Stepwise Hydrolysis of a Terminal Nitrosyl Ligand

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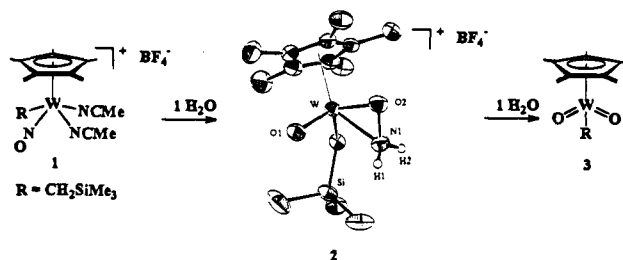Vancouver, British Columbia, Canada V6T 1Z1*

Nitric oxide, NO, is a versatile and important molecule that is gaining ever-increasing recognition for its physiological properties.[1] For instance, in the human body in measured doses, it helps maintain blood pressure by dilating blood vessels, helps fill foreign invaders in the immune response system, is a major biochemical mediator of male sexual function, and is probably a major biochemical component as a neurotransmitter of long-term memory.[2] Not surprisingly, the utilization of metallo-nitrosyl complexes as pharmaceutical agents capable of releasing NO in vivo has recently become a very active area of research.[3] However, the potential utility of many transition metal nitrosyl compounds is severely hampered by their hydrolytic instability. The mechanism by which hydrolysis of the nitrosyl group in such compounds occurs must be more thoroughly understood before attempts at blocking this route of decomposition may be undertaken. In this communication we wish to report the unprecedented stepwise hydrolysis of a terminal nitrosyl ligand which results first in the formation of an η^2-hydroxylamide group and then the liberation of the hydroxylammonium cation.[4]

The overall conversion of interest is the reaction of $[Cp^*W(NO)(CH_2SiMe_3)(NCMe)_2]BF_4$ (1) with excess water, which produces the known $Cp^*W(O)_2(CH_2SiMe_3)$ complex (3),[5] a common hydrolysis product for many other similar nitrosyl-containing compounds,[6] in virtually quantitative yields as judged by ^1H NMR spectroscopy. As shown in Scheme 1, careful control of the reaction stoichiometry permits the isolation of the intermediate salt, $[Cp^*W(O)(\eta^2-NH_2O)(CH_2SiMe_3)]BF_4$ (2), as yellow crystals. Subsequent treatment of complex 2 with one more equivalent of water leads to the formation of 3 and $[H_3NOH]BF_4$, which is detectable by ^1H NMR spectroscopy[7] but is unisolable since it does not persist in the presence of 3. The isolable nitrogen-containing product from the final reaction mixture is slightly impure $[NH_4][BF_4]$.[8]

The preparation of 1 is achieved in a manner analogous to that utilized for $[Cp^*W(NO)(CH_2CMe_3)(NCMe)_2]BF_4$.[8] Thus, chloride abstraction from $Cp^*W(NO)(CH_2SiMe_3)Cl$ with $AgBF_4$ in acetonitrile yields analytically pure, orange crystals of 1 in approximately 50% yield after workup. Even though many transition metal cationic complexes react readily with π-electron-rich substrates,[9] 1 shows no proclivity toward this mode of

(1) (a) Koshland, D. E., Jr. *Science* **1992**, *258*, 1861. (b) Culotta, E.; Koshland, D. E., Jr. *Science* **1992**, *258*, 1862.
(2) McCall, T.; Vallance, P. *Trends Pharmacol. Sci.* **1992**, *13*, 1.
(3) (a) Sadler, P. J. *Adv. Inorg. Chem.* **1991**, *36*, 1. (b) Clarke, M. J.; Gaul, J. B. *Structure Bonding* **1993**, *81*, 147.
(4) Elegant work by Meyer has demonstrated that a terminal nitrosyl ligand may be converted into an ammonia ligand by reduction in aqueous solutions, see: Younathan, J. N.; Wood, K. S.; Meyer, T. J. *Inorg. Chem.* **1992**, *31*, 3280 and references contained therein.
(5) Legzdins, P.; Hillips, E. C.; Rettig, S. J.; Sánchez, L. *Organometallics* **1989**, *8*, 940.
(6) Legzdins, P.; Lundmark, P. J.; Phillips, E. C.; Rettig, S. J.; Veltheer, J. E. *Organometallics* **1992**, *11*, 2991 and references contained therein.
(7) To a solution of 1 in DMSO-d_6 was added approximately 2 equiv of H_2O, and the progress of the reaction was monitored by ^1H NMR spectroscopy. The appearance and growth of a peak at 10.1 ppm was indicative of the presence of $[H_3NOH]BF_4$, which may also be synthesized independently by treating H_2NOH with HBF_4 in the same solvent.
(8) Characterization data for the ammonium salt: IR (Nujol) 3332, 1029 cm^{-1}; low-resolution mass spectrum (FAB$^-$) m/z 87 [BF$_4^-$]; ^1H NMR (DMSO-d_6) δ 7.08. Anal. Calcd for BF$_4$H$_4$N: C, 0.00; H, 3.85; N, 13.36. Found: C, 0.25; H, 3.81; N, 12.58. These spectroscopic properties are identical to those exhibited by an authentic sample of $[NH_4]BF_4$.

Scheme 1

reactivity. For instance, it is unreactive toward phenylacetylene, acetone, carbon monoxide, ethene, 1-pentyne, or butadiene in $CDCl_3$ up to 55 °C. We believe that this lack of reactivity is a manifestation both of the formal 18-valence-electron configuration at the metal center and of the presence of two stabilizing acetonitrile ligands which render the metal center coordinatively saturated. Interestingly, the two acetonitrile ligands may be displaced by one trimethylphosphine molecule, i.e.,
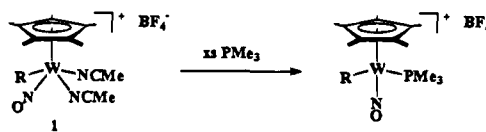
This preference of the cation in 1 for σ-base ligands led us to attempt the reaction of 1 with water. Treatment of either Me-CN or CH_2Cl_2 solutions of 1 with 1 equiv of H_2O (as a dilute solution in Et_2O) at room temperature results in the production of the intermediate complex 2 in 78% isolated yield. This product may be crystallized by slow evaporation of a saturated solution in chloroform/toluene (1:1). The exact nature of compound 2 could not be unambiguously established by spectroscopic means alone, and so a single-crystal X-ray crystallographic analysis of the complex has been performed.[11] An ORTEP drawing of the organometallic cation in 2 is shown in Scheme 1. Comparisons of the metrical parameters of this cation with those exhibited by other hydroxylamido complexes reveal that the bond lengths of the η^2-NH$_2$O ligand are normal.[12] The N—O bond length of 1.423(4) Å is typical of a N—O single bond, and both the W—O and the W—N distances (W—O(2) = 1.942(3) Å, W—N(1) = 2.124(4) Å) are also those expected for normal single bonds. The dihapto hydroxylamido ligand thus appears to be functioning as a formal three-electron donor to the tungsten center. Both hydrogen atoms of the η^2-NH$_2$O group were found and fully refined, and one is clearly hydrogen-bonded to the BF$_4^-$ counterion.

A plausible mechanism for the transformation of 1 into 2 is presented in Scheme 2. Since compound 1 is unreactive when treated with HBF$_4$, it is unlikely that the incoming water molecule is functioning as a protonic acid.[13] Rather, it first functions as a Lewis base and displaces both acetonitrile ligands from the organometallic cation in a manner analogous to that

(9) Debad, J. D.; Legzdins, P.; Rettig, S. J.; Veltheer, J. E. *Organometallics* **1993**, *12*, 2714.
(10) For recent examples, see: (a) Alelyunas, Y. W.; Baenziger, N. C.; Bradley, P. K.; Jordan, R. F. *Organometallics* **1994**, *13*, 148. (b) Odenkirk, W.; Rheingold, A. L.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 6392. (c) Faller, J. W.; Ma, Y. *J. Am. Chem. Soc.* **1991**, *113*, 1579. (d) Brookhart, M.; Hauptman, E.; Lincoln, D. M. *J. Am. Chem. Soc.* **1992**, *114*, 10394.
(11) Crystals of $[Cp^*W(O)(\eta^2-NH_2O)(CH_2SiMe_3)]BF_4 \cdot 1/2CH_3C_6H_5$ are triclinic, $P\bar{1}$, $a = 10.528(1)$ Å, $b = 14.206(1)$ Å, $c = 8.3003(5)$ Å, $\alpha = 97.145(6)°$, $\beta = 104.896(7)°$, $\gamma = 77.855(9)°$, $Z = 2$. Data were corrected for 6.5% linear decay, absorption (empirical, azimuthal scans for three reflections), and Lorentz and polarization effects. The structure was solved by the Patterson method and was refined by full-matrix least-squares procedures to $R = 0.026$ and $R_w = 0.024$ for 4599 reflections with $I \geq 3\sigma(I)$. Complete details of the structure analysis are included as supplementary material.
(12) Moller, E. R.; Jorgensen, K. A. *J. Am. Chem. Soc.* **1993**, *115*, 11814.

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Communications to the Editor

Scheme 2
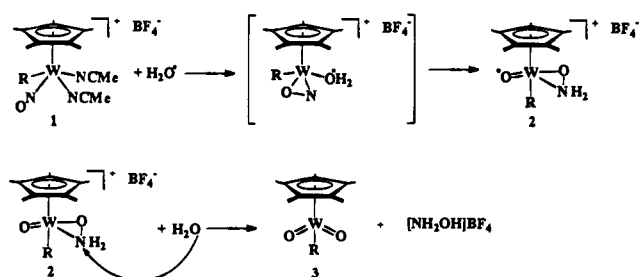
observed with PMe$_3$ (eq 1). This is followed by hydrogen atom transfer from the coordinated water to the nitrosyl nitrogen atom, a process that may be facilitated by the NO group adopting an η^2 mode of coordination to the electronically unsaturated metal center. Consistent with this mechanism is the fact that reaction of **1** with $^{18}OH_2$ yields the ^{18}O-labeled analogue of **2**, namely **2′**. The FAB$^+$ mass spectrum of the labeled complex indicates incorporation of only one ^{18}O atom. Furthermore, the IR spectrum of **2′** as a Nujol mull exhibits a shift of the $\nu_{W=O}$ band from 927 cm^{-1} in **2** to 902 cm^{-1} in **2′**, thereby indicating that it is the oxo oxygen in the organometallic cation of **2** that has its origins in the incoming water molecule (Scheme 2).

As indicated in Scheme 1, isolated **2** reacts with a further equivalent of water to form **3**, thereby completing the hydrolysis of the original NO ligand. Labeling studies with $^{18}OH_2$ do not provide further insight into this conversion's mechanism due to scrambling of the labels in the final product.[14] We believe, however, that the reaction proceeds via direct nucleophilic attack

by H$_2$O on the η^2-NH$_2$O ligand in the cation of **2** (as shown in Scheme 2), since the latter compound exhibits no tendency to form metal-centered adducts with typical Lewis bases. The isolated nitrogen-containing product, namely [NH$_4$]BF$_4$, probably results from decomposition of its less thermodynamically stable hydroxylammonium analogue, a process evidently facilitated by **3**.[15]

In summary, this study has demonstrated the first stepwise hydrolysis of a nitrosyl ligand in a cationic complex. Since other cationic aquonitrosyl complexes of later transition metals do not undergo similar transformations,[10b,16] the conclusion that logically follows is that the chemistry reported here is facilitated by the oxophilic nature of the metal center. Complexes containing such metal centers are therefore probably not suitable candidates for delivering NO intact to living systems. Studies are currently in progress to test the validity of this conclusion as well as to establish the generality of the chemistry reported in this communication for other nitrosyl complexes.

Supplementary Material Available: Experimental procedures and characterization data for all complexes and full details of the crystal structure analysis including associated tables for Cp*W(O)(η^2-ONH$_2$)(CH$_2$SiMe$_3$)BF$_4$ (**2**) (31 pages); tables of measured and calculated structure factor amplitudes for **2** (25 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(13) Other workers have previously effected the conversion of a terminal M−NO linkage to a M(η^2-ONH$_2$) grouping by employing H$^+$ (Wieghardt, K.; Quilitzsch, U. Z. *Naturforsch.* **1981**, *B36*, 683), N$_2$H$_4$ (Sellmann, D.; Seubert, B.; Moll, M.; Knoch, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1164), or electrochemical methods (Barley, M. H.; Takeuchi, K. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 5876).

(14) Full details of these experiments are provided in the supplementary material.

(15) Solutions of [H$_3$NOH]BF$_4$ in MeCN persist. However, solutions of [H$_3$NOH]BF$_4$ in MeCN containing **3** readily decompose. [H$_3$NOH]BF$_4$ is known to be less thermodynamically stable than [NH$_4$]BF$_4$, see: Shriver, D. F.; Atkins, P.; Langford, C. H. *Inorganic Chemistry*, 2nd ed.; Freeman: New York, 1994; p 301.

(16) Hauptman, E.; Brookhart, M.; Fagan, P. J.; Calabrese, J. C. *Organometallics* **1994**, *13*, 774.