet) and ^{19}F NMR spectra (−89.49 ppm, doublet) are also consistent with the presence of the monodentate difluorophosphate group. The J_{P-F} coupling constant of 985 Hz is within the range commonly found for difluorophosphoric acid and its salts.[41,50] Not surprisingly, the UV−vis spectrum of $(OEP)Os(NO)(O_2PF_2)$ is similar to that of (OEP)Os(NO)-($OClO_3$).[13a]

The molecular structure of $(OEP)Os(NO)(O_2PF_2)$ is shown in Figure 2, and selected bond lengths and angles are listed in Tables 2−4. The Os−N(por) bond length of 2.06 Å (av) appears longer than those observed for other $(OEP)Os^{II}$ complexes, with the possible exception of the $(OEPMe_2)Os(CO)$-(py) derivative (2.069(3) and 2.065(3) Å).[32b] The Os atom is displaced by 0.16 Å from the four-nitrogen porphyrin plane toward the NO ligand, and the Os−O(difluorophosphate) bond length of 2.046(5) Å is longer than that of (OEP)Os(NO)(O-*n*-Bu) described earlier but is similar to the Os−O bond lengths of the only other structurally characterized Os^{II} porphyrin complex containing axial Os−O bonds, namely, (OEP)Os-$(OPPh_3)_2$ (2.036(7) Å). It is also longer than the observed axial Os−O bonds for the structurally characterized Os^{IV} porphyrin alkoxides (1.909−1.938 Å) or Os^{VI} porphyrin dioxo derivatives (1.74 Å) (Table 3). The Os−N−O bond is essentially linear with a bond angle of 174.3(6)°. The O−P−O bond angle of 118.4(4)° is larger than the F−P−F angle of 101.1(4)°, and this observation is not uncommon for transition metal difluorophosphate complexes (Table 4). The difluorophosphate P atom essentially eclipses a porphyrin nitrogen, with the N4−Os−O2−P1 torsion angle of 10.3°. Importantly, although the difluorophosphate anion forms complexes with other transition metals,[39−41,49,51] main group metals,[47,48,52,53] the ammonium cation,[54] and even the nitrosonium cation,[55] to the best of our knowledge this is the first reported example of a metalloporphyrin difluorophosphate derivative.

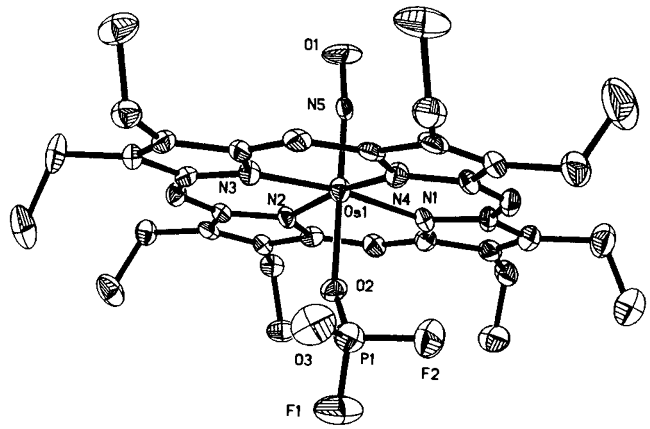


Figure 2. Molecular structure of $(OEP)Os(NO)(O_2PF_2)$.

Investigation of the Reaction Pathway for RSNO Addition. We sought to explore further the reaction pathway for RSNO addition to metalloporphyrins. In particular, we invoked the well-used concept of the "element displacement principle"[56] to investigate the nature of RSNO additions to osmium porphyrins. We sought out chemical comparisons of PhSNO with compounds of the form PhSN═NAr (phenyl arylazo sulfides),[18,57]

(27) Rudnitskaya, O. V.; Buslaeva, T. M.; Stash, A. I.; Kisin, A. V. *Russ. J. Coord. Chem.* **1995**, *21*, 136.

(28) (a) Herberhold, M.; Hill, A. F.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Wright, A. H. *Organometallics* **1989**, *8*, 2483. (b) Hill, A. F.; Roper, W. R.; Waters, J. M.; Wright, A. H. *J. Am. Chem. Soc.* **1983**, *105*, 5939.

(29) Fergusson, J. E.; Robinson, W. T.; Coll, R. K. *Inorg. Chim. Acta* **1991**, *181*, 37.

(30) Czeska, B.; Dehnicke, K.; Fenske, D. *Z. Naturforsch. B.* **1983**, *38*, 1031.

(31) Clark, G. R.; Waters, J. M.; Whittle, K. R. *J. Chem. Soc., Dalton Trans.* **1975**, 463.

(32) Other structurally characterized osmium porphyrins include the following. (a) $(OEP)Os(PPh_3)_2$: ref 33. (b) $(OEPMe_2)Os(CO)(py)$: Buchler, J. W.; Lay, K. L.; Smith, P. D.; Scheidt, W. R.; Rupprecht, G. A.; Kenny, J. E. *J. Organomet. Chem.* **1976**, *110*, 109. (c) $(TTP)Os(4\text{-pic})_2$: Djukic, J.-P.; Young, V. G., Jr.; Woo, L. K. *Organometallics* **1994**, *13*, 3995. (d) $(TTP)Os(Cl)_2$: Smieja, J. A.; Omberg, K. M.; Busuego, L. N.; Breneman, G. L. *Polyhedron* **1994**, *13*, 339. (e) $(TTP)Os(CH_2SiMe_3)_2$: Leung, W.-H.; Hun, T. S. M.; Wong, K.-Y.; Wong, W.-T. *J. Chem. Soc., Dalton Trans.* **1994**, 2713. (f) $(TTP)Os(p\text{-}NC_6H_4NO_2)_2$: Smieja, J. A.; Omberg, K. M. *Inorg. Chem.* **1994**, *33*, 614.

(33) Che, C.-M.; Lai, T.-F.; Chung, W.-C.; Schaefer, W. P.; Gray, H. B. *Inorg. Chem.* **1987**, *26*, 3907.

(34) Scheidt, W. R.; Nasri, H. *Inorg. Chem.* **1995**, *34*, 2190.

(35) Collman, J. P.; Bohle, D. S.; Powell, A. K. *Inorg. Chem.* **1993**, *32*, 4004.

(36) Che, C.-M.; Huang, J.-S.; Li, Z.-Y.; Poon, C.-K.; Tong, W.-F.; Lai, T.-F.; Cheng, M.-C.; Wang, C.-C.; Wang, Y. *Inorg. Chem.* **1992**, *31*, 5220.

(37) Nasri, H.; Scheidt, W. R. *Acta Crystallogr.* **1990**, *C46*, 1096.

(38) Che, C.-M.; Chung, W.-C.; Lai, T.-F. *Inorg. Chem.* **1988**, *27*, 2801.

(39) Bauer, H.; Nagel, U.; Beck, W. *J. Organomet. Chem.* **1985**, *290*, 219

(40) Bruno, G.; Schiavo, S. L.; Piraino, P.; Faraone, F. *Organometallics* **1985**, *4*, 1098.

(41) Fernández-Galán, R.; Manzano, B. R.; Otero, A.; Lanfranchi, M.; Pellinghelli, M. A. *Inorg. Chem.* **1994**, *33*, 2309.

(42) The reaction of (OEP)Ru(CO) with $NOBF_4$ also generates [(OEP)-Ru(NO)]BF_4, which is converted to $[(OEP)Ru(NO)(H_2O)]BF_4$ in air (see ref 6b).

(43) Bühler, K.; Bues, W. *Z. Anorg. Allg. Chem.* **1961**, *308*, 62.

(44) Schmutzler, R. In *Advances in Fluorine Chemistry*; Stacey, M., Tatlow, J. C., Sharpe, A. G., Eds.; Butterworth: London, 1965; Vol. 5, p 252.

(45) The $Cp_2Rh_2(\mu\text{-CO})(\mu\text{-dppm})(\mu\text{-AgO}_2PF_2)$ complex contains disordered O and F atoms in the O_2PF_2 group (ref 40).

(46) Bidentate (refs 47 and 48) and tridentate (ref 49) O_2PF_2 groups have also been structurally characterized.

(47) Powell, J.; Horvath, M. J.; Lough, A. *J. Chem. Soc., Dalton Trans.* **1996**, 1669.

(48) Granier, P. W.; Durand, J.; Cot, L.; Galigné, J. L. *Acta Crystallogr.* **1975**, *B31*, 2506.

(49) Begley, M. J.; Dove, M. F. A.; Hibbert, R. C.; Logan, N.; Nunn, M.; Sowerby, D. B. *J. Chem. Soc., Dalton Trans.* **1985**, 2433.

(50) Reference 44, p 262.

(51) Legzdins, P.; Oxley, J. C. *Inorg. Chem.* **1984**, *23*, 1053.

(52) Tan, T. H.; Dalziel, J. R.; Yeats, P. A.; Sams, J. R.; Thompson, R. C.; Aubke, F. *Can. J. Chem.* **1972**, *50*, 1843.

(53) Thompson, R. C.; Reed, W. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 581.

(54) Harrison, R. W.; Trotter, J. *J. Chem. Soc. A* **1969**, 1783.

(55) Babaeva, V. P.; Rosolovskii, V. Y. *Russ. J. Inorg. Chem.* **1971**, *16* (4), 471.

(56) Haas, A. *Adv. Inorg. Chem. Radiochem.* **1984**, *28*, 167.

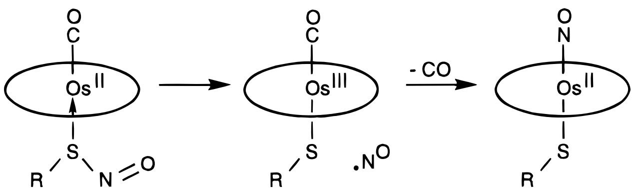
(57) Dell'Erba, C.; Houmam, A.; Morin, N.; Novi, M.; Petrillo, G.; Pinson, J.; Rolando, C. *J. Org. Chem.* **1996**, *61*, 929.

Table 4. Metric Parameters (in Å and deg) for Transition Metal η^1-OP(=O)F_2 Complexes

	(OEP)Os(NO)(O_2PF_2)[a]	Ir(O_2PF_2)(PPh_3)$_2$(H)(Cl)(CO)[b]	Pd(O_2PF_2)(η^3-2-MeC_3H_4)(PCy_3)[c,d]
M−O	2.046(5)	2.201(8)	2.314(6) [2.126(5)]
O−P	1.477(5)	1.456(7)	1.471(5) [1.455(5)]
P−F	1.511(6), 1.531(5)	1.499(10), 1.529(12)	
P=O	1.454(7)	1.421(8)	1.468(8) [1.441(8)]
M−O−P	138.7(3)	127.0(4)	125.4(3) [124.7(3)]
O−P=O	118.4(4)	122.1(6)	123.3(4) [122.1(4)]
F−P−F	101.1(4)	95.4(7)	97.2(5) [96.0(4)]
O−P−F	108.2(3)	108.3(4), 107.4(5)	
O=P−F	111.2(4), 108.3(4)	112.1(5), 108.3(6)	

[a] This work. [b] Reference 39. [c] Reference 41. [d] There are two independent molecules present. The data in brackets are for the second molecule.

Scheme 2



where a simple replacement of the oxygen atom in PhSNO with the valence isoelectronic NAr group will generate the "equivalent" phenyl arylazo sulfide. This concept has been utilized successfully in metal-nitrosyl (M−NO) and metal-aryldiazonium (M−N_2Ar) comparisons.[58]

thionitrite arylazo sulfide

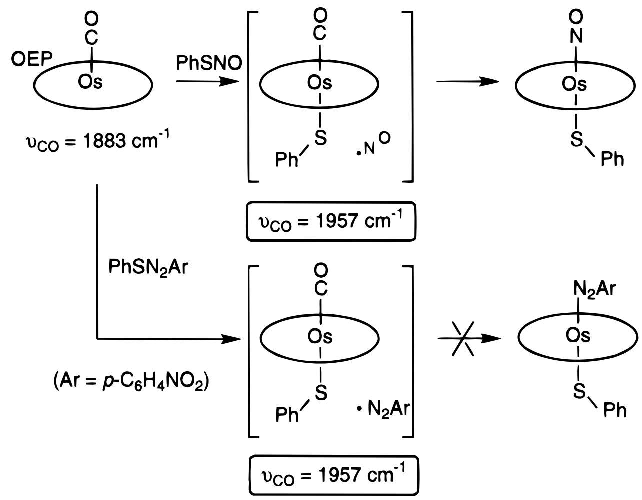
Not surprisingly, the reaction of (OEP)Os(CO) with PhSNO gave, after workup, the (OEP)Os(NO)(SPh) thiophenolate product in 45% isolated yield. In contrast to the other nitrosyl thiolates obtained in our laboratory, this nitrosyl thiophenolate is moderately air-sensitive. This dark-red product is soluble in CH_2Cl_2 and benzene but is rather insoluble in hexane. The υ_{NO} of 1766 cm^{-1} in CH_2Cl_2 is ca. 10 cm^{-1} higher than that of the related alkanethiolate (OEP)Os(NO)(S-*i*-C_5H_{11}), although the υ_{NO}'s of both nitrosyl thiolates as KBr pellets are virtually identical.

IR monitoring of the reaction of PhSNO with (OEP)Os(CO) in CH_2Cl_2 reveals that, in addition to the υ_{CO} band of starting (OEP)Os(CO) (at 1883 cm^{-1}) and the υ_{NO} band of the thiophenolate (OEP)Os(NO)(SPh) product at 1766 cm^{-1}, a new *higher* band at 1957 cm^{-1} is observed. This new band is attributed (consistent with earlier similar results)[9b] to an intermediate carbonyl Os^{III} complex. In time, only the product band remains.

We have proposed earlier (based on IR spectroscopy) that thionitrites react with group 8 metalloporphyrins probably via *S*-coordination of the RSNO group (Scheme 2) followed by homolytic cleavage of the RS−NO bond.

In this pathway, rapid diffusion of the stable NO radical to the metal site results in a substitution of CO to give the final nitrosyl thiolate product. To test this proposed reaction pathway, we employed the valence isoelectronic PhSN=NC_6H_4(*p*-NO_2) compound in place of PhSNO. We rationalized that the success of proposed Scheme 2 depends on the known stability of the NO radical, enabling it to displace the bound carbonyl from the osmium center. Since the ·N_2Ar radical is generally not

Scheme 3



expected to be stable,[59] it would not be expected to survive the reaction conditions to displace CO (Scheme 3, bottom) to form the (OEP)Os(N_2Ar)(SPh) addition product.[60] If this is so, then any observed band in the carbonyl region of the IR spectrum should be due to υ_{CO} and not υ_{NO}, since there is no NO present in the reaction mixture.

Indeed, IR monitoring of the reaction of (OEP)Os(CO) with PhSN=NC_6H_4(*p*-NO_2) reveals the formation of the band at 1957 cm^{-1} assigned to the intermediate carbonyl (OEP)Os(CO)(SPh) complex (Scheme 3, bottom). We have not been able to isolate this thermally unstable intermediate. However, reaction of this intermediate with NO gas (2 min) gives a 1:1 mixture of (OEP)-Os(NO)(SPh) and the known (OEP)Os$(NO)_2$.[13b] This latter compound forms from the attack of NO on unreacted (OEP)-Os(CO)[13b] and (OEP)Os(NO)(SPh). A similar reaction involving (TTP)Os(NO)(S-isoamyl) has been reported.[9b]

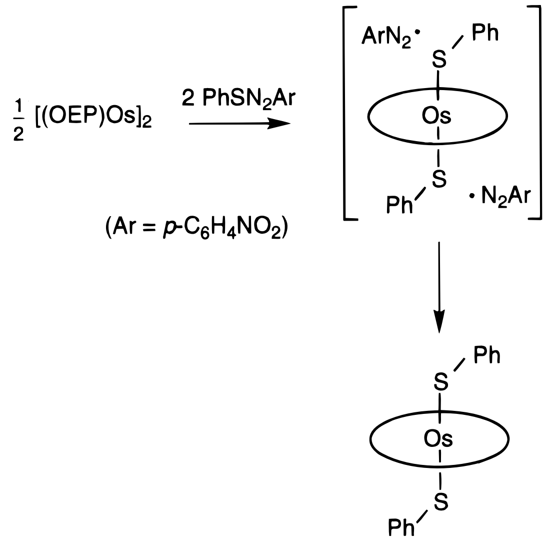
To further confirm the similarity of *S*-binding of PhSNO and PhSN=NAr to give the (OEP)Os(CO)(SR) thiolate initial products, we proceeded to employ the non-carbonyl-containing $[(OEP)Os]_2$ dimer, with the intention of incorporating *two* *S*-bonded ligands on opposite ends of the Os center. Remarkably, the reaction of $[(OEP)Os]_2$ with 4 equiv of PhSN=NAr (i.e., 2 equiv per Os center) gives (OEP)Os$(SPh)_2$ in 41% isolated yield, presumably via a bis-adduct intermediate which undergoes homolytic cleavage of the S−N bonds to give the known bisthiolate species[17] (Scheme 4). Importantly, the success of the reaction in Scheme 4 provides further chemical evidence for the *S*-binding of RSNO to osmium porphyrins.

(58) Sutton, D. *Chem. Soc. Rev.* **1975**, *4*, 443.

(59) Suehiro, T.; Masuda, S.; Nakausa, R.; Taguchi, M.; Mori, A.; Koike, A.; Date, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3321.

(60) Aryldiazonium adducts of metalloporphyrins are known: Farrell, N.; Neves, A. A. *Inorg. Chim. Acta* **1981**, *54*, L53.

Scheme 4



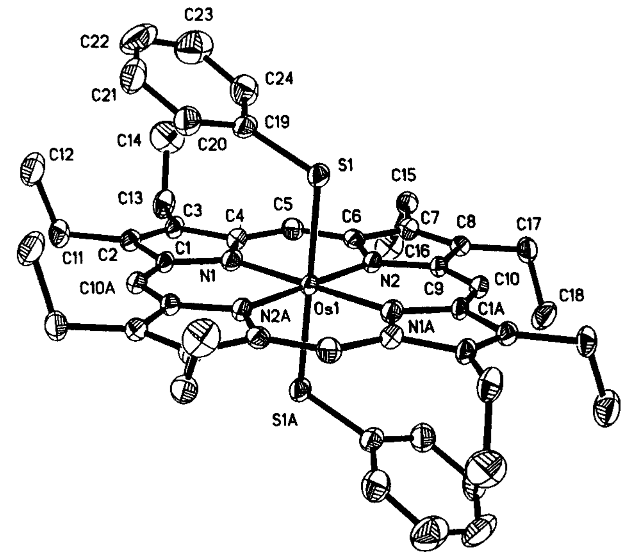


Figure 3. Molecular structure of $(OEP)Os(SPh)_2$.

We were able to obtain suitable crystals of the moderately air-stable bisthiolate Os^{IV} porphyrin complex by slow evaporation of a CH_2Cl_2/toluene solution of the compound. The molecular structure of the complex is shown in Figure 3. The Os−N(por) bond lengths are 2.047(4) and 2.050(4) Å. The Os−S and S−C bond lengths are 2.295(1) and 1.782(5) Å, respectively. The Os−S−C thiolate angle is 110.9(2)° and is within the range found for other osmium aryl thiolates (107.0−123.9°)[35,61] or alkanethiolates (102.5−111.8°).[9b,62] The thiolate ligands nearly eclipse diagonal porphyrin nitrogens, with the N1−Os−S1−C19 torsion angle of 14.2°. The structure is essentially similar to that of the related $(TTP)Os(SC_6F_4H)_2$ reported by Collman and synthesized by the reaction of $(TTP)Os(O)_2$ with thiol.[35]

Conclusion. In summary, we have provided new insight into the reactions of thionitrites and alkyl nitrites with osmium porphyrins. Whereas nitrosyl thiolates and alkoxides are produced in the reactions of thionitrites and alkyl nitrites with Os^{II} porphyrins, only the osmium nitrosyl difluorophosphate complex is isolated in the case of Os^{III}. This work also adds to the sparse structural data currently available for osmium nitrosyl porphyrins: prior to this work, only one other osmium nitrosyl porphyrin had been structurally characterized.[9b] By using the valence isoelectronic phenyl arylazo sulfide in place of PhSNO, we have been able to isolate and characterize the bisthiolate adduct, thereby giving more spectroscopic and chemical evidence that RSNO binds through the sulfur atom to the osmium porphyrin center. These results may have mechanistic implications for the further study of thionitrite and alkyl nitrite vasodilators with heme and other heme models.

Acknowledgment. We are grateful to the National Institutes of Health (FIRST Award 1R29 GM53586-01A1) and the National Science Foundation (CAREER Award CHE-9625065) for funding for this research. We also thank Dr. P. C. Ford for providing us with his results on ruthenium porphyrins (ref 10a) prior to publication.

Supporting Information Available: Drawings and listings of crystal data, atomic coordinates, anisotropic displacement parameters, bond lengths and angles, hydrogen coordinates and isotropic displacement parameters, torsion angles, and least-squares planes (47 pages). Ordering information is given on any current masthead page.

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(61) (a) Che, C.-M.; Cheng, W.-K.; Mak, T. C. W. *Inorg. Chem.* **1986**, *25*, 703. (b) Cruz-Garritz, D.; Gelover, S.; Torrens, H.; Leal, J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1988**, 2393. (c) Cruz-Garritz, D.; Sosa, P.; Torrens, H.; Hills, A.; Hughes, D. L.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1989**, 419. (d) Hills, A.; Hughes, D. L.; Richards, R. L.; Arroyo, M.; Cruz-Garritz, D.; Torrens, H. *J. Chem. Soc., Dalton Trans.* **1991**, 1281. (e) Arroyo, M.; Chamizo, J. A.; Hughes, D. L.; Richards, R. L.; Roman, P.; Sosa, P.; Torrens, H. *J. Chem. Soc., Dalton Trans.* **1994**, 1819.

(62) Lynch, W. E.; Lintvedt, R. L.; Shui, X. Q. *Inorg. Chem.* **1991**, *30*, 1014.