Synthesis of Molybdenum and Tungsten Complexes That Contain Triamidoamine Ligands of the Type $(C_6F_5NCH_2CH_2)_3N$ and Activation of Dinitrogen by Molybdenum

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Abstract: Three new ligands of the type $(ArNHCH_2CH_2)_3N$ (Ar = 3,5-bis(trifluoromethyl)phenyl, 2-(trifluoromethyl)-phenyl, and pentafluorophenyl) have been prepared. Only Mo and W complexes containing the $[(C_6F_5NCH_2CH_2)_3N]^{3-}$ ($[N_3N]^{3-}$) ligand were found to be stable. Stable complexes that have been prepared include $Mo[N_3N](NMe_2)$, $M[N_3N]Cl$ (M = Mo or W), $Mo[N_3N](OTf)$ (M = Mo or W), $[N_3N]M{\equiv}N$ (M = Mo or W), and $\{[N_3N]Mo{=}NMe\}$-(OTf). An X-ray study of $Mo[N_3N]Cl$ showed it to be a monomeric distorted trigonal bipyramidal species having a pseudo-C_3 symmetry (space group $P\bar{1}$, a = 11.265(2) Å, b = 11.371(2) Å, c = 21.805(4) Å, α = 82.40(1)°, β = 79.07(1)°, γ = 74.89(1)°, V = 2637.4 Å^3, Z = 4, fw = 772.75, ρ(calcd) = 1.946 g/cm^3, R = 0.032, R_w = 0.034). Reduction of $Mo[N_3N](OTf)$ with 1 equiv of sodium amalgam yields a dinuclear bridging dinitrogen species, $[N_3N]Mo(\mu-N_2)Mo[N_3N]$. In the presence of 2 equiv of sodium amalgam in ether $Mo[N_3N](OTf)$ is reduced to $[N_3N]Mo(N_2)[Na(ether)_x]$ ($1 < x < 2$). A more stable 15-crown-5 derivative can be prepared and more fully characterized. $[N_3N]Mo(\mu-N_2)Mo[N_3N]$ can be reduced to $[N_3N]Mo(N_2)[NaL_x]$ by sodium amalgam under dinitrogen and the latter can be oxidized to the former by ferrocenium triflate or air. $[N_3N]Mo(N_2)[NaL_x]$ reacts with $Mo[N_3N](OTf)$ to give $[N_3N]Mo(\mu-N_2)Mo[N_3N]$, with triisopropylsilyl chloride to give $[N_3N]MoN{=}NSi(i\text{-}Pr)_3$, and with tributyltin chloride to give $[N_3N]MoN{=}NSn(Bu)_3$. An X-ray study of $[N_3N]MoN{=}NSi(i\text{-}Pr)_3$ (space group $P2_1/n$, a = 13.524(3) Å, b = 18.016(4) Å, c = 16.248(3) Å, β = 98.74(2)°, V = 3913(1) Å^3, Z = 4, fw = 922.67, ρ(calcd) = 1.566 g/cm^3, R = 0.069, R_w = 0.072) showed it to be a trigonal bipyramidal complex containing a slightly bent diazenido ligand (Mo–N_α = 1.788(9) Å, Mo–N_α–N_β = 171.1(8)°, N_α–N_β–Si = 154(1)°).

Introduction

Ligands of the type $[RNCH_2CH_2)_3N]^{3-}$ (R = H[1], methyl[2], benzyl,[3] or trialkylsilyl[1,4-7]) have been found to form complexes with first,[5,8] second,[8] or third[6,7] row transition metals or main group elements.[9-11] These tetradentate "triamidoamine" ligands[12] yield relatively rigid distorted trigonal bipyramidal transition metal complexes when the amine coordinates to the metal in an apical position. When R is a sterically bulky group such as trimethylsilyl or *tert*-butyldimethylsilyl, rarely observed types of complexes can be prepared, e.g., a tantalum phosphinidene,[6] a titanium(IV) hydride,[5] a V=NH complex,[13] a Ta=Se or Ta=Te complex,[7] or an iron(IV) cyanide complex.[14] "Trigonal monopyramidal" complexes also can be prepared (for first row metals Ti through Fe[4]), i.e., complexes that have no ligand in the apical site trans to the amine donor.

In the last few years we have been studying the activation of dinitrogen[15-18] and NH_x derivatives by high oxidation state complexes that contain Nb or Ta,[19] Mo or W,[20-23] or Re.[24] Most recently we have concentrated on systems that contain the MCp^*Me_3 core (M = W, Mo, or Re; $Cp^* = \eta^5\text{-}C_5Me_5$). When the MCp^*Me_3 fragment assumes a square pyramidal shape with an empty basal coordination site, then N_2H_x fragments can be stabilized in an asymmetric manner employing two π bonding orbitals and one σ bonding orbital. Trigonal monopyramidal complexes that contain tetradentate $[(RNCH_2CH_2)_3N]^{3-}$ ligands also have a $2\pi,1\sigma$ set of orbitals directed toward the apical position. Therefore we felt that high oxidation state complexes that contain $[(RNCH_2CH_2)_3N]^{3-}$ ligands have the potential to bind and activate dinitrogen and its partially hydrogenated (N_2H_x) derivatives. Attempts to synthesize $[(RNCH_2CH_2)_3N]^{3-}$ derivatives of molybdenum and tungsten in which R is a silyl group so

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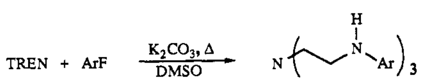
(1) Gudat, D.; Verkade, J. G. *Organometallics* **1989**, *8*, 2772.
(2) Lensink, C.; Xi, S. K.; Daniels, L. M.; Verkade, J. G. *J. Am. Chem. Soc.* **1989**, *111*, 3478.
(3) Naiini, A. A.; Menge, W. M. P. B.; Verkade, J. G. *Inorg. Chem.* **1991**, *30*, 5009.
(4) Cummins, C. C.; Lee, J.; Schrock, R. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *32*, 1501.
(5) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Organometallics* **1992**, *11*, 1452.
(6) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 756.
(7) Christou, V.; Arnold, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1450.
(8) Plass, W.; Verkade, J. G. *J. Am. Chem. Soc.* **1992**, *114*, 2275.
(9) Verkade, J. G. *Acc. Chem. Res.* **1993**, *26*, 483.
(10) Wan, Y.; Verkade, J. G. *Inorg. Chem.* **1993**, *32*, 79.
(11) Pinkas, J.; Gaul, B.; Verkade, J. G. *J. Am. Chem. Soc.* **1993**, *115*, 3925.
(12) Verkade[3] has called titanium complexes, for example, that contain the $(OCH_2CH_2N)_3N$ ligand "titanatranes" and titanium complexes that contain the $(RNCH_2CH_2N)_3N$ ligand "azatitanatranes". We prefer the more generic description of ligands of this type.
(13) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1994**, *33*, 1448.
(14) Cummins, C. C.; Schrock, R. R. *Inorg. Chem.* **1994**, *33*, 395.
(15) Shilov, A. E. In *Energy Resources through Photochemistry and Catalysis*; Gratzel, M., Ed.; Academic Press: New York, 1983; p 535.
(16) Leigh, G. J. *J. Mol. Catal.* **1988**, *47*, 363.
(17) Henderson, R. A. *Transition Met. Chem.* **1990**, *15*, 330.
(18) Pelikan, P.; Boca, R. *Coord. Chem. Rev.* **1984**, *55*, 55.
(19) Rocklage, S. M.; Turner, H. W.; Fellmann, J. D.; Schrock, R. R. *Organometallics* **1982**, *1*, 703.
(20) O'Regan, M. B.; Liu, A. H.; Finch, W. C.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 4331.
(21) Schrock, R. R.; Glassman, T. E.; Vale, M. G.; Kol, M. *J. Am. Chem. Soc.* **1993**, *115*, 1760.
(22) Glassman, T. E.; Vale, M. G.; Schrock, R. R. *Organometallics* **1991**, *10*, 4046.
(23) Vale, M. G.; Schrock, R. R. *Inorg. Chem.* **1993**, *32*, 2767.
(24) Vale, M. G.; Schrock, R. R. *Organometallics* **1993**, *12*, 1140.

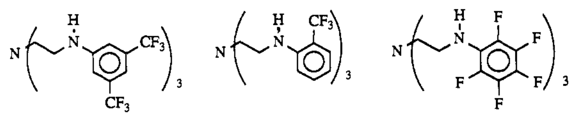
0002-7863/94/1516-4382$04.50/0

far have met with limited success, although a bimetallic dinitrogen complex has been prepared in low yield when R is a *tert*-butyldimethylsilyl group.[25] We felt that a triamidoamine ligand that might be amenable to forming high oxidation state Mo or W complexes would be one in which R is an electron-withdrawing aromatic ring. Complexes containing such ligands should be more resistant to reactions that result in loss of silyl groups from the amido nitrogen atoms and the aromatic ring should be sufficiently bulky to protect the position trans to the amine donor ligand and prevent rapid intermolecular decomposition reactions. In this paper we describe the synthesis of three such ligands and a variety of molybdenum and tungsten complexes that contain one of them. Perhaps the most interesting finding is that dinitrogen can be activated to give either a bridging dinitrogen complex or a terminal dinitrogen complex, and that the two can be interconverted in a redox process.

Results

Synthesis of Ligands and Some $[N_3N]MX$ Complexes (M = Mo or W). 2,2′,2″-Tris[(3,5-bis(trifluoromethylphenyl)amino]-triethylamine, 2,2′,2″-tris[(2-(trifluoromethyl)phenyl)amino]triethylamine, and 2,2′,2″-tris[(pentafluorophenyl)amino]triethylamine were prepared by nucleophilic attack by 2,2′,2″-triaminotriethylamine (TREN) on the corresponding electron-deficient arenes (eq 1).[26] The yields of $H_3[N_3NF18]$ and

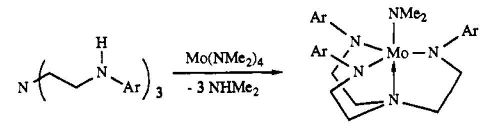

(1)



$H_3[N_3NF18]$ $H_3[N_3NF9]$ $H_3[N_3N]$

$H_3[N_3N]$ are high and reactions can be carried out on a 50–100-g scale. $H_3[N_3NF9]$ is obtained in lower yield, perhaps because longer reaction times are required to drive the reaction to completion and therefore more side reactions take place to a more significant degree. Standard workup followed by flash vacuum chromatography on alumina proved to be an efficient method of purifying up to 50 g of $H_3[N_3NF18]$ and $H_3[N_3N]$. $H_3[N_3NF9]$ was obtained in a yield of 28% after a similar chromatographic purification. All three TREN derivatives are white crystalline solids that are highly soluble in ether but only slightly soluble in hydrocarbon solvents. Stable trilithium salts of these derivatives could not be prepared, most likely because the aromatic ring is subject to further nucleophilic attack. In contrast, trilithium salts of silyl-substituted TREN derivatives can be prepared readily and are highly crystalline and soluble in hydrocarbons.[4,5]

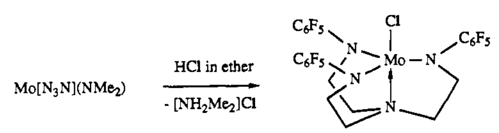
The two approaches we took to prepare complexes that contain the triamidoamine ligands were (i) reaction of the ligands with metal amides and (ii) reaction of the ligands with metal halides in the presence of a base such as triethylamine. The first approach was successful for molybdenum in the case of $H_3[N_3N]$, only partially successful in the case of $H_3[N_3NF18]$, and not successful at all in the case of $H_3[N_3NF9]$. Molybdenum tetrakis-(dimethylamide) reacted with $H_3[N_3NF18]$ in pentane to give $Mo[N_3NF18](NMe_2)$ (**1b**) as a dark green, pentane-soluble crystalline solid that decomposed slowly, even at −35 °C under nitrogen (eq 2). The analogous $[N_3N]^{3-}$ derivative (**1a**) was


(2)

(**1a**) Ar = C_6F_5
(**1b**) Ar = $3,5\text{-}(CF_3)_2C_6H_3$

obtained in a similar manner as a purple, pentane-soluble crystalline solid that exhibited a similar thermal instability. Both complexes are diamagnetic and have 3-fold symmetry on the NMR time scale; the methyl groups in the dimethylamido ligand are equivalent in each case. We believe that **1a** and **1b** are monomers in solution in view of their high solubility and by analogy with the structure of a chloride derivative (see below). Their diamagnetism can be ascribed to the fact that the d_{xz} and d_{yz} orbitals (taking the C_3 axis as the z axis), which are degenerate in C_{3v} symmetry, become inequivalent as a consequence of interaction of the lone electron pair on the dimethylamido ligand with the metal. However, there apparently is insufficient steric hindrance to rotation of the amido ligand about the Mo–N axis, and the methyl groups therefore are equivalent on the NMR time scale.

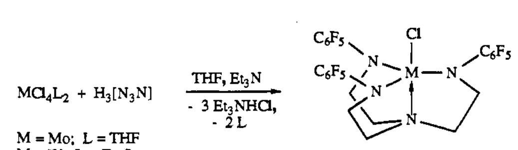
Addition of HCl to **1a** yields a chloride derivative, **2a** (eq 3). In contrast to **1a**, **2a** is paramagnetic, exhibiting only two broad peaks for the methylene protons in the ligand in the high-field


(3)

2a

region of the proton NMR spectrum. The paramagnetic nature of **2a** can be ascribed to the fact that any π bonding between the chloride ligand and the metal would involve both d_{xz} and d_{yz} orbitals equally, so these orbitals consequently are still degenerate. Complex **2a** is soluble in THF, toluene, and dichloromethane, slightly soluble in ether, but insoluble in pentane. Attempts to prepare $Mo[N_3NF18]Cl$ were not successful; only decomposition was observed.

Molybdenum (**2a**) or tungsten (**2b**) chloride complexes containing the $[N_3N]$ ligand can be prepared by the direct reaction between $H_3[N_3N]$ and $MoCl_4(THF)_2$[27] or $WCl_4(Et_2S)_2$,[28] respectively, in the presence of triethylamine (eq 4). Interestingly, **2a** also can be prepared from $MoCl_5$ in moderate yield in the presence of triethylamine (eq 5). In this case the solvent of choice


(4)

2a M = Mo
2b M = W

$$MoCl_5 + H_3[N_3N] \xrightarrow{\text{ether, } Et_3N} \mathbf{2a} \qquad (5)$$

is diethyl ether. The solubility characteristics of **2b** are similar to those of **2a**. Complex **2b**, like **2a**, is paramagnetic, consistent with degeneracy of the d_{xz} and d_{yz} orbitals and resulting high-spin d^2 ground state. The IR spectra of **2a** and **2b** are virtually superimposable. Attempts to prepare analogous Mo or W

(25) Shih, K.-Y.; Kempe, R.; Schrock, R. R. Unpublished results.
(26) Bader, H.; Hansen, A. R.; McCarty, F. J. *J. Org. Chem.* **1966**, *31*, 2319.
(27) Dilworth, J. R.; Richards, R. L.; Chen, G. J.; McDonald, J. W. *Inorg. Synth.* **1980**, *20*, 119.
(28) Schaeffer King, M. A.; McCarley, R. E. *Inorg. Chem.* **1973**, *12*, 1972.

Table 1. Selected Bond Lengths and Bond Angles for the Two Independent Molecules of **2a**

Bond Distances (Å)								
Mo–N(1)	1.962(3)	1.961(3)	Mo–N(3)	1.964(3)	1.978(3)	N(1)–C(1)	1.406(5)	1.395(5)
Mo–N(2)	1.957(3)	1.955(3)	Mo–Cl	2.367(1)	2.365(1)	Mo–N(4)	2.182(3)	2.182(3)
Bond Angles (deg)								
Mo–N(1)–C(1)	127.8(3)	128.1(3)	Cl–Mo–N(3)	100.9(1)	101.5(1)	N(2)–Mo–N(3)	117.4(1)	116.6(1)
Mo–N(2)–C(7)	125.9(3)	125.4(3)	Cl–Mo–N(4)	177.97(9)	177.54(9)	N(1)–Mo–N(4)	80.8(1)	80.6(1)
Mo–N(3)–C(13)	124.6(2)	124.8(3)	N(1)–Mo–N(2)	119.0(1)	119.5(1)	N(2)–Mo–N(4)	80.8(1)	80.6(1)
Cl–Mo–N(1)	99.9(1)	99.5(1)	N(1)–Mo–N(3)	115.9(1)	115.8(1)	N(3)–Mo–N(4)	80.4(1)	80.1(1)
Cl–Mo–N(2)	97.2(1)	97.7(1)				C(22)–N(4)–C(20)	111.4(3)	111.5(3)
Dihedral Angles (deg)								
Cl–Mo–N(1)–C(1)	−5.1(3)	−11.1(3)	Cl–Mo–N(3)–C(13)	9.7(3)	6.7(3)	Mo–N(2)–C(7)–C(12)	−86.4(4)	−82.2(5)
Cl–Mo–N(2)–C(7)	11.8(3)	12.7(3)	Mo–N(1)–C(1)–C(2)	−58.5(5)	−53.5(5)	Mo–N(3)–C(13)–C(14)	−72.3(5)	−71.5(5)

[a] The sign is positive if when looking from atom 2 to atom 3 a clockwise motion of atom 1 would superimpose it on atom 4.

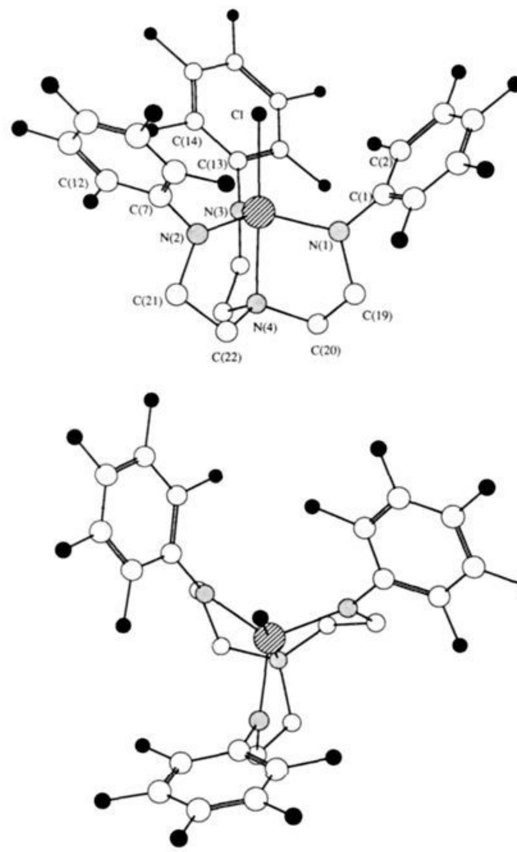


Figure 1. Two views of the structure of one of the two independent molecules of $[(C_6F_5NCH_2CH_2)_3N]MoCl$.

complexes containing $[N_3NF18]^{3-}$ or $[N_3NF9]^{3-}$ ligands by similar methods so far have not been successful.

An X-ray study of **2a** showed it to be approximately a trigonal bipyramid in which the molybdenum atom lies only ~0.32 Å above the plane of the three amido nitrogen atoms. Two views of the structure are shown in Figure 1. Bond lengths and angles for one of the two molecules in the asymmetric unit are listed in Table 1. The amido nitrogens are sp^2 hybridized with the maximum deviation of any nitrogen atom from the plane defined by the three atoms connected to it being 0.13 Å. The pentafluorophenyl rings form a bowl-like cavity around the apical chloride. The $Mo–N_{axial}$ bond length (2.182(3) Å) is significantly shorter than a dative bond in complexes that contain a non-fluorinated substituent bound to the amido nitrogen in the triamidoamine ligand (cf. 2.238(6) Å in $[(Me_3SiNCH_2CH_2)_3N]VCl$,[5] 2.321(6) Å in $[(MeNCH_2CH_2)_3N]V{=}O$,[8] 2.241(6) Å in $[(Me_3SiNCH_2CH_2)_3N]V{=}NH$,[13] 2.488 Å in $[(Me_3SiNCH_2CH_2)_3N]Ta{=}Te$,[7] and 2.29(1) Å in $\{[(t\text{-}BuMe_2SiNCH_2CH_2)_3N]Mo\}_2(\mu\text{-}N_2)$[25]), consistent with a more electron-poor character for the metal and the absence of a multiply-bound ligand trans to the amine donor atom. The $Mo–N_{eq}$ bond lengths also are significantly shorter than one would expect for typical Mo–N single bonds, consistent with some degree of $Mo–N_{eq}$ multiple bond character. Only two π bonds are possible, however. The symmetry of one of the three MO's that are created from the three p orbitals on the nitrogen atoms that lie in the plane defined by the three nitrogen atoms is not matched in symmetry by an orbital on the metal and therefore constitutes a ligand-centered nonbonding orbital. Therefore, the trianionic, tetradentate ligand can be regarded as a $12e^-$ ligand (at most) and **2a** as a $16e^-$ species (at most). It is interesting to note that if the axial amine were to dissociate from the metal, the resulting decrease in electron count could not be compensated by an increase in π bonding, if the complex retains its C_{3v} symmetry.

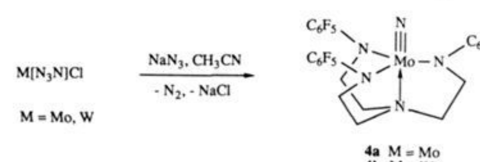
Complexes **2a** and **2b** react with trimethylsilyl triflate to afford the highly insoluble triflate complexes, **3a** and **3b** (eq 6), in high

$$M[N_3N]Cl \xrightarrow[\text{- TMSCl}]{\text{TMSOTf}} M[N_3N](OTf) \qquad (6)$$

3a M = Mo, orange
3b M = W, yellow

yield in 1–3 days. Analytically pure samples can be obtained simply by washing away impurities with dichloromethane and drying the resulting powders in vacuo. The IR spectra of **3a** and **3b** are almost superimposable. The strong triflate absorption at 1198 cm^{-1} is consistent with triflate being coordinated to the metal.[29]

Complexes **2a** and **2b** react with sodium azide to yield the nitride complexes (**4a** and **4b**, respectively) as the only isolable products (eq 7). The reaction is relatively slow, approximately



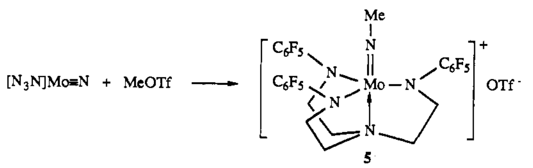
(7)

4a M = Mo
4b M = W

2 days being required for completion. We presume that azide complexes are intermediates from which dinitrogen is lost. (This type of reaction has considerable precedent.[30]) Both **4a** and **4b** are almost colorless solids which crystallize as long needles upon slow diffusion of pentane into a concentrated THF solution. Both are diamagnetic, have 3-fold symmetry on the NMR time scale, and are stable at room temperature in toluene-d_8 under dinitrogen for days. No metal–nitrogen triple bond stretch could be observed in the IR spectrum, as this region (around 1000 cm^{-1}) is masked by strong C–F absorptions. The Mo≡N stretching frequency in closely analogous $[(MeNCH_2CH_2)_3N]Mo{\equiv}N$ is found at 991 cm^{-1}.[8]

(29) Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17.
(30) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988.

Complex **4a** can be alkylated by methyl triflate in toluene to give the methylimido complex **5** in ~90% yield (eq 8). We propose



5 (8)

that **5** is a cationic species on the basis of its salt-like physical properties and 3-fold symmetry (on the NMR time scale). Threefold symmetry suggests that the triamidoamine ligand is tetradentate. It seems more likely that the imido ligand would form a pseudo triple bond with the metal in a cationic species than to remain bent in a complex that also contains coordinated triflate and a tetradentate triamidoamine ligand. Attempts to protonate **4a** with triflic acid or tetrafluoroboric acid were not successful; the expected Mo=NH complex could not be observed, even at −78 °C in CD_2Cl_2.

Synthesis of Dinitrogen Complexes. Reduction of $[(C_6F_5NCH_2CH_2)_3N]Mo(OTf)$ (**3a**) in THF with 1 equiv of sodium amalgam under 1 atm of dinitrogen yields a paramagnetic purple solid (**6**) nearly quantitatively that is only slightly soluble in THF. An analogous product is obtained if lithium amalgam or sodium naphthalenide is used as the reducing agent, but sodium amalgam seems to give the cleanest reactions. If the reduction is conducted under argon or in vacuo, the reaction mixture turns brown slowly, and no **6** can be isolated. The stoichiometry of the reaction and elemental analysis suggest that **6** contains 1 equiv of dinitrogen per two molybdenum atoms (eq 9). Only two broad resonances

$$\underset{\textbf{3a}}{Mo[N_3N](OTf)} \xrightarrow[THF,\ N_2]{1\ equiv\ Na/Hg} \underset{\textbf{6}}{0.5\ [N_3N]Mo(\mu\text{-}N_2)Mo[N_3N]} \quad (9)$$

are observed in the high-field region of the ^1H NMR spectrum (at −21.8 and −14.4 ppm) and no triflate nor N–N peaks are observed in the IR spectrum. Reduction of **3a** under $^{15}N_2$ yielded an analogous product (**6**-$^{15}N_2$). The IR spectrum of **6**-$^{15}N_2$ is virtually identical to the IR spectrum of the $^{14}N_2$ compound; the region where one might expect to see a relatively weak band characteristic of a $M(\mu\text{-}N_2)M$ mode in a high oxidation state dinitrogen complex (~850 cm^{-1})[19,31,32] is too complex. Reduction of **3b** under conditions similar to those that yield **6** from **3a** did not yield any products that could be identified. It should be noted that **6** is nominally a dimer of **4a**, yet the two do not appear to interconvert readily.

When **3a** is reduced under dinitrogen in THF, dimethoxyethane, or ether by two or more equivalents of sodium amalgam, the final product (after recrystallization from ether) is a diamagnetic, red solid that we propose is a sodium derivative of the "molybdenum(II) dinitrogen complex", "$[Mo[N_3N](N_2)]^-$" (**7a**, eq 10).

$$\underset{\textbf{3a}}{Mo[N_3N](OTf)} \xrightarrow[THF,\ N_2,\ ether]{2\ equiv\ Na/Hg} \underset{\textbf{7a}}{[N_3N]Mo(N_2)[Na(ether)_x]} \quad (10)$$

Reduction of **6** with 1 equiv of sodium amalgam under dinitrogen also yields **7a** quantitatively. **7a** is stable only in the presence of coordinating solvents such as THF, DME, or ether; it decomposes upon attempted dissolution in noncoordinating solvents such as toluene and is extremely sensitive to oxidation by air to give **6**. Plate-like red crystals could be grown from a mixture of ether and pentane, but elemental analyses were variable and in general were too low in nitrogen. We suspect that **7a** loses ether and/or dinitrogen in vacuo or is simply too air sensitive to analyze accurately. Part of the problem may be associated with the fact that the amount of ether present in crystalline samples varied from sample to sample (according to NMR spectra); the amount was always greater than 1 equiv and was usually less than 2 equiv. The ether can be replaced by other solvents; for example, when the THF-d_8 was removed from a sample of **7a** in vacuo and the spectrum recorded again in THF-d_8, no ether was observed. Unfortunately, samples containing THF or DME did not appear to be any more stable than **7a**. According to quenching experiments with electrophiles (see below) we can be confident that **7a** forms in 75–80% yield. Proton NMR spectra of **7a** in THF-d_8 show ligand resonances in the normal region for a diamagnetic 3-fold symmetric complex at 3.86 (6, t, J = 5.2 Hz) and 2.64 ppm (6, t, J = 5.4 Hz). Oxidation of **7a** by ferrocenium triflate yielded **6**. Oxidation of **7a** by slow reaction with oxygen in a capped NMR tube over a period of 2 days also yielded **6**, although **6** also decomposed upon further exposure to air. IR spectra of **7a** show a strong absorption at 1769 cm^{-1} that can be ascribed to ν_{NN} in a non-centrosymmetric environment.

A relatively stable derivative, $[N_3N]Mo(N_2)[Na(15\text{-crown-}5)]$ (**7b**), can be obtained by adding 15-crown-5 to **7a**. The elemental analytical data for **7b** (including sodium analysis) are consistent with the proposed formulation, although the analysis for nitrogen is still low. The IR spectrum of **7b** shows ν_{NN} at 1848 cm^{-1}. Because the values for ν_{NN} in **7a** and **7b** are so different, but not as low as diazenido derivatives (see below), we hesitate to propose that the sodium is bound covalently to N_β. In fact the value of ν_{NN} for **7a** is much closer to that of the anionic vanadium complexes, $[Na][V(N_2)_2(dmpe)_2]$[33] (1763 cm^{-1}) or $[Na(THF)][V(N_2)_2(dppe)_2]$ (1790 cm^{-1}),[34] than neutral mononuclear dinitrogen complexes of the type *trans*-$[Mo(N_2)_2(dppe)_2]$ (2020, 1970 cm^{-1})[35] or *trans*-$[MoCl(N_2)(dppe)_2)]^+$ (1966 cm^{-1}).[36] A crystal structure of $[Na(THF)][V(N_2)_2(dppe)_2]$ (1790 cm^{-1})[34] revealed that the sodium ion is 2.45 Å from the metal, a distance that the authors proposed was consistent with a contact ion pair. Therefore we feel that "ionic" descriptions of **7a** and **7b** may be more valid. Unfortunately, no crystals suitable for X-ray studies have yet been obtained.

Reactions between **7a** and electrophiles are consistent with the nucleophilic character of the β nitrogen atom. For example, **7a** reacts with **3a** to produce **6** (eq 11). Triisopropylsilyl chloride reacts with **7a** to give diamagnetic **8a** (eq 12). Highly soluble

$$\underset{\textbf{7a}}{[N_3N]Mo(N_2)[Na(ether)_x]} + \underset{\textbf{3a}}{Mo[N_3N](OTf)} \longrightarrow \underset{\textbf{6}}{[N_3N]Mo(\mu\text{-}N_2)Mo[N_3N]} \quad (11)$$

$$\underset{\textbf{7a}}{[N_3N]Mo(N_2)[Na(ether)_x]} + (i\text{-}Pr)_3SiCl \longrightarrow \underset{\textbf{8a}}{[N_3N]Mo\text{-}N{=}N\text{-}Si(i\text{-}Pr)_3} \quad (12)$$

8a can be isolated by extracting the crude reaction mixture with pentane. The ^1H, ^{13}C, ^{29}Si, and ^{19}F NMR spectra of **8a**, as well as its IR spectrum (a strong band at 1687 cm^{-1}), are all consistent with its formulation as a diazenido derivative. The ^{15}N NMR spectrum of **8a**-$^{15}N_2$ showed two doublets at 366 and 228 ppm (J_{NN} = 15 Hz) corresponding to the α and β nitrogens of the diazenido ligand, respectively,[37] while the IR spectrum of **8a**-$^{15}N_2$ showed that the absorption attributable to an N–N stretch had shifted to lower values (1628 cm^{-1} with a shoulder at 1658 cm^{-1}), as expected. Reduction of **6**-$^{15}N_2$ by sodium amalgam under $^{14}N_2$ followed by addition of excess $(i\text{-}Pr)_3SiCl$ yielded a 1:1 mixture of **8a**-$^{15}N_2$ and **8a**-$^{14}N_2$ (by IR) that was identical

(31) Rocklage, S. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 3077.
(32) Turner, H. W.; Fellmann, J. D.; Rocklage, S. M.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1980**, *102*, 7809.
(33) Woitha, C.; Rehder, D. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1438.
(34) Rehder, D.; Woitha, C.; Priebsch, W.; Gailus, H. *J. Chem Soc., Chem. Commun.* **1992**, 364.
(35) Hidai, M.; Tominari, K.; Uchida, Y.; Misono, A. *Inorg. Synth.* **1975**, *15*, 25.
(36) Day, V. W.; George, T. A.; Iske, S. D. A. *J. Am. Chem. Soc.* **1975**, *97*, 4127.
(37) Haymore, B. L.; Hughes, M.; Mason, J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1988**, 2935.

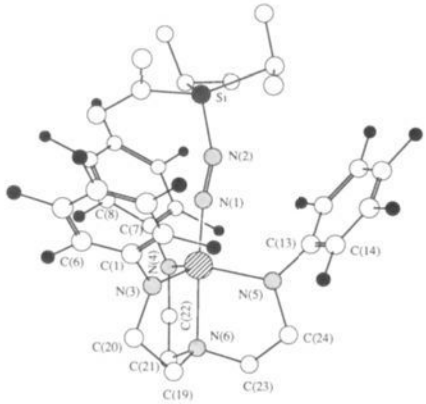


Figure 2. Structure of $[(C_6F_5NCH_2CH_2)_3N]MoN{=}NSi(i\text{-}Pr)_3$.

Table 2. Selected Bond Lengths, Bond Angles, and Dihedral Angles for **8a**

Bond Distances (Å)

Mo–N(1)	1.788(9)	Mo–N(3)	1.978(9)	Mo–N(5)	2.001(9)
N(1)–N(2)	1.20(1)	Mo–N(4)	1.987(9)	Mo–N(6)	2.218(9)
N(2)–Si	1.67(1)			N(4)–C(7)	1.39(2)

Bond Angles (deg)

Mo–N(1)–N(2)	171.1(8)	N(3)–Mo–N(4)	119.6(4)
Mo–N(3)–C(1)	126.9(8)	N(3)–Mo–N(5)	116.4(4)
Mo–N(4)–C(7)	124.6(7)	N(4)–Mo–N(5)	116.2(4)
Mo–N(5)–C(13)	127.3(9)	N(3)–Mo–N(6)	80.3(4)
N(1)–N(2)–Si	154(1)	N(4)–Mo–N(6)	80.1(4)
N(1)–Mo–N(3)	102.1(4)	N(5)–Mo–N(6)	81.5(4)
N(1)–Mo–N(4)	96.4(4)	C(22)–N(4)–C(7)	117.4(9)
N(1)–Mo–N(5)	99.5(4)	C(20)–N(3)–C(1)	117.1(9)
N(1)–Mo–N(6)	176.4(4)	C(24)–N(5)–C(13)	116(1)

Dihedral Angles (deg)

N(1)–Mo–N(3)–C(1)	−6(1)	Mo–N(3)–C(1)–C(2)	−69(1)
N(1)–Mo–N(5)–C(13)	−3(1)	Mo–N(4)–C(7)–C(8)	−65(1)
N(1)–Mo–N(4)–C(7)	0(1)	Mo–N(5)–C(13)–C(14)	108(1)

[a] The sign is positive if when looking from atom 2 to atom 3 a clockwise motion of atom 1 would superimpose it on atom 4.

(by IR) to an authentic mixture of **8a**-$^{15}N_2$ and **8a**-$^{14}N_2$ (eq 13).

$$[N_3N]Mo(\mu\text{-}^{15}N_2)Mo[N_3N]\ (\mathbf{6}\text{-}^{15}N_2) \xrightarrow[\text{2. excess (i-Pr)}_3\text{SiCl}]{\text{1. Na/Hg; }^{14}N_2\text{ atm}} [N_3N]Mo\text{-}^{14}N{=}^{14}N\text{-}Si(i\text{-}Pr)_3 + [N_3N]Mo\text{-}^{15}N{=}^{15}N\text{-}Si(i\text{-}Pr)_3 \quad (13)$$

This experiment proves that **6** contains one dinitrogen per two molybdenum atoms and also suggests that exchange between free and coordinated dinitrogen in **6** or **8** is slow ($\gg \sim 25$ min). Tri-*n*-butyltin chloride reacts rapidly with **7a** to yield a diamagnetic tributyltin derivative (**8b**) analogous to **8a** ($\nu_{NN} = 1692$ cm^{-1}). However, **8b** is unstable at room temperature, decomposing over a period of several hours to give **6** as the only identifiable product.

An X-ray study of **8a** revealed it to have the structure shown in Figure 2. Selected bond distances, angles, and dihedral angles are listed in Table 2. The most notable features of the structure are a short Mo–N_α distance (1.788(9) Å), an almost linear Mo–N_α–N_β angle (171.1(8)°), a short N_α–N_β bond (1.20(1) Å), and a N_α–N_β–Si angle of 154(1)°, all of which suggest that this compound belongs to the general category of singly bent diazenido complexes.[37] The short N–Si bond (1.67(1) Å) suggests some $p\pi$–$d\pi$ interaction between nitrogen and silicon. Similar bond lengths and angles were found for $[WI(NNSiMe_3)(PMe_2Ph)_4]$.[38] The molybdenum–ligand core in **8a** is similar to that of the Mo[N_3N]Cl, except the four ligand Mo–N bonds are all slightly longer in **8a**, perhaps because the metal in **8a** is not as electron poor as the metal in **2a**. The triisopropylsilyl unit caps the cavity that contains the N_2 fragment, and the three isopropyl groups lie more or less over the three C_6F_5 rings (view not shown), not between the rings, which one might have expected on steric grounds.

8a could not be reduced readily by hydrogen gas, hydrazine, or lithium aluminum hydride. It could be oxidized to **3a** quantitatively by 2 equiv of ferrocenium triflate, but **6** could not be identified as an intermediate in the oxidation pathway. Addition of cesium fluoride to **8a** in THF at 25 °C yielded a red solution after 12 h, which when quenched with trimethylsilyl chloride yielded a product that (by ^{1}H NMR) consisted of a 1:1 mixture of **8a** and the analogous trimethylsilyl derivative (eq 14). We presume that the cesium analog of **7a** is the intermediate in this reaction.

$$\underset{\mathbf{8a}}{[N_3N]Mo\text{-}N{=}N\text{-}Si(i\text{-}Pr)_3} \xrightarrow[\text{2. TMSCl}]{\text{1. CsF}} \underset{\mathbf{8c}}{[N_3N]Mo\text{-}N{=}N\text{-}SiMe_3} \quad (14)$$

Discussion

The most interesting of the reactions described here is the formation of dinitrogen complexes upon reduction of **3a**. An important question is when does dinitrogen coordinate to molybdenum? One possibility is that dinitrogen binds to the one electron reduction product (after triflate ion is lost), i.e., "Mo[N_3N]". "Mo[N_3N]" is the second row analog of Cr[(t-BuMe$_2$SiNCH$_2$CH$_2$)$_3$N], a member of a series of d^3 trigonal monopyramidal high-spin complexes of that type that have been prepared for the first row metals Ti through Fe.[4] If two electrons were transferred from the metal to the dinitrogen, a cationic Mo(V) center and a negatively-charged β nitrogen atom would be a valid description, as shown in eq 15. Subsequent attack by N_β on **3a** followed by addition of a second electron would yield **6** (eq 16). This mechanism is analogous to that proposed for formation of $Cp^*Me_3W{=}NN{=}WCp^*Me_3$ upon reduction of $Cp^*WMe_3(OTf)$ by sodium amalgam under dinitrogen,[20] except that dinitrogen is activated at a d^3 Mo center instead of a d^2 W center. A second possibility is that Mo[N_3N] is reduced rapidly by a second electron to give "$\{Mo[N_3N]\}^-$" before dinitrogen is bound to give **7a** (eq 17). In this scenario dinitrogen would be activated by a d^4 Mo(II) center. The reaction between **7a** and **3a** would then give **6**. Although it has long been presumed that more highly reduced metal complexes will bind dinitrogen more rapidly, in part because the vast majority of *isolated* dinitrogen complexes contain the metal in a low oxidation state (zerovalent in typical Mo or W tetraphosphine dinitrogen complexes studied primarily by Hidai and Chatt and co-workers[39–41]), quantitative data that support that view are lacking. In short, it is not possible at this stage to choose between activation of dinitrogen by d^3 Mo[N_3N] or by d^4 $\{Mo[N_3N]\}^-$. (A similar ambiguity exists over activation of dinitrogen by d^2 WCp^*Me_3 and d^3 "$[WCp^*Me_3]^-$", although the possibility shown in eq 18 was not considered at the time.[20])

$$Mo[N_3N] + N_2 \longrightarrow [N_3N]Mo(N_2) \text{ or } [N_3N]\overset{(+)}{Mo}\text{-}N{=}\overset{(-)}{N} \quad (15)$$

$$[N_3N]\overset{(+)}{Mo}\text{-}N{=}\overset{(-)}{N} + Mo[N_3N](OTf) \xrightarrow{-\,OTf^-} \{[N_3N]Mo\text{-}N{=}N\text{-}Mo[N_3N]\}^+ \xrightarrow{1e} \mathbf{6} \quad (16)$$

$$Mo[N_3N] \xrightarrow{1e} \{Mo[N_3N]\}^- \xrightarrow{N_2} \{Mo[N_3N](N_2)\}^- \quad (17)$$

$$Cp^*WMe_3(OTf) \xrightarrow[-\,OTf^-]{+\,2e\,+\,N_2} [Cp^*WMe_3(N_2)]^- \xrightarrow[-\,OTf^-]{Cp^*WMe_3(OTf)} [Cp^*WMe_3]_2(\mu\text{-}N_2) \quad (18)$$

Questions concerning the spin state of d^3 Mo[N_3N] or d^4 $\{Mo[N_3N]\}^-$ cannot yet be addressed. (We feel that a low-spin

(38) Hidai, M.; Komori, K.; Kodama, T.; Jin, D.; Takahashi, T.; Sugiura, S.; Uchida, Y.; Mizobe, Y. *J. Organomet. Chem.* **1984**, *272*, 155.

(39) Richards, R. L. *Chem. Br.* **1988**, *24*, 133.
(40) Leigh, G. J. *Acc. Chem. Res.* **1992**, *25*, 177.
(41) Henderson, R. A.; Leigh, G. J.; Pickett, C. J. *Adv. Inorg. Chem. Radiochem.* **1983**, *27*, 197.

configuration having a highly electrophilic orbital may be an important feature of dinitrogen activation.) Some circumstantial evidence that dinitrogen is reduced at a Mo(II) center is that the tungsten analog of **3a** reacts with sodium amalgam, but dinitrogen complexes analogous to **6** or **7a** have not yet been observed. In contrast, in the Cp*MMe_3 system it is reduction of Cp*WMe_3(OTf) under dinitrogen that succeeds and reduction of Cp*$MoMe_3$(OTf) that fails. We do not ascribe any great significance to these apparent contradictions, as the rate of side reactions is often the limiting feature of homologous chemistry, and we know relatively little about side reactions in either system.

To our knowledge interconversion of a dinuclear "μ-dinitrogen" complex (**6**) and a mononuclear "terminal dinitrogen" complex (**7a**) in a redox process (one electron per metal) has not been observed before. So-called tungsten(VI) and molybdenum(VI) hydrazido(4–) complexes that contain Cp*MMe_3 moieties at each end of dinitrogen are not reduced by sodium amalgam;[20,42] therefore such species become "sinks" as far as dinitrogen reduction is concerned. A detail of the reduction of **6** or the oxidation of **7a** that may be important is whether the amine donor in the triamidoamine ligand remains bound at all times. For example, we have found via an X-ray study that the amine donor in $Ta[(Me_3SiNCH_2CH_2)_3N](Me)(OTf)$ is *not* bound to the metal.[43] Dissociation of the apical amine donor would have profound steric and electronic implications as far as reactions of $Mo[N_3N]X$ complexes in general are concerned. Interestingly, attempts to model **6** using bond distances found in the structure of $Mo[N_3N]Cl$ resulted in severe nonbonding repulsions between the pentafluorophenyl rings. Such repulsions could be minimized by dissociating the amine donor and forming approximately a tetrahedral coordination geometry about molybdenum. Therefore we must consider the possibility that amine dissociation is an important feature of reactions involving triamidoamine ligands, although at present we have no evidence other than that cited above for tantalum to support that hypothesis. Whether the apical nitrogen is coordinated or not is known to have important consequences in main group "azaatrane" chemistry.[9]

The paramagnetism of **6** can be rationalized readily. Two sets of degenerate (orthogonal) π molecular orbitals can be constructed from two d orbitals and two p orbitals on each nitrogen atom into which 10 π electrons must be placed, which leaves two unpaired electrons in the orbital set with the third highest energy. Extended Hückel calculations on "$[Mo(NH_2)_3(NH_3)]_2(\mu\text{-}N_2)$" (two ends staggered) using bond distances and angles for the MoN_4 core found in **2a** and Mo—N=N—Mo distances found in $[Mo(t\text{-}BuMe_2SiNCH_2CH_2)_3N]_2(\mu\text{-}N_2)$[25] were consistent with this point of view. The occupied π orbitals of the idealized S6 fragment which appear in Figure 3 consist of doubly degenerate sets. (The degenerate set of totally symmetric occupied MO's is not shown.) The lower set of orbitals (HOMO-1) is a bonding combination of molybdenum d_{xz} and d_{yz} with the π* orbitals of dinitrogen. The higher set (HOMO) is mostly d_{xz} and d_{yz} in character, with a small antibonding contribution from the dinitrogen π orbitals. The degeneracy of the latter set is responsible for the paramagnetic character of **6**. Reduction of **6** by two electrons would fill the HOMO level and lead to Mo–N antibonding interactions, a consequence that may in part be responsible for Mo–N cleavage to give **7a**. As we noted above, dissociation of the apical amine may be an important feature of reduction of **6** that we have not taken into account in this analysis.

An interesting finding that should be compared with the reducibility of **6** is that $[Mo(t\text{-}BuMe_2SiNCH_2CH_2)_3N]_2(\mu\text{-}N_2)$ is not reduced by sodium amalgam readily.[25] Therefore pentafluorophenyl substituents may be required for facile reduction of **6** and Mo–N cleavage; they lower the energy of the partially

(42) Schrock, R. R.; Kolodziej, R. M.; Liu, A. H.; Davis, W. M.; Vale, M. G. *J. Am. Chem. Soc.* **1990**, *112*, 4338.
(43) Cummins, C. C. Unpublished results.

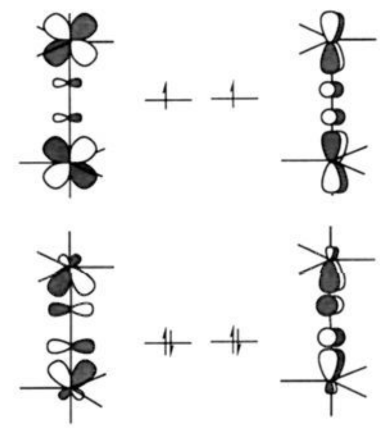


Figure 3. HOMO (–8.0 eV) and HOMO-1 (–10.9 eV) in "$(NH_3)(NH_2)_3Mo(\mu\text{-}N_2)Mo(NH_2)_3(NH_3)$" (staggered configuration) according to extended Hückel calculations.

occupied HOMO and/or provide a pathway for more facile electron transfer.

The structure of nitrogenase in its resting state is now known down to a resolution of 2.2 Å.[44,45] One of the controversies that has been generated as a consequence of the structural findings is whether dinitrogen is reduced at iron centers (two to six) or at the octahedrally coordinated molybdenum at one end of the metal system.[46–48] Molybdenum is coordinated by three sulfurs, a nitrogen donor from a histidine residue, and a chelating homocitrate. The argument against activation by molybdenum centers on its octahedral coordination. What appears to be missing in such arguments is that the coordination number of molybdenum could change upon addition of electrons and protons to the system. Therefore octahedral coordination of molybdenum in the resting state should not preclude reduction of dinitrogen at the molybdenum center, which is a very slow catalytic reaction ($\sim 5\ s^{-1}$) in any case.[29] Another argument against reduction of dinitrogen at molybdenum is that a nitrogenase is known that contains only iron.[49] However, there is nothing wrong with the proposition that there is no single universal mechanism for dinitrogen reduction. It is interesting to point out that the coordination at molybdenum in nitrogenase could be viewed as a "three anion (sulfide) plus one donor (nitrogen)" type of coordination environment that is related to the type that we are exploring here, even though the nitrogen donor does not lie on a C_3 axis in nitrogenase. A working hypothesis is that the homocitrate is labilized by electrons and/or protons in molybdenum nitrogenase during the reduction cycle and that dinitrogen is reduced at what is essentially a "$Mo[S_3N]$" site.

There are many questions raised in this study. The possibility that the apical nitrogen atom in such species can dissociate to form a pyramidal three-coordinate, pseudotetrahedral four-coordinate, or pseudotrigonal bipyramidal five-coordinate species is an unanticipated but potentially extremely important feature of such systems. Even though the equilibrium may lie far toward the form containing a coordinated apical nitrogen, and the "off" rate is not large, (slow) catalytic reactions may still take place at a practical rate, in part also because the metal is stabilized sterically toward intermolecular decomposition reactions when the apical nitrogen is bound. We hope to address such issues in future studies of these and related species containing triamidoamine and related ligands.

(44) Kim, J.; Rees, D. C. *Nature* **1992**, *360*, 553.
(45) Chan, M. K.; Kim, J. S.; Rees, D. C. *Science* **1993**, *260*, 792.
(46) Sellmann, D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 64.
(47) Orme-Johnson, W. H. *Science* **1992**, *257*, 1639.
(48) Deng, H.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1062.
(49) Chisnell, J. R.; Premakumar, R.; Bishop, P. E. *J. Bacteriol.* **1988**, *170*, 27.

Experimental Section

General Procedures. Solvents were dried and degassed prior to use and distilled from molten sodium (toluene), sodium/benzophenone (ether, THF, 1,2-dimethoxyethane, pentane), calcium hydride (dichloromethane), or P_2O_5 (acetonitrile). (Pentane was first washed with 5% HNO_3/H_2SO_4, dried over calcium chloride, and distilled from sodium/benzophenone/tetraglyme.) All metal complex preparations were conducted under a nitrogen atmosphere in a Vacuum Atmospheres drybox, under argon when using Schlenck techniques, or on a high-vacuum line ($<10^{-4}$ Torr). Ligands were prepared using bench-top techniques.

DMSO, 2,2′,2″-triaminotriethylamine, hexafluorobenzene, 2-(trifluoromethyl)fluorobenzene, 3,5-bis(trifluoromethyl)aniline, and anhydrous HCl in ether (1 M) were used as received. Triethylamine was distilled from CaH_2 and stored over 4-Å sieves. $MoCl_4(THF)_2$,[27] $Mo(NMe_2)_4$,[50] and $WCl_4(Et_2S)_2$[28] were prepared according to published procedures. $^{15}N_2$ was purchased from Isotec in a pressurized cylinder and used without further purification. Deuterated solvents were dried by passage through alumina and storage over 4-Å molecular sieves.

NMR operating frequencies and reference standards for heteronuclei on the scale of ^{1}H (300 MHz, $SiMe_4$ = 0 ppm) are as follows: ^{13}C (75.5 MHz, $SiMe_4$ = 0 ppm), ^{15}N (30.40 MHz, NH_2Ph = 56.5 ppm), and ^{19}F (282.21 MHz, $CFCl_3$ = 0 ppm). Proton and carbon spectra were referenced using the partially deuterated solvent as an internal referenece. Fluorine NMR spectra were referenced externally to the compounds indicated in the same solvent where possible. Chemical shifts are in ppm and coupling constants and line widths are in hertz. All spectra were acquired at ~22 °C unless otherwise noted.

All IR spectra were recorded as Nujol mulls between KBr plates in an airtight cell. Microanalyses were performed on a Perkin-Elmer PE2400 microanalyzer or by Schwarzkopf. High resolution mass-spectra were measured on a Finnigan-MAT system 8200 and are reported in (m/z). Melting points were measured in capillaries and are uncorrected.

Preparation of Ligands. 2,2′,2″-Tris[(3,5-bis(trifluoromethyl)phenyl)amino]triethylamine. Hydrochloric acid (160 mL, 6 N) was added to 3,5-bis(trifluoromethyl)aniline (22.9 g, 100 mmol). The solution was cooled to 0–5 °C and sodium nitrite (10.4 g, 150 mmol) in 25 mL of water was added, followed by sodium tetrafluoroborate (15.2 g, 138 mmol) in 30 mL of water. A white salt precipitated and the reaction mixture was stirred at 0 °C for 15 min. The salt was separated by filtration under vacuum, washed sequentially with cold water (30 mL), cold methanol (30 mL), and cold ether (30 mL), and dried overnight in vacuo at room temperature to yield 27 g of the tetrafluoroborate diazonium salt (82%).

The salt was thermolyzed at ca. 200 °C using a distillation assembly containing a cooled collecting flask attached to a 10% sodium hydroxide trap. The crude distillate was washed three times with 10% sodium hydroxide solution and then with brine and dried over magnesium sulfate. Distillation (108 °C, 1 atm) yielded 13.5 g (58% from the aniline) of 3,5-bis(trifluoromethyl)fluorobenzene as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.706 (1, s), 7.542 (2, d, $^3J_{HF}$ = 7.8); ^{19}F NMR ($CDCl_3$) δ −63.65 (CF_3), −108.07 (arom F, t, $^3J_{HF}$ = 7.8).

In a dry 250-mL round-bottomed flask were placed 2,2′,2″-triaminotriethylamine (4.5 g, 30.8 mmol), 3,5-bis(trifluoromethyl)fluorobenzene (30 g, 129 mmol), potassium carbonate (14.5 g), and dimethyl sulfoxide (100 mL, distilled from calcium hydride), and the reaction mixture was heated to 110–120 °C for 2 days. The crude suspension was added to ~1 L of water and extracted with chloroform. The organic layer was dried with calcium chloride, and the solvent was removed under vacuum to afford practically pure 2,2′,2″-tris[(3,5-bis(trifluoromethyl)phenyl)amino]triethylamine as a yellow oil which crystallized slowly, in 99% yield. The material was further purified by flash vacuum chromatography on alumina, using a 1:1 mixture of chloroform and hexane as eluent: ^{1}H NMR ($CDCl_3$) δ 7.17 (3, s), 6.80 (6, s), 4.50 (3, t, J = 4.7), 3.28 (6, q, J = 5.5), 2.93 (6, t, J = 5.5); ^{13}C NMR ($CDCl_3$) δ 40.99, 52.30 (2 × CH_2), 110.96 (C_p), 111.95 (C_o), 124.07 (CF_3, $^1J_{CF}$ = 271), 133.04 (CCF_3, $^2J_{CF}$ = 34), 148.74 (CNH); ^{19}F NMR ($CDCl_3$) δ −63.90; IR 3408 cm^{-1} (NH); MS 782.1708 (calcd 782.1714); mp 79.5–81.0 °C. Anal. Calcd for $C_{30}H_{24}N_4F_{18}$: C, 46.05; H, 3.09; N, 7.16. Found: C, 45.93; H, 3.19; N, 6.74.

2,2′,2″-Tris[(2-(trifluoromethyl)phenyl)amino]triethylamine. This ligand was synthesized in a manner similar to that used to prepare 2,2′,2″-tris[(3,5-bis(trifluoromethyl)phenyl)amino]triethylamine starting from 2,2′,2″-triaminotriethylamine (3.27 g, 22.36 mmol) and 2-(trifluoromethyl)fluorobenzene (18.73 g, 114 mmol). The reaction mixture was heated to 110 °C for 1 week. The pure ligand was obtained in 28% yield (after chromatography on alumina) as a pale yellow oil that crystallized upon standing: ^{1}H NMR ($CDCl_3$) δ 7.43 (3, d, J = 7.5), 7.07 (3, t, J = 7.5), 6.48 (6, m), 4.70 (3, br t), 3.29 (6, q, J = 5.5), 2.86 (6, t, J = 5.5); ^{19}F NMR ($CDCl_3$) δ −63.08; IR 3442 cm^{-1} (NH); mp 105.5–106.5 °C; MS 578.2089 (calcd 578.2092). Anal. Calcd for $C_{27}H_{27}N_4F_9$: C, 56.06; H, 4.70; N, 9.68. Found: C, 56.15; H, 5.09; N, 9.72.

2,2′,2″-Tris[(pentafluorophenyl)amino)triethylamine. This ligand was synthesized in a manner similar to that used to prepare 2,2′,2″-tris[(3,5-bis(trifluoromethyl)phenyl)amino]triethylamine starting from 2,2′,2″-triaminotriethylamine (11.35 g, 77.6 mmol) and hexafluorobenzene (52 g, 279 mmol). The reaction was heated to 70 °C for 24 h. The pure ligand was obtained in 73% yield (after chromatography on alumina with 20% chloroform in hexane as eluent) as a colorless oil which crystallized upon standing: ^{1}H NMR ($CDCl_3$) δ 4.04 (3, br s), 3.42 (6, q, J = 6), 2.80 (6, t, J = 6); ^{13}C NMR (C_6D_6) δ 43.68, 53.78 (2 × CH_2), 124.14 (C_{ipso}), 133.81 (C_p, $^1J_{CF}$ = 244), 138.14 (C_o, $^1J_{CF}$ = 230), 138.62 (C_m, $^1J_{CF}$ = 249); ^{19}F NMR ($CDCl_3$) δ −160.54 (6, d, $^3J_{FF}$ = 21), -164.61 (6, t, $^3J_{FF}$ = 21), −171.62 (3, t, $^3J_{FF}$ = 21); IR 3377 (NH), 3313 cm^{-1} (m, NH); mp 39.5–40.5 °C; MS 644.1055 (calcd 644.1057). Anal. Calcd for $C_{24}H_{15}N_4F_{15}$: C, 44.73; H, 2.35; N, 8.69. Found: C, 44.95; H, 2.59; N, 8.49.

Mo[N$_3$N](NMe$_2$) (1a). $H_3[N_3N]$ (5.50 g, 8.54 mmol) was added as a solid to a precooled solution of $Mo(NMe_2)_4$ (2.32 g, 8.53 mmol) in 70 mL of pentane and the reaction mixture was stirred at room temperature for 6 h. The mixture was filtered and the precipitate washed with cold pentane to give a solution from which **1a** crystallized as a dark purple solid (5.38 g, 76%) which was pure by proton NMR. Recrystallization from cold toluene/pentane afforded an analytically pure sample: ^{1}H NMR (C_6D_6) δ 3.67 (6, s), 3.04 (6, t, J = 6), 2.52 (6, t, J = 6); ^{13}C NMR (C_6D_6) δ 12.80 (CH_3N), 56.82, 65.04 (CH_2), 137.70 (d, J = 249), 138.12 (d, J = 254), 144.74 (d, J = 249); ^{19}F NMR (C_6D_6) δ −149.31 (6, d, $^3J_{FF}$ = 17), −164.02 (3, t, $^3J_{FF}$ = 22), −165.11 (6, t, $^3J_{FF}$ = 20). Anal. Calcd for $C_{26}H_{18}N_5F_{15}Mo$: C, 39.97; H, 2.32; N, 8.96. Found: C, 40.26; H, 2.58; N, 8.85.

Mo[N$_3$NF18](NMe$_2$) (1b). $H_3[N_3NF18]$ (982 mg, 1.256 mmol) was added as a solid to a precooled solution of $Mo(NMe_2)_4$ (341 mg, 1.254 mmol) in 50 mL of pentane and the reaction mixture was stirred at room temperature overnight. The crude reaction mixture consisted of a dark green solution and a brown precipitate. The mixture was filtered and the precipitate extracted with pentane. The combined filtrates were reduced in volume and cooled to give the molybdenum amido complex as a dark green microcrystalline solid (1.00 g, 87%). Attempted recrystallization of **1b** resulted in some decomposition: ^{1}H NMR (C_6D_6) δ 7.40 (3, s), 6.78 (6, s), 2.89 (6, t, J = 6), 2.82 (6, s), 2.32 (6, t, J = 6); ^{13}C NMR (C_6D_6) δ 12.78 (CH_3N), 55.90, 60.82 (CH_2), 114.42, 121.99 (arom CH), 124.13 (CF_3, $^1J_{CF}$ = 271), 131.95 (CCF_3, $^2J_{CF}$ = 30); ^{19}F NMR (C_6D_6) δ −62.82. Anal. Calcd for $C_{32}H_{27}N_5F_{18}Mo$: C, 41.80; H, 2.96; N, 7.62. Found: C, 41.45; H, 2.99; N, 7.16.

Mo[N$_3$N]Cl (2a). (a) From MoCl$_4$(THF)$_2$. Triethylamine (3.50 g, 34.6 mmol) in 20 mL of THF and $H_3[N_3N]$ (6.60 g, 10.25 mmol) in 15 mL of ether were added sequentially to a suspension of $MoCl_4(THF)_2$ (3.80 g, 9.95 mmol) in 40 mL of THF. After the reaction mixture was stirred at room temperature for 3 h, it was filtered through Celite and the insoluble ammonium salt was extracted with THF. The solvent was removed from the filtrate in vacuo. The crude product was taken up in 1,2-dimethoxyethane, the solution was filtered through Celite, and the solvent was removed from the filtrate under vacuum. The solid thus obtained was washed with pentane and ether to afford 6.50 g of orange-red crystalline $Mo[N_3N]Cl$ which was pure by ^{1}H NMR (85%). Analytically pure samples were prepared by recrystallization from cold THF–ether mixtures: ^{1}H NMR (C_6D_6) δ -76.02 (br, $w_{1/2}$ = 700), −15.97 (br, $w_{1/2}$ = 700); ^{19}F NMR (C_6D_6) δ −84.0 (br s, $w_{1/2}$ = 200), −131.7 (br s, $w_{1/2}$ = 40), −144.7 (br s, $w_{1/2}$ = 30). Anal. Calcd for $C_{24}H_{12}N_4F_{15}MoCl$: C, 37.30; H, 1.57; N, 7.25. Found: C, 37.28; H, 1.85; N, 7.12.

(b) From 1a. A 1 M solution of HCl in ether (2.97 mL, 2.97 mmol) was added to a precooled solution of **1a** (2.28 g, 2.92 mmol) in 40 mL of ether, and the reaction mixture was stirred at room temperature overnight. The resulting precipitate was collected by filtration, washed with dichloromethane, ether, and pentane, and dried under vacuum to yield 744 mg (33%) of orange product.

W[N$_3$N]Cl (2b). A solution of $H_3[N_3N]$ (5.44 g, 8.44 mmol) and triethylamine (2.8 g, 27.7 mmol) in 20 mL of ether was added to a precooled solution of $WCl_4(Et_2S)_2$ (4.0 g, 8.44 mmol) in 80 mL of ether. A yellow precipitate formed and redissolved after 20 min to give an orange reaction mixture. The reaction was stirred overnight at room temperature and the orange precipitate was collected by filtration, washed with ether, and

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extracted with THF. The orange product was obtained by removing the THF in vacuo; yield 4.6 g (63%). Analytically pure samples were prepared by crystallization from a mixture of dichloromethane and ether: ^{1}H NMR (CD_2Cl_2) δ -53.3 (br, $w_{1/2}$ = 50), -21.8 (br, $w_{1/2}$ = 75). Anal. Calcd for $C_{24}H_{12}N_4F_{15}WCl$: C, 33.49; H, 1.41; N, 6.51. Found: C, 33.65; H, 1.59; N, 6.30.

Mo[N$_3$N](OTf) (3a). Trimethylsilyl trifluoromethanesulfonate (2.2 g, 9.91 mmol) was added to a solution of Mo[N$_3$N]Cl (3.36 g, 4.35 mmol) in 40 mL of dichloromethane and the reaction mixture was stirred at room temperature for 2 days. The insoluble Mo[N$_3$N](OTf) was collected by filtration and washed with dichloromethane and pentane. Drying under vacuum afforded analytically pure **3a** as a fine orange solid; yield 3.13 g (81%). Anal. Calcd for $C_{25}H_{12}N_4F_{18}MoSO_3$: C, 33.88; H, 1.36; N, 6.32. Found: C, 33.54; H, 1.54; N, 6.10.

W[N$_3$N](OTf) (3b). Trimethylsilyl triflate (600 μL, 3.11 mmol) was added to a solution of W[N$_3$N]Cl (1.88 g, 2.19 mmol) in 70 mL of dichloromethane and the reaction mixture was stirred at room temperature for 2 days. The yellow insoluble W[N$_3$N](OTf) that formed was collected by filtration and washed with dichloromethane. Trimethylsilyl triflate (500 μL) was added to the orange filtrate, which was stirred for another day at room temperature. The combined yellow precipitates were washed with methylene chloride until the washings were colorless and dried in vacuo to afford analytically pure W[N$_3$N](OTf) as a fine yellow solid (1.63 g, 77%): IR 1351, 1198, 627 (OTf). Anal. Calcd for $C_{25}H_{12}N_4F_{18}WSO_3$: C, 30.82; H, 1.24; N, 5.75. Found: C, 30.92; H, 1.50; N, 5.53.

[N$_3$N]Mo≡N (4a). Sodium azide (425 mg, 6.54 mmol, excess) was added to a solution of Mo[N$_3$N]Cl (3.08 g, 3.98 mmol) in 70 mL of acetonitrile, and the reaction mixture was stirred at room temperature for 2 days. The mixture was filtered through Celite and the solvent was removed from the filtrate slowly under vacuum, which caused fine light orange microcrystals to form (2.19 g). The orange needles were recrystallized from a mixture of THF and pentane to yield fine light yellow needles (1.97 g, 65%): ^{1}H NMR (C_6D_6) δ 1.99 (6, t, J = 5.5), 3.17 (6, t, J = 5.5); ^{1}H NMR (CD_2Cl_2) δ 3.11 (6, t, J = 5.5), 3.88 (6, t, J = 5.5); ^{13}C NMR (CD_2Cl_2) δ 51.28, 57.87 (CH_2), 137.85 (d, J = 245), 138.50 (d, J = 249), 142.00 (d, J = 255); ^{19}F NMR (CD_2Cl_2) δ -148.82 (6), -161.72 (3), -163.56 (6). Anal. Calcd for $C_{24}H_{12}N_5F_{15}Mo$: C, 38.37; H, 1.61; N, 9.32. Found: C, 38.71; H, 1.87; N, 9.31.

[N$_3$N]W≡N (4b). Sodium azide (95 mg, 1.46 mmol) was added to a solution of W[N$_3$N]Cl (890 mg, 1.03 mmol) in 50 mL of acetonitrile, and the reaction mixture was stirred at room temperature overnight. The solvent was removed under vacuum, the resulting solid was extracted with THF, and the extract was filtered through Celite. The THF was removed in vacuo and the residue was recrystallized from a mixture of THF and ether to yield fine off-white needles (550 mg, 63%): ^{1}H NMR (CD_3CN) δ 3.11 (6, t, J = 5.6), 4.00 (6, t, J = 5.6); ^{1}H NMR ($CDCl_3$) δ 3.10 (6, t, J = 5.5), 3.99 (6, t, J = 5.5); ^{19}F NMR (CD_3CN) δ -149.63 (6, ortho F), -162.67 (3, para), -165.16 (6, meta).

{[N$_3$N]Mo=NMe}(OTf) (5). Neat methyl triflate (310 mg, 1.89 mmol) was added to a cold solution of [N$_3$N]Mo≡N (779 mg, 1.036 mmol) in 20 mL of toluene and the reaction mixture was stirred at room temperature for 5 h. The yellow precipitate was collected on a frit, washed with toluene and pentane, and dried in vacuo to yield 868 mg of **5** (91% yield). The product was recrystallized by slow diffusion of pentane into a concentrated dichloromethane solution: ^{1}H NMR (CD_2Cl_2) δ 3.17 (3, s), 3.80 (6, t, J = 5.5), 4.34 (6, t, J = 5.5); ^{19}F NMR (CD_2Cl_2) δ -78.4 (s, OTf), -148.14 (6, d), -155.01 (3, t), -159.91 (6, t); IR 1268, 637 cm^{-1} (OTf). Anal. Calcd for $C_{26}H_{15}N_5F_{15}SO_3Mo$: C, 34.11; H, 1.65; N, 7.65. Found: C, 34.18; H, 1.87; N, 7.55.

[N$_3$N]Mo(μ-N$_2$)Mo[N$_3$N] (6). Mo[N$_3$N](OTf) (887 mg, 1.00 mmol) in 10 mL of THF was added within 5 min to 1 equiv of sodium amalgam (24 mg of Na in 4.50 g of Hg), and the heterogeneous mixture was stirred at room temperature. A purple color appeared at the interface between the mercury and THF after 5 min. After 15 min, **6** was consumed and the reaction mixture was dark purple and contained purple microcrystals. The suspension was decanted and the solvent removed under vacuum. The crude purple solid was washed with ether and cold THF to yield 716 mg of **6** as fine purple solid (95% yield), which was pure by elemental analysis. Attempts to crystallize 6 from a variety of solvents resulted in precipitation of a fine blue solid: ^{1}H NMR (THF-d_8) δ -21.8 ($w_{1/2}$ = 660), -14.4 ($w_{1/2}$ = 660). Anal. Calcd for $C_{48}H_{24}N_{10}F_{30}Mo_2$: C, 38.37; H, 1.61; N, 9.32. Found: C, 38.66; H, 1.91; N, 8.87.

[N$_3$N]Mo(N$_2$)[Na(ether)$_x$] (7a). Solid Mo[N$_3$N](OTf) (430 mg, 0.485 mmol) was added gradually to a stirred mixture of sodium amalgam (0.5%, 7 g, 1.52 mmol) covered with 5 mL of THF. The reaction mixture turned purple and then red within 20 min. The red supernatant was decanted, and the solvent was removed under vacuum. The resulting red solid was extracted with ether, the solution was filtered through Celite, and the ether was removed under vacuum to yield 380 mg of red crystals. Plate-like red crystals could be grown from a mixture of ether and pentane: ^{1}H NMR of etherate (THF-d_8) δ 3.86 (6, t, J = 5.2), 2.64 (6, t, J = 5.4), 3.36 (q, ether), 1.12 (t, ether); the ether resonances were absent after the THF-d_8 was removed in vacuo and the spectrum recorded again in THF-d_8; ^{13}C NMR (THF-d_8) δ 54.84 (CH_2), 56.47 (CH_2), 136.5, 136.7, 140.0, 140.9, 144.1; ^{19}F NMR (THF-d_8) δ -152.9 (2, d), -169.3 (2, t), -174.5 (1, t). Elemental analyses were variable and irreproducible.

Reduction of 6 under Dinitrogen. **6** (415 mg, 0.276 mmol) was added to a stirred mixture of sodium amalgam (0.5%, 4.4 g, 0.96 mmol) covered with 18 mL of THF, and the reaction mixture was stirred under dinitrogen for 1 h. The resulting red solution was decanted, and the solvent was removed from the filtrate under vacuum. The resulting red solid was extracted with ether, the solution was filtered through Celite, and the ether was removed in vacuo to afford 448 mg of red crystalline solid that was identical in all respects to other samples of **7a**.

Oxidation of 7a to 6. Solid ferrocenium triflate (12 mg, 0.036 mmol) was added to a sample of **7a** (50 mg, 0.065 mmol) dissolved in 5 mL of DME. The reaction mixture gradually turned to purple-red upon being stirred at room temperature for 2 h. The solvent was removed in vacuo and the residue was washed with ether and cold THF to yield 20 mg of a purple insoluble solid that was identical to an authentic sample of **6**. Similar results were obtained when the oxidation was performed under argon.

Reaction of 7a with 3a. **3a** (129 mg, 0.145 mmol) was added to a solution of crude **7a** (220 mg, excess) in 8 mL of THF. The reaction mixture was stirred for 10 min and the solvent was removed in vacuo. The crude product was washed with ether and cold THF to afford a fine purple solid identical to other samples of **6** (187 mg, 85% yield).

[N$_3$N]Mo(N$_2$)[Na(15-crown-5)] (7b). A sample of **7a** (260 mg) was dissolved in 6 mL of ether, and the solution was cooled to -35 °C. To the solution was added 80 mg of 15-crown-5 and the ether was removed in vacuo. The red product was washed with pentane and dissolved in toluene. The solution was filtered through Celite. Pentane was added and the solution was cooled to afford 140 mg (1st crop) plus 85 mg (2nd crop) of intense-red plate-like crystals: ^{1}H NMR (toluene-d_8) δ 2.13 (6, t, J = 5.5); 3.08 (20, s); 3.75 (6, t, J = 5.5), ^{19}F NMR (toluene-d_8) δ -174.0 (3, t, J = 22), -167.8 (6, d, J = 22), -152.2 (6, d, J = 22); IR 1848 cm^{-1} (s). Anal. Calcd for $C_{34}H_{32}N_6F_{15}MoNaO_5$: C, 40.49; H, 3.20; N, 8.33; Na, 2.28. Found: C, 40.44; H, 3.21; N, 6.59; Na, 2.33.

Preparation of [N$_3$N]MoN=NSi(i-Pr)$_3$ (8a). **3a** (338 mg, 0.381 mmol) was added to excess sodium amalgam (0.5%, 6 g) in THF under 1 atm of N$_2$, and the reaction mixture was stirred for 10 min. The resulting dark red solution of **7a** was filtered through Celite and cooled to -35 °C. Neat triisopropylsilyl chloride (100 μL, 0.467 mmol, 1.22 equiv) was added to the cold THF solution. The reaction mixture turned dark yellow within 30 s and was stirred for another 10 min. The solvent was removed in vacuo and the resulting dark yellow solid was extracted with pentane. The pentane was removed from the extract in vacuo to afford fine yellow crystalline **8a**, which was pure by NMR (270 mg, 77% yield relative to **3a**). Recrystallization by slow diffusion of pentane into a concentrated etheral solution afforded analytically pure yellow crystals: ^{1}H NMR ($CDCl_3$) δ 0.39 (3, sept, J = 7), 0.61 (18, d, J = 7), 3.12 (6, t, J = 5.5), 3.92 (6, t, J = 5.5); ^{13}C NMR ($CDCl_3$) δ 12.94 (CH), 17.03 (CH_3), 53.42 (CH_2), 56.68 (CH_2), 131.55 (br s), 137.63 (br d, $^1J_{CF}$ = 251), 142.21 (br d, $^1J_{CF}$ = 244); ^{19}F NMR (C_6D_6) δ -150.26 (d), -164.26 (m); ^{29}Si NMR ($CDCl_3$) δ 2.48 (s); IR 1715, 1687 cm^{-1} (strong). Anal. Calcd for $C_{33}H_{33}N_6F_{15}MoSi$: C, 42.96; H, 3.60; N, 9.11. Found: C, 43.01; H, 3.69; N, 8.93.

Preparation of [N$_3$N]Mo^{15}N=^{15}NSi(i-Pr)$_3$ (8a-^{15}N$_2$). **3a** (420 mg, 0.47 mmol) was added to excess sodium amalgam (0.5%, 6.8 g) in 8 mL of THF under 1 atm of ^{15}N$_2$, and the reaction mixture was stirred at room temperature. After the characteristic color change had taken place (yellow to purple to dark red), neat triisopropylsilyl chloride (150 μL, 0.70 mmol) was added via syringe. The reaction mixture turned dark yellow-brown within 5 s, and after 5 min, the solvent was removed under vacuum. The resulting brown solid was extracted with pentane and the pentane was removed in vacuo to afford fine brown-yellow crystals (234 mg). The crude product was recrystallized by slowly diffusing pentane into a concentrated etheral solution. Yellow crystals were obtained whose proton NMR spectrum was identical to the spectrum of **8a** (180 mg, 41% relative to **3a**): ^{15}N NMR ($CDCl_3$) δ 228.0 (d, J = 15), 366.0 (d, J = 15); IR 1658, 1628 cm^{-1} (s).

Reduction of $[N_3N]Mo(\mu\text{-}^{15}N_2)Mo[N_3N]$ under $^{14}N_2$. A slurry of 50 mg of **6**-$^{15}N_2$ in 10 mL of THF was added to 20 mg of Na amalgam in 2.5 g of Hg, and the reaction mixture was stirred at 25 °C for 25 min. Excess $(i\text{-}Pr)_3SiCl$ (60 μL) was added to the red mixture to give a yellow mixture. The solvent was removed from the reaction mixture in vacuo and the solid was extracted with pentane. The pentane was removed under vacuum and the crude product was washed twice with cold pentane and dried to afford yellow crystalline product (45 mg). An IR spectrum of the product was identical to that of a 1:1 mixture of **8b** and **8b**-$^{15}N_2$.

Preparation of $[N_3N]MoN{=}NSn(n\text{-}Bu)_3$ (8b). A sample of **7a** (197 mg, ~0.23 mmol) was dissolved in 8 mL of ether and the solution was cooled to −35 °C. Neat $(n\text{-}Bu)_3SnCl$ (62 μL, 0.23 mmol) was added to the dark red solution. The reaction mixture turned yellow-black rapidly. The solution was allowed to warm to room temperature. It was then filtered through Celite and the ether was removed from the filtrate in vacuo. The crude product was extracted with pentane. Light yellow crystals of **8b** were obtained upon removing pentane in vacuo (152 mg, 0.144 mmol, 63%). **8b** is not stable thermally; with time it decomposes to give **6**: ^1H NMR (C_6D_6) δ 0.70 (6, t, J = 8), 0.92 (9, t, J = 7), 1.23 (12, m), 2.04 (6, t, J = 5.5), 3.42 (6, t, J = 5.5); ^{19}F NMR (C_6D_6) δ −155.64 (2, d), −169.58 (2, t), −170.61 (1, t); IR 1692 cm^{-1} (strong). Elemental analyses of **8b** were variable.

Reaction of 8a with Ferrocenium Triflate. A solution of ferrocenium triflate in dichloromethane was added to a solution of **8a** (50 mg, 0.054 mmol) in 5 mL of dichloromethane. The blue color of the ferrocenium triflate disappeared and an orange solid precipitated. The addition was carried out until an end point was observed (~35–40 mg). The product was washed with dichloromethane until the washings were colorless and dried in vacuo to afford 47 mg of fine orange solid that was identical in all respects to other samples of **3a**.

Reaction of 8a with CsF; Observation of 8c. Excess cesium fluoride (80 mg) was added to a solution of **8a** (34 mg, 0.037 mmol) in 6 mL of THF, and the reaction mixture was stirred at room temperature for 24 h. Trimethylsilyl chloride was added to the resulting red solution; the reaction turned yellow-brown rapidly. The reaction mixture was filtered and the solvents were removed from the filtrate in vacuo. A proton NMR spectrum of the crude product showed it to consist of a mixture of **8a** and the corresponding trimethylsilyl derivative (~1:1) accompanied by some decomposition products.

X-ray Structure of 2a. Suitable orange-red crystals of **2a** were grown by slow diffusion of ether into a concentrated THF solution. A crystal having approximate dimensions of 0.3 × 0.4 × 0.5 mm was mounted on a glass fiber. Data were collected at −72 ± 1 °C on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71069 Å). Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range 18.00 < 2θ < 26.00°, corresponded to a a triclinic cell: a = 11.265(2) Å, b = 11.371(2) Å, c = 21.805(4) Å, α = 82.40(1)°, β = 79.07(1)°, γ = 74.89(1)°, V = 2637.4 Å^3, Z = 4, fw = 772.75, ρ(calcd) = 1.946 g/cm^3. On the basis of packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $P\bar{1}$.

A total of 7293 reflections were collected in the range 2θ < 44.9°, with 6872 being unique. An empirical absorption correction was applied, using the program DIFABS,[51] which resulted in transmission factors ranging from 0.96 to 1.12. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 0.95387 × 10^{-6}). The structure was solved by the Patterson method. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation in idealized positions. The final cycle of full-matrix least-squares refinement was based on 5948 observed reflections ($I > 3.00\sigma(I)$) and 812 variable parameters and converged with R = 0.032 and R_w = 0.034. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.54 and −0.47 e/Å^3. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corp.

X-ray Structure of 8a. Suitable light orange crystals were grown by slow diffusion of pentane into a concentrated ether solution of **8a**. A crystal having approximate dimensions of 0.4 × 0.4 × 0.5 mm was mounted in a glass capillary. Data were collected at 23 ± 1 °C on a RIGAKU AFC6R diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71069 Å). Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 20 carefully centered reflections in the range 24.99 < 2θ < 28.82°, corresponded to a monoclinic cell with parameters a = 13.524(3) Å, b = 18.016(4) Å, c = 16.248(3) Å, β = 98.74(2), V = 3913(1) Å^3, Z = 4, fw = 922.67, ρ(calcd) = 1.566 g/cm^3. On the basis of the systematic absences of $h0l$ where $h + l \neq 2n$ and $0k0$ where $k \neq 2n$ the space group is $P2_1/n$. A total of 8559 reflections were collected in the range 2θ < 55°, with 8180 being unique. An empirical absorption correction was applied, based on azimuthal scans of several reflections, which resulted in transmission factors ranging from 0.91 to 1.00. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 0.20976 × 10^{-5}). The structure was solved by a combination of the Patterson method and direct methods. All non-hydrogen atoms were refined anisotropically, except for the isopropyl groups, which were constrained as rigid groups. Disorder within the $Si(i\text{-}Pr)_3$ group limited the overall quality of the structure. The isopropyl methine protons were not located. The final cycle of full-matrix least-squares refinement was based on 3369 observed reflections ($I > 3.00\sigma(I)$) and 452 variable parameters and converged with R = 0.069 and R_w = 0.072. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.69 and −0.57 e/Å^3, respectively. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corp.

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Supplementary Material Available: Experimental details and tables of labeled ORTEP drawings and final positional and thermal parameters for **2a** (two independent molecules) and **8a** (21 pages); listing of and final observed and calculated structure factors (63 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.

(51) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.