O-Protonation of a Terminal Nitrosyl Group To Form an η^1-Hydroxylimido Ligand

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Nitric oxide (NO) has a rich chemistry within living organisms and continues to gain ever increasing recognition for the physiological roles it plays in biological systems.[1] Since some of its chemistry in these environments is mediated by transition metals, studies of the chemistry and biochemistry of NO bound to a metal center as the nitrosyl ligand are also experiencing a renaissance. For instance, Shiro and co-workers have recently studied the nitric oxide reductase (Nor) enzyme isolated from the denitrifying fungus *Fusarium oxysporum*.[2] By utilizing resonance Raman and crystallographic techniques, they have concluded that for this cytochrome P450-type heme enzyme (P450nor) it is probably the protonation of a terminal heme-nitrosyl oxygen by water that constitutes one of the key mechanistic steps during its catalysis of the reduction of NO to N_2O. Such complexation of H^+ has been unequivocally demonstrated for the more basic doubly and triply bridging NO groups,[3] but to date it has only been inferred,[4a,5a,b] sometimes incorrectly,[4b,5c] for terminal NO ligands. We now wish to report the first definitively characterized examples of O-protonated terminal nitrosyl ligands and the changes to the metal−NO bonding interactions that occur within the resulting η^1-hydroxylimido−metal linkages.

$$Cp^*WR_2(NO) + [H(OEt_2)_2]^+ \rightarrow [Cp^*WR_2(NOH{\cdot}OEt_2)]^+ + Et_2O \quad (1)$$

Reaction of 1 equiv of the oxonium acids $[H(OEt_2)_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ ($HBAr^f_4$)[6] or $[H(OEt_2)_2][B(C_6F_5)_4]$ ($HB\phi^f_4$),[7] with the bis(hydrocarbyl) nitrosyl complexes, $Cp^*WR_2(NO)$ (**1**, R = CH_2SiMe_3 (**a**), CH_2Ph (**b**)),[8] results in quantitative formation of the corresponding cations $[Cp^*WR_2(NOH{\cdot}OEt_2)]$ **2a** and **2b** (eq 1). Similarly, reaction of **1b** with triflic acid generates the unsolvated complex $[Cp^*WBz_2(NOH{\cdot}OTf)]$ (**3**). Crystallographic and spectral data indicate that the WNOH linkages in these complexes are best viewed as involving hydroxylimido ligands, i.e., W≡N−OH.

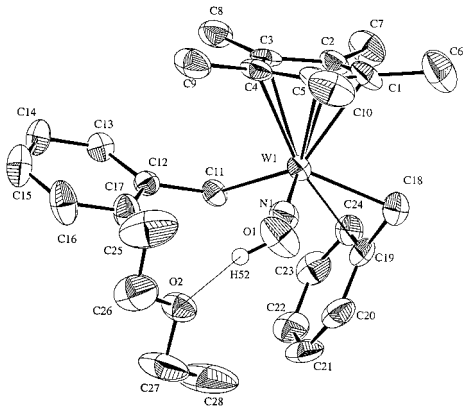

Figure 1. The solid-state molecular structure of cation **2b** in **2b**[BAr^f_4]; 50% probability thermal ellipsoids are shown.

A single-crystal X-ray crystallographic analysis of **2b**[BAr^f_4][9] (Figure 1) reveals that the metrical parameters of the $Cp^*W(\eta^1\text{-}CH_2Ph)(\eta^2\text{-}CH_2Ph)$ fragment of cation **2b** are generally similar to those exhibited by its neutral precursor **1b** (W(1)−C(19) = 2.509 Å).[8] However, the W−N bond in **2b** is significantly shorter than that extant in **1b** (W(1)−N(1) = 1.716(5) (**2b**), 1.752(3) Å (**1b**)) and within the range typical of W≡N(imido) bond lengths,[10] whereas the N−O bond is significantly longer (N(1)−O(1) = 1.339(6) (**2b**), 1.239(5) Å (**1b**)). The proton of the hydroxylimido ligand in **2b** was refined isotropically, thereby permitting an estimation of its distance from the nitrosyl oxygen atom (i.e. 0.90(7) Å) and the N(1)−O(1)−H(52) bond angle (103(4)°). Finally, a molecule of Et_2O within the crystal lattice is hydrogen bonded to the hydroxylimido proton with a O(2)−H(52) contact of 1.71(8) Å.

The ν(NO) of the hydroxylimido ligand is obscured by counterion absorptions in the IR spectra of **2a**[BAr^f_4], **2b**[BAr^f_4], and **3** as KBr pellets. However, a band at 1303 cm^{-1} that shifts under a counterion band at 1270 cm^{-1} in the IR spectrum (KBr) of **2b**[$B\phi^f_4$]-^{15}N can be assigned to the N−O stretch of **2b**[$B\phi^f_4$]. This absorption is ca. 250 cm^{-1} lower in energy than the ν(NO) of **1b** (1556 cm^{-1}).[8] Such a change is indicative of a highly reduced N−O bond order and reinforces the description of these complexes as containing terminal hydroxylimido ligands.[11]

The ^1H and ^{13}C NMR spectra of complexes **2** and **3** are qualitatively similar to those of their precursor nitrosyl complexes **1** and indicate that they retain their $Cp^*W(\eta^1\text{-}CH_2Ph)(\eta^2\text{-}CH_2Ph)$ cores in solutions. Resonances due to the coordinated Et_2O molecule are evident in the NMR spectra of **2** but not in the spectra of **3**, thereby indicating that in **3** the triflate anion probably remains hydrogen bonded to the hydroxylimido proton.[12] A signal due to the −NOH proton is evident between 12.5 and 14.5 ppm in the ^1H NMR spectra of **2** and **3** obtained in $Et_2O\text{-}d_{10}$ or chlorinated solvents.[13] Interestingly, the ambient-temperature ^1H

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(9) Crystal data for **2b**[BAr^f_4]: $C_{60}H_{52}NO_2F_{24}WB$, T = 173 K, M_r = 1469.70, yellow, block, orthorhombic, $Pna2_1$ (No. 33), a = 26.696(1) Å, b = 12.9115(3) Å, c = 17.5937(8) Å, V = 6064.3(9) Å^3, Z = 4, R = 0.049, R_w = 0.066, GOF = 0.65.

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(11) ^{15}N labeling studies revealed no bands attributable to W≡N stretches in the IR spectra of these compounds.

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NMR spectra of equimolar mixtures of either **2** or **3** and the corresponding free acid exhibit a single broad resonance situated in a position intermediate to those of the hydroxylimido proton and the free acid. This observation indicates that in acidic solution the −NOH proton exchanges with free acid. Decoalescence of these signals occurs upon cooling of the solutions.[14] The ^{15}N NMR spectra of isotopically labeled **2a/b-^{15}*N*** exhibit signals that are shifted ca. 30 ppm upfield relative to those of **1**, but these values of δ are still within the range associated with the sp-hybridized N atoms of linear, terminal nitrosyls.[15] No ^{15}N−^{1}H coupling between the hydroxylimido proton and the labeled nitrosyl nitrogen is evident even at −70 °C.

The hydroxylimido protons in **2** and **3** are acidic and can be readily abstracted by basic reagents such as pyridine to reform the neutral nitrosyl species. Furthermore, these complexes are unstable with respect to protonolysis of a hydrocarbyl ligand under appropriate conditions. For instance, dissolution of **2b** and **3** in acetonitrile for 24 h leads to the clean formation of the known cationic complex $[Cp^*W(Bz)(NO)(NCMe)]^+$.[16] This observation suggests that in MeCN solution the coordination of H^+ to the nitrosyl is reversible and ultimately leads to protonolysis.

The reaction of **1b** with HCl generates the known benzyl chloro complex, Cp*W(Bz)Cl(NO), with no observable hydroxylimido intermediate.[17] It thus appears that the counterion of the acid plays a key role in permitting the isolation of the product resulting from the kinetic site of protonation, namely the nitrosyl ligand.

Surprisingly, a different mode of reactivity occurs during the reaction of the oxonium acid, $HBF_4{\cdot}OEt_2$, with complexes **1**. In this instance the nitrosyl−boron trifluoride adducts, $Cp^*WR_2(NOBF_3)$ (**4**, R = CH_2SiMe_3 (**a**), CH_2Ph (**b**)) (eq 2) are

$$Cp^*WR_2(NO) + HBF_4 \rightarrow Cp^*WR_2(NOBF_3) \qquad (2)$$

immediately and quantitatively formed. The complexes **4** display physical properties and spectroscopic features akin to those exhibited by the hydroxylimido complexes. The NO-derived IR stretching frequencies for **4a** (1389 cm^{-1}) and **4b** (1378 cm^{-1}) in KBr have been definitively assigned by comparison of their spectra with those of isotopically labeled **4a/b**-^{15}*N*. As expected, there is a decrease in ν(NO) upon complexation of the nitrosyl ligand, but the softer Lewis acid BF_3 effects less of a decrease than does a proton. A single-crystal X-ray crystallographic analysis of **4a** has been performed, and the results are shown in Figure 2.[18]

A comparison of the solid-state molecular structure of **4a** with those of other crystallographically characterized Cp*W(hydrocarbyl)$_2$(NO) species reveals that the nitrosyl-derived ligand is again distorted with a slightly shorter W(1)−N(1) distance (1.740(2) Å) and longer N(1)−O(1) distance (1.303(3) Å) as compared to an uncomplexed nitrosyl ligand. The N−O−B angle

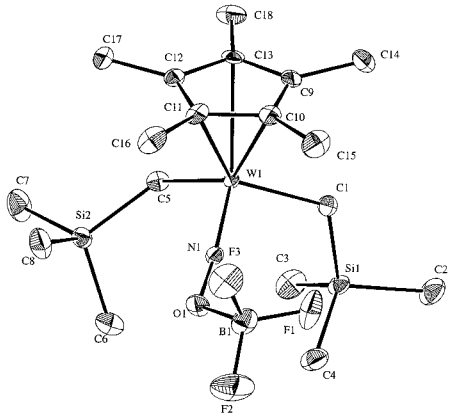

Figure 2. The solid-state molecular structure of **4a**; 50% probability thermal ellipsoids are shown.

is sharply bent at an angle of 118.0(2)°. These distortions to the bond lengths and angles are similar to those reported for the two other nitrosyl−borane adducts that have been structurally characterized and, consistent with the IR spectroscopic evidence, display less alteration than that evident in the structure of **2b**[BAr^f_4].[19]

The complexes **4** are probably formed via a reaction pathway that transiently involves analogues of **3**. The BF_4-counterion is known to hydrogen bond to the proton of an η^3-hydroxylimido proton.[3e] It is therefore not unreasonable that an initially formed hydroxylimido species such as $[Cp^*WR_2(NOH{\cdot}F_nBF_{4-n})]$ decomposes via HF elimination to afford the neutral isonitrosyl complexes **4**.

In summary, we have presented here the first well-characterized examples of compounds containing the biologically relevant η^1-hydroxylimido ligand. While reasonably thermally stable, the ligand itself is acidic and prone to transfer its proton to basic substrates. Furthermore, the stabilization of this ligand is dependent on the nature of the acid used to effect the protonation of the nitrosyl precursor. Our investigations of the reactivity of terminal nitrosyl ligands with other important electrophiles are currently in progress.

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Supporting Information Available: Experimental procedures and complete characterization data for complexes **2**, **3**, and **4** and full details of the crystal structure analyses of **2b**[BAr^f_4] and **4a** including associated tables (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) ^{1}H NMR (NO*H*) δ: **2a**[BAr^f_4] 13.97 (Et_2O-d_{10}), **2b**[BAr^f_4] 13.60 (Et_2O-d_{10}), **2b**[$B\phi^f_4$] 12.82 (CD_2Cl_2), **3** 14.32 ($CDCl_3$). **2a**[$B\phi^f_4$] has not yet been isolated analytically pure.

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(18) Crystal data for **4a**: $C_{18}H_{37}NOSi_2WBF_3$, T = 173 K, M_r = 591.32, orange, block, monoclinic, $P2_1/n$ (No. 14), a = 9.5887(4) Å, b = 17.2976(6) Å, c = 14.7882(6) Å, β = 97.574(3)°, V = 2431.4(1) Å^3, Z = 4, R = 0.036, R_w = 0.052, GOF = 0.94.

(19) $CpRe(SiMe_2Cl)(PPh_3)(NOBCl_3)$: (a) Lee, K. E.; Arif, A. M.; Gladysz, J. A. *Inorg. Chem.* **1990**, *29*, 2885. (b) Lee, K. E.; Arif, A. M.; Gladysz, J. A. *Chem. Ber.* **1991**, *124*, 309. $Re(H)(P^iPr_3)(NO)(NOBF_3)$: (c) Gusev, D.; Llamazares, A.; Artus, G.; Jacobsen, H.; Berke, H. *Organometallics* **1999**, *18*, 75. The bond lengths exhibited in the M−N−O−B fragment reported in refs 19a,b are more drastically distorted from those of the parent nitrosyl than are those presented here or in ref 19c. The authors of ref 19c suggest that this may be due to the relatively low quality data set that was used for the X-ray analysis of $CpRe(SiMe_2Cl)(PPh_3)(NOBCl_3)$.