Activation of Thionitrites and Isoamyl Nitrite by Group 8 Metalloporphyrins and the Subsequent Generation of Nitrosyl Thiolates and Alkoxides of Ruthenium and Osmium Porphyrins

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Ruthenium and osmium porphyrins of the form (por)M(CO) (por = octaethylporphyrinato dianion (OEP), tetratolylporphyrinato dianion (TTP)) react with thionitrites (RSNO) and isoamyl nitrite (RONO) to give the (por)M(NO)(SR) and (por)M(NO)(OR) addition products. Reaction of *S*-nitroso-*N*-acetyl-L-cysteine methyl ester with (TPP)Fe(THF)$_2$ (TPP = tetraphenylporphyrinato dianion) gives (TPP)Fe(NO) in high yield. The related reaction of isoamyl nitrite with [(TPP)Fe(THF)$_2$]$^+$ gives the nitrosyl alcohol product [(TPP)Fe(NO)(HO-*i*-C$_5$H$_{11}$)]$^+$. The solid state structures of (OEP)Ru(NO)(NACysMe-*S*) (NACysMe = *N*-acetyl-L-cysteinate methyl ester), (TTP)Os(NO)(S-*i*-C$_5$H$_{11}$), and [(TPP)Fe(NO)(HO-*i*-C$_5$H$_{11}$)]$^+$ have been determined by X-ray diffraction.

Introduction

Nitric oxide (NO) chemistry and biochemistry received a surge of renewed interest about a decade ago when it was proposed that the radical species referred to as the endothelium-derived relaxing factor (EDRF) was NO.[1] It is now known that NO activates guanylyl cyclase (GC) by binding to its heme moiety.[2] Also, the biosynthesis of NO involves the heme-containing NO synthase, whose active site is similar to that of cytochrome P450 and contains a (porphyrin)Fe(thiolate) group.[3] Thus, it has been established that the heme group is vital in NO biochemistry and pharmacology in both NO consumption (by GC) and production (by NO synthase).

Thionitrites (RSNO) are a class of compounds containing the *S*-nitroso functional group,[4] and their pharmacological properties are invariably linked to the chemistry and biochemistry of NO.[5,6] Important questions have been raised over the last few years as to the true identity of EDRF. While it is generally accepted that EDRF is NO, there are a few published reports that show some thionitrites as possessing EDRF-like properties.[7−9] For example, RSNO is found to effect bronchodilation in a manner independent of NO activation.[9] Interestingly, nitroprusside ([Fe(CN)$_5$NO]$^{2-}$)[10] and other nitrovasodilators such as isoamyl nitrite are physiologically active only in the presence of thiols, consistent with the proposed intermediacy of RSNO.[11] Some alkyl nitrites (RONO) are also known to readily nitrosate thiols and cysteine derivatives.[12]

Protein thiols may be nitrosated under physiological conditions to produce *S*-nitroso derivatives,[13] although the direct reaction of thiols with NO to produce RSNO has been questioned.[14] The reported role of thionitrites (RSNO) as NO-storage and NO-carrier entities *in vivo* is also intriguing. Hemoglobin is also reported to be an NO carrier by using its cysteine groups on the protein to form RSNO groups.[15] Furthermore, the ability of nitrosomethane to bind directly to the heme of GC has also prompted the suggestion that RSNO may actually be able to bind directly to the heme site in GC.[16] It has also been suggested that one of the possible pathways

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for the NO activation of GC is its binding to a non-heme site followed by transfer of the NO group to the heme iron.[17]

Recent investigations into RSNO stability revealed that the presence of trace Cu^+ (even in distilled water) plays an important role in RSNO decomposition catalysis.[18] Thus, removal of trace metal ions (e.g., by EDTA addition) markedly enhances RSNO stability. This finding thus raises the question of the role of iron and copper metal ions in RSNO pharmacology.[19]

The possibility of a direct interaction of RSNO with heme led us to investigate the chemical reactions of RSNO with synthetic metalloporphyrins of the group 8 metals. We recently showed that nitrosamines (*N*-nitroso),[20] nitrosoarenes (*C*-nitroso),[21] and cupferron (*N*-nitroso)[22] compounds bind intact to iron porphyrins. We now report the results of our work with the related *S*-nitroso and *O*-nitroso derivatives. We show that the latter nitroso derivatives are activated by the metal centers in Fe, Ru, and Os porphyrins via an unusual formal *trans* addition process. A preliminary report on the Ru work has been communicated.[23]

Experimental Section

All reactions were performed under an atmosphere of prepurified nitrogen using standard Schlenk glassware and/or in an Innovative Technology Labmaster 100 dry box. Solutions for spectral studies were also prepared under a nitrogen atmosphere. Solvents were distilled from appropriate drying agents under nitrogen just prior to use: CH_2Cl_2 (CaH_2), toluene (Na), and hexane (Na/benzophenone/tetraglyme). Anhydrous deaerated methanol was purchased from Aldrich Chemical Co. and used as received.

Chemicals. (TTP)Ru(CO)[24] and (TTP)Os(CO)[25] were prepared by reaction of $TTPH_2$[26] with $Ru_3(CO)_{12}$ (Strem) and $Os_3(CO)_{12}$ (Strem), respectively (TTP = 5,10,15,20-tetra-*p*-tolylporphyrinato dianion). (TPP)FeCl (TPP = 5,10,15,20-tetraphenylporphyrinato dianion), (OEP)Ru(CO) (OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion), isoamyl nitrite (*i*-$C_5H_{11}ONO$, 97%), 2,2,2-trifluoroethanethiol (95%), and isoamyl mercaptan (*i*-$C_5H_{11}SH$, 97%) were purchased from Aldrich Chemical Co. Chloroform-*d* (99.8%, Cambridge Isotope Laboratories) was vacuum-distilled from CaH_2 under nitrogen prior to use. Elemental analyses were performed by Atlantic Microlab, Norcross, GA. Nitric oxide (98%, Matheson Gas) was passed through KOH pellets and a cold trap (dry ice/acetone, −78 °C) to remove higher nitrogen oxides.

Instrumentation. Infrared spectra were recorded on a Bio-Rad FT-155 FTIR spectrometer. Proton NMR spectra were obtained on a Varian XL-300 spectrometer and the signals referenced to the residual signal of the solvent employed. All couplings are in hertz. FAB mass spectra were obtained on a VG-ZAB-E mass spectrometer. UV−vis spectra were recorded on a Hewlett Packard Model 8452A diode array instrument.

Preparation of Thionitrites. *N*-Acetyl-L-cysteine methyl ester (NACysMe = *N*-acetyl-L-cysteinate methyl ester) was prepared by reaction of the precursor *N*-acetyl-L-cysteine (Aldrich) with diazomethane as previously reported.[27] The *S*-nitroso derivative was prepared by a published procedure.[28] The preparation of the remaining thionitrites (*i*-$C_5H_{11}SNO$ and CF_3CH_2SNO) followed established routes from their precursor thiols.[29] The following example is representative: Isoamyl mercaptan (0.418 g, 4.011 mmol) in acetic acid (2 mL) was treated with a solution (1 mL) of $NaNO_2$ (0.277 g, 4.015 mmol) in water at 0 °C. The solution turned deep red immediately. After 2 min of stirring, the red product was rapidly extracted with CH_2Cl_2 (20 mL) and the solution washed with aqueous $NaHCO_3$. The IR spectrum of *i*-$C_5H_{11}SNO$ in CH_2Cl_2 shows a characteristic peak at 1520 cm^{-1} for ν_{NO}, and the UV−vis spectrum of *i*-$C_5H_{11}SNO$ in CH_2Cl_2 shows two characteristic maxima at 334 nm and 548 nm for the thionitrite group.[30]

Preparation of (OEP)Ru(NO)(NACysMe-*S*) (NACysMe = *N*-Acetyl-L-cysteinate Methyl Ester). To a solid mixture of (OEP)Ru(CO) (0.100 g, 0.151 mmol) and *S*-nitroso-*N*-acetyl-L-cysteine methyl ester (0.032 g, 0.155 mmol) was added CH_2Cl_2 (10 mL). The mixture was stirred for 10 min, during which it turned from red to dark purple. The solvent was then removed in vacuo, the residue was dissolved in CH_2Cl_2/hexane (10 mL/5 mL), and crystals were obtained by slow evaporation of the solvent mixture in air to give (OEP)Ru(NO)(NACysMe-*S*)·0.4CH_2Cl_2 (0.103 g, 0.118 mmol, 78% isolated yield).

Anal. Calcd for $C_{42}H_{54}O_4N_6RuS·0.4CH_2Cl_2$: C, 58.26; H, 6.32; N, 9.61; Cl, 3.25; S, 3.67. Found: C, 58.50; H, 6.38; N, 9.54; Cl, 3.06; S, 3.59. IR (KBr, cm^{-1}): ν_{NO} = 1791 s; ν_{CO} = 1755 m, 1683 m; also 2962 m, 2929 w, 2869 m, 1498 m, 1466 m, 1450 m, 1428 m, 1372 m, 1363 m, 1353 m, 1316 w, 1353 m, 1302 w, 1269 m, 1241 w, 1229 w, 1206 m, 1165 m, 1152 m, 1112 m, 1057 s, 1020 s, 992 m, 961 m, 922 w, 868 w, 839 s, 746 s, 732 s, 725 s, 713 s, 698 w, 542 m . ^{1}H NMR ($CDCl_3$): δ 10.29 (s, 4H, *meso*-H of OEP), 5.28 (s, 0.8H, CH_2Cl_2), 4.17 (m, 16H, CH_2CH$_3$ of OEP), 2.88 (s, 3H, OCH_3 of NACysMe), 2.39 (br d, J = 7, 1H, N*H*CH of NACysMe), 1.99 (t, J = 7, 24H, CH_2CH_3 of OEP), 1.48 (m (apparent q), 1H, C*H*NH of NACysMe), 1.19 (s, 3H, C(O)CH_3 of NACysMe), −2.61 (dd, J = 7/13, 1H, C$H_\alpha H_\beta$ of NACysMe), −3.16 (dd, J = 5/13, 1H, C$H_\alpha H_\beta$ of NACysMe). Low-resolution mass spectrum (FAB): *m/z* 810 [(OEP)Ru(NACysMe-*S*)]$^+$ (18%), 664 [(OEP)Ru(NO)]$^+$ (100%), 634 [(OEP)Ru]$^+$ (50%).

Preparation of (OEP)Ru(NO)(SCH_2CF_3). To a stirred CH_2Cl_2 (5 mL) solution of (OEP)Ru(CO) (0.030 g, 0.045 mmol) was added excess CF_3CH_2SNO (> 10 equiv) in CH_2Cl_2 (5 mL). The mixture was stirred for 10 min, and the solvent was then removed in vacuo. Analysis of the residue by IR and ^{1}H NMR spectroscopy showed quantitative formation of the previously reported (OEP)Ru(NO)(SCH_2CF_3) compound.[20b]

Preparation of (TTP)Ru(NO)(O-*i*-C_5H_{11}). A CH_2Cl_2 solution (10 mL) of (TTP)Ru(CO) (0.100 g, 0.029 mmol) and *i*-$C_5H_{11}ONO$ (0.50 mL, ca. 3.6 mmol) was stirred at reflux for 10 min, during which the mixture turned from red to reddish brown. The solvent was removed in vacuo, the residue was redissolved in CH_2Cl_2 (10 mL), and the solution was filtered through a column of neutral alumina (1.5 × 15 cm). The volume of the filtrate was reduced to ca. 5 mL, and a mixture of hexanes (5 mL) was added. Crystals were obtained by slow evaporation of the solvent mixture at room temperature in air to give (TTP)Ru(NO)(O-*i*-C_5H_{11})·0.5CH_2Cl_2 (0.065 g, 0.070 mmol, 58% isolated yield).

Anal. Calcd for $C_{53}H_{47}O_2N_5Ru·0.5CH_2Cl_2$: C, 69.13; H, 5.20; N, 7.53; Cl, 3.82. Found: C, 68.80; H, 5.32; N, 7.53, Cl, 3.93. IR (KBr,

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Table 1. Crystal Data and Structure Refinement Parameters

	(OEP)Ru(NO)(NACysMe-*S*)	(TTP)Os(NO)(S-*i*-C_5H_{11})	[(TPP)Fe(NO)(HO-*i*-C_5H_{11})]ClO_4
formula	$C_{42}H_{54}N_6O_4SRu$	$C_{53}H_{47}N_5OSOs$	$C_{54}H_{39}N_5Cl_3O_6Fe$
fw	840.04	992.22	1016.10
T, K	203(2)	188(2)	153(2)
crystal system	monoclinic	triclinic	monoclinic
space group	$P2_1$	$P\bar{1}$	$P2_1/c$
unit cell dimens			
a, Å	8.2810(10)	11.084(2)	12.711(2)
b, Å	19.455(3)	11.190(2)	19.067(5)
c, Å	12.670(2)	11.687(2)	20.138(3)
α, deg	90	68.80(2)	90
β, deg	90.71(1)	73.11(1)	96.76(1)
γ, deg	90	83.31(1)	90
V, Å^3; *Z*	2041.1(5); 2	1292.8(4); 1	4847(2); 4
D(calcd), g/cm^3	1.367	1.274	1.393
abs coeff, mm^{-1}	0.484	2.545	0.533
F(000)	880	500	2092
crystal size, mm^3	0.22 × 0.36 × 0.44 mm	0.58 × 0.46 × 0.32 mm	0.46 × 0.42 × 0.28 mm
θ range for data collection, deg	1.61 to 28.41	2.23 to 27.00	1.93 to 25.00
index ranges	$0 \le h \le 10, 0 \le k \le 26, -16 \le l \le 16$	$0 \le h \le 14, -13 \le k \le 13, -14 \le l \le 14$	$0 \le h \le 15, 0 \le k \le 22, -23 \le l \le 23$
reflns collected	5147	5726	8851
independent reflns	4823 [*R*(int) = 0.0482]	5629 [*R*(int) = 0.0331]	8435 [*R*(int) = 0.0367]
data/restraints/parameters	4816/1/487	5612/323/552	8406/43/703
goodness-of-fit on F^2	1.079	1.133	1.030
final *R* indices [$I > 2\sigma(I)$][a,b]	R1 = 0.0465, wR2 = 0.1047	R1 = 0.0455, wR2 = 0.1188	R1 = 0.0645, wR2 = 0.1718
R indices (all data)[a,b]	R1 = 0.0639, wR2 = 0.1249	R1 = 0.0493, wR2 = 0.1335	R1 = 0.0923, wR2 = 0.2213
largest diff peak and hole, e/Å^3	1.401 and −0.433	2.172 and −1.187	0.731 and −0.748

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

cm^{-1}): ν_{NO} = 1809 s; also 3025 w, 2952 w, 2918 w, 2865 w, 1525 w, 1489 w, 1455 w, 1362 w, 1348 m, 1303 w, 1261 m, 1212 m, 1183 m, 1112 m, 1072 s, 1015 s, 976 w, 869 w, 847 w, 796 s, 736 m, 717 m, 711 m, 648 w, 597 m, 560 w, 521 m, 510 m, 478 w, 451 w. ^{1}H NMR ($CDCl_3$): *δ* 8.92 (s, 8H, pyrrole H, TTP), 8.12 (app t (overlapping d's), 8H, *o*/*o*′-H of TTP), 7.56 (d, *J* = 8, 8H, *m*-H of TTP), 5.28 (s, 1H, C*H*$_2$Cl$_2$), 2.70 (s, 12H, C*H*$_3$ of TTP), −0.59 (d, *J* = 7, 6H, (C*H*$_3$)$_2$CHCH$_2$CH$_2$O), −1.02 (m, 1H, (CH$_3$)$_2$C*H*CH$_2$CH$_2$O), −2.34 (t, *J* = 7, 2H, (CH$_3$)$_2$CHCH$_2$C*H*$_2$O), −2.78 (dt, *J* = 7/7, 2H, (CH$_3$)$_2$CHC*H*$_2$CH$_2$O). Low-resolution mass spectrum (FAB): *m*/*z* 887 [(TTP)Ru(NO)(O-*i*-C_5H_{11})]$^+$ (8%), 800 [(TTP)Ru(NO)]$^+$ (100%), 770 [(TTP)Ru]$^+$ (71%).

Preparation of (TTP)Os(NO)(S-*i*-C_5H_{11}). A CH_2Cl_2 solution (10 mL) of (TTP)Os(CO) (0.100 g, 0.113 mmol) was reacted with *i*-C_5H_{11}SNO (ca. 3 mmol in 20 mL of CH_2Cl_2), and the mixture was stirred for 10 h, during which its color turned from purple to brown. After all volatiles were removed in vacuo, the residue was dissolved in a CH_2Cl_2/hexane mixture (1:5, 12 mL), and the solution was transferred to the top of an alumina column (1.5 × 15 cm) and eluted with CH_2Cl_2/hexane (ca. 50−100 mL). A resulting green band was separated from a slow-moving brown band and collected. The solvent was removed in vacuo and the product identified as (TTP)Os(NO)(S-*i*-C_5H_{11})·0.3CH_2Cl_2 (0.023 g, 0.023 mmol, 20% isolated yield).

Anal. Calcd for $C_{53}H_{47}ON_5OsS$·0.3CH_2Cl_2: C, 62.90; H, 4.71; N, 6.88. Found: C, 62.99; H, 5.09; N, 6.61. IR (KBr, cm^{-1}): ν_{NO} = 1760 s; also 2955 m, 2921 w, 2869 w, 1574 m, 1542 w, 1516 m, 1467 w, 1352 m, 1307 w, 1275 w, 1214 w, 1181 m, 1107 w, 1072 m, 1018 s, 798 s, 764 w, 750 m, 720 w, 668 w, 525 m. ^{1}H NMR ($CDCl_3$): *δ* 8.93 (s, 8H, pyrrole H, TTP), 8.10 (app t (overlapping d's), 8H, *o*/*o*′-H of TTP), 7.56 (m (overlapping d's), 8H, *m*/*m*′-H of TTP), 5.28 (s, 0.6H, C*H*$_2$Cl$_2$), 2.70 (s, 12H, C*H*$_3$ of TTP), −0.26 (d, *J* = 3, 6H, (C*H*$_3$)$_2$CHCH$_2$CH$_2$S), −1.01 (m, 1H, (CH$_3$)$_2$C*H*CH$_2$CH$_2$S), −1.60 (m, 2H, (CH$_3$)$_2$CHC*H*$_2$CH$_2$S), −2.73 (t, *J* = 7, 2H, (CH$_3$)$_2$CHCH$_2$C*H*$_2$S). Low-resolution mass spectrum (FAB): *m*/*z* 992 [(TTP)Os(NO)(S-*i*-C_5H_{11})]$^+$ (5%), 890 [(TTP)Os(NO) + H]$^+$ (100%), 860 [(TTP)Os + H]$^+$ (22%).

Preparation of (TTP)Os(NO)(O-*i*-C_5H_{11}). A CH_2Cl_2 solution (10 mL) of (TTP)Os(CO) (0.065 g, 0.073 mmol) was reacted with *i*-C_5H_{11}ONO (0.20 mL, 1.4 mmol). The solution was gently heated and left to stir for 15 min. The color of the solution did not change very much (from red to purplish red). All of the solvent was then removed in vacuo. The residue was dissolved in toluene (2 mL), a mixture of hexanes (5 mL) was added, and the resultant mixture was kept overnight at −20 °C. The supernatant solution was discarded, and the purple crystalline solid was washed with hexanes (3 × 5 mL) and dried in vacuo for 3 h to give (TTP)Os(NO)(O-*i*-C_5H_{11}) (0.041 g, 0.042 mmol, 57% yield).

Anal. Calcd for $C_{53}H_{47}O_2N_5Os$: C, 65.21; H, 4.85; N, 7.17. Found: C, 65.15; H, 4.93; N, 7.13. IR (KBr, cm^{-1}): ν_{NO} = 1770 s; also 3024 w, 2947 w, 2918 w, 2865 w, 1806 w, 1528 w, 1512 w, 1494 w, 1455 w, 1365 w, 1351 m, 1306 w, 1214 m, 1183 m, 1110 w, 1075 m, 1018 s, 978 w, 848 w, 798 s, 719 m, 644 m, 599 w, 594 w, 523 m. IR (CH_2Cl_2, cm^{-1}): ν_{NO} = 1766 s. ^{1}H NMR ($CDCl_3$): *δ* 8.93 (s, 8H, pyrrole H of TTP), 8.12 (app t (overlapping d's), 8H, *o*/*o*′-H of TTP), 7.56 (m (overlapping d's), 8H, *m*/*m*′-H of TTP), 2.70 (s, 12H, C*H*$_3$ of TTP), −0.61 (d, *J* = 7, 6H, (C*H*$_3$)$_2$CHCH$_2$CH$_2$O), −1.07 (m, 1H, (CH$_3$)$_2$C*H*CH$_2$CH$_2$O), −2.27 (t, *J* = 7, 2H, (CH$_3$)$_2$CHCH$_2$C*H*$_2$O), −2.82 (dt (app q), *J* = 7/7, 2H, (CH$_3$)$_2$CHC*H*$_2$CH$_2$O). Low-resolution mass spectrum (FAB): *m*/*z* 977 [(TTP)Os(NO)(O-*i*-C_5H_{11}) + H]$^+$ (24%), 890 [(TTP)Os(NO) + H]$^+$ (100%), 859 [(TTP)Os]$^+$ (33%).

Reaction of (TPP)Fe(THF)$_2$ with *S*-Nitroso-*N*-acetyl-L-cysteine Methyl Ester. A CH_2Cl_2 solution (10 mL) of (TPP)Fe(THF)$_2$ (0.080 g, 0.099 mmol)[31] and *S*-nitroso-*N*-acetyl-L-cysteine methyl ester (0.021 g, 0.11 mmol) was stirred for 30 min, during which the mixture turned from red to purple. After removal of solvent in vacuo, the residue was redissolved in CH_2Cl_2 (10 mL) and MeOH (10 mL), and ca. half the solvent was removed in vacuo. The resulting suspension was filtered through a cotton plug, and the trapped solid was washed with MeOH to remove any side products. The remaining purple residue on the cotton plug was then eluted with CH_2Cl_2 and the filtrate collected. Solvent removal from this filtrate gave (TPP)Fe(NO) (0.065 g, 0.093 mmol, 94% yield), identified by its characteristic IR (ν_{NO} = 1699 cm^{-1} (KBr)) and UV−vis spectra (CH_2Cl_2: 406, 474 (sh), 538, 608 nm).[32]

Reaction of [(TPP)Fe(THF)$_2$]ClO_4 with *i*-C_5H_{11}ONO. To a CH_2Cl_2 solution (10 mL) of [(TPP)Fe(THF)$_2$]ClO_4 (0.100 g, 0.114 mmol)[20a] was added *i*-C_5H_{11}ONO (0.5 mL, ca. 4 mmol). After 30 min of stirring, hexane (5 mL) was added to the solution, and the mixture was kept at −20 °C for 2 weeks. The resulting crystalline precipitate was collected and identified as [(TPP)Fe(NO)(HO-*i*-C_5H_{11})]ClO_4·CH_2Cl_2·H_2O (0.88 g, 0.089 mmol, 78% yield). Anal. Calcd for $C_{49}H_{40}N_5O_6ClFe$·CH_2Cl_2·H_2O: C, 60.71; H, 4.48; N, 7.08; Cl, 10.77. Found: C, 60.61; H, 4.61; N, 6.50, Cl, 11.16. IR (KBr, cm^{-1}): ν_{NO} = 1935 s; also 1597 w, 1577 vw, 1484 w, 1466 vw, 1440 m, 1342 m, 1311 w, 1268 m,

(31) Reed, C. A.; Mashiko, T.; Scheidt, W. R.; Spartalian, K.; Lang, G. *J. Am. Chem. Soc.* **1980**, *102*, 2302.
(32) Scheidt, W. R.; Frisse, M. E. *J. Am. Chem. Soc.* **1975**, *97*, 17.

1227 w, 1200 m, 1177 m, 1160 vw, 1106 s, br, 1074 s, br, 1046 s, br, 1005 s, br, 925 m, 870 m, 848 w, 833 w, 801 s, 753 s, 735 s, 702 s, 662 m, 620 s, 566 m, 524 s, 461 s, 407 s. Low-resolution mass spectrum (FAB): *m/z* 668 $[(TPP)Fe]^+$ (100%). This complex is thermally unstable in solution, slowly releasing NO.

Structural Determinations by X-ray Crystallography. All crystal data were collected on a Siemens P4 diffractometer with Mo Kα radiation ($\lambda = 0.710\,73$ 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)*. Thermal ellipsoid plots are drawn at 35% probability.

i. (OEP)Ru(NO)(NACysMe-*S*). A crystal of (OEP)Ru(NO)(NACysMe-*S*) was grown from a CH_2Cl_2/hexane solution (1:1) left in air overnight. The data were corrected for Lorentz and polarization effects. No absorption correction was applied since it was judged to be insignificant. Details of crystal data and refinement are given in Table 1, and selected bond lengths and angles are collected in Table 2.

ii. (TTP)Os(NO)(S-*i*-C_5H_{11}). A crystal was grown from a saturated solution of CH_2Cl_2/hexane (1:2) left for 2 d at −20 °C. Some parts of the structure are affected by disorder. In particular, the carbon atoms C(53), C(52), C(50), and C(49) of the axial thiolate group (S-*i*-C_5H_{11}) are severely disordered as evident from the very high thermal motions displayed by these atoms. Details of crystal data and refinement are given in Table 1, and selected bond lengths and angles are collected in Table 3.

iii. [(TPP)Fe(NO)(*i*-$C_5H_{11}OH$)]ClO_4. A crystal was grown from a concentrated solution of CH_2Cl_2/hexane (2:1) left for 2 weeks at −20 °C. The asymmetric unit contains a cation with a completely disordered *i*-C_5H_{11} group in the axial position. In addition to the cation, the asymmetric unit also contains a disordered perchlorate anion, a disordered dichloromethane molecule, and a disordered solvent molecule. Because of the extreme disorder of the solvent (refined as a hydrocarbon), it was not possible to clearly identify it. The six peaks were refined as carbon atoms with C(51) and C(52) with full occupancy and C(53), C(54), C(55), and C(56) with 0.5 occupancy. Completely labeled diagrams of the cation, anion, and solvent molecules are available as Supporting Information. In the final cycles of refinement, hydrogen atoms were included in the idealized positions for the cation. Details of crystal data and refinement are given in Table 1, and selected bond lengths and angles are collected in Table 4.

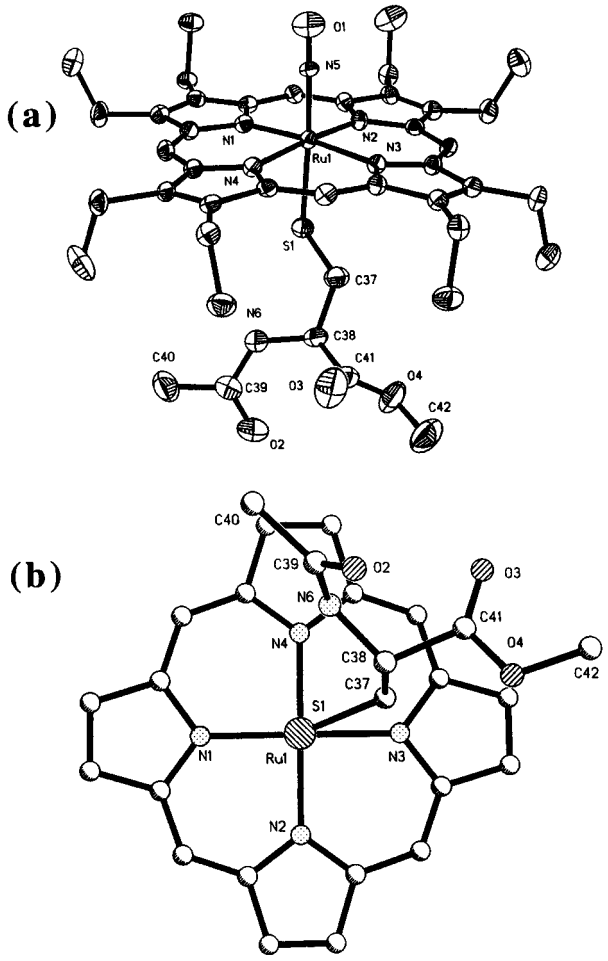

Figure 1. (a) Molecular structure of (OEP)Ru(NO)(NACysMe-*S*). Hydrogen atoms have been omitted for clarity. (b) View along the S(1)−Ru(1) bond showing the orientation of the axial thiolate ligand. The ethyl substituents on the porphyrin have been omitted.

Results

Ruthenium Complexes. Reaction of (OEP)Ru(CO) with 1 equiv of solid *S*-nitroso-*N*-acetyl-L-cysteine methyl ester in CH_2Cl_2 at room temperature results in an instantaneous color change from red to dark purple and the replacement of the 1919 cm^{-1} band in the IR spectrum of the reaction mixture (due to ν_{CO} of (OEP)Ru(CO)) with a new band at 1805 cm^{-1} assigned to ν_{NO} of the nitrosyl product. The reaction generates the nitrosyl thiolate (OEP)Ru(NO)(NACysMe-*S*) complex resulting from a formal *trans* addition in 78% yield after workup.

$$(OEP)Ru(CO) + RSNO \rightarrow (OEP)Ru(NO)(SR) \qquad (1)$$

SR = NACysMe-*S* (*N*-acetyl-L-cysteinate methyl ester)

This product is recrystallized from CH_2Cl_2/hexanes in air and is air-stable in solution and in the solid state, not showing any signs of decomposition in the solid state for at least 2 weeks. It is readily soluble in chlorinated solvents such as CH_2Cl_2 and $CHCl_3$ but is insoluble in hydrocarbon solvents such as hexanes and benzene. The ν_{NO} of 1791 cm^{-1} (KBr) is similar to those of other (OEP)Ru(NO)(SR) nitrosyl thiolates generated by us previously (SR = SCH_2CF_3 (1782 cm^{-1}), SC_6F_4H (1798 cm^{-1})) from the reaction of the respective thiolate anions with $[(OEP)Ru(NO)(H_2O)]^+$.[20b] The (OEP)Ru(NO)(NACysMe-*S*) complex also displays ν_{CO} bands at 1755 and 1683 cm^{-1} due to the coordinated cysteinate ligand. The mass spectrum (FAB) does not show the parent ion but shows ion fragments due to loss of the NO ligand (*m/z* 810) or loss of the cysteinate ligand (*m/z* 664). The sharpness of the peaks in the ^1H NMR spectrum of the complex in $CDCl_3$ is consistent with the expected diamagnetic nature of the formal Ru^{II} product (with the linear nitrosyl ligand regarded as NO^+).[33] When the reagents of eq 1 (or (OEP)Ru(CO) with CF_3CH_2SNO) are combined in CD_2Cl_2 in an NMR tube and the ^1H NMR spectrum is collected immediately afterward, only the peaks of the nitrosyl thiolate product are observed, indicating the quantitative nature of the reaction.

In order to unambiguously determine the mode of attachment of the multi-heteroatom cysteinate ligand in (OEP)Ru(NO)(NACysMe-*S*), we subjected a suitable crystal to a single-crystal X-ray crystallographic analysis. The molecular structure is shown in Figure 1. Selected bond lengths and angles are collected in Table 2. The axial Ru−N(O) bond length is 1.790(5) Å, and the N−O bond length is 1.123(8) Å. The Ru−N−O linkage is essentially linear, with a bond angle of 174.8(6)°. The Ru−S bond length is 2.362(2) Å, and the Ru−S−C(37) bond angle is 107.1(3)°.

The related reaction between (OEP)Ru(CO) and excess isoamyl nitrite (*i*-$C_5H_{11}ONO$) gives a product that was very difficult to isolate or purify (ν_{NO} 1790 cm^{-1} (CH_2Cl_2)). However, replacement of OEP with TTP results in the successful

(33) Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyls*; Oxford University Press: New York, 1992.

Table 2. Selected Bond Lengths and Angles for (OEP)Ru(NO)(NACysMe-*S*)

Bond Lengths (Å)			
Ru(1)−N(5)	1.790(5)	N(1)−C(1)	1.382(8)
Ru(1)−N(2)	2.043(4)	N(2)−C(6)	1.374(8)
Ru(1)−N(3)	2.045(6)	N(2)−C(9)	1.388(8)
Ru(1)−N(1)	2.057(5)	N(3)−C(14)	1.375(8)
Ru(1)−N(4)	2.068(4)	N(3)−C(11)	1.380(8)
Ru(1)−S(1)	2.362(2)	N(4)−C(19)	1.373(8)
S(1)−C(37)	1.814(8)	N(4)−C(16)	1.376(8)
O(1)−N(5)	1.123(8)	N(6)−C(39)	1.324(11)
O(2)−C(39)	1.206(12)	N(6)−C(38)	1.431(10)
O(3)−C(41)	1.181(10)	C(37)−C(38)	1.532(10)
O(4)−C(41)	1.301(10)	C(38)−C(41)	1.540(11)
O(4)−C(42)	1.420(12)	C(39)−C(40)	1.494(14)
N(1)−C(4)	1.367(8)		
Bond Angles (deg)			
N(5)−Ru(1)−N(2)	94.2(3)	C(37)−S(1)−Ru(1)	107.1(3)
N(5)−Ru(1)−N(3)	92.3(3)	C(41)−O(4)−C(42)	115.2(9)
N(2)−Ru(1)−N(3)	90.4(2)	O(1)−N(5)−Ru(1)	174.8(6)
N(5)−Ru(1)−N(1)	93.7(2)	C(39)−N(6)−C(38)	122.1(7)
N(2)−Ru(1)−N(1)	89.3(2)	C(38)−C(37)−S(1)	111.9(5)
N(3)−Ru(1)−N(1)	174.0(2)	N(6)−C(38)−C(37)	110.7(6)
N(5)−Ru(1)−N(4)	90.5(3)	N(6)−C(38)−C(41)	109.9(6)
N(2)−Ru(1)−N(4)	175.2(4)	C(37)−C(38)−C(41)	106.3(6)
N(3)−Ru(1)−N(4)	89.7(2)	O(2)−C(39)−N(6)	120.8(10)
N(1)−Ru(1)−N(4)	90.2(2)	O(2)−C(39)−C(40)	121.6(10)
N(5)−Ru(1)−S(1)	177.0(2)	N(6)−C(39)−C(40)	117.6(9)
N(2)−Ru(1)−S(1)	88.0(2)	O(3)−C(41)−O(4)	124.0(9)
N(3)−Ru(1)−S(1)	89.6(2)	O(3)−C(41)−C(38)	124.5(8)
N(1)−Ru(1)−S(1)	84.3(2)	O(4)−C(41)−C(38)	111.3(7)
N(4)−Ru(1)−S(1)	87.2(2)		

isolation of the analytically pure nitrosyl alkoxide product (TTP)Ru(NO)(O-*i*-C_5H_{11}) in 58% yield after workup (eq 2).

$$(TTP)Ru(CO) + i\text{-}C_5H_{11}ONO \rightarrow (TTP)Ru(NO)(O\text{-}i\text{-}C_5H_{11}) \quad (2)$$

The reaction is slower than that described in eq 1, and mild heating is required for the reaction to proceed to completion in a 10 min period.[34] Indeed, when the reaction is run at room temperature and monitored by IR spectroscopy, an intermediate is seen to form (ν_{CO} 2006 cm^{-1} (CH_2Cl_2), Figure 2). This intermediate has been tentatively assigned as the *carbonyl* alkoxide (TTP)Ru(CO)(O-*i*-C_5H_{11}) complex (see Discussion).

The spectroscopic data for the final (TTP)Ru(NO)(O-*i*-C_5H_{11}) product are entirely consistent with its formulation as a nitrosyl alkoxide. Thus, the ν_{NO} of 1809 cm^{-1} is close to that recently reported for the crystallographically characterized (TTP)Ru(NO)(OMe) (ν_{NO} 1800 cm^{-1}),[35] and the mass spectrum of (TTP)Ru(NO)(O-*i*-C_5H_{11}) also shows a parent ion at *m/z* 887.

Osmium Complexes. The analogous reaction of (TTP)Os(CO) with isoamyl thionitrite in CH_2Cl_2 results in the replacement of the ν_{CO} of 1899 cm^{-1} for (TTP)Os(CO) in its IR spectrum with a new band at 1770 cm^{-1} assigned to ν_{NO} of the formal *trans*-addition product (eq 3).

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

When the reaction described in eq 3 is performed under a nitrogen purge and monitored by IR spectroscopy, an intermediate is seen to form (1937 cm^{-1}, Figure 3). In the presence of excess RSNO, the nitrosyl thiolate product is then formed (ν_{NO} 1770 cm^{-1}). When all volatiles are removed from the reaction mixture after initial RSNO addition and the residue[36] redissolved in CH_2Cl_2 and NO gas added, two products are formed: the expected nitrosyl thiolate (ν_{NO} 1770 cm^{-1}) and the nitrosyl nitrito (TTP)Os(NO)(ONO) complex (ν_{NO} 1818 cm^{-1})[37] as shown in Figure 4. An independent reaction of authentic (TTP)Os(NO)(S-*i*-C_5H_{11}) with NO gas also produces (TTP)Os(NO)(ONO) quantitatively.[37,38]

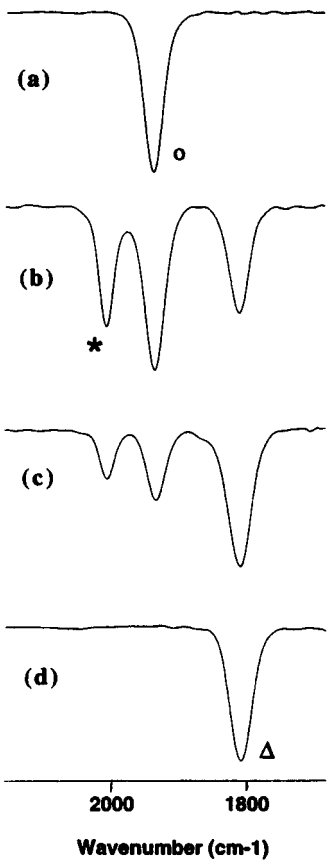

Figure 2. IR monitoring (in CH_2Cl_2) of the reaction of (TTP)Ru(CO) (labeled o in spectrum a; ν_{CO} 1934 cm^{-1}) with isoamyl nitrite to give (TTP)Ru(NO)(O-*i*-C_5H_{11}) (Δ in spectrum d; ν_{NO} 1809 cm^{-1}). Spectrum b: after addition of isoamyl nitrite, showing the intermediacy of (TTP)Ru(CO)(O-*i*-C_5H_{11}) (*; ν_{CO} 2006 cm^{-1}), starting (TTP)Ru(CO), and product (TTP)Ru(NO)(O-*i*-C_5H_{11}). Spectrum c: after further reaction of the sample of spectrum b for 50 min.

The final nitrosyl thiolate product of eq 3 is very soluble in benzene and in polar solvents such as CH_2Cl_2 and is moderately soluble in hexanes. The product is obtained pure after chromatography and is isolated as an analytically pure solid in somewhat low yield. Unlike the ruthenium analog, this compound is air-sensitive in solution, which, together with its high solubility, probably accounts for partial loss of product during isolation procedures. In any event, the spectroscopic

(34) The expectation of a slower reaction of RONO compared with RSNO has some precedent.[12a]

(35) (a) Bohle, D. S.; Goodson, P. A.; Smith, B. D. *Polyhedron* **1996**, *15*, 3147. (b) Bohle, D. S. Personal communication.

(36) Low-resolution mass spectral data for the solid residue formulated as (TTP)Os(CO)(S-*i*-C_5H_{11}): FAB^+ *m/z* 886 $[(TTP)Os(CO)]^+$; EI (20 eV) *m/z* 206 $[(SC_5H_{11})_2]^+$ 88%, 103 $[SC_5H_{11}]^+$ 7%, 71 $[C_5H_{11}]^+$ 100%.

(37) Data for (TTP)Os(NO)(ONO) are as follows. IR (KBr, cm^{-1}): ν_{NO} = 1805 s; also ν_{ONO} 1530, 920 cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.00 (s, 8H, pyrrole H of TTP), 8.15 (d, J = 8, 4H, *o*-H of TTP), 8.05 (d, J = 8, 4H, *o*′-H of TTP), 7.56 (app t (overlapping d's), 8H, *m*/*m*′-H of TTP), 2.67 (s, 12H, CH_3 of TTP). Low-resolution mass spectral data (FAB): *m/z* 905 $[(TTP)Os(ONO)]^+$ (4%), 889 $[(TTP)Os(NO)]^+$ (11%). Manuscript in preparation.

(38) We and others[35a,39] have reported on the synthesis of the Ru analogs: 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.

(39) Ford, P. C. Personal communication.

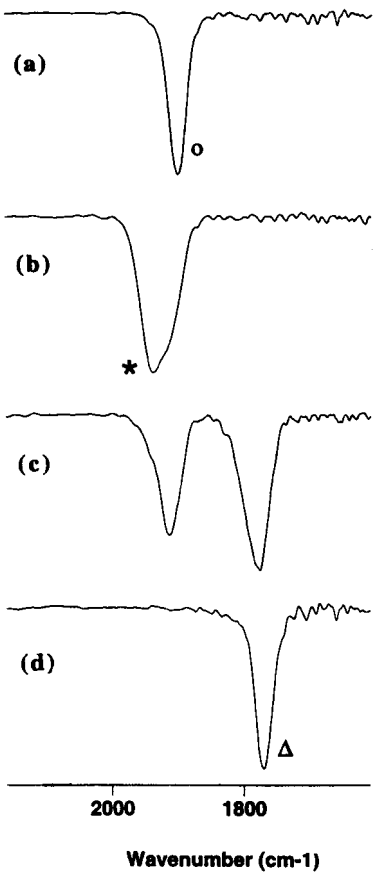

Figure 3. IR monitoring (in CH_2Cl_2) of the reaction of (TTP)Os(CO) (labeled o in spectrum a; υ_{CO} 1899 cm^{-1}) with isoamyl thionitrite to give (TTP)Os(NO)(S-*i*-C_5H_{11}) (Δ in spectrum d; υ_{NO} 1770 cm^{-1}). Spectrum b: after addition of isoamyl thionitrite while the sample was purged with N_2, showing the formation of intermediate (TTP)Os(CO)-(S-*i*-C_5H_{11}) (*; υ_{CO} 1937 cm^{-1}). Spectrum c: after addition of excess isoamyl thionitrite without purging with N_2, showing formation of the (TTP)Os(NO)(S-*i*-C_5H_{11}) product.

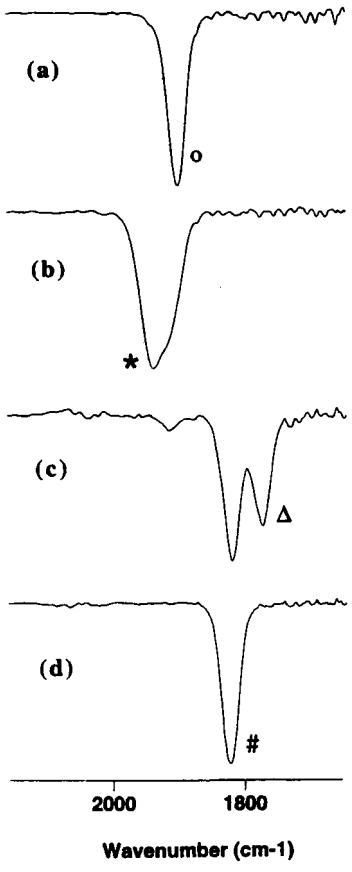

Figure 4. IR monitoring (in CH_2Cl_2) of the reaction of (TTP)Os(CO) (labeled o in spectrum a; υ_{CO} 1899 cm^{-1}) with isoamyl thionitrite followed by NO gas to eventually give (TTP)Os(NO)(ONO) (# in spectrum d; υ_{NO} 1818 cm^{-1}). Spectrum b: after addition of isoamyl thionitrite while the sample was purged with N_2, showing the formation of intermediate (TTP)Os(CO)(S-*i*-C_5H_{11}) (*; υ_{CO} 1937 cm^{-1}). Spectrum c: further reaction of a CH_2Cl_2 solution of the dried residue from the sample of spectrum b with NO gas to give a mixture of (TTP)Os(NO)-(S-*i*-C_5H_{11}) (△; υ_{NO} 1770 cm^{-1}) and (TTP)Os(NO)(ONO) (#; υ_{NO} 1818 cm^{-1}).

properties of (TTP)Os(NO)(S-*i*-C_5H_{11}) are also consistent with its formulation as a nitrosyl thiolate. The mass spectrum shows a parent ion at *m/z* 992, and the ν_{NO} of the complex is at 1760 cm^{-1} (KBr).

A suitable crystal was subjected to a single-crystal X-ray diffraction analysis, and the molecular structure is shown in Figure 5. Selected bond lengths and angles are collected in Table 3. To the best of our knowledge, this is the first reported X-ray structural determination of an osmium nitrosyl porphyrin.[33] The axial Os−N(O) and nitrosyl N−O bond lengths are 2.041(7) and 1.086(10) Å, respectively, and the Os−N−O bond angle of 172.0(9)° indicates linearity of the nitrosyl linkage. The axial Os−S bond distance is 2.209(3) Å, and the Os−S−C angle is 111.8(5)°. The osmium atom is displaced 0.03 Å out of the four-nitrogen porphyrin plane toward the nitrosyl ligand. The axial S−Os−N(O) group is linear (178.1(2)°), and the thiolate C(49) atom is essentially eclipsed by the porphyrin N(5) atom (with a N(5)−Os−S−C(49) torsion angle of 6.5°).

The related reaction of (TTP)Os(CO) with isoamyl nitrite gives, after workup, the nitrosyl alkoxide (TTP)Os(NO)(O-*i*-C_5H_{11}) in 57% yield (eq 4). An intermediate for eq 4 is

$$(TTP)Os(CO) + i\text{-}C_5H_{11}ONO \rightarrow (TTP)Os(NO)(O\text{-}i\text{-}C_5H_{11}) \quad (4)$$

observed to form when the reaction is monitored by IR spectroscopy: a new band appears in the IR spectrum at 1968 cm^{-1} in CH_2Cl_2 and is tentatively assigned as the ν_{CO} of the intermediate (TTP)Os(CO)(O-*i*-C_5H_{11}) complex (cf 1898 cm^{-1} for (TTP)Os(CO)). The spectroscopic properties of (TTP)Os-(NO)(O-*i*-C_5H_{11}) are similar to those of the thiolate analog described in the preceding paragraphs. The ν_{NO} is 1770 cm^{-1}, higher than that of the thiolate analog (ν_{NO} 1760 cm^{-1}) and higher than that of the related octaethylporphyrin methoxy complex (OEP)Os(NO)(OMe) (ν_{NO} 1745 cm^{-1} (KBr)).[40]

Iron Complexes. Unlike the reactions with Ru^{II} and Os^{II} described above, the reaction of the Fe^{II} porphyrin (TPP)Fe-$(THF)_2$ with RSNO (*S*-nitroso-*N*-acetyl-L-cysteine methyl ester) in CH_2Cl_2 generates the known five-coordinate (TPP)Fe(NO) complex in 94% isolated yield (eq 5). Although the related

$$(TPP)Fe(THF)_2 + RSNO \rightarrow (TPP)Fe(NO) \quad (5)$$

SR = NACysMe-*S* (*N*-acetyl-L-cysteinate methyl ester)

reaction of the *ferric* $[(TPP)Fe(THF)_2]ClO_4$ derivative with RSNO did not yield any isolable products, the IR spectrum of the reaction solution (CH_2Cl_2) revealed the formation of a mixture of (TPP)Fe(NO) (ν_{NO} 1685 cm^{-1}), free NO (ν_{NO} 1845 cm^{-1}), and $[(TPP)Fe(NO)(L)]^+$ (ν_{NO} 1919 cm^{-1}; L = unknown)

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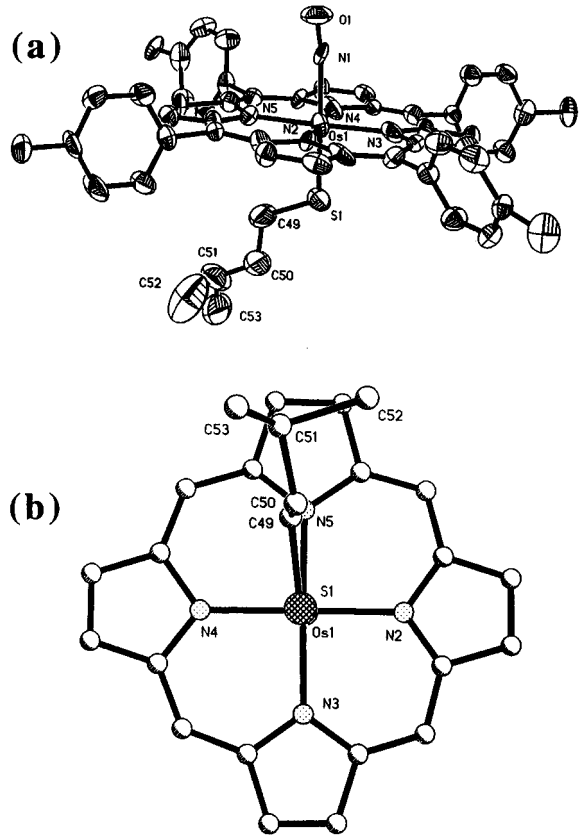

Figure 5. (a) Molecular structure of (TTP)Os(NO)(S-*i*-C_5H_{11}). Hydrogen atoms have been omitted for clarity. (b) View along the S(1)−Os(1) bond showing the orientation of the axial thiolate ligand. The tolyl substituents on the porphyrin have been omitted.

Table 3. Selected Bond Lengths and Angles for (TTP)Os(NO)(S-*i*-C_5H_{11})

Bond Lengths (Å)			
Os(1)−N(2)	2.035(5)	Os(1)−N(4)	2.076(9)
Os(1)−N(1)	2.041(7)	N(1)−O(1)	1.086(10)
Os(1)−N(5)	2.049(6)	Os(1)−S(1)	2.209(3)
Os(1)−N(3)	2.074(8)	S(1)−C(49)	1.81(2)
Bond Angles (deg)			
O(1)−N(1)−Os(1)	172.0(9)	N(5)−Os(1)−N(4)	90.4(3)
N(2)−Os(1)−N(1)	89.7(2)	N(3)−Os(1)−N(4)	90.6(3)
N(2)−Os(1)−N(5)	90.1(2)	N(2)−Os(1)−S(1)	92.2(2)
N(1)−Os(1)−N(5)	85.5(2)	N(1)−Os(1)−S(1)	178.1(2)
N(2)−Os(1)−N(3)	88.9(3)	N(5)−Os(1)−S(1)	94.3(2)
N(1)−Os(1)−N(3)	92.6(2)	N(3)−Os(1)−S(1)	87.6(2)
N(5)−Os(1)−N(3)	177.9(2)	N(4)−Os(1)−S(1)	89.4(3)
N(2)−Os(1)−N(4)	178.3(2)	C(49)−S(1)−Os(1)	111.8(5)
N(1)−Os(1)−N(4)	88.8(3)	C(50)−C(49)−S(1)	116.4(13)

which could not be separated. However, the analogous reaction with isoamyl nitrite generates the cationic [(TPP)Fe(NO)(HO-*i*-C_5H_{11})]$^+$ product in 78% isolated yield (eq 6). Presumably, adventitious protons (from glass surfaces or solvents) are involved in the formation of the isolated product.

$$[(TPP)Fe(THF)_2]^+ + i\text{-}C_5H_{11}ONO \rightarrow [(TPP)Fe(NO)(HO\text{-}i\text{-}C_5H_{11})]^+ \quad (6)$$

The nitrosyl alcohol product is air-sensitive in the solid state and more so in solution. The product is also thermally unstable, readily losing the nitrosyl ligand. The ν_{NO} of 1935 cm^{-1} (KBr) of the complex is similar to that of the known aqua complex [(TPP)Fe(NO)(H_2O)]ClO_4 reported by Scheidt and Hatano (1937 cm^{-1} (KBr))[41a] and other cationic iron nitrosyl complexes reported by Kadish.[41b] The ν_{OH} band was not observed.[42] The IR spectrum also reveals bands at 1106−1069 cm^{-1} due to uncoordinated perchlorate anion.[43] The molecular structure is shown in Figure 6.

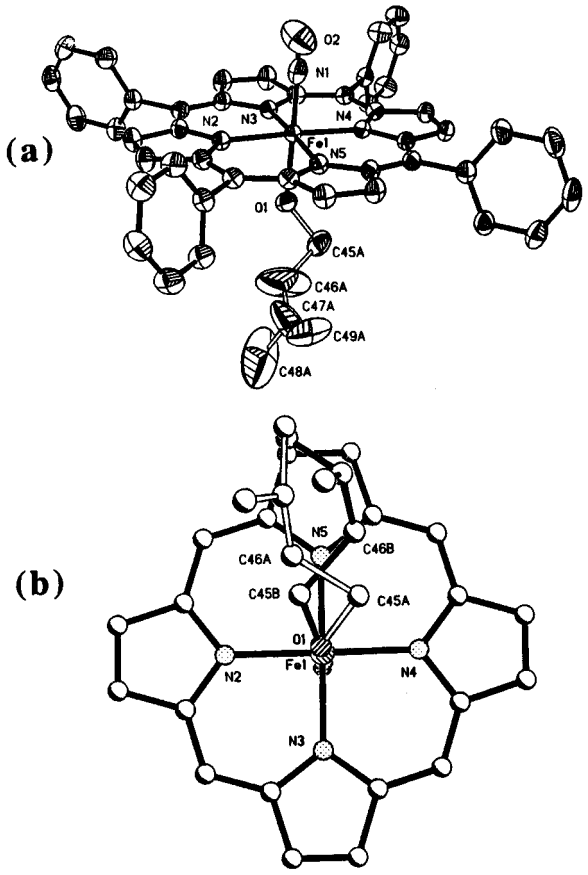

Figure 6. (a) Molecular structure of the [(TPP)Fe(NO)(*i*-$C_5H_{11}OH$)]$^+$ cation showing only one of the disordered O-*i*-C_5H_{11} groups for the sake of clarity. Hydrogen atoms have been omitted. (b) View along the axial O(1)−Fe(1) bond showing the orientation of the disordered alcohol ligand. The phenyl substituents on the porphyrin have been omitted.

Table 4. Selected Bond Lengths and Angles for [(TPP)Fe(NO)(HO-*i*-C_5H_{11})]ClO_4

Bond Lengths (Å)			
Fe(1)−N(1)	1.776(5)	Fe(1)−N(5)	2.016(3)
Fe(1)−N(2)	2.014(3)	N(1)−O(2)	0.925(6)
Fe(1)−N(3)	2.012(3)	Fe(1)−O(1)	2.063(3)
Fe(1)−N(4)	2.010(3)	O(1)−C(45A)	1.450(12)
Bond Angles (deg)			
Fe(1)−N(1)−O(2)	177.1(7)	N(4)−Fe(1)−O(1)	89.41(13)
N(1)−Fe(1)−O(1)	177.2(2)	N(3)−Fe(1)−O(1)	85.64(13)
N(1)−Fe(1)−N(4)	90.6(2)	N(2)−Fe(1)−O(1)	88.41(13)
N(1)−Fe(1)−N(3)	91.6(2)	N(5)−Fe(1)−O(1)	90.89(13)
N(1)−Fe(1)−N(2)	91.6(2)	Fe(1)−O(1)−C(45A)	127.8(6)
N(1)−Fe(1)−N(5)	91.9(2)	Fe(1)−O(1)−C(45B)	131.8(6)

Selected bond lengths and angles are collected in Table 4. The Fe−N−O linkage is linear (bond angle of 177.1(7)°). The

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(42) This is not unusual for metalloporphyrin complexes. For example, we do not see the ν_{OH} in the spectra of our related [(por)Ru(NO)(H_2O)]$^+$ complexes.[20b,38] The ν_{OH} bands for the related [(TPP)Fe(NO)(H_2O)]$^+$,[41a] [(TPP)Fe(H_2O)$_2$]$^+$,[42a] and [(TPP)Fe(EtOH)$_2$]$^+$ [42b] were also not reported: (a) Scheidt, W. R.; Cohen, I. A.; Kastner, M. E. *Biochemistry* **1979**, *18*, 3546. (b) Einstein, F. W. B.; Willis, A. C. *Inorg. Chem.* **1978**, *17*, 3040.
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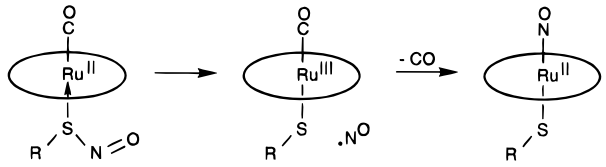
Scheme 1



Fe−N(O) and N−O bond lengths are 1.776(5) and 0.925(6) Å, respectively. The Fe atom is displaced from the four-nitrogen porphyrin plane by 0.05 Å toward the NO ligand. The Fe−O axial bond length is 2.063(3) Å and is longer than the axial Fe−O bond length in the related aqua cation $[(TPP)Fe(NO)(H_2O)]^+$ (2.001(5) Å, Fe−N−O = 174.4(10)°).[41a]

Discussion

As stated in the Introduction, heme plays an important role in the binding of NO and in the RSNO-induced activation of GC presumably by direct interaction with the heme iron. The unusual, yet clean, formal *trans* addition of RSNO and RONO to Ru and Os porphyrins thus raises intriguing questions about metalloporphyrin-catalyzed decompositions of RSNO and RONO. In the case of the Ru alkyl nitrite reaction, a short-lived intermediate was observed by IR spectroscopy (Figure 2) and assigned as the carbonyl alkoxide (por)Ru(CO)(OR). The higher ν_{CO} of 2006 cm^{-1} relative to that of the parent (por)Ru(CO) (ν_{CO} = 1934 cm^{-1}) is consistent with the increased oxidation state of Ru^{III} in the carbonyl alkoxide relative to Ru^{II} in (por)Ru(CO), resulting in diminished back-bonding to carbonyl. Similar intermediates of the form (por)Os(CO)X (X = thiolate, alkoxide) are also observed in the Os reactions (Figures 4 and 5). The Os six-coordinate carbonyl intermediates also have higher ν_{CO} bands relative to the starting (por)Os(CO), consistent with the increased oxidation state of Os^{III} in the carbonyl alkoxide/thiolate relative to Os^{II} in (por)Os(CO). Additional support for our Os^{III} formulation comes from a recent report by Gross, who isolated authentic (TMP)Os(CO)(Br) (TMP = tetramesitylporphyrin), which has a ν_{CO} of 1933 cm^{-1}, higher than that of the parent (por)Os(CO) at 1920 cm^{-1}.[44]

We thus propose that, in the case of Ru and Os porphyrins, the RSNO incoming group binds to the sixth coordination site via S-coordination.[45] Homolysis of the S−NO bond then liberates NO, which reacts with the (por)M(CO)(SR) intermediate to generate the final nitrosyl product (Scheme 1).

Analogous (but *anionic*) Ru carbonyl thiolate complexes of the form $[(por)Ru(CO)(SR)]^-$ have been generated by thiolate attack on (por)Ru(CO) or by deprotonation of (por)Ru(CO)(RSH).[46] Notably, the ν_{CO} of $[(OEP)Ru(CO)(SR)]^-$ is shifted 25 cm^{-1} to *lower* wavenumber relative to (por)Ru(CO).[46a] Returning to Scheme 1, however, we note that S-bound RSNO ligands have been proposed in Hg^{2+}-catalyzed RSNO decompositions.[47,48] However, N-bound RSNO ligands have been proposed in intermediate complexes of the form $[Fe(CN)_5\{N(O)SR\}]^{3-}$ obtained from reactions of nitroprusside with thiolate anions.[10,49] Since Ru forms strong Ru−NO linkages,[33] N-coordination of RSNO to the (por)Ru(CO) complex would be expected to result in (por)Ru(CO)(NO) formation and •SR release. We could not detect either •SR (or the disulfide) or the as-yet unknown (por)Ru(CO)(NO) complex in either the bench-scale reactions or the NMR tube reactions.[50] In fact, the results of IR monitoring of the Ru and Os reactions are consistent with our proposal in Scheme 1. We also propose a similar reaction pathway for the RONO reactions.[51]

The solid state structures of the Ru and Os nitrosyl thiolates represent the first crystal structures of the form (por)M(NO)(SR) that are potential models for the NO adducts of cytochrome P450 and NO synthase. Although a number of Ru thiolate structures are known,[53] only three Ru *alkane*thiolate structures were reported prior to our study, and they all involve *tertiary* alkyl groups bound to sulfur (Table 5). To the best of our knowledge, no Ru porphyrin thiolate structures were known prior to this work. The Ru−S bond length of 2.362 Å in (OEP)Ru(NO)(NACysMe-*S*) is within the 2.195−2.522 Å range for Ru−S bond lengths of thiolate complexes whose X-ray structures have been determined (Table 5).[64] However, the Ru−S−C bond angle of 107.1° is smaller than those seen for Ru *alkane*thiolates (in the 112−120° range for three complexes). The Os−S bond length of 2.209(3) Å in (TTP)Os(NO)(S-*i*-C_5H_{11}) is shorter than that for the only other structurally characterized Os porphyrin thiolate ($(TTP)Os(SC_6F_4H)_2$, 2.294(3) Å),[66] which contains *arene*thiolate ligands and is also shorter than the Os *alkane*thiolate bond length in $Os(SCH_2Ph)_2$-

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Table 5. Representative Structural Data for Monometallic Ru η^1-Thiolates[a,b]

	M−S, Å	M−S−C angle(s), deg	ref
$[(\eta^5\text{-}C_5H_5)Ru(PPh_2OMe)_2(SBu^t)]PF_6$	2.274(1)	120.1(1)	54
$[(\eta^5\text{-}C_5H_5)Ru(NO)(PPh_3)(SCMe_3)_2]BF_4$	2.386(2)	112.3(3)[c]	55
$(\eta^5\text{-}C_5Me_5)Ru(NO)(SCMe_3)_2$	2.371(1)	112.07(22)[c]	56
	2.401(1)	118.01(16)[c]	
$(\eta^6\text{-cymene})Ru(SC_6H_3Me_2)$	2.311(6)	114.2(8)	57
	2.263(7)	108.9(8)	
$[Ru(SC_6HMe_4)_3(MeCN)_2]PF_6$	2.195(8)	111.5(8)	58
	2.198(8)	111.9(8)	
	2.208(8)	110.7(8)	
cis-$(DMPE)_2Ru(Et)(SC_6H_4Me)$	2.522(3)	116.6(4)	59
trans-$(DMPE)_2Ru(SPh)_2$	2.472(1)	122.3(1)	60
	2.466(1)	123.8(1)	
cct-$Ru(SC_6H_4Me)_2(CO)_2(PPh_3)_2$	2.450(2)	113.6(2)	61
	2.470(2)	113.0(2)	
$Ru(SC_6F_5)_2(PPh_3)_2$	2.334(5)	102.9(5)	62
	2.333(4)	102.2(6)	
$Ru(pyS)(SC_5H_4N)(CO)_2(PPh_3)$	2.419(1)	109.6(2)	63

[a] Abbreviations: DMPE = 1,2-bis(dimethylphosphino)ethane; *cct* = *cis*,*cis*,*trans*.; pyS = η^2-SC_5H_4N. [b] References to other monometallic Ru thiolate structures are given in ref 64. [c] Obtained from deposited Supporting Information via the Internet.

Table 6. Structural Data for Monometallic Os η^1-Thiolato Complexes[a]

	Os−S, Å	Os−S−C angle(s), deg	ref
$Os(SCH_2Ph)_2[(BA)_2en]$	2.298(3)	107.8(4)	65
	2.315(3)	102.5(4)	
$(TTP)Os(SC_6F_4H)_2$	2.294(3)	107.8(3)	66
trans-Os(salen)$(SPh)_2$	2.298(2)	112.4(2)	67
	2.343(2)	112.1(2)	
mer-$OsCl(SC_6H_5)(N_2)(PMe_2Ph)_3$	2.507(1)	123.9(2)	68
ttt-$Os(SC_6F_5)_2(CO)_2(PEt_2Ph)_2$	2.477(1)	114.3(2)	69
$Os(pyS)(SC_5H_4N)(CO)_3$	2.424(3)	109.7(4)	70
$Os(SC_6F_5)_2(O_2CPh)(PMe_2Ph)_2$	2.329(1)	107.6(1)	71
	2.335(1)	107.0(1)	
$OsCl(SC_6F_5)_3(PMe_2Ph)$	2.196(1)	114.4(1)	71
	2.195(1)	113.4(1)	
	2.201(1)	112.9(1)	
$Os(SC_6F_4H)_4(PPh_3)_3$	2.414(5)	117.6(7)	72
	2.203(6)	119.6(7)	
	2.195(7)	117.8(8)	
	2.220(6)	111.3(8)	
$OsCl(SC_6F_5)_2(SC_6H_4\text{-}p\text{-}CF_3)(PMe_2Ph)$	2.207(2)	111.2(3)	72
	2.204(2)	110.5(3)	
	2.187(2)	113.9(3)	

[a] Abbreviations: *ttt* = *trans*,*trans*,*trans*; pyS = η^2-SC_5H_4N; $(BA)_2$en = bis(benzoylacetone) ethylenediimine dianion; salen = *N*,*N*′-ethylenebis(salicyclideneaminate).

$[(BA)_2en]$ (2.298(3), 2.315(3) Å).[65] The Os−S−C bond angle (111.8(5)°) of (TTP)Os(NO)(S-*i*-C_5H_{11}) is, however, within the range found for other Os thiolates whose solid state structures have been determined by X-ray diffraction (Table 6).

We could not obtain analogous nitrosyl thiolate complexes with iron porphyrins. NO forms adducts with NO synthase[73] and cytochrome P450.[74] However, some of these NO adducts are known to decompose to form the five-coordinate (por)Fe(NO).[75]

Table 7. Structural Data for Fe, Ru, and Os Nitrosyl Porphyrins[a]

	n in $\{M(NO)\}^n$	M−N−O angle, deg	ref
Iron			
$[(TPP)Fe(NO)(H_2O)]^+$	6	174.4(10)	41a
$[(TPP)Fe(NO)(HO\text{-}i\text{-}C_5H_{11})]^+$	6	177.1(7)	this work
$[(OEP)Fe(NO)]^+$	6	176.9(3)	41a
(TPP)Fe(NO)	7	149.2(6)	32
(TDCPP)Fe(NO)	7	138.8(9)	77
(OBTPP)Fe(NO)	7	146.4(24)	77
(TpivPP)Fe(NO)	7	143, 131	78
(TPP)Fe(NO)(1-MeIm)	7	142.1(6), 138.3(11)	79
(TPP)Fe(NO)(4-MeIm)	7	143.7(6)	80
(TPP)Fe(NO)(4-MeIm)·$CHCl_3$	7	138.5(11)	80
Ruthenium			
$[(OEP)Ru(NO)(H_2O)]^+$	6	171.0(7)	20b
(TPP)Ru(NO)(ONO)	6	180.0	38
(TTP)Ru(NO)(OMe)	6	180.0	35
(OEP)Ru(NO)(NACysMe-*S*)	6	174.8(6)	this work
(TTP)Ru(NO)(*p*-C_6H_4F)	6	152.2(5)[b]	81
Osmium			
(TTP)Os(NO)(S-*i*-C_5H_{11})	6	172.0(9)	this work

[a] Abbreviations: TDCPP = tetrakis(*o*/*o*′-difluorophenyl)porphyrinato dianion; OBTPP = octabromotetraphenylporphyrinato dianion; TpivPP = tetrakis(*o*-pivalamidophenyl)porphyrinato dianion. [b] The bent geometry may be influenced by crystal packing forces.[81]

Interestingly, the six-coordinate nitrosyl alcohol complex $[(TPP)Fe(NO)(HO\text{-}i\text{-}C_5H_{11})]^+$ was isolated from the reaction of ferric $[(TPP)Fe(THF)_2]^+$ with isoamyl nitrite. The linearity of the Fe−NO link is consistent with its formulation as a $\{Fe(NO)\}^6$ complex using the Enemark−Feltham notation.[76] Indeed, all three crystal structures reported in this study belong to the $\{M(NO)\}^6$ class and contain linear metal−NO linkages (Table 7). Conversely, $\{M(NO)\}^7$ compounds would be expected to contain bent M−N−O groups, as is borne out in Table 7.

Conclusion

Although RSNO and RONO are important in pharmacology and biochemistry, chemical information on their reactions with metalloporphyrins was lacking. We have shown for the first time that RSNO and RONO will react with Fe, Ru, and Os

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porphyrins to produce isolable five-coordinate (Fe only) or six-coordinate (Fe (RONO only), Ru, Os) nitrosyl derivatives. We have also reported the first crystal structures of the type (por)M-(NO)(SR), which are potential structural models for the NO adducts of cytochrome P450 and NO synthase. A related but distinct goal that now needs to be addressed is the study of the kinetics of the reactions of RSNO and RONO with metalloporphyrins.

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Note Added in Proof. As an addendum to Table 7, the solid state crystal structure of (TTP)Ru(NO)(NSO) was reported recently: Bohle, D. S.; Hung, C.-H.; Powell, A. K.; Smith, B. D.; Wocadlo, S. *Inorg. Chem.* **1997**, *36*, 1992.

Supporting Information Available: Additional structural diagrams and listings of crystal data, non-hydrogen atomic coordinates, anisotropic displacement parameters, bond lengths and angles, hydrogen coordinates and isotropic displacement parameters, torsion angles, and least-squares planes (39 pages). Ordering information is given on any current masthead page.

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