

Cleavage of the Nitrous Oxide NN Bond by a Three-Coordinate Molybdenum(III) Complex

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Received January 13, 1995

Of great significance in both biological and synthetic systems are two-electron processes in which a divalent atom such as oxygen is completely transferred between two reaction partners.¹ Until now, the endogenous three-electron atom transfer process has been limited to examples of intermetallic nitrogen atom transfer as exemplified by the reaction $(\text{TTP})\text{Cr} + \text{N}=\text{Mn}(\text{TTP}) \rightarrow (\text{TTP})\text{Cr}=\text{N} + \text{Mn}(\text{TTP})$.² In the present work we establish a three-electron redox process in which a nitrogen atom from nitrous oxide is transferred to a molybdenum(III) coordination complex.

The complex $\text{Mo}(\text{NRAr})_3$ (**1**; R = $\text{C}(\text{CD}_3)_2\text{CH}_3$, Ar = 3,5- $\text{C}_6\text{H}_3\text{Me}_2$) was prepared for this work since d^3 **1** could conceivably engage in three-electron redox processes. Of the various possibilities, N-atom transfer was a particularly attractive target since stable nitrido complexes of the kind $\text{N}=\text{MoX}_3$ (X = alkyl,³ amide,⁴ or alkoxide⁵) are known. In a typical preparation, $\text{MoCl}_3(\text{THF})_3$ (4.164 mmol) and $\text{Li}(\text{NRAr})(\text{OEt}_2)$ (8.315 mmol) were added to 70 mL of cold (-100°C) ether, and the mixture was stirred for 2.5 h after warming to 28°C . The precipitated LiCl and excess $\text{MoCl}_3(\text{THF})_3$ were removed by filtration. Analysis of the filtrate by ^2H NMR spectroscopy showed only one major product, with a relatively sharp ($\Delta\nu_{1/2} = 35$ Hz) signal at 64.6 ppm corresponding to the ^2H -labeled *tert*-butyl groups in paramagnetic $\text{Mo}(\text{NRAr})_3$.⁸ The filtrate was concentrated and cooled to -35°C under an argon atmosphere to produce orange-red, crystalline $\text{Mo}(\text{NRAr})_3$ (mp $126\text{--}128^\circ\text{C}$, yield 70%).⁹ $\text{Mo}(\text{NRAr})_3$ (**1**) is extremely oxygen- and

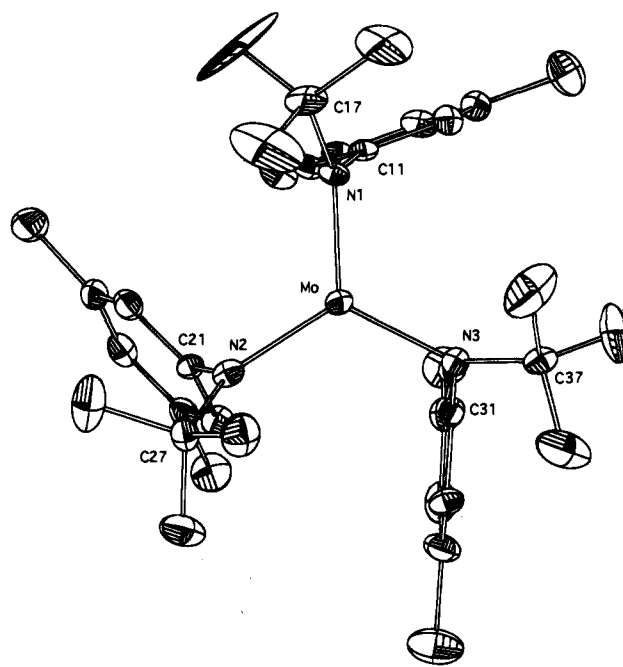


Figure 1. Structural diagram of $\text{Mo}(\text{NRAr})_3$ (**1**) with thermal ellipsoids at the 30% probability level. Selected bond distances (\AA): Mo–N(1), 1.960(7); Mo–N(2), 1.964(7); Mo–N(3), 1.977(7); N(1)–C(11), 1.42(1); N(1)–C(17), 1.50(1); N(2)–C(21), 1.44(1); N(2)–C(27), 1.49(1); N(3)–C(31), 1.43(1); N(3)–C(37), 1.49(1). Selected bond angles (deg): N(1)–Mo–N(2), 120.4(3); N(1)–Mo–N(3), 118.0(3); N(2)–Mo–N(3), 119.3(3); Mo–N(1)–C(11), 110.2(5); Mo–N(1)–C(17), 131.7(6); C(11)–N(1)–C(17), 118.1(7); Mo–N(2)–C(21), 111.5(5); Mo–N(2)–C(27), 130.7(6); C(21)–N(2)–C(27), 117.7(7); Mo–N(3)–C(31), 108.9(5); Mo–N(3)–C(37), 132.0(6); C(31)–N(3)–C(37), 119.0(7).

moisture-sensitive, but is stable for extended periods at 25°C in an inert atmosphere.

The monomeric nature of **1** was verified by X-ray crystallography (Figure 1).¹⁰ Compound **1** exhibits a trigonal-planar MoN_3 core with no Mo–C contacts shorter than 2.7 \AA . Ranging between 1.956(7) and 1.977(7) \AA , the Mo–N bond lengths are slightly shorter than the sum of Mo and N covalent radii (2.0 \AA). Each nitrogen atom exhibits a trigonal-planar geometry with large Mo–N– $\text{C}_{t\text{-Bu}}$ angles of $\sim 130^\circ$, small Mo–N– C_{aryl} angles of $\sim 110^\circ$, and normal $\text{C}_{t\text{-Bu}}$ –N– C_{aryl} angles of $\sim 120^\circ$. These values differ little from those for other metal complexes of the NRAr ligand.⁷ Given the approximate C_3 symmetry of **1**, an $a(n)^1e(n)^2$ electronic configuration is anticipated in the absence of significant out-of-plane N→Mo $p\pi\text{--}d\pi$ bonding. Magnetic studies reveal a μ_{eff} of 3.56 μ_{B} in benzene- d_6 at 23°C , indicating the presence of three unpaired electrons.¹¹ $\text{Mo}(\text{NRAr})_3$ (**1**) may be viewed as a monomeric relative of the ubiquitous $\text{X}_3\text{M}=\text{MX}_3$ (M = Mo, W; X = alkyl, amide, alkoxide) dimers.¹²

Exposure of degassed solutions of **1** (0.157 mmol, 20 mL of Et_2O , 25°C) to an excess (3–4 equiv) of electronic grade N_2O resulted in a color change from red-orange to amber over 5–10 min. Upon removal of all volatile material in vacuo, a crystalline residue with a 1:1 ratio of the terminal nitrido complex **2** and the nitrosyl complex **3** was obtained (Scheme

(10) Crystal data: $a = 13.736(4)\text{ \AA}$, $b = 15.948(4)\text{ \AA}$, $c = 16.187(7)\text{ \AA}$, $\alpha = 88.93(2)^\circ$, $\beta = 84.46(2)^\circ$, $\gamma = 88.35(2)^\circ$, $V = 3527(4)\text{ \AA}^3$, space group $P1$, $Z = 4$, mol wt = 642.90 for $\text{C}_{36}\text{H}_{36}\text{D}_{18}\text{N}_3\text{Mo}$, and $d(\text{calcd}) = 1.210\text{ g/cm}^3$; $R = 0.066$ and $R_w = 0.065$.

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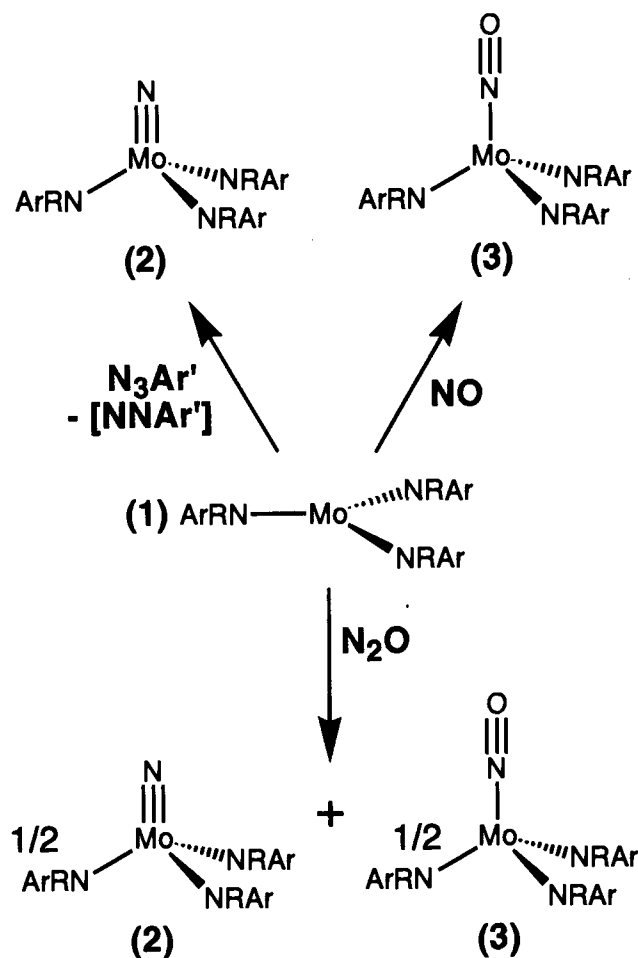
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(9) Anal. Calcd for $\text{C}_{36}\text{H}_{36}\text{D}_{18}\text{MoN}_3$: C, 67.26; H, 8.47; N, 6.54. Found: C, 67.61; H, 8.38; N, 6.40.

Scheme 1



1). Complete consumption of paramagnetic **1** was determined by the absence of its signature 2H NMR resonance at 64.6 ppm, and the 2H NMR spectrum of the mixture indicated only **2** and **3**. That diamagnetic **2** and **3** are the only significant products of the reaction between $Mo(NRAr)_3$ (**1**) and N_2O was also indicated by sharp 1H NMR resonances in spectra of the mixture and negligible residual paramagnetic susceptibility. Experiments are underway to determine whether or not this dissociation of N_2O requires two molybdenum centers.

Aryl azides were employed in an independent synthesis of nitride **2** (Scheme 1). Mesityl azide (0.997 mmol) reacted with **1** (0.686 mmol in 10 mL of Et_2O , 25 °C) to give pure amber **2** in 73% yield after one recrystallization (Et_2O , -35 °C).¹³ Preparation of $^{15}N \equiv Mo(NRAr)_3$ (**2**- ^{15}N) was accomplished similarly, employing selectively-labeled $^{15}NNN(p-C_6H_4Me)$.¹⁴ Incorporation of the label into **2**- ^{15}N was ascertained by comparison of high-resolution electron impact mass spectrometry data for the complex with those for unlabeled **2**. A strong infrared band at 1042 cm^{-1} for unlabeled **2** shifted to 1014 cm^{-1} upon incorporation of the label; this spectroscopic signature is characteristic of the terminal nitride functionality ($Mo \equiv N$).¹⁵ The relative instability of $NNAr$ radicals compared to nitric

(13) Anal. Calcd for $C_{36}H_{36}D_{18}MoN_4$: C, 65.82; H, 8.29; N, 8.53. Found: C, 66.14; H, 7.90; N, 8.45.

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oxide accounts for production of $N \equiv Mo(NRAr)_3$ (**2**) as the only molybdenum-containing entity in reactions between $Mo(NRAr)_3$ (**1**) and aryl azides.¹⁶

Nitrosyl **3** was synthesized independently by exposure of **1** (0.547 mmol, 25 mL of Et_2O , 25 °C) to 1.5 equiv of nitric oxide (Scheme 1). This resulted in an immediate color change from red-orange to brown-yellow. Subsequent removal of all volatile material left a yellow crystalline residue consisting of pure **3** (verified by 1H and 2H NMR analysis).¹⁷ We ascribe an infrared band at 1604 cm^{-1} to ν_{NO} for the nitrosyl complex, the low value indicating that $Mo(NRAr)_3$ is a strong π donor. This synthesis of **3** can be compared to the preparation of monomeric $(ON)Mo(OR)_3(py)_2$ ($R = SiMe_2-t-Bu$, $py =$ pyridine) by scission of the $Mo \equiv Mo$ triple bond in $Mo_2(OR)_6$ upon NO exposure in the presence of pyridine.¹⁸ It is also directly related to the classic synthesis of $(ON)Cr[N(SiMe_3)_2]_3$ by NO addition to monomeric $Cr[N(SiMe_3)_2]_3$.¹⁹

The independent syntheses of nitride **2** and nitrosyl **3** serve to cement our interpretation of the nitrous oxide NN cleavage reaction promoted by $Mo(NRAr)_3$ (**1**). The reaction stands in stark contrast to previous metal-mediated cleavage reactions of N_2O , in which nitrous oxide is a source of an oxygen atom and molecular nitrogen.²⁰ Scant precedent exists for cleavage of the nitrous oxide NN bond aside from its reaction with excited atomic oxygen (1D), a reaction that is thought to be the sole source of stratospheric nitric oxide.²¹

Acknowledgment. For financial support, C.C.C. thanks the MIT Department of Chemistry, C.E.L. thanks the MIT Undergraduate Research Opportunities Program, and J.D.P. thanks the CWRU Department of Chemistry. For stimulating discussions, C.C.C. thanks Professors S. L. Buchwald, A. Davison, M. L. H. Green, G. L. Hillhouse, S. J. Lippard, R. R. Schrock, and P. T. Wolczanski.

Supplementary Material Available: Experimental details for the X-ray structure of $Mo(NRAr)_3$, tables of positional parameters and bond lengths and angles for $Mo(NRAr)_3$, and preparative details for all new compounds (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(17) **3** was isolated in 78% yield after recrystallization (Et_2O , -35 °C). Anal. Calcd for $C_{36}H_{36}D_{18}MoN_4O$: C, 64.26; H, 8.09; N, 8.33. Found: C, 64.51; H, 8.15; N, 8.27.

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