

Preparation of a Nitroxyl (HN=O) Complex of Rhenium by Selective Oxidation of Coordinated Hydroxylamine

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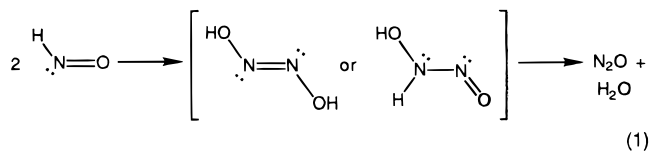
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The discovery that nitric oxide (NO) plays key roles in mammalian biochemistry has spurred significant recent work aimed at elucidating the bioinorganic chemistry of NO. The diatomic radical has been shown to be responsible for numerous physiological functions, and it is particularly important as a cell-signaling agent, which includes its role as the endothelium-derived relaxing factor (EDRF) responsible for triggering smooth muscle relaxation. In this sense, NO functions as a vasodilator, helping to lower blood pressure; in the stomach, it promotes the relaxation component of peristalsis; and it is the neurotransmitter in males responsible for translating sexual excitement into tumescence.¹ It has been suggested that the 1-e⁻ redox relatives of NO, the nitrosonium cation (NO⁺), and the nitroside anion (NO⁻) as well as the conjugate acid of NO⁻, nitroxyl (HN=O), may be responsible for certain aspects of the rich biological chemistry of nitric oxide.^{1a,b} In addition to its biological relevance, HN=O has been postulated as an intermediate in photochemical and free-radical reactions,² and its formation and decomposition may play a role in mechanisms for the combustion of nitrogen-containing fuels and the oxidation of atmospheric nitrogen.³

Nitroxyl is a reactive molecule that was first proposed in 1903 as an intermediate in the decomposition of sodium trioxodinitrate(II) (Na₂N₂O₃) in aqueous media.⁴ The first reports of direct spectroscopic observation of HN=O appeared in 1958 from gas-phase work by Dalby² and, independently, from argon-matrix-isolation experiments (by the photolysis of methyl nitrite) by Pimentel.⁵ However, despite its very simple constitution and structure, a facile synthesis for this triatomic molecule remains elusive. While HN=O is thought to readily decompose in a bimolecular fashion to give N₂O (eq 1),⁶ its stability, like that



of the isoelectronic 1,2-diazene (NH=NH),^{7–9} can be greatly

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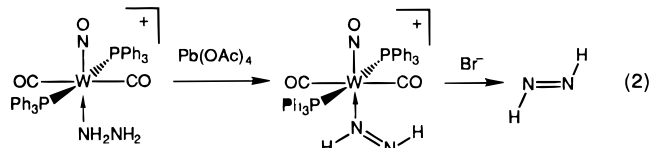
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enhanced by coordination to a transition metal. There are a few reported examples of nitroxyl complexes,^{10,11} most notably Roper's OsCl₂(CO)(NH=O)(PPh₃)₂, produced by reaction of OsCl(CO)(NO)(PPh₃)₂ with anhydrous HCl.¹¹

Our group has been actively involved in synthetic and reactivity studies of cationic complexes of 1,2-diazene in d⁶-transition-metal systems (W, Re, Ru, Os).^{7–9} We have shown NH=NH can indeed be stabilized by complexation and, furthermore, that these complexes can serve as clean sources of the free NH=NH molecule (as illustrated for W in eq 2). Since HN=O is isoelectronic with diazene, we have explored the use of a similar synthetic approach for the preparation of stable coordination complexes of nitroxyl, with an eye on ultimately using such complexes as HN=O synthons.



Of the W, Re, Ru, and Os series of cationic, d⁶ diazene complexes, the Re derivative [mer,trans-Re(CO)₃(NH=NH)(PPh₃)₂]⁺[SO₃CF₃⁻] is by far the most thermally robust,⁸ so our initial synthetic efforts have concentrated on preparing an HN=O analogue of this compound. Herein we report the first synthesis of a nitroxyl complex prepared by the selective oxidation of coordinated hydroxylamine. The Re(I) hydride mer,trans-ReH(CO)₃(PPh₃)₂ reacts with trifluoromethanesulfonic acid to give dihydrogen and mer,trans-Re(η¹-OSO₂CF₃)(CO)₃(PPh₃)₂ (**1**);⁸ alternatively, **1** can be synthesized in good yield by the reaction of mer,trans-ReCl(CO)₃(PPh₃)₂¹² with silver triflate, with silver chloride being the byproduct. The weakly-bound triflate ligand of **1** is displaced by hydroxylamine to give the cationic rhenium-hydroxylamine complex [mer,trans-Re(CO)₃(NH₂OH)(PPh₃)₂]⁺[SO₃CF₃⁻] (**2**) as an analytically pure white crystalline compound in 85% yield (Scheme 1). Complex **2** was characterized by standard spectroscopic methods (IR; ¹H and ³¹P NMR), elemental analysis, and a single-crystal X-ray diffraction study.^{13,14} The ¹H NMR spectrum (CD₂Cl₂, 20 °C) of **2** exhibits resonances for the hydroxylamine ligand at δ 7.67 (br s, Re–NH₂OH) and δ 5.62 (t, ReNH₂OH, ³J_{PH} = 3.8 Hz),

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(13) For **2**: ¹H NMR (CD₂Cl₂, 20 °C): δ 7.67 (br s, 1 H, NH₂OH), 7.60–7.35 (m, 30 H, Ph), 5.62 (t, 2 H, NH₂OH, ³J_{PH} = 3.8 Hz). ³¹P{¹H} NMR (CD₂Cl₂, 20 °C): δ 16.5 (s). IR: ν(NH), ν(OH) 3235 (w, br), 3205 (w, br), 3139 (w, br); ν(CO) 2061 (w), 1966 (s), 1926 (s) cm⁻¹. Anal. Calcd for C₄₀H₃₃O₇NSF₃P₂Re: C, 49.18; H, 3.40; N, 1.43. Found: C, 49.16; H, 3.26; N, 1.24. For **2**-¹⁵N: ¹H NMR (CD₂Cl₂, 20 °C): δ 7.68 (br s, 1 H, NH₂OH), 7.60–7.35 (m, 30 H, Ph), 5.62 (dt, 2 H, NH₂OH, ³J_{PH} = 3.6 Hz, ¹J_{NH} = 73.2 Hz).

(14) Crystal data for **2**, C₄₀H₃₃F₃NO₇P₂ReS: triclinic, $\bar{P}1$, $a = 11.123(2)$ Å, $b = 12.299(10)$ Å, $c = 15.668(9)$ Å, $\alpha = 96.585(6)^\circ$, $\beta = 96.620(10)^\circ$, $\gamma = 109.224(9)^\circ$, $Z = 2$, $\mu(\text{Mo K}\alpha) = 32.60 \text{ cm}^{-1}$, $T = 241 \text{ K}$. Of 6145 data collected (colorless crystal, $2.04^\circ \leq \theta \leq 22.50^\circ$), 5177 were independent and 5173 were observed with $I > 2\sigma(I)$. An empirical correction for absorption was performed. All non-hydrogen atoms were anisotropically refined, and hydrogen atoms were idealized except for those of the hydroxylamine ligand which were located and refined. $R(F) = 5.30\%$ and $R(wF) = 5.63\%$.

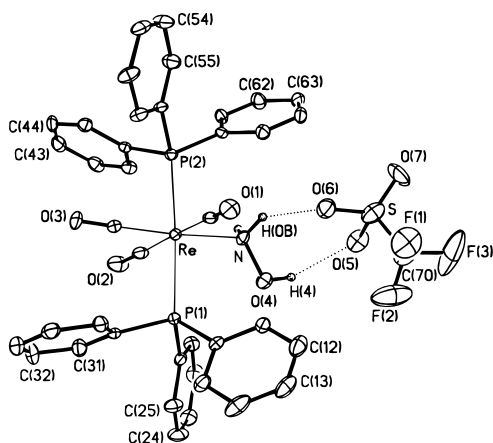
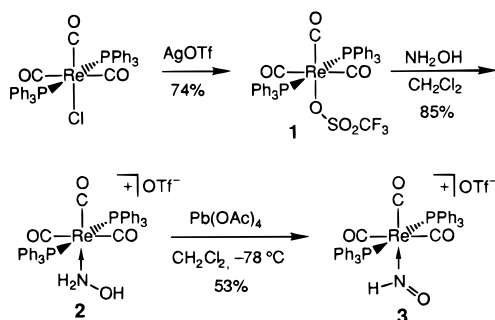


Figure 1. A perspective view of the molecular structure of **2** showing the atom-labeling scheme. Selected metrical parameters are given in the text.

Scheme 1



and in the labeled isotopomer [*mer,trans*-Re(CO)₃(¹⁵NH₂OH)-(PPh₃)₂⁺][SO₃CF₃⁻] (**2**-¹⁵N), the NH₂ resonance exhibits a $|^1J_{\text{NH}}| = 73.2$ Hz.

The molecular structure of **2**, determined by X-ray diffraction analysis, is shown in Figure 1. The complex cation has pseudooctahedral geometry with meridional carbonyl ligands, *trans* triphenylphosphine ligands, and a monohapto, N-bound hydroxylamine ligand whose hydrogen atoms were located and refined and were found to be hydrogen bonded to the oxygen atoms of the triflate counterion (CF₃SO₂O...H-X contacts in **2** are ~3.4 Å, X = N, O). Significant ion-pairing is also reflected in the high solubility of **2** in relatively nonpolar solvents like benzene. The N-O bond length (1.422(5) Å) in **2** is similar to that found in [Ni(NH₂OH)₆²⁺][SO₄²⁻] (mean distance 1.44 Å)¹⁵ and is shorter than that found for NH₂OH in the gas phase (1.453 Å).¹⁶ The Re-N bond length (2.222(4) Å) is reasonable for a Re-N(sp³) dative bond, and the Re-N-O angle (116.4(3)°) is opened somewhat from the ideal tetrahedral value.

Lead tetracetate reacts with **2** in CH₂Cl₂ solution at low temperature (-78 °C) to effect selective oxidation of the coordinated hydroxylamine ligand, forming [*mer,trans*-Re(CO)₃(NH=O)(PPh₃)₂⁺][SO₃CF₃⁻] (**3**), which was isolated as an analytically pure compound in good yield (Scheme 1).¹⁷ The reaction appears to be specific for Pb(OAc)₄, with attempts to carry out oxidation of the hydroxylamine ligand with other oxidants like MnO₂ or HgO being unsuccessful. The ¹H NMR

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(17) For **3**: δ 21.67 (s, 1 H, NH=O), 7.58–7.35 (m, 30 H, Ph). ³¹P{¹H} NMR (CD₂Cl₂, 20 °C): δ 12.3 (s). IR: ν (NH) 3056 (w); ν (CO) 2082 (w), 2007 (s), 1977 (s); ν (NO) 1391 (m) cm⁻¹. Anal. Calcd for C₄₀H₃₁O₇NSF₃P₂Re: C, 49.28; H, 3.20; N, 1.44. Found: C, 48.99; H, 3.08; N, 1.31. For **3**-¹⁵N: ¹H NMR (CD₂Cl₂, 20 °C): δ 21.67 (d, NH=O, 1 H, $|^1J_{\text{NH}}| = 72.5$ Hz), 7.58–7.35 (m, 30 H, Ph).

spectrum (CD₂Cl₂ solution, 20 °C) of **3** shows a diagnostic singlet for the HN=O proton at δ 21.7, an extraordinary downfield shift for a diamagnetic molecule. The isotopically labeled complex [*mer,trans*-Re(CO)₃(¹⁵NH=O)(PPh₃)₂⁺][SO₃CF₃⁻] (**3**-¹⁵N) was prepared analogously from **2**-¹⁵N and Pb(OAc)₄ and showed $|^1J_{\text{NH}}| = 72.5$ Hz, as expected for a proton attached to an sp²-hybridized nitrogen coordinated to a transition metal.^{7,18,19} (This $|^1J_{\text{NH}}$ also confirms that the HN=O ligand is N-bound; if it were coordinated to Re through oxygen, the nitrogen atom would possess an uncomplexed lone pair and the magnitude of $|^1J_{\text{NH}}|$ would be substantially reduced to ~45 Hz.^{7,18,20}) These values are nearly identical with those found for the nitroxyl proton resonance in *cis,trans*-OsCl₂(CO)-(¹⁵NH=O)(PPh₃)₂ (δ 21.2, $|^1J_{\text{NH}}| = 75$ Hz),^{11b} and similar to those observed for the α -diazanyl proton resonances in related η^1 -NH=NH complexes.^{7–9} The infrared spectrum of **3** exhibits a medium-intensity ν (NO) at 1391 cm⁻¹ and a weak ν (NH) at 3056 cm⁻¹, values that are in the range found in other nitroxyl^{10,11} and nitrosoalkane²¹ complexes. These vibrations are significantly perturbed in the coordination complexes as compared to the analogous modes in free HN=O, which exhibits ν (NO) at 1563 cm⁻¹ and ν (NH) at 2717 cm⁻¹ in an argon matrix,²² indicative of weaker N-O and stronger N-H bonds for coordinated HN=O with respect to the free species.

Preliminary studies indicate that cationic, d⁶ nitroxyl complexes like **3** might indeed serve as viable precursors to free HN=O. While **3** is stable in the solid state under an inert atmosphere and in solution for extended periods at low temperatures (CH₂Cl₂, -78 °C), it is unstable in solution at ambient temperature, slowly undergoing a clean thermal decomposition to give the triflate complex **1**. Moreover, addition of tetrabutylammonium bromide to methylene chloride solutions of **3** results in clean formation of *mer,trans*-ReBr(CO)₃(PPh₃)₂. Unfortunately, under these conditions we have not been able to trace the fate of the displaced HN=O ligand. We are currently exploring the scope of this chemistry in an effort to access a system in which HN=O displacement can be carried out at substantially lower temperatures which might allow for a study of its solution reactivity (cf., bromide reacts with [*cis,trans*-Mo(NH=NPh)(CO)₂(NO)(PPh₃)₂⁺] at -40 °C with rapid, quantitative displacement of NH=NPh).²³

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Supporting Information Available: Experimental, spectroscopic, analytical, and crystallographic details and tables of atomic coordinates, bond angles and distances, anisotropic thermal parameters, and hydrogen atom coordinates (12 pages). See any current masthead page for ordering and Internet access information.

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(19) Due to the anisotropic-lone-pair effect on $|^1J_{\text{NH}}$ for an sp²-hybridized nitrogen,²⁰ the magnitudes of $|^1J_{\text{NH}}$ for the coordinated NH₂OH in **2** and the coordinated HN=O in **3** are very similar; analogous similarities between sp²- and sp³-hybridized NH couplings were observed in the related W and Os NH₂NH₂ and NH=NH complexes. (a) Cheng, T.-Y. Ph. D. Thesis, The University of Chicago, 1994. (b) See ref 7.

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