Redox-Catalyzed Binding of Dinitrogen by Molybdenum *N-tert*-Hydrocarbylanilide Complexes: Implications for Dinitrogen Functionalization and Reductive Cleavage

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Abstract: The splitting of dinitrogen (1 atm, THF, 25 °C) by $Mo(N[R]Ar)_3$ (R = $C(CD_3)_2CH_3$, Ar = 3,5-$C_6H_3Me_2$) giving 2 equiv of nitride $N\equiv Mo(N[R]Ar)_3$ is found to be accelerated in the presence of sodium amalgam. Careful control of the $Mo(N[R]Ar)_3$ concentration led to the isolation and characterization of the anionic dinitrogen complex, $[(THF)_xNa][(N_2)Mo(N[R]Ar)_3]$, where x is from 0 to 3. Via electrochemical experiments and synthetic studies, $[(THF)_xNa][(N_2)Mo(N[R]Ar)_3]$ is found to be a key intermediate in the acceleration of N_2 splitting by $Mo(N[R]Ar)_3$ in the presence of sodium amalgam. Accordingly, in the presence of an electron acceptor, $[(THF)_xNa][(N_2)Mo(N[R]Ar)_3]$ reacts with $Mo(N[R]Ar)_3$ to give the neutral N_2-bridged complex $(\mu\text{-}N_2)\{Mo(N[R]Ar)_3\}_2$, which in turn splits to 2 equiv of nitride $N\equiv Mo(N[R]Ar)_3$. It is seen that the function of sodium amalgam in this system is as a redox catalyst, accelerating the conversion of $Mo(N[R]Ar)_3$ to $(\mu\text{-}N_2)\{Mo(N[R]Ar)_3\}_2$, a dinuclear dinitrogen complex that does not lose N_2 readily. Electrochemical or chemical outer-sphere oxidation of $[(THF)_xNa][(N_2)Mo(N[R]Ar)_3]$ leads to rapid N_2 evolution with regeneration of $Mo(N[R]Ar)_3$, presumably via the neutral mononuclear dinitrogen complex $(N_2)Mo(N[R]Ar)_3$. In situ generated $[(THF)_xNa][(N_2)Mo(N[R]Ar)_3]$ was efficiently trapped by $ClSiMe_3$ to give $(Me_3SiNN)Mo(N[R]Ar)_3$. This complex underwent reaction with methyl triflate to give the dimethyl hydrazido cationic species, $[(Me_2NN)Mo(N[R]Ar)_3][OTf]$. The synthesis of the monomethyl complex $(MeNN)Mo(N[R]Ar)_3$ also was achieved. Experiments designed to trap the neutral mononuclear dinitrogen complex $(N_2)Mo(N[R]Ar)_3$ gave rise to efficient syntheses of heterodinuclear dinitrogen complexes including $(Ph[^tBu]N)_3Ti(\mu\text{-}N_2)Mo(N[R]Ar)_3$, which also was synthesized in its $^{15}N_2$-labeled form. Synthesis and characterization data for the new *N*-adamantyl-substituted three-coordinate molybdenum(III) complex $Mo(N[Ad]Ar)_3$ (Ad = 1-adamantyl, Ar = 3,5-$C_6H_3Me_2$) are presented. The complex is found to react with dinitrogen (1 atm, THF, 25 °C) in the presence of sodium amalgam to give the dinitrogen anion complex $[(THF)_xNa][(N_2)Mo(N[Ad]Ar)_3]$; the synthesis does not require careful regulation of the $Mo(N[Ad]Ar)_3$ concentration. Indeed, under no conditions has $Mo(N[Ad]Ar)_3$ been observed to split dinitrogen or to give rise to a dinuclear $\mu\text{-}N_2$ complex; this striking contrast with the reactivity of $Mo(N[R]Ar)_3$ (R = $C(CD_3)_2CH_3$) is attributed to the enhanced steric protection at Mo afforded by the 1-adamantyl substituents.

Introduction

It has been reported that the three-coordinate molybdenum-(III) complex $Mo(N[R]Ar)_3$ (**1**, R = $C(CD_3)_2CH_3$, Ar = 3,5-$C_6H_3Me_2$) effects the six-electron reductive cleavage of dinitrogen (Figure 1),[1−3] thus providing a homogeneous-solution analogue to the proposed rate-determining step in the Haber−Bosch ammonia synthesis.[4−6] The splitting of N_2 by niobium calixarene complexes also has been documented,[7] and atomic scandium has been shown to split N_2 to give scandium(III) nitride via a putative dinuclear intermediate.[8]

A key intermediate in the binding and splitting of dinitrogen by **1** is the dinuclear complex $(\mu\text{-}N_2)\{Mo(N[R]Ar)_3\}_2$ (**3**), which is formed during a slow (~76 h) incubation period at −35 °C (1 atm N_2, OEt_2 or toluene).[2] The dimolybdenum dinitrogen complex **3** then converts to 2 equiv of the terminal nitrido derivative $N\equiv Mo(N[R]Ar)_3$ (**4**) with a first-order kinetic profile, a fragmentation reaction constituting the final step in the splitting of dinitrogen by **1**. Although the fragmentation of **3** to 2 equiv of **4** is facile at 28 °C and above, the reaction is slow at −35 °C. The kinetic profile of the steps in Figure 1 has facilitated the study of the properties of dinuclear **3** and its conversion to **1**. These reactions also have been the subject of theoretical scrutiny.[9−11]

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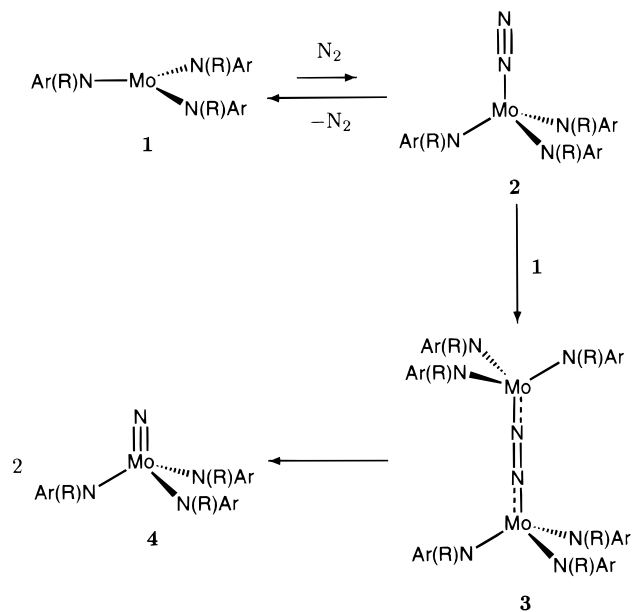(11) Hahn, J.; Landis, C. R.; Nasluzov, V. A.; Neyman, K. M.; Rösch, N. *Inorg. Chem.* **1997**, *36*, 3947.

Figure 1. Reaction of Mo(N[R]Ar)$_3$ (**1**) with dinitrogen in the absence of added reagents. Reaction conditions for complete conversion of **1** to **3**: 1 atm of N$_2$, Et$_2$O or toluene, −35 °C, ∼72 h. At 25 °C under otherwise identical conditions, consumption of **1** is negligible over ∼24 h. Conversion of **3** to **4** at 25 °C occurs with $t_{1/2} \approx 30$ min.

Since the slow step in the binding and splitting of dinitrogen by **1** appears to be the formation of dinuclear **3**,[2] it was of interest to see whether the binding of N$_2$ could be accelerated by some means. In this regard, the reaction of **1** with N$_2$ in the presence of reducing equivalents has been examined both chemically and electrochemically.

A further point of interest is whether the formation of a dinuclear dinitrogen complex such as **3** could be avoided entirely, to give rise to a manifold of chemistry in which the N$_2$ to Mo ratio would be 1:1. Such a manifold of chemistry might be fruitful in terms of obtaining complexes of functionalized N$_2$-derived ligands. This particular goal has been achieved straightforwardly through the use of more sterically demanding (adamantyl-substituted[12,13]) ligands, and less-straightforwardly via careful control of reaction conditions.

The results described in this paper bear on both of the preceding points, namely (i) the acceleration of N$_2$ splitting by **1** as a consequence of accelerated N$_2$ uptake in the presence of reducing agents and (ii) diversion of the N$_2$ chemistry of **1** into a manifold where N$_2$ functionalization is possible and where the N$_2$ to Mo ratio is 1:1.

Of course, the new N$_2$ coordination chemistry described here is complementary to work from the groups of Floriani,[7,14−16] Fryzuk,[17−20] Gambarotta,[21−25] Schrock,[26−29] Scott,[30−34] and

others who study dinitrogen chemistry involving metal complexes supported by hard π-donor ligands.[35] Alternative synthetic approaches to nitrogen fixation, including those involving organophosphine-stabilized systems, have been reviewed.[36−39]

Results and Discussion

(1) Reaction of Mo(N[R]Ar)$_3$ with Dinitrogen in the Presence of Sodium Amalgam. Stirring THF solutions of **1** over stoichiometric Na/Hg under a dinitrogen atmosphere resulted in a rapid transformation at 25 °C (Figure 2). Initially displaying the bright orange color of **1**, such solutions acquired the intense purple of intermediate **3** within 1 h. ^{2}H NMR spectroscopy revealed that a steady consumption of orange **1** coincided with the formation of the neutral dinuclear complex **3**. A new, sharper peak at 1.5 ppm, indicative of a diamagnetic species, also was observed.

An FTIR spectrum of this solution featured an intense ν_{NN} vibration at 1761 cm^{-1}. Other stretches appearing in this spectrum are typical of complexes bearing the N(R)Ar ligand.[2,40,41] The most prominent are those at 1596 and 1583 cm^{-1} arising from aryl ν_{CC} vibrations.

As the reaction mixture was stirred over a period of several hours, the intense purple color gradually diminished, and the final solution acquired a red-brown color. ^{2}H NMR spectroscopy of the crude product mixture revealed complete consumption of both the starting material **1** and intermediate **3**. A ^{1}H NMR spectrum of said mixture indicated that nitride **4** had formed in 85% yield. Approximately 10% of a new diamagnetic product also was present, displaying a single set of anilido ligand resonances along with resonances for solvated THF. A solution FTIR spectrum of this mixture still showed the presence of ν_{NN} at 1761 cm^{-1}, its intensity diminished relative to data acquired at earlier reaction times. In part on the basis of the literature precedent provided by Schrock and co-workers,[27,42,43] we assign the new diamagnetic product as the sodium salt of the anionic dinitrogen complex [(THF)$_x$Na][(N$_2$)Mo(N[R]Ar)$_3$] (**5**). These observations are depicted in Figure 2.

The product ratio of neutral **4** to salt **5** produced in the reaction system of Figure 2 was found critically to be dependent

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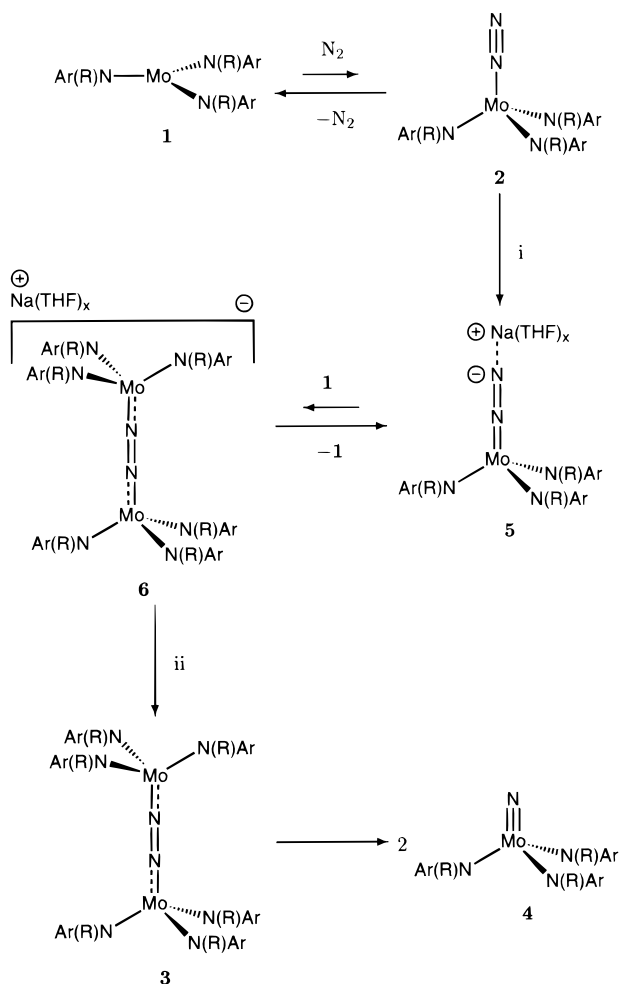
Figure 2. Reaction of **1** with dinitrogen (1 atm, 28 °C, THF solvent) in the presence of sodium amalgam. (i) Na/Hg or **6** generated *in situ*; (ii) compound **2** or possibly Hg. Note that intermediates **6** and **2** are not observed. Conditions can be optimized for isolation of either **5** or **4** (see text).

upon factors including (i) the rate of stirring, (ii) the concentration of **1**, and (iii) the quantity of Na/Hg employed.

Experiments resulting in virtually quantitative formation of nitride **4** were those in which compound **1** was added all at once to 1 equiv of Na/Hg in THF with moderate stirring. On the other hand, slow addition of **1** to an excess of Na/Hg in THF with rapid stirring gave rise to good yields of the anionic N_2 complex **5**.

The reaction scheme of Figure 2 accounts for the observation that high concentrations of **1** lead via reaction of **1** with **5** (in the presence of an oxidant) to good yields of nitride **4**. On the other hand, slow addition of **1** in the presence of an excess of Na/Hg minimizes the pathway for conversion of **5** to **3**, thereby affording a route to good yields of dinitrogen complex **5**. Rapid stirring presumably increases the rate at which N_2 is taken up. Thus, the scheme of Figure 2 provides a tunable product distribution via careful control of the reaction conditions.

To this point our discussion of the reactions in Figure 2 has focused on experiments carried out at ~28 °C under 1 atm of dinitrogen. Our attention now turns to control experiments carried out under argon.

(2) Treatment of Mo(N[R]Ar)₃ with Sodium Amalgam under Argon. Compound **1** was found to be stable to excess sodium amalgam under an argon atmosphere. Less than 5% decay of **1** was observed in THF over a period of 24 h at 25 °C

when stirred over 0.4% Na/Hg. This amount of decay was indistinguishable from that observed in the absence of Na/Hg under otherwise identical conditions.

The lack of reactivity between **1** and sodium amalgam in the absence of N_2, as well as the electrochemical stability of **1** at potentials as low as -2.8 V in THF (vide infra), precludes direct reduction of **1** to its corresponding anion under the conditions of Figure 2. Rather, the unobserved neutral dinitrogen complex **2** is implicated as the electron-accepting species.

In a full paper, which included electrochemical data, Floriani and co-workers reported recently that the anionic d^3 species $[(THF)V(Mes)_3]^-$ (Mes = 2,4,6-Me₃C₆H₂) binds N_2 readily.[15]

(3) Synthesis and Characterization of $[(THF)_xNa][(N_2)Mo(N[R]Ar)_3]$ (5). The clean isolation of **5** relied upon circumventing a subsequent bimolecular reaction between **1** and **5**. In a typical synthetic run, a dilute solution of **1** was added dropwise, very slowly, to a vigorously stirred mixture of Na/Hg in THF under a dinitrogen atmosphere. The rate of addition was determined empirically by an array of attempts until conditions were found in which the intense purple color of the undesired bridged species **3** was no longer noticeable throughout the addition. A 10-h dropwise addition of **1** to a stirring amalgam under N_2 reproducibly converted ~0.01 mmol of **1** to **5** in good isolated yield (e.g., 69%). Syringe pump addition of a THF solution of **1** to the Na/Hg mixture at 25 °C under 1 atm N_2 was found to be optimal.

A ^{1}H NMR spectrum of the crude product mixture showed that **5** formed in ~96% yield under the above conditions with only trace impurities of nitride **4** and the free ligand HN(R)Ar. Consistent with earlier observations, pure **5** showed an intense ν_{NN} at 1761 cm^{-1} in THF. Dinitrogen complex $[(THF)_xNa][(N_2)Mo(N[R]Ar)_3]$ was scarlet in the presence of donor solvents such as THF and OEt₂. Upon trituration, pentane solutions of **5** acquired an orange color and the THF was effectively removed. Recrystallization from pentane afforded the stable, solvent-free derivative $[(THF)_xNa][(N_2)Mo(N[R]Ar)_3]$ (**5**; $x = 0$) in 69% yield. The latter species is likely to be dimeric in nature.[41,44]

(4) Synthesis and Structure of $[Na(12-crown-4)_2][(N_2)Mo(N[R]Ar)_3]$ (7). Solvent-free $[(THF)_xNa][(N_2)Mo(N[R]Ar)_3]$ (**5**; $x = 0$) was moderately soluble in pentane but precipitated upon addition of 2 equiv of 12-crown-4. An intense violet solid was easily isolated, which was insoluble in pentane, benzene, and OEt₂, reflecting its distinctly ionic nature, formulated as $[Na(12-crown-4)_2][(N_2)Mo(N[R]Ar)_3]$ (**7**). Complex **7** was solubilized by tetrahydrofuran, and a single crystal suitable for an X-ray diffraction study was obtained by storing a THF/pentane solution at -35 °C. The solid-state structure confirmed assignment of **7** as the salt $[Na(12-crown-4)_2][(N_2)Mo(N[R]Ar)_3]$.

A thermal ellipsoid representation of **7** is given in Figure 3. The complex, displaying a terminally bound dinitrogen ligand, adopts the expected geometry in which the dinitrogen ligand resides on the pseudo-C_3 axis of the Mo(N[R]Ar)₃ template and is centered within the C_3 propeller of the ^{t}Bu substituents. The N(4)−N(5) bond distance of 1.171(14) Å seems to be shorter than that found in (Ph[^{t}Bu]N)₃Ti(μ-N₂)Mo(N[R]Ar)₃ (**14**, d_{NN} = 1.229(4) Å, vide infra) but the difference is not statistically significant. This may reflect a greater degree of N_2 reduction in **14**, further manifested by the respective ν_{NN} stretching frequencies for the two complexes: 1761 cm^{-1} for **7** vs 1575 cm^{-1} for **14**.

(5) Ferrocenium Oxidation of $[(THF)_xNa][(N_2)Mo(N[R]Ar)_3]$ (5). With the key compound $[(THF)_xNa][(N_2)Mo(N[R]-Ar)_3]$

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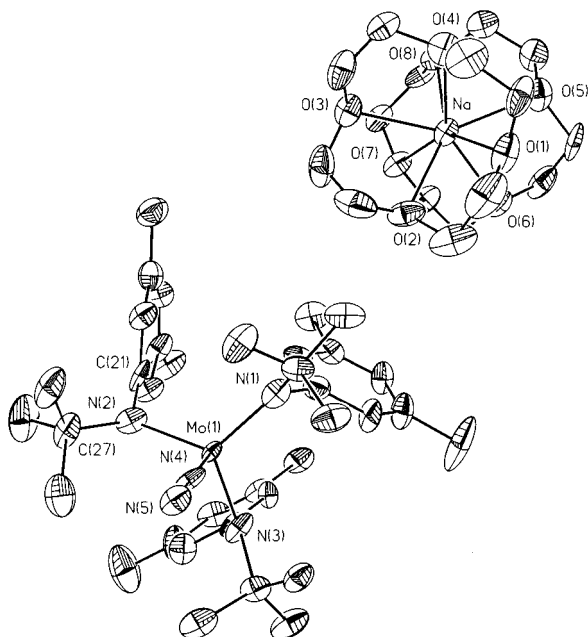
Figure 3. Structural drawing of **7** with ellipsoids at the 35% probability level. Selected bond distances (Å) and angles (deg): Mo(1)−N(1), 1.994(12); Mo(1)−N(2), 2.016(11); Mo(1)−N(3), 1.999(11); Mo(1)−N(4), 1.840(11); N(4)−N(5), 1.171(14); N(4)−Mo(1)−N(3), 98.8(4); N(4)−Mo(1)−N(1), 97.1(5); N(4)−Mo−N(2), 96.7(4); N(3)−Mo(1)−N(2), 118.8(5); N(3)−Mo(1)−N(1), 116.5(5); N(1)−Mo(1)−N(2), 119.6(5).

Ar)$_3$] (**5**) in hand, it was possible to access the neutral N_2 complex **2** from the other side of the proposed equilibrium for N_2 binding (Figure 1). Ferrocenium triflate[45] ([Cp$_2$Fe][OTf]) was selected as an appropriate one-electron oxidant. Fast addition of a scarlet solution of **5** to an intense blue THF solution of [Cp$_2$Fe][OTf] effected the rapid oxidation of **5**.

Effervescence was observed upon mixing, indicating dissociation of the coordinated dinitrogen ligand. FTIR spectra of the crude mixture acquired just after mixing showed that the intense ν_{NN} band of **5** at 1761 cm^{-1} had completely decayed to baseline. No stretches were observed that might have corresponded to the neutral dinitrogen complex **2** in question. A ^{2}H NMR spectrum of the crude mixture corroborated this by showing that Mo(N[R]Ar)$_3$ had been generated cleanly and quantitatively by the chemical oxidation. The oxidation proceeded analogously when carried out at −35 °C. It is apparent that **5** spontaneously and rapidly loses dinitrogen upon chemical oxidation and that neutral **2** is not a chemically isolable species.

Interestingly, O'Donoghue and Schrock reported that oxidation of the related complex {[(Me$_3$SiNCH$_2$CH$_2$)$_3$N]Mo(N$_2$)}$_2$-Mg(THF)$_2$ gave a moderately stable dinitrogen adduct [(Me$_3$-SiNCH$_2$CH$_2$)$_3$N]Mo(N$_2$).[26,27] This complex was structurally characterized and formulated as a low-spin neutral dinitrogen complex of molybdenum(III). Apparently, the apical donor atom, provided by the triamidoamine ligand and absent in our trisamido system, provides just enough electron density at the metal center to make the N$_2$ adduct of the [(Me$_3$SiNCH$_2$CH$_2$)$_3$N]-Mo core stable.[9] Electrochemical experiments comparing the two systems suggest that the trianionic (Me$_3$SiNCH$_2$CH$_2$)$_3$N ancillary ligand set is appreciably more reducing than the trisanilido ligand set employed here. For example, the reduction potential of N≡Mo(N[R]Ar)$_3$ (**4**) was found to be −2.7 V, whereas the reduction potential for the related complex [[Me$_3$-
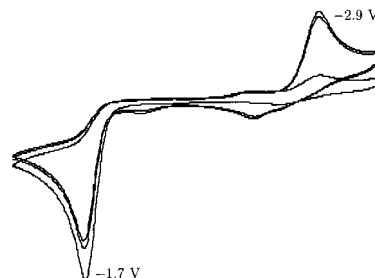
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Figure 4. Cyclic voltammogram of **5** in THF with [N(*n*-Bu)$_4$][PF$_6$] electrolyte. Potentials indicated are vs ferrocene/ferrocenium. See text for assignments.

SiNCH$_2$CH$_2$)$_3$N]Mo≡N was measured to be −2.9 V (THF, [N(*n*-Bu)$_4$][PF$_6$], vs ferrocene/ferrocenium).

(6) Electrochemistry of Mo(N[R]Ar)$_3$ (1) and [(THF)$_x$Na]-[(N$_2$)Mo(N[R]Ar)$_3$] (5). The inherent instability of neutral (N$_2$)-Mo(N[R]Ar)$_3$ (**2**) prompted us to utilize another technique for its study. Due to the inherent redox nature of the Na/Hg-facilitated N$_2$ cleavage reaction, an electrochemical study was deemed appropriate.

Cyclic voltammetry of a THF solution of [(THF)$_x$Na][(N$_2$)-Mo(N[R]Ar)$_3$] (**5**; see Figure 4) revealed a distinct oxidation wave at −1.7 V. No return wave was observable at scan rates ranging from 0.1 to 10 V/s, indicating that the oxidation product was unstable and had decayed completely before the scan was reversed. This irreversible process is assigned to the oxidation of the anionic component of [(THF)$_x$Na][(N$_2$)Mo(N[R]Ar)$_3$] (**5**) to generate neutral (N$_2$)Mo(N[R]Ar)$_3$ (**2**). The latter quickly decays through loss of N$_2$ to afford Mo(N[R]Ar)$_3$ (**1**). On the basis of this result, the $t_{1/2}$ for neutral **2** appears to be less than 1 s.

A reduction wave was observed at −2.9 V. Through successive scans it was found that the wave at −1.7 V gradually decayed while the wave at −2.9 V increased, confirming that the latter belongs to the decomposition product of **2**, namely **1**. Independent electrochemical study of a solution of **1** corroborated the assignment of the −2.9-V wave. A further noteworthy feature of the −2.9-V wave is that it was found to be irreversible. The latter observation is suggestive of fast uptake of N$_2$ (or, indeed, some other chemical process) by a highly reactive reduced molybdenum(II) species "[Mo(N[R]Ar)$_3$]$^-$".

Exhaustive electrolysis of a solution of **1** confirmed that the final product, under a dinitrogen atmosphere, contained the anionic component of **5**. When a potential of −3.0 V was maintained for extensive periods, the solution color changed from the bright orange of **1** to the scarlet of **5**. At this point, the current had reached a plateau and 1 equiv of electrons (based on **1**) had passed through the cell. The electrochemical response confirmed the presence of the anionic component of **5**. As expected, returning this solution to a potential of −1.3 V reverted the process, oxidizing **5** and regenerating the orange solution of **1**. Thus, the electrochemistry of **1** and **5** dramatically illustrates the redox chemistry outlined in Figure 2.

Fruitless attempts have been made to prepare synthetically a reduced trisanilido molybdenum species "[Mo(N[R]Ar)$_3$]$^-$" in the absence of N$_2$ using solid sodium as the reductant. An important subtlety of the chemistry described here is that **1** is not itself reduced by 0.5% Na/Hg. Electrochemically, **1** is reduced at −2.9 V, at which point it picks up dinitrogen. When subjected to less reducing conditions (0.5% Na/Hg can be estimated at ~−2.4 V vs ferrocene/ferrocenium in THF), the data indicate that **5** is formed by reduction of **2**, the potential for which is a mere −1.7 V.

(7) Reaction of Mo(N[R]Ar)₃ (1) with [(THF)ₓNa][(N₂)-Mo(N[R]Ar)₃] (5). The foregoing results establish that dinitrogen cleavage is dramatically accelerated at ambient temperatures by the presence of 0.5% Na/Hg. It is presumed (Figure 2) that salt **5** reacts directly with **1** in solution to generate dinuclear **3**, with the aid of an oxidant. With the key compound **5** having been isolated, this model became subject to direct testing.

Mixing stoichiometic amounts of **1** and **5** in THF under a dinitrogen atmosphere at 25 °C resulted in a steady buildup of intense purple **3** within 1 h (²H NMR). IR spectroscopy confirmed that a significant amount of **5** was present throughout the course of the reaction.

Analysis of the final reaction products by ¹H NMR spectroscopy after 14 h showed a mixture of N≡Mo(N[R]Ar)₃ and **5** in an approximate 2:1 ratio. Inclusion of an internal integration standard indicated that ∼90% of the starting materials were accounted for by ¹H NMR spectroscopy. Additionally, a small amount of free ligand, HN(R)Ar, was observed. Notably, the reaction proceeded in similar fashion even when carried out in the presence of added mercury.

The described reactions demonstrate clearly that **5** reacts readily with Mo(N[R]Ar)₃, (**1**), to generate (μ-N₂){Mo(N[R]-Ar)₃}₂ (**3**), en route to the irreversible formation of N≡Mo-(N[R]Ar)₃ (**4**). This is as depicted in Figure 2. Hence, reactions in which the redox catalyst [(THF)ₓNa][(N₂)Mo(N[R]Ar)₃] (**5**) is formed in the presence of **1** are expected to generate the nitride product **4**.

(8) Effect of Other Reducing Agents. In our efforts to explore the diverse reaction chemistry of Mo(N[R]Ar)₃, several one-electron reductants, in addition to Na/Hg, have been observed to facilitate the dinitrogen cleavage reaction. A particularly clean instance of this occurred upon interaction of sodium triethylborohydride (superhydride) with **1** under N₂.

When a homogeneous THF solution of Mo(N[R]Ar)₃ and an excess of superhydride were stirred under an atmosphere of dinitrogen at 25 °C, nitride **4** was formed quantitatively over a period of 24 h. ¹H NMR and IR spectroscopies of the final crude mixture showed neither [(THF)ₓNa][(N₂)Mo(N[R]Ar)₃] (**5**) nor any free HN(R)Ar ligand. As was the case for the Na/Hg-facilitated cleavage reaction, the intense purple of the N₂-bridged intermediate **3** was observed during the course of the reaction. The purple color dissipated gradually over 24 h, consistent with its decay to N≡Mo(N[R]Ar)₃.

Undoubtedly, a plethora of reaction pathways may be postulated to account for formation of the observed nitride product in the superhydride-mediated reaction. To date, no intermediates have been observed.

(9) Attempted Synthesis of [(THF)ₓNa][(μ-N₂){Mo(N[R]-Ar)₃}₂] (6). A salt such as [(THF)ₓNa][(μ-N₂){Mo(N[R]Ar)₃}₂] (**6**) as invoked in Figure 2, seemed a likely intermediate in the generation of (μ-N₂){Mo(N[R]Ar)₃}₂ from the bimolecular reaction between **1** and **5**. It was therefore of interest to discover whether a dinitrogen-free THF mixture of **5** and Mo(N[R]Ar)₃ would contain detectable concentrations of **6**.

To address this question, rigorously degassed THF was vacuum transferred into an NMR tube containing stoichiometric amounts (as solids) of **5** and **1**. ²H NMR spectra acquired after mixing showed no evidence for the presence of **6**. Both starting materials, **5** and **1**, were observed, in addition to a small amount (<10%) of the neutral bridged complex (μ-N₂){Mo(N[R]Ar)₃}₂. A similar experiment carried out with the crown-containing salt **7** and Mo(N[R]Ar)₃ likewise did not show signals indicative of formation of an N₂-bridged dimolybdenum anion.
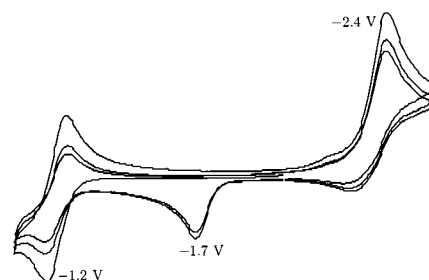

Figure 5. Cyclic voltammogram of **3** in THF with [N(*n*-Bu)₄][PF₆] electrolyte. Potentials indicated are vs ferrocene/ferrocenium. See text for assignments.

Though its intermediacy remains likely, [(THF)ₓNa][(μ-N₂)-{Mo(N[R]Ar)₃}₂] (**6**) does not appear to be an isolable or observable complex, at least under the reaction conditions of the redox-facilitated cleavage reaction. Thus, it may be concluded that **6** dissociates readily to **1** and **5** in the absence of a (N₂)Mo(N[R]Ar)₃ oxidant (Figure 2). As described below, the electrochemical data support this notion.

(10) Electrochemistry of (μ-N₂){Mo(N[R]Ar)₃}₂ (3). In the cyclic voltammogram of a freshly prepared THF solution of (μ-N₂){Mo(N[R]Ar)₃}₂ (**3**) (see Figure 5), a cathodic wave at −2.4 V is clearly in evidence. It was not possible to detect the corresponding anodic wave at scan rates between 0.1 and 10 V/s. However, a new anodic peak was detected at −1.7 V concomitant with the irreversible reduction process at −2.4 V. The peak at −1.7 V also displayed a lack of reversibility and is readily assigned to oxidation of the dinitrogen complex anion **5**, an oxidation that we have already analyzed chemically (section 5). Repetitive reductive scans effected a decrease in the magnitude of the wave at −2.4 V and a corresponding increase in the wave at −1.7 V.

Thus may be assigned the cathodic wave at −2.4 V to the reductive conversion of **3** to its corresponding unstable anion, the same N₂-bridged dimolybdenum anion considered above (**6**, section 9). Consistent with the chemical instability of dinuclear anion **6**, the species was unstable on the electrochemical time scale, splitting apart into the mononuclear anionic component of **5** along with neutral Mo(N[R]Ar)₃ (**1**).

Dinitrogen anion **5** was indeed detected at −1.7 V subsequent to a sequence of reductive scans. On the basis of its independent electrochemical investigation described above (section 6), we know that **1** itself is not electroactive through the potential window under consideration here. When more positive anodic potentials were investigated, a reversible wave at −1.2 V was detected. The intensity of the latter wave decreased along with consumption of **3**, as judged by decay of the peak at −2.4 V. Thus we assign the −1.2-V anodic wave to the electrochemically reversible conversion of **3** to its corresponding monocation, an entity that has not yet been subjected to attempted synthesis and characterization.

(11) Observation of Intermetal N₂⁻ Transfer. Having been unable directly to observe [(THF)ₓNa][(μ-N₂){Mo(N[R]Ar)₃}₂] (**6**; sections 9 and 10) it was desirable to secure further indirect evidence for its proposed intermediacy in the reaction scheme of Figure 2.

Because the deuterated anilide ligand N(R)Ar (R = C(CD₃)₂-CH₃, Ar = 3,5-C₆H₃Me₂) can be prepared readily in its natural-isotopic-abundance form, e.g., N(ᵗBu)Ar, it was possible to do a crossover experiment.

²H NMR spectroscopy showed clearly that Mo(N[R]Ar)₃ (**1**) was generated upon mixing a THF solution of stoichiometric Mo(N[ᵗBu]Ar)₃ and **5** under vacuum (Figure 6). Integration of
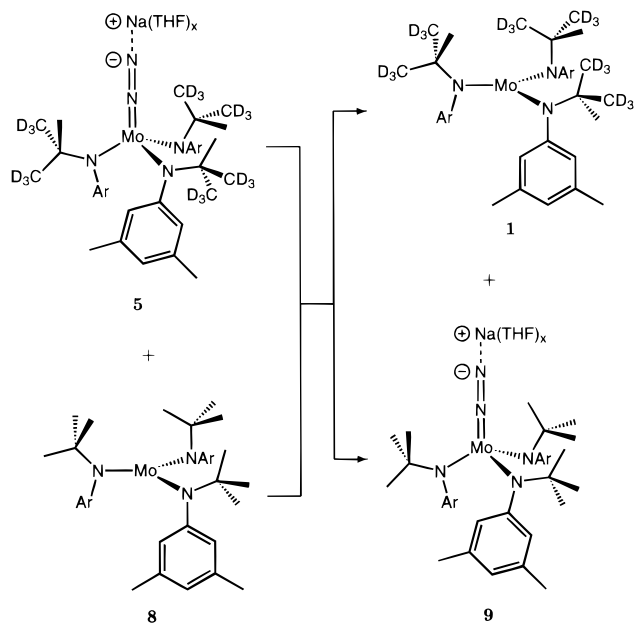
Figure 6. Reaction in THF and in the absence of N_2 of Mo(N[ᵗBu]-Ar)₃ with [(THF)$_x$Na][(N₂)Mo(N[R]Ar)₃]. The reaction constitutes an example of degenerate [N₂]⁻ transfer. Detection of progress in the forward direction is by ²H NMR spectroscopy.

the ²H NMR signals for the respective N(R)Ar ligands revealed that ∼38.5% of the deuterium-labeled **5** was converted to deuterium-labeled **1**.

In accord with the above observation, ¹H NMR spectroscopy confirmed that [(THF)$_x$Na][(N₂)Mo(N[ᵗBu]Ar)₃] (**9**) also was generated. Control experiments have shown that **5** is stable for days in THF at 25 °C with no appreciable decomposition to three-coordinate **1**. Hence, transfer of the dinitrogen ligand from **5** to Mo(N[ᵗBu]Ar)₃ (**8**) is best explained by the intermediate formation of an anionic N₂-bridged species, [(Ar[*t*-Bu]N)₃Mo-(μ-N₂)Mo(N[R]Ar)₃]⁻, identical to **6** but for the consideration of deuterium substitution.

Despite repeated attempts to generate an ideal 1:1 mixture of **5** and **9**, the ²H NMR spectra of such solutions typically showed that a small amount of dinuclear **3** (∼7%) had been generated. As mentioned above (section 7), this was also observed when **5** was mixed with **1**.

Note that the result summarized by Figure 6 constitutes an example of intermetal dinitrogen monoanion (N₂⁻) transfer. A conceivable extension of this type of reaction is to systems for the cooperative reduction of N₂ by two different metal complexes or to catalytic systems in which the transfer of N₂⁻ provides a means for regenerating **1**. The transfer of N₂⁻ from one metal complex to another is reminiscent of intermetal nitrogen atom-transfer reactions, a class of reactions that have undergone intense scrutiny in recent years.[46−55]

(12) A Titanium/Molybdenum Heterodinuclear Dinitrogen Complex. In effect, the new chemistry of Figure 2 represents

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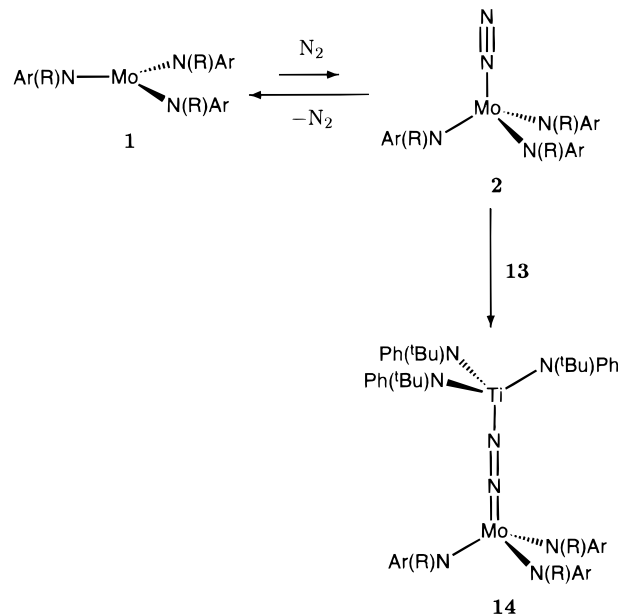

Figure 7. Reaction of **1** with Ti(N[ᵗBu]Ph)₃ (**13**) to give the molybdenum/titanium μ-dinitrogen complex **14**. The high-yield formation of **14** (25 °C, 1 atm N₂, 4 h) suggests that **13** is a far more efficient trap of putative **2** than is **1** itself. The data do not, however, rule out initial binding of N₂ by **13**.

the consequences of the interception of **2** by the reducing agent, sodium amalgam. Now, it seemed likely that reducing agents other than sodium amalgam might also be capable of intercepting **2**. A sterically demanding titanium(III)-based reducing agent we have studied in the past is the complex Ti(N[ᵗBu]Ph)₃ (**13**).[56] In this section is described the cooperative binding of N₂ by **1** and **13**.

A 1:1 mixture of **1** and **13**[56] were stirred in OEt₂ under a dinitrogen atmosphere at 25 °C, giving initially an olive-green solution which gradually lightened in color. Over the course of a 15-h period, a deep-orange solid determined to be (Ph[ᵗ-Bu]N)₃Ti(μ-N₂)Mo(N[R]Ar)₃ (**14**) precipitated and was isolated in 81% yield (Figure 7).

Complex **14** was found to be robust both in solution and in the solid state, as expected given the π⁸ electronic configuration for this system. The designation π⁸ refers to the fact that in C₃$_v$ symmetry the π molecular orbitals for the linear Mo−N−N−Ti moiety occur as four increasingly energetic doubly degenerate levels, which in the Ti/Mo case are populated with eight electrons. The corresponding dimolybdenum complex **3** carries a corresponding π¹⁰ designation, accounting for its paramagnetism and (in part) its propensity to split to 2 equiv of **4**. Other examples of stable π⁸ systems are the linear nitrosyl complex (ON)Mo(N[R]Ar)₃,[57] the isoelectronic Mo−N₂ anion in **5**, and the terminal phosphorus monoxide complex (OP)Mo(N[R]-Ar)₃.[58] Note that 2 equiv of **4** together constitutes a π⁸ system. A further interesting way to think about these systems is to note that, while d³ **1** can be regarded as isolobal with a quartet-state nitrogen atom, the π⁸ systems are isolobal with N₂O, azide ion, and CO₂. The very stable terminal nitride **4** is isolobal with dinitrogen itself.

¹H NMR spectroscopy supports our formulation for **14**, it being the case that two inequivalent ligand environments are

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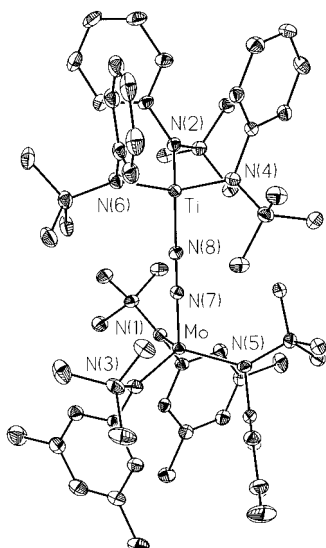(58) Johnson, M. J. A.; Odom, A. L.; Cummins, C. C. *Chem. Commun.* **1997**, 1523.

Figure 8. A 35% thermal ellipsoid representation of (Ph[^{t}Bu]N)$_3$Ti-(μ-N$_2$)Mo(N[R]Ar)$_3$, **14**, from X-ray coordinates. Selected distances (Å) and angles (deg): Mo−N(7), 1.787(3); Ti−N(8), 1.880(3); N(7)−N(8), 1.229(4); Mo−N(1), 1.969(3); Mo−N(3), 1.971(3); Mo−N(5), 1.963(3); Ti−N(2), 1.956(3); Ti−N(4), 1.951(3); Ti−N(6), 1.954(3); N(7)−Mo-N(1), 102.59(13); N(7)−Mo−N(3), 103.17(13); N(7)-Mo−N(5), 104.03(13); N(5)−Mo−N(1), 113.23(13); N(5)−Mo−N(3), 115.22(13); N(1)−Mo−N(3), 116.25(13). N(8)−Ti−N(6), 109.87(87); N(8)−Ti−N(2), 111.11(13); N(8)−Ti−N(4), 109.98(13); N(4)−Ti−N(6), 109.09(13); N(4)−Ti−N(2), 108.80(13); N(6)−Ti−N(2), 107.93-(13).

in evidence in a 1:1 ratio. Broad resonances observed at room temperature for the ortho protons of the 3,5-C$_6$H$_3$Me$_2$ residues of **14** are taken to be a reflection of the gearing effect involving the six ^{t}Bu groups inhibiting rapid interconversion of two degenerate C_{3v} enantiomers.[55] Along these lines, note that low-temperature ^{1}H NMR spectra of X-M(N[R]Ar)$_3$ complexes are consistent with C_3 symmetry,[55] with three aryl resonances observed in a 1:1:1 ratio for the Ar substituents. The two resonances for the ortho protons coalesce to a single signal upon warming. Indeed, in the case of **14**, the broad ortho signals sharpened upon warming.

An FTIR spectrum of **14** confirmed the presence of the bridging dinitrogen ligand with a ν_{NN} at 1575 cm^{-1}, to be compared with the 1630-cm^{-1} ν_{NN} observed by Raman spectroscopy for **3**.[2] Because this region of the spectrum is complicated by the presence of rather intense anilido ν_{CC} vibrations, a ^{15}N$_2$-labeled derivative **15**, (Ph[^{t}Bu]N)$_3$Ti(μ-^{15}N$_2$)-Mo(N[R]Ar)$_3$, was prepared. A shift in ν_{NN} from 1575 to 1524 cm^{-1} was consistent with the simple harmonic oscillator model (calculated 1522 cm^{-1}). The ^{15}N NMR spectrum of **15** showed doublets at 437.15 and 433.09 ppm relative to liquid ammonia (0 ppm) with a $^1J_{NN}$ of 12.6 Hz. These shifts can be compared with the large downfield ^{15}N NMR shifts found for terminal nitrido derivatives of chromium[59] and molybdenum.[54]

Heterodinuclear **14** was crystallized from pentane, and single crystals suitable for an X-ray diffraction study were obtained from a pentane solution stored at −35 °C. A thermal ellipsoid representation of **14** is presented in Figure 8. The complex displays a dinitrogen ligand suspended linearly between the Mo and Ti centers. Both metal centers adopt a pseudotetrahedral geometry, and the N$_2$ ligand rests in the aliphatic pocket provided by the six *tert*-butyl groups. The *tert*-butyl groups all

are directed proximal to the N$_2$ molecule, a typical conformational motif for X−M(N[R]Ar)$_3$ complexes.[3] The ligands adopt a moderately staggered disposition, with an average N−Ti−Mo−N dihedral angle of ∼18°. The Mo−N(7) bond length of 1.787(3) Å is indicative of substantial π bonding to the dinitrogen ligand by the Mo(N[R]Ar)$_3$ portion of the complex. This distance is significantly shorter than the Mo−N bonding distances to the anilido ligands (average 1.968 Å). The Ti−N(8) distance of 1.880(3) Å suggests a lesser degree of π bonding between the Ti(N[^{t}Bu]Ph)$_3$ fragment and the N$_2$ ligand, but this distance nonetheless is appreciably shorter than the average Ti−N$_{anilide}$ distance of 1.954 Å. The N(8)−N(7) bond length of 1.229(4) Å reflects an appreciable degree of cooperative dinitrogen reduction by the respective trisanilido molybdenum and titanium fragments. By way of comparison, the N−N distance in **3** is ∼1.20 Å, a distance identified with an N−N bond order of 2.

In an important control experiment, the trisanilido complexes **13** and **1** were found not to react with each other when stirred in OEt$_2$ at 25 °C in the absence of dinitrogen (1 atm of argon). While it is known that low-valent N-donor-stabilized complexes of titanium can exhibit dinitrogen chemistry,[60,61] studies of the solution chemistry of **13**[56] and related Ti(N[R]Ar)$_3$[40] have not revealed any independent propensity for reactivity with dinitrogen. Similarly, dinitrogen chemistry was not reported for Wolczanski's siloxide Ti(OSi^{t}Bu$_3$)$_3$.[62−64] Taken collectively, these results indicate that the formation of **14** (Figure 7) results from the capture of (N$_2$)Mo(N[R]Ar)$_3$ (**2**) by reactive Ti(N[^{t}-Bu]Ph)$_3$ (**13**). Like the reductant sodium amalgam, **13** efficiently intercepts **2** at 25 °C on a time scale much faster than formation (Figure 1) of the dimolybdenum N$_2$ complex **3**.

(13) Synthesis and Structure of (Me$_3$SiNN)Mo(N[R]Ar)$_3$ (12). The synthesis of **12** was accomplished by trapping the in situ generated anionic dinitrogen complex with the electrophile chlorotrimethylsilane. The optimized procedure involved addition of complex **1** to a THF solution of ClSiMe$_3$ while stirring over sodium amalgam under dinitrogen (1 atm; see Figure 9). Allowing the reaction to proceed for 2 h prior to filtration led to the best results. Silyldiazenido complex **12** is readily obtained in pure form upon crystallization from pentane solution. An alternative approach to the synthesis of (Me$_3$SiNN)Mo(N[R]-Ar)$_3$ was found to involve the addition of equimolar amounts of **5** and ClSiMe$_3$ to a vessel containing ether.

Infrared spectra (THF, KBr) of **12** showed a signature band at 1650 cm^{-1} for the ν_{NN} vibration of the N$_2$ ligand.

X-ray diffraction studies were carried out using a single crystal of silyldiazenido **12** grown from a chilled pentane solution. A thermal ellipsoid representation of **12** is presented in Figure 10. The complex displays a dinitrogen ligand suspended between the Mo and Si centers. The Mo−N(4) bond length of 1.753(2) Å is indicative of substantial π bonding to the dinitrogen ligand by the Mo(N[R]Ar)$_3$ fragment. This distance is significantly shorter than the Mo−N bonding distances to the anilido ligands (average 1.970 Å). The N(4)−N(5) bond length of 1.221(3) Å reflects an appreciable degree of dinitrogen reduction relative to free dinitrogen and taken together with the observed ν_{NN} frequency indicates an N−N

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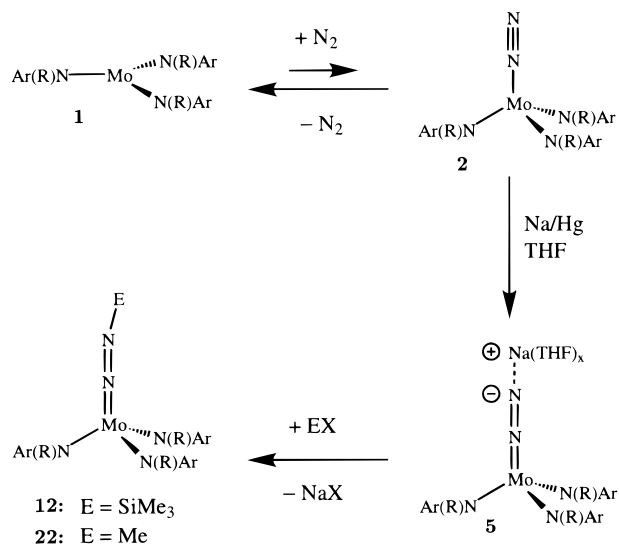
Figure 9. One-pot syntheses of **12** and **22** by silylation or methylation, respectively, of **5** generated by *in situ* reduction of the dinitrogen adduct of **1**. Note that the success of this procedure relies on the fact that the electrophile (EX = ClSiMe₃ or MeOTs) reacts at a negligible rate with the reductant (0.5% Na/Hg) under the reaction conditions (1 atm of N₂, 28 °C, THF solvent).
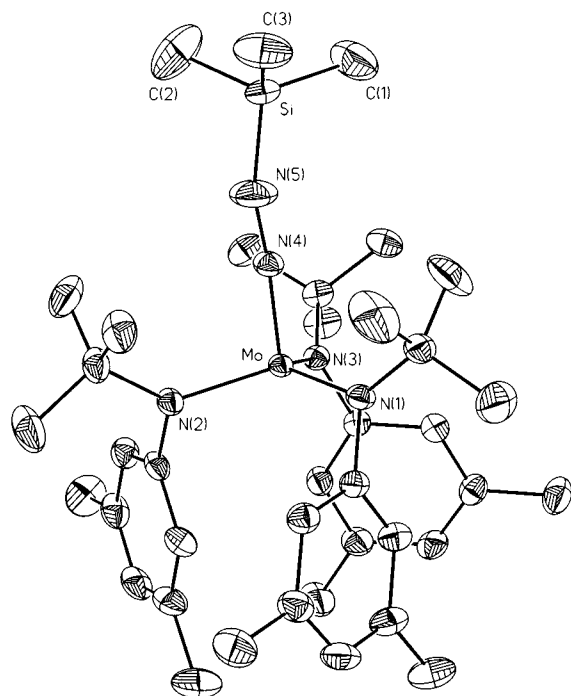

Figure 10. Structural drawing of (Me₃SiNN)Mo(N[R]Ar)₃ (**12**) with ellipsoids at the 35% probability level. Selected distances (Å) and angles (deg): Mo−N(1), 1.977(2); Mo−N(2), 1.970(2); Mo−N(3), 1.970(2); Mo−N(4), 1.753(2); N(4)−N(5), 1.221(3); N(5)−Si, 1.678(3); N(4)−Mo−N(3), 100.68(9); N(4)−Mo−N(2), 99.21(9); N(3)−Mo−N(4), 115.98(8); N(4)−Mo−N(1), 99.85(9); N(5)−N(4)−Mo, 173.7(2); N(4)−N(5)−Si 157.0(3).

bond order of ∼2. Recently, Schrock et al.[26] synthesized and structurally characterized an analogous silyldiazenido compound, [N₃N]MoN₂SiMe₃, where [N₃N] = [(Me₃SiNCH₂CH₂)₃N]³⁻. The reported core bond distances for [N₃N]MoN₂SiMe₃ were as follows: Mo−N$_\alpha$ = 1.803(7) Å; N−N = 1.206(9) Å; and N$_\beta$−Si = 1.670(9) Å. Although the N−N and N$_\beta$−Si bond distances are essentially identical (within experimental error) for the two systems, the Mo−N$_\alpha$ bond distance for **12** is
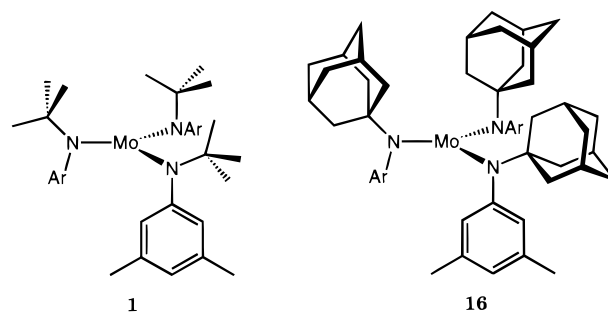

Figure 11. Skeletal drawing of **1** and **16**. Whereas **1** forms the μ-dinitrogen complex **3**, an analogous dinuclear N₂-bridged species derived from **16** does not form; this result is attributable to the increased steric requirements of the 1-adamantyl groups in **16**. Ar = 3,5-C₆H₃-Me₂.

marginally shorter (by ∼0.05 Å) than that found for [N₃N]MoN₂-SiMe₃.

(14) Methylation of the Dinitrogen Ligand. The cationic dimethylhydrazido complex [(Me₂NN)Mo(N[R]Ar)₃][OTf] (**21**) was synthesized by adding the silyldiazenido precursor **12** to a pentane solution containing 7 equiv of methyl triflate. Reaction occurs with precipitation of the red-orange product **21** over a period of 6 h. A 79% yield of pure diamagnetic **21** was obtained in one crop.

A corresponding monomethylated complex, namely, the neutral species (MeNN)Mo(N[R]Ar)₃ (**22**), also has been synthesized and characterized (see Figure 9). The first preparation of methyldiazenido **22** comprised a one-pot synthesis in which Mo(N[R]Ar)₃ was added slowly to a rapidly stirred solution of excess methyl tosylate in THF over sodium amalgam. This procedure provides the desired monomethylated product; however, its separation from impurities proved somewhat troublesome using this regimen. Therefore a second, preferred procedure was developed, involving the reaction of preisolated **9** with 1 equiv of methyl tosylate in OEt₂. The latter reaction was run for 2 h, and it produced the desired compound in spectroscopically and analytically pure form. The IR spectrum of **22** revealed a ν_{NN} at the relatively low frequency of 1538 cm⁻¹. It should be noted that the one-pot syntheses of the silyl- and methyldiazenido derivatives **12** and **22** are interesting in that the reactions involve both N₂ uptake and N−E (E = SiMe₃ or Me) bond formation. Additionally, both of the successful one-pot procedures employ electrophiles that fail to react with complex **1** and also fail to react with sodium amalgam under the conditions of the experiment, while the in situ generated anionic N₂ complex is readily derivatized by these electrophiles.

(15) An *N*-Adamantyl-Substituted Three-Coordinate Molybdenum(III) Complex. The successful trapping (section 12) of transient (N₂)Mo(N[R]Ar)₃ (**2**) by the titanium(III) reductant **13** was an advance consistent with the interpretation given above (section 3) for the formation of **5**. The chemistry of Mo(N[R]-Ar)₃ (**1**) in the presence of N₂ and sodium amalgam is complex and quite dependent upon the reaction conditions, primarily because the size requirements of the ᵗBu substituents are not sufficient to rule out dinuclear binding of N₂ (Figure 2). Providing the anilido ligands with an even greater degree of steric bulk was to allow the clean generation of a molybdenum dinitrogen anion species without the complication of bimetallic reaction pathways (see Figure 11 for a skeletal structural comparison between the two systems).

A preparation of the new three-coordinate molybdenum complex Mo(N[Ad]Ar)₃ (**16**) (Ad = 1-adamantyl,[12,13] Ar = 3,5-C₆H₃Me₂) was developed as a modification of the synthetic protocol[2] for **1**.
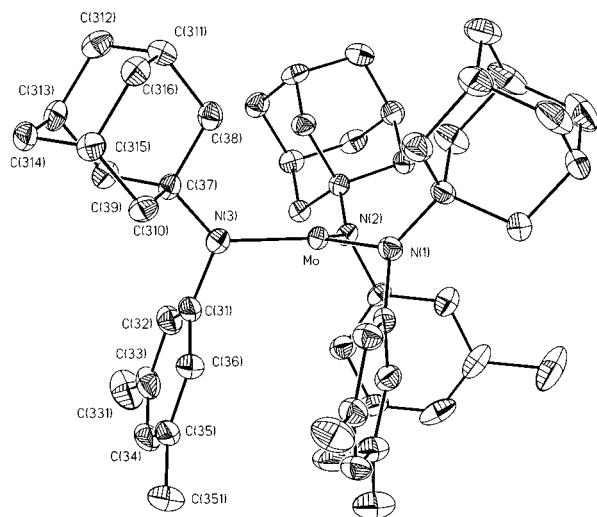
Figure 12. Structural drawing of Mo(N[Ad]Ar)$_3$ (**16**) with ellipsoids at the 35% probability level. Selected distances (Å) and angles (deg): Mo−N(1), 1.989(3); Mo−(N2), 1.974(3); Mo−N(3), 1.958(3); N(1)−C(11), 1.429(5); N(1)−C(17), 1.485(5); N(2)−C(21), 1.435(5); N(2)−C(27), 1.481(5); N(3)−C(31), 1.450(5); N(3)−C(37), 1.484(5); N(3)−Mo−N(2), 121.55(13); N(3)−Mo−N(1), 118.01(14); N(2)−Mo−N(1), 120.17(13); C(11)−N(1)−C(17), 122.3(3); C(11)−N(1)−Mo, 109.5-(2); C(17)−N(1)−Mo, 128.1(2); C(21)−N(2)−C(27), 117.9(3); C(21)−N(2)−Mo, 109.9(2); C(27)−N(2)−Mo, 132.2(2); C(31)−N(3)−C(37), 118.9(3); C(31)−N(3)−Mo, 110.0(2); C(37)−N(3)−Mo, 131.0(3).

(16) Synthesis and Properties of Mo(N[Ad]Ar)$_3$ (16; Ad = 1-Adamantyl). The synthesis of **16** entails addition of 2 equiv of the lithium salt Li(N[Ad]Ar)[12,13] to MoCl$_3$(THF)$_3$[65] in OEt$_2$ to effect the desired salt-elimination reaction. After removal of LiCl and excess molybdenum(III) chloride, the crude product is extracted into a pentane/benzene mixture and filtered through Celite to remove residual impurities including the free ligand HN(Ad)Ar. The use of benzene serves selectively to solubilize **16**, helping to separate it from the impurities. The purification can be somewhat problematic because both **16** and HN(Ad)Ar have limited solubility in pentane and in OEt$_2$. However, multigram quantities of **16** have been obtained reproducibly in yields typically ranging from 35 to 50% based on the starting lithium salt. Analytically pure samples of solid **16** are bright yellow-orange, appreciably lighter in hue than **1**.

A solution magnetic susceptibility measurement obtained by the method of Evans[66,67] for **16** was consistent with a quartet ground state (μ_{eff} = 3.96 μB), as expected.

Infrared spectra (CaF$_2$, THF) of **16** showed two signature bands at 1597 and 1583 cm^{-1} for the aryl ν_{CC} vibrations of the N(Ad)Ar ligands. Compound **16** was stable in the solid state for long periods at 25 °C and, once properly purified, provided a sturdy manifold for the molybdenum(III) dinitrogen chemistry of interest (vide infra).

Single crystals of **16** suitable for an X-ray diffraction study were deposited from an OEt$_2$ solution on standing at 25 °C. A thermal ellipsoid representation of **16** is shown in Figure 12. As anticipated, the molybdenum center adopts a trigonal planar geometry and the small-molecule binding pocket is in a cage consisting of the highly encumbering and preorganized adamantyl substituents.

In stark contrast to observations involving **1**, three-coordinate **16** proved to be stable indefinitely under the conditions for conversion of **1** to **3** (1 atm of N$_2$, toluene, −35 °C; see Figure
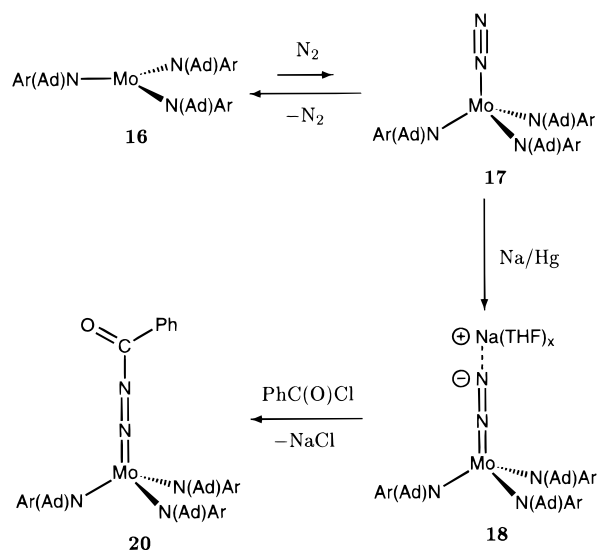
(65) Dilworth, J. R.; Zubieta, J. *Inorg. Synth.* **1986**, *24*, 193.
(66) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.
(67) Sur, S. K. *J. Magn. Reson.* **1989**, *82*, 169.

Figure 13. Synthesis of **18** proceeding in a fashion similar to that for **5** (1 atm of N$_2$, 28 °C), except that the adamantyl-substituted molybdenum complex **16** need not be added slowly to the Na/Hg/THF mixture. Putative **17** is not observed. The synthesis of **20** by addition of benzoyl chloride to an isolated sample of **18** went in 45% isolated yield (OEt$_2$, −35 → 25 °C).

1). Inspection of Figure 12 indicates that steric factors are prohibitive with regard to assembling two molecules of **16** about a single dinitrogen molecule.

Accordingly, no special precautions are required with respect to the handling of **16** under dinitrogen, and under no circumstances has **16** been observed to convert to its corresponding molybdenum(VI) nitride as a consequence of simple exposure to dinitrogen.

(17) Binding of N$_2$ by Mo(N[Ad]Ar)$_3$ (16) upon Na/Hg Reduction. When a THF solution of **16** was stirred over 0.4% Na/Hg under a dinitrogen atmosphere at 25 °C, the anionic dinitrogen complex [(THF)$_x$Na][(N$_2$)Mo(N[Ad]Ar)$_3$] (**18**) was the major product (Figure 13). While the lack of deuterium incorporation in the N(Ad)Ar ligands obviated ^{2}H NMR spectroscopy as a viable spectroscopic probe, it was found that the formation of **18** was easily monitored by IR spectroscopy. Dinitrogen complex **18** evinces two prominent ν_{NN} bands at 1783 and 1757 cm^{-1} in THF solution, and its formation was determined to be complete within several hours.

The observation of two ν_{NN} bands for **18** was unexpected, since only one band at 1761 cm^{-1} was observed under similar conditions for **5**. It is tempting to suggest that this phenomenon arises as a consequence of the presence of two conformational isomers being present in solution, isomers that are easily discriminated on the fast time scale of IR spectroscopy. For example, isomers of both C_3 and C_s symmetries may be present in significant concentrations in solution, despite the fact that pseudo-C_3 symmetry is often manifested in the solid state (see, e.g., Figure 12).

Dinitrogen complex **18** is scarlet in the presence of donor solvents such as THF or OEt$_2$ but precipitates as an orange solid when added to hydrocarbon solvents such as pentane or benzene. ^{1}H NMR spectroscopy showed that this color change coincided with complete or near-complete loss of the donor solvent molecules which solvate the sodium cation. The orange, THF-free solid was virtually insoluble in pentane, and its isolation and purification as the solvent-free complex **18** ($x = 0$) in ~64% yield was straightforward. Orange **18** ($x = 0$) is stable in the solid state, both under a dinitrogen atmosphere and under
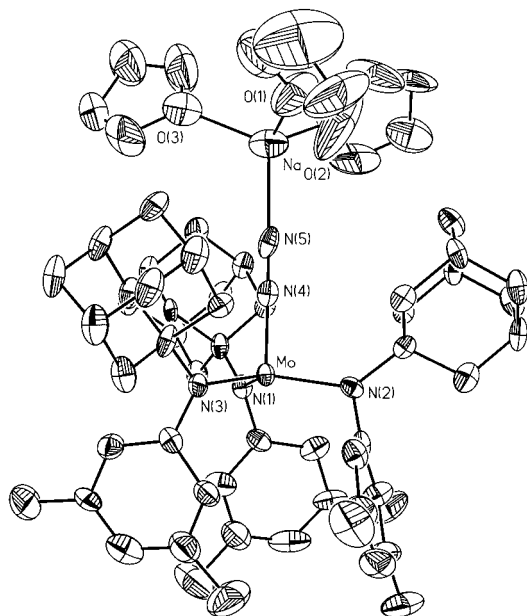
Figure 14. Structure of **18** with ellipsoids at the 35% probability level. Selected bond distances (Å) and angles (deg): Mo−N(1), 2.003(5); Mo−N(2), 2.002(5); Mo−N(3), 2.038(6); Mo−N(4), 1.830(8); N(4)−N(5), 1.152(8); Na−O(1), 2.193(10); Na−O(2), 2.254(10); Na−O(3), 2.221(10); Na−N(5), 2.227(9); N(1)−Mo−N(3), 115.8(2); N(1)−Mo−N(2), 119.1(2); N(2)−Mo−N(3), 119.9(2); N(4)−Mo−N(1), 98.3(2); N(4)−Mo−N(2), 96.8(2); N(4)−Mo−N(3), 97.7(2); N(4)−N(5)−Na, 177.6(6); N(5)−N(4)−Mo, 179.2(6); O(1)−Na−N(5), 110.0(4); O(2)−Na−N(5), 110.4(3); O(3)−Na−N(5), 113.(4).

vacuum. Its scarlet color is regenerated upon dissolution in OEt$_2$ or THF. As was found to be the case for **1** (section 2), three-coordinate **16** exhibited no reaction with 0.4% Na/Hg under an argon atmosphere, suggesting that the N$_2$-binding step precedes reduction in the generation of **18** (as indicated for **1** in Figure 2).

(18) X-ray Structure of [(THF)$_x$Na][(N$_2$)Mo(N[Ad]Ar)$_3$] (18). An X-ray diffraction study on a single crystal of **18** ($x = 3$), grown from heptane/THF, revealed an ion-paired dinitrogen complex in which a sodium cation is ligated by three THF molecules in addition to the β-nitrogen atom of the terminally coordinated N$_2$ ligand, with a Na···N(5) distance of 2.227(9) Å (Figure 14). The dinitrogen ligand itself resides along the pseudo-C_3 axis of the Mo(N[Ad]Ar)$_3$ fragment and does not protrude from the completely adamantyl-caged binding site. The structure observed for **18** (Figure 14) offers a forceful graphic illustration of how the steric constraints of the Mo(N[Ad]Ar)$_3$ system render the synthesis of **18** straightforward relative to that of **5** (compare section 3), by preventing the assembly of dimolybdenum N$_2$-bridged systems.

While bimetallic complexes featuring a bridging dinitrogen ligand are ubiquitous, structurally characterized examples where one of the metal centers is an alkali metal are rare. Schrock et al. reported in 1994 that, under appropriate conditions, Na/Hg effected the transformation of a molybdenum(IV) triflato complex to a corresponding anionic dinitrogen complex, formulated with a Mo=N=N···Na core.[43] Although structural data were not reported for the latter complex, the reaction chemistry served to demonstrate nucleophilic character for the β-nitrogen atom of the coordinated dinitrogen ligand. Silylation and stannylation were achieved at the β-N atom upon reaction with ClSi(iPr)$_3$ and ClSn(nBu)$_3$, respectively.

Recently, O'Donoghue and Schrock have extended this work to a host of related dinitrogen complexes bearing a [(Me$_3$-

SiNCH$_2$CH$_2$)$_3$N]Mo(N$_2$) core.[26,27] The chemistry of such complexes, which employ triamidoamine supporting ligands, was reviewed recently.[28]

(19) Reaction of [(THF)$_x$Na][(N$_2$)Mo(N[Ad]Ar)$_3$] (18) with Electrophiles. Addition of ClSiMe$_3$ to an ethereal solution of **18** unveiled the nucleophilic nature of this anionic dinitrogen complex. A change in color from the scarlet of ethereal **18** to bright yellow occurred upon mixing at 25 °C. Following salt removal a ^{1}H NMR spectrum of the crude product mixture showed the expected resonance for a Si*Me*$_3$ group and confirmed a nearly quantitative conversion to the anticipated silyldiazenido complex (Me$_3$SiNN)Mo(N[Ad]Ar)$_3$ (**19**).

An IR spectrum of **19** evinced a dramatic shift from the intense ν_{NN} vibration at 1761 cm^{-1} for **18** to a very broad absorbance centered at 1646 cm^{-1}.

The addition of benzoyl chloride to a cold ethereal solution of **18** effected N−C bond formation with concomitant salt elimination. The reaction was not quantitative, and the orange, crystalline benzoyldiazenido product (PhC(O)NN)Mo(N[Ad]Ar)$_3$ (**20**) was obtained in 45% yield from the green-tinted reaction mixture (Figure 13). By analogy with the Curtius rearrangement, it was thought that **20** might exhibit a tendency to rearrange thermally to phenylisocyanate and N≡Mo(N[Ad]Ar)$_3$. However, N≡Mo(N[Ad]Ar)$_3$ was not observed and **20** was not consumed when a benzene solution of the latter was maintained at 75 °C for 2 h.

The reactions of ClSiMe$_3$ and benzoyl chloride with **18** represent examples of N−Si and N−C bond formation stemming from a nucleophilic coordinated dinitrogen ligand.[68,69]

The use of transition metals to coordinate and activate molecular nitrogen toward functionalization remains an intense and challenging area of study. The construction of N−C and N−Si bonds from dinitrogen bound to zero-valent d^6 Mo and W complexes has been reported for metal centers bearing phosphine and macrocyclic thioether coligands. Chatt and co-workers reported the first examples of N−C bond formation from metal-coordinated dinitrogen in 1972.[70] Hidai[69] reported the molecular structure of a group 6 benzoyldiazenido complex obtained by functionalization of coordinated N$_2$. Noteworthy for comparison, the complexes trans-[M(N$_2$)$_2$(diphos)$_2$] (M = Mo, W) undergo reaction with iodotrimethylsilane at 50 °C in benzene to afford silyldiazenido complexes, but chlorotrimethylsilane under otherwise identical conditions was unable to effect the silylation.[68]

(20) Chemical Oxidation of [(THF)$_x$Na][(N$_2$)Mo(N[Ad]Ar)$_3$] (18). As was the case for **5** (section 5), **18** was readily oxidized by ferrocenium triflate. Such a proclivity towards redox chemistry was also manifested in a brief study of the chemistry of **18** as follows.

We were interested in the possibility of using simple salt-elimination reactions to furnish connections between the (Ar[Ad]N)$_3$Mo=N=N$^-$ moiety and transition metal centers such as Mo, Re, or W. Though this concept remains to be explored in detail, initial probe reactions indicate that redox-susceptible metal halides such as MoCl$_3$(THF)$_3$ can oxidize **18** to liberate N$_2$.

A few attempts were made to protonate **18**. The hope was to generate a parent diazenido species, (HNN)Mo(N[Ad]Ar)$_3$, but the attempts evidently resulted in undesired redox chemistry.

(68) Hidai, M.; Komori, K.; Kodama, T.; Jin, D. M.; Takahashi, T.; Sugiura, S.; Uchida, Y.; Mizobe, Y. *J. Organomet. Chem.* **1984**, *272*, 155.
(69) Hidai, M.; Sato, M.; Kodama, T.; Uchida, Y. *J. Organomet. Chem.* **1978**, *152*, 239.
(70) Chatt, J.; Heath, G. A.; Leigh, G. J. *J. Chem. Soc., Chem. Commun.* **1972**, 444.

Addition of sterically hindered 2,6-di-*tert*-butylphenol to an ethereal solution of **18** resulted in a gradual color change from scarlet to green. IR spectra showed complete consumption of starting material **18** and no new ν_{NN} vibrations, consistent with redox-triggered dissociation of N_2. *tert*-Butyl iodide also was investigated as a potential proton source. It was found, however, that addition of this reagent to **18** also effected the ejection of N_2.

Concluding Remarks

The chemistry of $Mo(N[R]Ar)_3$ (**1**) and related complexes of three-coordinate molybdenum(III) represents a unique chapter in coordination chemistry and in the chemistry of dinitrogen. Several reports have documented the binding and splitting of dinitrogen by **1** in the absence of added reagents.[1-3,35,54] Such reactivity represents a solution-chemistry analogue of the rate-determining step in Haber–Bosch nitrogen fixation,[4-6] namely, the dissociative adsorbtion of N_2.

With the present work we have shown that the binding of N_2 by **1** and its analogues is accelerated dramatically by the judicious utilization of appropriate reducing agents. The electrochemistry of several of the relevant dinitrogen complexes, mononuclear and dinuclear, has been investigated thoroughly, such that a detailed understanding is now available of the redox-catalyzed splitting of N_2 by **1**. Furthermore, in the case of the adamantyl-substituted system (section 16) it has been demonstrated that steric control afforded by synthesis can be exerted to shut down the dinitrogen-splitting pathway, which requires dinuclear N_2 complex intermediates.

In the course of investigating the intricacies of the redox chemistry of **1** in the presence of dinitrogen, syntheses of formally molybdenum(II) anionic dinitrogen complexes have been developed, and structural characterization by X-ray diffraction has been achieved.

A related advance is the development of rational high-yield routes to heterodinuclear Mo/M (M = Ti, U[71]) dinitrogen complexes, arising as a consequence of experiments designed to intercept the elusive neutral dinitrogen complex **2**.

The chemistry of Figure 2 constitutes a succinct summary of the basis for the wealth of fundamentally new dinitrogen chemistry included in this paper. Among other things, the first clear instance of intermetal dinitrogen–monoanion transfer has been documented, a new principle for the high-yield assembly of heterodinuclear N_2 complexes has been espoused, and the critical role of the state of charge with respect to N_2 binding has been made abundantly clear.

Experimental Section

General Considerations. Unless stated otherwise, all operations were performed in a Vacuum Atmospheres drybox under an atmosphere of purified nitrogen or using standard Schlenk techniques under an argon or dinitrogen atmosphere. Anhydrous OEt_2 and toluene were purchased from Mallinckrodt; *n*-pentane and *n*-hexane were purchased from EM Science. Ether was purified according to the procedure of Grubbs et al.[72] Aliphatic hydrocarbon solvents were distilled under a nitrogen atmosphere from sodium/benzophenone ketyl solubilized with a small quantity of tetraglyme. Distilled solvents were transferred under vacuum into Teflon-stopcocked glass vessels and stored, prior to use, in a Vacuum Atmospheres drybox. C_6D_6 was degassed and dried over activated molecular sieves (4 Å) and transferred under vacuum into a storage vessel. Molecular sieves (4 Å), Celite, and alumina were

(71) Odom, A. L.; Arnold, P. L.; Cummins, C. C. *J. Am. Chem. Soc.* **1998**, *120*, 5836.

(72) Pangborn, A.; Giardello, M.; Grubbs, R.; Rosen, R.; Timmers, F. *Organometallics* **1996**, *15*, 1518.
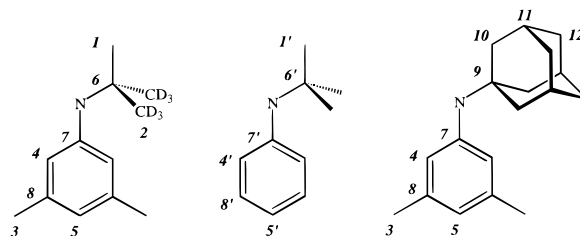
Figure 15. Numbering scheme for ^1H and ^{13}C NMR assignments.

activated in vacuo overnight at a temperature above 180 °C. Compounds **1**,[2] **13**,[40] ferrocenium triflate,[45] and $LiN(Ad)Ar$[12] were prepared according to published procedures. ^{15}N-Labeled N_2 gas was purchased form Cambridge Isotope Laboratory (CIL). $ClSiMe_3$ and benzoyl chloride were degassed and dried over molecular sieves (4 Å) prior to use. Other chemicals were purified and dried by standard procedures or were used as received. The syringe pump used was a KD Scientific model 200 Jen Houser Series infusion pump. Infrared spectra were recorded on a Bio-Rad 135 Series FTIR spectrometer. UV–visible spectra were recorded on a Hewlett-Packard 8453 diode-array spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-500, Varian XL-300, or Varian Unity-300 spectrometer. ^1H and ^{13}C NMR chemical shifts are reported with reference to solvent resonances (residual C_6D_5H in C_6D_6, 7.15 ppm; C_6D_6, 128.0 ppm; $CHCl_3$ in $CDCl_3$, 7.24 ppm; $CDCl_3$, 77.0 ppm). ^{15}N NMR spectra are referenced as reported previously.[59] ^{19}F NMR referenced against $CFCl_3$, 0.0 ppm. ^2H NMR chemical shifts are reported with respect to external C_6D_6 (7.15 ppm). Solution magnetic susceptibilities were determined by ^1H NMR at 300 MHz using the method of Evans.[66,67] Routine coupling constants are not reported. Combustion analyses (C, H, N) were performed by Microlytics (South Deerfield, MA) and Mikroanalytisches Labortorium (Mülheim, Germany). X-ray diffraction data were collected on a Siemens Platform goniometer with a charge coupled device (CCD) detector. Structures were typically solved by direct methods (SHELXTL V5.0, G. M. Sheldrick and Siemens Industrial Automation, Inc., 1995) unless otherwise noted. Peaks in the ^1H and ^{13}C NMR spectra are denoted according to Figure 15.

Electrochemical Measurements. Electrochemical measurements were performed in THF solution containing the desired compounds and 0.5 M $[N(n-Bu)_4][PF_6]$. In a typical procedure, 5 mg of the complex was dissolved in 0.75 mL of THF. To the solution was added 0.75 mL of a saturated THF solution of $[N(n-Bu)_4][PF_6]$. A platinum disk (1.6 mm diameter, Bioanalytical Systems), a platinum wire, and a silver wire were employed as the working electrode, the auxiliary, and the reference, respectively. The electrochemical response was collected with the assistance of an Eco-Chemie Autolab potentiostat (pgstat20) and the GPES 4.3 software. An IR correction drop was always employed due to the high resistance of the solutions. A typical resistance value measured with the positive feedback technique for these solutions was 975 Ω. All of the potentials are reported against the ferrocenium/ferrocene couple measured in the same solution.

Reaction of $Mo(N[R]Ar)_3$ (1) with Na/Hg (1 Equiv) under 1 atm of N_2. A 0.40% Na/Hg was prepared by dissolving Na metal (5.7 mg, 0.2479 mmol) in Hg (1.41 g, 7.03 mmol) in a 20-mL scintillation vial. THF was added (5 mL) and the amalgam was stirred for 5 min, followed by addition of solid orange **1** (173.4 mg, 0.2697 mmol) at 22 °C. Vigorous stirring was continued and within 1 h the solution had acquired an intense purple color, indicative of formation of **3**, an interpretation confirmed by a ^2H NMR spectrum acquired at this time. **1** had been consumed after 1 h (~3% remaining). An FTIR spectrum showed a ν_{NN} band at 1761 cm^{-1} consistent with the presence of **5**. Stirring was continued for 7 h, by which time the purple color had faded and the solution had turned orange-red. The solution was filtered through Celite, and solvent was removed in vacuo from the filtrate, yielding an orange-red solid. A ^1H NMR spectrum of the orange solid showed it to consist of 85% nitride **4** and 10% dinitrogen anion **5**, the independent characterization of which is described below.

Reaction of $Mo(N[R]Ar)_3$ (1) with $[Na][Et_3BH]$ under 1 atm of N_2. Compound **1** (**1**, 61.8 mg, 0.0961 mmol) was dissolved in THF (2 mL) in a 20-mL scintillation vial equipped with a magnetic stir bar.

Under a dinitrogen atmosphere, 480 mL of NaEt₃BH (0.480 mmol, 1 M solution in toluene) was added directly to the stirring orange solution at 22 °C. A gradual change in color resulting in an intense purple solution was observed during the first few hours. After 24 h, the purple color had dissipated and the solution was light-brown in color. Volatile material was removed in vacuo, and spectroscopic analysis (¹H NMR) indicated quantitative formation of nitride **4** relative to an internal integration standard of O(SiMe₃)₂.

Reaction of Mo(N[R]Ar)₃ (1) with Na/Hg under Argon. A 0.4% Na/Hg was prepared in a 50-mL round-bottom flask equipped with a side arm and stopcock by dissolving solid sodium (22 mg, 0.957 mmol) in Hg (5.44 g). THF (8 mL) was added to the flask, followed by solid **1** (1 equiv) under argon counterflow. The vessel was sealed, and stirring was continued under an Ar atmosphere for 22 h at 25 °C. The reaction mixture retained an orange color throughout. After 22 h, the solvent was removed in vacuo and the resulting orange residue was extracted into pentane and filtered away from the amalgam. A ²H NMR spectrum of this pentane solution showed unreacted **1** along with a small quantity of a diamagnetic entity ($\delta = 1.8$ ppm). A ¹H NMR spectrum of the residue reconstituted with C₆D₆ showed the diamagnetic product to be the free ligand HN(R)Ar. The estimated amount of HN(R)Ar was less than 10%.

Reaction of Mo(N[R]Ar)₃ (1) with Na under Argon. Sodium metal (111 mg, 4.828 mmol) was weighed into a 50-mL flask equipped with a side arm and stopcock. The sodium was spread around the base of the flask into a thin film to expose a high degree of surface area. THF (10 mL) was then added, and the mixture was stirred vigorously under Ar for 5 min. Compound **1** was added as a solid all at once under Ar counterflow, and the initially orange solution turned sienna within the first 30 min of stirring. After 2.5 h, the mixture was dried in vacuo and the resulting residue was extracted with pentane, the extract was filtered through Celite, and volatile matter was removed from the filtrate in vacuo. The process was repeated, and upon the second filtration, 185 mg of a black, hydrocarbon-insoluble solid was removed, affording a dark orange filtrate. This filtrate was stored at −35 °C and decanted twice away from a small amount of precipitate that had settled out. The filtrate was dried in vacuo and a ¹H NMR spectrum of the resulting orange-brown solid was acquired (C₆D₆), the spectrum evincing resonances consistent with one N(R)Ar ligand environment and coordinated THF. A ²H NMR spectrum showed a single resonance at 1.5 ppm. No ν_{NN} stretch was observed by infrared spectroscopy. The coordinated THF was not removed upon lyophilization (benzene). Analogous ¹H NMR spectra were obtained in several independent experiments. ¹H NMR (300 MHz, C₆D₆, 25 °C) $\delta = 6.24$ (s, 4), 5.82 (5), 3.24 (t, THF), 2.25 (3), 1.45 (1), 1.23 (m, THF). No change was observed in the ¹H NMR spectrum of the orange-brown material after exposure to N₂ for a period of 1 h. Addition of 2 equiv of 12-crown-4 to a sample of this solid in THF resulted in a complex mixture of products. An attempt to regenerate **1** by oxidation of the orange-brown compound with stoichiometric ferrocenium triflate in OEt₂ led to a complex mixture of products including a substantial quantity of the free ligand, HN(R)Ar. The orange-brown compound reacted slowly with carbon monoxide over a period of 30 min but did not afford the expected anionic CO derivative of **1**, which has been characterized independently.[41] Additionally, the orange-brown compound did not react with N₂ to form **5**. X-ray-quality crystals of the orange-brown compound were never obtained.

Synthesis of (Ph[ᵗBu]N)₃Ti(μ-N₂)Mo(N[R]Ar)₃ (14). Compound **1** (187.5 mg, 0.293 mmol) and green Ti(N[ᵗBu]Ph)₃[40] (**13**, 144 mg, 0.293 mmol) were weighed into a 20-mL scintillation vial containing a stir bar. Ether (3.5 mL) was added to the vial and the contents were stirred at 25 °C, initially giving a dark, green-orange solution. The reaction mixture was stirred under an atmosphere of dinitrogen for 36 h and the reaction progress was monitored by ²H NMR, such that the gradual depletion of paramagnetic **1** ($\delta = 64.5$ ppm) and the formation of a single new product with a single resonance ($\delta = 1.8$ ppm) was observed. After 36 h, **1** had been completely consumed, and a large amount of an orange precipitate was evident in the vessel. This bright orange powder was collected on a sintered glass frit by filtration, and the filtrate was concentrated to its solid form. The solids were combined, and a ¹H NMR spectrum of the crude material evinced clean production

of a single diamagnetic product exhibiting two ligand environments. A small quantity of the free ligands HN(R)Ar and HN(ᵗBu)Ph were also discernable. The crude material was extracted into pentane (15 mL) and recrystallized (two crops) to afford 267 mg (81%) of deep-orange, crystalline **14**: ¹H NMR (300 MHz, C₆D₆, 45 °C) δ 7.20 (m, 8′ and 5′), 7.09 (m, 8′ and 5′), 7.00 (m, 8′ and 5′), 6.73 (s, 5), 6.55 (br s, 4), 5.92 (br s, 4′), 2.11 (s, 3), 1.56 (s, 1), 1.49 (s, 1′); ¹³C NMR (125.66 MHz, C₆D₆, 25 °C) δ 154.00 (aryl), 148.78 (aryl), 137.26 (aryl), 132.27 (aryl), 128.97 (aryl), 127.69 (aryl), 124.86 (aryl), 65.24 (6 or 6′), 62.25 (6 or 6′), 32.33 (2), 32.07 (2′), 21.86 (3); UV−vis (OEt₂) λ 306 ($\epsilon = 34\,800$), 449 nm ($\epsilon = 32\,000$); FTIR (CH₂Cl₂, CaF₂) ν_{NN} 1575 cm⁻¹. Anal. Calcd for C₆₆H₇₈D₁₈N₈MoTi: C, 68.13; H, 8.32; N, 9.63. Found: C, 68.31; H, 8.40; N, 9.54.

Synthesis of (Ph[ᵗBu]N)₃Ti(μ-¹⁵N₂)Mo(N[R]Ar)₃ (15). A 100-mL vessel containing ¹⁵N₂ gas at 1 atm (∼4.1 mmol) was attached to a 50-mL round-bottom Schlenk flask containing a stir bar. The two vessels were separated by a break-seal. Ether (8 mL) was added to the Schlenk flask, which was subsequently degassed. Under a counterflow of argon, 200 mg of solid **1** (0.311 mmol) and 153 mg of **13** were added to the Schlenk flask. The break-seal was broken with the stir bar in order to expose the solution to ¹⁵N₂. The reaction workup followed the same protocol as that described above for **14**: FTIR (CH₂-Cl₂, CaF₂) 1524 cm⁻¹ (ν¹⁵N¹⁵N, calcd 1522 cm⁻¹); ¹⁵N NMR (50.65 MHz, C₆D₆, 25 °C) δ 437.15 (d, ¹$J_{NN} = 12.6$ Hz), 433.09 (d, ¹$J_{NN} = 12.6$ Hz). ¹⁵NH₂Ph was used as reference at 55 ppm relative to liquid ammonia at 0 ppm.[59]

X-ray structure of (Ph[ᵗBu]N)₃Ti(μ-N₂)Mo(N[R]Ar)₃ (14). Deep orange crystals were grown slowly from a pentane solution at −35 °C. The crystals were quickly moved from a scintillation vial to a microscope slide containing Paratone N oil (an Exxon product). Under the microscope, an orange plate was selected and mounted on a glass fiber using wax. A total of 31 317 reflections were collected (−17 ≤ h ≤ 13, −21 ≤ k ≤ 21, −28 ≤ l ≤ 27) in the θ range of 1.32−23.26° of which 11 068 were unique ($R_{int} = 0.0616$). The structure was solved by direct methods in conjunction with standard difference Fourier techniques. Hydrogen atoms were placed in calculated ($d_{C-H} = 0.96$ Å) positions. The largest peak and hole in the difference map were 0.405 and −0.354 e·Å⁻³, respectively. A semiempirical absorption correction was applied based on pseudo-ψ scans with maximum and minimum transmission equal to 0.1513 and 0.0954, respectively. A solvent pentane molecule was located in the difference map of the asymmetric unit and included during refinement. The least-squares refinement converged normally with residuals of R (based on F) = 0.0579, wR (based on F^2) = 0.1326, and GOF = 1.086 (based on $I >$ 2$\sigma(I)$). Crystal data for C₇₁H₁₀₇MoN₈Ti: monoclinic, space group = $P2_1/n$, $z = 4$, $a = 15.679(2)$ Å, $b = 19.580(4)$ Å, $c = 25.319(3)$ Å, $\beta = 95.61(2)°$, $V = 7736(2)$ Å³, $\rho_{calc} = 1.045$ g·cm⁻³, $F(000) = 2612$.

Synthesis of Mo(N[Ad]Ar)₃ (16). To a 500-mL flask was added 7.44 g of Li(N[Ad]Ar)[12] (7.44 g, 28.5 mmol) and 150 mL of OEt₂. The mixture was stirred for 5 min at 25 °C, and then MoCl₃(THF)₃[65] (5.96 g, 14.2 mmol) was added in one portion. The reaction mixture darkened and attained a light-brown color after 5 h, at which time it was filtered through Celite. The filtrate was stored at −35 °C to precipitate out a small quantity of solid. The mixture was then filtered through a sintered glass frit, and the filter cake was washed with pentane until the washings were colorless. The orange washings and filtrate were combined, and the cooling/filtration/extraction process was repeated. After solvent removal in vacuo, the residue was extracted with ether (50 mL). The extract was stored at ∼28 °C until a light orange solid precipitated. The solid (3.1 g) was collected on a frit and dried in vacuo. The ¹H NMR spectrum (C₆D₆) of the material revealed ∼2% impurity of the free ligand HN(Ad)Ar. The orange solid was dissolved in a 50:50 pentane/benzene mixture, and the resulting solution was filtered through Celite. Solvent was removed from the filtrate in vacuo, affording 2.85 g of a light orange-yellow powder (35% yield): μ_{eff} (C₆D₆) 2.96 μ_B. Anal. Calcd for C₅₄H₇₂MoN₃: C, 75.49; H, 8.45; N, 4.89. Found: C, 75.33; H, 8.45; N, 4.68.

X-ray Structure of Mo(N[Ad]Ar)₃ (16). Orange crystalline slabs were grown slowly from an ethereal solution at 25 °C. The crystals were quickly moved from a scintillation vial to a microscope slide

containing Paratone N oil (an Exxon product). Under the microscope an orange plate was selected and mounted on a glass fiber using wax. A total of 19 029 reflections were collected ($-10 \leq h \leq 20$, $-14 \leq k \leq 13$, $-23 \leq l \leq 21$) in the θ range of $1.14-23.25°$ of which 6804 were unique ($R_{int} = 0.0469$). The structure was solved by direct methods in conjunction with standard difference Fourier techniques. Hydrogen atoms were placed in calculated ($d_{C-H} = 0.96$ Å) positions. The largest peak and hole in the difference map were 0.357 and -0.504 e·Å^{-3}, respectively. A semiempirical absorption correction was applied based on pseudo-ψ scans with maximum and minimum transmission equal to 0.6720 and 0.6191, respectively. The least-squares refinement converged normally with residuals of R (based on F) = 0.0535, wR (based on F^2) = 0.1040, and GOF = 1.274 (based on $I > 2\sigma(I)$). Crystal data for C$_{47}$H$_{72}$MoN$_3$: monoclinic, space group = P2$_1$/c, z = 4, a = 18.874(3) Å, b = 12.6894(11) Å, c = 20.947(5) Å, β = 108.805(13)°, V = 4749.0(13) Å^3, ρ_{calc} = 1.202 g·cm^{-3}, $F(000)$ = 1836.

Synthesis of [(THF)$_x$Na][(N$_2$)Mo(N[Ad]Ar)$_3$] (18). A 0.4% Na/Hg was prepared by dissolving 100 mg of Na metal (4.350 mmol) in 25 g of Hg in a 50-mL round-bottom flask charged with a stir bar. THF (17 mL) was added to the amalgam and the mixture was stirred for 5 min, after which time solid orange **16** (895 mg, 1.045 mmol) was added directly to the vigorously stirring mixture. The reaction flask was plugged with a rubber septum fitted with a needle inlet, providing constant exposure to a dinitrogen atmosphere. The reaction mixture acquired a scarlet color within 10 h. The mixture was stirred for 35 h, after which time the deep scarlet supernatant was decanted away from the amalgam and dried in vacuo. The residue was subsequently extracted into ether (40 mL) and filtered through Celite. The filtrate was again divested of solvent in vacuo. Pentane (10 mL) was added to the resulting scarlet solid, effecting the precipitation of a bright orange solid from a solution which was now red-orange. The orange solid was collected on a sintered frit and washed twice with 10 mL of pentane. Solvent removal afforded 610 mg (64%) of the THF-free species [(THF)$_x$Na]-[(N$_2$)Mo(N[Ad]Ar)$_3$] (x = 0). This solid was virtually insoluble in all hydrocarbon solvents including benzene and was found (not unexpectedly) to be unstable in CH$_2$Cl$_2$ and CHCl$_3$. Spectroscopic characterization was carried out on samples crystallized from ether at -35 °C, which produced a scarlet crystalline material in good yield. Drying under ambient pressure of such a solid, and subsequent extraction into C$_6$D$_6$, afforded homogeneous solutions amenable to spectroscopic analysis. A ^{1}H NMR spectrum of such a sample showed shifted OEt$_2$ resonances (there were ~9 OEt$_2$ molecules for each Mo atom): ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C) δ = 6.88 (s, *4*), 6.63 (s, *5*), 3.25 (q, OEt$_2$), 2.24 (s, *3*), 2.18 (s, Ad), 1.93 (s, Ad), 1.67 (s, Ad), 1.11 (t, OEt$_2$); ^{13}C NMR (125.66 MHz, C$_6$D$_6$, 25 °C) δ 136.89 (aryl), 131.45 (aryl), 121.76 (aryl), 118.11 (aryl), 68.24 (OEt$_2$), 66.3, 61.7, 45.9, 44.3, 37.80, 37.17, 32.63, 31.73, 30.55, 26.18, 23.46, 23.08, 21.93, 15.96 (OEt$_2$), 14.72 (OEt$_2$); FTIR (THF, KBr) ν_{NN} 1783, 1757 cm^{-1}; UV–vis (OEt$_2$) λ_{max} = 465 nm (ϵ = 4000). A sample appropriate for microanalysis was obtained as the discrete salt complex [Na(12-crown-4)$_2$][(N$_2$)Mo(N[Ad]Ar)$_3$] by addition of 2 equiv of a benzene solution of 12-crown-4 to a scarlet solution of **18** in THF/benzene. The resulting violet solution was dried in vacuo and washed thoroughly with pentane to afford a violet powder. Recrystallization from a toluene/THF mixture at -35 °C afforded [Na(12-crown-4)$_2$][(N$_2$)Mo(N[Ad]Ar)$_3$]. Anal. Calcd for C$_{70}$H$_{104}$N$_5$MoNaO$_8$: C, 66.59; H, 8.30; N, 5.55. Found: C, 65.95; H, 8.41; N, 5.43.

X-ray Structure of [(THF)$_x$Na][(N$_2$)Mo(N[Ad]Ar)$_3$] (18). Deep scarlet crystals were grown slowly by slow diffusion of heptane into a scarlet THF solution at 25 °C. The crystals were quickly moved from a scintillation vial to a microscope slide containing Paratone N oil. Under the microscope, a scarlet plate was selected and mounted on a glass fiber using wax. A total of 26 843 reflections were collected ($-34 \leq h \leq 33$, $-31 \leq k \leq 34$, $-14 \leq l \leq 16$) in the θ range of $1.31-20.00°$ of which 7153 were unique ($R_{int} = 0.0835$). The structure was solved by direct methods in conjunction with standard difference Fourier techniques. Non-hydrogen atoms were refined anisotropically. Two Na-bound THF moieties were severely disordered, and attempts to model the problem were unsuccessful. The model that is reported uses the geometry of the one *good* THF as a basis for constraining the disordered ligands. Thermal motion was also constrained for those THF moieties

through the final refinement. All hydrogen atoms were placed in calculated ($d_{C-H} = 0.96$ Å) positions. The largest peak and hole in the difference map were 0.486 and -0.346 e·Å^{-3}, respectively. The least-squares refinement converged normally with residuals of R (based on F) = 0.0799, wR (based on F^2) = 0.1829, and GOF = 1.048 based upon $I > 2\sigma(I)$. Crystal data for C$_{66}$H$_{95}$MoN$_5$NaO$_3$: trigonal, space group = P$\bar{3}$, z = 6, a = 31.1129(8) Å, b = 31.1129(8) Å, c = 14.9633-(6) Å, V = 12544.1(7) Å^3, ρ_{calc} = 0.894 g·cm^{-3}, $F(000)$ = 3618.

Synthesis of (Me$_3$SiNN)Mo(N[Ad]Ar)$_3$ (19). In a 20-mL scintillation vial, solid orange **18** (34.5 mg, 0.0379 mmol) was dissolved in ether (2.5 mL) to form a scarlet solution. A separate ether solution (2 mL) of chlorotrimethylsilane (6 mg, 0.0552 mmol) was prepared, and the solutions were then mixed at -35 °C. The stirring mixture attained a bright yellow within 5 min. After 15 min the mixture was filtered through Celite, abandoning a yellow filter cake, which was washed with benzene (2 mL) until the washings were colorless. Volatile material was removed in vacuo, and the resulting yellow residue was recrystallized from pentane in two crops affording 21 mg (58%) of crystalline yellow **19**: ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C) δ 6.89 (s, *5*), 6.33 (s, *4*), 2.16 (s, *3*), 2.12 (s, Ad), 2.06 (s, Ad), 1.68 (dd, Ad), 0.39 (s, SiMe$_3$); ^{13}C NMR (125.66 MHz, C$_6$D$_6$, 25 °C) δ 137.31 (aryl), 131.74 (aryl), 121.78 (aryl), 118.13 (aryl), 66.77 (*9*), 46.30 (Ad), 44.33 (Ad), 37.39 (Ad), 37.16 (Ad), 31.67 (Ad), 30.54 (Ad), 23.07 (*3*), 21.95; FTIR (THF, KBr) ν_{NN} 1646 cm^{-1} (br). Anal. Calcd for C$_{57}$H$_{81}$N$_5$MoSi: C, 71.29; H, 8.50; N, 7.29. Found: C, 71.22; H, 8.38; N, 7.19.

Synthesis of (PhC(O)NN)Mo(N[Ad]Ar)$_3$ (20). In a 20-mL scintillation vial, solid orange **18** (92.3 mg, 0.101 mmol) was dissolved in ether (4 mL), giving a scarlet solution. A separate ether solution (2 mL) of benzoyl chloride (15.1 mg, 0.107 mmol) was prepared. Both solutions were chilled to -35 °C, and the solution of benzoyl chloride was then added quickly to the stirring solution of **18**, eliciting a rapid color change to dark olive-green. The reaction mixture was allowed to stir for an additional 24 h, and then it was filtered through Celite. A bright orange solid was obtained by crystallization from pentane in several crops from the green filtrate (45 mg, 45%). A benzene solution of this solid was thermally stable at 75 °C for 2 h: ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C) δ 8.73 (d, phenyl para), 7.24 (m, phenyl meta), 6.69 (*5*), 6.15 (*4*), 2.31 (Ad), 2.17 (Ad), 2.09 (*3*), 1.80 (Ad), 1.57 (Ad); ^{13}C NMR (125.66 MHz, C$_6$D$_6$, 25 °C) δ 146.98 (aryl), 137.79 (aryl), 131.58 (aryl), 129.61 (aryl), 129.34 (aryl), 121.77 (aryl), 118.13 (aryl), 65.74 (*9*), 45.54 (Ad), 44.31 (Ad), 37.19 (Ad), 31.74 (Ad), 30.54 (Ad), 21.84 (*3*). Anal. Calcd for C$_{61}$H$_{77}$N$_5$MoO: C, 73.84; H, 7.82; N, 7.06. Found: C, 73.22; H, 7.88; N, 6.99.

Synthetic Procedures for [(THF)$_x$Na][(N$_2$)Mo(N[R]Ar)$_3$] (5) and [Na(12-crown-4)$_2$][(N$_2$)Mo(N[R]Ar)$_3$] (7). The following preparation was carried out in a drybox under 1 atm of dinitrogen. A 0.44% Na/Hg solution was prepared by dissolving Na (400 mg, 0.0174 mol) in Hg (91 g, 0.454 mol) in a 250-mL round-bottom flask. The amalgam was allowed to cool to ambient temperature, and THF (60 mL) was then added to the flask. The contents were stirred vigorously for 5 min. Orange **1** (620 mg, 0.0965 mmol) was dissolved in THF (40 mL, 0.024 M), and this solution was placed in a dropping funnel equipped with a stopcock. The orange solution of **1** was added dropwise, very slowly, to the vigorously stirring solution containing the amalgam at 25 °C. The addition rate was adjusted such that the addition took place over a period of 10 h. During the addition, the solution acquired a scarlet color. The reaction mixture was stirred for an additional 12 h at 25 °C, after which time the solvent was removed in vacuo. The resulting residue was extracted with pentane (30 mL), and the extract was decanted away from the amalgam. The orange extract was filtered through Celite and dried to a fine orange powder. Spectroscopic analysis (^{1}H NMR) revealed near-quantitative conversion (96% crude) to the desired product [(THF)$_x$Na][(N$_2$)Mo(N[R]Ar)$_3$] (**5**), with only 2% free ligand HN(R)Ar and 2% nitride **4** present as side products. The orange powder was recrystallized from pentane in 69% yield, affording pure **5** (x = 0) containing a trace amount of THF: ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C) δ 6.804 (s, *4*), 6.63 (s, *5*), 2.22 (s, *3*), 1.38 (s, *1*); ^{13}C NMR (125.66 MHz, C$_6$D$_6$, 25 °C) δ 156.2 (aryl), 137.0 (aryl), 130.1 (aryl), 124.3 (aryl), 60.9 (*6*), 34.8 (*1*), 33.0 (*2*), 23.1 (*3*), 21.8 (*3*); FTIR (THF, KBr) ν_{NN} 1761 cm^{-1}. Addition of 2 equiv of 12-crown-4 afforded the discrete violet salt [Na(12-crown-4)$_2$][(N$_2$)Mo(N[R]Ar)$_3$] (**7**). This

salt was highly insoluble in solvents such as pentane, diethyl ether, and benzene but dissolved readily in THF and was recrystallized nearly quantitatively from a pentane/THF mixture; FTIR (THF, KBr) ν_{NN} 1761 cm^{-1}. Anal. Calcd for C$_{52}$H$_{68}$D$_{18}$N$_5$O$_8$MoNa: C, 59.69; H, 8.28; N, 6.69. Found: C, 59.46; H, 8.26; N, 6.61.

Syringe Pump Synthesis of [(THF)$_x$Na][(N$_2$)Mo(N[^{t}Bu]Ar)$_3$] (9). Mo(N[^{t}Bu]Ar)$_3$ (**8**, identical to **1** but for lack of deuterium enrichment in the *tert*-butyl group, 1.098 g, 1.76 mmol) was divided into two equal portions. Each portion was dissolved in THF (40 mL) and loaded into an air-tight glass syringe (two syringes being used simultaneously). The syringes were mounted on top of a dual-infusion pump that was set to add the solution continuously for 10 h. Two 250-mL Erlenmeyer filter flasks each were charged with 30 equiv 0.5% of Na/Hg prepared by dissolving Na (606 mg, 52.8 mmol) in Hg (121 g). These flasks were mounted on individual magnetic stir plates set for rapid stirring. Teflon tubing is used to connect the syringes to their respective flasks. The tubing is inserted through the side arm on the flask and allowed to hang downward toward the amalgam. The top of the flasks are capped to obviate spillage of the rapidly stirring mixture. After complete addition, the solutions were combined and worked up as one. The scarlet THF solution was decanted from the amalgam and filtered through Celite on a sintered glass frit. Solvent was removed in vacuo from the filtrate. The resulting solid residue was dissolved in pentane. The pentane solution was filtered through Celite, and volatile material was removed in vacuo from the filtrate. Spectroscopic analysis (^{1}H NMR) revealed quantitative conversion (99+% crude) to the desired product [(THF)$_x$Na][(N$_2$)Mo(N[^{t}Bu]Ar)$_3$] (**9**, $x = 0$), with less than 1% nitride **4** present as a side product. The crude product may be crystallized in 77% yield by dissolving in pentane (16 mL) and storing at −35 °C for 48 h. Spectroscopic properties are essentially the same as for **5** above.

X-ray Structure of [Na(12-crown-4)$_2$][(N$_2$)Mo(N[R]Ar)$_3$] (7). Deep violet crystals were grown slowly from a pentane/THF solution at −35 °C. The crystals were quickly moved from a scintillation vial to a microscope slide containing Paratone N. Under the microscope a violet plate was selected and mounted on a glass fiber using wax. A total of 9132 reflections were collected ($-13 \leq h \leq 13$, $-16 \leq k \leq 18$, $-13 \leq l \leq 19$) in the θ range of 1.49−20.00° of which 5796 were unique ($R_{int} = 0.0690$). The structure was solved by direct methods in conjunction with standard difference Fourier techniques. Hydrogen atoms were placed in calculated ($d_{C-H} = 0.96$ Å) positions. The largest peak and hole in the difference map were 0.632 and −0.552 e·Å^{-3}, respectively. No absorption correction was applied. The least-squares refinement converged normally with residuals of R (based on F) = 0.1156, wR (based on F^2) = 0.2431, and GOF = 1.117 (based on $I > 2\sigma(I)$). Crystal data for C$_{52}$H$_{86}$MoN$_5$NaO$_8$: triclinic, space group = P1, $z = 2$, $a = 12.3630(8)$ Å, $b = 16.2797(11)$ Å, $c = 17.8547(12)$ Å, $\alpha = 71.3237(12)°$, $\beta = 87.1904(7)°$, $\gamma = 80.7164(12)°$, $V = 3359.7(4)$ Å^3, $\rho_{calc} = 1.016$ g·cm^{-3}, $F(000) = 1100$.

[(THF)$_x$Na][(N$_2$)Mo(N[R]Ar)$_3$] (5) + [Cp$_2$Fe][O$_3$SCF$_3$]. A scarlet solution of [(THF)$_x$Na][(N$_2$)Mo(N[R]Ar)$_3$] (36.0 mg, 0.0519 mmol) in 1.5 mL of THF was prepared in a small vial equipped with a stir bar. A separate deep blue solution of ferrocenium triflate, [Cp$_2$Fe][O$_3$SCF$_3$] (17.4 mg, 0.0519 mmol), in 1.5 mL of THF was similarly prepared. The scarlet solution was added quickly at 25 °C to the intense blue solution of [Cp$_2$Fe][O$_3$SCF$_3$]. Effervescence was observed at once, and the resulting homogeneous solution was orange-red. After filtration, the volatiles were removed in vacuo, and spectroscopic analysis (FTIR, ^{1}H NMR, ^{2}H NMR) of the crude mixture confirmed complete consumption of **5** and stoichiometric formation of Mo(N[R]Ar)$_3$ and Cp$_2$Fe. An analogous experiment carried out at low temperature (−35 °C) proceeded similarly.

Mo(N[R]Ar)$_3$ (1) + [(THF)$_x$Na][(N$_2$)Mo(N[R]Ar)$_3$] (5) under N$_2$. Scarlet **5** (27 mg, 0.0390 mmol) was dissolved in THF (2 mL) in a 20-mL scinitillation vial equipped with a stir bar. An orange solution of Mo(N[R]Ar)$_3$ (25 mg, 0.0389 mmol) in THF (1.5 mL) was added dropwise to the stirring scarlet solution over a period of ∼30 s. No color change was observed after the first few minutes had passed. Within 30 min, however, the solution was an intense purple. A ^{2}H NMR spectrum of the reaction mixture after 1.5 h indicated the presence of the paramagnetic dinuclear complex (μ-N$_2$){Mo(N[R]Ar)$_3$}$_2$ (∼13 ppm) and a diamagnetic species (1.7 ppm) in a 1:7 ratio. All of the starting

Mo(N[R]Ar)$_3$ (**1**) had been consumed by this time. The reaction mixture was dried in vacuo after 7 h, by which time the intense purple color of (μ-N$_2$){Mo(N[R]Ar)$_3$}$_2$ (**3**) had faded. A ^{1}H NMR spectrum of the crude mixture showed N≡Mo(N[R]Ar)$_3$ (**4**, 62.4%), [(THF)$_x$Na][(N$_2$)Mo-(N[R]Ar)$_3$] (**5**, 35.3%), and HN(R)Ar (2.3%).

Mo(N[R]Ar)$_3$ (1) + [(THF)$_x$Na][(N$_2$)Mo(N[R]Ar)$_3$] (5) + Hg under N$_2$. In a 20-mL scintillation vial, orange Mo(N[R]Ar)$_3$ (**1**) (23.2 mg, 0.0360 mmol) was dissolved in THF (1.5 mL) and 207 mg of mercury was added to the stirring solution at 25 °C. A solution of [(THF)$_x$Na][(N$_2$)Mo(N[R]Ar)$_3$] (25 mg, 0.0360 mmol) in THF (2 mL) was then added quickly via pipet. An intense purple color developed during the first hour of stirring. After 14 h, the solution was dried in vacuo. Addition of pentane (4 mL) to the dried residue resulted in an orange solution which was decanted away from a gray particulate residue at the base of the vial. The mercury was washed further with pentane until the washings were colorless. The orange solution was dried and weighed at 44.8 mg. ^{1}H NMR analysis of the crude orange solid (in C$_6$D$_6$ with an internal integration standard of hexamethyld-isiloxane) showed the spectroscopically identifiable products to be N≡Mo(N[R]Ar)$_3$ (60%), [(THF)$_x$Na][(N$_2$)Mo(N[R]Ar)$_3$] (28%), and HN-(R)Ar (6.5%). A ^{2}H NMR spectrum of this solid (in THF) revealed that ∼5% of (μ-N$_2$){Mo(N[R]Ar)$_3$}$_2$ remained. The gray particulate that remained in the original reaction vial was tested for its activity to facilitate dinitrogen binding and cleavage by preparing a fresh solution of Mo(N[R]Ar)$_3$ (23.2 mg, 0.0360 mmol) in THF (2 mL) and adding it to the original reaction vial containing the gray particulate. The contents of the vial were stirred for several hours. The solution remained orange throughout, and after 7 h a ^{1}H NMR spectrum of the crude mixture revealed only ∼8% N≡Mo(N[R]Ar)$_3$. Starting Mo(N[R]Ar)$_3$ was the only other species detectable (∼90% of the mixture).

Reaction of [(THF)$_x$Na][(N$_2$)Mo(N[R]Ar)$_3$] (5) with Mo(N[^{t}Bu]-Ar)$_3$ (8) in Vacuo. Solid orange Mo(N[^{t}Bu]Ar)$_3$ (**8**; 14.0 mg, 0.0224 mmol) and solid scarlet **5** (17.1 mg, 0.0246 mmol) were carefully weighed into a sealable NMR tube. Rigorously degassed THF was subsequently vacuum distilled into the evacuated tube at −196 °C and the frozen vessel was flame-sealed. Upon thawing, the mixture went homogeneous and ^{2}H NMR spectroscopy was used to analyze the deuterium-labeled species present. The spectra obtained clearly showed the presence of paramagnetic Mo(N[R]Ar)$_3$ at 65 ppm (∼38.5%) as well as diamagnetic [(THF)$_x$Na][(N$_2$)Mo(N[^{t}Bu]Ar)$_3$] at 1.0 ppm (∼54.5%). A small amount of bridged (μ-N$_2$){Mo(N[R]Ar)$_3$}$_2$ was observed at 13 ppm (∼7%). A ^{1}H NMR spectrum of the mixture, reconstituted in C$_6$D$_6$, confirmed that [(THF)$_x$Na][(N$_2$)Mo(N[^{t}Bu]Ar)$_3$] (**9**) had formed. This result was reproduced in two subsequent independent experiments.

Attempted Synthesis of [Na(12-crown-4)$_2$][(μ-N$_2$){Mo(N[R]-Ar)$_3$}$_2$] (11). Solid violet [Na(12-crown-4)$_2$][(N$_2$)Mo(N[R]Ar)$_3$] (**7**; 44.0 mg, 0.0421 mmol) and orange Mo(N[R]Ar)$_3$ (**1**; 27.1 mg, 0.0421 mmol) were weighed carefully into a sealable NMR tube. The tube was evacuated and rigorously degassed. THF (1.2 mL) was then vacuum distilled into the the tube at −196 °C. The tube was flame-sealed and transferred directly to a −78 °C dry ice/2-propanol bath. The cold sample was then quickly analyzed by ^{2}H NMR spectroscopy. Both starting materials were present in near-stoichiometric amounts (assign-ments at $\delta = 65$ ppm for Mo(N[R]Ar)$_3$ and $\delta = 2.2$ ppm for [Na(12-crown-4)$_2$][(N$_2$)Mo(N[R]Ar)$_3$]). A small amount of the neutral bridged complex (μ-N$_2$){Mo(N[R]Ar)$_3$}$_2$ was observed ($\delta = 13$ ppm). No other resonances were observed. Upon standing at 25 °C, the resonance at 13 ppm decayed to a new peak at 2 ppm, consistent with formation of N≡Mo(N[R]Ar)$_3$ (the signals for diamagnetic [Na(12-crown-4)$_2$][(N$_2$)-Mo(N[R]Ar)$_3$] and N≡Mo(N[R]Ar)$_3$ are coincident by ^{2}H NMR spectroscopy). The relative ratios of starting Mo(N[R]Ar)$_3$ and [Na-(12-crown-4)$_2$][(N$_2$)Mo(N[R]Ar)$_3$] remained constant over a period of 24 h at 25 °C. This experiment was repeated several times and always showed small but varying amounts of **3**. A signal assignable to [Na-(12-crown-4)$_2$][(μ-N$_2$){Mo(N[R]Ar)$_3$}$_2$] was not spectroscopically ob-served. A similar experiment performed with the ion-pair species [(THF)$_x$Na][(N$_2$)Mo(N[R]Ar)$_3$] and Mo(N[R]Ar)$_3$ behaved analogously.

Synthesis of (Me$_3$SiNN)Mo(N[R]Ar)$_3$ (12). Sodium amalgam (1%, 10 equiv) was prepared by dissolving Na metal (107.0 mg, 4.652 mmol) in Hg (10.1877 g) in a 20-mL scintillation vial. Chlorotrimethylsilane

(358.0 mg, 3.295 mmol) was dissolved in THF and added to the amalgam. While stirring, solid orange Mo(N[R]Ar)₃ (302.1 mg, 0.4702 mmol) was added to the reaction mixture at 25 °C under a dinitrogen atmosphere. The orange solution gradually turned yellow-brown. After 6 h, the reaction mixture was filtered through Celite removing a gray solid. The filtrate was dried in vacuo to a yellow-brown residue. Spectroscopic analysis (^{1}H, ^{2}H NMR) of the crude material showed a relatively clean transformation to a single diamagnetic product. The crude product was redissolved in pentane and filtered again through Celite to ensure complete removal of salts. Removal of solvent and recrystallization from pentane at −35 °C afforded 275.3 mg (79%) of an orange, crystalline material: ^{1}H NMR (300 MHz, C₆D₆, 25 °C) δ = 6.07 (s, *4*), 6.64 (s, *5*), 2.07 (s, *3*), 1.50 (s, *1*), 0.49 (s, 9H, Si*Me₃*); ^{13}C NMR (125.66 MHz, C₆D₆, 25 °C) δ 150.11 (aryl), 137.60 (aryl), 130.89 (aryl), 124.3 (aryl), 63.5 (*6*), 33.37 (*1*), 32.5 (*2*), 21.84 (*3*), 3.57 (Si*Me₃*); FTIR (THF, KBr) ν_{NN} 1650 cm⁻¹. Anal. Calcd for C₃₉H₄₅D₁₈N₅-MoSi: C, 62.95; H, 8.53; N, 9.41. Found: C, 63.18; H, 8.62; N, 9.49.

X-ray Structure of (Me₃SiNN)Mo(N[R]Ar)₃ (12). Orange crystals were grown slowly from a pentane solution at −35 °C. The crystals were quickly moved from a scintillation vial to a microscope slide containing Paratone N. Under the microscope, an orange plate was selected and mounted on a glass fiber using wax. A total of 16 637 reflections were collected (−12 ≤ h ≤ 16, −10 ≤ k ≤ 14, −23 ≤ l ≤ 22) in the θ range of 1.81−23.26° of which 5976 were unique (R_{int} = 0.0241). The structure was solved by direct methods in conjunction with standard difference Fourier techniques. Hydrogen atoms were placed in calculated ($d_{C−H}$ = 0.96 Å) positions. The largest peak and hole in the difference map were 0.411 and −0.275 e·Å⁻³, respectively. No absorption correction was applied. The least-squares refinement converged normally with residuals of R (based on F) = 0.0287, wR (based on F^2) = 0.0798, and GOF = 1.020 (based upon I > 2σ(I)). Crystal data for C₃₉H₆₃MoN₅Si: monoclinic, space group = P2₁/c, z = 4, a = 15.03890(10) Å, b = 13.3531(2) Å, c = 20.7912(2) Å, α = 90°, β = 91.23°, γ = 90°, V = 4174.24(8) Å³, ρ_{calc} = 1.155 g·cm⁻³, F(000) = 1552.

Synthesis of [(Me₂NN)Mo(N[R]Ar)₃][OTf] (21). Methyl triflate (MeOTf, where OTf = [O₃SCF₃]) was weighed as a liquid (347 mg, 2.116 mmol) into a 20-mL scintillation vial and subsequently dissolved by stirring in pentane (5 mL). Solid orange (Me₃SiNN)Mo(N[R]Ar)₃ (**12**; 258 mg, 0.346 mmol) was added, at once, to the stirring solution of MeOTf at 22 °C. The resulting golden solution gradually deposited a red-orange precipitate over a period of 6 h. The precipitate was collected on a sintered glass frit, washed with pentane, and dried in vacuo. This first crop of 233 mg (79%) was judged to be both spectroscopically and analytically pure: ^{1}H NMR (300 MHz, C₆D₆, 25 °C) δ 6.65 (s, *5*), 6.25 (s, *4*), 3.73 (s, MoNN*Me₂*), 2.11 (s, *3*), 1.06 (s, *1*); ^{13}C NMR (125.66 MHz, C₆D₆, 25 °C) δ 147.82 (aryl), 138.52 (aryl), 129.63 (aryl), 65.32 (*6*), 46.25 (Mo(NN*Me₂*), 30.78 (*1*), 30.15 (*2*), 21.28 (*3*); ^{19}F NMR (300 MHz, C₆D₆, 20 °C) δ −76.92 (O₃SCF₃). Anal. Calcd for C₃₉H₄₂D₁₈F₃MoN₅O₃: C, 55.11; H, 7.11; N, 8.24. Found: C, 55.32; H, 6.63; N, 8.12.

Na/Hg Reduction of [(Me₂NN)Mo(N[R]Ar)₃][OTf] (21). In an isolated reaction vessel, [(Me₂NN)Mo(N[R]Ar)₃][OTf] (**21**; 27 mg, 0.032 mmol) was stirred over a 0.5% Na/Hg (1.0 mg, 0.043 mmol of Na; and 197 mg of Hg) in C₆D₆. After stirring at 22 °C for 3 h, the volatiles were vacuum-transferred to a sealable NMR tube. The NMR tube was flame-sealed, and spectroscopic analysis (^{1}H, ^{13}C NMR) of the isolated volatiles indicated that dimethylamine (HNMe₂) was produced cleanly. This was verified by comparison to spectra of an authentic sample of HNMe₂. Workup of the nonvolatile products consisted of redissolving the remaining residue in THF and filtering through Celite to remove an insoluble gray material. The filtrate was dried in vacuo, producing a pale beige solid. This solid was extracted into pentane, filtered through Celite, and dried in vacuo to a weight of

18.7 mg. Spectroscopic analysis verified this beige solid to be pure N≡Mo(N[R]Ar)₃ (**4**; isolated in ~88% yield).

One-Pot Synthesis of (MeNN)Mo(N[R]Ar)₃ (22). The predried THF used in this protocol was filtered through a column of activated alumina just prior to use. A 0.5% Na/Hg was prepared by slowly dissolving sodium (331 mg, 14.41 mmol) in mercury (64 g) in a 250-mL Erlenmeyer flask equipped with a stir bar. The amalgam was allowed to cool and then a solution of methyl tosylate, CH₃SO₃−*p*-C₆H₄Me (869 mg, 4.67 mmol), dissolved in THF (5 mL) was added to it. An orange solution of Mo(N[R]Ar)₃ (**1**; 870 mg, 0.467 mmol) dissolved in THF (25 mL) was added dropwise to the stirring reaction mixture over a period of 1.5 h. The reaction mixture was allowed to stir an additional 2.5 h, maintaining a red-yellow color throughout. A gray residue was then removed by filtration of the reaction mixture through Celite. The filtrate was dried in vacuo, affording a yellow-red solid. This solid was redissolved in pentane and once again filtered through Celite to remove a small amount of additional gray material. Subsequent drying of the filtrate in vacuo produced 287 mg of a crude product which was yellow-red. Spectroscopic analysis (^{1}H, ^{2}H NMR) of this crude material showed a single ligand environment and some ligand degradation byproduct, HN(R)Ar. Purification for elemental analysis was not achieved using this synthetic protocol, but see the section below on synthesis of **23** for a successful synthesis of the pure material: ^{1}H NMR (300 MHz, C₆D₆, 25 °C) δ 6.68 (s, *5*), 6.29 (s, *4*), 3.75 (s, MoNN*Me*), 2.11 (s, *3*), 1.45 (s, *1*); FTIR (THF, KBr) ν_{NN} 1539 cm⁻¹ (br).

Synthesis of (MeNN)Mo(N[ᵗBu]Ar)₃ (23). A solution of **9** (1.121 g, 1.66 mmol) in 12 mL of diethyl ether was prepared. To the solution was added methyl tosylate (309 mg, 1.66 mmol) as a solution in ether (3 mL) at 25 °C. After 2 h, the mixture was filtered through Celite on a sintered glass frit. Volatile material was removed from the filtrate, producing a brown-orange solid residue. The residue was extracted into pentane, the extract was filtered through Celite, and volatile material was again removed in vacuo. The crude product thus obtained was spectroscopically pure (^{1}H NMR) and the yield was 89% (986 mg). Further purification was achieved by dissolution in pentane (6 mL), followed by cooling to ~−70 °C. The resulting analytically pure precipitate was collected and dried. Crystals of **23** were grown by storing the mother liquor at −30 °C for 24 h: ^{1}H NMR (300 MHz, C₆D₆) δ 6.68 (*5*), 6.29 (*4*), 3.74 (N₂C*H₃*), 2.11 (*3*), 1.45 (*1*). ^{13}C NMR (125.66 MHz, C₆D₆, 25 °C): δ 150.3 (aryl *ipso*), 137.7 (*4*), 130.7 (*5*), 128.0 (*8*), 62.6 (*6*), 43.8 (N₂C*H₃*), 32.9 (*1*), 21.9 (*3*); FTIR (KBr windows, THF solution) ν_{NN} 1538 cm⁻¹ also 1585, 1285, 1276, 1146, 701, 638, 572 cm⁻¹. Anal. Calcd for C₃₇H₅₇N₅Mo: C, 66.54; H, 8.60; N, 10.49. Found: C, 66.67; H, 8.68; N, 10.41.

Supporting Information Available: Tables of bond lengths, bond angles, atomic coordinates, and anisotropic displacement parameters for the structures of **7**, (Ph[ᵗBu]N)₃Ti(μ-N₂)Mo(N[R]-Ar)₃ (**14**), (Me₃SiNN)Mo(N[R]Ar)₃ (**12**), Mo(N[Ad]Ar)₃ (**16**), and [(THF)ₓNa][(N₂)Mo(N[Ad]Ar)₃] (**18**); the details of the structure of **7** have been deposited with the Cambridge Crystal-lographic Database. This information is available free of charge via the Internet at http://pubs.acs.org.

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