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Derivatization of Dinitrogen by Molybdenum in Triamidoamine Complexes

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The reduction of $[N_3N]MoCl$ by an excess of Mg powder in THF under dinitrogen (1 atm) yields the diazenido species $\{[N_3N]Mo{-}N{=}N\}_2Mg(THF)_2$ (**1**), which reacts with $MCl_2(PPh_3)_2$ (M = Ni or Pd) or $ZnCl_2$ to yield $[N_3N]Mo(N_2)$ (**2**). Heating toluene solutions of **2** under dinitrogen yields the homobimetallic dinitrogen complex $[N_3N]Mo{-}N{=}N{-}Mo[N_3N]$ (**3**). Derivatization of dinitrogen is achieved by reaction of **1** with (TMS)Cl to yield the diazenido complex $[N_3N]Mo{-}N{=}N{-}TMS$ (**4**). **4** reacts with an excess of MeOTf to give two products, the dimethyl hydrazido complex $\{[N(CH_2CH_2NSiMe_3)_2(CH_2CH_2NCH_3)]Mo{=}N{-}NMe_2\}OTf$ (**5**) and the diazenido complex $\{[(Me_3SiNCH_2CH_2)_2NCH_2CH_2NMe_2]Mo{-}N{=}NSiMe_3\}OTf$ (**6**). Both **5** and **6** react readily with MeMgCl to yield products arising from methylation at molybdenum, $[N(CH_2CH_2NSiMe_3)_2(CH_2CH_2NMe_2)]Mo(CH_3)(N_2\text{-}TMS)$ (**7**) and $[N(CH_2CH_2NSiMe_3)_2(CH_2CH_2NMe)]Mo(CH_3)(NNMe_2)$ (**8**), respectively. In **7**, the dimethylamino group is not bound to the metal. Compound **8** is thermally unstable, decomposing via N−N bond cleavage to yield the nitrido complex $[(Me_3SiNCH_2CH_2)_2N(CH_2CH_2NMe)]Mo{\equiv}N$ (**9**). X-ray studies are reported for compounds **1**, **2**, **5**, **6**, and **7**.

Introduction

Ligands of the type $[(RNCH_2CH_2)_3N]^{3-}$ can bind to a variety of main group elements[1] or transition metals[2] in oxidation state 3+ or higher. When R is a sterically bulky group such as trimethylsilyl, we have had the opportunity to study rarely observed complexes and decomposition pathways. Examples include a tantalum phosphinidene complex,[3] molybdenum and tungsten terminal phosphido and arsenido complexes,[4] and a demonstration that certain molybdenum and tungsten alkyl complexes decompose via α-elimination by as much as 6 orders of magnitude faster than via β-elimination.[5,6] The first reported uranium(III) complex that contains molecular nitrogen also contains a silyl-substituted triamidoamine ligand.[7]

Triamidoamine ligands usually bind to transition metals in a tetradentate manner, thus creating a sterically protected, 3-fold symmetric pocket in which to bind small molecules. We have been interested in exploiting the sterically protected apical site and the orbital arrangement in this pocket to bind and activate dinitrogen. The orbitals available in the pocket consist of a σ orbital (approximately d_{z^2}) and two degenerate π orbitals (approximately d_{xz} and d_{yz}). Therefore triamidoamine complexes would appear to be well-suited to bind dinitrogen if the energies of the σ and π orbitals on the metal and dinitrogen are relatively well-matched. Binding of dinitrogen appears to be facile since $[N_3N_F]MoOTf$ ($[N_3N_F]^{3-} = [(C_6F_5NCH_2CH_2)_3N]^{3-}$) can be reduced with sodium under dinitrogen by two electrons to give the sodium "diazenido" complex $[N_3N_F]Mo{-}N{=}N{-}Na(ether)_x$ and by one electron per Mo to give the bimetallic "diazenido" complex $[N_3N_F]Mo{-}N{=}N{-}Mo[N_3N_F]$.[8] Furthermore, a neutral Re(III) complex $[N_3N_F]Re(N_2)$, can be isolated.[9] Using $[N_3N]MoCl$ ($[N_3N]^{3-} = [(Me_3SiNCH_2CH_2)_3N]^{3-}$) as a starting material, we recently showed that $[N_3N]MoCl$ could be reduced by magnesium to give the dinitrogen-containing complex $\{[N_3N]Mo{-}N{=}N\}_2Mg(THF)_2$ (**1**).[10] This diazenido complex has proved to be a versatile starting material for $[N_3N]Mo$ dinitrogen chemistry. We have used **1** for two purposes, to synthesize a variety of heterobimetallic dinitrogen complexes[11] and to provide an entry into the derivatization of dinitrogen at a single metal center. This paper details our progress in the reduction and functionalization of dinitrogen at a $[N_3N]Mo$ site.

Results

Activation of Dinitrogen. A solution of $[N_3N]MoCl$ in THF is reduced cleanly by magnesium powder under dinitrogen to give a mixture of two diamagnetic products in a ratio of 1:3, according to their respective $[N_3N]^{3-}$ ligand TMS resonances in proton NMR spectra. Addition of 1,4-dioxane to a toluene solution of the mixture allows one of the products to be isolated in high yield (90%). The ^1H NMR spectrum of this product, $\{[N_3N]Mo{-}N{=}N\}_2Mg(THF)_2$ (**1**; eq 1), consists of a single

$$2[N_3N]MoCl \xrightarrow[\text{1,4-dioxane}]{\text{Mg, THF, }N_2} \underset{\mathbf{1}}{\{[N_3N]Mo{-}N{=}N\}_2Mg(THF)_2} + MgCl_2(dioxane) \quad (1)$$

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Table 1. Crystallographic Data for **1**, **2**, **5**, **6**, and **7**[a]

	1	**2**	**5**	**6**	**7**
formula	$C_{40}H_{99}MgMo_2N_{12}O_{2.5}Si_6$	$C_{15}H_{39}MoN_6Si_3$	$C_{16}H_{39}F_3MoN_6O_3SSi_2$	$C_{18}H_{45}F_3MoN_6O_3SSi_3$	$C_{18}H_{49}MoN_6Si_3$
fw	1173.00	483.73	604.71	662.87	529.84
space group	$P\bar{1}$	*Pbca*	*Pbca*	*Pbca*	$P2_1/c$
a (Å)	10.1540(2)	17.0164(2)	14.723(3)	15.610(3)	10.235(3)
b (Å)	16.4300(3)	16.9922(3)	14.417(3)	12.478(3)	14.315(7)
c (Å)	19.8388(5)	34.251	26.243(4)	34.085(5)	20.277(7)
α (deg)	89.4350(10)	90	90	90	90
β (deg)	84.1230(10)	90	90	90	103.80(2)
γ (deg)	82.19	90	90	90	90
V ($Å^3$)	3261.77(12)	9903.7(2)	5571(2)	6639(2)	2885(2)
Z	2	16	8	2	4
D_{calc} ($Mg/m^{3)}$	1.193	1.298	1.442	1.326	1.220
μ (mm^{-1})	0.543	0.686	0.679	0.611	0.594
$R\ [I > 2\sigma(I)]^b$	0.0907	0.0459	0.0851	0.0452	0.0251
R_w (all data)[c]	0.2435	0.1060	0.1589	0.1609	0.0750

[a] All structures were solved on a Siemens SMART/CCD diffractometer at 183 K using 0.710 73 Å Mo Kα radiation. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

TMS resonance and a pair of triplets for the methylene protons on the ligand backbone, characteristic of compounds in which the $[N_3N]Mo$ portion of **1** is C_3-symmetric.[2] The ^1H NMR spectrum also showed there to be one molecule of THF present per $[N_3N]Mo$ unit. If the compound is prepared under $^{15}N_2$, the ^{15}N NMR spectrum in C_6D_6 consists of a pair of doublets at 377.0 and 304.4 ppm ($J_{NN} = 12$ Hz) corresponding to N_α and N_β of **1**-$^{15}N_2$ respectively.[12] The IR spectrum of **1** has a strong broad stretch at 1719 cm^{-1} that shifts to 1662 cm^{-1} in **1**-$^{15}N_2$. The other product present in approximately 25% yield before the addition of dioxane is proposed to be $\{[N_3N]Mo{-}N{=}N\}MgCl(THF)_2$, and the yield of **1** is believed to be raised to 90% (isolated) as a consequence of a Schlenk-like equilibrium that produces **1** and $\{MgCl_2(dioxane)\}_x$. Further support for this suggestion comes from the observation that addition of Me_3SiCl to a mixture of **1** and $\{[N_3N]Mo{-}N{=}N\}MgCl(THF)_2$ (before addition of dioxane) yielded $[N_3N]Mo{-}N{=}N{-}SiMe_3$ (see below) as the sole product in high yield. The reduction that yields **1** is unaffected by the presence of excess magnesium powder. Sodium amalgam and sodium naphthalenide have not yielded reproducible results, although there is evidence (see below) that sodium naphthalenide does yield the sodium analogue of **1**, $\{[N_3N]Mo(N_2)\}Na$, in situ (cf. $\{[(C_6F_5NCH_2CH_2)_3N]Mo(N_2)Na(ether)_x{}^8\}$).

A toluene-d_8 solution of **1** shows no signs of decomposition upon being heated to 82 °C under dinitrogen for 24 h. Furthermore, a solution of **1** stored at room temperature under dinitrogen remained unchanged over a period of 2 weeks (according to ^1H NMR data). However, **1** apparently decomposes rapidly in the solid state when exposed to high vacuum. No products of this decomposition reaction could be identified. Loss of dinitrogen would seem to be the significant step that leads to decomposition in the solid state in vacuo.

Crystals of **1** suitable for an X-ray study were grown from saturated diethyl ether solutions at −20 °C; half a molecule of ether was found in the unit cell. Crystallographic data are given in Table 1. The molecular structure of **1**, along with the atom-labeling scheme, is shown in Figure 1, while selected bond lengths and bond angles are listed in Table 2. **1** is composed of two $\{[N_3N]Mo(N_2)\}^-$ units bound to pseudotetrahedral magnesium, the coordination sphere being completed by two molecules of THF. The N−Mg−N bond angle opens to 134.7° in order to accommodate the sterically bulky $\{[N_3N]Mo(N_2)\}^-$ "ligands", while the O(1)−Mg−O(2) angle closes to 94.7(5)°. The Mo−N−N−Mg linkages are essentially linear. The N−N bond lengths (1.164(13) and 1.195(13) Å) are indicative of some reduction of the dinitrogen ligands in **1** compared with free dinitrogen (1.098 Å) and are consistent with the formulation of **1** as a diazenido complex of Mo(IV).[13−17] The N−N distance in **1** should be compared with the N−N bond distance in other diazenido-like substituted TREN complexes, e.g., $[(C_6F_5NCH_2CH_2)_3N]Mo{-}N{=}N{-}Si(i\text{-}Pr)_3$ (1.20(1) Å)[8] or $\{[(t\text{-}BuMe_2SiNCH_2CH_2)_3N]Mo\}_2(\mu\text{-}N_2)$ (1.20(2) Å).[18] We have found that the twisting of a given TMS group out of the $N_{ax}{-}M{-}N_{eq}$ plane and the resulting decrease in the $N_{ax}{-}M{-}N_{eq}{-}Si$ dihedral angle are a useful measure of the degree of steric strain in the pocket in $[N_3N]$ complexes. For example, in $[N_3N]Mo$(cyclohexyl), this angle was found to range from 129 to 136° as a consequence of the steric interaction between the cyclohexyl ring and the TMS groups of the ligand.[5] In **1** the $N_{ax}{-}M{-}N_{eq}{-}Si$ angles are uniformly near 180°, consistent with there being little steric pressure in the pocket.

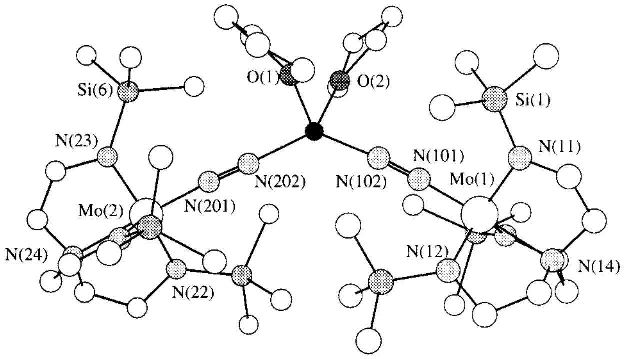

Figure 1. View of the structure of $\{[N_3N]Mo(N_2)\}_2Mg(THF)_2$ (**1**).

Paramagnetic $[N_3N]Mo(N_2)$ (**2**) is formally the one-electron-oxidation product of $\{[N_3N]Mo(N_2)\}^-$. It has been isolated in moderate yield upon reduction of $[N_3N]MoCl$ in THF by sodium naphthalenide. Unfortunately, this reaction is neither clean nor reproducible. The reaction appears to be sensitive to temperature, efficiency of stirring, and rate of addition of the reductant.

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Table 2. Selected Bond Lengths and Bond Angles for **1**

Bond Distances (Å)					
Mo(1)–N(101)	1.876(11)	Mo(2)–N(201)	1.842(10)		
N(101)–N(102)	1.164(13)	N(201)–N(202)	1.193(13)		
Mg–N(102)	1.973(11)	Mg–N(202)	1.966(11)	Mo(1)–N(14)	2.215(10)
Mo(2)–N(24)	2.252(9)	Mo(1)–N(11)	1.998(12)	Mo(1)–N(12)	2.001(11)
Mo(1)–N(13)	2.010(11)	Mo(2)–N(21)	1.979(10)	Mo(2)–N(22)	2.017(9)
Mo(2)–N(23)	2.027(10)	Mg–O(1)	2.041(10)	Mg–O(2)	2.019(10)
Bond Angles (deg)					
Mo(1)–N(101)–N(102)	175.6(9)	Mo(2)–N(201)–N(202)	177.0(9)		
Mg–N(102)–N(101)	178.2(9)	Mg–N(202)–N(201)	166.6(9)		
Mo(1)–N(11)–Si(1)	127.7(6)	Mo(2)–N(23)–Si(6)	126.0(6)		
N(102)–Mg–N(202)	134.7(5)	O(1)–Mg–O(2)	94.7(5)		
N(102)–Mg–O(1)	107.9(4)	N(102)–Mg–O(2)	104.5(4)		
N(202)–Mg–O(1)	105.1(4)	N(202)–Mg–O(2)	102.8(4)		
Dihedral Angles (deg)[a]					
N(14)–Mo(1)–N(11)–Si(1)	179.5	N(14)–Mo(1)–N(13)–Si(3)	180.0		
N(24)–Mo(2)–N(21)–Si(5)	167.4	N(24)–Mo(2)–N(22)–Si(4)	171.1		

[a] Obtained from a Chem-3D drawing.

For example, if 1 equiv of sodium naphthalenide is added to $[N_3N]MoCl$ in THF *all at once*, the main product of the reaction is **2**, but it is contaminated with $[N_3N]MoCl$. However, if 1 equiv of sodium naphthalenide is added *dropwise* to a THF solution of $[N_3N]MoCl$, followed by addition of Me_3SiCl, the ^1H NMR spectrum of the crude reaction mixture shows 0.5 equiv of $[N_3N]MoCl$ and 0.5 equiv of $[N_3N]Mo{-}N{=}N{-}TMS$ (**4**) (see below) to be present, indicating that the reaction has consisted exclusively of a two-electron reduction of $[N_3N]MoCl$ in the presence of dinitrogen to yield the sodium analogue of **1**.

A cleaner, high-yield route to **2** was the consequence of an attempted formation of a palladium complex that would contain the $\{[N_3N]Mo(N_2)\}^-$ "ligand", as found in $\{[N_3N]Mo(N_2)\}_3Fe$.[10] Two equivalents of $\{[N_3N]Mo(N_2)\}^-$ is oxidized by Ni(II) or Pd(II), as shown in eq 2. **2** can be isolated as burgundy-colored crystals from this reaction in >80% yield. However, the preferred route to **2** is an analogous reaction between **1** and $ZnCl_2$ in THF. Zinc metal and $MgCl_2$ are the only other products, so isolation of **2** is not complicated by the presence of phosphine ligand or reduced metal complexes.

$$\{[N_3N]Mo{-}N{=}N\}_2Mg(THF)_2 + ML_2\,Cl_2 \xrightarrow{THF} MgCl_2 + \underset{\mathbf{2}}{2[N_3N]Mo(N_2)} + ML_x \quad (2)$$

$$M = Pd, Ni;\ x \text{ is unknown}$$

The ^1H NMR spectrum of **2** consists of two broad resonances at 14.02 and −40.57 ppm for the methylene protons of the $[N_3N]^{3-}$ ligand and a sharper resonance at −4.53 ppm assigned to the TMS groups of the $[N_3N]^{3-}$ ligand. Spectra exhibiting one high-field and one low-field resonance for the ligand methylene protons is also characteristic of $[N_3N]W(L)$[19] and $[N_3N_F]W(L)$[20] complexes. (Often both methylene resonances are shifted to high field.) The IR spectrum of **2** in pentane has a strong ν_{NN} absorption at 1934 cm^{-1} that shifts to 1870 cm^{-1} in **2**-$^{15}N_2$, while the IR spectrum of **2** in Nujol consists of two strong absorptions at 1910 and 1901 cm^{-1}. We attribute the two absorptions in the solid-state spectrum to the presence of two molecules in the unit cell, as confirmed in an X-ray study (see below). SQUID magnetic susceptibility data for solid **2** are plotted versus temperature in Figure 2. These data can be fit to a Curie–Weiss law ($\chi = \mu^2/8(T - \Theta)$) over the temperature range 5–300 K to yield $\mu = 1.77(1)\ \mu_B$ and $\Theta = -0.22(2)$ K, consistent with one unpaired spin. This result is sensible since in trigonal bipyramidal **2** the lowest lying orbitals should be the degenerate d_{xz} and d_{yz} pair and the energy gap to the next highest energy orbitals with substantial d character should be large with respect to the electron-pairing energy. Therefore, the three electrons occupy these two orbitals to give a low-spin species. Although **2** is stable under dinitrogen, dinitrogen does exchange slowly. If a toluene solution of **2** is stirred under an atmosphere of $^{15}N_2$ for 1 week, the IR spectrum of the resulting solid in Nujol reveals four strong absorptions at 1910, 1901, 1846, and 1839 cm^{-1}, consistent with exchange of $^{14}N_2$ with $^{15}N_2$ to yield a roughly 2:1 mixture of **2**-$^{14}N_2$ and **2**-$^{15}N_2$. The rate of exchange cannot be accelerated by heating the reaction mixture, since when solutions of **2** are heated, a bimetallic dinitrogen complex (see below) is formed irreversibly. We have found that the lability of N_2 in **2** can be exploited to isolate other Mo(III) complexes, which will be the subject of a future report. As expected, **2** is reduced readily by magnesium powder in THF to give **1** in high yield.

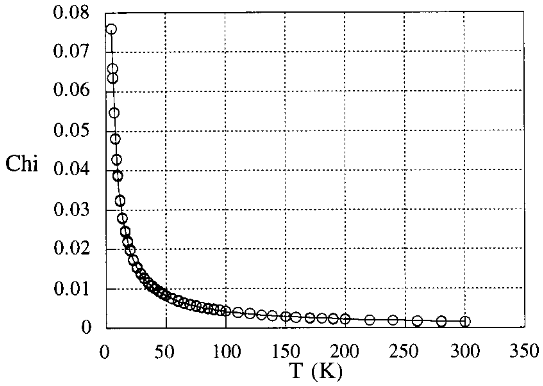

Figure 2. Plot of χ (corrected for diamagnetism) versus T for $[N_3N]Mo(N_2)$.

Single crystals of **2** grown from saturated diethyl ether solutions at −20 °C were employed in an X-ray study. Crystallographic data are given in Table 1. The molecular structure of **2**, along with the atom-labeling scheme, is shown in Figure 3 while selected bond lengths and bond angles are listed in Table 3. Two statistically identical molecules were found in the unit cell; selected data for both are listed in Table 3. **2** contains an "end-on" dinitrogen ligand with a linear Mo–N–N linkage. The N(5A)–N(6A) bond length (1.085(5) Å) is not statistically different (within 3σ) from that of free

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Table 3. Selected Bond Lengths and Bond Angles for **2**

Bond Distances (Å)					
N(5A)−N(6A)	1.085(5)	N(5B)−N(6B)	1.083(6)	Mo(1)−N(5A)	1.990(4)
Mo(2)−N(5B)	1.995(4)	Mo(1)−N(4A)	2.197(3)	Mo(2)−N(4B)	2.183(4)
Mo(1)−N(1A)	1.989(4)	Mo(1)−N(2A)	1.995(4)	Mo(1)−N(3A)	1.994(4)
Mo(2)−N(1B)	2.000(4)	Mo(2)−N(2B)	1.994(4)	Mo(2)−N(3B)	1.986(4)

Bond Angles (deg)			
Mo(1)−N(5A)−N(6A)	179.1(4)	Mo(2)−N(5B)−N(6B)	179.4(4)
N(4A)−Mo(1)−N(5A)	179.36(14)	N(4B)−Mo(2)−N(5B)	179.1(2)
Mo(1)−N(1A)−Si(1A)	127.3(2)	Mo(2)−N(1B)−Si(1B)	128.1(2)
N(1A)−Mo(1)−N(2A)	118.4(2)	N(1B)−Mo(2)−N(2B)	120.6(2)

Dihedral Angles (deg)[a]			
N(4A)−Mo(1)−N(1A)−Si(1A)	175.5	N(4A)−Mo(1)−N(2A)−Si(2A)	180.0
N(4A)−Mo(1)−N(3A)−Si(3A)	177.7	N(4B)−Mo(2)−N(1B)−Si(1B)	174.1
N(4B)−Mo(2)−N(2B)−Si(2B)	173.1	N(4B)−Mo(2)−N(3B)−Si(3B)	173.4

[a] Obtained from a Chem 3D drawing.

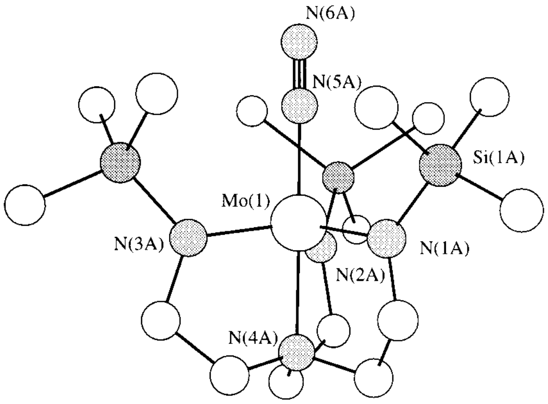

Figure 3. View of the structure of $[N_3N]Mo(N_2)$ (**2**).

dinitrogen, which suggests that there is little reduction of the dinitrogen in **2** and that **2** is best viewed as a low-spin Mo(III) dinitrogen complex. (The Mo(1)−N(5A) distance (1.990(4) Å) is also consistent with this interpretation.) The N_{ax}−M−N_{eq}-Si dihedral angles in **2** are all consistent with an "upright" orientation of the TMS groups, suggesting that there is little steric hindrance within the trigonal pocket.[5,6]

When a toluene solution of **2** is heated to 84 °C under dinitrogen, a dramatic color change from orange-red to royal purple is observed over the course of 40 h as $[N_3N]Mo{-}N{=}N{-}Mo[N_3N]$ (**3**) is formed (eq 3). **3** can be isolated as virtually

$$2[N_3N]Mo(N_2) \xrightarrow[-N_2]{\text{toluene, 84 °C}} \underset{\mathbf{3}}{[N_3N]Mo{-}N{=}N{-}Mo[N_3N]} \tag{3}$$

black microcrystals in 78% yield. The ^1H NMR spectrum of paramagnetic **3** in C_6D_6 exhibits three broad, shifted resonances, consistent with a species in which the $[N_3N]Mo$ portion is C_3-symmetric. The UV−visible spectrum of **3** in pentane has an intense absorption at 542 nm ($\epsilon = 17\,900$). SQUID magnetic susceptibility data for solid **3** can be fit to the equation $\chi = \mu^2/8(T - \Theta)$ over the temperature range 50−300 K to yield $\mu = 3.24(2)\ \mu_B$ and $\Theta = -1.1(5)$ K. The value for μ is close to the spin-only value for a system containing two unpaired electrons (2.83 μ_B), as predicted on the basis of **3** being a Mo(IV) diazenido (N_2^{2-}) complex analogous to crystallographically characterized $\{[(t\text{-}BuMe_2SiNCH_2CH_2)_3N]Mo\}_2(\mu\text{-}N_2)$.[18] In a Mo−N=N−Mo complex, one can construct two sets of degenerate π orbitals from the d_{xz} and d_{yz} orbitals on molybdenum and the p_x and p_y orbitals on the nitrogen atoms. Addition of 10 electrons to this degenerate π orbital system would result in two unpaired spins.[8] Two unpaired spins would also be predicted if one were to propose that each molybdenum is low-spin Mo(III) and the bridging dinitrogen is not reduced. However, on the basis of the N−N bond length in an analogous species, $\{[(t\text{-}BuMe_2SiNCH_2CH_2)_3N]Mo\}_2(\mu\text{-}N_2)$ (1.20 Å),[18] $[(C_6F_5NCH_2CH_2)_3N]Mo{-}N{=}N{-}Si(i\text{-}Pr)_3$ (1.20(1) Å),[8] and other "diazenido" compounds described here, the Mo(IV) proposal is the more likely. A toluene-d_8 solution of **3** shows no signs of decomposition upon being heated to 105 °C under dinitrogen for 72 h. In particular, **3** is stable toward decomposition to $[N_3N]Mo{\equiv}N$, a known compound,[4] via homolytic N−N bond cleavage, a type of reaction that has been documented for $Mo[N(t\text{-}Bu)(3,5\text{-}Me_2C_6H_3)]_3$[21] and similar species. No reaction was observed upon attempted reduction of **3** with Mg in THF. We propose that **3** forms via loss of dinitrogen from $[N_3N]Mo(N_2)$ to give "$[N_3N]Mo$", which then attacks N_β in $[N_3N]Mo(N_2)$.

The reaction between **1** and 2 equiv of Me_3SiCl yields $[N_3N]Mo{-}N{=}N{-}SiMe_3$ (**4**) as a yellow, pentane-soluble solid in 88% yield (eq 4). Compound **4** also can be obtained in high yield

$$\{[N_3N]Mo{-}N{=}N\}_2Mg(THF)_2 + 2TMSCl \xrightarrow{THF} \underset{\mathbf{4}}{2[N_3N]Mo{-}N{=}NTMS} + MgCl_2 \tag{4}$$

from the reduction of $[N_3N]MoCl$ by magnesium powder in the presence of Me_3SiCl. The IR spectrum of **4** has a strong broad absorption at 1712 cm^{-1} that shifts to 1654 cm^{-1} in **4**-$^{15}N_2$. The ^{15}N NMR spectrum of **4**-$^{15}N_2$ in C_6D_6 consists of a pair of doublets ($J_{NN} = 12$ Hz) at 356.9 and 238.1 ppm. For comparison, in $[(C_6F_5NCH_2CH_2)_3N]Mo{-}N{=}N{-}Si(i\text{-}Pr)_3$ the ν_{NN} IR absorption is found at 1687 cm^{-1} and in the ^{15}N NMR spectrum the two resonances for the hydrazido nitrogens are found at 366 and 228 ppm ($J_{NN} = 15$ Hz).[8]

1 also reacts cleanly with (TMS)OTf to give **4**. However, when other electrophiles are used, the reactions are more complicated and mixtures result. For example, reaction of MeOTf with **1** yields two diamagnetic products in addition to **2**. Since the IR spectrum of the product mixture has a strong stretch at 1713 cm^{-1}, one of the diamagnetic products is tentatively formulated as a species that contains a Mo−N=N−Me linkage. However, the nature of the supporting ligand in such circumstances cannot be stated with certainty in view of the tendency for the relatively small methyl electrophile to attack imido nitrogens in the triamidoamine ligand (see below). **1** reacts with 2 equiv of MeI to give a mixture of as yet

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(21) 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.

Table 4. Selected Bond Lengths and Bond Angles for **5**

Bond Distances (Å)

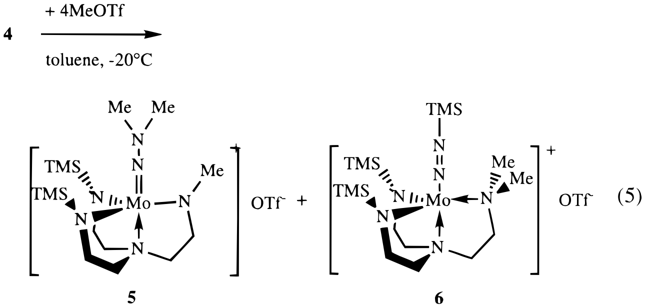
Mo(1)−N(5)	1.747(10)	Mo(1)−N(1)	1.960(9)	Mo(1)−N(2)	1.950(9)
Mo(1)−N(3)	1.962(9)	Mo(1)−N(4)	2.235(9)	N(5)−N(6)	1.334(13)

Bond Angles (deg)

Mo(1)−N(5)−N(6)	173.6(8)	Mo(1)−N(1)−Si(1)	129.5(5)
Mo(1)−N(3)−C(31)	128.5(8)	Mo(1)−N(2)−Si(2)	125.1(5)
N(5)−N(6)−C(7)	119.1(10)	N(5)−N(6)−C(8)	115.9(10)
N(1)−Mo(1)−N(5)	103.5(4)	N(3)−Mo(1)−N(5)	94.5(4)

unidentified diamagnetic and paramagnetic species (according to proton NMR).

Efforts to functionalize the dinitrogen ligand further have consisted of alkylations of **4**. Compound **4** does not react readily with (TMS)OTf, (TMS)I, or MeI. However, it does react with excess MeOTf (4 equiv) in toluene over 12 h to give a mixture of two diamagnetic products, **5** and **6** (eq 5), typically in a ratio



(5)

of 1:3. These two products can be separated by fractional crystallization. When THF/ether solutions of the product mixture are cooled, **5** can be isolated as an orange, crystalline solid in 20% yield. The ^{19}F NMR spectrum of **5** in C_6D_6 reveals a singlet at −77.3 ppm for the triflate ion. The ^1H NMR spectrum of **5** in THF-d_8 has multiple resonances for the methylene protons of the ligand backbone, consistent with the fact that it is not a C_3-symmetric species. A singlet at 3.72 ppm integrates as three protons and is assigned to the amido methyl group. The presence of a plane of symmetry in **5** is confirmed by the ^{13}C NMR spectrum which exhibits four resonances for the methylene backbone carbons of the ligand. The ^{15}N NMR spectrum of **5**-$^{15}N_2$ in THF-d_8 consists of a pair of doublets at 374.8 and 157.2 ppm attributed to N_α and N_β of a hydrazido(2−) ligand, respectively.[12,17,22,23] No ν_{NN} absorption could be assigned in an IR spectrum of **5** in THF.

Single crystals of **5** suitable for an X-ray study were grown from THF/pentane solutions at −20 °C. Crystallographic data are given in Table 1. The molecular structure of **5** (two views), along with the atom-labeling scheme, is shown in Figure 4 while selected bond lengths and bond angles are listed in Table 4. The Mo−N(5)−N(6) linkage is essentially linear (173.6(8)°), and the N−N bond length (1.334(13) Å) is similar to that found in a wide variety of other hydrazido(2−) complexes.[13,15,24] The short Mo−N(5) bond length (1.747(10) Å) is also consistent with formulation of **5** as a 2,2-dimethylhydrazido(2−) complex. N(6) is essentially planar, as is the norm in hydrazido(2−) complexes, with the sum of the angles being 353°. However, there is some deviation from planarity as a consequence of steric interactions between the NMe_2 groups and the TMS groups on N(1) and N(2), as shown in the top view in Figure 4. The two methyl groups of the hydrazido ligand are oriented roughly in a plane that passes between N(3) and N(1)/N(2), and the $NNMe_2$ moiety is tilted ~10° toward the methylated ligand arm (N(5)−Mo−N(3) = 94.5(4), N(5)−Mo−N(1) = 103.5(4), N(5)−Mo−N(2) = 104.6(4)°). Both features can be attributed to greater steric demands of Si(1) and Si(2) compared to the methyl group on the third equatorial amido nitrogen. We can be certain that there is no proton present on N(3) in view of the virtual identity of the Mo−N(1), Mo−N(2), and Mo−N(3) bond lengths and the fact that they are all similar to Mo−N_{amido} bond lengths in many other triamidoamine complexes.[2]

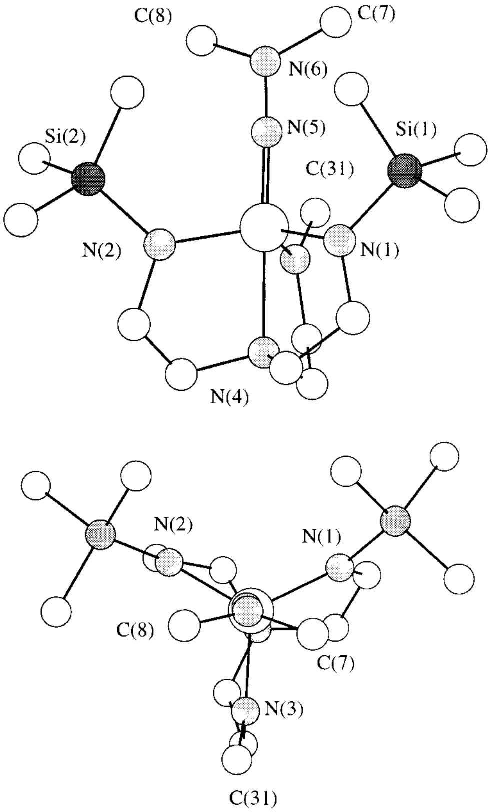


Figure 4. Two views of the structure of **5** (triflate ion omitted).

The second product (**6**) of the reaction between **4** and MeOTf can be isolated in 35% yield as red crystals from THF/pentane solutions at −20 °C. NMR data are consistent with its formulation as the Mo(IV) diazenido complex $\{[(Me_3SiNCH_2CH_2)_2NCH_2CH_2NMe_2]Mo{-}N{=}NSiMe_3\}OTf$. A singlet at 0.34 ppm in the proton NMR spectrum of **6** in THF-d_8 integrates as 27 protons and is assigned to three TMS groups, the resonances for which apparently are accidentally equivalent. (In benzene-d_6 two resonances are observed at 0.29 ppm (area 18) and 0.16 ppm (area 9).) A second singlet at 2.76 ppm integrates as six protons but is 1 ppm upfield of the methyl amido protons of **5**. There are five sets of multiplets for the 12 methylene protons of the ligand backbone, and so **6** also is not a C_3-symmetric complex. The ^{13}C NMR spectrum of **6** taken in THF-d_8 reveals TMS groups in two different environments and four methylene

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(22) Chatt, J.; Fakley, M. E.; Richards, R. L.; Mason, J.; Stenhouse, I. A. *J. Chem. Res., Miniprint* **1979**, 3701.

(23) Mason, J. *Chem. Rev.* **1981**, *81*, 205.

(24) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589.

Table 5. Selected Bond Lengths and Bond Angles for **6**

Bond Distances (Å)

Mo(1)−N(5)	1.803(7)	Mo(1)−N(1)	1.958(5)	Mo(1)−N(2)	1.950(5)
Mo(1)−N(3)	2.181(5)	Mo(1)−N(4)	2.229(6)	N(5)−N(6)	1.206(9)
N(1)−Si(1)	1.744(6)	N(2)−Si(2)	1.745(6)	N(6)−Si(3)	1.670(9)

Bond Angles (deg)

N(5)−Mo(1)−N(3)	95.2(2)	N(5)−Mo(1)−N(1)	100.3(3)
N(5)−Mo(1)−N(2)	100.8(3)	N(2)−Mo(1)−N(3)	116.5(2)
N(3)−Mo(1)−N(4)	80.2(2)	N(6)−N(5)−Mo(1)	172.8(7)
N(5)−N(6)−Si(3)	170.5(8)	N(4)−Mo(1)−N(5)	175.4(2)

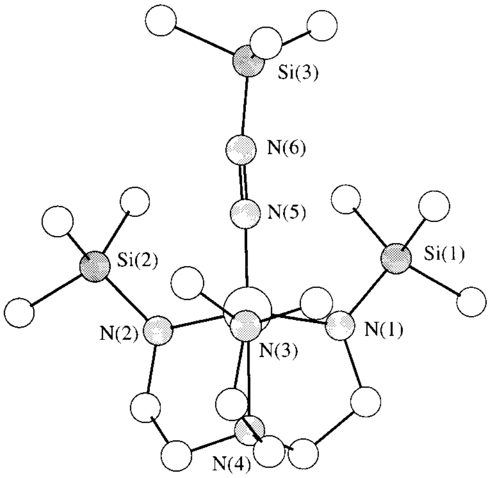
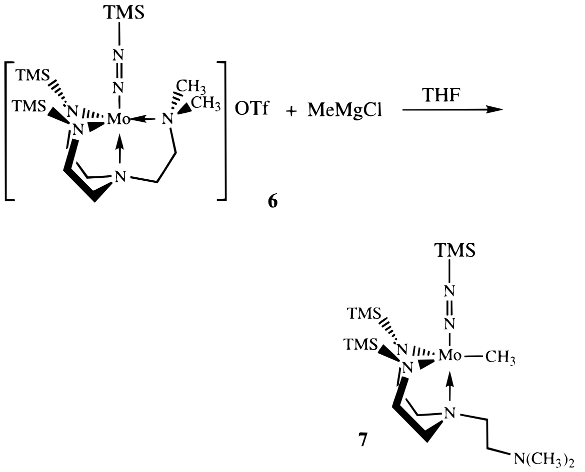


Figure 5. View of the structure of **6** (triflate ion omitted).

carbon resonances, which suggests that **6** has a plane of symmetry. The IR spectrum of **6** has a strong broad absorption at 1724 cm^{-1} that shifts to 1668 cm^{-1} in **6**-$^{15}N_2$, and the ^{15}N NMR spectrum reveals resonances at 361.5 and 244.3 ppm (J_{NN} = 13 Hz) (cf. **1** and **4**).

X-ray-quality crystals of **6** were obtained from THF/pentane at −20 °C. Crystallographic data are given in Table 1. The molecular structure of **6**, along with the atom labeling scheme, is shown in Figure 5, while selected bond lengths and bond angles are listed in Table 5. The most important feature of **6** is the double methylation of one of the ligand arms, thereby converting the triamidoamine ligand into a diamidodiamine ligand, and the survival of the diazenido ligand with the TMS substituent intact. The Mo−N(3) bond length (2.181(5) Å) is typical of a dative amine bond and should be compared with the Mo−N(4) bond length of 2.229(6) Å. The dinitrogen bond length of 1.206(9) Å is within the range of N−N bond lengths of other crystallographically characterized diazenido complexes in TREN[8,18] and other systems.[13,15,16,24]

We began to explore the reactivity of **5** and **6** with MeMgCl in order to determine whether an alkyl nucleophile would add to N$_\alpha$, to N$_\beta$, or to the metal center. **6** reacts instantly with MeMgCl in THF to give diamagnetic **7** (eq 6). ^{1}H and ^{13}C NMR spectra of **7** suggest that alkylation has occurred at molybdenum. In the ^{1}H NMR spectrum of **7** in C_6D_6, the resonance due to the methyl groups of the amine ligand arm appears at 1.90 ppm, which is somewhat upfield of the corresponding resonance of **6** (2.76 ppm). The IR spectrum of **7** in Nujol shows a strong, broad absorption at 1640 cm^{-1} (1577 cm^{-1} in **7**-$^{15}N_2$) while the ^{15}N NMR spectrum taken in C_6D_6 consists of two doublets at 374.6 and 239.5 ppm (J_{NN} = 15 Hz), all of which are consistent with an intact diazenido ligand. **7** decomposes to a black, oily solid upon prolonged exposure to vacuum (1 h), but a satisfactory elemental analysis was obtained for a sample of **7** that was subjected to vacuum-drying for only ~10 min. All data are consistent with a dimethylamine donor that is not bound to the metal on the NMR time scale, as a molecule with no symmetry would result if the dimethylamine donor were bound to the metal.



6

7

(6)

Single crystals of **7** were grown from saturated hexamethyldisiloxane solutions at −20 °C. Crystallographic data are given in Table 1. The molecular structure of **7**, along with the atom-labeling scheme, is shown in Figure 6 while selected bond lengths and bond angles are listed in Table 6. The trigonal bipyramidal environment around the metal center in **7** confirms that alkylation has occurred at molybdenum and that the amine ligand arm is not bound to the metal. The Mo−N(5)−N(6) linkage is linear, and the N(5)−N(6) bond length (1.229(3) Å) is consistent with **7** being a diazenido complex. However, the diazenido ligand in **7** in quite bent at N$_\beta$, with N(5)−N(6)−Si(2) = 137.0(2)° compared to the corresponding angle in **6**, which is essentially linear (170.5(8)°). We attribute the bending of the diazenido ligand to the nontrigonally symmetric axial coordination site and the resulting steric influence of TMS groups containing Si(1) and Si(3) on the TMS group containing Si(2). The environment above C(7) is relatively open, so the trimethylsilyl group of the diazenido ligand bends toward C(7). A comparison of the ^{15}N NMR chemical shifts and the IR stretches for the diazenido ligands in **1**, **5**, **6**, and **7** suggests that, for triamidoamine complexes of the type being investigated here, ^{15}N NMR and IR data are not reliable parameters on which to base any conclusion as to whether the diazenido ligand is bent at N$_\beta$ or not in the solid state, a topic of some discussion in the past.[17]

Addition of MeMgCl to a THF solution of **5** at −20 °C resulted in an immediate color change to blood red. The ^{1}H NMR spectrum in C_6D_6 shown on the lower half of Figure 7 is consistent with **8** being a complex with no symmetry. There are 10 sets of resonances for the 12 methylene protons of the ligand backbone, and the singlet at 0.18 ppm suggests that the methyl group has added to molybdenum (cf. a chemical shift for MoMe of 0.74 ppm in **7**). Both the ^{1}H and ^{13}C NMR spectra

Table 6. Selected Bond Lengths and Bond Angles for **7**

Bond Distances (Å)

Mo(1)−N(5)	1.789(2)	Mo(1)−N(1)	1.983(2)	Mo(1)−C(7)	2.153(3)
Mo(1)−N(3)	1.981(2)	Mo(1)−N(4)	2.312(2)	N(5)−N(6)	1.229(3)
N(6)−Si(2)	1.726(2)				

Bond Angles (deg)

N(5)−Mo(1)−N(1)	98.65(8)	N(3)−Mo−(1)−N(1)	123.99(9)
N(5)−Mo(1)−C(7)	91.69(10)	N(3)−Mo(1)−C(7)	114.47(11)
C(4)−N(4)−Mo(1)	117.34(14)	N(6)−N(5)−Mo(1)	179.5(2)
N(5)−N(6)−Si(2)	137.0(2)		

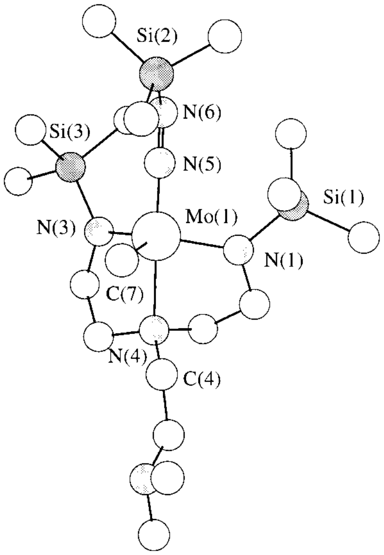
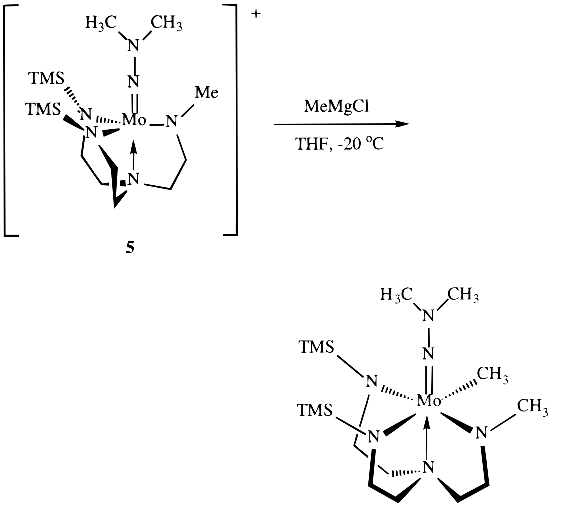


Figure 6. View of the structure of $[N(CH_2CH_2NTMS)_2(CH_2CH_2NMe_2)]Mo(CH_3)(N_2TMS)$ (**7**).

of **8** show that the TMS groups are inequivalent. The ^{15}N NMR spectrum of **8**-$^{15}N_2$ consists of two sets of doublets ($J_{NN} = 12$ Hz) at 355 and 142 ppm. These data suggest that **8** is the pseudooctahedral methyl hydrazido complex shown in eq 7.



5

8

(7)

Alkylation between TMS-substituted and Me-substituted amido nitrogens in **5** is sterically more likely than alkylation between two TMS-substituted amido nitrogens to give a derivative with mirror symmetry, even though steric crowding in that alternative structure may be less significant than it is in **8**.

Compound **8** is thermally unstable, even at room temperature. Over 24 h, the color of a C_6D_6 solution of **8** changed from blood red to orange-brown. This transformation is accelerated by heating a sample to 65 °C. If the solvent is removed and the residue is extracted with pentane, a pale yellow, crystalline solid (**9**) can be isolated. The ^1H NMR spectrum of **9** is shown on the upper half of Figure 7. It is apparent from this spectrum that **9** is a complex with mirror symmetry on the NMR time scale. There is a single resonance for the TMS groups and a singlet at 4.08 ppm that is assigned to the methyl group on a triamidoamine ligand arm. Spectroscopic data and elemental analysis support the formulation of **9** as $[(Me_3SiNCH_2CH_2)_2N(CH_2CH_2NMe)]Mo{\equiv}N$ (eq 8). The ^1H NMR spectrum

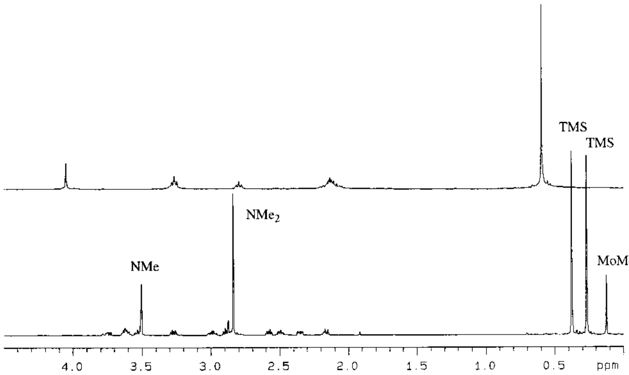
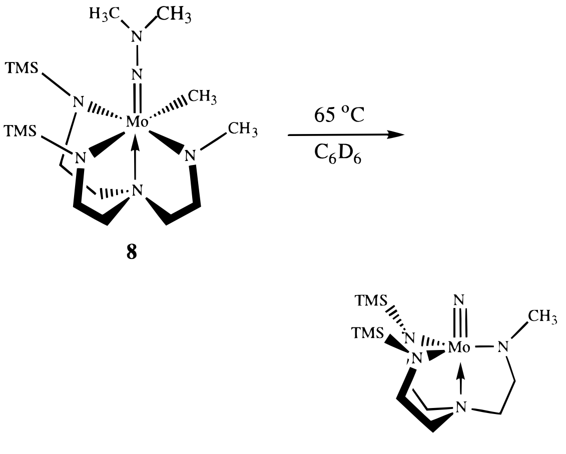


Figure 7. ^1H NMR spectra of **8** (lower spectrum) and **9** (upper spectrum) taken in C_6D_6.



8

9

(8)

of **9** is a hybrid of that of $[(Me_3SiNCH_2CH_2)_3N]Mo{\equiv}N$[4] and that of $[(MeNCH_2CH_2)_3N]Mo{\equiv}N$.[25] The IR spectra of **9** and **9**-$^{15}N_2$ are superimposable except for a single absorption at 1002 cm^{-1} in the spectrum of **9** that shifts to 977 cm^{-1} in the spectrum of **9**-$^{15}N_2$, and that can be assigned to a M≡N stretch.[26] Finally, the ^{15}N NMR spectrum of **9**-$^{15}N_2$ reveals a singlet at 866.1 ppm, consistent with a metal nitride complex.[26] The yield of **9** (versus

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(25) Plass, W.; Verkade, J. G. *J. Am. Chem. Soc.* **1992**, *114*, 2275.

(26) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988.

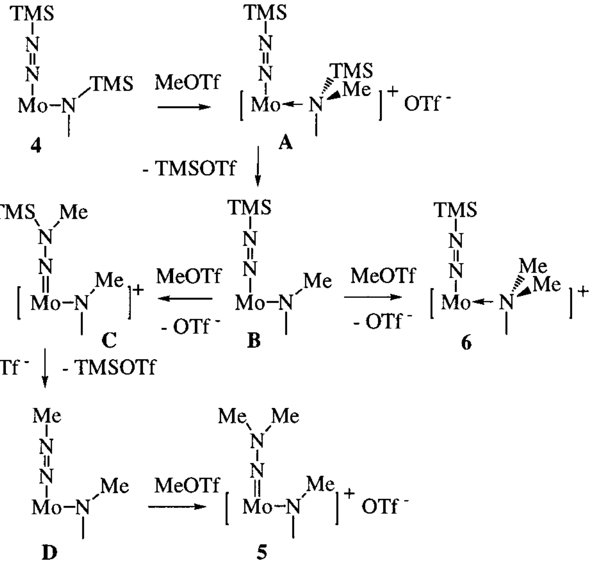
an internal standard) obtained from the thermolysis of **8** in THF-d_8 is 67%. Among the non-metal-containing products are methane (16% in solution) and dimethylamine (38% in solution), according to NMR comparison with authentic samples and according to proton NMR measurements employing an internal standard. No other products have been identified, and it is clear from the complexity of the NMR spectrum of decomposed **8** that a fraction of the triamidoamine ligand originally present has been attacked in some significant manner. In view of the long and low-yield route to **8** and the complexity of its decomposition, it unfortunately was impractical to explore the decomposition reaction in more detail.

Discussion

The synthesis of **1** is noteworthy in several respects. First, **1** provides us with a relatively facile entry into dinitrogen chemistry in the TMS−TREN system. Second, **1** is the first crystallographically characterized example in the triamidoamine family of complexes of what could be called salts of a parent diazenido complex, even though $\{[N_3N]Mo(N_2)\}^-$ has magnesium bound to N_β. Other transition metal complexes of dinitrogen that contain magnesium bound to N_β are known, for example $[Co(PPh_3)_2(N_2)]_2[Mg(THF)_4]$[27,28] and related metalated versions of "$[Co(PPh_3)_2(N_2)]^-$".[28−30] In the $[Li(ether)_3]^+$ derivative, the N−N distance is 1.167(16) Å and the Co−N distance is 1.707(11) Å.[27] Third, **1** can be oxidized by one electron to afford the neutral terminal dinitrogen complex **2** in high yield. Finally, it should be noted that heterobimetallic dinitrogen complexes containing earlier transition metals (Zr,[11] V,[11] Fe,[11] and Mn[31]) can be prepared by employing $\{[N_3N]Mo(N_2)\}^-$ as a nucleophile in the form of **1**, although the stability of both $[N_3N]Mo(N_2)$ and the $\{[N_3N]Mo(N_2)\}^-$ is a complicating feature of chemistry involving later transition metals such as iron.[10] We suspect that we will be able to isolate and structurally characterize some example of a metal-free $\{[triamidoamine]Mo(N_2)\}^-$ species and that $[N_3N]Mo(N_2)$ and $\{[N_3N]Mo(N_2)\}^-$ then could be viewed as potential ligands that differ by one electron in metal-free form. The $[N_3N]Mo(N_2)$/$\{[N_3N]Mo(N_2)\}^-$ redox couple and also the $[N_3N]Mo(N_2)$/$\{[N_3N]Mo(N_2)\}^+$ redox couple or redox couples in analogous triamidoamine complexes will be the subject of future investigations in view of the central role they will play in the functionalization of terminally bound dinitrogen.

It seems likely that the dinitrogen ligand in **2** is labile to some degree, as suggested by slow exchange of $^{14}N_2$ in **2** with $^{15}N_2$ and by decomposition of **2** to give **3**. However, the "$[N_3N]$Mo" formed upon dissociation of dinitrogen from **2** we speculate is a relatively high-energy and reactive species. We would expect that the d_{z^2} orbital in "$[N_3N]$Mo" formed upon loss of dinitrogen from **2** is pushed well above the energy of the d_{xz} and d_{yz} orbitals as a consequence of the binding of the amine donor to one of the apical sites. Consequently "$[N_3N]$Mo" could be a low-spin species and its high energy and reactivity in part a consequence of its low-spin configuration. In contrast, the trigonal complex $Mo[N(t\text{-}Bu)(3,5\text{-}Me_2C_6H_3)]_3$ has a high-spin configuration, presumably as a consequence of the relatively small energy difference between the d_{z^2} orbital and degenerate d_{xz} and d_{yz} orbitals.[21] This difference between the tris(anilide) and triamidoamine complexes we believe to be the one which differentiates their chemistry with dinitrogen. In particular, a monometallic dinitrogen adduct of $[(t\text{-}Bu)ArN]_3Mo$ (Ar = 3,5-$Me_2C_6H_3$) has not yet been observed, and the observable $[(t\text{-}Bu)ArN]_3Mo(\mu\text{-}N_2)Mo[NAr(t\text{-}Bu)]_3$ species is unstable with respect to homolytic cleavage of the dinitrogen to give 2 equiv of $[(t\text{-}Bu)ArN]_3Mo{\equiv}N$.[21] Coordination of the apical nitrogen donor in "$[N_3N]$Mo" may also promote more efficient back-bonding to dinitrogen and, it has been proposed,[32] might account for the calculated endothermicity of the homolytic dinitrogen cleavage reaction in $Mo(\mu\text{-}N_2)Mo$ in the triamidoamine family.

Scheme 1



The replacement of trimethylsilyl groups by methyl groups using good electrophiles such as methyl triflate has given rise to new types of diamido/bis(donor) complexes (i.e., **6**) that may prove to be of use in the future, if more direct ways can be found to prepare the ligands and starting materials that contain such a ligand. A plausible mechanism for the formation of **5** and **6** is shown in Scheme 1. The first step is proposed to be alkylation of N_{eq} to give unstable **A**, which is susceptible to attack by the triflate ion on the amino trimethylsilyl group to give **B**. **B** is probably even more susceptible to alkylation at the now more accessible methylated amido atom to give **6**. Alkylation at N_β of the diazenido ligand in **B** would have to compete with formation of **6** in order to give **C** and ultimately **5** from **B**. Whether this proposal is correct or not, it is clear that alkylations at N_{eq} and N_β of the diazenido ligand are not clearly differentiable in terms of rate, at least when electrophiles as strong as methyl triflate are required. It should be noted that, of the three combinations of the p orbitals on the equatorial amido nitrogen atoms in triamidoamine complexes, one cannot overlap with a metal orbital and therefore is a ligand-centered nonbonding orbital. Presumably it is the relatively ready accessibility of this orbital that leads to alkylation at N_{eq} of **4** and **B**. The low yields of **5** and **6** suggest that other reactions, e.g., alkylation of **D** at the methylated N_{eq}, might be taking place also, but the consequence of such alkylations so far has not been documented. Formation of **5** and **6** is the first instance of which we are aware where recordable chemistry has taken place

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at N_{eq} in triamidoamine complexes outside of protonation.[9,33] Formation of **6** suggests that future efforts to synthesize diamido/bis(donor) ligands and complexes thereof, especially those that do not contain silyl substituents on nitrogen centers, may be a fruitful undertaking.

The decomposition of **8** to give **9** is intriguing, even though the long sequence of reactions required to produce **8** (via **5**) so far have prevented a detailed investigation of this decomposition reaction and even though a relatively stable nitrido complex is formed. We hope to establish the mechanism or mechanisms by which more readily accessible species analogous to **8** decompose in future studies and to return to the question concerning the means by which nitrido ligands might be removed from the metal to give a nitrogen-containing product from the second half of dinitrogen and return to a point where a potential catalytic cycle might be possible.[4]

Despite the limitations of TMS−TREN as a robust ligand, the present study demonstrates the feasibility of the stepwise reduction and functionalization of dinitrogen in molybdenum triamidoamine complexes. The difficulties that we have encountered with lability of TMS groups on the $[N_3N]^{3-}$ ligand have prompted us to revisit the C_6F_5−TREN system[8] and to develop methods of preparing new triamidoamine ligands that contain aryl substituents other than C_6F_5 on amido nitrogens. Preliminary results suggest that this approach will be successful. For example, $[N_3N_F]Mo{-}N{=}N{-}SiMe_3$ has been found to react cleanly with 2 equiv of MeOTf to give $\{[N_3N_F]Mo{=}NNMe_2\}$-OTf in high yield.[34] Therefore, future work will be aimed largely toward the derivatization of dinitrogen in triamidoamine and related complexes that do not contain trimethylsilyl groups on amido nitrogens in the triamidoamine ligand.

Experimental Procedures

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques unless otherwise specified. Pentane was washed with sulfuric acid/nitric acid (95/5 v/v), sodium bicarbonate, and water, stored over calcium chloride, and distilled from sodium benzophenone ketyl under nitrogen. Reagent grade tetrahydrofuran was distilled from sodium benzophenone ketyl under nitrogen. Toluene was distilled from sodium, and CH_2Cl_2 was distilled from CaH_2. Reagent grade diethyl ether was sparged with nitrogen and passed through two columns of activated alumina. Hexamethyldisiloxane was purchased from Aldrich, dried over sodium, and then vacuum-transferred into a small storage flask and stored over molecular sieves. $[N_3N]MoCl$ was prepared as described in the literature.[5]

NMR data were obtained at 300 or 500 MHz (^1H), 75.4 MHz (^{13}C), and 50.7 MHz (^{15}N). Chemical shifts are listed in parts per million downfield from tetramethylsilane for proton and carbon. ^{15}N chemical shifts are referenced to external CH_3NO_2, whose shift is +380.2 ppm with respect to liquid ammonia. Coupling constants are listed in hertz. Spectra were obtained at 25 °C unless otherwise noted. Benzene-d_6 and toluene-d_8 were predried with CaH_2, vacuum-transferred onto sodium and benzophenone, stirred under vacuum for 2 days, and then vacuum-transferred into small storage flasks and stored over molecular sieves.

UV/visible spectra were recorded on an HP 8452 diode array spectrophotometer using a Hellma 221-QS quartz cell (path length = 10 mm) sealed to a gas adapter fitted with a Teflon stopcock. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. Elemental analyses (C, H, N) were performed in our laboratory using a Perkin-Elmer 2400 CHN analyzer or by Microlytics or Schwarzkopf. X-ray data were collected on a Siemens SMART/CCD diffractometer, and the structures were solved by methods analogous to those described elsewhere.[33]

SQUID Magnetic Susceptibility Measurements. Measurements were carried out on a Quantum Design SQUID magnetometer at a field strength of 5000 G as described elsewhere.[5] Two runs were performed on each sample, one from 5 to 300 K and a second from 300 to 5 K. Measurements were made at the following increments: 5−10 K (every 1 K), 10−20 K (every 2 K), 20−50 K (every 3 K), 50−100 K (every 5 K), 100−200 K (every 10 K), 200−300 K (every 20 K).

$\{[N_3N]MoN_2\}_2Mg(THF)_2$ (1). $[N_3N]MoCl$ (785 mg, 1.60 mmol) was dissolved in 30 mL of THF, and magnesium powder (100 mg, 4.16 mmol) was added. The mixture was then stirred for 17 h. THF was removed in vacuo, and the residue was extracted with 30 mL of toluene. 1,4-Dioxane (560 mg, 6.37 mmol) was added, and the solution was stirred for 30 min. $MgCl_2$(dioxane) was removed by filtration through a pad of Celite. Toluene was removed from the filtrate in vacuo, and the orange solid was crystallized from diethyl ether: yield 820 mg (90%); ^1H NMR (C_6D_6) δ 3.98 (m, 8, THF), 3.60 (t, 12, NCH_2CH_2N), 2.21 (t, 12, NCH_2CH_2N), 1.46 (m, 8, THF), 0.61 (s, 54, $NSiMe_3$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 71.0 (THF), 54.7 (NCH_2CH_2N), 52.0 (NCH_2CH_2N), 25.6 (THF), 4.8 ($NSiMe_3$); IR (THF) 1719 cm^{-1} ($N{=}N$). Anal. Calcd for $C_{38}H_{94}N_{12}Si_6O_2Mo_2Mg$: C, 40.18; H, 8.34; N, 14.80. Found: C, 40.35; H, 8.13; N, 14.76.

$\{[N_3N]Mo^{15}N_2\}_2Mg(THF)_2$ (1-$^{15}N_2$). $[N_3N]MoCl$ (520 mg, 1.06 mmol) was dissolved in 10 mL of THF, and the solution was placed in a glass bomb with a stirring bar and an excess of magnesium powder. The vessel was subjected to three freeze−pump−thaw cycles to remove any $^{14}N_2$ present. $^{15}N_2$ (1 atm) was introduced, and the solution was stirred for 20 h. The product was isolated in a manner analogous to that described for $\{[N_3N]MoN_2\}_2Mg(THF)_2$: ^{15}N NMR (C_6D_6) δ 377.0 (J_{NN} = 12), 304.4 (J_{NN} = 12); IR (THF) 1662 cm^{-1} ($N{=}N$).

$[N_3N]Mo(N_2)$ (2). Method 1. $\{[N_3N]MoN_2\}_2Mg(THF)_2$ (302 mg, 0.27 mmol) was dissolved in 10 mL of THF, and the solution was cooled to −20 °C. $Pd(PPh_3)_2Cl_2$ (187 mg, 0.27 mmol) was added all at once as a solid to the stirred solution of **1**. Within 1 min, the solution had become deep green. After 45 min, the solvent was removed and the residue extracted with 40 mL of pentane. The mixture was filtered through Celite, and part of the pentane was removed from the filtrate in vacuo to yield red crystals: yield 205 mg (80%); ^1H NMR (C_6D_6) δ 14.02 (CH_2), −4.53 (TMS), −40.57 (CH_2); IR (pentane) 1934 cm^{-1} ($N{=}N$); IR (Nujol) 1910, 1900 cm^{-1} ($N{=}N$). The reaction employing $Ni(PPh_3)_2Cl_2$ is entirely analogous. The product prepared using method 1 tends to be contaminated by a small amount of $[N_3N]MoCl$.

Method 2. $\{[N_3N]MoN_2\}_2Mg(THF)_2$ (302 mg, 0.27 mmol) was dissolved in 10 mL of THF, and anhydrous $ZnCl_2$ (36 mg, 0.27 mmol) was dissolved in 2 mL of THF. Both solutions were cooled to −20 °C, and the $ZnCl_2$ solution was added to the stirring solution of $\{[N_3N]MoN_2\}_2Mg(THF)_2$. After 4 h, the reaction solution was filtered through Celite and the solvent was removed in vacuo. The residue was extracted with 20 mL of pentane, and the extract was filtered through Celite. The solvent was removed from the filtrate in vacuo, and the residue was recrystallized from diethyl ether to afford the product as red crystals; yield 181 mg (70%, two crops). Method 2 is simpler and the product is not contaminated with $[N_3N]MoCl$.

$[N_3N]Mo(^{15}N_2)$ (2-$^{15}N_2$). This compound was prepared in a manner analogous to the synthesis of **2** using $\{[N_3N]Mo^{15}N_2\}_2Mg(THF)_2$: IR (pentane) 1870 cm^{-1} ($N{=}N$); IR (Nujol) 1846, 1839 cm^{-1} ($N{=}N$). Anal. Calcd for $C_{15}H_{39}N_4{}^{15}N_2Si_3Mo$: C, 37.09; H, 8.09; N, 17.71. Found: C, 37.08; H, 8.49; N, 17.50.

$[N_3N]Mo{-}N{=}N{-}Mo[N_3N]$ (3). $[N_3N]Mo(N_2)$ (200 mg,0.41 mmol) was dissolved in 5 mL of toluene, and the solution was placed in a glass bomb along with a stirring bar. The bomb was sealed and heated to 84 °C for 40 h. During this time, the reaction mixture turned deep purple. The toluene was removed in vacuo, and the residue was extracted with ether. The mixture was filtered, and the filtrate was reduced in volume and cooled to −20 °C to give the product as a black microcrystalline solid: yield 152 mg (78%); ^1H NMR (C_6D_6) δ 3.74 (TMS), −17.05 (NCH_2CH_2N), −30.77 (NCH_2CH_2N); UV−vis (toluene) λ = 542 nm, ϵ = 17 872. Anal. Calcd for $C_{30}H_{78}N_{10}Si_6Mo_2$: C, 38.36; H, 8.37; N, 14.91. Found: C, 38.09; H, 8.45; N, 14.48.

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[N$_3$N]MoN$_2$SiMe$_3$ (4). [N$_3$N]MoCl (100 mg, 0.20 mmol) was dissolved in 5 mL of THF. Magnesium powder (large excess, ∼100 mg) and Me$_3$SiCl (80 mg, 0.74 mmol) were added, and the mixture was stirred for 5 h. After 20 h, the THF was removed from the yellow solution and the residue was extracted into pentane. The mixture was filtered through Celite, the volume of the filtrate was reduced, and the filtrate was cooled to −30 °C to give a yellow solid: yield 100 mg (88%); ^{1}H NMR (C$_6$D$_6$) δ 3.38 (t, 6, NCH$_2$CH$_2$N), 2.10 (t, 6, NCH$_2$CH$_2$N), 0.49 (s, 27, NSiMe$_3$), 0.49 (s, 9, N$_2$SiMe$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 54.1 (NCH$_2$CH$_2$N), 52.1 (NCH$_2$CH$_2$N), 4.1 (NSiMe$_3$), 4.0 (N$_2$SiMe$_3$); IR (THF) 1714 cm^{-1} (N═N). Anal. Calcd for C$_{18}$H$_{48}$N$_6$Si$_4$Mo: C, 38.82; H, 8.69; N, 15.09. Found: C, 38.86; H, 8.73; N, 15.02.

[N$_3$N]Mo^{15}N$_2$SiMe$_3$ (4-^{15}*N*$_2$). This compound was prepared in a manner analogous to the preparation of **4**: ^{15}N$_2$ NMR (C$_6$D$_6$) δ 356.9 (J_{NN} = 12), 238.1 (J_{NN} = 12); IR (THF) 1654 cm^{-1} (N═N).

{[N(CH$_2$CH$_2$NSiMe$_3$)$_2$(CH$_2$CH$_2$NCH$_3$)]MoN$_2$(CH$_3$)$_2$}OTf(THF)$_{0.5}$ (5). [N$_3$N]Mo−N═NTMS (500 mg, 0.90 mmol) was dissolved in 30 mL of toluene, and the solution was cooled to −20 °C. A solution of methyl triflate (408 μL, 3.60 mmol) in 15 mL of toluene was cooled to −20 °C, and the solution was added dropwise to the stirred solution of [N$_3$N]MoN═NTMS. After 18 h, the toluene was removed in vacuo and the residue was washed with 7 mL of pentane in order to remove any unreacted [N$_3$N]Mo−N═NTMS (50 mg, 0.09 mmol). The brown-red solid was dissolved in minimum THF, and the solution was filtered. Ether was added, and the solution was stored at −20 °C to give 102 mg of orange crystals (20%): ^{1}H NMR (THF-d_8) δ 3.96−3.79 (m, 6, NCH$_2$CH$_2$), 3.73 (s, 3, NCH$_3$), 3.72 (s, 6, N(CH$_3$)$_2$), 3.43−3.26 (m, 8, NCH$_2$CH$_2$, THF), 1.58 (m, THF), 0.27 (s, 18, NTMS); ^{13}C NMR (THF-d_8) δ 71.50 (t, $^1J_{\mathrm{CH}}$ = 138, THF), 64.10 (t, $^1J_{\mathrm{CH}}$ = 138, NCH$_2$CH$_2$N), 56.79 (t, $^1J_{\mathrm{CH}}$ = 140, NCH$_2$CH$_2$N), 55.50 (q, $^1J_{\mathrm{CH}}$ = 136, NCH$_3$), 54.26 (t, $^1J_{\mathrm{CH}}$ = 140, NCH$_2$CH$_2$N), 53.09 (t, $^1J_{\mathrm{CH}}$ = 140, NCH$_2$CH$_2$N), 46.15 (q, $^1J_{\mathrm{CH}}$ = 141, N(CH$_3$)$_2$), 27.82 (t, $^1J_{\mathrm{CH}}$ = 127, THF), 2.73 (q, $^1J_{\mathrm{CH}}$ = 119, NTMS); ^{19}F NMR (C$_6$D$_6$) δ −77.3 (s, CF$_3$SO$_3$). Anal. Calcd for C$_{18}$H$_{43}$F$_3$Si$_2$N$_6$MoO$_{3.5}$S: C, 33.74; H, 6.76; N, 13.12. Found: C, 33.61; H, 6.83; N, 12.93.

5-^{15}*N*$_2$. This complex was synthesized in a manner analogous to the preparation of **5**: ^{15}N NMR (THF-d_8) δ 374.81 (d, $^1J_{\mathrm{NN}}$ = 12), 157.15 (d, $^1J_{\mathrm{NN}}$ = 12).

{[N(CH$_2$CH$_2$NSiMe$_3$)$_2$(CH$_2$CH$_2$NMe$_2$)]MoN$_2$TMS}OTf (6). After isolation of **5** from the reaction mixture, pentane was added to the mother liquor, and the solution was then cooled to −20 °C. The resulting red solid was subjected to a second crystallization from THF/pentane to give **6** as a pink-red solid: ^{1}H NMR (THF-d_8) δ 4.17 (m, 2, NCH$_2$CH$_2$N), 3.93 (m, 2, NCH$_2$CH$_2$N), 3.35 (m, 2, NCH$_2$CH$_2$N), 3.24 (m, 4, NCH$_2$CH$_2$N), 2.96 (m, 2, NCH$_2$CH$_2$N), 2.76 (s, 6, N(CH$_3$)$_2$), 0.34 (s, 27, NTMS); ^{13}C{^{1}H} NMR (THF-d_8) δ 61.42 (NCH$_2$CH$_2$N), 54.79 (NCH$_2$CH$_2$N), 54.40 (NCH$_2$CH$_2$N), 51.38 (NCH$_2$CH$_2$N), 48.26 (N(CH$_3$)$_2$), 2.99 (NTMS), 2.57 (NTMS). Anal. Calcd for C$_{18}$H$_{45}$F$_3$Si$_3$N$_6$MoO$_3$S: C, 32.62; H, 6.84; N, 12.68. Found: C, 32.59; H, 6.93; N, 12.56.

6-^{15}*N*$_2$ was synthesized in an analogous manner: ^{15}N NMR (THF-d_8) δ 361.50 (d, $^1J_{\mathrm{NN}}$ = 13), 244.34 (d, $^1J_{\mathrm{NN}}$ = 13).

[N(CH$_2$CH$_2$NSiMe$_3$)$_2$(CH$_2$CH$_2$NMe$_2$)]Mo{N$_2$TMS}(CH$_3$) (7). {[N(CH$_2$CH$_2$NSiMe$_3$)$_2$(CH$_2$CH$_2$NMe$_2$)]MoN$_2$TMS}OTf (200 mg, 0.302 mmol) was dissolved in 5 mL of diethyl ether, and the solution was cooled to −20 °C. MeMgCl (96 μL, 3.14M) was added dropwise to the stirred solution. After 20 min, the solvent was removed in vacuo and the residue was extracted with pentane. The extract was filtered through Celite, and the pentane was removed from the filtrate in vacuo to give the product as an orange-red solid: yield 153 mg (96%); ^{1}H NMR (C$_6$D$_6$) δ 3.54 (t, 1, CH$_2$), 3.49 (t, 1, CH$_2$), 3.35 (t, 1, CH$_2$), 3.31 (t, 1, CH$_2$), 2.97 (t, 2, CH$_2$), 2.43 (t, 4, CH$_2$), 2.03 (t, 2, CH$_2$), 1.90 (s, 6, NCH$_3$), 0.74 (s, 3, MoCH$_3$), 0.53 (s, 18, NTMS), 0.50 (s, 9, NTMS); ^{13}C NMR (C$_6$D$_6$) δ 53.84 (t, J_{CH} = 138, NCH$_2$CH$_2$N), 52.86 (t, J_{CH} = 138, NCH$_2$CH$_2$N), 52.08 (t, J_{CH} = 134, NCH$_2$CH$_2$N), 51.65 (t, J_{CH} = 138, NCH$_2$CH$_2$N), 45.93 (q, J_{CH} = 135, CH$_3$NNCH$_3$), 23.92 (q, J_{CH} = 121, MoCH$_3$), 3.90 (q, J_{CH} = 118, NTMS), 3.56 (q, J_{CH} = 118, NTMS); IR (Nujol) 1640 cm^{-1} (N═N). Anal. Calcd for C$_{18}$H$_{48}$Si$_3$N$_6$Mo: C, 40.88; H, 9.15; N, 15.89. Found: C, 40.72; H, 8.97; N, 15.55.

7-^{15}*N*$_2$ was synthesized in an analogous manner: ^{15}N NMR (C$_6$D$_6$) δ 374.62 (d, $^1J_{\mathrm{NN}}$ = 15), 239.46 (d, $^1J_{\mathrm{NN}}$ = 15); IR (Nujol) 1577 cm^{-1} (N═N).

[N(CH$_2$CH$_2$NSiMe$_3$)$_2$(CH$_2$CH$_2$NCH$_3$)]Mo{NN(CH$_3$)$_2$}(CH$_3$) (8). A sample of **5** (190 mg) was dissolved in 7 mL of THF, and the solution was cooled to −20 °C. MeMgCl (98 μL, 1.05 mmol in THF) was added to 3 mL of THF, and the solution was cooled to −20 °C. Addition of the MeMgCl solution to the solution of **5** resulted in an immediate change in color from orange to blood red. After 20 min, the solvent was removed in vacuo and the residue was extracted with pentane. The extract was filtered through Celite, and the pentane was removed in vacuo to give the product as a red film: yield 125 mg (90%); ^{1}H NMR (C$_6$D$_6$) δ 3.79−3.72 (m, 1, CH$_2$), 3.66−3.58 (m, 2, CH$_2$), 3.56−3.52 (m, 1, CH$_2$), 3.51 (s, 3, NCH$_3$), 3.30−3.24 (m, 1, CH$_2$), 3.02−2.95 (m, 1, CH$_2$), 2.91−2.89 (m, 2, CH$_2$), 2.84 (s, 6, N(CH$_3$)$_2$), 2.61−2.55 (m, 1, CH$_2$), 2.52−2.46 (m, 1, CH$_2$), 2.38−2.33 (m, 1, CH$_2$), 2.20−2.14 (m, 1, CH$_2$), 0.38 (s, 9, NTMS), 0.27 (s, 9, NTMS), 0.18 (s, 3, MoCH$_3$); ^{13}C NMR (C$_6$D$_6$) δ 67.19 (t, CH$_2$, J_{CH} = 129), 66.21 (t, CH$_2$, J_{CH} = 133), 64.76 (t, CH$_2$, J_{CH} = 136), 60.91 (t, CH$_2$, J_{CH} = 136), 56.29 (t, CH$_2$, J_{CH} = 131), 54.00 (q, NCH$_3$, J_{CH} = 136), 52.94 (t, CH$_2$, J_{CH} = 131), 44.30 (q, N(CH$_3$)$_2$, J_{CH} = 136), 17.79 (q, MoCH$_3$, J_{CH} = 124), 3.01 (q, NTMS, J_{CH} = 118), 2.54 (q, NTMS, J_{CH} = 118). Due to the thermal instability of **8**, a recrystallized sample could not be obtained.

8-^{15}*N*$_2$ was synthesized in a manner analogous to the preparation of **8**: ^{15}N NMR (THF-d_8) δ 354.85 (d, $^1J_{\mathrm{NN}}$ = 12), 141.97 (d, $^1J_{\mathrm{NN}}$ = 12).

[N(CH$_2$CH$_2$NSiMe$_3$)$_2$(CH$_2$CH$_2$NCH$_3$)]Mo≡N (9). A sample of **8** (115 mg, 0.24 mmol) was dissolved in 1.5 mL of C$_6$D$_6$, and the solution was placed in a glass bomb along with a stirring bar. The bomb was sealed, removed from the drybox, and heated to 84 °C for 15 h. The volatile components were vacuum-transferred into an NMR tube, which was then sealed. The bomb was returned to the drybox, the residue was extracted with pentane, and the extract was filtered. The volume of the filtrate was reduced in vacuo, and the solution was chilled to −20 °C to give the product as yellow needles: yield 30 mg (30%); ^{1}H NMR (C$_6$D$_6$) δ 4.08 (s, 3, NCH$_3$), 3.25 (t, 4, NCH$_2$CH$_2$N), 2.78 (t, 2, NCH$_2$CH$_2$N), 2.20−2.00 (m, 6, NCH$_2$CH$_2$N), 0.59 (s, 18, NTMS); ^{13}C NMR (C$_6$D$_6$) δ 60.38 (q, NCH$_3$), 59.73 (t, NCH$_2$CH$_2$N), 52.77 (t, NCH$_2$CH$_2$N), 51.17 (t, NCH$_2$CH$_2$N), 49.81 (t, NCH$_2$CH$_2$N), 3.18 (q, NTMS); IR (Nujol) 1002 cm^{-1} (Mo≡N). Anal. Calcd for C$_{13}$H$_{33}$Si$_2$N$_5$Mo: C, 37.94; H, 8.08; N, 17.02. Found: C, 37.96; H, 7.51; N, 16.69.

9-^{15}*N*$_2$ was synthesized in a manner analogous to that described for **9**: ^{15}N NMR (C$_6$D$_6$) δ 866.08 (s); IR (Nujol) 977 cm^{-1} (Mo≡N).

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Supporting Information Available: X-ray crystallographic files, in CIF format, for complexes **5**−**7** are available on the Internet only. Access information is given on any current masthead page. Supporting Information for compounds **1** and **2** was submitted with the preliminary communication.[10]

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