

“Fixation” of Dinitrogen by Molybdenum and the Formation of a Trigonal Planar Iron–Tris[molybdenum(dinitrogen)] Complex

Myra B. O'Donoghue, Nadia C. Zanetti,
William M. Davis, and Richard R. Schrock*

Department of Chemistry, 6-331
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received November 4, 1996

We recently showed that $[\text{N}_3\text{N}_F]\text{MoCl}$ ($[\text{N}_3\text{N}_F]^{3-} = [(\text{C}_6\text{F}_5\text{NCH}_2\text{CH}_2)_3\text{N}]^{3-}$) could be reduced with sodium under dinitrogen by 2e to give the sodium “diazenido” complex $[\text{N}_3\text{N}_F]\text{Mo}-\text{N}=\text{N}-\text{Na}(\text{ether})_x$ and by 1e to give the bimetallic diazenido complex $[\text{N}_3\text{N}_F]\text{Mo}-\text{N}=\text{N}-\text{Mo}[\text{N}_3\text{N}_F]$.¹ It also has been shown that the reaction between $\text{MoCl}_3(\text{THF})_3$ and $\text{Li}_3[(t\text{-BuMe}_2\text{SiNCH}_2\text{CH}_2)_3\text{N}]$ yields the crystallographically characterized dimolybdenum diazenido complex $\{[(t\text{-BuMe}_2\text{SiNCH}_2\text{CH}_2)_3\text{N}]\text{Mo}\}_2(\text{N}_2)$ in low yield,² and that trigonal planar complexes such as $\text{Mo}[\text{N}(t\text{-Bu})(3,5\text{-C}_6\text{H}_3\text{Me}_2)]_3$ react with dinitrogen to yield first the dimolybdenum diazenido complexes $\{[\text{N}(t\text{-Bu})(3,5\text{-C}_6\text{H}_3\text{Me}_2)]_3\text{Mo}\}_2(\text{N}_2)$ and then, in a symmetrical cleavage reaction, 2 equiv of the nitrido complex $[\text{N}(t\text{-Bu})(3,5\text{-C}_6\text{H}_3\text{Me}_2)]_3\text{Mo}\equiv\text{N}$.^{3,4} We became interested in determining whether the as yet unobserved trigonal monopyramidal complex “[$\text{N}_3\text{N}]\text{Mo}” ($[\text{N}_3\text{N}]^{3-} = [(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]^{3-}$), an analog of known first-row complexes containing Ti through Fe,⁵ could be prepared by reducing some suitable $[\text{N}_3\text{N}]\text{MoX}$ species, and whether d^3 $[\text{N}_3\text{N}]\text{Mo}$ would bind dinitrogen.$

Reduction of $[\text{N}_3\text{N}]\text{MoCl}$ in THF with an excess of magnesium powder under dinitrogen (1 atm) proceeds smoothly over a period of 17 h to give two diamagnetic products whose TMS resonances are in a ratio of ~1:3. Addition of 1,4-dioxane to the mixture (in order to remove MgCl_2) allows one of these products to be isolated from diethyl ether in moderate yield (60%). An X-ray study⁶ revealed the product to be the $\{\text{Mg}(\text{THF})_2\}^{2+}$ salt of the $\{[\text{N}_3\text{N}]\text{Mo}(\text{N}_2)\}^-$ ion (Figure 1). On the basis of bond distances and angles in the $\text{Mo}-\text{N}-\text{N}$ portion of $[\text{N}_3\text{N}_F]\text{Mo}-\text{N}=\text{N}-\text{Si}(i\text{-Pr})_3$ ¹ and $\{[(t\text{-BuMe}_2\text{SiNCH}_2\text{CH}_2)_3\text{N}]\text{Mo}\}_2(\text{N}_2)$,² the product is best described as the diazenido species $\{[\text{N}_3\text{N}]\text{Mo}-\text{N}=\text{N}\}_2\text{Mg}(\text{THF})_2$ (**1**). The IR spectrum of **1** shows a ν_{NN} stretch at 1719 cm^{-1} (in THF) that shifts to 1662 cm^{-1} in $\mathbf{1}\text{-}^{15}\text{N}_2$, while the ^{15}N NMR spectrum of $\mathbf{1}\text{-}^{15}\text{N}_2$ in C_6D_6 shows two resonances at 377.0 and 304.4 ppm ($J_{\text{NN}} = 12\text{ Hz}$). We speculate that the other diamagnetic product, whose NMR and IR spectra are similar to those of **1**, and which disappears upon addition of dioxane, is $\{[\text{N}_3\text{N}]\text{Mo}-\text{N}=\text{N}\}\text{MgCl}(\text{THF})_2$.

The reaction between **1** and FeCl_2 in THF at -20°C produces a product (**2**) that can be isolated from a pentane extract of the crude reaction product as plum-colored, paramagnetic crystals. An X-ray study⁷ revealed **2** to be $\{[\text{N}_3\text{N}]\text{Mo}(\text{N}_2)\}_3\text{Fe}$ (Figure 2), in which the core of the complex has trigonal planar

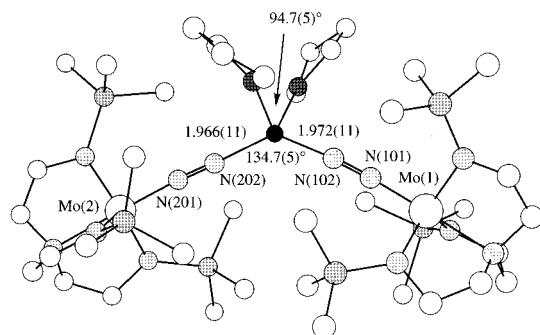


Figure 1. Structure of $\{[\text{N}_3\text{N}]\text{Mo}(\text{N}_2)\}_2\text{Mg}(\text{THF})_2$: $\text{Mo}(1)-\text{N}(101) = 1.877(11)\text{ \AA}$, $\text{N}(101)-\text{N}(102) = 1.164(13)\text{ \AA}$, $\text{Mo}(2)-\text{N}(201) = 1.840(10)\text{ \AA}$, $\text{N}(201)-\text{N}(202) = 1.195(13)\text{ \AA}$, $\text{Mo}(1)-\text{N}(101)-\text{N}(102) = 175.7(9)^\circ$, $\text{Mo}(2)-\text{N}(201)-\text{N}(202) = 177.0(9)^\circ$, $\text{Mg}-\text{N}(102)-\text{N}(101) = 178.2(9)^\circ$, $\text{Mg}-\text{N}(202)-\text{N}(201) = 166.6(9)^\circ$.

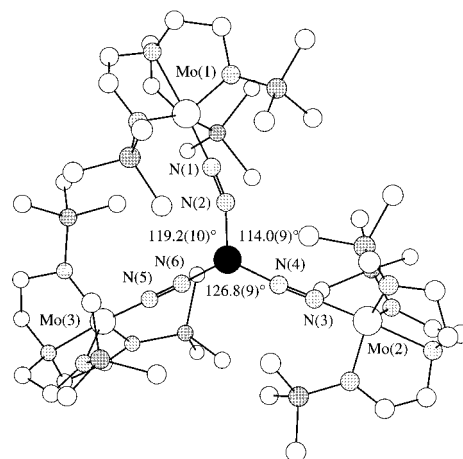
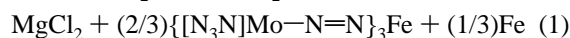
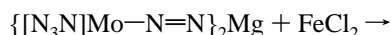


Figure 2. Structure of $\{[\text{N}_3\text{N}]\text{Mo}(\text{N}_2)\}_3\text{Fe}$: $\text{Mo}(1)-\text{N}(1)-\text{N}(2) = 174(2)^\circ$, $\text{Mo}(2)-\text{N}(3)-\text{N}(4) = 175(2)^\circ$, $\text{Mo}(3)-\text{N}(5)-\text{N}(6) = 179(2)^\circ$, $\text{Fe}-\text{N}(2)-\text{N}(1) = 156(2)^\circ$, $\text{Fe}-\text{N}(4)-\text{N}(3) = 175(2)^\circ$, $\text{Fe}-\text{N}(6)-\text{N}(5) = 176(2)^\circ$, $\text{Fe}-\text{N}(2) = 1.86(2)\text{ \AA}$, $\text{Fe}-\text{N}(4) = 1.84(2)\text{ \AA}$, $\text{Fe}-\text{N}(6) = 1.82(2)\text{ \AA}$, $\text{Mo}(1)-\text{N}(1) = 1.86(2)\text{ \AA}$, $\text{Mo}(2)-\text{N}(3) = 1.81(2)\text{ \AA}$, $\text{Mo}(3)-\text{N}(5) = 1.82(2)\text{ \AA}$, $\text{N}(1)-\text{N}(2) = 1.20(3)\text{ \AA}$, $\text{N}(3)-\text{N}(4) = 1.25(2)\text{ \AA}$, $\text{N}(5)-\text{N}(6) = 1.27(2)\text{ \AA}$.

coordination geometry. One of the $\text{Mo}-\text{N}-\text{N}-\text{Fe}$ linkages is significantly bent at the nitrogen bound to iron ($\text{Fe}-\text{N}(2)-\text{N}(1) = 156(2)^\circ$), while the other two are essentially linear, characteristic of diazenido linkages. In view of the relatively large errors we cannot say that distances within the $[\text{N}_3\text{N}]\text{Mo}(\text{N}_2)$ units are statistically different. Since a black magnetic solid (presumably iron) is formed in this reaction, the “ideal” stoichiometry would be that shown in eq 1. SQUID magnetic



susceptibility data on solid **2** can be fit to a Curie–Weiss equation ($\chi = 8/(T - \theta) + C$) over the temperature range 5–300 K to give $\mu = 6.03(3)\mu_{\text{B}}$, $\theta = 0.74(5)\text{ K}$, and $C = -0.003(1)$. An IR spectrum of **2** in Nujol shows primarily an absorption at 1703 cm^{-1} , although weaker absorptions are present between 1600 and 1703 cm^{-1} . The visible spectrum of **2** in pentane shows an intense absorption at 516 nm ($\epsilon = 22\,800$).

The reaction shown in eq 1 is actually relatively complex. Two other products appear to be formed in varying amounts,

(1) Kol, M.; Schrock, R. R.; Kempe, R.; Davis, W. M. *J. Am. Chem. Soc.* **1994**, *116*, 4382.

(2) Shih, K.-Y.; Schrock, R. R.; Kempe, R. *J. Am. Chem. Soc.* **1994**, *116*, 8804.

(3) Laplaza, C. E.; Johnson, M. J. A.; Peters, J. C.; Odom, A. L.; Kim, E.; Cummins, C. C.; George, G. N.; Pickering, I. J. *J. Am. Chem. Soc.* **1996**, *118*, 8623.

(4) Laplaza, C. E.; Cummins, C. C. *Science* **1995**, *268*, 861.

(5) Cummins, C. C.; Lee, J.; Schrock, R. R.; Davis, W. M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1501.

(6) Empirical formula $\text{C}_{40}\text{H}_{100}\text{MgMo}_2\text{N}_{12}\text{O}_{25}\text{Si}_6$, FW = 1174.01, space group $P1$, $a = 10.1540(2)\text{ \AA}$, $b = 16.4300(3)\text{ \AA}$, $c = 19.8388(5)\text{ \AA}$, $\alpha = 89.4350(10)^\circ$, $\beta = 84.1230(10)^\circ$, $\gamma = 82.19^\circ$, $V = 3261.77(12)\text{ \AA}^3$, $Z = 2$, $D_{\text{calcd}} = 1.193\text{ Mg/m}^3$, $R1$ (all data) = 0.1018. The unit cell contains 0.5 molecule of diethyl ether.

(7) Empirical formula $\text{C}_{46.25}\text{H}_{120}\text{FeMo}_3\text{N}_{18}\text{Si}_9$, FW = 1525.02, space group $P1$, $a = 10.4926(2)\text{ \AA}$, $b = 14.33000(10)\text{ \AA}$, $c = 26.8775(6)\text{ \AA}$, $\alpha = 97.2850(10)^\circ$, $\beta = 93.2670(10)^\circ$, $\gamma = 90.163(2)^\circ$, $V = 4001.93(12)\text{ \AA}^3$, $Z = 2$, $D_{\text{calcd}} = 1.262\text{ Mg/m}^3$, $R1$ (all data) = 0.1896. The unit cell contains 0.25 molecule of pentane.

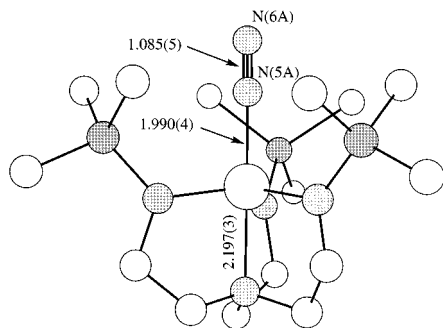
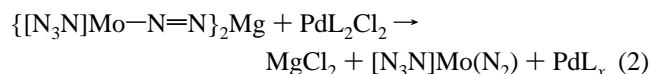


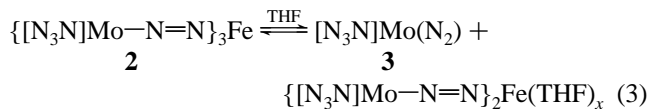
Figure 3. Structure of $[\text{N}_3\text{N}]\text{Mo}(\text{N}_2)$: $\text{Mo}-\text{N}(5\text{A})-\text{N}(6\text{A}) = 179.1(4)^\circ$.

depending on subtle differences (including workup solvent and procedure) from one reaction to another. $[\text{N}_3\text{N}]\text{Mo}(\text{N}_2)$ (**3**) is one of the two other products (according to IR and NMR spectra of product mixtures), but it cannot be isolated in good yield by this method. The best method of preparing **3** that we have found so far is to add $\text{PdCl}_2(\text{PPh}_3)_2$ to **1** in THF (eq 2; $\text{L} = \text{PPh}_3$; x



unknown). **3** can be isolated as deep burgundy-colored crystals from this reaction in >80% yield. An X-ray study⁸ revealed two molecules in the unit cell that are statistically identical; one of them is shown in Figure 3. **3** contains an “end-on” dinitrogen ligand^{9,10} with $\text{Mo}-\text{N}(5\text{A}) = 1.990(4) \text{ \AA}$, $\text{N}(5\text{A})-\text{N}(6\text{A}) = 1.085(5) \text{ \AA}$, and $\text{Mo}-\text{N}(5\text{A})-\text{N}(6\text{A}) = 179.1(4)^\circ$. Other distances and angles are typical of $[\text{N}_3\text{N}]^{3-}$ ligands of this general type.¹¹ The IR spectrum of **3** in pentane reveals that $\nu_{\text{NN}} = 1934 \text{ cm}^{-1}$ (1870 cm^{-1} for $3\text{-}^{15}\text{N}_2$), while in THF $\nu_{\text{NN}} = 1917 \text{ cm}^{-1}$. SQUID magnetic susceptibility measurements on solid **3** produce data that can be fit to the Curie–Weiss law over the temperature range 5–300 K ($\mu = 1.77(1) \mu_{\text{B}}$, $\theta = -0.22(2) \text{ K}$), consistent with one unpaired electron being present. Reduction of **3** in THF with an excess of magnesium powder gives **1** cleanly. We were surprised to find that **3** is stable, as the monomeric complex formed by addition of dinitrogen to $\text{Mo}[\text{N}(t\text{-Bu})(3,5\text{-C}_6\text{H}_3\text{Me}_2)]_3$ has not yet been observed,¹² even though it can be trapped to form $\{[\text{N}(t\text{-Bu})(3,5\text{-C}_6\text{H}_3\text{Me}_2)]_3\text{Mo}\}_2(\text{N}_2)$.³ We speculate that the presence of the nitrogen donor in $[\text{N}_3\text{N}]\text{Mo}$ destabilizes d_{z^2} more than d_{xz} or d_{yz} and therefore stabilizes the low spin configuration (d_{z^2})⁰-(e)³ (where e is the d_{xz}/d_{yz} set), a configuration that would appear to be optimal to bind dinitrogen.

The third species that is often present as a product of the reaction in eq 1 has characteristic, broad, as yet unidentified resonances in its proton NMR spectrum. It can be shown by NMR that this third species reacts with **3** to give free THF and **2**, and that **2** reacts with THF to give this third species and **3** (eq 3). Therefore, we speculate that the third species is a THF



adduct of “ $\{[\text{N}_3\text{N}]\text{Mo}-\text{N}=\text{N}\}_2\text{Fe}$ ”. All three species appear to be thermally stable and in ready equilibrium, according to NMR studies. These proposals are supported by reports in the literature concerning the behavior of several two-coordinate¹³ and three-coordinate¹⁴ iron(II) complexes.¹⁵ All of our observations so far suggest that $\{[\text{N}_3\text{N}]\text{Mo}-\text{N}=\text{N}\}_3\text{Fe}$ is best formulated in the solid state as an iron(II) species containing two $\{[\text{N}_3\text{N}]\text{Mo}-\text{N}=\text{N}\}^-$ ligands and one $[\text{N}_3\text{N}]\text{Mo}(\text{N}_2)$ ligand, and that, in the presence of THF, $[\text{N}_3\text{N}]\text{Mo}(\text{N}_2)$ is lost and $\{[\text{N}_3\text{N}]\text{Mo}-\text{N}=\text{N}\}_2\text{Fe}(\text{THF})_x$ is formed reversibly. Since two-coordinate complexes such as $\text{Fe}(2,4,6\text{-C}_6\text{H}_2\text{-}t\text{-Bu}_3)_2$ ^{16,17} are known, we cannot yet exclude the possibility that solvent-free, monomeric $\{[\text{N}_3\text{N}]\text{Mo}-\text{N}=\text{N}\}_2\text{Fe}$ might be accessible.

Crystallographically characterized heterobimetallic complexes containing bridging dinitrogen ligands are rare.^{9,18} To our knowledge **2** is the only reported example of a structurally characterized iron–molybdenum dinitrogen complex, a type of species that perhaps is especially relevant in view of the structure of Fe/Mo nitrogenase in one resting state.^{19–21} However, compound **2** is remarkable for other reasons: (i) trigonal coordination about iron is a type of geometry that is relatively rare in general,^{13,14,20,22} (ii) the three ligands around iron are all formed from dinitrogen; and (iii) the dinitrogen-containing ligands exist in both “anionic” and “neutral” forms.

We expect that other $\{[\text{N}_3\text{N}]\text{Mo}(\text{N}_2)\}_3\text{M}$ species can be prepared, as well as other types of complexes that contain $\{[\text{tri-amidoamine}]\text{Mo}(\text{N}_2)\}^-$ or $[\text{tri-amidoamine}]\text{Mo}(\text{N}_2)$ “ligands”, including those in which the triamidoamine ligand is not $[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]^{3-}$.¹¹ We will be especially interested in reactions in which the “dinitrogen” within the ligand becomes susceptible to further reactions at one or both of the nitrogen atoms, especially reactions that lead to N–N cleavage and further reduction.

Acknowledgment. R.R.S. is grateful to the National Institutes of Health (Grant GM 31978) for research support, while N.C.Z. thanks Ciba-Geigy for postdoctoral support through a Ciba-Geigy Jubiläums Stiftung. R.R.S. also thanks the National Science Foundation for funds to help purchase a departmental Siemens SMART/CCD diffractometer. M.B.O'D. thanks Scott W. Seidel for help with SQUID measurements.

Supporting Information Available: Experimental details, crystal data, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **1**, **2**, and **3** (32 pages). See any current masthead page for ordering and Internet access instructions. This information is also available in CIF format.

JA963822Y

(13) Power, P. P. *Chemtracts-Inorg. Chem.* **1994**, *6*, 181.

(14) Eller, P. G.; Bradley, D. C.; Hursthouse, M. B.; Meek, D. W. *Coord. Chem. Rev.* **1977**, *24*, 1.

(15) Stokes, S. L.; Davis, W. M.; Odom, A. L.; Cummins, C. C. *Organometallics* **1996**, *15*, 4521.

(16) Müller, H.; Seidel, W.; Görls, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *36*, 325.

(17) Wehmschulte, R. J.; Power, P. P. *Organometallics* **1995**, *14*, 3264.

(18) Mizobe, Y.; Yokobayashi, Y.; Oshita, H.; Takahashi, T.; Hidai, M. *Organometallics* **1994**, *13*, 3764.

(19) Kim, J.; Rees, D. C. *Nature* **1992**, *360*, 553.

(20) Kim, J.; Woo, D.; Rees, D. C. *Biochemistry* **1993**, *32*, 7104.

(21) Chen, J.; Christiansen, J.; Campobasso, N.; Bolin, J. T.; Tittsworth, R. C.; Hales, B. J.; Rehr, J. J.; Cramer, S. P. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1592.

(22) Power, P. P. *Comments Inorg. Chem.* **1989**, *8*, 177.

(8) Empirical formula $\text{C}_{15}\text{H}_{39}\text{MoN}_6\text{Si}_3$, FW = 483.73, space group *Pbca*, $a = 17.0164(2) \text{ \AA}$, $b = 16.9922(3) \text{ \AA}$, $c = 34.251(6) \text{ \AA}$, $V = 9903.7(2) \text{ \AA}^3$, $Z = 16$, $D_{\text{calcd}} = 1.298 \text{ Mg/m}^3$, $R1$ (all data) = 0.0554.

(9) Hidai, M.; Mizobe, Y. *Chem. Rev.* **1995**, *95*, 1115.

(10) Richards, R. L. *Chem. Br.* **1988**, *24*, 133.

(11) Schrock, R. R. *Acc. Chem. Res.* **1997**, *90*, 9.

(12) Cummins, C. C. Private communication.