

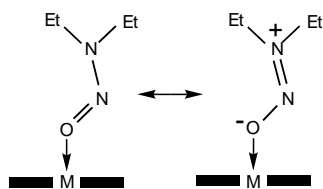
RECENT RESEARCH RESULTS

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Portions of this work have been described in a recent *Acc. Chem. Res.* article [1].

1 Metalloporphyrin Nitrosamine Complexes: We have successfully prepared the first isolable metalloporphyrin nitrosamine complexes of Fe, Ru, and Os [2]. To date, these are the only nitrosamine complexes of heme models to be reported. We have shown, by IR spectroscopy and X-ray crystallography, that the O-binding nature of Et₂NNO (Fig. 1) is general for (i) high-spin ferric porphyrins of the form [(por)Fe(ONNEt₂)₂]⁺, and (ii) diamagnetic ruthenium and osmium porphyrins of the form (por)M(CO)(ONNEt₂) and [(por)M(NO)(ONNEt₂)]⁺. We also prepared the *thionitrosamine* complex [(TPP)Fe(SNNMe₂)₂]ClO₄. The IR spectrum (KBr) of this complex shows bands at 1120 and 766 cm⁻¹ assigned to ν_{NN} and ν_{NS} , respectively, of the bound dimethylthionitrosamine (consistent with S-binding, and is consistent with a contribution of the dipolar ⁻S-N=N⁺Me₂ form (similar to that seen in the nitrosamine shown in Fig. 1).

Figure 1



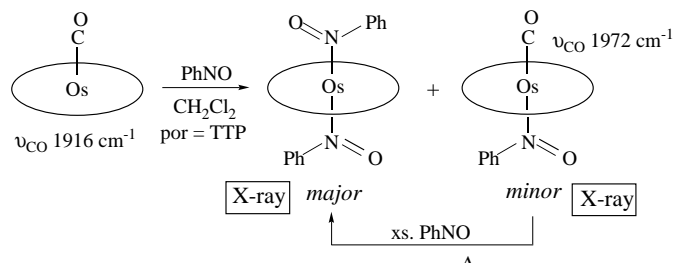
Reaction of (por)Os(CO)(ONNEt₂) (por = OEP) with the nitrosonium cation NO⁺ gives [(por)Os(NO)(ONNEt₂)]⁺. The observed *smaller* | $\nu_{\text{NO}} - \nu_{\text{NN}}$ | value of 44 cm⁻¹ for the bound nitrosamine in [(OEP)Os(NO)(ONNEt₂)]⁺ (ν_{NO} 1241 cm⁻¹, ν_{NN} 1197 cm⁻¹) compared with the corresponding value of 72 cm⁻¹ for the parent isoelectronic (OEP)Os(CO)(ONNEt₂) analogue is

suggestive of an increased contribution of the Et₂N⁺=NO⁻ resonance form in the cationic product (Fig. 1). Indeed, the | $\nu_{\text{NO}} - \nu_{\text{NN}}$ | value is negligible in the case of [(TPP)Fe(ONNEt₂)₂]⁺ ($\nu_{\text{NO}} \approx \nu_{\text{NN}} = 1270$ cm⁻¹), whose X-ray structure is known and is suggestive of a large Et₂N⁺=NO⁻ dipolar contribution. The crystal structure of (TTP)Os(CO)(ONNEt₂) confirms the η^1 -O binding mode.

The syntheses of these complexes are of fundamental importance because (i) these were the first metalloporphyrin nitrosamine complexes to be isolated, and (ii) the X-ray structural studies have provided us with information on how nitrosamine groups could bind to ferric heme centers.

2 Metalloporphyrin Nitrosoarene Complexes:[3] Nitrosoarenes (ArNO; Ar = Ph, *o*-tol) add to (por)Os(CO) (por = TPP, TTP, OEP, TMP; TTP = tetratolylporphyrinato dianion; TMP = tetramesitylporphyrinato dianion) to generate N-bound complexes. When (TTP)Os(CO) is reacted with 1 equiv. of PhNO in CH₂Cl₂, a 1:3 mixture of (TTP)Os(CO)(PhNO) and (TTP)Os(PhNO)₂ is generated (Fig. 2). Interestingly, the ν_{CO} of (TTP)Os(CO)(PhNO) is 56 cm⁻¹ *higher* in energy than that of (TTP)Os(CO). This observation is consistent with PhNO acting as a π -acid ligand

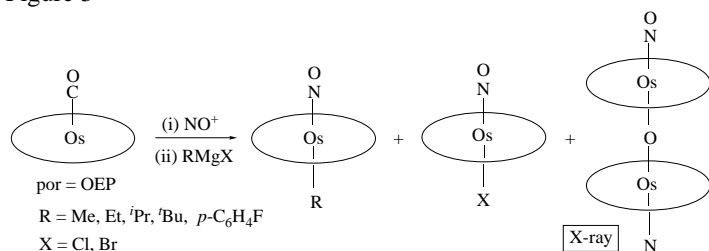
Figure 2



towards the "(TTP)Os(CO)" fragment, making less electron density available for Os^{II}-CO back-donation, thereby raising ν_{CO} (in general, binding of Lewis bases decreases ν_{CO}). X-ray structures of five of these (por)Os(ArNO)-containing complexes reveal the η^1 -N binding mode, and suggest that the bound ArNO ligands orient themselves in a manner that maximizes their orbital overlap with the (por)M HOMO (d_{xz}, d_{yz}) orbitals.

3 Organoosmium Nitrosyl Porphyrins:[4] The sequential reaction of (OEP)Os(CO) with NOPF₆

Figure 3



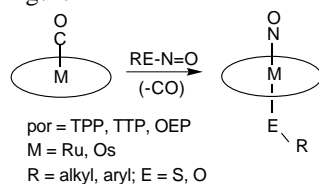
followed by RMgX gave variable isolated yields of the (OEP)Os(NO)R (5–44%), (OEP)Os(R)₂ (1–10%; not shown), (OEP)Os(NO)X (14–19%), and [(OEP)Os(NO)]₂(μ–O) (up to 24%) compounds depending on the reaction conditions and the nature of R and X (Fig. 3). The organometallic (OEP)Os(NO)R compounds are convenient precursors for the study of insertion reactions into the Os–R bonds. Unlike other metalloporphyrin μ-oxo dimers, the bridging oxo ligand in [(OEP)Os(NO)]₂(μ–O) is fairly unreactive towards acid, and this is attributed to the presence of two axial/trans NO ligands that withdraw electron density from the μ–O ligand. The solid-state structures of [(OEP)Os(NO)]₂(μ–O) and the related thionitrosyl (OEP)Os(NS)Cl and (OEP)Os(NS)Me were determined by single-crystal X-ray diffraction.

4 RSNO/RONO Chemistry:[5-10] We have synthesized Ru and Os compounds of the form

(por)M(NO)(SR) by the unusual formal *trans* additions of thionitrites (RSNO) to their carbonyl precursors

(e.g., Figs. 4 and 5). The formal *trans* addition of RSNO and RONO was unprecedented in chemistry and biochemistry. We are also pursuing research into the metal-assisted transformations of isolable RSNO compounds (an X-ray structure of a typical example of a heteroatom-containing RSNO is shown in Fig. 5).

Figure 4



The reaction of the ferrous complex (TPP)Fe(THF)₂ with *S*-nitroso-*N*-acetyl-L-cysteine methyl ester results in the formation of the known five-coordinate (TPP)Fe(NO) complex in very high isolated yield. On the other hand, the reaction of ferric [(TPP)Fe(THF)₂]⁺ with isoamyl nitrite results in the formation of the nitrosyl alcohol complex [(TPP)Fe(NO)(HO-*i*-C₅H₁₁)]⁺ (X-ray structure obtained).

Figure 5

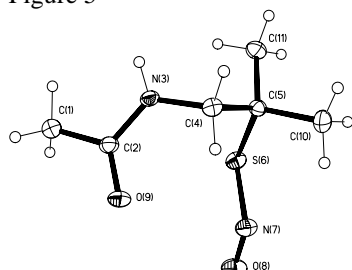
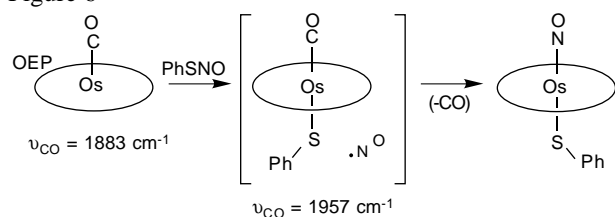


Figure 6

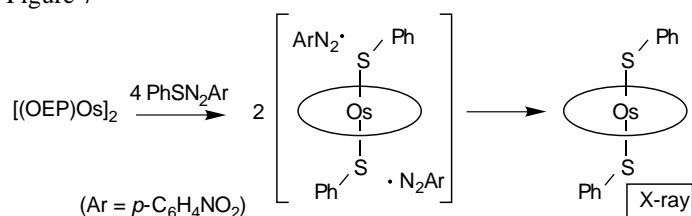


IR spectroscopic monitoring of the reaction of (OEP)Os(CO) with PhSNO reveals the formation of an intermediate complex (OEP)Os(CO)(SPh) (Fig. 6). The higher ν_{CO} of this intermediate compared to (OEP)Os(CO) is consistent with moving from the Os^{II} oxidation state in the precursor (OEP)Os(CO) to the Os^{III} oxidation state in the (OEP)Os(CO)(SPh) intermediate. The final nitrosyl (OEP)Os(NO)(SPh) product results from carbonyl replacement in (OEP)Os(CO)(SPh) by the *in situ*-generated NO radical. A similar reaction occurs with alkyl nitrites (RONO) to give (OEP)Os(NO)(OR).

To further examine the RSNO (PhSNO) addition reaction, we employed the valence

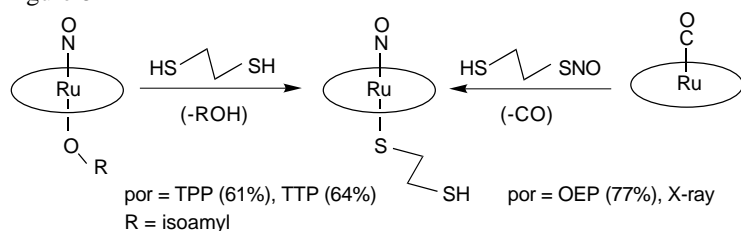
isoelectronic phenyl aryl azo sulfide ($\text{PhSN}=\text{NAr}$; $\text{Ar} = p\text{-C}_6\text{H}_4\text{NO}_2$) in place of "RSNO"; the same $(\text{OEP})\text{Os}(\text{CO})(\text{SPh})$ intermediate was seen to form. Thus, we propose that the reaction proceeds via a sulfur

Figure 7



attack (and not nitrogen attack from the RSNO reagent) at the osmium center. Furthermore, we envisaged that the use of the non-carbonyl-containing $[(\text{OEP})\text{Os}]_2$ dimer should then generate the bis-thiolate species shown as the final product in Fig. 7, which in fact was the case.

Figure 8

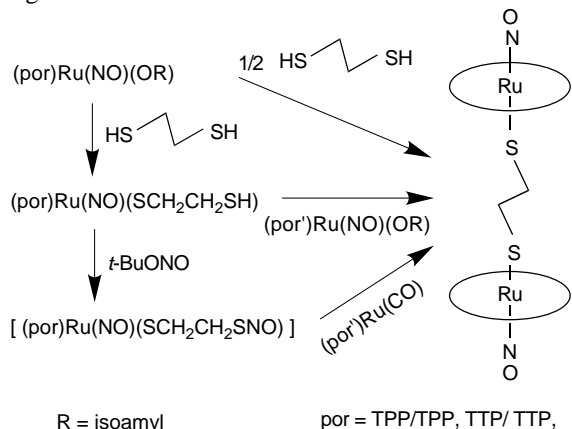


Monometallic Thiolate-thiol

Complexes. The $(\text{TPP})\text{Ru}(\text{NO})\text{-(O-}i\text{-C}_5\text{H}_{11})$ isoamyl alkoxide complex undergoes reaction

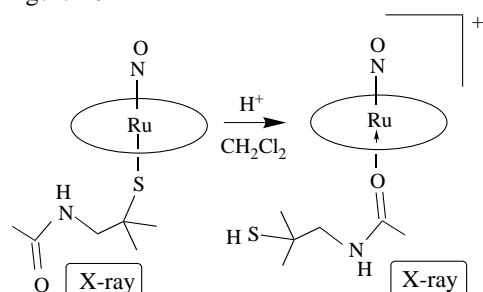
with 1,2-ethanedithiol to generate the thiolate-thiol derivatives (Fig. 8). We were not able to prepare the OEP derivative by the method described on the left side of Fig. 8. However, the reaction of $(\text{OEP})\text{Ru}(\text{CO})$ with $\text{HSCH}_2\text{CH}_2\text{SNO}$ gave the desired product (Fig. 8, right side) via the formal *trans* addition of the RSNO across the metal center (similar to Fig. 4).

Figure 9



We also prepared novel bimetallic porphyrin complexes of Ru and Os containing μ -dithiolate ligands (Fig. 18). The most noticeable spectral difference between these bimetallic derivatives and their monometallic analogues (Fig. 17, middle) lies in their ^1H NMR spectra.

Figure 10



a remarkable ligand rearrangement (*S*-bound to *O*-bound), and the Ru example is shown in Fig. 10.

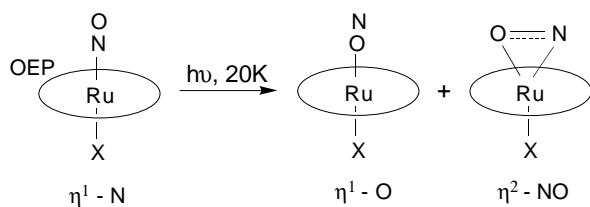
We prepared the analogous 3-carbon (μ -propanedithiolate) and 4-carbon (μ -butanedithiolate) bridged dithiolate derivatives of the "TTP/TTP" dimer, and the unsymmetrical $(\text{TPP})(\text{NO})\text{Ru}(\text{SCH}_2\text{CH}_2\text{S})\text{Ru}(\text{NO})(\text{OEP})$ bimetallic complex.

We also explored the reaction chemistry of the resulting six-coordinate (porphyrin) $\text{M}(\text{NO})(\text{SR})$ compounds. The preliminary results of the reaction chemistry of the nitrosyl thiolates are quite interesting. For example, protonation of the complexes containing an amide-thiol ligand results in a

5 Photoinduced Metastable Iron and Ruthenium Nitrosyl Porphyrins:

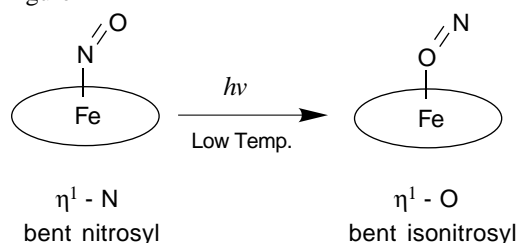
Infrared spectroscopic results demonstrate that metastable η^1 -O and η^2 -NO linkage isomers are formed when the (OEP)Ru(NO)X (X = O-*i*-C₅H₁₁, SCH₂CF₃, Cl, or [py]⁺) complexes are irradiated at low temperature (Fig. 11) [11]. For example, irradiation of (OEP)Ru(NO)(O-*i*-C₅H₁₁) [ν_{NO} 1791 cm⁻¹ (KBr pellet); 330 < λ < 460 nm; Xe lamp] at 20K for 15 min results in IR spectral changes that are attributed to the formation of the metastable η^1 -O (ν_{NO} 1645 cm⁻¹; $\nu_{15\text{NO}}$ 1609 cm⁻¹) and η^2 -NO (ν_{NO} 1497 cm⁻¹; $\nu_{15\text{NO}}$ 1480 cm⁻¹) linkage isomers. These linkage isomers are stable at low temperature, but convert to the starting Ru-NO compound upon warming (without dissociation of NO). Importantly, this was the first report of the existence of nitrosyl linkage isomers for metalloporphyrins.

Figure 11



We have extended this study to iron nitrosyl porphyrins. We reported that low temperature irradiation of the five-coordinate (por)Fe(NO) compounds (por = OEP, TTP) results in the first observation of iron isonitrosyl porphyrin derivatives (Fig. 12) [12].

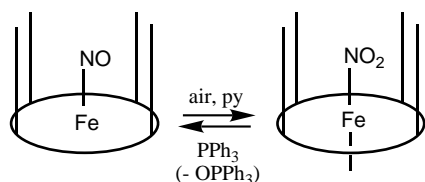
Figure 12



These results have been confirmed by Density Functional calculations, which show that the O-bound isonitrosyl conformation is a local minimum on the potential energy curve. These results are very relevant to heme NO chemistry and biochemistry, and to kinetic studies involving combination, dissociation, and recombination of the NO ligand with the metal center in heme and heme models. Surprisingly, such linkage isomers had not been previously considered in metalloporphyrin-NO chemistry. This research was performed in collaboration with the Coppens and Bagley groups in Buffalo, N.Y.

6 A High-Yield Iron Nitrosyl-to-Nitrite Conversion: We have recently reported that exposure of a five-coordinate (por)Fe(NO) complex (por = picket fence porphyrinato dianion) to air and pyridine results in its quantitative conversion to the isolable nitrite derivative [13]. The

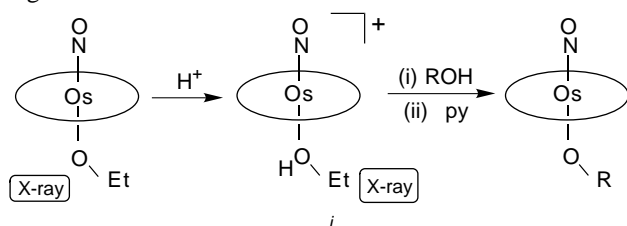
Figure 13



deoxygenation of the bound nitrite by triphenylphosphine (as an O-atom acceptor) to regenerate the nitrosyl precursor is also a high yield process. The implications for the reactivity of (por)Fe(NO) groups in aerobic environments are enormous, and suggest that an iron-bound nitrite could be one of several stable intermediates in NO oxidation chemistry in biology.

7 Osmium Nitrosyl Alcohol Complexes: We have prepared new alkoxide (OEP)Os(NO)(OR) (R = ethyl, isopropyl, hexyl, cyclohexyl) compounds and alcohol [(OEP)Os(NO)(HOR)]⁺ complexes (R = methyl, ethyl, isopropyl, hexyl, cyclohexyl) in high yields [14]. The (OEP)Os(NO)(OEt) compound and the cationic aqua and alcohol [(OEP)Os(NO)(HOR)]⁺ complexes

Figure 14



aqua and alcohol [(OEP)Os(NO)(HOR)]⁺ complexes (R = H, ethyl, isopropyl, hexyl) were characterized by single-crystal X-ray crystallography; the latter represent the first osmium alcohol structures to be reported. Interestingly, the electrophilic [(OEP)Os(NO)]⁺ fragment in the [(OEP)Os(NO)(HOR)]⁺ complexes renders the coordinated alcohol ligands susceptible to deprotonation by pyridine to produce the

corresponding alkoxide (OEP)Os(NO)(OR) derivatives. A one-pot reaction sequence for the preparation of new (OEP)Os(NO)(OR) complexes from (OEP)Os(NO)(OEt) was developed, which was based on (i) initial protonation of the ethoxide compound to give [(OEP)Os(NO)(HOEt)]⁺, (ii) alcohol substitution by ROH to give [(OEP)Os(NO)(HOR)]⁺, and (iii) deprotonation of the latter by pyridine to give (OEP)Os(NO)(OR) (Fig. 14).

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