Synthesis, Structure, and Electrochemical Studies of Molybdenum and Tungsten Dinitrogen, Diazenido, and Hydrazido Complexes That Contain Aryl-Substituted Triamidoamine Ligands

George E. Greco and Richard R. Schrock*

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

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One-electron reduction of [ArN_3N]MoCl complexes (Ar = C_6H_5, 4-FC_6H_4, 4-t-BuC_6H_4, 3,5-$Me_2C_6H_3$) yields complexes of the type [ArN_3N]Mo−N═N−Mo[ArN_3N], while two-electron reduction yields {[ArN_3N]Mo−N═N}$^-$ derivatives (Ar = C_6H_5, 4-FC_6H_4, 4-t-BuC_6H_4, 3,5-$Me_2C_6H_3$, 3,5-$Ph_2C_6H_3$, and 3,5-(4-t-BuC_6H_4)$_2C_6H_3$). Compounds that were crystallographically characterized include {[t-$BuC_6H_4N_3N$]Mo}$_2$(N_2), Na(THF)$_6${[PhN_3N]Mo−N═N}$_2$Na(THF)$_3$, [t-$BuC_6H_4N_3N$]Mo−N═N−Na(15-crown-5), and {[$Ph_2C_6H_3N_3N$]MoNN}$_2$Mg(DME)$_2$. Compounds of the type [ArN_3N]Mo−N═N−Mo[ArN_3N] do not appear to form when Ar = 3,5-$Ph_2C_6H_3$ or 3,5-(4-t-BuC_6H_4)$_2C_6H_3$, presumably for steric reasons. Treatment of diazenido complexes (e.g., [ArN_3N]Mo−N═N−Na(THF)$_x$) with electrophiles such as Me_3SiCl or MeOTf yielded [ArN_3N]Mo−N═NR complexes (R = $SiMe_3$ or Me). These species react further to yield {[ArN_3N]Mo−N═NMe_2}$^+$ species in the presence of methylating agents. Addition of anionic methyl reagents to {[ArN_3N]Mo−N═NMe_2}$^+$ species yielded [ArN_3N]Mo(N═NMe_2)(Me) complexes. Reduction of [4-t-$BuC_6H_4N_3N$]WCl under dinitrogen leads to a rare {[t-$BuC_6H_4N_3N$]W}$_2$(N_2) species that can be oxidized by two electrons to give a stable dication (as its BPh_4^- salt). Reduction of hydrazido species leads to formation of Mo≡N in low yields, and only dimethylamine could be identified among the many products. Electrochemical studies revealed expected trends in oxidation and reduction potentials, but also provided evidence for stable neutral dinitrogen complexes of the type [ArN_3N]Mo(N_2) when Ar is a relatively bulky terphenyl substituent.

Introduction

We have been interested in exploring the chemistry of transition metal complexes containing triamidoamine ([$(RNCH_2CH_2)_3N$]$^{3-}$ = [RN_3N]$^{3-}$) ligands,[1] in part with respect to activation and further reactions of dinitrogen. The first dinitrogen complex containing a [RN_3N]$^{3-}$ ligand, {[t-$BuMe_2SiN_3N$]Mo}$_2$(μ-N_2) was isolated as a byproduct of the synthesis of [t-$BuMe_2SiN_3N$]MoCl from Li_3[t-$BuMe_2SiN_3N$] and $MoCl_3(THF)_3$.[2] More rational syntheses of dinitrogen complexes were accomplished in systems that employed the [$C_6F_5N_3N$]$^{3-}$ ligand.[3] For example, reduction of [$C_6F_5N_3N$]Mo(OTf) with 2 equiv of sodium amalgam yielded diazenido complexes of the type [$C_6F_5N_3N$]Mo−N═N−Na(THF)$_x$ (*x* unknown), which could be treated with i-Pr_3SiCl to yield [$C_6F_5N_3N$]Mo−N═NSi(i-Pr)$_3$ in high yield.[4] More recent work has involved the synthesis of dinitrogen complexes from [Me_3SiN_3N]MoCl. For example, reduction of [Me_3SiN_3N]MoCl by magnesium in THF in the presence of dinitrogen led to {[Me_3SiN_3N]Mo−N═N}$_2$Mg(THF)$_2$ in high yield. A number of heterobimetallic dinitrogen complexes could be prepared employing the magnesium species such as {[Me_3SiN_3N]Mo−N═N}$_3$Fe, {[Me_3SiN_3N]Mo−N═N}$_2$$ZrCl_2$, {[$Me_3SiN_3N$]Mo−N═N}$_2$VCl(THF), and {[$Me_3SiN_3N$]Mo−N═N}$_3$VCl.[5] During the course of our research on dinitrogen and other types of complexes that contain a [$C_6F_5N_3N$]$^{3-}$ or [Me_3SiN_3N]$^{3-}$ ligand, several drawbacks were revealed. For example, several [Me_3SiN_3N]$^{3-}$ complexes were found to decompose by loss of a TMS group or by CH activation within a TMS group.[4,6−9] The primary drawback of the C_6F_5 ligand was proposed to be its instability toward strongly nucleophilic reagents, although no direct evidence for that statement has yet come to light.[10] The C_6F_5 groups also produce a relatively electron deficient metal center, which can be undesirable if strong π back-donation into a ligand in the coordination pocket is desired, as in dinitrogen binding. For this reason we turned to the synthesis of triamidoamine ligands substituted with ordinary aryl groups ([$(ArNCH_2CH_2)_3N$]$^{3-}$ = [ArN_3N]$^{3-}$) and the preparation of Mo and W complexes that would be useful for exploring dinitrogen chemistry, namely, monochloride complexes, [ArN_3N]MCl. In the preceding paper in this issue[11]

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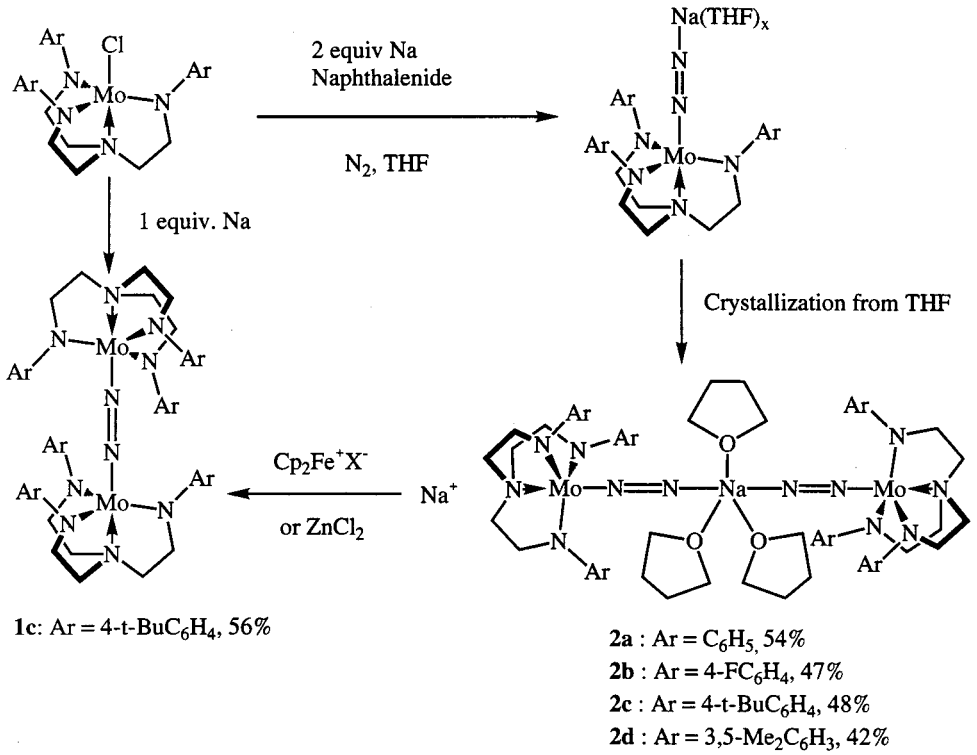
Scheme 1



we report the synthesis of eight such ligands from triethylenetetraamine by coupling an aryl bromide to the terminal amine functionalities, where Ar = C_6H_5, 4-FC_6H_4, 4-t-BuC_6H_4, 3,5-$Me_2C_6H_3$, and 3,5-$Ph_2C_6H_3$, 3,5-(4-t-$BuC_6H_4)_2C_6H_3$, 2,4,6-$Me_3C_6H_2$, and 2-MeC_6H_4. A "direct" synthesis of complexes of the type [ArN_3N]MCl from the corresponding tetrachlorides of Mo or W was possible with the first six of these ligands. In this paper we report the synthesis of dinitrogen complexes containing several of these ligands, and in particular how the chemistry of such species changes with the steric bulk of the triamidoamine ligands and their electronic characteristics.

Results and Discussion

Dimolybdenum Bridging Dinitrogen Complexes. Reduction of [ArN_3N]MoCl complexes by one electron under dinitrogen results in the formation of dimolybdenum bridging dinitrogen complexes of type **1** (Scheme 1). Magnesium, sodium amalgam, and sodium naphthalenide are all effective reducing agents, although we have obtained the cleanest reductions with sodium naphthalenide. Compounds **1** are purple paramagnetic solids which are relatively insoluble in common organic solvents (THF, methylene chloride, DMF, hot toluene, chlorobenzene, acetonitrile, and 1,4-dioxane), except for **1c**, which is soluble in benzene, toluene, and THF. Therefore only **1c** can be separated from the NaCl or $MgCl_2$ salts that are also formed in the reaction.

The best method of preparing **1c** (in 56% yield) is by addition of 1 equiv of sodium naphthalenide to a solution of [t-$BuC_6H_4N_3N$]MoCl in THF at −40 °C. The anionic diazenido complex (**2c**, see below) was not formed, according to ^{1}H NMR spectra. The ^{1}H NMR spectrum of **1c** is characteristic of a paramagnetic species. The resonance for the meta hydrogen of the ligand aryl group is relatively sharp and shifted downfield, while the resonances for the methylene protons of the ligand backbone are shifted upfield. The backbone resonance that is furthest upfield is the broadest. None of the peaks is shifted as much from its normal diamagnetic position as the corresponding peak in [t-$BuC_6H_4N_3N$]MoCl.

Stirring a THF solution of [t-$BuC_6H_4N_3N$]MoCl overnight over 1 equiv of Na/Hg under dinitrogen results in the formation of **1c** in 27% yield. The remainder of the material consists of unidentified ether-soluble material. Unlike in the case of compounds containing the C_6F_5 ligand,[3] the reaction is not rapid. The purple color begins to appear after several hours, but at least 12 h are required for complete reaction. If 2.5 equiv of Na/Hg is employed, a 3:2 mixture of **1c** and **2c** is obtained, according to ^{1}H NMR spectra, while 5 equiv of Na/Hg yields a 1:2 mixture of **1c** and **2c**. We have not been able to convert **1c** to **2c** with a large excess of sodium amalgam, in contrast to complexes containing the $[C_6F_5N_3N]^{3-}$ ligand.[3] A Raman spectrum of **1c** in THF solution showed a sharp peak at 1681 cm^{-1} that can be assigned to the N−N stretch. For comparison, the N−N stretch is found at 1630 cm^{-1} in the Raman spectrum of [Mo(N([R]Ar)$_3$]$_2$(μ-N_2).[12]

X-ray quality crystals of **1c** were grown from a saturated THF solution at −35 °C. Crystallographic data, collection parameters, and refinement parameters are collected in Table 1, while selected bond lengths and angles can be found in Table 2. One molecule of THF is present in the unit cell. Side and end views of the molecule are depicted in Figure 1. The crystallographic inversion center is located at the midpoint of the N−N bond. Most of the bond lengths and angles are typical for five-coordinate Mo complexes containing triamidoamine ligands.[1] The Mo−N−N−Mo axis is linear, and the N═N bond length is 1.19 Å, both of which are typical of bridging dinitrogen complexes in this category. In another structurally characterized bridging N_2 dimer of Mo containing [t-$BuMe_2SiN_3N$]$^{3-}$ ligands, the N−N bond length is 1.195 Å.[2] As can be seen from the top view in Figure 1, the two halves of the molecule are staggered

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Table 1. Crystallographic Data, Collection Parameters, and Refinement Parameters for [t-BuC$_6$H$_4$N$_3$N]Mo−N═N−Mo[t-BuC$_6$H$_4$N$_3$N] (**1c**) and Na(THF)$_6${[PhN$_3$N]Mo−N═N[Na(THF)$_3$]N═N−Mo[PhN$_3$N]} (**2a**)[a]

	1c	**2a**
empirical formula	$C_{40}H_{59}MoN_5O$	$C_{96}H_{102}Mo_2N_{12}Na_2O_{10}$
formula w	721.86	1831.52
space group	$P\bar{1}$	$R\bar{3}c$
a (Å)	11.1627(2)	13.3659(15)
b (Å)	13.19800(10)	13.3659(15)
c (Å)	14.0430(3)	93.012(13)
α (deg)	76.8720(10)	90
β (deg)	86.3670(10)	90
γ (deg)	78.3060(10)	120
V (Å^3)	1972.67(6)	14390(3)
Z	2	6
temp (K)	183(2)	183(2)
R1 [$I > 2\sigma(I)$]	0.0615	0.0544
wR2 [$I > 2\sigma(I)$]	0.1302	0.1314
R1 (all data)	0.0669	0.0856
wR2 (all data)	0.1330	0.1471

[a] All structures were solved on a Bruker SMART/CCD diffractometer using 0.710 73 Å Mo Kα radiation. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [t-BuC$_6$H$_4$N$_3$N]Mo−N═N−Mo[t-BuC$_6$H$_4$N$_3$N] (**1c**) and Na(THF)$_6${[PhN$_3$N]Mo−N═N[Na(THF)$_3$]N═N−Mo[PhN$_3$N]} (**2a**)

1c		**2a**	
N(5)−N(5A)	1.186(7)	N(1)−N(2)	1.195(13)
Mo−N(5)	1.930(4)	Mo−N(1)	1.862(13)
Mo−N(1)	1.996(4)	Mo−N(3)	2.034(5)
Mo−N(2)	2.014(4)	Mo−N(4)	2.209(9)
Mo−N(3)	2.015(4)	Na−N(2)	2.160(14)
Mo−N(4)	−2.253(4)	Na−O(2)	2.532(13)
N(5)−Mo−N(4)	178.40(16)	N(1)−Mo−N(4)	180.0
N(1)−Mo−N(2)	115.98(17)	N(3)−Mo−N(4)	80.77(16)
N(2)−Mo−N(3)	117.75(17)	N(2)−Na−O(2)	90.000(4)
N(1)−Mo−N(3)	116.00(18)	N(2)−N(1)−Mo	180.0
C(1)−N(1)−Mo	130.2(3)	N(1)−N(2)−Na	180.0
C(13)−N(2)−Mo	131.0(3)	C(1)−N(3)−Mo	130.4(5)
C(25)−N(3)−Mo	131.5(3)		
N(5A)−N(5)−Mo	178.9(5)		

with respect to each other, a consequence of the steric demand of each [t-BuC$_6$H$_4$N$_3$N]Mo unit.

Anionic Molybdenum Diazenido Complexes. Reduction of [ArN$_3$N]MoCl complexes with 2 equiv of sodium naphthalenide under dinitrogen produces diamagnetic anionic diazenido complexes (**2a**−**d**) in yields ranging from 42 to 54% (Scheme 1). The choice of reducing agent is very important for this reaction; in our hands sodium naphthalenide is the only reducing agent that leads to yields greater than 20%. Unlike reductions that employ Na/Hg or Mg (vide infra), there is no evidence of any **1** present in the reaction mixture, and the reaction is very rapid, even at −40 °C. Exactly 2 equiv of sodium naphthalenide should be employed in order to obtain the highest yield, since some decomposition occurs in the presence of any excess.

The IR spectra of **2a**−**d** in THF contain N═N stretching absorptions in the region 1813−1818 cm^{-1} (Table 6). Since these frequencies approximately match those of the structurally characterized monomeric 15-crown-5 derivative **3c** (vide infra), we believe that **2a**−**d** are monomers of the form [ArN$_3$N]Mo−N═N−Na(THF)$_x$ in THF. THF solutions of pure **2a**−**d** are purple. If THF is removed and the residue is washed with ether (or toluene for **2b**), pink solids can be isolated. The solid-state IR spectra of these pink solids contain N═N absorptions in the region from 1741 to 1752 cm^{-1}. The N═N absorption of **2c** is found at 1745 cm^{-1} in benzene, which suggests that the solid-state structure is preserved in benzene. Proton NMR spectra of **2c** and **2d** in C$_6$D$_6$ revealed the presence of one molecule of THF per [RN$_3$N]$^{3-}$ ligand. Attempts to grow crystals of the pink solids from mixtures of toluene and pentane resulted only in the formation of red oils.

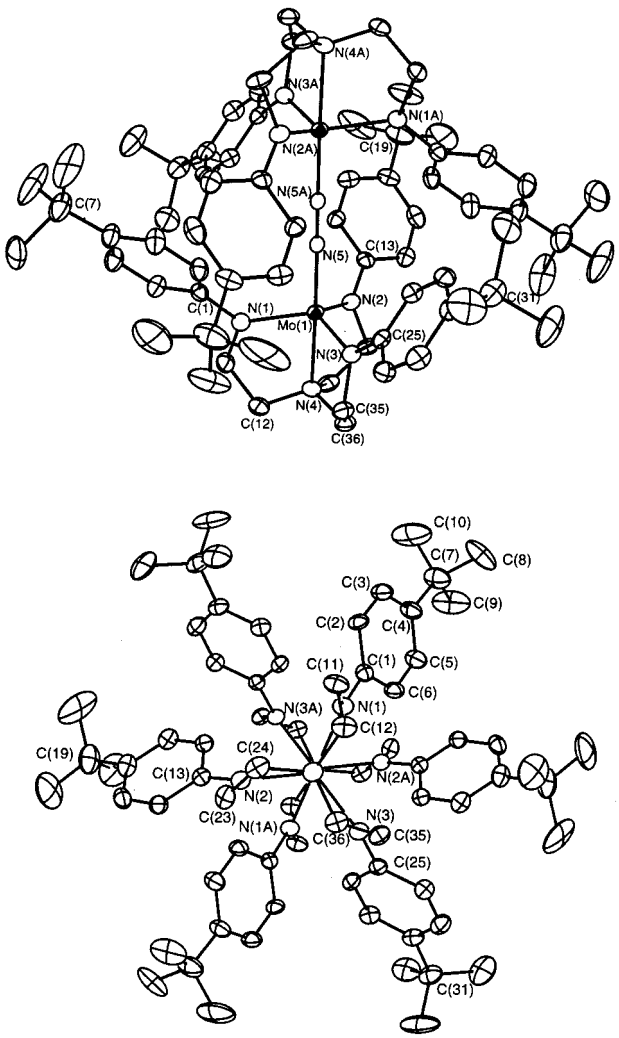

Figure 1. Two views of the structure of [t-BuC$_6$H$_4$N$_3$N]Mo−N═N−Mo[t-BuC$_6$H$_4$N$_3$N] (**1c**).

Single crystals of **2a** could be grown from THF. Crystallographic data, collection parameters, and refinement parameters are collected in Table 1, while selected bond lengths and angles can be found in Table 2. As can be seen from the ORTEP drawing in Figure 2, **2a** is a monoanionic dimolybdenum species in the solid state, with two {[t-BuC$_6$H$_4$N$_3$N]Mo−N═N}$^-$ units bound to a central sodium along with three molecules of THF. The sodium counterion is surrounded by six molecules of THF. One molecule of unbound THF is contained in the lattice. The structure is highly symmetric with the crystallographically imposed 3-fold axis coincident with the Mo−N═N−Na−N═N−Mo axis of the molecule. The presence of an inversion center at sodium means that the two N═N and Mo−N bond lengths are identical, at 1.195(13) and 1.862(13) Å, respectively. Other bond distances and angles are similar to what has been seen in other triamidoamine complexes of this general nature.[4,5,13]

We presume that **2b**−**d**, if they have been crystallized from THF, all have structures in the solid state similar to that found

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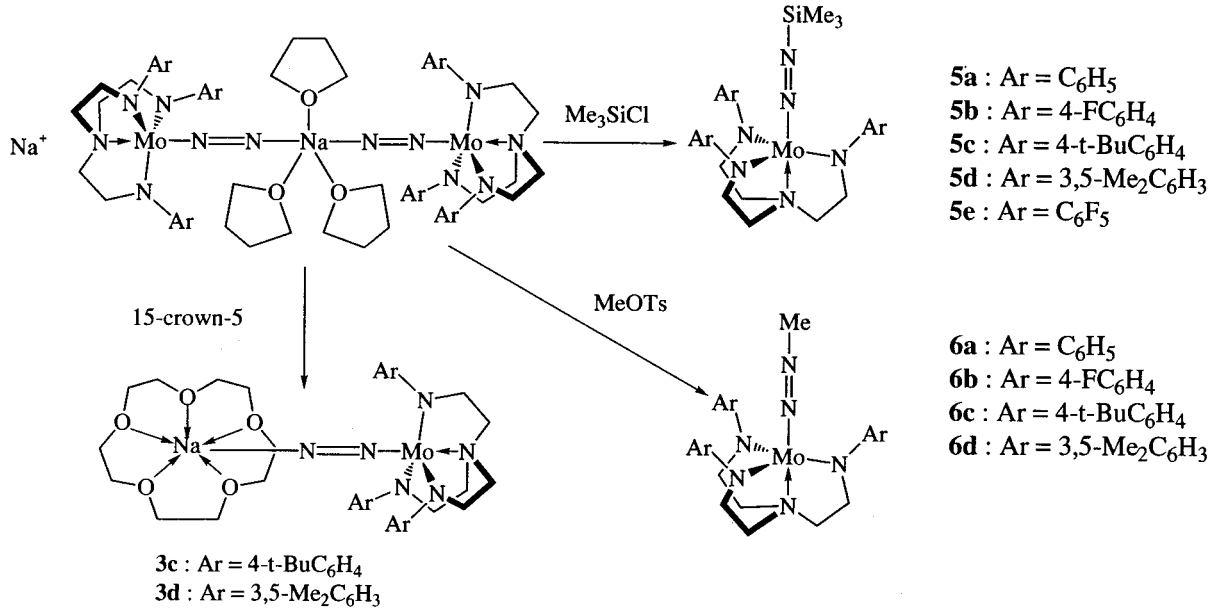
Scheme 2



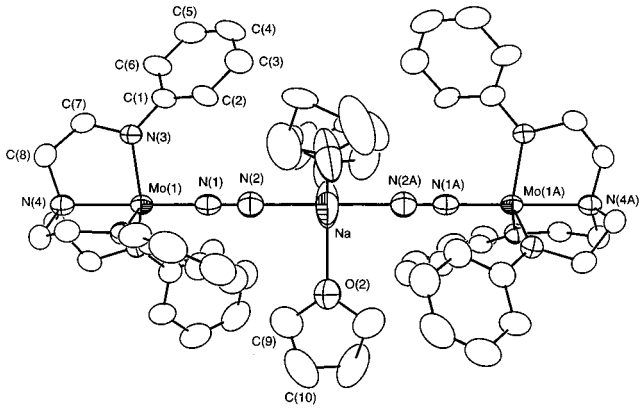


Figure 2. ORTEP drawing of the anion in $Na(THF)_6\{[PhN_3N]Mo{-}N{=}N\}_2Na(THF)_3$ (**2a**).

for **2a**, based on similar solubility properties and IR spectra. Since ^{1}H NMR spectra of vacuum-dried powders indicate that only one THF is present per Mo, most of the THF in the crystal must be relatively labile. Indeed, if the single crystals of **2a** that were employed for the X-ray study are exposed to pentane, they immediately disintegrate to give a powder.

Reduction of $[t\text{-}BuC_6H_4N_3N]MoCl$ with 2 equiv of sodium naphthalenide under $^{15}N_2$ produced $Na\{[t\text{-}BuC_6H_4N_3N]Mo\text{-}^{15}N{=}^{15}N\}_2Na(THF)_2$ (**2c-^{15}N**). The N−N stretch in the IR spectrum of **2c**-^{15}N was found at 1688 cm^{-1} in the solid state and 1755 cm^{-1} in THF solution, which correspond to shifts of 53 and 60 cm^{-1}, respectively, compared to **2c**. The ^{15}N NMR[14] spectrum of **2c**-^{15}N consists of two doublets at 374.44 and 336.07 ppm, which we assign to the α− and β-nitrogens, respectively. The one-bond N−N coupling constant is 10 Hz. The ^{15}N chemical shifts and coupling constants of all compounds reported in this paper are consistent with those of the analogous compounds containing the $[(TMS)N_3N]^{3-}$ ligand[4] and related complexes in the literature.[14−16]

Compound **2c** was oxidized with Cp_2FeOTf and $ZnCl_2$ in the hope of obtaining a terminal dinitrogen complex, "$[t\text{-}BuC_6H_4N_3N]Mo(N_2)$". However, in both cases, **1c** was the only product, with no sign of $[t\text{-}BuC_6H_4N_3N]Mo(N_2)$ by IR or NMR. We propose that $[t\text{-}BuC_6H_4N_3N]Mo(N_2)$ is the initial product of oxidation and that it begins to lose dinitrogen to yield $[t\text{-}BuC_6H_4N_3N]Mo$. A reaction between $[t\text{-}BuC_6H_4N_3N]Mo$ and $[t\text{-}BuC_6H_4N_3N]Mo(N_2)$ could then lead to **1c** directly, even though each is present in only a low concentration. Alternatively $[t\text{-}BuC_6H_4N_3N]Mo$ could react with some source of $\{[t\text{-}BuC_6H_4N_3N]Mo{-}N{=}N\}^-$ (e.g., **2c**) to yield $\{[t\text{-}BuC_6H_4N_3N]Mo{-}N{=}N{-}Mo[t\text{-}BuC_6H_4N_3N]\}^-$, which could be oxidized readily to yield **1c**. In a later section we present electrochemical studies of compounds of types **1** and **2** that (inter alia) include the formation of $\{[t\text{-}BuC_6H_4N_3N]Mo{-}N{=}N{-}Mo[t\text{-}BuC_6H_4N_3N]\}^-$ and its fate. The main message at this point is that steric factors do not prevent formation of **1c**, so species of this general type form rapidly, perhaps by multiple pathways and are kinetic "sinks" that cannot be reduced readily to compounds of type **2**.

Addition of 1 equiv of 15-crown-5 to **2c** or **2d** results in conversion to compounds of the type $[ArN_3N]Mo{-}N{=}N{-}Na$-(15-crown-5) (**3c** and **3d**) (Scheme 2). The ^{1}H NMR resonance for the crown ether occurs at δ 3.04 ppm in **2c** and at δ 2.91 ppm in **2d**, and it integrates to 20 protons. If an excess of crown ether is present, the crown ether resonance is broadened and shifted closer to the position of the resonance for free 15-crown-5 at δ 3.50 ppm, behavior which suggests that crown ether exchange is facile. The N=N stretching absorptions can be observed at 1815 cm^{-1} in the IR spectra of both **3c** and **3d**, and they do not change significantly when the spectra are recorded in THF. Therefore, the solid state and solution structures are likely to be the same. IR spectra do not change when crown ether is added, which suggests that a compound in which the sodium is removed from the β-nitrogen and ligated by two molecules of the crown ether[17] is not formed in this system, or at least it is not an observable, stable entity.

An X-ray diffraction study of **3c** was carried out on crystals that had been grown from a mixture of THF and pentane at

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Table 3. Crystallographic Data, Collection Parameters, and Refinement Parameters for [t-BuC$_6$H$_4$N$_3$N]Mo−N═N−Na(15-crown-5) (**3c**) and {[Ph$_2$C$_6$H$_3$N$_3$N]Mo−N═N}$_2$Mg(DME)$_2$ (**4f**)[a]

	3c	**4f**
empirical formula	$C_{46}H_{71}MoN_6NaO_5$	$C_{150}H_{132}MgMo_2N_{12}O_6$
fw	907.02	2414.87
space group	$P4_3$	$P2_1/c$
a (Å)	17.1059(7)	25.316(4)
b (Å)	17.1059(7)	16.114(2)
c (Å)	16.8153(10)	33.761(5)
β (deg)	90	99.927(3)°
V (Å^3)	4920.4(4)	13567(4)
Z	4	4
temp (K)	183(2)	183(2)
R1 [$I > 2\sigma(I)$]	0.0398	0.0981
wR2 [$I > 2\sigma(I)$]	0.0807	0.2167
R1 (all data)	0.0602	0.1602
wR2 (all data)	0.0858	0.2489

[a] All structures were solved on a Bruker SMART/CCD diffractometer using 0.710 73 Å Mo Kα radiation. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2}$.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for [t-BuC$_6$H$_4$N$_3$N]Mo−N═N−Na(15-crown-5) (**3c**)

Bond Lengths (Å)			
N(5)−N(6)	1.161(5)	Mo−N(3)	2.033(4)
Mo−N(5)	1.898(5)	Mo−N(4)	2.219(4)
Mo−N(1)	2.008(4)	Na−N(6)	2.362(5)
Mo−N(2)	2.063(4)		

Bond Angles (deg)			
N(5)−Mo−N(4)	177.20(18)	C(13)−N(2)−Mo	130.8(3)
N(1)−Mo−N(2)	120.97(17)	C(25)−N(3)−Mo	126.3(3)
N(2)−Mo−N(3)	117.77(16)	N(6)−N(5)−Mo	178.2(5)
N(1)−Mo−N(3)	113.12(18)	N(5)−N(6)−Na(1)	163.1(4)
C(1)−N(1)−Mo	129.3(4)		

Dihedral Angles (deg)			
N(4)−Mo−N(1)−C(1)	177.2(5)	N(4)−Mo−N(3)−C(25)	156.0(4)
N(4)−Mo-N(2)−C(13)	161.3(4)		

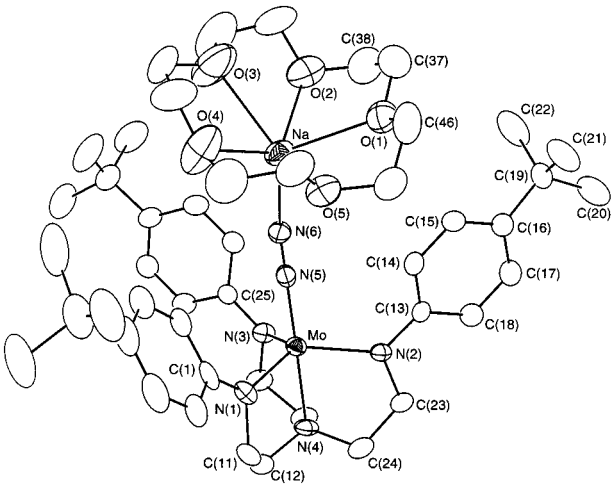


Figure 3. ORTEP drawing of the structure of [t-BuC$_6$H$_4$N$_3$N]Mo−N═N−Na(15-crown-5) (**3c**).

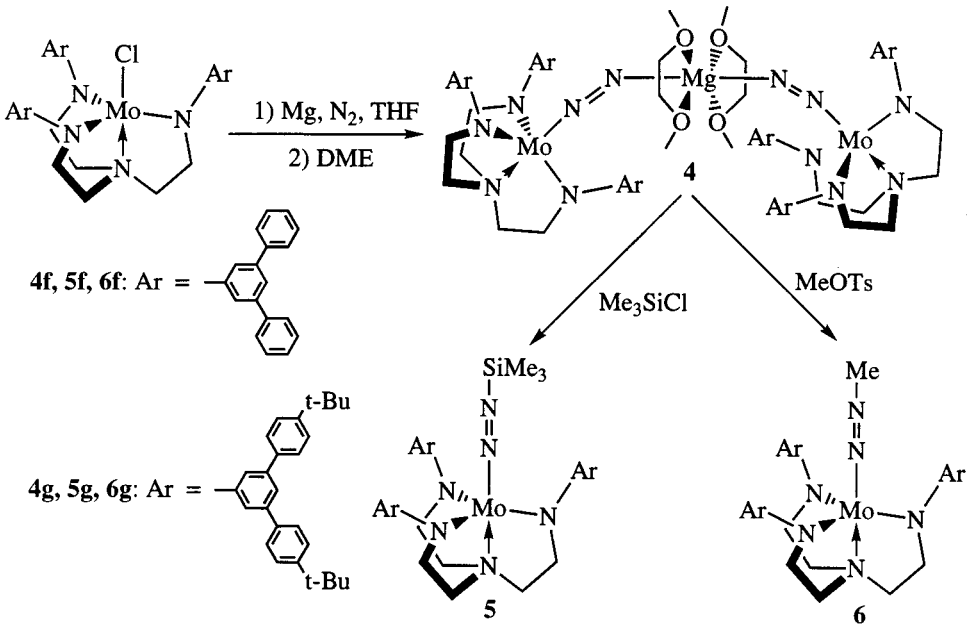
−35 °C. Crystallographic data, collection parameters, and refinement parameters are collected in Table 3, while selected bond lengths and angles can be found in Table 4. Figure 3 contains an ORTEP drawing of the structure, with thermal ellipsoids at the 35% probability level. One molecule of crown ether is bound to the sodium, and the sodium atom is bound to the β-nitrogen with a Na−N(6) bond length (2.362(5) Å) that is significantly longer than the Na−N(2) distance found in **2a** (2.160(14) Å). The N═N bond length is 1.16 Å, as expected for a diazenido complex. For comparison, two related sodium diazenido complexes prepared by Cummins and co-workers have N−N bond lengths of 1.17 and 1.15 Å.[17] The bent geometry at the β-nitrogen can be ascribed in part to crystal packing. Examination of the packing diagram (not shown) reveals that the crown ether fits between two of the ligand arms of an adjacent molecule, an arrangement that is best achieved if the bond angle at N(6) is not 180°.

Various [ArN$_3$N]MoCl complexes were reduced with magnesium under dinitrogen in an effort to obtain a Mg diazenido complex {[ArN$_3$N]Mo−N═N}$_2$Mg(L)$_x$ (**4**) analogous to that obtained in the [Me$_3$SiN$_3$N]$^{3-}$ system.[4,13] In all cases described thus far (Ar = C$_6$H$_5$, 4-FC$_6$H$_4$, 4-t-BuC$_6$H$_4$, and 3,5-Me$_2$C$_6$H$_3$) reduction of the [ArN$_3$N]MoCl complexes yields a mixture of **1** and **4**. Since **1c** (Ar = 4-t-BuC$_6$H$_4$) is soluble in C$_6$D$_6$, it was possible to determine the ratio of **1c** to **4c** by ^{1}H NMR. Reduction of [t-BuC$_6$H$_4$N$_3$N]MoCl with 3 equiv of magnesium powder under dinitrogen yields a mixture of **1c** and two diamagnetic compounds after 16 h, one of which is **4c**. Addition of 2 equiv of 1,4-dioxane resulted in conversion of the unknown compound to **4c**. This result suggests, by analogy with what was observed for complexes containing the [Me$_3$SiN$_3$N]$^{3-}$ ligand,[4,13] that one of the compounds is {[t-BuC$_6$H$_4$N$_3$N]Mo−N═N}MgCl(THF)$_x$, while the other is {[t-BuC$_6$H$_4$N$_3$N]Mo−N═N}$_2$Mg(THF)$_y$. Examination of the crude reaction mixture by ^{1}H NMR at this point indicated a 2:1 ratio of **4c** to **1c**. We found it difficult to separate **4c** and **1c**, since their solubilities are similar in common solvents. It was possible to obtain a mixture enriched in **4c** by adding ether to a concentrated toluene solution of the mixture, which results in the selective precipitation of **1c**. However, even after two iterations of this process, the material obtained was only 90% pure **4c**. Therefore it would appear that sodium is the reducing agent of choice for the preparation of anionic diazenido complexes containing the relatively "small" [ArN$_3$N]$^{3-}$ ligands.

When [ArN$_3$N]MoCl complexes containing the larger [Ph$_2$C$_6$H$_3$N$_3$N]$^{3-}$ ([TerN$_3$N]$^{3-}$) or [(4-t-BuC$_6$H$_4$)$_2$C$_6$H$_3$N$_3$N]$^{3-}$ ([t-BuTerN$_3$N]$^{3-}$) ligands are reduced under dinitrogen, one compound can be isolated when Mg is used as the reducing agent (Scheme 3). Stirring a suspension of [TerN$_3$N]MoCl and Mg powder in THF overnight yielded a soluble anionic diazenido complex of the form {[TerN$_3$N]Mo−N═N}$_2$Mg(THF)$_x$(**4f**-THF) in 87% yield. This material is not highly crystalline, and it is not known how many molecules of THF are coordinated to magnesium, but on the basis of the structure of the DME adduct discussed below, we assume that $x = 4$. Complex **4f**-THF is soluble in THF and benzene and is red in solution. ^{1}H and ^{13}C NMR spectra differ from those of other anionic diazenido complexes only by the additional resonances due to the [TerN$_3$N]$^{3-}$ ligand. The N−N stretch in the IR spectrum is centered at 1775 cm^{-1} in the solid state, and at 1789 cm^{-1} in THF solution, but both peaks are broad. Therefore, we assume that the solid-state and solution values are identical within experimental error. This observation contrasts with the large difference in the position of the N−N stretch between the solid state and solution for compounds of type **2**. Apparently a dimeric complex with Mg^{2+} at the center is the only readily accessible form when the [TerN$_3$N]$^{3-}$ ligand is present.

When [t-BuTerN$_3$N]MoCl is stirred with an excess of magnesium powder under dinitrogen, {[t-BuTerN$_3$N]Mo−N═N}$_2$Mg(THF)$_x$ (**4g**-THF) is formed in good yield. Complex **4g**-THF is highly soluble in most organic solvents and moderately soluble in pentane. The N−N stretch can be found at 1782 cm^{-1} in the solid-state IR spectrum and at 1805 cm^{-1} in

Scheme 3



THF solution. Once again, both peaks are broad, so differences between the solid state and solution probably are not significant.

When **4f**-THF and **4g**-THF are dissolved in DME, the color of the solutions darken as they are converted into $\{[ArN_3N]Mo-N{=}N\}_2Mg(DME)_2$ (**4f**-DME, **4g**-DME) species. The solubility of **4f**-DME in organic solvents is low; it crystallizes out of DME as it is formed. It can be dissolved in THF to give a red solution, but partial reversion to the THF adduct takes place. If the cycle of dissolving **4f**-DME or **4g**-DME in THF and removing THF in vacuo is repeated three times, the THF adduct is the only species present. Compound **4g**-DME was soluble enough in C_6D_6 to obtain a ^1H NMR spectrum, which indicated that one molecule of DME was present per ligand. The N−N stretch for **4f**-DME is found at 1785 cm^{-1} in the solid state and at 1789 cm^{-1} in THF solution, which suggests that major structural changes are not taking place upon replacement of THF by DME.

A crystal of **4f**-DME suitable for an X-ray diffraction study was grown by allowing a warm, dilute solution of **4f**-DME in dimethoxyethane to cool to room temperature. Crystallographic data, collection parameters, and refinement parameters are collected in Table 3, while selected bond lengths and angles can be found in Table 5. Figure 4 contains an ORTEP drawing of the structure, with thermal ellipsoids at the 35% probability level. The Mg atom is six-coordinate, with two diazenido ligands occupying axial sites and two DME ligands occupying equatorial sites. The Mo−N=N−Mg−N=N−Mo axis of the molecule is

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $\{[Ph_2C_6H_3N_3N]Mo-N{=}N\}_2Mg(DME)_2$ (**4f**-DME)

		Bond Lengths (Å)	
N(5)−N(6)	1.166(12)	N(7)−N(8)	1.173(12)
Mo−N(5)	1.884(12)	Mo(2)−N(8)	1.879(12)
Mo−N(1)	1.999(9)	Mo(2)−N(9)	2.004(10)
Mo−N(2)	2.007(11)	Mo(2)−N(11)	2.006(10)
Mo−N(3)	2.011(10)	Mo(2)−N(10)	2.020(10)
Mo−N(4)	2.221(9)	Mo(2)−N(12)	2.227(9)
Mg−N(6)	2.120(12)	Mg−N(7)	2.136(12)
		Bond Angles (deg)	
N(4)−Mo−N(5)	173.0(4)	N(8)−Mo(2)−N(9)	98.6(4)
Mo−N(5)−N(6)	172.0(10)	N(8)−Mo(2)−N(10)	96.0(4)
N(5)−N(6)−Mg	160.3(10)	N(8)−Mo(2)−N(11)	103.8(4)
N(6)−Mg−N(7)	174.8(5)	N(9)−Mo(2)−N(10)	123.7(4)
Mg−N(7)−N(8)	160.3(10)	N(9)−Mo(2)−N(11)	117.7(4)
N(7)−N(8)−Mo(2)	172.5(10)	N(10)−Mo(2)−N(11)	110.7(4)
N(8)−Mo(2)−N(12)	174.4(4)	N(9)−Mo(2)−N(12)	80.3(4)
N(5)−Mo−N(1)	99.0(4)	N(10)−Mo(2)−N(12)	80.3(4)
N(5)−Mo−N(2)	95.1(4)	N(11)−Mo(2)−N(12)	81.4(4)
N(5)−Mo−N(3)	105.1(4)	C(1)−N(1)−Mo	129.2(8)
N(1)−Mo−N(2)	122.0(4)	C(21)−N(2)−Mo	129.1(8)
N(1)−Mo−N(3)	117.8(4)	C(41)−N(3)−Mo	131.6(8)
N(2)−Mo−N(3)	111.9(4)	C(61)−N(9)−Mo(2)	130.5(8)
N(1)−Mo−N(4)	79.4(4)	C(81)−N(10)−Mo(2)	129.8(9)
N(2)−Mo−N(4)	80.2(4)	C(101)−N(11)−Mo(2)	129.1(8)
N(3)−Mo−N(4)	81.6(4)		
		Dihedral Angles (deg)	
N(4)−Mo−N(1)−C(1)	175.6(12)	N(12)−Mo(2)−N(9)−C(61)	177.8(13)
N(4)−Mo−N(2)−C(21)	155.4(11)	N(12)−Mo(2)−N(10)−C(81)	156.5(11)
N(4)−Mo−N(3)−C(41)	171.6(11)	N(12)−Mo(2)−N(11)−C(101)	166.2(11)

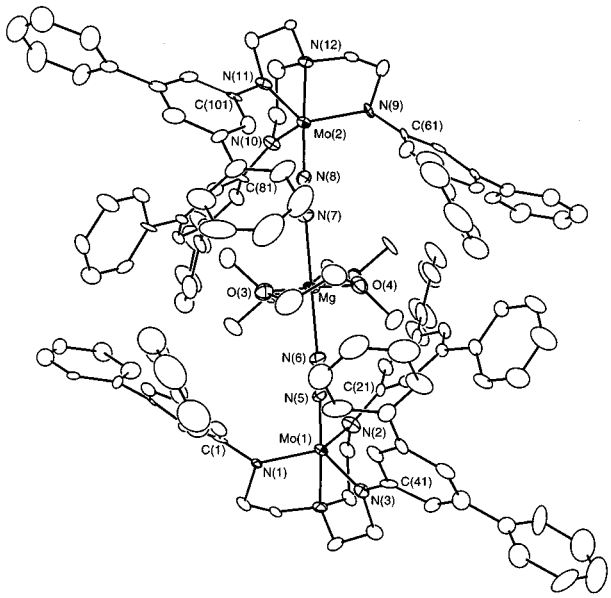


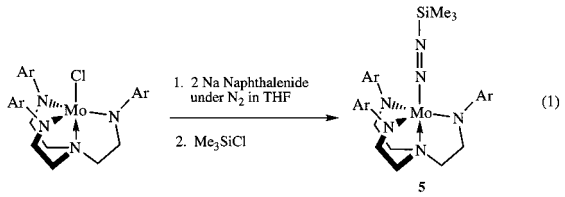
Figure 4. ORTEP drawing of the structure of $\{[Ph_2C_6H_3N_3N]MoNN\}_2$-$Mg(DME)_2$ (**4f**-DME).

bent slightly at each nitrogen atom. The deviation from linearity is most pronounced at N(6) and N(7), where the N(5)−N(6)−Mg and Mg−N(7)−N(8) bond angles are both 160°. The geometry at magnesium is essentially linear (174.8(5)°), which contrasts sharply with the 135° N−Mg−N angle in $\{[N_3N]$-$(TMS)Mo{-}N{=}N\}_2Mg(THF)_2$, in which the Mg atom is four-coordinate and in which the bond angles at the β-nitrogens are 178 and 166°.[4,13] Most of the metrical parameters are similar in the two halves of **4f**-DME. The two N−N bond lengths are statistically identical at 1.17 Å, which is essentially the same bond length as found in **3c** (1.16 Å) and **2a** (1.19 Å) and other published molybdenum diazenido complexes containing amido ligands.[2,3,13,17]

Attempts to isolate a terminal dinitrogen complex by reducing $[TerN_3N]MoCl$ with 1 equiv of sodium naphthalenide were unsuccessful. This observation contrasts with the behavior of complexes containing the $[Me_3SiN_3N]^{3-}$ ligand.[4] Later in this paper we will confirm through electrochemical studies that terminal dinitrogen complexes are not stable for the majority of triamidoamine Mo complexes that contain aryl-substituted ligands.

Neutral Molybdenum Diazenido Complexes. Addition of Me_3SiCl to **2** or **4** in THF leads to neutral trimethylsilyl diazenido complexes $[ArN_3N]Mo{-}N{=}N{-}SiMe_3$ (**5**) in yields ranging from 73 to 86% (Schemes 2 and 3). Diazenido complexes **5** also can be formed in one pot from $[ArN_3N]MoCl$ by reduction under dinitrogen with sodium naphthalenide or magnesium, depending on the ligand, followed by reaction with Me_3SiCl (eq 1). However, for most ligands **2** is easier to purify than **5**, the conversion of **2** to **5** is trivial, and **2** is a more versatile compound since it can be treated with other electrophiles. Complex **5e** was prepared from $[C_6F_5N_3N]Mo(OTf)$ using the literature procedure for closely related $[C_6F_5N_3N]Mo{-}N{=}NSi(i\text{-}Pr)_3$.

Compounds **5** are all yellow, C_3-symmetric, diamagnetic solids, with ^1H and ^{13}C NMR spectra that are typical of such species. The peaks in the IR spectra that correspond to N−N stretches are very broad, and there is sometimes a significant difference between the position of the peak in the solid state and in THF solution (e.g., 87 cm^{-1} for **5c**, Table 6). Compound **5c** that has been labeled with ^{15}N has its N−N stretch in the IR



spectrum at 1679 cm^{-1} in the solid state (vs 1738 cm^{-1} for **5c**) and at 1615 cm^{-1} in THF (vs 1651 cm^{-1} for **5c**). The ^{15}N NMR spectrum of labeled **5c** consists of two doublets at 374.39 and 220.72 ppm (with $J_{NN} = 13$) for the α− and β-nitrogens, respectively, consistent with the diazenido ligand being linear at the α-nitrogen.[16] In the ^{13}C NMR spectrum of **5c**-^{15}**N** the trimethylsilyl carbon resonance is split into a doublet by a two-bond $^{15}N{-}^{13}C$ coupling with a coupling constant of 3.4 Hz.

Addition of exactly 1 equiv of MeOTs to **2** or **4** produces neutral methyl diazenido complexes $[ArN_3N]Mo{-}N{=}N{-}Me$ (**6**) in yields ranging from 37 to 69% (Schemes 2 and 3). Unlike the reaction with Me_3SiCl, the reaction with MeOTs requires several hours to go to completion. If too much MeOTs is added, a mixture of **6** and $\{[ArN_3N]Mo{=}N{-}NMe_2\}OTs$ (**7**) results, and it is difficult to separate the two compounds. When the proper stoichiometry is maintained, the primary byproduct in the synthesis of **6** is **1**, formed by oxidation of **2**. However, **1** is considerably less soluble than **6**, so it can be removed by filtration. Compounds **6a**−**f** represent the first examples of methyl diazenido complexes that contain triamidoamine ligands, but a similar Mo complex containing three N(R)Ar ligands has been reported.[17] Like compounds **5**, **6a**−**f** are also yellow, C_3-symmetric, diamagnetic compounds, with unremarkable ^1H NMR spectra. It is interesting to note that the N=N stretching frequencies in the IR spectra of compounds **6**, which do not differ greatly between the solid-state and THF solution, are lower than those of any other compound. However, it is likely that the observed IR stretch is not a pure N=N stretch; i.e., it may also contain the Mo−N and N−C modes. For this reason it would not be appropriate to attempt to correlate the frequency of the "N−N stretch" with the degree of N−N bond reduction without additional detailed knowledge.

^{15}N-labeled **6c** (Ar = 4-t-BuC_6H_4) was prepared by treating **2c**-^{15}N with MeOTs. The N−N stretch in the IR spectrum shifts from 1585 to 1542 cm^{-1} in the solid state upon labeling. The ^{15}N NMR spectrum consists of two doublets at 407.02 and 231.94 ppm ($J_{NN} = 16$ Hz) for the α− and β-nitrogens, respectively. The *N*-methyl resonance in the ^{13}C NMR spectrum of **6c**-^{15}N is a doublet of doublets by virtue of coupling between ^{13}C and both labeled nitrogens. The one-bond coupling constant to the β-nitrogen is 8.8 Hz, while the two-bond coupling constant to the α-nitrogen is 4.5 Hz. The resonance for the protons on the methyl group bound to the β-nitrogen is also a doublet of doublets, with a two-bond $^1H{-}^{15}N(\beta)$ coupling constant of 3 Hz, and a three-bond $^1H{-}^{15}N(\alpha)$ coupling constant of 0.6 Hz.

Molybdenum Hydrazido and Nitride Complexes. Alkylation of neutral diazenido complexes **5** and **6** produces cationic hydrazido complexes in high yield (Scheme 4). The product that is obtained depends strongly on the starting material and the reaction conditions. The simplest case involves complexes that contain the 4-*tert*-butylphenyl ligand. Reaction of **5c** with 2 equiv of methyl triflate in toluene produces the dimethyl hydrazido complex $\{[t\text{-}BuC_6H_4N_3N]Mo{=}N{-}NMe_2\}^+OTf^-$ (**8c**) in 62% yield. Complex **8c** does not react further with methyl triflate, so an excess of methyl triflate is employed in order to ensure complete reaction. Complex **8c** is soluble in benzene and toluene, but insoluble in ether. Therefore, it can be isolated

Table 6. N−N Stretching Frequency in the IR Spectra of Diazenido Complexes

compd	ν(N−N) (Nujol)	ν(N−N) (THF)	ref
$[Me_3SiN_3N]MoN{\equiv}N$	1910, 1900	1934 (pentane)	
$[C_6F_5N_3N]MoN{=}N-Na$(15-crown-5)	1848		3
$[Me_2C_6H_3N_3N]Mo-N{=}N-Na$(15-crown-5) (**3d**)	1815	1832	
$[t\text{-}BuC_6H_4N_3N]Mo-N{=}N-Na$(15-crown-5) (**3b**)	1815	1815	
$[Me_3SiN_3N]MoN{=}N-Na$(15-crown-5)	1791		25
$[(N[R]Ar)_3Mo-N{=}N][Na(12\text{-crown-}4)_2]$		1761	17
$\{[TerN_3N]MoNN\}_2Mg(THF)_x$ (**4f**-THF)	1775	1789	
$\{[TerN_3N]MoNN\}_2Mg(DME)_2$ (**4f**-DME)	1785	1789	
$\{[t\text{-}BuTerN_3N]MoNN\}_2Mg(THF)_x$ (**4g**-THF)	1782	1805	
$\{[t\text{-}BuTerN_3N]MoNN\}_2Mg(DME)_2$ (**4g**-DME)	1787		
$\{[t\text{-}BuC_6H_4N_3N]MoNN\}_2Mg(THF)_x$ (**4c**)	1758		
$\{[Me_3SiN_3N]MoN{=}N\}_2Mg(THF)_2$		1719	4
$Na\{[FC_6H_4N_3N]MoNN\}_2Na(THF)_2$ (**2b**)	1752	1813	
$Na\{[PhN_3N]MoNN\}_2Na(THF)_2$ (**2a**)	1750	1818	
$Na\{[Me_2C_6H_3N_3N]MoNN\}_2Na(THF)_2$ (**2d**)	1742	1816	
$Na\{[t\text{-}BuC_6H_4N_3N]MoNN\}_2Na(THF)_2$ (**2c**)	1741	1815	
$Na\{[t\text{-}BuC_6H_4N_3N]Mo^{15}N^{15}N\}_2Na(THF)_2$ (**2c**-^{15}N)	1688	1755	
$[Na][(N{=}N)Mo(N[R]Ar)_3]$		1761	17
$[t\text{-}BuC_6H_4N_3N]Mo-N{=}N-SiMe_3$ (**5c**)	1738	1651	
$[Me_2C_6H_3N_3N]Mo-N{=}N-SiMe_3$ (**5d**)	1722	1657	
$[Me_3SiN_3N]Mo-N{=}N-SiMe_3$	1712	1714	4
$[t\text{-}BuC_6H_4N_3N]Mo\text{-}^{15}N{=}^{15}N-SiMe_3$ (**5c**-^{15}N)	1679	1615	
$[FC_6H_4N_3N]MoN{=}N-SiMe_3$ (**5b**)	1674	1657	
$[C_6F_5N_3N]Mo-N{=}N-SiMe_3$ (**5e**)	1672		
$[TerN_3N]Mo-N{=}N-SiMe_3$ (**5f**)	1646	1645	
$[PhN_3N]Mo-N{=}N-SiMe_3$ (**5a**)	1643	1663	
$[t\text{-}BuTerN_3N]Mo-N{=}N-SiMe_3$ (**5g**)	1642	1648	
$(N[R]Ar)_3Mo-N{=}N-SiMe_3$		1650	17
$[Me_2C_6H_3N_3N]Mo-N{=}N$-Me (**6d**)	1603	1602	
$[PhN_3N]Mo-N{=}N$-Me (**6a**)	1598	1601	
$[TerN_3N]Mo-N{=}N$-Me (**6f**)	1596	1596	
$[t\text{-}BuC_6H_4N_3N]Mo-N{=}N-Me$ (**6c**)	1585	1579	
$[FC_6H_4N_3N]Mo-N{=}N-Me$ (**6b**)	1581	1582	
$[t\text{-}BuC_6H_4N_3N]Mo-^{15}N{=}^{15}N-Me$ (**6c**-^{15}N)	1542		
$(N[R]Ar)_3Mo-N{=}NMe$		1538	17

by removing toluene and washing the crude residue with ether, or by growing crystals from a mixture of THF and pentane.

Treatment of **6c** with 1 equiv of methyl triflate also produces **8c** in 95% yield. ^{15}N labeled **8c** was also prepared by this method from **6c**-^{15}N. The two-step yield of **8c** from **2c** is virtually identical whether **5c** or **6c** is an intermediate. If **5c** is the intermediate, a high-yielding first step is followed by a moderate yield for the second step. If **6c** is employed as the intermediate, the opposite is true. The clean preparation of **8c** in high yield stands in sharp contrast with syntheses of $[Me_3SiN_3N]^{3-}$ complexes, where the yield is only ~20% after fractional crystallization, and compounds in which one of the trimethylsilyl groups on the ligand has been replaced by a methyl group are also formed.[4]

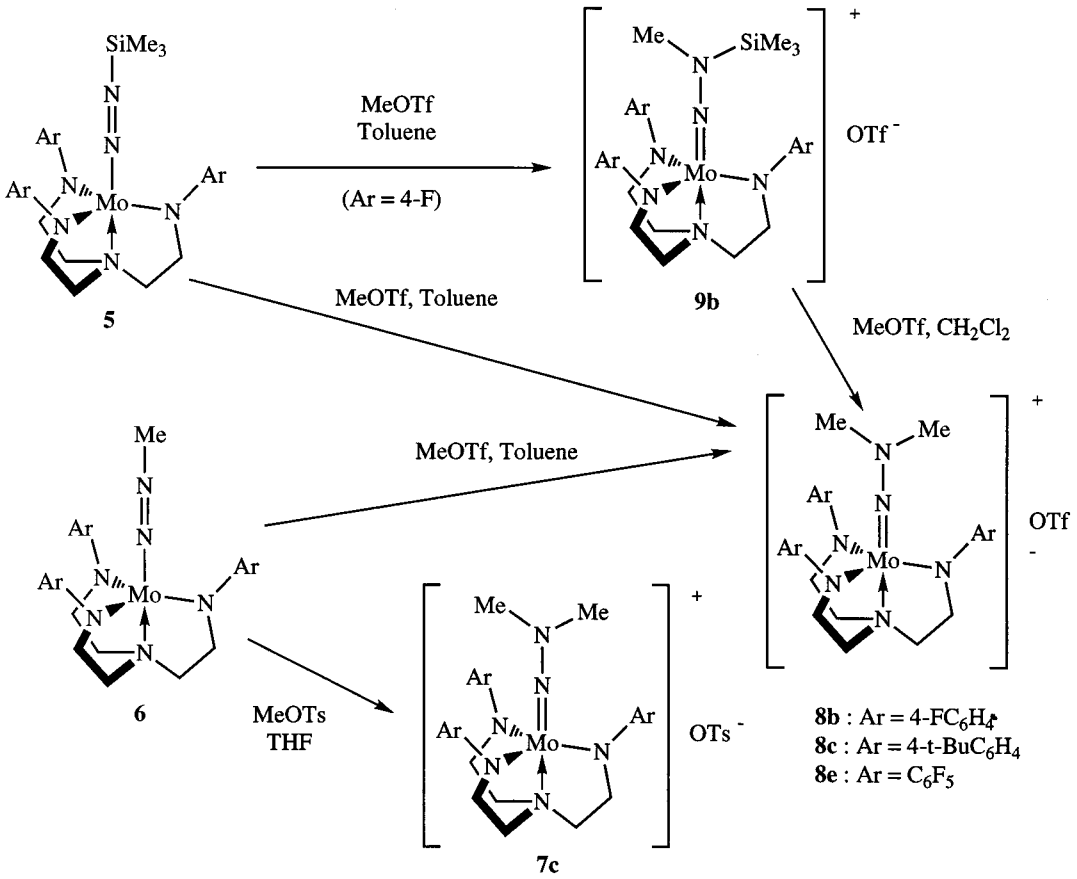
All cationic hydrazido complexes reported here are diamagnetic species that are soluble and stable in $CDCl_3$. Therefore, ^{1}H NMR spectra of **8c** were recorded both in $CDCl_3$ and in C_6D_6. The chemical shifts for all aryl protons are accidentally coincident in C_6D_6, so only a singlet integrating as 12 protons is observed. However, in $CDCl_3$ the normal pattern of two doublets is observed for the aryl protons. In both solvents, the backbone proton resonances of the ligand are shifted downfield relative to where they are found in related neutral complexes. The ^{15}N NMR spectrum of **8c**-^{15}N consists of two doublets at 368.27 and 154.40 ppm (J_{NN} = 11 Hz) for the α− and β-nitrogens, respectively. The *N*-methyl resonance in the ^{13}C NMR spectrum of **8c**-^{15}N is a doublet with $^1J(^{13}C,^{15}N)$ = 9.2 Hz. Two-bond coupling to ^{15}N was not observed in either ^{13}C or ^{1}H NMR spectra of **8c**-^{15}N. No peak that can be assigned to an N−N stretch is readily apparent in the IR spectrum of **8c**, since the spectra of **8c** and **8c**-^{15}N are essentially identical.

As was discussed briefly in the context of the synthesis of compounds **6**, treatment of **6c** with 1 equiv of methyl tosylate, which is a milder electrophile than methyl triflate, produces $\{[t\text{-}BuC_6H_4N_3N]Mo{=}N-NMe_2\}^+OTs^-$ (**7c**) in 64% yield (Scheme 4). Complex **7c** is much more soluble in organic solvents than complex **8c** (triflate counterion), and even though it is cationic, it is soluble in ether, whereas neutral **6c** is not. Complex **7c** was isolated by crystallization from a concentrated ether solution. The ^{1}H NMR spectrum of **7c** is consistent with it being a cationic species in that the ligand backbone resonances are shifted downfield relative to neutral complexes.

Reaction of **5e** (Ar = C_6F_5) with 3 equiv of methyl triflate in toluene produces **8e** (Scheme 4). Higher temperatures and longer reaction times are needed for the synthesis of **8e**, in part because the electron-withdrawing C_6F_5 groups on the $[RN_3N]^{3-}$ ligand render the β-nitrogen of **5e** less nucleophilic than that of **5c**. A 96% yield is obtained after overnight reaction at 50 °C in a pressure tube. Compound **8e** precipitates out of toluene, so it can be isolated simply by filtering the reaction mixture. Complex **8e** is insoluble in ether and sparingly soluble in THF. As with **8c**, no degradation of the ligand occurs, the ligand backbone resonances are shifted downfield in the ^{1}H NMR spectrum, and no N−N stretch can be found in the IR spectrum. No reaction is observed when **5c** is treated with an excess of methyl tosylate under similar conditions.

Treatment of **5b** (Ar = 4-FC_6H_4) with an excess of methyl triflate in toluene results in the immediate precipitation of an orange powder. On the basis of the solubility properties of **8e**, it was assumed that the orange powder was **8b**. However, examination of the ^{1}H NMR spectrum (recorded in $CDCl_3$), reveals that the orange powder is actually $[FC_6H_4N_3N]Mo{=}$

Scheme 4



N−N(Me)($SiMe_3$) (**9b**) (Scheme 4). The isolated yield of **9b** is 99%. If a solution of **9b** in dichloromethane is allowed to stir overnight with an excess of methyl triflate, it is converted into **8b**. However this reaction is not clean, and **8b** is isolated in only 42% yield after removing CH_2Cl_2 and washing away the more soluble byproducts with THF.

The formation of **9b** and its conversion into **8b** suggest that the first step in formation of **8** from **5** in general is electrophilic attack of methyl triflate on the β-nitrogen of **5** to produce **9**. Since **9b** precipitates from solution, alkylation does not proceed further. However, when **9** remains in solution, a second equivalent of methyl triflate reacts with **9** to yield **8**. The mechanistic details of this second step are not clear. Compound **8b** can be produced cleanly in 81% yield from **6b** under the same reaction conditions used to convert **6c** into **8c**.

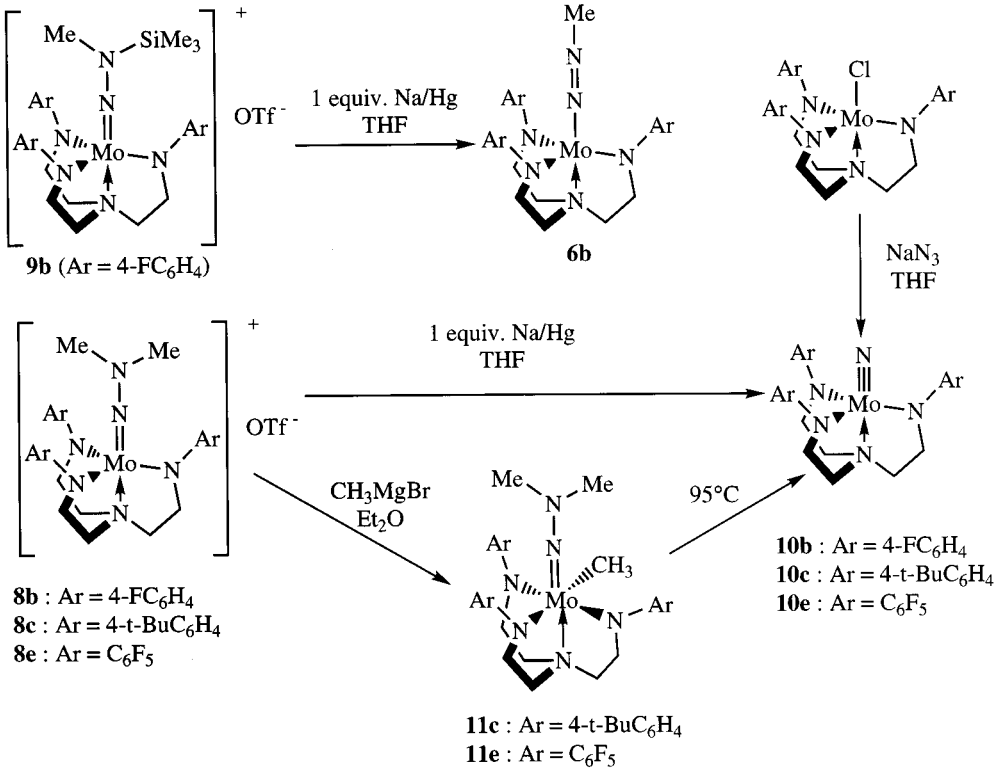
Reduction of **8b**, **8c**, or **8e** with 1 equiv of sodium amalgam in THF produces a mixture of products, but [ArN_3N]Mo≡N (**10**) is the major metal-containing product (Scheme 5). However, the NMR yield of **10b** is only 28% (by integration against the triflate resonance). The large number of peaks in the crude NMR spectra of these reductions is consistent with extensive decomposition. Nitride **10e** is a known compound.[3] Nitrides **10b** and **10c** also were prepared by treating [ArN_3N]MoCl with NaN_3 (Scheme 5). The yield of **10b** is 57%, and **10c** is obtained in 58% yield after 2 days. Both compounds are yellow solids which are soluble in THF and toluene, but insoluble in ether and pentane. Dark red byproducts can be washed away with ether, and the nitrides can be recrystallized from a mixture of toluene and pentane.

A ^{13}C-labeled version of **8c** was prepared by treating **6c** with $^{13}CH_3OTf$. Reduction of **8c**-^{13}C with Na/Hg was carried out in an NMR tube in THF and monitored by ^{13}C NMR. The major peak in the ^{13}C NMR spectrum is at 38.62 ppm, which is the chemical shift for the methyl carbon in a sample of dimethylamine in THF obtained independently. Our hypothesis is that the first step in the conversion of **8** to **10** is the reduction of **8** to a neutral Mo(V) dimethyl hydrazido complex. As we will show later, the Mo(V) dimethylhydrazido species is stable on the CV time scale (500 mV/s), but we do not know about its longer term stability. The Mo(V) dimethylhydrazido species also can be reduced to give an unstable anion. If the Mo(V) dimethylhydrazido species ultimately decomposes via homolytic N−N bond cleavage, it would yield **10** and a dimethylamine radical. In solvents such as THF or toluene, which are good hydrogen atom donors relative to C_6D_6, the dimethylamine radical would abstract a hydrogen atom from the solvent to give dimethylamine. However, the dimethylamine radical is also likely to react in other more destructive ways, thereby leading to a large number of byproducts. It is also possible that **10** forms in a more complex manner after the Mo(V) dimethylhydrazido species is reduced further.

Chemical reduction of **9b** with sodium amalgam in THF produced **6b** in 42% yield (Scheme 5), along with about 10% unidentified paramagnetic material (by ^{19}F NMR). As in the reduction of **8**, an unstable Mo(V) intermediate is postulated. However, in this case, the weakest bond is the Si−N bond, so the Mo(V) intermediate decomposes by Si−N bond cleavage to give the methyl diazenido complex. Si−N bond cleavage is a common, undesired side reaction for compounds containing the [Me_3SiN_3N]$^{3-}$ ligand.[4,6,8]

Alkylation of **8c** or **8e** with methylmagnesium bromide (3.0 M in ether) at −40 °C immediately yields the neutral trimethylhydrazido complexes, [ArN_3N]Mo(Me)($NNMe_2$) (**11**) (Scheme 5). Conversion of **8e** to **11e** proceeds rapidly in ether even

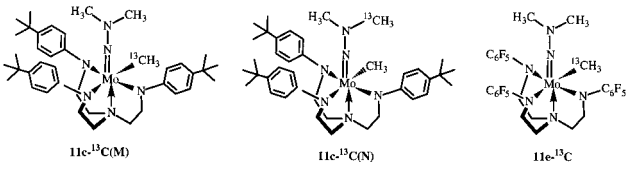
Scheme 5



though **8e** is insoluble in ether. Complex **11c** is pentane soluble, and midnight blue in solution, while complex **11e** is burgundy colored. Complex **11c** was isolated in 86% yield by crystallization from pentane at −40 °C, while complex **11e** was isolated in 79% yield by washing the crude residue with pentane after filtering off Mg salts and removing ether in vacuo. Precedent for the conversion of **8** to **11** exists for complexes containing the $[Me_3SiN_3N]^{3-}$ ligand.[4] The ^{1}H NMR spectrum of **11c** is characteristic of a C_s-symmetric complex. The resonances at 0.60 ppm in the ^{1}H NMR spectrum and 18 ppm in the ^{13}C NMR spectrum are assigned to the methyl group bound to the metal. The ^{1}H and ^{19}F NMR spectra of **11e** (Ar = C_6F_5) at elevated temperatures show evidence for a reversible fluxional process (broadened resonances) that was not studied further.

Both **11c** and **11e** decompose upon heating to give the corresponding nitride as the major metal-containing product. Heating **11e** to 50 °C overnight is sufficient to promote its complete decomposition, but **11c** must be heated to 90 °C for 2 days before it is all consumed. Three separate decompositions were carried out on **11e** in sealed NMR tubes, two in toluene-d_8 and one in THF. In all three experiments, the color of the solution changes from blood red to yellow-orange. In the THF experiment and in one of the toluene experiments, two new trigonally symmetric, diamagnetic products are formed in about a 1:1 ratio. One of the products is nitride **10e**, but the identity of the other compound is unknown. The second toluene decomposition reaction was carried out using analytically pure **11e**; in this case nitride **10e** was the only metal-containing product that could be identified. We conclude that the thermolysis reaction is sensitive to the purity of the starting material (inter alia). Nitride **10c** is by far the major metal-containing product in the decomposition of **11c** in C_6D_6 (by ^{1}H NMR), but a close examination of the *tert*-butyl region of the NMR spectrum indicates that no fewer than nine other products are present in small amounts. The presence of peaks in the vinylic region of the spectrum suggests that one of the decomposition pathways is abstraction of a hydrogen atom from the ligand backbone and subsequent cleavage of a C−N bond, as was observed for certain Ta complexes containing the $[Me_3SiN_3N]^{3-}$ ligand.[18,19]

Two ^{13}C-labeling labeling studies were carried out in an attempt to gain more insight into the organic products of the thermolysis of **11**. One experiment involved ^{13}C labeling the methyl group bound to the metal. Compounds **11c**-^{13}C(M) and **11e**-^{13}**C** were prepared in the same manner as unlabeled material using $^{13}CH_3MgI$. Thermolyses were performed in C_6D_6 and monitored by both ^{1}H and ^{13}C NMR. Both spectra indicate that nitride is the major product after decomposition is complete, and the most intense peak in both ^{13}C NMR spectra is that of methane. A second resonance for a labeled methyl group can be found at 22.7 ppm, but the identity of this product could not be established. The absence of a peak at 48 ppm indicates that trimethylamine is not one of the products.

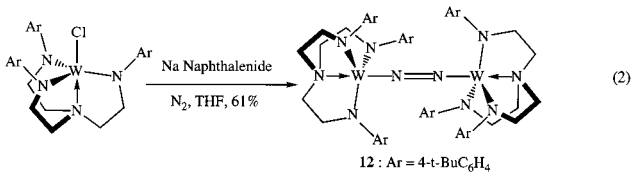


The other labeling experiment involved ^{13}C labeling one of the methyl groups bound to the β-nitrogen. Compound **11c**-^{13}C(N) was prepared from **8c**-^{13}C by reaction with unlabeled methylmagnesium bromide; a resonance for the labeled methyl group could be observed at 43.34 ppm in the ^{13}C NMR spectrum. After decomposition of **11c**-^{13}C(N) was complete, 14

(18) Freundlich, J. S.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3643.
(19) Freundlich, J. S.; Schrock, R. R.; Davis, W. M. *Organometallics* **1996**, *15*, 2777.

resonances were observed in the ^{13}C NMR spectrum in the region from 30 to 50 ppm. Dimethylamine is one of the products, but it is by no means a major product, at least when C_6D_6 is the solvent.

Tungsten Dinitrogen Complexes. Simultaneous addition of a solution of [t-Bu$C_6H_4N_3$N]WCl and a solution of sodium naphthalenide to a flask containing vigorously stirred THF resulted in the formation of pink, paramagnetic [t-Bu$C_6H_4N_3$N]W−N═N−W[t-Bu$C_6H_4N_3$N] (**12**) in 61% yield (eq 2). Elemental analysis, ^1H NMR spectroscopy, and cyclic voltammetry (see later) all support the proposed composition of this species. Similar ditungsten bridging dinitrogen complexes appear to be formed upon reduction of [ArN_3N]WCl complexes containing the phenyl, 4-fluorophenyl, or 3,5-dimethylphenyl ligands, but since they are insoluble in all organic solvents, they could not be characterized. As with Mo compounds **1** (Scheme 1), no N−N stretch is expected in the IR spectrum of **12**, and none was observed. Recently Scheer has published the X-ray structure of {[($Me_3CCH_2NCH_2CH_2$)$_3$N]W}$_2$(μ−N_2), which presumably is an analogue of **12**; it was isolated in low yield as a byproduct during the synthesis of ($Me_3CCH_2NCH_2CH_2$)$_3$]WCl from W(dme)Cl_4 and Li$_3$[($Me_3CCH_2NCH_2CH_2$)$_3$N].[20]



(2)

12 : Ar = 4-t-BuC_6H_4

The ^1H NMR spectra of **1c** and **12** display many similarities. Both spectra contain a relatively sharp resonance at 12.22 ppm corresponding to the meta hydrogens on the aryl rings of the ligand. However, due to the sharper resonances for paramagnetic W complexes, it is possible to resolve a doublet with a coupling constant of 8.4 Hz. Another doublet with the same coupling constant can be found at 2.63 ppm which is assigned to the ortho hydrogens on the aryl rings. The ligand backbone resonances occur in a region of the spectrum similar to those in **1c**, and as with **1c**, the upfield resonance is much broader than the downfield one. A C_6D_6 solution of **12** remained unchanged upon heating to 90 °C for several days.

Electrochemical (CV) studies (see below) first established that compound **12** could be oxidized readily by two electrons. We found that it can be oxidized cleanly by Cp_2FeBPh_4 in dichloromethane to give {[t-Bu$C_6H_4N_3$N]W−N═N−W[t-Bu$C_6H_4N_3$N]}(BPh_4)$_2$ (**13**) in 85% yield (eq 3). Compound **13** is diamagnetic, as expected for a MNNM system that contains 8 π electrons.[3,12,21] The ligand backbone resonances in the ^1H NMR spectrum are found at 4.18 and 2.84 ppm, similar to other cationic diamagnetic complexes containing a triamidoamine ligand reported here. Unfortunately, several attempts to grow X-ray quality crystals of **12** and **13** were unsuccessful.

Since ditungsten bridging dinitrogen complexes are formed by the one-electron reduction of [ArN_3N]WCl, we hoped that anionic diazenido complexes of W could be produced by the two-electron reduction of [ArN_3N]WCl. [ArN_3N]WCl (Ar = 4-FC_6H_4, 3,5-$Me_2C_6H_3$, 3,5-$Ph_2C_6H_3$) was treated with 2 equiv of sodium naphthalenide, and the reactions were worked up in the same manner as the analogous Mo reactions, but no compounds similar to **2** (Scheme 1) could be isolated, and no diamagnetic material was observed in crude ^1H NMR spectra. Addition of Me_3SiCl to crude reaction mixtures did not produce compounds analogous to **5**.

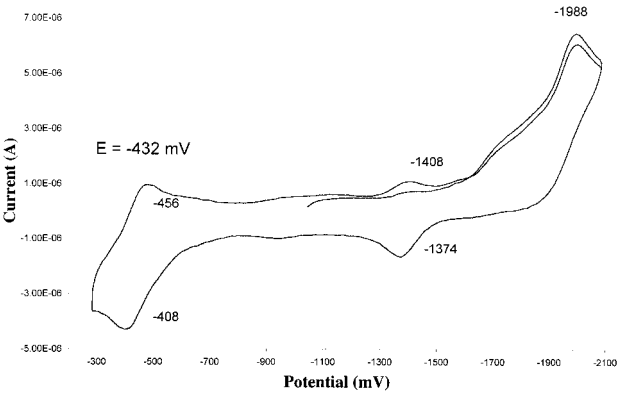


Figure 5. CV of [$C_6F_5N_3$N]Mo−N═N−Mo[$C_6F_5N_3$N] (**1e**).

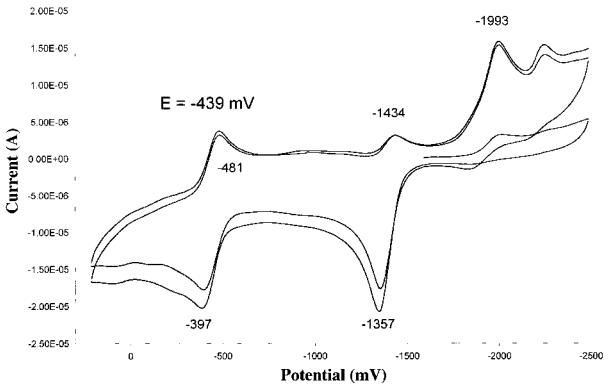
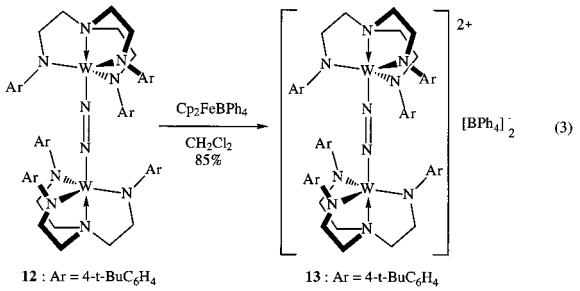


Figure 6. CV of [$C_6F_5N_3$N]Mo−N═N−Na(15-Crown-5) (**2e**).



(3)

12 : Ar = 4-t-BuC_6H_4 **13** : Ar = 4-t-BuC_6H_4

Electrochemical Studies. In Figures 5 and 6 are shown CV scans of **1e** and **2e**. During the initial reductive scan for {[$C_6F_5N_3$N]Mo(N_2)}$^-$ (**2e**), no cathodic waves are present out to −2500 mV. On the anodic scan {[$C_6F_5N_3$N]Mo(N_2)}$^-$ is oxidized at −1357 mV. Only a small return wave is observed for this oxidation because "[$C_6F_5N_3$N]Mo(N_2)" is unstable, we propose toward loss of dinitrogen to yield "[$C_6F_5N_3$N]Mo". Apparently "[$C_6F_5N_3$N]Mo(N_2)" and "[$C_6F_5N_3$N]Mo" combine under these conditions to yield **1e**, since the anodic wave at −439 mV and the irreversible cathodic wave at −1993 mV in Figure 6 can also be found in the CV of **1e**, as shown in Figure 5. Compound **1e** (Figure 5) is reduced irreversibly at −1988 mV to what we presume is {[$C_6F_5N_3$N]Mo−N═N−Mo-[$C_6F_5N_3$N]}$^-$. Apparently, however, {[$C_6F_5N_3$N]Mo−N═N−Mo[$C_6F_5N_3$N]}$^-$ decomposes to {[$C_6F_5N_3$N]Mo(N_2)}$^-$ and "[$C_6F_5N_3$N]Mo", which at this potential and under dinitrogen is reduced to a second equivalent of {[$C_6F_5N_3$N]Mo(N_2)}$^-$. The anodic wave of low intensity that is observed at −1374 mV in Figure 5 corresponds to the oxidation of {[$C_6F_5N_3$N]Mo(N_2)}$^-$ to "[$C_6F_5N_3$N]Mo(N_2)", the same process that can be seen more

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(21) Sanner, R. D.; Duggan, D. M.; McKenzie, T. C.; Marsh, R. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 8358.

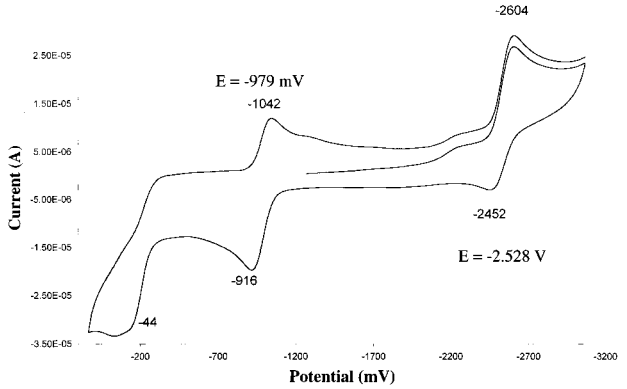

Figure 7. CV of [t-Bu$C_6H_4N_3N$]Mo−N═N−Mo[t-Bu$C_6H_4N_3N$] (**1c**).

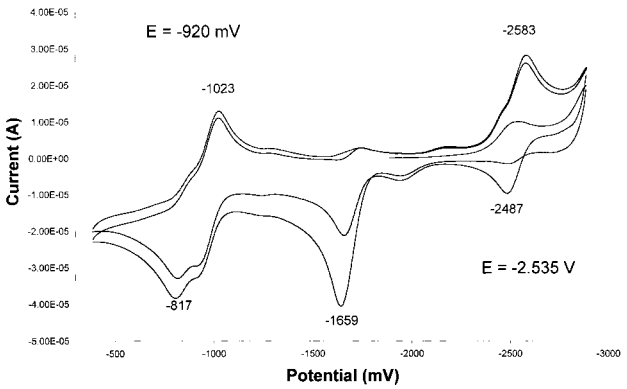

Figure 8. CV of [t-Bu$C_6H_4N_3N$]Mo−N═N−Na$(THF)_x$ (**2c**).

clearly in Figure 6. The anodic wave at −432 mV in Figure 5 corresponds to the oxidation of [$C_6F_5N_3N$]Mo−N═N−Mo[$C_6F_5N_3N$] to {[$C_6F_5N_3N$]Mo−N═N−Mo[$C_6F_5N_3N$]}$^+$, in a reversible manner on this time scale. Note that in Figure 6 the cathodic peak that corresponds to an irreversible reduction of **1e** at −1993 mV is not present during the initial reductive scan. These data support the chemical observation that oxidation of **2e** generates **1e** and reduction of **1e** generates **2e** and suggest that "[$C_6F_5N_3N$]Mo(N_2)" and {[$C_6F_5N_3N$]Mo−N═N−Mo[$C_6F_5N_3N$]}$^-$ are both unstable on the time scale employed. No effort was made to isolate {[$C_6F_5N_3N$]Mo−N═N−Mo[$C_6F_5N_3N$]}$^+$, and if the potential is scanned to more positive values than those shown in Figure 5, irreversible anodic waves characteristic of decomposition are observed. Therefore hypothetical {[$C_6F_5N_3N$]Mo−N═N−Mo[$C_6F_5N_3N$]}$^{2+}$, a variation of which can be observed in CV studies of tungsten species (see below) and which can be isolated (see above), is not stable.

The CV of **1c** is shown in Figure 7. Compound **1c** is reduced at −2523 mV, compared with −1988 mV for **1e**, as one might expect on the basis of the greater electron withdrawing power of the pentafluorophenyl group. However, the reduction of **1c** is more reversible than it is for **1e**. Apparently {[t-Bu$C_6H_4N_3N$]Mo−N═N−Mo[t-Bu$C_6H_4N_3N$]}$^-$ is not transformed readily into 2 equiv of {[$C_6F_5N_3N$]Mo(N_2)}$^-$. An anodic wave that corresponds to the relatively reversible oxidation of {[t-Bu$C_6H_4N_3N$]Mo−N═N−Mo[t-Bu$C_6H_4N_3N$]} to {[t-Bu$C_6H_4N_3N$]Mo−N═N−Mo[t-Bu$C_6H_4N_3N$]}$^+$ is observed at −986 mV, again about 500 mV more negative than the oxidation of **1e**. The second oxidation (at −44 mV) in Figure 7 is clearly irreversible, which suggests that {[t-Bu$C_6H_4N_3N$]Mo−N═N−Mo[t-Bu$C_6H_4N_3N$]}$^{2+}$ is unstable on the CV time scale. No peak is observed during the initial cathodic scan out to −2900 mV in the CV of {[t-Bu$C_6H_4N_3N$]Mo(N_2)}$^-$ (**2c**, Figure 8), while irreversible oxidation is observed at −1659 mV. Only a tiny return wave that corresponds to the reduction of "[t-Bu$C_6H_4N_3N$]Mo(N_2)" is observed, consistent with the ready loss of dinitrogen to yield "[t-Bu$C_6H_4N_3N$]Mo". A reaction between "[t-Bu$C_6H_4N_3N$]Mo(N_2)" and "[t-Bu$C_6H_4N_3N$]Mo" then yields **1c** and in subsequent scans the waves that correspond to the oxidation and reduction of **1c** shown in Figure 7 are observed.

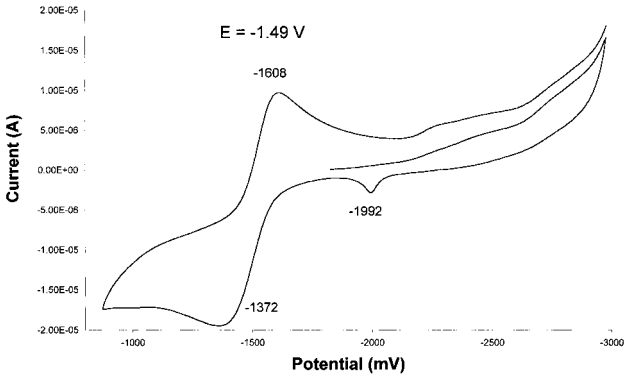

Figure 9. CV of {[$Ph_2C_6H_3N_3N$]Mo−N═N}$_2$Mg$(THF)_x$ (**4f**).

The CV of **2d** is similar to that of **2c**. (See Figure 1S in Supporting Information.) No reduction is observed in the initial cathodic scan, while an oxidation wave for **2d** is observed at −1623 mV. Decomposition of "[$Me_2C_6H_3N_3N$]Mo(N_2)" to "[$Me_2C_6H_3N_3N$]Mo" then leads to **1d**, which is reduced at −2.37 V and oxidized at −0.99 and −0.30 V. The second oxidation (of {[$Me_2C_6H_3N_3N$]Mo−N═N−Mo[$Me_2C_6H_3N_3N$]}$^+$ to {[$Me_2C_6H_3N_3N$]Mo−N═N−Mo[$Me_2C_6H_3N_3N$]}$^{2+}$) is irreversible at low scan rates. (Data not shown in Figure 1S.)

The CVs of **2a** (Figure 2S, Supporting Information) and **2b** show waves for the oxidation of the anion to the neutral dinitrogen complex clearly at −1572 and −1555 mV, respectively. However, the reduction and oxidation(s) of the bridging dinitrogen complexes are not readily observed as a consequence of the insolubility of these bridging dinitrogen complexes. Visual examination of the working electrode after completion of the experiment whose CV is shown in Figure 2S reveals a coating of what we presume to be **1a** on the electrode. Electrochemical studies of **1a** and **1b** therefore are also not practical for that reason.

The CV trace for **4f** is shown in Figure 9. That for **4g** is similar, although the reduction wave is more pronounced in the CV of **4g**. No wave is observed upon initially scanning to negative potentials. The main feature in Figure 9 is a *relatively reversible* oxidation of {[TerN_3N]Mo(N_2)}$^-$ to "[TerN_3N]Mo(N_2)" at −1.49 V (−1.54 V for **4g**). The X-ray structure of **4f** suggests that formation of a bridging dimolybdenum dinitrogen complex analogous to **1c** or **1e** would be difficult. In short, [ArN_3N]Mo(N_2) is relatively stable when the Ar group is sterically relatively bulky because even if [ArN_3N]Mo(N_2) loses dinitrogen to yield "[ArN_3N]Mo", which we suspect it does, [ArN_3N]Mo(N_2) and [ArN_3N]Mo cannot combine (for steric reasons) to yield a compound of type **1**. Therefore, at least under an atmosphere of dinitrogen, [ArN_3N]Mo(N_2) appears to be relatively stable.

An electrochemical study was carried out on **12** in order to compare the behavior of the tungsten complex with its molybdenum analogue, **1c** (Figure 7). A CV of **12** is shown in Figure 10. Compound **12** is reduced cleanly at −3.03 V, which is considerably more negative than the reduction wave for **1c**. It is important to note that {[t-Bu$C_6H_4N_3N$]W−N═N−W[t-Bu$C_6H_4N_3N$]}$^-$ apparently is stable toward W−N cleavage to give {[t-Bu$C_6H_4N_3N$]W−N═N}− and "W[t-Bu$C_6H_4N_3N$]". It

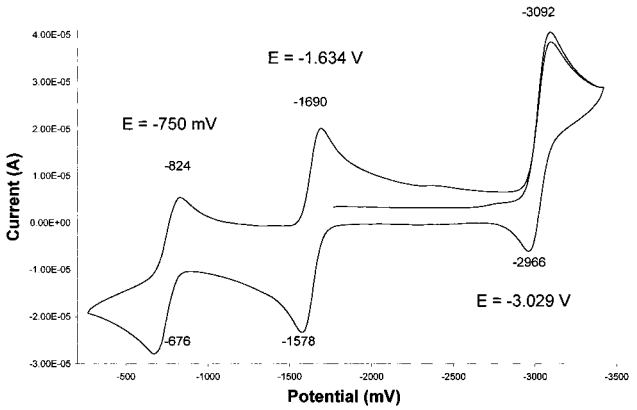

Figure 10. CV of [t-BuC$_6$H$_4$N$_3$N]W−N═N−W[t-BuC$_6$H$_4$N$_3$N] (**12**).

should also be noted that two reversible oxidations are observed at −1.63 and −0.75 V. The CV of isolated {[t-BuC$_6$H$_4$N$_3$N]W−N═N−W[t-BuC$_6$H$_4$N$_3$N]}$^{2+}$ (**13**, Figure 3S, Supporting Information) is identical to the CV shown in Figure 10. The initial cathodic scan reveals a reduction of {[t-BuC$_6$H$_4$N$_3$N]W−N═N−W[t-BuC$_6$H$_4$N$_3$N]}$^{2+}$ to {[t-BuC$_6$H$_4$N$_3$N]W−N═N−W[t-BuC$_6$H$_4$N$_3$N]}$^{+}$, a reduction of {[t-BuC$_6$H$_4$N$_3$N]W−N═N−W[t-BuC$_6$H$_4$N$_3$N]}$^{+}$ to {[t-BuC$_6$H$_4$N$_3$N]W−N═N−W[t-BuC$_6$H$_4$N$_3$N]}, and a reduction of {[t-BuC$_6$H$_4$N$_3$N]W−N═N−W[t-BuC$_6$H$_4$N$_3$N]} to {[t-BuC$_6$H$_4$N$_3$N]W−N═N−W[t-BuC$_6$H$_4$N$_3$N]}$^{-}$, followed by the expected waves in the return anodic scan. The greater W−N bond strength (vs Mo−N) results in the integrity of the W−N−N−W core being maintained through three one-electron processes.

CV studies also were carried out on **8b** (Ar = 4-FC$_6$H$_4$; Figure 4S, Supporting Information), **8c** (Ar = 4-t-BuC$_6$H$_4$; Figure 5S, Supporting Information), and **8e** (Ar = C$_6$F$_5$; Figure 6S, Supporting Information). All three compounds display a relatively reversible reduction, which is the most facile for **8e** (E = −1.22 V) followed by **8b** (E = −1.60 V) and **8c** (E = −1.68 V). Irreversible second reductions, presumably to produce a Mo(IV) monoanion, are observed at −2.61 V for **8b**, −2.76 V for **8c**, and −2.49 V for **8e**. Apparently the neutral Mo(V) dimethylhydrazido species, [ArN$_3$N]Mo═N−NMe$_2$, which are 17 electron species counting one triamidoamine π bond and donation of an electron pair from Nα to the metal, are relatively stable on the electrochemical time scale. They can be reduced further to 18e {[ArN$_3$N]Mo═N−NMe$_2$}$^{-}$ species, but not reversibly. The mode of decomposition of the 18e species is not known.

Conclusions

We have found that [ArN$_3$N]MoCl complexes (Ar = C$_6$H$_5$, 4-FC$_6$H$_4$, 4-t-BuC$_6$H$_4$, 3,5-Me$_2$C$_6$H$_3$, 3,5-Ph$_2$C$_6$H$_3$, and 3,5-(4-t-BuC$_6$H$_4$)$_2$C$_6$H$_3$) can be reduced to give various Mo−N═N-M (M = Na, Mg) diazenido complexes. Dimolybdenum diazenido complexes are readily formed when Ar = C$_6$H$_5$, 4-FC$_6$H$_4$, 4-t-BuC$_6$H$_4$, or 3,5-Me$_2$C$_6$H$_3$, but for steric reasons not when Ar = 3,5-Ph$_2$C$_6$H$_3$ or 3,5-(4-t-BuC$_6$H$_4$)$_2$C$_6$H$_3$. Conversely, only when the terphenyl-substituted ligands are present is there any indication that [ArN$_3$N]Mo(N$_2$) complexes are stable under dinitrogen; i.e., they are not readily converted into Mo−N═N−Mo species. Addition of electrophiles to various Mo−N═N−M species proceeds relatively smoothly to give first [ArN$_3$N]-Mo−N═N−E species (E = electrophile) followed by {[ArN$_3$N]Mo═N−NE$_2$}$^{+}$ species, in contrast to similar reactions in [Me$_3$SiN$_3$N]$^{3-}$ systems where trimethylsilyl groups are lost. A ditungsten diazenido complex that contains the [4-t-BuC$_6$H$_4$N$_3$N]$^{3-}$ ligand can be prepared, but W−N═N−M diazenido complexes have not yet been observed. The W−N═N−W linkage is strong enough to survive both a one-electron reduction and two one-electron oxidations, and [{[4-t-BuC$_6$H$_4$N$_3$N]W}$_2$-(N$_2$)]$^{2+}$ (as its BPh$_4$ salt) can be isolated. Reduction of Mo−N═N−M and Mo═N−NE$_2$ hydrazido species leads to formation of Mo≡N in low yields, but N$_\beta$ appears to end up in many products, of which only dimethylamine could be identified. Electrochemical studies reveal expected trends in oxidation and reduction potentials, but also provide insight into the stabilities of various intermediates, in particular, neutral dinitrogen complexes of the type [ArN$_3$N]Mo(N$_2$). Since the chemistry of complexes that contain the sterically more bulky terphenyl-substituted ligands appears to be restricted to the mononuclear species, i.e., bimetallic diazenido complexes are avoided, we plan to employ sterically more protective ligands of this general type in future studies.

Experimental Section

General Procedures. All reactions were conducted under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using Schlenk techniques. Ether, toluene, and pentane were sparged with nitrogen for 45 min followed by passage through a 1 gallon column of activated alumina as described in the literature.[22] Tetrahydrofuran, dimethoxyethane, and 1,4-dioxane were distilled from sodium benzophenone ketyl, and dichloromethane was distilled from CaH$_2$. C$_6$D$_6$ was sparged with nitrogen and stored over 4 Å molecular sieves. CDCl$_3$ was dried over CaH$_2$, vacuum transferred to a solvent storage flask, stored at −35 °C, and passed through a plug of alumina before use. [ArN$_3$N]MoCl and [ArN$_3$N]WCl complexes were prepared as described in the preceding paper in this issue.[11] [C$_6$F$_5$N$_3$N]Mo(OTf)[3] and Cp$_2$FeBPh$_4$[23] were prepared as described in the literature. Sodium naphthalenide was prepared by stirring sodium sand and naphthalene overnight in THF; it was titrated with n-PrOH before use. ^{13}CH$_3$MgI was prepared in the usual fashion in diethyl ether from ^{13}CH$_3$I. All other starting materials are commercially available and were used as received.

^{1}H NMR spectra were recorded at an operating frequency of 300 or 500 MHz, and ^{13}C NMR spectra were recorded at an operating frequency of 75.5 or 125.8 MHz. The residual protons or carbon-13 atoms of the deuterated solvents were used as internal references. ^{19}F NMR spectra were recorded at an operating frequency of 282.2 MHz, and were referenced externally using CFCl$_3$ (0 ppm). ^{15}N NMR spectra were recorded at an operating frequency of 50.7 MHz and were referenced externally using nitromethane (380.2 ppm). Chemical shifts are reported in parts per million, and coupling constants are in hertz. All spectra were acquired at ca. 22 °C. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. Elemental analyses (C, H, N) were performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany. X-ray data were collected on a Bruker SMART/CCD diffractometer, and general experimental details are described in the literature.[24]

[t-BuC$_6$H$_4$N$_3$N]Mo−N═N−Mo[t-BuC$_6$H$_4$N$_3$N] (1c). A solution of [t-BuC$_6$H$_4$N$_3$N]MoCl (218 mg, 0.325 mmol) in THF (7 mL) was cooled to −35 °C. A 0.65 M stock solution of sodium naphthalenide (0.5 mL, 0.325 mmol) in THF was diluted to 3 mL and cooled to −35 °C. The sodium naphthalenide solution was added dropwise to the solution of [t-BuC$_6$H$_4$N$_3$N]MoCl, and the reaction mixture was allowed to warm to room temperature while being stirred over a period of 2 h. The color changed from red to deep purple. The THF was removed in vacuo, the residue was dissolved in toluene, and the mixture was filtered through Celite. Toluene was removed from the extract in vacuo, and the product

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was washed with ether and dried in vacuo; yield 119 mg (0.092 mmol, 56% based on Mo). ^{1}H NMR (C_6D_6): δ 11.02 (s, 12, meta), 4.29 (br s, 12, ortho), 1.76 (s, 54, t-Bu), −8.46 (br s, 12, CH_2), −36 (br, 12, CH_2). Anal. Calcd for $C_{72}H_{102}N_{10}Mo_2$: C, 66.55; H, 7.91; N, 10.78. Found: C, 66.42; H, 7.82; N, 10.66.

Na({[PhN$_3$N]Mo−N═N}$_2$Na)(THF)$_2$ (2a). A 0.33 M stock solution of sodium naphthalenide (7.25 mL, 2.40 mmol) in THF was diluted to 20 mL and cooled to −35 °C. [PhN$_3$N]MoCl (604 mg, 1.20 mmol) was added as a solid, and the reaction was allowed to warm to room temperature with stirring for 1 h. The color became burgundy. The reaction mixture was filtered through Celite to remove salts. The filtrate was concentrated to 4 mL, during which time purple crystals formed. The crystals were collected, washed with ether, and dried in vacuo; yield = 384 mg (0.65 mmol, 54%). ^{1}H NMR (C_6D_6 spiked with THF): δ 7.28 (t, 12, meta), 7.16 (d, 12, ortho), 6.91 (t, 6, para), 3.67 (t, 12, CH_2), 3.53 (THF), 2.15 (t, 12, CH_2), 1.43 (THF). ^{13}C NMR (THF): δ 160.24 (C_{ipso}), 126.44 (C_o), 119.59 (C_m), 115.31 (C_p), 67.15 (THF), 54.44 (CH_2), 53.52 (CH_2), 25.37 (THF). IR (cm^{-1}): 1750 (Nujol), 1818 (THF). Anal. Calcd for $C_{56}H_{70}N_{12}O_2Na_2Mo_2$: C, 56.95; H, 5.970; N, 14.23. Found: C, 57.11; H, 6.06; N, 14.18.

Na({[FC$_6$H$_4$N$_3$N]Mo−N═N}$_2$Na)(THF)$_2$ (2b). A 0.54 M stock solution of sodium naphthalenide (6.0 mL, 3.24 mmol) in THF was diluted to 50 mL and cooled to −35 °C. [FC$_6$H$_4$N$_3$N]MoCl (902 mg, 1.62 mmol) was added as a solid, and the reaction was allowed to warm to room temperature with stirring for 1 h. The plum colored reaction mixture was filtered through Celite, and the filtrate was concentrated in vacuo to give a brown oily residue. The residue was washed with pentane in order to remove naphthalene. The rust colored solid was washed with toluene to yield a magenta solid. Analytically pure material was obtained by recrystallization from a mixture of THF and pentane at −35 °C; yield 490 mg (0.76 mmol, 47%). ^{1}H NMR (C_6D_6 spiked with THF): δ 7.18 (dd, 12, Ar), 6.97 (t, 12, Ar), 3.64 (t, 12, CH_2), 3.54 (THF), 2.18 (t, 12, CH_2), 1.43 (THF). ^{13}C NMR (THF): δ 157.48 (s, C_{ipso}), 155.82 (d, C_p, J_{CF} = 232), 120.39 (d, C_o, J_{CF} = 7), 113.17 (d, C_m, J_{CF} = 21), 67.72 (THF), 55.39 (CH_2), 53.99 (CH_2), 25.88 (THF). ^{19}F NMR (C_6D_6 spiked with THF): δ −129.76 (br s). IR (cm^{-1}): 1752 (Nujol), 1813 (THF). Anal. Calcd for $C_{56}H_{64}F_6N_{12}O_2Na_2Mo_2$: C, 52.18; H, 5.00; N, 13.04. Found: C, 52.28; H, 4.87; N, 13.12.

Na({[t-BuC$_6$H$_4$N$_3$N]Mo−N═N}$_2$Na)(THF)$_2$ (2c). A 0.65 M stock solution of sodium naphthalenide (20.0 mL, 13.0 mmol) in THF was diluted to 80 mL and cooled to −40 °C. A separate solution of [t-BuC$_6$H$_4$N$_3$N]MoCl (4.36 g, 6.50 mmol) in 40 mL of THF was also cooled to −40 °C. The Mo solution was added dropwise over a period of 15 min to the sodium naphthalenide with vigorous stirring. The reaction mixture was allowed to warm to room temperature and was stirred for 1 h. The volume was reduced to 10 mL in vacuo, and the reaction mixture was filtered through Celite to remove NaCl. Pentane (15 mL) was added, and the solution was stirred at −35 °C for 3 h to yield pink crystals (1.53 g). The filtrate was concentrated to dryness in vacuo, and the residue was triturated with pentane to yield another 809 mg of powder which was spectroscopically identical to the crystallized product; total yield 2.34 g. (3.09 mmol, 48%). ^{1}H NMR (C_6D_6): δ 7.29 (d, 12, meta), 7.13 (d, 12, ortho), 3.66 (t, 12, CH_2), 3.42 (m, 8, THF), 2.15 (t, 12, CH_2), 1.34 (s, 54, t-Bu), 1.32 (m, 8, THF). ^{13}C NMR (C_6H_6): δ 158.05 (C_{ipso}), 140.43 (C_p), 124.97 (C_o), 120.11 (C_m), 67.84 (THF), 55.39 (CH_2), 53.16 (CH_2), 34.04 (t-Bu), 31.88 (t-Bu Me), 25.37 (THF). ^{13}C NMR (THF): δ 158.33 (C_{ipso}), 136.72 (C_p), 123.11 (C_o), 119.15 (C_m), 67.16 (THF), 54.74 (CH_2), 53.36 (CH_2), 33.28 (t-Bu), 31.24 (t-Bu Me), 25.37 (THF). IR (cm^{-1}): 1741 (Nujol), 1815 (THF), 1745 (benzene). Anal. Calcd for $C_{80}H_{118}N_{12}O_2Na_2Mo_2$: C, 63.31; H, 7.84; N, 11.07. Found: C, 63.26; H, 7.91; N, 10.89.

Na({[t-BuC$_6$H$_4$N$_3$N]Mo−^{15}N═^{15}N}$_2$Na)(THF)$_2$ (2c-^{15}N). One chamber of a two-chamber reaction vessel was charged with a solution of [t-BuC$_6$H$_4$N$_3$N]MoCl (671 mg, 1.00 mmol) in 10 mL of THF, and the other chamber was charged with a solution of sodium naphthalenide (4.0 mL of a 0.50 M stock solution, 2.0 mmol) in 10 mL of THF. The vessel was sealed and degassed on the Schlenk line by the freeze−pump−thaw method. When the vessel was evacuated, $^{15}N_2$ was introduced directly from a breakseal flask through a piece of rubber tubing. The contents of the two chambers were mixed, and the reaction mixture was stirred under $^{15}N_2$ for 1 h. The vessel was resealed and returned to the glovebox (under $^{14}N_2$) for the remainder of the workup, which was performed in an analogous manner as for the unlabeled material; yield 225 mg (0.148 mmol, 30%). ^{15}N NMR (C_6D_6/THF): δ 374.44 (d, N_α, J_{NN} = 10), 336.07 (d, N_β, J_{NN} = 10). IR (cm^{-1}): 1688 (Nujol), 1755 (THF).

Na({[Me$_2$C$_6$H$_3$N$_3$N]Mo−N═N}$_2$Na)(THF)$_2$ (2d). A 0.42 M stock solution of sodium naphthalenide (7.50 mL, 3.15 mmol) in THF was diluted to 20 mL and cooled to −35 °C. [Me$_2$C$_6$H$_3$N$_3$N]MoCl (925 mg, 1.57 mmol) was added as a solid, and the reaction was allowed to warm to room temperature with stirring for 1 h, after which time the solution was plum colored. The reaction mixture was filtered through Celite and concentrated to dryness to yield a black oily residue. The residue was washed with pentane to remove naphthalene and red impurities. The resulting pink solid was pure by NMR, but analytically pure material was obtained by recrystallization from a mixture of THF and pentane at −40 °C; yield 445 mg (0.66 mmol, 42%). ^{1}H NMR (C_6D_6): δ 6.98 (s, 12, ortho), 6.47 (s, 6, para), 3.70 (t, 12, CH_2), 3.46 (m, 8, THF), 2.25 (s, 36, 3,5-Me_2), 2.19 (t, 12, CH_2), 1.36 (m, 8, THF). ^{13}C NMR (THF): δ 160.57 (C_{ipso}), 134.83 (C_p), 118.37 (C_o), 117.39 (C_m), 67.15 (THF), 55.03 (CH_2), 53.33 (CH_2), 25.37 (THF), 21.12 (3,5-Me_2). IR (cm^{-1}): 1742 (Nujol), 1816 (THF). Anal. Calcd for $C_{68}H_{94}N_{12}O_2Na_2Mo_2$: C, 60.53; H, 7.02; N, 12.46. Found: C, 60.39; H, 6.88; N, 12.35.

[t-BuC$_6$H$_4$N$_3$N]Mo−N═N−Na(15-crown-5) (3c). 15-Crown-5 (66 mg, 0.3 mmol) was dissolved in 2 mL of THF and added dropwise to a solution of **2c** (228 mg, 0.3 mmol) in 6 mL of THF. The reaction was stirred at room temperature for 2 h, then THF was removed, and the residue was dissolved in 2 mL of toluene. Pentane was added until crystals began to form. The reaction was cooled to −35 °C for 2 h to complete crystallization. The mother liquor was decanted off, and the purple crystals were washed three times with ether; yield = 209 mg (0.23 mmol, 77%). ^{1}H NMR (C_6D_6): δ 7.67 (d, 6, meta), 7.37 (d, 6, ortho), 3.83 (t, 6, CH_2), 3.04 (s, 20, crown), 2.16 (t, 6, CH_2), 1.48 (s, 27, t-Bu). ^{13}C NMR (C_6D_6/THF): δ 159.86 (C_{ipso}), 137.42 (C_p), 124.52 (C_m), 120.14 (C_o), 70.10 (crown), 56.07 (CH_2), 53.94 (CH_2), 34.40 (t-Bu), 32.42 (t-Bu). IR (cm^{-1}): 1815 (Nujol), 1815 (THF). Anal. Calcd for $C_{46}H_{71}N_6O_5NaMo$: C, 60.91; H, 7.89; N, 9.27. Found: C, 61.11; H, 7.96; N, 9.21.

[Me$_2$C$_6$H$_3$N$_3$N]Mo−N═N−Na(15-crown-5) (3d). 15-Crown-5 (76 mg, 0.34 mmol) was dissolved in 2 mL of THF and added dropwise to a solution of **2d** (216 mg, 0.32 mmol) in 6 mL of THF. The color changed immediately from purple to black. The reaction was stirred at room temperature for 30 min, then THF was removed, and the residue was washed with pentane to give a black solid. This material was recrystallized from a mixture of ether and toluene to give purple crystals, which were washed with ether until the washings were colorless and dried in vacuo; yield 69 mg. (0.084 mmol, 26%). ^{1}H NMR (C_6D_6): δ 7.43 (s, 6, ortho), 6.47 (s, 3, para), 3.92 (t, 6, CH_2), 2.91 (s, 20, crown), 2.41 (s, 18, 3,5-Me_2), 2.20 (t, 6, CH_2). ^{13}C NMR (C_6D_6/THF): δ 161.82 (C_{ipso}), 136.28 (C_m), 119.17 (C_o), 118.03 (C_p), 69.66 (crown), 56.14 (CH_2), 53.74 (CH_2), 22.46 (Ar CH_3). IR (cm^{-1}): 1815 (Nujol), 1832 (THF). Anal. Calcd for $C_{40}H_{59}N_6O_5NaMo$: C, 58.39; H, 7.23; N, 10.21. Found: C, 58.46; H, 7.18; N, 10.17.

{[t-BuC$_6$H$_4$N$_3$N]Mo−N═N}$_2$Mg(THF)$_2$ (4c). A 20 mL reaction vial was charged with a solution of [t-BuC$_6$H$_4$N$_3$N]MoCl (200 mg, 0.30 mmol) in 5 mL of THF and Mg powder (24 mg, 1.0 mmol). The reaction was stirred overnight at room temperature, and the color became pinkish purple. A 1 mL aliquot of 1,4-dioxane was added, and the reaction was allowed to stir for 1 more hour. THF was removed in vacuo, and the residue was dissolved in toluene. Filtration of the extract through Celite removed $MgCl_2$(dioxane). The toluene was removed in vacuo, and the residue was washed with ether to yield a peach colored ether-insoluble solid (~100 mg?) which was collected and dried in vacuo. This material could not be purified to homogeneity. ^{1}H NMR (C_6D_6): δ 7.41 (br s, 6, meta), 7.36 (br s, 6, ortho), 3.79 (br s, 6, CH_2), 3.25 (m, 4, THF), 2.26 (br s, 6, CH_2), 1.28 (s, 27, t-Bu). IR (Nujol; cm^{-1}) 1758.

{[TerN$_3$N]Mo−N═N}$_2$Mg(THF)$_4$ (4f-THF). A suspension of [TerN$_3$N]MoCl (441 mg, 0.46 mmol) in THF (12 mL) was stirred over Mg powder (100 mg, 4.16 mmol) under dinitrogen overnight. All of

the Mo starting material dissolved as it reacted to produce a scarlet red solution. Addition of 1,4-dioxane (1 mL) resulted in the precipitation of $MgCl_2$(dioxane), which was filtered off. The solvent was removed from the filtrate in vacuo and the residue was washed with pentane. The red insoluble product was collected and dried in vacuo; yield 443 mg (0.20 mmol, 87%). ^{1}H NMR (C_6D_6): δ 7.72 (d, 24, 3,5-ortho), 7.60 (s, 12, ortho), 7.48 (s, 6, para), 7.21 (t, 24, 3,5-meta), 7.07 (t, 12, 3,5-para), 3.87 (t, 12, CH_2), 3.18 (br s, THF), 2.36 (t, 12, CH_2), 1.04 (br s, THF). ^{13}C NMR (THF): δ 161.91 (C_{ipso}), 141.94 (C_m), 140.73 (3,5-ipso), 128.12 (3,5-meta), 126.78 (3,5-ortho), 126.15 (3,5-para), 120.11(C_o), 116.64 (C_p), 57.11 (CH_2), 53.77 (CH_2). IR (cm^{-1}):1775 (Nujol), 1789 (THF).

{[TerN$_3$N]Mo−N=N}$_2$Mg(DME)$_2$ (4f-DME). Compound **4f**-THF (110 mg, 0.050 mmol) was dissolved in DME (8 mL). Purple crystals formed over the course of several hours. The mother liquor was decanted off and the crystals were washed with pentane and dried in vacuo; yield 98 mg (0.046 mmol, 93%). ^{1}H NMR (C_6D_6/DME): δ 7.42 (d, 24, 3,5-ortho), 7.32 (s, 12, H_o), 7.16 (s, 6, H_p), 7.14 (t, 24, 3,5-meta), 7.06 (t, 12, 3,5-para). IR (cm^{-1}): 1785 (Nujol), 1789 (THF). Anal. Calcd for $C_{128}H_{122}N_{12}O_4MgMo_2$: C, 72.91; H, 5.83; N, 7.97. Found: C, 73.08; H, 5.75; N, 8.08.

{[(t-BuC$_6$H$_4$)$_2$C$_6$H$_3$N$_3$N]Mo−N=N}$_2$Mg(THF)$_4$ (4g-THF). A solution of [(t-BuC$_6$H$_4$)$_2$C$_6$H$_3$N$_3$N]MoCl (555 mg, 0.43 mmol) in THF (12 mL) was stirred over Mg powder (50 mg, 2.08 mmol) under dinitrogen overnight. 1,4-Dioxane (0.5 mL) was added, and the mixture was stirred for 30 more minutes. Insoluble material was filtered off, and THF was removed to yield a red oil. The oil was dissolved in pentane, and more salts were filtered off. Storage of the pentane solution at −40 °C overnight resulted in the formation of orange crystals. The mother liquor was decanted off and the crystals were washed with pentane and dried in vacuo; yield 499 mg (0.33 mmol, 78%). ^{1}H NMR (C_6D_6): δ 7.78 (d, 24, 3,5-meta), 7.69 (s, 12, H_o), 7.61 (s, 6, H_p), 7.35 (d, 24, 3,5-ortho), 3.92 (t, 12, CH_2), 3.32 (br s, THF), 2.35 (t, 12, CH_2), 1.25 (s, 108, t-Bu), 1.14 (br s, THF). ^{13}C NMR (C_6D_6): δ 162.25 (C_{ipso}), 149.86 (3,5-para), 142.01 (C_m), 140.42 (3,5-ipso), 127.76 (3,5-meta), 126.31 (3,5-ortho), 120.26 (C_o), 117.95 (C_p), 69.32 (THF), 56.78 (CH_2), 54.58 (CH_2), 34.83 (t-Bu), 31.89 (t-Bu), 25.80 (THF). IR (cm^{-1}): 1782 (Nujol), 1805 (THF).

{[(t-BuC$_6$H$_4$)$_2$C$_6$H$_3$N$_3$N]Mo−N=N}$_2$Mg(DME)$_2$ (4g-DME). Compound **4g**-THF (90 mg, 0.031 mmol) was dissolved in DME (4 mL). The solvent was removed, and the residue was washed with pentane. The lavender, pentane-insoluble product was collected and dried in vacuo; yield 70 mg (0.025 mmol, 81%). ^{1}H NMR (C_6D_6): δ 7.65 (d, 24, 3,5-meta), 7.58 (s, 12, H_o), 7.42 (d, 30, 3,5-ortho, and H_p), 3.79 (t, 12, CH_2), 2.34 (s, 8, DME), 2.26 (s, 12, DME). 2.12 (t, 12, CH_2), 1.34 (s, 108, t-Bu). ^{13}C NMR (C_6D_6): δ 163.34 (C_{ipso}), 149.95 (3,5-para), 141.65 (C_m), 140.41 (3,5-ipso), 127.74 (3,5-meta), 126.26 (3,5-ortho), 121.57 (C_o), 117.18 (C_p), 69.84 (DME), 60.24 (DME), 58.04 (CH_2), 54.55 (CH_2), 34.92 (t-Bu), 32.05 (t-Bu). IR (cm^{-1}): 1787 (Nujol).

[PhN$_3$N]Mo−N=N−SiMe$_3$ (5a). A solution of **2a** (154 mg, 0.13 mmol) in 8 mL of THF was cooled to −40 °C. Me_3SiCl (48 mg, 0.44 mmol) was dissolved in 1 mL of THF, cooled to −40 °C, and added to the reaction mixture. The color immediately changed from purple to yellow. THF was removed, and the residue was dissolved in toluene. NaCl was filtered off, and yellow crystals formed upon concentration of the toluene solution. The crystals were collected, washed with ether, and dried in vacuo; yield 124 mg (0.22 mmol, 84%). ^{1}H NMR (C_6D_6): δ 7.26 (d, 12, H_o and H_m), 6.90 (septet, 3, H_p), 3.55 (t, 6, CH_2), 2.15 (t, 6, CH_2), −0.08 (s, 9, $SiMe_3$). ^{13}C NMR (C_6D_6): δ 159.05 (C_{ipso}), 129.19 (C_m), 122.29 (C_o), 121.79 (C_p), 56.61 (CH_2), 53.28 (CH_2), 1.44 ($SiMe_3$). IR (cm^{-1}): 1643 (Nujol), 1663 (THF). Anal. Calcd for $C_{27}H_{36}N_6SiMo$: C, 57.03; H, 6.38; N, 14.78. Found: C, 57.12; H, 6.31; N, 14.70.

[FC$_6$H$_4$N$_3$N]Mo−N=N−SiMe$_3$ (5b). A solution of sodium naphthalenide (7.5 mL of a 0.17 M solution) was diluted to 20 mL with THF and cooled to −40 °C. A separate solution of [FC$_6$H$_4$N$_3$N]MoCl (278 mg, 0.5 mmol) in 10 mL of THF was prepared, cooled to −40 °C, and added dropwise to the naphthalenide solution, causing a color change from green to red. The reaction mixture was allowed to warm to room temperature with stirring for 30 min; then it was cooled to −40 °C and added slowly to a solution of Me_3SiCl (87 mg, 0.8 mmol) in THF (5 mL). The reaction mixture was allowed to warm to room temperature with stirring for 30 min; then the THF was removed in vacuo. The residue was extracted with ether and the extract was filtered. The dark yellow filtrate was concentrated to dryness in vacuo, and the resulting residue was washed with pentane and dried in vacuo; yield 175 mg (0.28 mmol, 56%). ^{1}H NMR (C_6D_6): δ 6.85−7.00 (m, 12, Ar), 3.40 (t, 6, CH_2), 2.11 (t, 6, CH_2), −0.17 (s, 9, $SiMe_3$). ^{13}C NMR (THF): δ 158.49 (d, C_p, J_{CF} = 239), 155.46 (d, C_{ipso}, J_{CF} = 2), 122.94 (d, C_o, J_{CF} = 7), 115.08 (d, C_m, J_{CF} = 21), 57.27 (CH_2), 53.69 (CH_2), 0.93 ($SiMe_3$). ^{19}F NMR (C_6D_6): δ −122.72 (7 lines). IR (cm^{-1}): 1674 (Nujol), 1657 (THF). Anal. Calcd for $C_{27}H_{33}F_3N_6SiMo$: C, 52.09; H, 5.34; N, 13.50. Found: C, 51.96; H, 5.27; N, 13.38.

[t-BuC$_6$H$_4$N$_3$N]Mo−N=N−SiMe$_3$ (5c). (a) From [t-BuC$_6$H$_4$N$_3$N]-MoCl. A solution of sodium naphthalenide in THF (5.0 mL of a 0.28 M solution, 1.4 mmol) was diluted to 20 mL and cooled to −35 °C. A separate solution of [t-BuC$_6$H$_4$N$_3$N]MoCl (376 mg, 0.56 mmol) in THF (10 mL) was also cooled to −35 °C. This solution was added dropwise to the sodium naphthalenide solution with vigorous stirring. The reaction mixture was allowed to warm to room temperature with stirring for 1 h; then it was cooled back down to −35 °C. A solution of Me_3SiCl (122 mg, 1.12 mmol) in THF (5 mL) was added dropwise. THF was removed in vacuo, and the residue was dissolved in toluene. NaCl was removed by filtration of the extract through Celite. Toluene was removed from the filtrate in vacuo, and the residue was washed with pentane to yield a yellow solid (185 mg, 45%), which was collected and dried in vacuo. Analytically pure material was obtained by recrystallization from a mixture of toluene and pentane. ^{1}H NMR (C_6D_6): δ 7.32 (s, 12, aryl), 3.63 (t, 6, CH_2), 2.20 (t, 6, CH_2), 1.29 (s, 27, t-Bu), −0.12 (s, 9, $SiMe_3$). ^{13}C NMR (C_6D_6/THF): δ 156.87 (C_{ipso}), 143.17 (C_p), 125.52 (C_m), 121.73 (C_o), 57.13 (CH_2), 53.80 (CH_2), 34.67 (t-Bu), 32.07 (t-Bu), 1.23 ($SiMe_3$). IR (cm^{-1}): 1738 (Nujol), 1651 (THF). Anal. Calcd for $C_{39}H_{60}N_6SiMo$: C, 63.56; H, 8.21; N, 11.40. Found: C 63.38; H, 8.16; N, 11.30.

(b) From 2c. A solution of **2c** (380 mg, 0.25 mmol) in THF (10 mL) was cooled to −35 °C. A separate solution of Me_3SiCl (82 mg, 0.75 mmol) in THF (1 mL) was also cooled to −35 °C and added dropwise to the solution of **2c**; the color changed immediately from purple to yellow. THF was removed in vacuo and the residue was dissolved in toluene. The solution was filtered through Celite, and the toluene filtrate was concentrated to 3 mL in vacuo. Pentane (10 mL) was added in order to complete the formation of yellow crystals. The red mother liquor was decanted away from the crystals, which were washed twice with pentane and dried in vacuo; yield 315 mg (0.427 mmol, 85%).

[t-BuC$_6$H$_4$N$_3$N]Mo-^{15}N=^{15}N−SiMe$_3$ (5c-15N). This material was prepared in a manner identical to that used to prepare unlabeled material starting from **2c**-^{15}N (68 mg, 0.045 mmol) and Me_3SiCl (13 mg, 0.12 mmol); yield 50 mg (0.068 mmol, 75%). ^{15}N NMR (C_6D_6/THF): δ 374.39 (d, N_α, J_{NN} = 13), 220.72 (d, N_β, J_{NN} = 13). ^{13}C NMR (C_6D_6/THF): δ 1.174 (d, ^{15}N−SiMe$_3$, ^2J(^{13}C,^{15}N) = 3.4). IR (cm^{-1}): 1679 (Nujol), 1615 (THF).

[Me$_2$C$_6$H$_3$N$_3$N]Mo−N=N−SiMe$_3$ (5d). (a) From [Me$_2$C$_6$H$_3$N$_3$N]-MoCl. A 0.42 M stock solution of sodium naphthalenide (4.0 mL, 1.68 mmol) in THF was diluted to 10 mL and cooled to −35 °C. [Me$_2$C$_6$H$_3$N$_3$N]MoCl (493 mg, 0.84 mmol) was added as a solid, and the reaction was allowed to warm to room temperature with stirring for 2 h. A solution of Me_3SiCl (200 mg, 1.84 mmol) in THF (2 mL) was then added to the plum colored solution resulting in a color change to dark yellow. After 15 min, the reaction mixture was filtered through Celite and the THF was removed in vacuo. The residue was washed with pentane to yield a yellow solid which was pure by NMR; yield 234 mg (0.36 mmol, 43%). Analytically pure yellow crystals were obtained by recrystallization from a mixture of toluene and pentane at −35 °C. ^{1}H NMR (C_6D_6): δ 7.02 (s, 6, ortho), 6.59 (s, 3, para), 3.65 (t, 6, CH_2), 2.29 (s, 18, 3,5-Me_2), 2.25 (t, 6, CH_2), −0.14 (s, 9, $SiMe_3$). ^{13}C NMR (THF): δ 158.67 (C_{ipso}), 136.57 (C_p), 122.29 (C_m), 120.10 (C_o), 56.61 (CH_2), 52.75 (CH_2), 20.84 (3,5-Me_2), −0.59 ($SiMe_3$). IR (cm^{-1}): 1722 (Nujol); 1657 (THF). Anal. Calcd for $C_{33}H_{48}N_6MoSi$: C, 60.72; H, 7.41; N, 12.87. Found: C, 60.59; H, 7.47; N, 12.97.

(b) From 2d. A solution of **2d** (81 mg, 0.060 mmol) in THF (6 mL) was cooled to −40 °C. A separate solution of Me_3SiCl (22 mg,

0.20 mmol) in THF (1 mL) was also cooled to −40 °C, and added to the reaction mixture. The color changed immediately from purple to yellow. THF was removed in vacuo, and the residue was dissolved in toluene. The extract was filtered, and the filtrate was stored at −40 °C. The crystals were collected, washed with ether, and dried in vacuo; yield 57 mg (0.087 mmol, 73%).

[$C_6F_5N_3N$]Mo−N═N−SiMe$_3$ (5e). Sodium amalgam (0.5%, 7 g, 1.5 mmol Na) was covered with THF. [$C_6F_5N_3N$]MoOTf (443 mg, 0.50 mmol) was added as a solid, and the reaction was stirred at room temperature for 3 h. The insoluble Mo triflate dissolved, and the color of the reaction turned red. The solution was decanted from the mercury, and the solvent was removed in vacuo. The residue was dissolved in ether, the ether solution was cooled to −40 °C, and a −40 °C solution of Me_3SiCl (68 mg, 0.625 mmol) in THF was added. The color turned orange immediately, but the reaction was allowed to warm to room temperature over a period of 30 min. Addition of a small amount of pentane led to precipitation of sodium salts as well as some black material, which was removed by filtration. The ether solution was then concentrated, and pentane was added. The solution was cooled to −40 °C to yield crystals (277 mg, 0.33 mmol, 67%). ^{1}H NMR (C_6D_6): δ 3.31 (t, 6, CH_2). 2.01 (t, 6, CH_2), −0.37 (s, 9, $SiMe_3$). ^{13}C NMR (THF): δ 142.67 (d, J_{CF} = 245.1), 138.44 (d, J_{CF} = 241.3), 137.52 (d, J_{CF} = 246.4), 132.65 (br s, ipso), 56.95 (CH_2), 53.81 (CH_2), −0.09 ($SiMe_3$). ^{19}F NMR (THF): δ −151.39 (d, 6, ortho), −166.93 (t, 6, meta), −167.58 (t, 3, para). IR (Nujol; cm^{-1}): 1672 (N═N).

[TerN$_3$N]Mo−N═N−SiMe$_3$ (5f). A solution of **4f**-DME (137 mg, 0.065 mmol) in THF (6 mL) was cooled to −40 °C. A separate solution of Me_3SiCl (26 mg, 0.24 mmol) in THF (1 mL) was cooled to −40 °C and then added to the reaction mixture; the color changed from red to yellow. NaCl was filtered off, and crystals formed in the filtrate during the process. The crystals were collected, washed with ether, and dried in vacuo; yield 115 mg (0.112 mmol, 86%). ^{1}H NMR (C_6D_6): δ 7.83 (t, 12, 3,5-ortho), 7.71 (s, 6, ortho), 7.61 (s, 3, para), 7.20 (t, 12, 3,5-meta), 7.13 (t, 6, 3,5-para), 3.68 (t, 6, CH_2), 2.30 (t, 6, CH_2), −0.36 (s, 9, $SiMe_3$). ^{13}C NMR (C_6D_6/THF): δ 159.90 (C_{ipso}), 142.79 (C_m), 142.70 (3,5-ipso), 129.04 (3,5-meta), 128.05 (3,5-ortho), 127.53 (3,5-para), 121.01(C_o), 119.52(C_p), 57.39 (CH_2), 53.68 (CH_2), 0.11 ($SiMe_3$). IR (cm^{-1}): 1646 (Nujol), 1645 (THF). Anal. Calcd for $C_{63}H_{60}N_6MoSi$: C, 73.81; H, 5.90; N, 8.20. Found: C, 73.94; H, 6.03; N, 8.11.

[(t-BuC$_6$H$_4$)$_2$C$_6$H$_3$N$_3$N]Mo−N═N−SiMe$_3$ (5g). A solution of [(t-BuC$_6$H$_4$)$_2$C$_6$H$_3$N$_3$N]MoCl (259 mg, 0.20 mmol) in THF (6 mL) was stirred over Mg powder (24 mg, 1.00 mmol) under dinitrogen overnight. The reaction mixture was cooled to −40 °C, and a solution of Me_3SiCl (26 mg, 0.24 mmol) in THF (1 mL) was added. After 30 min 1,4-dioxane (0.5 mL) was added. The reaction mixture was filtered through Celite and concentrated to dryness in vacuo. The residue was dissolved in ether and filtered again to remove more insoluble white powder. The ether was removed from the filtrate in vacuo, and the residue was washed with pentane. A pentane-insoluble orange solid was collected, washed with pentane, and dried in vacuo; yield 162 mg (0.119 mmol, 59%). Analytically pure material was obtained by recrystallization from a mixture of toluene and pentane. ^{1}H NMR (C_6D_6): δ 7.90 (d, 12, 3,5-ortho), 7.80 (s, 6, ortho), 7.75 (s, 3, para), 7.35 (d, 12, 3,5-meta), 3.72 (t, 6, CH_2), 2.30 (t, 6, CH_2), 1.27 (s, 54, t-Bu), −0.25 (s, 9, $SiMe_3$). ^{13}C NMR (THF): δ 159.79 (C_{ipso}), 150.27 (3,5-para), 142.54 (C_m), 140.09 (3,5-ipso), 127.87 (3,5-meta), 126.10 (3,5-ortho), 120.62 (C_o), 119.09 (C_p), 57.21 (CH_2), 53.37 (CH_2), 35.07 (t-Bu), 31.86 (t-Bu), 0.24 ($SiMe_3$). IR (cm^{-1}): 1642 (Nujol), 1648 (THF). Anal. Calcd for $C_{87}H_{108}N_6MoSi$: C, 76.73; H, 7.99; N, 6.17. Found: C, 76.48; H, 7.86; N, 6.08.

[PhN$_3$N]Mo−N═N-Me (6a). Solid methyl tosylate (56 mg, 0.3 mmol) was added to a solution of **2a** (177 mg, 0.15 mmol) in THF (12 mL). The reaction was stirred at room temperature for 6 h. (A solution IR study of an aliquot after 3 h suggested incomplete reaction). The THF was removed, and the residue was dissolved in toluene. Insoluble material was filtered off to yield a clear yellow solution. The solvent was removed in vacuo, and the residue was washed with ether to give 89 mg (0.174 mmol, 58%) of the product as a yellow powder. Analytically pure material was obtained by recrystallization from toluene. ^{1}H NMR (C_6D_6): δ 7.24 (t, 6, meta), 7.17 (d, 6, ortho), 6.88 (t, 3, para), 3.52 (t, 6, CH_2), 2.99 (s, 3, NCH_3), 2.18 (t, 6, CH_2). ^{13}C NMR (THF): δ 159.06 (C_{ipso}), 127.46 (C_m), 121.07 (C_o), 120.40 (C_p), 55.97 (CH_2), 53.27 (CH_2), 39.53 (NCH_3). IR (cm^{-1}): 1598 (Nujol), 1601 (THF). Anal. Calcd for $C_{25}H_{30}N_6Mo$: C, 58.82; H, 5.92; N, 16.46. Found: C, 58.75; H, 6.08; N, 16.55.

[FC$_6$H$_4$N$_3$N]Mo−N═N−Me (6b). This material was synthesized in a manner similar to that used to prepare **6a**, starting from **2b** (338 mg, 0.262 mmol) and methyl tosylate (97 mg, 0.52 mmol). Three hours were sufficient for complete reaction; yield 180 mg (0.319 mmol, 61%). ^{1}H NMR (C_6D_6): δ 6.98 (dd, 6, Ar), 6.87 (t, 6, Ar), 3.36 (t, 6, CH_2), 2.89 (s, 3, N-Me), 2.14 (t, 6, CH_2). ^{13}C NMR (THF): δ 157.76 (d, C_p, J_{CF} = 238), 155.35 (d, C_{ipso}, J_{CF} = 2), 121.98 (d, C_o, J_{CF} = 8), 113.78 (d, C_m, J_{CF} = 22), 56.35 (CH_2), 53.22 (CH_2), 39.54 (NCH_3). ^{19}F NMR (C_6D_6): δ −122.30 (7 lines). ^{19}F NMR (THF): δ −124.25 (7 lines). IR (cm^{-1}): 1581 (Nujol), 1582 (THF). Anal. Calcd for $C_{25}H_{27}F_3N_6Mo$: C, 53.20; H, 4.82; N, 14.89. Found: C, 53.31; H, 4.83; N, 14.96.

[t-BuC$_6$H$_4$N$_3$N]Mo−N═N−Me (6c). A 20 mL reaction vial was charged with **2c** (760 mg, 1.0 mmol), methyl tosylate (186 mg, 1.0 mmol), and THF (25 mL). The reaction was stirred at room temperature for 3 h during which time the color changed from violet to dark yellow. THF was removed in vacuo, and the residue was dissolved in toluene. The solution was filtered through Celite to remove NaOTs, and the toluene solution was concentrated to 5 mL. Addition of 15 mL of pentane resulted in the formation of yellow-green crystals. The burgundy colored mother liquor was decanted off, and the crystals were washed with pentane and dried in vacuo; yield 417 mg (0.61 mmol, 61%). ^{1}H NMR (C_6D_6): δ 7.27 (s, 12, aryl), 3.60 (t, 6, CH_2), 2.91 (s, 3, N-Me), 2.23 (t, 6, CH_2), 1.26 (s, 27, t-Bu). ^{13}C NMR (THF): δ 156.56 (C_{ipso}), 142.69 (C_p), 124.19 (C_m), 120.63 (C_o), 56.10 (CH_2), 53.04 (CH_2), 39.05 (NCH_3), 33.53 (t-Bu), 30.97 (t-Bu Me). IR (cm^{-1}):1585 (Nujol), 1579 (THF). Anal. Calcd for $C_{37}H_{54}N_6Mo$: C, 65.47; H, 8.02; N, 12.38. Found: C 65.59; H, 8.04; N, 12.27.

[t-BuC$_6$H$_4$N$_3$N]Mo−^{15}N═^{15}N−Me (6c-^{15}N). This material was prepared in amanner identical to that used to prepare unlabeled material starting from **2c**-^{15}N (103 mg, 0.068 mmol) and MeOTs (26 mg, 0.14 mmol); yield 53 mg (0.078 mmol, 57%). ^{1}H NMR (C_6D_6): δ 2.908 (dd, ^{15}N−CH$_3$, $^2J_{H,^{15}N}$ = 3, $^3J_{H,^{15}N}$ = 0.6). ^{15}N NMR (C_6D_6/THF): δ 407.02 (d, N$_\alpha$, J_{NN} = 16), 231.94 (d, N$_\beta$, J_{NN} = 16). ^{13}C NMR (C_6D_6/THF): δ 40.188 (dd, ^{15}N−CH$_3$, $^1J_{^{13}C,^{15}N}$ = 8.8, $^2J_{^{13}C,^{15}N}$ = 4.5). IR (Nujol; cm^{-1}): 1542.

[Me$_2$C$_6$H$_3$N$_3$N]Mo−N═N−Me (6d). This material was synthesized in a manner similar to that used to prepare **6a**, starting from **2d** (236 mg, 0.175 mmol) and methyl tosylate (65 mg, 0.35 mmol). Three hours were sufficient for complete reaction; yield 78 mg (0.13 mmol, 37%). ^{1}H NMR (C_6D_6): δ 7.01 (s, 6, ortho), 6.57 (s, 6, para), 3.64 (t, 6, CH_2), 3.11 (s, 6, N-Me), 2.28 (t, 6, CH_2), 2.23 (s, 18, 3,5-Me_2). ^{13}C NMR (C_6D_6): δ 159.50 (C_{ipso}), 137.28 (C_p), 123.61 (C_m), 120.13 (C_o), 56.33 (CH_2), 53.36 (CH_2), 40.57 (NCH_3), 21.66 (3,5-Me_2). IR (cm^{-1}): 1603 (Nujol), 1602 (THF). Anal. Calcd for $C_{31}H_{42}N_6Mo$: C, 62.61; H, 7.12; N, 14.13. Found: C, 62.48; H, 7.19; N, 14.02.

[TerN$_3$N]Mo−N═N-Me (6f). A 20 mL reaction vial was charged with **4f**-DME (316 mg, 0.15 mmol), methyl tosylate (56 mg, 0.30 mmol), and THF (6 mL). The reaction mixture was stirred for 4 h, during which time the color lightened from dark burgundy to yellow. 1,4-Dioxane (0.5 mL) was added. The white precipitate was filtered off, and THF was removed from the filtrate in vacuo. The residue was washed three times with ether, and dried in vacuo; yield 200 mg (0.207 mmol, 69%). Analytically pure material was obtained by recrystallization from toluene. ^{1}H NMR (C_6D_6): δ 7.77 (d, 12, 3,5-ortho), 7.67 (s, 6, ortho), 7.57 (s, 3, para), 7.20 (t, 12, 3,5-meta), 7.13 (t, 3, 3,5-para), 3.66 (t, 6, CH_2), 2.83 (s, 3, N-Me), 2.36 (t, 6, CH_2). ^{13}C NMR (THF): δ 159.36 (C_{ipso}), 141.77 (C_m), 141.61 (3,5-ipso), 128.25 (3,5-meta), 127.07 (3,5-ortho), 126.59 (3,5-para), 119.35 (C_o), 118.62 (C_p), 56.30 (CH_2), 52.83 (CH_2), 38.79 (NCH_3). IR (cm^{-1}):1596 (Nujol), 1596 (THF). Anal. Calcd for $C_{61}H_{54}N_6Mo$: C, 75.76; H, 5.63; N, 8.69. Found: C, 75.58; H, 5.68; N, 8.59.

{[t-BuC$_6$H$_4$N$_3$N]Mo═N−NMe$_2$}OTs (7). Solid methyl tosylate (67 mg, 0.36 mmol) was added to a solution of **6c** (204 mg, 0.3 mmol) in THF (10 mL). No immediate color change was observed. The ^{1}H NMR spectrum of an aliquot taken after 2 h indicated 50% conversion to product. Another 25 mg (0.05 mmol, 17 equiv) of MeOTs were added, and the reaction was stirred for 36 h. Proton NMR indicated the reaction

to be 93% complete. THF was removed in vacuo, and the residue was dissolved in ether. The ether solution was filtered through Celite. Pentane was added to the filtrate, and the mixture was stored at −35 °C for several weeks to yield 167 mg of purple crystals of product (0.193 mmol, 64%). ^{1}H NMR (C_6D_6): δ 8.24 (d, 2, Ts), 7.25 (d, 6, Ar), 7.22 (d, 6, Ar), 6.96 (d, 2, Ts), 3.94 (t, 6, CH_2), 2.90 (t, 6, CH_2), 2.45 (s, 6, NMe_2), 2.02 (s, 3, Ts Me), 1.22 (s, 27, t-Bu). ^{13}C NMR (C_6D_6): δ 156.97 (C_{ipso}), 145.44 (C_p), 138.54 (Ts), 128.76 (Ts), 128.35 (Ts), 127.25 (Ts), 125.52 (C_o), 121.98 (C_m), 59.02 (CH_2), 55.88 (CH_2), 41.72 (NCH_3), 34.26 (t-Bu), 31.72 (t-Bu Me), 21.24 (Ts Me). Anal. Calcd for $C_{45}H_{64}N_6O_3SMo$: C, 62.48; H, 7.46; N, 9.72. Found: C, 62.52; H, 7.40; N, 9.64.

{[$FC_6H_4N_3N$]Mo═N−NMe_2}OTf (8b). (a) From 6b. This material was synthesized in a manner similar to that used to prepare **7**, starting from **6b** (153 mg, 0.271 mmol) and methyl triflate (51 mg, 0.31 mmol); yield 160 mg (0.22 mmol, 81%). ^{1}H NMR ($CDCl_3$): δ 7.08 (dd, 6, Ar), 6.98 (t, 6, Ar), 4.22 (t, 6, CH_2), 3.64 (t, 6, CH_2), 2.24 (s, 6, N-Me_2). ^{13}C NMR (CH_2Cl_2): δ 160.21 (d, C_p, J_{CF} = 244), 154.31 (d, C_{ipso}, J_{CF} = 3), 124.57 (d, C_o, J_{CF} = 8), 115.68 (d, C_m, J_{CF} = 22), 60.80 (CH_2), 54.61 (CH_2), 41.17 (NCH_3). ^{19}F NMR ($CDCl_3$): δ −77.97 (OTf), −116.71 (7 lines). Anal. Calcd for $C_{27}H_{30}F_6N_6O_3SMo$: C, 44.51; H, 4.15; N, 11.54. Found: C, 44.46; H, 4.21; N, 11.46.

(b) From 9b. An orange solution of **9b** (100 mg, 0.131 mmol) in CH_2Cl_2 (6 mL) was cooled to −35 °C. A separate solution of methyl triflate (43 mg, 0.262 mmol) in 2 mL of CH_2Cl_2 was cooled to −35 °C and added slowly to the reaction mixture. No color change was observed. ^{1}H and ^{19}F NMR spectra of an aliquot taken after 1 h indicated 25% conversion to product. An additional 60 mg of methyl triflate was added, and the reaction was allowed to stir overnight. NMR spectra taken at this time indicate complete consumption of starting material. The solvent was removed in vacuo, and the residue was extracted with a 1:1 mixture of THF and toluene. The insoluble orange powder was washed with toluene and pentane, and dried in vacuo; yield 40 mg (0.055 mmol, 42%).

{[t-Bu$C_6H_4N_3N$]Mo═N−NMe_2}OTf (8c). (a) From 5c. A solution of **5c** (315 mg, 0.426 mmol) in 12 mL of toluene was cooled to −35 °C. A separate solution of methyl triflate (197 mg, 1.2 mmol) in 3 mL of toluene was cooled to −35 °C and added dropwise to the solution of **5c**, resulting in an immediate color change from yellow to orange. The reaction was allowed to warm to room temperature over a period of 10 h. The volume was reduced to 1 mL in vacuo, and pentane was added. The orange crystals were collected, washed with ether, and dried in vacuo; yield 222 mg (0.263 mmol, 62%). ^{1}H NMR (C_6D_6): δ 7.21 (s, 12, aryl), 4.10 (t, 6, CH_2), 3.40 (t, 6, CH_2), 1.85 (s, 6, N-Me), 1.19 (s, 27, t-Bu). ^{1}H NMR ($CDCl_3$): δ 7.29 (d, 6, meta), 6.98 (d, 6, ortho), 4.24 (t, 6, CH_2), 3.67 (t, 6, CH_2), 2.10 (s, 3, N-Me), 1.27 (s, 27, t-Bu). ^{13}C NMR (THF): δ 156.00 (C_{ipso}), 147.35 (C_p), 125.27 (C_o), 122.37 (C_m), 60.01 (CH_2), 54.21 (CH_2), 40.12 (NCH_3), 33.95 (t-Bu), 30.82 (t-Bu Me). ^{19}F NMR (C_6D_6): δ −77.85. Anal. Calcd for $C_{39}H_{57}F_3N_6O_3SMo$: C, 55.57; H, 6.82; N, 9.97. Found: C, 55.41; H, 6.70; N, 9.88.

(b) From 6c. The procedure was identical starting with **6c** (271 mg, 0.4 mmol), and MeOTf (72 mg, 0.44 mmol); yield 320 mg (0.38 mmol, 95%).

{[t-Bu$C_6H_4N_3N$]Mo═N−N(CH_3)($^{13}CH_3$)}OTf (8c-^{13}C). This material was synthesized in a manner identical to that used to prepare unlabeled **8c** starting from **6c** (82 mg, 0.12 mmol), and $^{13}CH_3OTf$ (23 mg, 0.14 mmol); yield 88 mg (0.104 mmol, 87%).

{[t-Bu$C_6H_4N_3N$]Mo═^{15}N−^{15}NMe_2}OTf (8c-^{15}N). This material was synthesized in a manner identical to that used to prepare unlabeled **8c** starting from **6c**-^{15}N (40 mg, 0.058 mmol) and CH_3OTf (16 mg, 0.097 mmol); yield 49 mg (0.058 mmol, 100%):.^{15}N NMR (C_6D_6/THF): δ 368.27 (d, N_α, J_{NN} = 11), 154.40 (d, N_β, J_{NN} = 11). ^{13}C NMR (C_6D_6/THF): δ 41.04 (d, ^{15}N−CH_3, $^1J_{^{13}C,^{15}N}$ = 9.2).

{[$C_6F_5N_3N$]Mo═N−NMe_2}OTf (8e). Methyl triflate (1.28 g, 7.80 mmol) was added to a solution of **5e** (2.18 g, 2.60 mmol) in 40 mL of toluene. The reaction was heated to 45 °C overnight, during which time a yellow precipitate formed. The precipitate was collected, washed with ether to remove unreacted starting material and dried in vacuo; yield 2.36 g (2.50 mmol, 96%). ^{1}H NMR (CD_2Cl_2): δ 4.24 (t, 6, CH_2), 3.80 (t, 6, CH_2), 2.68 (s, 6, NCH_3). ^{13}C NMR (CH_2Cl_2): δ 143.16, 141.29, 139.57, 137.53 (aryl), 131.69 (ipso), 60.88 (CH_2), 54.74 (CH_2), 41.44 (NCH_3). ^{19}F NMR (CH_2Cl_2): δ −79.07 (s, triflate), −148.92 (d, 6, ortho), −157.13 (t, 3, para), −161.59 (t, 6, meta). Anal. Calcd for $C_{27}H_{18}F_{18}N_6O_3SMo$: C, 34.34; H, 1.92; N, 8.90. Found: C, 34.48. H, 2.05; N, 8.83.

{[$FC_6H_4N_3N$]Mo═N−N(Me)($SiMe_3$)}OTf(toluene)$_{0.5}$ (9b). A solution of **5b** (441 mg, 0.71 mmol) in toluene (10 mL) was cooled to −35 °C. A separate solution of methyl triflate (328 mg, 2.0 mmol) in toluene was cooled to −35 °C and added slowly to the reaction mixture. The color changed from yellow to orange and an orange powder precipitated before addition of the methyl triflate was complete. No further changes were observed over a period of 1 h. The toluene was decanted away from the product, which was washed with toluene and pentane and dried in vacuo; yield 555 mg (0.705 mmol, 99%). ^{1}H NMR ($CDCl_3$): δ 7.11 (dd, 6, Ar), 6.99 (t, 6, Ar), 4.23 (t, 6, CH_2), 3.62 (t, 6, CH_2), 2.04 (s, 3, N-Me), −0.38 (s, 9, $SiMe_3$). ^{13}C NMR (CH_2Cl_2): δ 160.30 (d, C_p, J_{CF} = 244), 154.26 (s, C_{ipso}), 125.20 (d, C_o, J_{CF} = 8), 115.85 (d, C_m, J_{CF} = 23), 61.31 (CH_2), 54.15 (CH_2), 36.35 (NCH_3), −2.72 ($SiMe_3$). ^{19}F NMR ($CDCl_3$): δ −77.97 (OTf), −116.81 (7 lines). Anal. Calcd for $C_{32}H_{40}F_6N_6O_3SSiMo$: C, 46.49; H, 4.88; N, 10.16. Found: C, 46.15; H, 4.71; N, 9.79.

[$FC_6H_4N_3N$]Mo≡N (10b). Solid sodium azide (52 mg, 0.8 mmol) was added to a solution of [$FC_6H_4N_3N$]MoCl (297 mg, 0.533 mmol) in THF (8 mL). The reaction was stirred for 2 days, during which time the color changed from orange to green. The reaction was filtered through Celite in order to remove NaCl. The THF was removed in vacuo and the residue was washed with ether. The red ether-soluble material was washed away to leave a yellow solid; yield 162 mg (0.303 mmol, 57%). Analytically pure material was obtained by recrystallization from toluene. ^{1}H NMR (C_6D_6): δ 7.38 (dd, 6, Ar), 6.80 (t, 6, Ar), 3.25 (t, 6, CH_2), 2.07 (t, 6, CH_2). ^{13}C NMR (THF): δ 158.76 (d, C_p, J_{CF} = 239), 157.08 (s, C_{ipso}), 121.20 (d, C_o, J_{CF} = 8), 113.70 (d, C_m, J_{CF} = 22), 56.32 (CH_2), 50.49 (CH_2). ^{19}F NMR (C_6D_6): δ −122.16 (7 lines). Anal. Calcd for $C_{24}H_{24}F_3N_5Mo$: C, 53.84; H, 4.52; N, 13.08. Found: C, 53.91; H, 4.40; N, 12.95.

[t-Bu$C_6H_4N_3N$]Mo≡N (10c). Solid sodium azide (49 mg, 0.75 mmol) was added to a solution of [t-Bu$C_6H_4N_3N$]MoCl (335 mg, 0.5 mmol) in THF (8 mL). The reaction was stirred for 2 days. The green reaction mixture was filtered through Celite. The THF was removed in vacuo, and the residue was washed with ether to give a yellow solid; yield 188 mg (0.29 mmol, 58%). Analytically pure material was obtained by recrystallization from a mixture of toluene and pentane. ^{1}H NMR (C_6D_6): δ 7.63 (d, 6, meta), 7.16 (d, 6, ortho), 3.50 (t, 6, CH_2), 2.16 (t, 6, CH_2), 1.24 (s, 27, t-Bu). ^{13}C NMR (C_6D_6): δ 159.22 (C_{ipso}), 145.50 (C_p), 125.53 (C_o), 121.02 (C_m), 56.61 (CH_2), 51.33 (CH_2), 34.71 (t-Bu), 32.23 (t-Bu Me). Anal. Calcd for $C_{36}H_{51}N_5Mo$: C, 66.55; H, 7.91; N, 10.78. Found: C 66.64; H, 7.85; N, 10.62.

[t-Bu$C_6H_4N_3N$]Mo(Me)$NNMe_2$ (11c). Solid **8c** (146 mg, 0.173 mmol) was suspended in 5 mL of ether, and the solution was cooled to −35 °C. An aliquot of MeMgBr (55 μL of a 3.0 M solution in ether, 0.165 mmol) was diluted to 1 mL, and the solution was added dropwise to the stirred reaction mixture to give a midnight blue solution. Addition of 1,4-dioxane (0.5 mL) resulted in the precipitation of a white powder, which was removed by filtration through Celite. The ether was removed in vacuo, and the residue was washed once with pentane. The product was soluble enough in pentane to turn the pentane dark blue, but the majority of the material did not dissolve. The pentane solution was removed by pipet, and the remaining material was dried in vacuo; yield 105 mg (0.148 mmol, 86%). ^{1}H NMR (C_6D_6): δ 7.27 (d, 4, Ar), 7.18 (d, 2, Ar), 7.10 (d, 4, Ar), 6.96 (d, 2, Ar), 3.84 (dd, 2, backbone), 3.63 (6 lines, 2, backbone), 3.38 (t, 2, backbone), 3.12 (6 lines, 2, backbone), 2.57 (s, 6, NMe_2), 2.54 (t, 2, backbone), 2.33 (dd, 2, backbone), 1.29 (s, 18, t-Bu), 1.22 (s, 9, t-Bu), 0.60 (s, 3, MoMe). ^{13}C NMR (THF): δ 156.68 (C_{ipso}), 155.82 (C_{ipso}), 140.59 (C_p), 138.27 (C_p), 124.14 (C_m), 124.03 (C_m), 117.98 (C_o), 117.39 (C_o), 62.65 (CH_2), 60.59 (CH_2), 57.83 (CH_2), 54.30 (CH_2), 41.77 (NCH_3), 33.58 (t-Bu), 33.47 (t-Bu), 31.08 (t-Bu Me), 31.01 (t-Bu Me), 16.48 (Mo−CH_3). Anal. Calcd for $C_{39}H_{60}N_6Mo$: C, 66.08; H, 8.53; N, 11.86. Found: C, 65.93; H, 8.40; N, 11.92.

[t-Bu$C_6H_4N_3N$]Mo($^{13}CH_3$)$NNMe_2$ (11c-^{13}C(M)). This material was prepared in a manner analogous to that used to prepare unlabeled material starting from **8c** (72 mg, 0.085 mmol) and $^{13}CH_3MgI$ (0.05

mL, 1.7 M in ether, 0.085 mmol). The crude product was subjected to thermolysis. ^{1}H NMR (C_6D_6): δ 0.59 (d, Mo^{13}CH$_3$, J_{CH} = 121). ^{13}C NMR (C_6D_6): δ 18.03 (Mo^{13}CH$_3$).

[t-BuC$_6$H$_4$N$_3$N]Mo(Me)NN(CH$_3$)(^{13}CH$_3$) (11c-^{13}C(N)). This material was prepared in a manner analogous to that used to prepare unlabeled material starting from **8c**-^{13}C (50 mg, 0.059 mmol) and CH$_3$MgBr (0.02 mL, 3.0 M in ether, 0.060 mmol). The crude product was subjected to thermolysis. ^{1}H NMR (C_6D_6): δ 2.566 (d, N^{13}CH$_3$, $^1J_{CH}$ = 139), 2.568 (d, NCH$_3$, $^3J_{CH}$ = 3). ^{13}C NMR (C_6D_6): δ 43.35 (N^{13}CH$_3$).

Thermolysis of 11c. A 20 mg sample of **11c** was dissolved in C_6D_6. The sample was transferred to an NMR tube which was flame sealed, and the tube was heated in an oil bath. Decomposition of **11c** required 2 days at 90 °C. Resonances in the NMR spectra of the final products matched those of **10**.

[C$_6$F$_5$N$_3$N]Mo(Me)NNMe$_2$ (11e). This material was prepared in a manner similar to that used to prepare **11c** starting from **8e** (368 mg, 0.39 mmol), and MeMgBr (0.13 mL of a 3.0 M solution in ether, 0.39 mmol). This compound is burgundy in color and completely insoluble in pentane, so the final pentane washings were colorless; yield 250 mg (0.308 mmol, 79%). ^{1}H NMR (toluene-d_8, −20 °C) :δ 3.98 (m, 2), 3.56 (m, 4), 2.98 (m, 2), 2.62 (m, 2), 2.17 (m, 2), 2.13 (s, 6, N−CH$_3$), 0.18 (s, 3, Mo−CH$_3$). ^{13}C NMR (toluene-d_8): δ 143.15 (d, J_{CF} = 243), 142.80 (d, C$_p$, J_{CF} = 244), 138.63 (d, J_{CF} = 249), 135.09 (br s, C$_{ipso}$), 62.97 (CH$_2$), 61.73 (CH$_2$), 60.78 (CH$_2$), 57.88 (CH$_2$), 39.77 (N−CH$_3$), 27.42 (Mo−CH$_3$). Anal. Calcd for $C_{27}H_{21}F_{15}N_6Mo$: C, 40.02; H, 2.61; N, 10.37. Found: C, 39.92; H, 2.65; N, 10.28.

[C$_6$F$_5$N$_3$N]Mo(^{13}CH$_3$)NNMe$_2$ (11e-^{13}C). This material was prepared in a manner analogous to that used to prepare unlabeled material starting from **8e** (80 mg, 0.085 mmol) and ^{13}CH$_3$MgI (0.05 mL, 1.7 M in ether, 0.085 mmol). The crude material was subjected to thermolysis. ^{1}H NMR (C_6D_6): δ 0.29 (d, Mo^{13}CH$_3$, J_{CH} = 124). ^{13}C NMR (C_6D_6): δ 27.35 (Mo^{13}CH$_3$).

Thermolysis of 11e. A 20 mg sample of **11e** was dissolved in C_6D_6, toluene-d_8, or THF. The sample was transferred to an NMR tube which was flame sealed, and the tube was heated in an oil bath. Decomposition of **11e** was complete after 24 h at 60 °C. Resonances in the NMR spectra of the final products matched those of **10**.

[t-BuC$_6$H$_4$N$_3$N]W−N═N−W[t-BuC$_6$H$_4$N$_3$N] (12). A solution of [t-BuC$_6$H$_4$N$_3$N]WCl (1.26 g, 1.66 mmol) in THF (10 mL) was cooled to −40 °C. A 0.33 M stock solution of sodium naphthalenide (6.00 mL, 1.98 mmol) in THF was diluted to 20 mL, and the solution was cooled to −40 °C. The two solutions were added simultaneously to a 100 mL flask containing THF (10 mL), which was being vigorously stirred. The reaction mixture was stirred for 2 h as it was allowed to warm to room temperature. It was filtered through Celite to remove NaCl. The solvent was removed from the filtrate in vacuo, and the residue was washed with pentane (to remove naphthalene), followed by ether (to remove dark red impurities). The resulting dark pink solid was collected and dried in vacuo; yield 755 mg (0.51 mmol, 62%). Analytically pure material was obtained by recrystallization from a mixture of THF and pentane. ^{1}H NMR (C_6D_6): δ 12.22 (d, 6, meta), 3.05 (s, 27, t-Bu), 2.63 (d, 6, ortho), −11.05 (br s, 6, CH$_2$), −16 (br, 6, CH$_2$). Anal. Calcd for $C_{72}H_{102}N_{10}W_2$: C, 58.62; H, 6.97; N, 9.49. Found: C, 58.54; H, 7.08; N, 9.38.

{[t-BuC$_6$H$_4$N$_3$N]W−N═N−W[t-BuC$_6$H$_4$N$_3$N]}(BPh$_4$)$_2$ (13). A solution of **12** (148 mg, 0.1 mmol) was dissolved in CH_2Cl_2, and the solution was cooled to −35 °C. Cp_2FeBPh_4 (101 mg, 0.2 mmol) was added as a solid, and the reaction mixture was allowed to warm to room temperature while being stirred over a period of 45 min. All of the ferrocenium salt dissolved, and the color of the reaction turned black. The reaction mixture was filtered through Celite. The solvent was removed from the filtrate in vacuo, and the oily residue was washed with pentane (to produce a solid), toluene (to remove any unreacted **12**), and pentane again (to remove toluene). The sample was dried in vacuo to yield 180 mg (0.085 mmol, 85%) of a black powder. Analytically pure material was obtained by recrystallization from a mixture of dichloromethane and toluene at −35 °C. ^{1}H NMR (CD_2Cl_2): δ 7.36 (br s, 16, BPh$_4$ ortho), 7.01 (t, 16, BPh$_4$ meta), 6.96 (d, 12, H$_m$), 6.85 (t, 8, BPh$_4$ para), 6.15 (d, 12, H$_o$), 4.18 (t, 12, CH$_2$), 2.84 (t, 12, CH$_2$), 1.20 (s, 54, t-Bu). ^{13}C NMR (CH_2Cl_2): δ 163.92 (q, BPh$_4$ ipso, J_{BC} = 49), 154.30 (C$_{ipso}$), 150.09 (C$_p$), 135.95 (BPh$_4$ meta), 126.44 (C$_m$), 125.80 (BPh$_4$ ortho), 122.00 (BPh$_4$ para), 121.38 (C$_o$), 61.68 (CH$_2$), 53.26 (CH$_2$), 34.49 (t-Bu), 31.33 (t-Bu). Anal. Calcd for $C_{120}H_{142}N_{10}B_2W_2$: C, 68.19; H, 6.77; N, 6.63. Found: C, 68.26; H, 6.84; N, 6.49.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **1c**, **2a**, **3c**, and **4f**. Figures showing the CV's of [Me$_2$C$_6$H$_3$N$_3$N]Mo−N═N−Na(THF)$_x$ (**2d**), [PhN$_3$N]Mo−N═N−Na(THF)$_x$ (**2a**), {[t-BuC$_6$H$_4$N$_3$N]W−N═N−W[t-BuC$_6$H$_4$N$_3$N]}(BPh$_4$)$_2$ (**13**), {[FC$_6$H$_4$N$_3$N]Mo═N−NMe$_2$}OTf (**8b**), {[t-BuC$_6$H$_4$N$_3$N]Mo═N−NMe$_2$}OTf (**8c**), and {[C$_6$F$_5$N$_3$N]Mo═N−NMe$_2$}OTf (**8e**). This material is available free of charge via the Internet at http://pubs.acs.org.

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