Synthesis, characterization, and molecular structures of nitrosyl nitrito complexes of osmium porphyrins: Disproportionation of nitric oxide in its reaction with Os(P)(CO) (P = porphyrinato dianion)

Felipe A. Leal, Ivan M. Lorkovic, Peter C. Ford, Jonghyuk Lee, Li Chen, Lindsey Torres, Masood A. Khan, and George B. Richter-Addo

Abstract: The Os(P)(NO)(ONO) compounds (P = TTP, TMP, OEP, TmTP; TTP = 5,10,15,20-tetra-*p*-tolylporphyrinato dianion, TMP = 5,10,15,20-tetramesitylporphyrinato dianion, OEP = octaethylporphyrinato dianion, TmTP = tetra(*m*-tolyl)porphyrinato dianion) have been prepared from the reaction of the precursor carbonyl complexes Os(P)(CO) with excess nitric oxide. Nitrous oxide was detected as a by-product of the reaction. The IR spectra of the Os(P)(NO)(ONO) compounds (as KBr pellets) reveal bands in the 1790–1804 cm⁻¹ range that are assigned to v_{NO} . The IR spectra also reveal two new bands for each complex in the 1495–1531 and 913–962 cm⁻¹ ranges indicative of O-bound nitrito ligands. The linearity of the bound NO groups and the O-binding of the *trans* nitrito ligands in the Os(P)(NO)(ONO) complexes are evident in the single-crystal X-ray crystal structures of the TTP and TMP derivatives. The kinetics of the reaction were studied by stopped-flow mixing techniques. Spectroscopic analysis of rapidly mixed solutions of Os(P)CO and NO in toluene showed a biphasic approach to the Os(P)(NO)(ONO) and N₂O products, owing to the starting material Os(P)CO scavenging CO formed during the reaction to give Os(P)(CO)₂ ($K_{CO} = 10^6 \text{ M}^{-1}$). The dicarbonyl was the only transient species observed. It is proposed that the rate-determining step of the reaction leading to Os(P)(NO)(ONO) is NO displacement of CO from Os(P)(CO) via initial formation of an unstable 19 electron Os(P)(NO)(CO) intermediate.

Key words: osmium, nitric oxide, X-ray, nitrosyl, porphyrin, kinetics.

Résumé : Les composés du type Os(P)(NO)(ONO), où P = TTP, TMP, OEP, TmTP; TTP= le dianion 5,10,15,20-tétra*p*-tolylporphyrinato, TMP = le dianion 5,10,15,20-tétramésitylporphyrinato, OEP = le dianion octaéthylporphyrinato, TmTP = le dianion tétra(m-tolyl)porphyrinato, ont été préparés à partir de la réaction des complexes carbonylés précurseurs OS(P)(CO) en présence d'un excès d'oxyde nitrique. On a détecté l'oxyde nitreux comme produit secondaire de la réaction. Les spectres IR des composés Os(P)(NO)(ONO) (sous forme de pastilles de KBr) révèlent des bandes dans la région de 1790–1804 cm⁻¹ que l'on attribue à la vibration v_{NO} Les spectres IR révèlent également, pour chaque complexe, deux nouvelles bandes dans les régions : 1495-1531 et 913-962 cm⁻¹ caractéristiques des ligands nitrito liés par l'oxygène. La linéarité des liens des groupes NO et le lien impliquant l'oxygène des ligands nitrito trans dans les complexes Os(P)(NO)(ONO) apparaissent clairement dans les structures des dérivés TTP et TMP déterminées par cristallographie de rayons X sur un monocristal. On a étudié la cinétique de la réaction par les techniques de mélange à flux stoppé. L'analyse spectroscopique des solutions OS(P)CO et de NO rapidement mélangées dans le toluène montrent une approche biphasique aux produits Os(P)(NO)(ONO) et N₂O à cause du produit de départ OS(P)CO qui piège le CO formé au cours de la réaction pour donner le $OS(P)(CO)_2$ ($K_{CO} = 10^6 \text{ M}^{-1}$). Le composé dicarbonylé est la seule espèce transitoire observée. On suggère que l'étape déterminante de la réaction conduisant au Os(P)(NO)(ONO) est le déplacement du CO par NO à partir du OS(P)(CO) via la formation initiale d'un intermédiaire instable Os(P)(NO)(CO) à 19 électrons.

Mots clés : osmium, oxyde nitrique, rayons X, nitrosyle, porphyrine, cinétique.

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F.A. Leal, I.M. Lorkovic, and P.C. Ford.¹ Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106, U.S.A.

J. Lee, L. Chen, L. Torres, M.A. Khan, and G.B. Richter-Addo.² Department of Chemistry and Biochemistry, University of Oklahoma, 620 Parrington Oval, Norman, Oklahoma 73019, U.S.A.

¹Corresponding author (e-mail: ford@chem.ucsb.edu).

²Corresponding author (e-mail: grichteraddo@ou.edu).

Introduction

Metalloporphyrin-induced NO \rightarrow N₂O conversions are very important biologically in the global nitrogen cycle (1). For example, nitric oxide reductase cytochrome P450nor from the fungus *Fusarium oxysporum* reduces NO to N₂O, and the enzyme contains heme at the active site (2, 3). The bacterial nitric oxide reductase from *Paracoccus denitrificans* also contains heme at the dinuclear active site and catalyzes the reduction of NO to N₂O (4, 5). The subject of biological NO reduction has been recently reviewed (1).

Heme-dependent NO oxidations are gaining widespread recognition in the chemistry of NO. For example, some flavohemoglobins have recently been described as NO dioxygenases (6, 7). Metal-assisted NO \rightarrow NO₂ conversions are also important in the biological and urban environment. In particular, knowledge of the efficiency of metal-assisted conversions of NO \rightarrow N_xO_y is an essential component in the design of catalytic converters for automobile engines (8). While the mechanisms of such conversions are not known with certainty, synthetic metal complexes that catalyze the formation of NO₂ (bound or free) from NO and vice versa, as well as the structures of metal-NO₂ coordination complexes, are of interest in this regard. In some instances, the addition of oxygen (or air) to the metal-NO precursor is necessary for the production of the metal-NO₂ complex. We recently demonstrated such a metal-NO to metal-NO₂ conversion using an iron nitrosyl porphyrin (9). Other metalloporphyrin-NO complexes of Co and Rh have been shown to behave similarly (10, 11).

There are many examples of non-heme transition metal complexes that promote NO disproportionation to give metal nitrite derivatives and N₂O (12). However, we have found that ferrous porphyrins do not promote NO disproportionation in the absence of oxygen; they react with NO to produce only mononitrosyl or weakly bound dinitrosyl complexes (13). The apparently contradictory results concerning the ability of iron porphyrins to promote the disproportionation of NO (in the presence or absence of trace air) are discussed in ref. 14. Iron porphyrin nitrite complexes containing the N-bound nitrite ligand are known, and their solid-state structures have been reviewed (15). We reported that ruthenium porphyrins react with NO in the absence of oxygen to produce the nitrosyl nitrito complexes Ru(P)(NO)(ONO) and N₂O (16-18), and we spectroscopically characterized a trans-dinitrosyl intermediate Ru(P)(NO)₂ during this NO disproportionation reaction (19, 20). The occurrence of NO disproportionation with ruthenium, but not with iron, led us to extend these studies to the osmium porphyrin congeners.

In this paper, we show that osmium porphyrins react with NO to give nitrosyl nitrito products with the release of N₂O. Solid-state molecular structures for two of these nitrosyl nitrito products have been obtained and, to the best of our knowledge, represent the first published osmium nitrito X-ray crystal structures to be reported. While the products are analogous to those found for the reaction of NO with similar ruthenium porphyrins Ru(P)(CO) (19, 20), unlike the ruthenium analogues, reactions of NO with Os(P)(CO) proceed without the generation of observable nitrosyl-containing intermediates. Instead, the CO released from reaction of NO

with Os(P)(CO) is scavenged by the remaining Os(P)(CO) to give the dicarbonyl complex $Os(P)(CO)_2$ in a "dead-end" equilibrium. The latter eventually is also converted to Os(P)(NO)(ONO).

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: benzene (Na), toluene (Na or CaH₂), hexane, chloroform, and cyclohexane (CaH₂).

Chemicals

The Os(P)(CO) compounds were prepared by literature methods (P = TTP, TMP, OEP, TmTP; TTP = 5,10,15,20tetra-*p*-tolylporphyrinato dianion, TMP = 5,10,15,20-tetramesitylporphyrinato dianion, OEP = octaethylporphyrinato dianion, TmTP = tetra(*m*-tolyl)porphyrinato dianion) (21). Os(OEP)(CO) was also purchased from Midcentury Chemicals. Chloroform-*d* (99.8%) was obtained from Cambridge Isotope Laboratories. Nitric oxide (98%, Matheson Gas) for the synthesis work was passed through KOH pellets and two cold traps (dry ice–acetone, -78° C) to remove higher nitrogen oxides. For experiments involving detection of evolved N₂O, NO was purified as described elsewhere (14).

Instrumentation

Infrared spectra were recorded on a Bio-Rad FT-155 FT-IR spectrometer. ¹H NMR spectra were obtained on Varian 300 MHz or 400 MHz spectrometers and the signals referenced to the residual signal of the solvent employed. All coupling constants are in Hz. FAB mass spectra were obtained on a VG-ZAB-E mass spectrometer.

Preparation of Os(TTP)(NO)(ONO)

A Schlenk flask was charged with Os(TTP)(CO) (0.055 g, 0.062 mmol) and benzene (30 mL). The mixture was stirred to generate an orange-red solution, and NO gas was then bubbled through the solution for ~15 min. The solvent was removed in vacuo, and the residue was redissolved in benzene (10 mL) and filtered through a neutral alumina column $(1.5 \times 15 \text{ cm})$. The red band was collected and dried in vacuo. The product was further purified by crystallization from a toluene-hexane mixture at -20°C to give Os(TTP)(NO)(ONO) (0.025 g, 0.027 mmol, 43% isolated yield). IR (KBr) (cm⁻¹): $v_{NO} = 1804$ (s), $v_{ONO} = 1528$ (m), 921 (m). ¹H NMR (CDCl₃) δ : 9.00 (s, 8H, *pyrrole*-H of TTP), 8.15 (d, *J* = 8 Hz, 4H, *o*-H of TTP), 8.05 (d, *J* = 8 Hz, 4H, o'-H of TTP), 7.56 (app t (overlapping d's), 8H, m/m'-H of TTP), 2.70 (s, 12H, CH₃ of TTP). Low-resolution FAB-MS m/z (%): 906 ([Os(TTP)(ONO)]⁺, 15%), 890 $([Os(TTP)(NO)]^+, 100\%), 860 ([Os(TTP)]^+, 18\%).$ This compound was prepared previously in low yield from the reaction of Os(TTP)(NO)(S-i-C₅H₁₁) with excess NO (22).

Preparation of Os(TMP)(NO)(ONO)

A Schlenk flask was charged with Os(TMP)(CO) (0.082 g, 0.082 mmol) and benzene (30 mL). The mixture was stirred to generate a dark orange-red solution, and NO gas was then bubbled through the solution for 30 min. During this time, the color of the reaction mixture turned bright red. The solvent was removed in vacuo, and the residue was redissolved in benzene (15 mL) and filtered through a neutral alumina column (2 \times 20 cm). The red band was collected, and the filtrate was dried in vacuo to give Os(TMP)(NO)(ONO) (0.077 g, 0.073 mmol, 90% isolated yield). IR (KBr) (cm⁻¹): $v_{NO} = 1799$ (s), $v_{ONO} = 1531$ (m), 919 (m). ¹H NMR (CDCl₃) δ : 8.77 (s, 8H, *pyrrole*-H of TMP), 7.29 (s, 4H, m-H of TMP), 7.26 (s, 4H, m'-H of TMP), 2.62 (s, 12H, *p*-CH₃ of TMP), 1.95 (s, 12H, *o*-CH₃ of TMP), 1.69 (s, 12H, o'-CH₃ of TMP). Low-resolution FAB-MS m/z (%): 1048 ([Os(TMP)(NO)(ONO)]⁺, 6%), 1019 $([Os(TMP)(ONO) + H]^+, 43\%), 1002 ([Os(TMP)(NO)]^+,$ 100%), 972 ([Os(TMP)]⁺, 13%).

The following two compounds were also prepared similarly.

Os(OEP)(NO)(ONO)

43% isolated yield. IR (KBr) (cm⁻¹): $v_{NO} = 1790$ (s), $v_{ONO} = 1495$ (m), 962 (s br (overlap with porphyrin band)). ¹H NMR (CDCl₃) & 10.41 (s, 4H, *meso*-H of OEP), 4.16 (q, J = 8 Hz, 16H, CH_2CH_3 of OEP), 2.00 (t, J = 8 Hz, 24H, CH_2CH_3 of OEP). This compound has similar spectral properties to a compound formulated as Os(OEP)(NO)₂ (23).

Os(TmTP)(NO)(ONO)

This compound was obtained in 95% yield (by ¹H NMR spectroscopy) when the reaction was performed in dry toluene or methylcyclohexane and in 25% yield (by ¹H NMR spectroscopy) when performed in CH₂Cl₂. The compound was further purified by chromatography over silica gel using a pentane–CH₂Cl₂ (2:1) solvent mixture. IR (KBr) (cm⁻¹): $v_{NO} = 1803$ (s), $v_{ONO} = 1528$ (m), 913 (m). IR (cyclohexane) (cm⁻¹): $v_{NO} = 1805$ (s), $v_{ONO} = 1540$ (m). ¹H NMR (CDCl₃) δ : 9.02 (s, 8H, *pyrrole*-H of TmTP), 8.10 (m, 4H, *o*-H of TmTP), 7.59–7.60 (m, 8H, *m/p*-H of TmTP), 2.66 (s, 6H, CH₃ of TmTP), 2.62 (s, 6H, CH₃ of TmTP).

Kinetics experiments

NO was plumbed via stainless steel lines through a stainless steel column of Ascarite (Thomas Scientific) to scrub out NO₂ and (or) N₂O₃. When desired, the N₂O impurity was removed by passage of NO through a cold (-78° C) activated silica column (6' × 1/4" i.d. stainless steel, Alltech). NO was quantified manometrically using known solubilities in toluene and cyclohexane (24) and transferred cryogenically to desired reaction flasks of known total volume and solution volume fitted with Teflon high vacuum stopcocks. Infrared solution spectra were recorded in amalgam-sealed cells with CaF₂ windows (ICL) on a Bio-Rad FTS-60 FT-IR instrument. Stopped-flow mixing experiments were performed on an Applied Photophysics SX17-MV instrument with custom made tonometers (20) for NO solution preparation and transfer to drive syringes. Flow IR experiments were performed with a home-built, manually actuated stopped-flow mixing apparatus utilizing gas tight syringes (Hamilton 5 mL) and PEEK tubing, valves, and fittings (Upchurch), connected after mixing to a standard amalgamsealed CaF₂ cell inserted into the FT-IR instrument. To avoid back-pressure-induced IR cell rupture, the stop syringe was disconnected and the output directed to a waste container. FT-IR spectra showing intermediate species in the reaction of Os(P)(CO) with NO were obtained by a single interferometric scan during constant flow of freshly mixed (aging time ~0.2 s) solutions through the cell.

CO binding equilibrium constant measurements

Carbon monoxide (Praxair, 99.5%) was added by gas-tight syringe to toluene solutions (~5 mL) of Os(OEP)(CO) and Os(TmTP)(CO) (~8 μ M) under Ar ($P_T = 760$ torr (1 torr = 133.322 Pa)) within special cuvette cells (~70 mL total volume) at 21 \pm 1°C. [CO] was calculated from the known solubility of CO in toluene (25) and the known volume of solution and headspace. Under these conditions the [CO] may be less than [Os] within the solution, but the total amount of CO within the closed system of the cell is always at least ten times greater than the amount of Os in the solution, and therefore [CO] may be considered to be constant, independent of the extent of reaction.

Structural determinations by X-ray crystallography

Crystal data were collected on a Siemens (Bruker) P4 diffractometer using monochromated Mo K α radiation ($\lambda = 0.71073$ Å).³ The data were corrected for Lorentz and polarization effects, and empirical absorption corrections based on ψ -scans were applied (26). The structures were solved by the heavy atom method using the SHELXTL 5.03 (Bruker) system and refined by full-matrix least squares on F^2 using all reflections (SHELXL-93). The thermal ellipsoids in Figs. 1 and 2 are drawn at the 35% probability level. Details of the crystal data and refinement are given in Table 1.

Os(TTP)(NO)(ONO)[•]toluene

A suitable crystal for structure determination was grown by recrystallization of the compound from toluene–hexane at -20° C. All the non-hydrogen atoms were refined anisotropically except the atoms (C25–C33) belonging to the disordered toluene molecules, which were refined isotropically. Hydrogen atoms were included in the refinement with idealized parameters; the hydrogen atoms for the disordered solvent molecules were not included.

Considerable difficulty was encountered during the refinement because of the disorder of the Os atom and the atoms belonging to the axial groups and the solvent molecules. The structure was solved initially in the non-centric space group Cc and gave very poor refinement with unreasonable N—O

³Supplementary data (drawings and tables of crystallographic data for Os(TTP)(NO)(ONO) and Os(TMP)(NO)(ONO)) may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically). CCDC 214514 and 214515 contain the supplementary data for this paper. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, U.K.; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

(a)



N1A

N24

and O-N-O bond lengths and several non-positive definite temperature factors. The structure was then solved and refined in the centric space group C2/c, where the molecule lies on the inversion center and only half of the molecule is unique. Thus, the axial NO and ONO groups are disordered over both sides of the porphyrin plane. The initial refinement used a model in which the Os atom was placed on a special position at the inversion center. This model gave elongated thermal ellipsoids for the Os atom, and the Os-N3 and Os-O2 distances were unreasonable. Finally, the Os atom was allowed to refine out of the porphyrin plane towards the NO ligand (0.241(3) Å out of the 24-atom mean porphyrin plane). In the final model, the Os atom and the NO and ONO groups are completely disordered over two sites. In addition to the disorder of the molecule, the crystal lattice contains two sites with partially disordered toluene solvent molecules. One of these toluene solvent sites is 50% populated, and the other site is also 50% populated; disorder at these sites results in the two sites having only 25% occupancy. The toluene solvent molecules were refined isotropically because of this disorder, and hydrogen atoms for these molecules were not included in the refinement. SHELXTL restraints (ISOR, DELU, SIMU, and DFIX) were needed to stabilize the refinement. The final values of R_1 =

Fig. 2. (*a*) Molecular structure of Os(TMP)(NO)(ONO). Hydrogen atoms have been omitted for clarity. Only one of the two disordered positions of the Os atom and the NO and ONO groups is shown; (*b*) View of the orientation of the nitrito ligand relative to the porphyrin skeleton. The porphyrin mesityl substituents and the *trans* NO ligand have been omitted for clarity.

(a)





0.0583 for 3651 "observed reflections" $[I > 2\sigma(I)]$ and $wR_2 = 0.1665$ for all reflections (4421 unique data) were obtained.

Os(TMP)(NO)(ONO)·3(benzene)

Suitable crystals for X-ray crystallography were grown by slow evaporation of a benzene solution of the compound at room temperature under inert atmosphere. All the nonhydrogen atoms were refined anisotropically, and the hydrogen atoms were included in the refinement with idealized parameters. The asymmetric unit contains one molecule of Os(TMP)(NO)(ONO) and three molecules of benzene. The Os atom and the NO and ONO groups are disordered over two sites along the axial direction. In addition, one of the benzene solvent molecules is disordered over two sites. Attempts to refine the two fragments did not yield a stable refinement. Thus, the geometry of the two fragments was idealized in the final cycles of refinement, and the thermal parameters were fixed at the values obtained from the earlier refinement cycles. The final values of $R_1 = 0.0374$ for 8660 "observed reflections" $[I > 2\sigma(I)]$ and $wR_2 = 0.1036$ for all reflections (10 961 unique data) were obtained.

Os(OEP)(NO)(ONO)

Both laboratories have independently crystallized this compound. Although we have not been able to grow high-

Table 1. Crystal data and structure refinement.

Compound	Os(TTP)(NO)(ONO)·toluene	Os(TMP)(NO)(ONO)·3(C ₆ H ₆)		
Formula (fw)	C ₅₅ H ₄₄ N ₆ O ₃ Os (1027.16)	C ₇₄ H ₇₀ N ₆ O ₃ Os (1281.56)		
<i>T</i> (K)	153(2)	173(2)		
Crystal system	Monoclinic	Triclinic		
Space group	C2/c	$P\overline{1}$		
Unit cell dimensions				
<i>a</i> (Å), α (°)	26.861(5), 90	12.1823(12), 81.362(9)		
<i>b</i> (Å), β (°)	9.947(2), 119.19(3)	13.031(2), 80.014(10)		
<i>c</i> (Å), γ (°)	21.933(4), 90	20.732(3), 76.857(10)		
V (Å ³), Z	5116.1(18), 4	3135.2(7), 2		
$D_{\text{calcd}} \text{ (g cm}^{-3})$	1.334	1.358		
Absorption coefficient (mm ⁻¹)	2.539	2.087		
<i>F</i> (000)	2064	1312		
Crystal size (mm)	0.48 imes 0.36 imes 0.28	$0.38 \times 0.36 \times 0.26$		
θ range for data collection (°)	2.13-24.99	1.80-25.00		
Index ranges	$0 \le h \le 31, \ 0 \le k \le 11, \ -26 \le l \le 22$	$-13 \le h \le 14, -14 \le k \le 15, -24 \le l \le 24$		
Reflections collected	4522	11 526		
Independent reflections	4421 ($R_{\rm int} = 0.0649$)	10 966 ($R_{\rm int} = 0.0337$)		
Absorption correction	Empirical	Semi-empirical		
Max. and min. transmission	0.8876 and 0.5998	0.4872 and 0.3951		
Data/restraints/parameters	4421/14/327	10 961/6/841		
Goodness-of-fit on F^2	1.172	1.068		
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0583, wR_2 = 0.1553$	$R_1 = 0.0374, wR_2 = 0.0858$		
R indices (all data)	$R_1 = 0.0732, wR_2 = 0.1665$	$R_1 = 0.0568, wR_2 = 0.1036$		
Largest diff. peak and hole (e $Å^{-3}$)	1.573 and -0.706	0.794 and -1.357		

quality, good-sized crystals, the results of separate preliminary X-ray crystallographic analyses (by both laboratories) on the crystals obtained to date unambiguously confirm the nitrosyl nitrito Os(OEP)(NO)(ONO) formulation.

Results and discussion

We reported that the Ru(P)(CO) compounds (P = OEP, TPP, TmTP) react with NO in solution to give the nitrosyl nitrito complexes Ru(P)(NO)(ONO) and N₂O as the final products (16, 17, 19, 20). Using similar methodologies, we have prepared the nitrosyl nitrito complexes of osmium porphyrins. Thus, the reaction of Os(TTP)(CO) with NO in benzene at ambient temperature for ~15 min gives, after workup, the nitrosyl nitrito product Os(TTP)(NO)(ONO) in 43% isolated yield. The product is soluble in dichloromethane, benzene, and toluene, but is insoluble in hexane. The IR spectrum of Os(TTP)(NO)(ONO) (as a KBr pellet) reveals a band at 1804 cm^{-1} assigned to $\upsilon_{NO}.$ This υ_{NO} band is of higher frequency than the corresponding bands for the alkoxide complex $Os(TTP)(NO)(O-i-C_5H_{11})$ (1770 cm⁻¹) (22), the thiolate derivative $Os(TTP)(NO)(S-i-C_5H_{11})$ (1760 cm^{-1}) (22), and the organometallic compound Os(TTP)(NO)Me (1732 cm⁻¹) (27). In addition, the IR spectrum indicates new bands at 1528 and 921 cm⁻¹ due to the O-bound nitrito ligand (28).

The ¹H NMR spectrum of Os(TTP)(NO)(ONO) (in CDCl₃) reveals peaks due to the pyrrole protons of the porphyrin macrocycle (at δ 9.00) and the tolyl substituents. The inequivalence of the *ortho* protons of the tolyl substituents suggests restricted rotation of the tolyl groups in this unsymmetrical Os(P)(NO)X compound; such a feature of restricted rotation is not uncommon for *p*-substituted tetraphenyl-

porphyrin complexes of the form M(P)(X)(Y) (29, 30). The FAB mass spectrum of Os(TTP)(NO)(ONO) reveals peaks due to loss of the NO and (or) ONO ligands.

We were also able to prepare other nitrosyl nitrito complexes of the type Os(P)(NO)(ONO), where P = TMP, OEP, and TmTP. The IR spectra of the complexes (as KBr pellets) reveal their nitrosyl v_{NO} bands at 1803 cm⁻¹ (TmTP), 1799 cm⁻¹ (TMP), and 1790 cm⁻¹ (OEP), reflecting the increasing electron donor properties of the porphyrin macrocycles along the series TTP \cong TmTP < TMP < OEP, as expected. The TMP, OEP, and TmTP derivatives also show medium intensity bands assignable to nitrito v_{N-O} . The N₂O gaseous by-product formed during the reaction was identified by IR spectroscopy as described previously (19).

Solid-state molecular structures

As mentioned in the Introduction, no X-ray crystal structures of osmium nitrito complexes had been reported prior to our study. Interestingly, there is only a single report of an osmium nitro (i.e., η^1 -N bound) structure in the literature, namely that for Os(H₂L)(PPh₃)₂(CO)(η^1 -NO₂)·H₂O (L = 3-ethyliminio-5-methyl-2-oxidophenyl-*C*¹,*O*) (31), although some bridging nitro moieties [Os-N(O)O-Os] have been characterized by crystallography (32–34).

We were successful in obtaining suitable crystals of two of the Os(P)(NO)(ONO) compounds for single-crystal X-ray diffraction studies. The solid-state molecular structure of Os(TTP)(NO)(ONO) is shown in Fig. 1*a*, and the axial nitrito ligand conformation is shown in Fig. 1*b*. As is evident in Fig. 1, the ONO group is bound to the Os center through an O-atom, and the ONO group essentially bisects adjacent porphyrin nitrogen atoms, with an N2-Os-O2-N4 torsion angle of 33° (Fig. 1*b*). The molecular structure of the related



Fig. 3. Structural data for Os(TTP)(NO)(ONO) and Os(TMP)(NO)(ONO). Selected bond lengths and angles are shown in the top sketches. Perpendicular atom displacements from the 24-atom porphyrin planes (in 0.01 Å units) are shown in the bottom sketches.

Os(TMP)(NO)(ONO) is shown in Fig. 2. In this compound, the nitrito ligand is also bound to osmium through an Oatom, and the ONO ligand essentially bisects adjacent porphyrin nitrogens, with an N1-Os-O1-N6 torsion angle of 46°. Selected bond lengths and angles for both compounds and atom displacements from the 24-atom mean porphyrin planes are displayed in Fig. 3.

There are several features to note from these solid-state structures. First, the nitrosyl Os-NO groups are essentially linear. Second, the Os atoms are displaced from the 24-atom mean porphyrin plane *towards* the axial NO ligand; 0.24 Å for the TTP compound and 0.22 Å (or 0.15 Å for the second disordered component) for the TMP compound. Third, the bond lengths within the nitrito ligand are consistent with the Os-O-N=O formulation; thus, the O-N bond lengths are longer than the nitrito N=O bond lengths. Surprisingly, this is not always the case for metal nitrito crystallographic data. Selected structural data for M(NO)(ONO)-containing complexes reported to date are collected in Table 2. However, there is little consistency in the reported bond lengths involving the ONO ligand, and this may be partly because of the fact that many of these structures suffer from ligand disorder problems.

Proposed reaction pathway for the formation of nitrosyl nitrito species

UV-vis spectroscopic monitoring of the reaction of a dilute solution of Os(OEP)(CO) in toluene with NO (Fig. 4, top) reveals an apparent clean conversion of Os(OEP)(CO) to Os(OEP)(NO)(ONO). Stopped-flow experiments monitored at several single-wavelengths suggest that the reaction is biphasic, involving the formation of a transient species with spectral features similar but not identical to that of Os(OEP)(CO) (Fig. 4, bottom and inset). Within a few seconds, this intermediate spectrum gives way to that of the final Os(OEP)(NO)(ONO) product. Isosbestic points for the slower and faster processes are observed at 536 and 553 nm and therefore the faster and slower processes may be individually followed at these monitoring wavelengths. Under these conditions, the reactions appeared to be first order with the respective rate constants $k_{obs}(536) = 7 \pm 1 \text{ s}^{-1}$ (fast) and $k_{\rm obs}(553) = 0.7 \pm 0.1 \text{ s}^{-1}$ (slow). Analogous UV–vis spectral features are observed for the TmTP derivative as well.

To gain further insight into these processes, stopped-flow mixing experiments coupled with FT-IR spectroscopic detection were performed on the more soluble TmTP and OEP derivatives. The FT-IR difference spectrum of the solution

Table 2. Selected structural data for metal nitrosyl nitrito complexes.

		M—ONO	MO—NO	MON—O	M-O-NO	MO-N-O	
Compound	cis–trans ^a	(Å)	(Å)	(Å)	(°)	(°)	Reference
CpCr(NO) ₂ (ONO)	cis	1.982(4)	1.292(8)	1.182(9)	125(1)	115(2)	39
$[Ni(NO)(ONO)dppe]_2^b$	cis	2.123(12)	1.097(14)	1.192(13)	109.0(12)	127.4(17)	40
[Fe(L)(NO)(ONO)(NO ₂)]ClO ₄ ^c	cis	1.914(3)	1.322(5)	1.216(6)	125.1(3)	116.3(4)	41
		[1.935(3)]	[1.305(5)]	[1.213(6)]	[125.7(3)]	[116.1(4)]	
Cr(py) ₃ (NO)(ONO) ₂ ·py	cis	1.96(1)	1.34(1)	1.13(1)	115.0(7)	112(1)	42
$[Ru(NO)(ONO)(2,2'-bpy)_2](PF_6)_2$	cis	2.030(8)	1.24(1)	1.17(1)	125.6^{d}	118(1)	43
$[Ru(NO)(ONO)(2,2'-bpy)(py)_2](PF_6)_2$	cis	2.033(4)	1.324(6)	1.227(7)	124.0^{d}	116.3(6)	43
$Mn(NO)_2(ONO)(PEt_3)_2$	cis	2.08	1.19	е	123	118	44
$Ru(sal_2en)(NO)(ONO)^f$	trans	2.011 avg.	е	е	е	116.5 avg.	37
[Mn(Pc)(NO)(ONO)](PNP) ^g	trans	1.953(8)	1.189(7)	1.165(7)	117.9(6)	108.2(8)	35
[Fe(TpivPP)(NO)(ONO)] ^{-h}	trans	2.080(8)	1.188(14)	1.28(2)	124.1(8)	112.2(14)	36
Ru(TPP)(NO)(ONO) ⁱ	trans	2.00(2)	0.94(5)	1.33(4)	137(3)	109(5)	16
Ru(TPP)(NO)(ONO) ⁱ	trans	1.90(2)	1.16(2)	1.23(2)	137.3(18)	108.0(30)	17
Ru(OEP)(NO)(ONO)	trans	1.984(6)	1.214(10)	1.188(9)	122.0(6)	117.3(9)	17
Ru(TTP)(NO)(ONO) ^{j,k}	trans	1.998(6)	1.148(18)	1.126(25)	124.0(11)	110.9(20)	38
			[1.136(35)]	[1.447(39)]	[128.0(18)]	[92.2(24)]	
Os(TTP)(NO)(ONO) ⁱ	trans	2.000(6)	1.296(11)	1.188(12)	123.2(7)	113.8(11)	This work
Os(TMP)(NO)(ONO) ⁱ	trans	2.020(4)	1.240(8)	1.179(8)	122.2(4)	115.1(7)	This work
		[1.996(4)]	[1.258(7)]	[1.154(8)]	[121.6(4)]	[113.4(6)]	

^aCis or trans with respect to NO and ONO.

 b dppe = Ph₂PCH₂CH₂PPh₂.

^cTwo molecules in the unit cell. The values for the second molecule are in brackets. L = 1,4,7-triazacyclononane.

^dData obtained from the Cambridge Structural Database.

^eMetrical data not reported.

 $f_{sal_2en} = N, N'$ -ethylenebis(salicylideneiminato). There are two molecules in the unit cell.

 $^{g}PNP = (Ph_{3}P)_{2}N^{+}.$

 h TpivPP = $\alpha, \alpha, \alpha, \alpha, \alpha$ -tetrakis(*o*-pivalamidophenyl)porphyrinato dianion. The ONO group is present as a linkage isomer together with the N-bound NO₂ group in the same molecule.

ⁱThe axial NO and ONO ligands are disordered over the two porphyrin faces.

The ONO ligand is disordered. The values for the second disordered component are in brackets.

^kTwo molecules in the unit cell, and only the values for molecule A are shown.

obtained from the reaction of Os(TmTP)(CO) in cyclohexane with NO (Fig. 5, top) revealed, in addition to Os(TmTP)(CO) (v_{CO} 1924 cm⁻¹) and the final product Os(TmTP)(NO)(ONO) (v_{NO} 1805 cm⁻¹; v_{ONO} 1540 cm⁻¹), a new species displaying a strong band at 1974 cm⁻¹.

Since the independent reaction of Os(TmTP)(CO) with added CO gave a new species displaying a v_{CO} band at 1974 cm⁻¹ twice as intense as that of Os(TmTP)(CO)(Fig. 5, bottom), we assign this band to the *trans* dicarbonyl complex $Os(TmTP)(CO)_2$. Therefore, its appearance as a transient in the reaction of NO with Os(TmTP)(CO) can be attributed to the Os(TmTP)(CO) scavenging the CO released during the reaction.

Formation of the dicarbonyl complexes $Os(P)(CO)_2$ (eq. [1]) was studied independently in toluene by probing optical spectrum changes upon addition of CO to toluene solutions of Os(P)(CO) (e.g., Fig. 6). In this manner the equilibrium constants $K_2 = 0.9 \pm 0.2 \times 10^6$ and $1.0 \pm 0.2 \times 10^6$ M⁻¹ were determined for P = TmTP and OEP, respectively. The latter value is ~10² larger than that observed for the corresponding Ru(OEP)(CO) complex $(1.1 \times 10^4 \text{ M}^{-1})$ (20).

[1]
$$Os(P)(CO) + CO \leftrightarrow Os(P)(CO)_2$$

The high affinity of Os(P)(CO) for CO explains the detection of $Os(P)(CO)_2$ as a transient in the stopped-flow experi-

ment described above. No other species with distinctive IR spectral signatures, such as expected for Os–nitrosyl intermediates, were detected during the stopped-flow study of the reaction of Os(P)(CO) with NO. This is in sharp contrast to the analogous reaction of Ru(P)(CO) with NO where the dinitrosyl complex Ru(P)(NO)₂ was a spectroscopically observable intermediate (20). Given that under the reaction conditions [NO] is always much greater than [CO], detecting Os(P)(CO)₂ as the only transient suggests that K_2 for CO binding to Os(P)(CO) is at least four orders of magnitude larger than the equilibrium constant for analogous binding of NO.

Scheme 1 is a proposed explanation for these kinetics and spectral observations during the formation of Os(P)(NO)(ONO) from Os(P)(CO) and NO. This is based largely on the behavior of the ruthenium analogues for which the dinitrosyl intermediate $Ru(P)(NO)_2$ was observed (19, 20). The initial step is very likely the reversible and endergonic formation of the 19-electron complex Os(P)(CO)(NO). Upon rate-limiting CO dissociation from Os(P)(CO)(NO), a rapid sequence of steps would lead to the disproportionation products. However, CO is also a product, and it will be rapidly scavenged by Os(P)(CO) to give the much less reactive $Os(P)(CO)_2$ in a dead-end equilibrium. Thus, the reaction slows, owing to the lower effective concentration of Os(P)(CO). Since no other transient species

Fig. 4. *Top*: UV–vis spectra of the reactant Os(OEP)(CO) in toluene and the product of its reaction with nitric oxide, Os(OEP)(NO)(ONO). *Bottom*: Spectral changes upon stoppedflow mixing of a solution of Os(OEP)(CO) (10 μ M in toluene after mix) with nitric oxide (5 mM after mix). The stacked plot shows no obvious intermediate, but single wavelength observation shows evidence for a fast (7 s⁻¹) and a slow (0.7 s⁻¹) process in this reaction. However, the two stages in the kinetics suggest the formation of an intermediate in solution whose spectrum is very similar to that of the starting solution.



Scheme 1.



Fig. 5. Top: Difference FT-IR spectrum of the solution obtained by mixing solutions of Os(TmTP)(CO) (~100 µM in cyclohexane after mix) with NO (~4 mM in cyclohexane after mix). The difference spectra shown are the result of subtracting the spectrum of the final product solution. Therefore, the υ_{NO} at 1805 cm^{-1} and v_{ONO} at 1540 cm⁻¹ for the product Os(TmTP)(NO)(ONO) are seen as negative peaks. The only observable new species in this reaction is the dicarbonyl Os(TmTP)(CO)₂ identified by its peak at 1974 cm⁻¹ (see below). The peak marked with an asterisk is a cyclohexane subtraction artifact and that marked "x" is suspended insoluble Os(TmPP)(CO). Bottom: Difference infrared spectrum of Os(TmTP)(CO)₂ in cyclohexane after CO addition to a solution of Os(TmTP)(CO), minus the spectrum observed prior to CO addition. The new species shows a single carbonyl band at 1974 cm⁻¹ that is twice as intense as that for the monocarbonyl (at 1924 cm⁻¹), consistent with a *trans*-dicarbonyl structure.



were observed in the stopped-flow IR experiments, we conclude that likely intermediates along the productive pathway — for example, the dinitrosyl $Os(P)(NO)_2$ — are too reactive to build to detectable steady-state concentrations.

This scheme would explain the observation of the twostage kinetics observed under a large excess of NO. Initially all the osmium carbonyl is in the monocarbonyl form, and the reaction proceeds rapidly. Since the fast reaction was monitored near the $Os(P)(CO)-Os(P)(CO)_2$ isosbestic point (Fig. 6), this will show (pseudo) first order kinetics for the **Fig. 6.** Measurement of the equilibrium constant for the reaction of CO with Os(OEP)(CO) in toluene. The inset shows a Lineweaver–Burke fit for the spectral change induced by addition of CO aliquots to a dry toluene solution of Os(OEP)(CO) (~10 μ M). The total amount of CO (most of which is contained in the headspace but in equilibrium with that in solution) available for the equilibrium reaction is much greater than the total amount of Os in the solution. Thus, [CO] in solution can be approximated as being constant, although it is much lower than [Os]. The measured equilibrium constant is $1.0 \pm 0.2 \times 10^6$ M⁻¹.



absorbance changes due to reaction along the productive pathway to give Os(P)(NO)(ONO) (reaction of Os(P)(CO) with the released CO is not observed owing to the isosbestic behavior at that wavelength). Once most of the remaining osmium carbonyl is sequestered as the dicarbonyl, further reaction will be slower, owing to the low steady-state concentration of the monocarbonyl. Consistent with this interpretation is the qualitative observation that the overall reaction is dramatically slowed in the presence of excess added CO. The slow second stage observed in the absence of added CO also appeared to follow first order kinetics; however, this may result from a fortuitous combination of conditions, since the continued production of CO should make the reaction auto-inhibitory.

Conclusion

We have successfully prepared several nitrosyl nitrito complexes of the form Os(P)(NO)(ONO) from the reaction of the precursor carbonyl complexes Os(P)(CO) with nitric oxide. Single-crystal X-ray crystallographic studies of two of these compounds confirm the O-binding modes of the nitrito ligands. To the best of our knowledge, these are the first X-ray crystal structures of osmium nitrito moieties to be reported.

Results from stopped-flow kinetics studies of the reactions suggest a mechanism in which initial adduct formation between Os(P)(CO) and NO is followed by a rate-determining replacement of CO by a second NO molecule. Subsequent reaction with more NO leads to an effective NO disproportionation to give the final nitrosyl nitrito product Os(P)(NO)(ONO) and nitrous oxide. The behavior of the osmium complexes is in marked contrast to the failure of Fe(P)(NO) analogs to promote such disproportionation in rigorously dried and deaerated solvents (14). A greater parallel can be drawn to the Ru(P)(CO) analogues (20); however, the likely osmium nitrosyl intermediates suggested by this analogy are apparently too reactive to build to detectable concentrations.

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