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Alkylation of Dinitrogen in $[(HIPTNCH_2CH_2)_3N]Mo$ Complexes (HIPT = 3,5-(2,4,6-*i*-$Pr_3C_6H_2)_2C_6H_3$)

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Abstract: In this paper we explore the ethylation of dinitrogen (employing $[Et_3O][BAr^f_4]$; Ar^f = 3,5-$(CF_3)_2C_6H_3$) in $[HIPTN_3N]Mo$ (**Mo**) complexes ($[HIPTN_3N]^{3-}$ = $[N(CH_2CH_2NHIPT)_3]^{3-}$; HIPT = 3,5-(2,4,6-*i*-$Pr_3C_6H_2)_2C_6H_3$) with the objective of developing a catalytic cycle for the conversion of dinitrogen into triethylamine. A number of possible intermediates in a hypothetical catalytic cycle have been isolated and characterized: **Mo**N=NEt, [**Mo**=$NNEt_2$][BAr^f_4], **Mo**=$NNEt_2$, [**Mo**=NEt][BAr^f_4], **Mo**=NEt, **Mo**NEt_2, and [**Mo**(NEt_3)][BAr^f_4]. Except for **Mo**NEt_2, all compounds were synthesized from other proposed intermediates in a hypothetical catalytic reaction. All alkylated species are significantly more stable than their protonated counterparts, especially the Mo(V) species, **Mo**=$NNEt_2$ and **Mo**=NEt. The tendency for both **Mo**=$NNEt_2$ and **Mo**=NEt to be readily oxidized by $[Et_3O][BAr^f_4]$ (as well as by $[H(Et_2O)_2][BAr^f_4]$, [**Mo**=NNH_2][BAr^f_4], and [**Mo**=NH][BAr^f_4]) suggests that their alkylation is unlikely to be part of a catalytic cycle. All efforts to generate NEt_3 in several stoichiometric or catalytic runs employing **Mo**N_2 and **Mo**≡N as starting materials were unsuccessful, in part because of the slow speed of most alkylations relative to protonations. In related chemistry that employs a ligand containing 3,5-(4-*t*-$BuC_6H_4)_2C_6H_3$ amido substituents alkylations were much faster, but a preliminary exploration revealed no evidence of catalytic formation of triethylamine.

Introduction

Ever since the discovery of the first transition metal dinitrogen complex, $[Ru(NH_3)_5(N_2)]^{2+}$,[1] scientists have been trying to reduce dinitrogen to ammonia or to prepare organic compounds from dinitrogen under mild conditions. Although the groups of Chatt and Hidai made significant advances toward the catalytic reduction of dinitrogen to ammonia,[2−9] no catalytic reduction under mild conditions was achieved. Chatt proposed that coordination of dinitrogen to the appropriate single metal could activate it toward addition of the first proton or electron and that subsequent alternating addition of a proton and an electron would result in formation of 2 equiv of ammonia.

Two systems are known in which dinitrogen is reduced under mild conditions. The first is one in which dinitrogen is reduced catalytically to a ∼10:1 mixture of hydrazine and ammonia in methanol employing a relatively strong reducing agent such as sodium amalgam.[10] The reaction requires molybdenum and is catalytic with respect to it. Hydrazine is the primary product, with ammonia being formed through a metal-catalyzed disproportionation of hydrazine to dinitrogen and ammonia. Shilov proposed that dinitrogen is bound and reduced to hydrazine between two metal centers.

The second system catalytically reduces dinitrogen to ammonia as the primary product at a molybdenum center in a complex that contains the $[HIPTN_3N]^{3-}$ ligand, where HIPT = 3,5-(2,4,6-*i*-$Pr_3C_6H_2)_2C_6H_3$ (HexaIsoPropylTerphenyl; see Figure 1).[11−18] The $[HIPTN_3N]^{3-}$ ligand discourages bimetallic chemistry by sterically protecting the metal coordination site and also provides increased solubility of Mo complexes in nonpolar solvents. The proposed catalytic reduction of dinitrogen to ammonia that involves $[HIPTN_3N]Mo$ complexes is shown in Figure 2 (R = H; $[HIPTN_3N]Mo$ = **Mo**). The oxidation states of molybdenum in the system range from Mo(III) to Mo(VI). Eight of these intermediates have been prepared and crystallographically characterized: **Mo**N_2, [**Mo**N_2]$^-$, **Mo**-N=NH, [**Mo**-N=NH_2]$^+$, **Mo**≡N, [**Mo**≡NH]$^+$, [**Mo**(NH_3)]$^+$, and **Mo**(NH_3). All hypothetical compounds that could not be observed and/or isolated were Mo(V) species, e.g., **Mo**=N-NH_2 (not observed)

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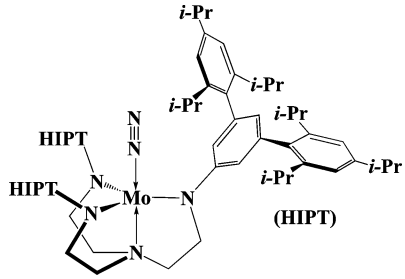

Figure 1. Drawing of **Mo**N_2.

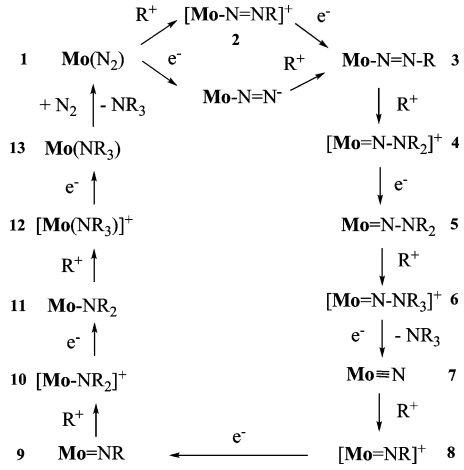

Figure 2. Possible intermediates in the reduction of dinitrogen to ammonia or a trialkylamine at a **Mo** center through the stepwise addition of R^+ (R = H or alkyl, respectively) and electrons.

and **Mo**=NH (observed, but not isolable). Calculations by Reiher and his group on complexes with the full $[HIPTN_3N]^{3-}$ ligand set are consistent with the proposed catalytic scheme.[19−21] Turnover employing $CrCp^*_2$ as the reducing agent and [2,6-Lut][BAr^f_4] (Ar^f = 3,5-$(CF_3)_2C_6H_3$) as the proton source in heptane is limited to approximately 4 equiv of dinitrogen out of a possible six, as a consequence, it is proposed, of the $[HIPTN_3N]^{3-}$ ligand being removed from the metal under catalytic conditions. The only other product of the catalytic reduction is dihydrogen.

We became interested in alkylation of dinitrogen and its derivatives in the $[HIPTN_3N]$Mo system for two reasons. First, alkylated dinitrogen and related ligands are likely to be much more robust than their protonated counterparts, a result that might lead to a more detailed understanding of the catalytic reduction of dinitrogen to ammonia. Second, trialkylamines might be synthesized directly from dinitrogen via a set of intermediates analogous to that proposed for reduction to ammonia (Figure 2; R = alkyl). Transition-metal-mediated reduction of dinitrogen to form amines under homogeneous catalysis conditions has been reported by Hidai[22] and by Mori.[23] Both processes require alkali metals as reducing agents, and mechanistic details are unknown. Although alkylations of dinitrogen and reduced dinitrogen fragments have been explored in the chemistry of relatively low oxidation state molybdenum and tungsten dinitrogen complexes,[2,5] similar alkylations of relatively high oxidation state molybdenum-based triamidoamine complexes has been investigated only sporadically.[24−26] In this paper we explore the possibility that triethylamine might be prepared catalytically in the $[HIPTN_3N]$Mo system.

Results and Discussion

Synthesis of [Et_3O][BAr^f_4]. The proton source that was chosen for the catalytic reduction of dinitrogen by $[HIPTN_3N]$Mo catalysts was [2,6-Lut][BAr^f_4] (2,6-Lut = 2,6-dimethylpyridinium). Since [2,6-Lut][BAr^f_4] is relatively insoluble in heptane (the reaction solvent), the direct reduction of protons to H_2 by $CrCp^*_2$, the reducing agent that is slowly added to the mixture, is minimized. Alkylating agents that contain the $[BAr^f_4]^-$ anion would be most desirable as they would perturb the system minimally. Therefore we turned to the possibility of employing [R_3O][BAr^f_4] reagents. All attempts to prepare [Me_3O][BAr^f_4] by treating commercially available [Me_3O][BF_4] with Na[BAr^f_4] under various conditions yielded only complex mixtures. [Et_3O][$B(C_6F_5)_4$] has been mentioned briefly in the literature, although experimental details of its synthesis were not provided.[27] The reaction between [Et_3O][BF_4] and 1.05 equiv of Na[BAr^f_4] proceeded smoothly in diethyl ether over a period of 3 days to give [Et_3O][BAr^f_4] in yields of 90−95% as a white solid. [Et_3O][BAr^f_4] became the reagent of choice for exploring dinitrogen alkylation reactions.

Synthesis of MoN=NEt. The first plausible intermediate in a hypothetical catalytic alkylation that begins with **Mo**N_2 is **Mo**N=NEt (**3** in Figure 2; R = Et). Diamagnetic **Mo**N=NEt is accessible through reduction of **Mo**Cl with excess Na sand under 1 atm of dry N_2 in THF to give $[\mathbf{Mo}N_2]^-$ in situ, followed by addition of [Et_3O][BAr^f_4] in diethyl ether; **Mo**N=NEt prepared in this manner can be isolated in a moderate yield (42%). The yield of **Mo**N=NEt is higher (69%) when [Bu_4N][**Mo**N_2] is first prepared and purified and then treated with [Et_3O][BAr^f_4] in ether (eq 1); this is the preferred method. **Mo**N=NEt also is obtained in 54% yield from **Mo**N_2, [Et_3O][BAr^f_4], and $CrCp^*_2$ in benzene at room temperature after 2 days. After recrystallization from heptane, **Mo**N=NEt was isolated as a pale yellow, crystalline solid.

$$[Bu_4N][\mathbf{Mo}N_2] + [Et_3O][BAr^f_4] \rightarrow \mathbf{Mo}N{=}NEt + [Bu_4N][BAr^f_4] + Et_2O \quad (1)$$

The ^{1}H NMR spectrum of **Mo**N=NEt in C_6D_6 displays a triplet at 0.87 ppm and a quartet at 3.31 ppm for the ethyl group, as well as the expected resonances for the $[HIPTN_3N]$Mo core. **Mo**N=NEt can be heated to 80 °C for several days in solution with no sign of decomposition. (**Mo**N=NH is known to decompose to **Mo**H under similar conditions.[16]) The oxidation of **Mo**N=NEt is fully reversible in PhF (0.1 M [Bu_4N][BAr^f_4]; $E_{1/2}$ = −0.18 V vs Fc/Fc^+) at scan rates between 50 and 700 mV/s (Table 1; Figure 3); the oxidized species is assigned as $[\mathbf{Mo}N{=}NEt]^+$. In contrast, oxidation of **Mo**N=NH begins near 0 V but is irreversible.[17] Attempts to prepare [**Mo**N=

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Table 1. Electrochemical Properties of Selected Protonated and Alkylated **Mo** Species[a]

couple	$E_{1/2}$ [V]	couple	$E_{1/2}$ [V]
$[\mathbf{Mo}{\equiv}NEt]^{+/0}$	–0.18	$[\mathbf{Mo}{\equiv}NH]^{+/0}$	$\sim 0^{d}$
$[\mathbf{Mo}{\equiv}NNEt_2]^{+/0}$	–1.76[b]	$[\mathbf{Mo}{\equiv}NNH_2]^{+/0}$	–1.56[e]
$[\mathbf{Mo}{\equiv}NEt]^{+/0}$	–1.64[c]	$[\mathbf{Mo}{\equiv}NH]^{+/0}$	–1.38[e]
$[\mathbf{Mo}NEt_2]^{+/0}$	–0.98		
$[\mathbf{Mo}(EtNH_2)]^{+/0}$	–1.83	$[\mathbf{Mo}(NH_3)]^{+/0}$	–1.63
$CrCp^*_2$	–1.63	$CoCp^*_2$	–2.01

[a] Potentials measured by cyclic voltammetry in 0.1 M $[Bu_4N][BAr^f_4]$ in PhF at a 3.0 mm glassy carbon disk under Ar and referenced to Fc/Fc^+. [b] Irreversible process ($I_{pc} = -1.87$ V). [c] Irreversible process for $[\mathbf{Mo}{\equiv}NEt][BAr^f_4]$ ($I_{pc} = -1.82$ V); reversible process for **Mo**≡NEt. [d] Onset of multiple irreversible oxidation waves. [e] Quasi-reversible process.

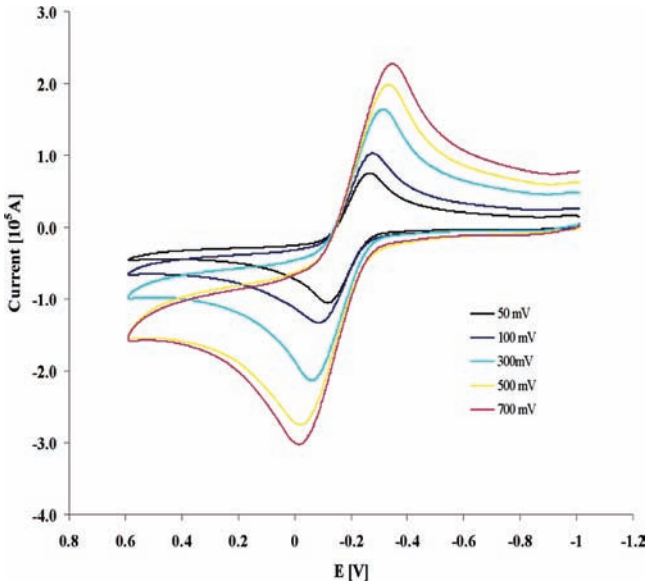

Figure 3. Cyclic voltammograms of **Mo**≡NEt in PhF (0.1 M $[Bu_4N][BAr^f_4]$ vs $FeCp_2/[FeCp_2]^+$).

$NEt][BAr^f_4]$ through oxidation of **Mo**≡NEt with $[Fc][BAr^f_4]$ ($Fc = FeCp_2$) or silver salts such as $Ag[BAr^f_4]$ in benzene, diethyl ether, or methylene chloride have been unsuccessful; only immediate decomposition to unidentified species was observed.

Two plausible products in a reaction between $\mathbf{Mo}N_2$ and $[Et_3O][BAr^f_4]$ are $[\mathbf{Mo}{\equiv}NEt][BAr^f_4]$ (**2** in Figure 2; R = Et) or a species in which an amido nitrogen is alkylated. The latter would be analogous to an unstable and potentially important intermediate observed when $\mathbf{Mo}N_2$ is treated with $[LutH][BAr^f_4]$ in fluorobenzene,[17] in which an amido nitrogen has been protonated. However, under a variety of conditions (solvent, temperature, stoichiometry) no significant amounts (<10%) of any identifiable alkylated species were formed. Since alkylation of an amido nitrogen is not likely to be reversible, the synthesis of **Mo**≡NEt from $\mathbf{Mo}N_2$, $[Et_3O][BAr^f_4]$, and $CrCp^*_2$ in benzene at room temperature noted above must proceed either through formation first of a small amount of $[\mathbf{Mo}{\equiv}NEt]^+$ (followed by reduction) or a small amount of $[\mathbf{Mo}N_2]^-$ (followed by alkylation).

Synthesis and Reduction of $[\mathbf{Mo}{\equiv}NNEt_2][BAr^f_4]$. Alkylation of **Mo**≡NEt with 1 equiv of $[Et_3O][BAr^f_4]$ in CH_2Cl_2 afforded diamagnetic $[\mathbf{Mo}{\equiv}NNEt_2][BAr^f_4]$ as an orange solid in 89% isolated yield (eq 2). According to ^1H NMR spectroscopy of the reaction mixture, the conversion proceeds without formation of any significant side products. The reaction is complete within 10−15 min at initial concentrations of 0.047 M in **Mo**≡NEt and $[Et_3O][BAr^f_4]$ and within 1 h at initial concentrations of 0.024 M of each. Disappearance of the proton resonances for $[Et_3O][BAr^f_4]$ were monitored by ^1H NMR in order to obtain a second-order rate constant of $k_2 = 0.23$ L mol^{-1} s^{-1}. The cyclic voltammogram of $[\mathbf{Mo}{\equiv}NNEt_2][BAr^f_4]$ in PhF (0.1 M $[Bu_4N][BAr^f_4]$) at a scan rate of 50 mV/s reveals an irreversible reduction at −1.87 V (I_{pc}; $E_{1/2} = -1.76$ V; vs Fc/Fc^+), which we assign to the $[\mathbf{Mo}{\equiv}NNEt_2]^{+/0}$ couple. This couple is shifted by about ∼200−300 mV compared to the $[\mathbf{Mo}{\equiv}NNH_2]^{+/0}$ couple (Table 1).[17] Like most of the other **Mo** compounds described here, $[\mathbf{Mo}{\equiv}NNEt_2][BAr^f_4]$ is highly soluble even in pentane, and X-ray quality crystals could not be obtained.

$$\mathbf{Mo}{\equiv}NEt + [Et_3O][BAr^f_4] \xrightarrow{Et_2O} [\mathbf{Mo}{\equiv}NNEt_2][BAr^f_4] \quad (2)$$

Reduction of $[\mathbf{Mo}{\equiv}NNEt_2][BAr^f_4]$ with 1 equiv of $CrCp^*_2$ in benzene yielded $[CrCp^*_2][BAr^f_4]$ and a red, paramagnetic species in ∼90% yield according to ^1H NMR spectroscopy of the reaction mixture (eq 3). This species is tentatively assigned as the neutral Mo(V) hydrazido complex, $\mathbf{Mo}{\equiv}NNEt_2$; $\mathbf{Mo}{\equiv}NNEt_2$ is much more stable than $\mathbf{Mo}{\equiv}NNH_2$, which cannot be observed upon attempts to generate it in situ.[17] The ^1H NMR spectrum of $\mathbf{Mo}{\equiv}NNEt_2$ displays only broad peaks in the diamagnetic region and no characteristic paramagnetically shifted resonances. Attempts to obtain analytically pure material have failed so far, in part because traces of $CrCp^*_2$ and $[CrCp^*_2][BAr^f_4]$ are present, but also because $\mathbf{Mo}{\equiv}NNEt_2$ decomposes slowly in solution over a period of days. Attempts to alkylate $\mathbf{Mo}{\equiv}NNEt_2$ with $[Et_3O][BAr^f_4]$ (**5** → **6** in Figure 2) resulted only in one-electron oxidation of $\mathbf{Mo}{\equiv}NNEt_2$ to reform $[\mathbf{Mo}{\equiv}NNEt_2][BAr^f_4]$ in 90−95% yield and butane, which was observed by ^1H NMR spectroscopy of the volatile products. As the electrochemical potentials suggest, $[\mathbf{Mo}{\equiv}NNH_2][BAr^f_4]$ should oxidize $\mathbf{Mo}{\equiv}NNEt_2$. It does so readily (eq 4). $\mathbf{Mo}{\equiv}NNEt_2$ is also oxidized by $[H(OEt_2)_2][BAr^f_4]$ in C_6D_6 and CD_2Cl_2 in virtually 100% yield.

$$[\mathbf{Mo}{\equiv}NNEt_2][BAr^f_4] + CrCp^*_2 \rightarrow \mathbf{Mo}{\equiv}NNEt_2 + [CrCp^*_2][BAr^f_4] \quad (3)$$

$$\mathbf{Mo} = NNEt_2 + [\mathbf{Mo}{\equiv}NNH_2][BAr^f_4] \rightarrow [\mathbf{Mo}{\equiv}NNEt_2][BAr^f_4] + \mathbf{Mo}{\equiv}NNH_2 \quad (4)$$

Synthesis of $[\mathbf{Mo}{\equiv}NEt][BAr^f_4]$ and Mo≡NEt. Treatment of **Mo**≡N with 1 equiv of $[Et_3O][BAr^f_4]$ in CH_2Cl_2 cleanly afforded diamagnetic $[\mathbf{Mo}{\equiv}NEt][BAr^f_4]$ in high yields (up to 93%) as the only product (eq 5). The reaction required about 13 h to go to completion at initial concentrations of 0.047 M.

$$\mathbf{Mo}{\equiv}N + [Et_3O][BAr^f_4] \xrightarrow{Et_2O} [\mathbf{Mo}{\equiv}NEt][BAr^f_4] \quad (5)$$

$[\mathbf{Mo}{\equiv}NEt][BAr^f_4]$ was isolated as an orange solid. The high solubility of $[\mathbf{Mo}{\equiv}NEt][BAr^f_4]$ in all common solvents and therefore failure to obtain single crystals suitable for an X-ray study again prevented structural elucidation. The electrochemistry of $[\mathbf{Mo}{\equiv}NEt][BAr^f_4]$ is comparable to that observed for $[\mathbf{Mo}{\equiv}NNEt_2][BAr^f_4]$. An irreversible reduction is observed at −1.82 V at a scan rate of 50 mV/s (I_{pc}; $E_{1/2} = -1.64$ V vs

Fc/Fc^+; recorded in PhF and 0.1 M $[Bu_4N][BAr^f_4]$); we assign this reduction to the $[\mathbf{Mo}{=}NEt]^{+/0}$ couple.

Despite the irreversible $[\mathbf{Mo}{=}NEt]^{+/0}$ couple observed in the CV of $[\mathbf{Mo}{=}NEt][BAr^f_4]$, $[\mathbf{Mo}{=}NEt][BAr^f_4]$ can be reduced with 1 equiv of $CrCp^*_2$ in benzene to give analytically pure **Mo**=NEt in virtually 100% yield (eq 6). **Mo**=NEt is stable both in the solid state and in solution over a period of several weeks at room temperature. The stability of **Mo**=NEt contrasts with the instability of **Mo**=NH,[17] which is prone to decomposition in the absence of excess reducing agent to form **Mo**≡N and $[\mathbf{Mo}(NH_3)]^+$. As expected for a paramagnetic Mo(V) d^1 species, the ^{1}H NMR Spectrum of **Mo**=NEt shows only broad resonances in the diamagnetic region. No characteristic, paramagnetically shifted resonances for either the ethylene backbone or the ethyl protons could be observed readily at room temperature. The electrochemical oxidation of **Mo**=NEt to $[\mathbf{Mo}{=}NEt]^+$ is fully reversible in PhF ($E_{1/2} = -1.64$ V vs Fc/Fc^+; 0.1 M $[Bu_4N][BAr^f_4]$, Table 1). We cannot explain why the reduction of $[\mathbf{Mo}{=}NEt][BAr^f_4]$ is irreversible (vide supra), while the oxidation of **Mo**=NEt is reversible.

$$[\mathbf{Mo}{=}NEt][BAr^f_4] \xrightarrow[-\,[CrCp^*_2][BAr^f_4]]{+\,CrCp^*_2} \mathbf{Mo}{=}NEt \qquad (6)$$

The reactivity of **Mo**=NEt toward protonation and alkylation is comparable to that observed for **Mo**=$NNEt_2$ described above. The reaction between **Mo**=NEt and 1 equiv of $[Et_3O][BAr^f_4]$ in various solvents at various temperatures only led to clean oxidation of **Mo**=NEt to $[\mathbf{Mo}{=}NEt][BAr^f_4]$ and formation of butane (by proton NMR; not quantitated). No evidence for formation of $[\mathbf{Mo}NEt_2][BAr^f_4]$ was obtained. Addition of $[H(OEt_2)_2][BAr^f_4]$ to **Mo**=NEt in C_6D_6 and CD_2Cl_2 also led simply to oxidation of **Mo**=NEt to $[\mathbf{Mo}{=}NEt][BAr^f_4]$. As expected on the basis of electrochemical potentials (Table 1), **Mo**=NEt readily reduces $[\mathbf{Mo}{=}NH][BAr^f_4]$ in benzene.

Synthesis of Cationic $[Mo(amine)]^+$ Complexes. We turned to reactions between **Mo**Cl and $Na[BAr_4]$ (Ar = Ph, Ar^f) in the presence of NR_3, R_2NH, or RNH_2 (R = Me, Et) in order to determine whether the crowded HIPT system would allow alkyl amines to coordinate to the metal, just as ammonia does.

$[\mathbf{Mo}(EtNH_2)][BAr^f_4]$ was isolated as a red-brown, crystalline solid in good yield (75%) as shown in eq 7 (amine = $EtNH_2$). Its ^{1}H NMR spectrum displays paramagentically shifted resonances for the ethylene backbone at −16.6 and − 98.9 ppm. Reduction of $[\mathbf{Mo}(EtNH_2)][BAr^f_4]$ with 1 equiv of $CrCp^*_2$ in C_6D_6 under 1 atm of N_2 afforded **Mo**N_2, $[CrCp^*_2][BAr^f_4]$, and free $EtNH_2$ in less than 15 min. The complete exchange of the ethylamine ligand in presumed intermediate $\mathbf{Mo}(EtNH_2)$ by dinitrogen contrasts with what is found for the reaction between $\mathbf{Mo}(NH_3)$ and N_2, a reaction for which $K_{eq} = 1.16(6)$ in benzene at 22 °C.[17] Whether the reaction between $\mathbf{Mo}(EtNH_2)$ and dinitrogen is zero order or first order in dinitrogen (as it is for the reaction between $\mathbf{Mo}(NH_3)$ and N_2) is not known. The CV of $[\mathbf{Mo}(EtNH_2)][BAr^f_4]$ under argon shows a quasireversible reduction couple in PhF ($E_{1/2} = -1.83$ V; 0.1 M $[Bu_4N][BAr^f_4]$; Table 1) that we assign as $[\mathbf{Mo}(EtNH_2)]^{+/0}$. Interestingly, even though $CrCp^*_2$ is technically not a good enough reducing agent in PhF to accomplish the reduction of $[\mathbf{Mo}(EtNH_2)][BAr^f_4]$ ($E_{1/2} = -1.63$ V; Table 1), the reduction proceeds quantitatively. Evidently precipitation of $[CrCp^*_2][BAr^f_4]$ provides the additional driving force to complete the reduction in PhF.[12,13,15,17,18] $[\mathbf{Mo}(MeNH_2)][BAr^f_4]$ and $[\mathbf{Mo}(Me_2NH)][BAr^f_4]$ could be generated and characterized in situ through ^{1}H NMR spectroscopy of the reaction mixtures by methods analogous to that shown in eq 7.

$$\mathbf{Mo}Cl \xrightarrow[-\,NaCl]{+\,Na[BAr^f_4]\,+\,amine} [\mathbf{Mo}(amine)][BAr^f_4] \qquad (7)$$

Reactions similar to that shown in eq 7 that involve Et_2NH, Et_3N, and Me_3N did not yield any $[\mathbf{Mo}(amine)][BAr^f_4]$ over a period of several days, even at elevated temperatures. We ascribe the failure to produce these $[\mathbf{Mo}(amine)][BAr^f_4]$ species by methods analogous to that shown in eq 7 to a failure to form what is proposed to be the required **Mo**(Cl)(amine) intermediate. We therefore turned to alternative approaches.

A successful synthesis of $[\mathbf{Mo}(Et_2NH)][BAr^f_4]$ is analogous to the reaction between **Mo**H and [2,6-LutH][$B(C_6F_5)_4$] to yield $[\mathbf{Mo}(2,6\text{-LutH})][B(C_6F_5)_4]$.[17] $[Et_2NH_2][BAr^f_4]$ and $[Et_3NH][BAr^f_4]$ were prepared by salt metathesis reactions of $Na[BAr^f_4]$ with either $[NEt_2H_2]Cl$ or $[Et_3NH]Cl$, respectively, and isolated as white solids in high yields. Treatment of a benzene solution of **Mo**H with 1.1 equiv of $[Et_2NH_2][BAr^f_4]$ at room temperature smoothly afforded $[\mathbf{Mo}(Et_2NH)][BAr^f_4]$ within 2 h (eq 8). $[\mathbf{Mo}(Et_2NH)][BAr^f_4]$ is the sole **Mo** species present at any significant concentration in the crude reaction mixture. $[\mathbf{Mo}(Et_2NH)][BAr^f_4]$ was isolated as an analytically pure red, crystalline solid in yields up to 84% after recrystallization from pentane. The ^{1}H NMR spectrum of $[\mathbf{Mo}(Et_2NH)][BAr^f_4]$ in C_6D_6 features two paramagnetically shifted resonances at −9.8 and −88.3 ppm, similar to those observed for the ethylene backbone protons in $[\mathbf{Mo}(EtNH_2)][BAr^f_4]$ (vide supra). The reduction of $[\mathbf{Mo}(Et_2NH)][BAr^f_4]$ with 1 equiv of $CrCp^*_2$ in C_6D_6 under 1 atm of N_2 produced $[CrCp^*_2][BAr^f_4]$, **Mo**N_2, and free Et_2NH within 15 min, as judged by ^{1}H NMR spectroscopy of the reaction mixture. The presumed intermediate ($\mathbf{Mo}(Et_2NH)$) was not observed.

$$\mathbf{Mo}H \xrightarrow[-\,H_2]{+\,[Et_2NH_2][BAr^f_4]} [\mathbf{Mo}(Et_2NH)][BAr^f_4] \qquad (8)$$

All efforts to prepare $[\mathbf{Mo}(NEt_3)][BAr^f_4]$ in a reaction between **Mo**H and $[Et_3NH][BAr^f_4]$ in several solvents (C_6H_6, CH_2Cl_2, PhF, NEt_3) were not successful, even at temperatures up to 100 °C.

Synthesis and Characterization of $MoNEt_2$. Because we could not prepare $[\mathbf{Mo}NEt_2][BAr^f_4]$ through the reaction of **Mo**=NEt with $[Et_3O][BAr^f_4]$ (vide supra), we did not have the option to prepare **Mo**NEt_2 through reduction of $[\mathbf{Mo}NEt_2]^+$. Therefore we had to devise an alternative synthesis of **Mo**NEt_2.

MoNEt_2 was isolated as a green solid in a yield of 54% upon treatment of $[\mathbf{Mo}(NH_3)][BPh_4]$ with $LiNEt_2$ in diethyl ether (eq 9). The reaction had to be conducted in the absence of N_2, otherwise significant amounts of **Mo**N_2 were formed as a side product. In the absence of N_2, the conversion proceeded cleanly in 2 h and the ^{1}H NMR spectrum of the crude reaction mixture indicated that **Mo**NEt_2 was present in a yield of 90−95%. **Mo**NEt_2 is noticeably more stable than **Mo**NH_2 (attempted isolation of which led to the formation of **Mo**≡N) and could be stored in the solid state for several weeks at −30 °C without decomposition. We could not prepare **Mo**NEt_2 through substitution of the chloride ligand in **Mo**Cl by $LiNEt_2$ or through deprotonation of $[\mathbf{Mo}(Et_2NH)][BAr^f_4]$ with $LiNEt_2$, Li[N-$(SiMe_3)_2$], or KO-*t*-Bu, an approach that was successful for preparing **Mo**NH_2.[17]

$$[\mathbf{Mo}(NH_3)][BPh_4] \xrightarrow[-\ Li[BPh_4]\ -\ NH_3]{+\ LiNEt_2} \mathbf{Mo}NEt_2 \qquad (9)$$

The ^{1}H NMR spectrum of **Mo**NEt$_2$ at room temperature features paramagnetically shifted resonances for the ethylene backbone at −6.5 and −39.5 ppm, which is suggestive of a ground-state high-spin d^2 Mo configuration or a high-spin/low-spin equilibrium, as found in the related compounds [(RNCH$_2$CH$_2$)$_3$N]MoNMe$_2$ (R = SiMe$_3$[24] or C$_6$F$_5$[24,28]). The resonances of the ethyl groups are also significantly shifted to −1.0 ppm (NCH$_2$C*H*$_3$) and −66.6 ppm (NC*H*$_2$CH$_3$). The temperature dependence of the four resonances observed in the ^{1}H NMR spectrum of **Mo**NEt$_2$ in the range −70 to +80 °C allowed us to determine the spin multiplicity of **Mo**NEt$_2$ in the ground state. A plot of the chemical shift of each resonance versus 1/*T* revealed a linear relationship for all, as expected for a Curie−Weiss paramagnet in solution (Figure 4). The methyl resonances in the diethylamide group were almost independent of *T* as a consequence of their being further away from Mo than the C$_2$H$_4$ protons in the ligand and the methylene protons in the diethylamide group. Thus, in contrast to the *low*-spin ground-state d^2 configurations found for [(RNCH$_2$CH$_2$)$_3$N]-MoNMe$_2$ (R = SiMe$_3$[24] or C$_6$F$_5$[24,28]), **Mo**NEt$_2$ has a *high*-spin ground-state d^2 configuration.

The second temperature-dependent process that is observed in NMR spectra of **Mo**NEt$_2$ is loss of C_3 symmetry at low temperature (Figure 5). As the temperature is lowered, the ligand is locked into a C_3 configuration and the dimethylamido group no longer freely rotates. At 200 K at least nine resonances are observed for the two former ethylene backbone protons.

The cyclic voltammogram of **Mo**NEt$_2$ in PhF (0.1 M [Bu$_4$N][BAr$^f_4$]) reveals a quasireversible oxidation process at $E_{1/2}$ = −0.98 V (vs Fc/Fc$^+$), as well as an irreversible process at −1.74 V (I_{pc} vs Fc/Fc$^+$; scan rate 50 mV/s; Table 1). We assign the former to the one-electron oxidation of **Mo**NEt$_2$ to [**Mo**NEt$_2$]$^+$, while the nature of the latter is not known. Chemical oxidation of **Mo**NEt$_2$ with [Fc][BAr$^f_4$] in toluene over a period of 3 days is accompanied by a gradual color change of the deep blue solution to deep red. Ferrocene is formed along with a new species with paramagnetically shifted resonances at −8.2, −21.3, −35.7, and −104.3 ppm. Unfortunately, side products are also formed in minor amounts upon oxidation of **Mo**NEt$_2$, and the identity of the major product, which we propose is [**Mo**NEt$_2$]$^+$, therefore cannot be confirmed.

To be able to compare compounds that contain the same dialkylamido ligand, **Mo**NMe$_2$ was prepared through reaction of [**Mo**(NH$_3$)][BPh$_4$] with LiNMe$_2$ in diethyl ether in the absence of dinitrogen. **Mo**NMe$_2$ was obtained as a dark green solid in a moderate yield (39%). **Mo**NMe$_2$ is significantly less stable than **Mo**NEt$_2$ both in the solid state and in solution. Decomposition of **Mo**NMe$_2$ to undefined products was observed within 24 h in C$_6$D$_6$ solution and within 5 d in the solid state. The ^{1}H NMR spectrum of **Mo**NMe$_2$ in C$_6$D$_6$ displays paramagnetically shifted resonances for the ethylene backbone at −3.0 and −40.4 ppm at room temperature, as well as for the amine methyl groups at −28.3 ppm. Variable-temperature proton NMR spectra of **Mo**NMe$_2$ in toluene-d_8 in a range of −20 to +80 °C (Figure 6) are analogous to those obtained for **Mo**NEt$_2$. Therefore, we conclude that **Mo**NMe$_2$ also has a *high*-spin ground state d^2 configuration. A *low*-spin d^2 configuration (e.g., for [(RNCH$_2$-CH$_2$)$_3$N]MoNMe$_2$ (R = SiMe$_3$[24] or C$_6$F$_5$[24,28])) would suggest that the amido ligand is planar, while a *high*-spin d^2 configuration for **Mo**NEt$_2$ and **Mo**NMe$_2$ would suggest that the amido ligand is not planar but rather pyramidal. We propose that a planar geometry for a diethylamino or dimethylamido group in **Mo**NEt$_2$ and **Mo**NMe$_2$ must not be possible because of steric interaction with the isopropyl HIPT substituents. It should be noted that the energy difference between high-spin and low-spin forms of [(RNCH$_2$CH$_2$)$_3$N)MoNMe$_2$] (R = SiMe$_3$[24] or C$_6$F$_5$[24,28]) is small (~2 kcal/mol), so the steric interaction that is required for the lowest energy state to be high-spin instead of low-spin need not be dramatic.

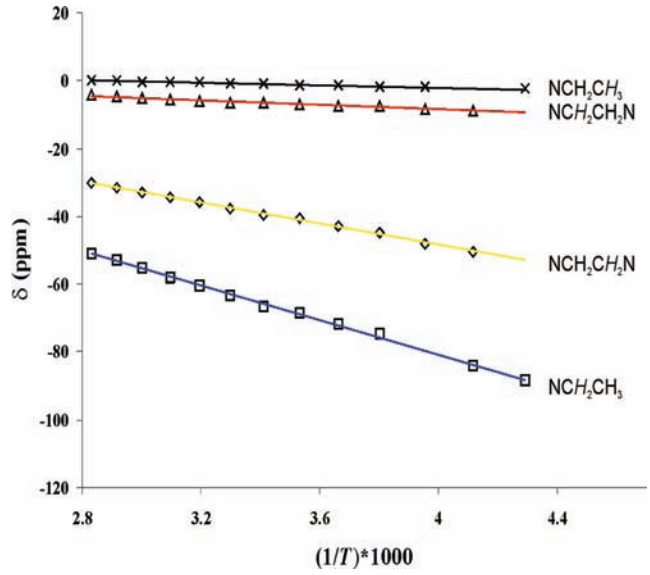

Figure 4. Plot of the chemical shift of selected resonances in **Mo**NEt$_2$ versus 1/*T*.

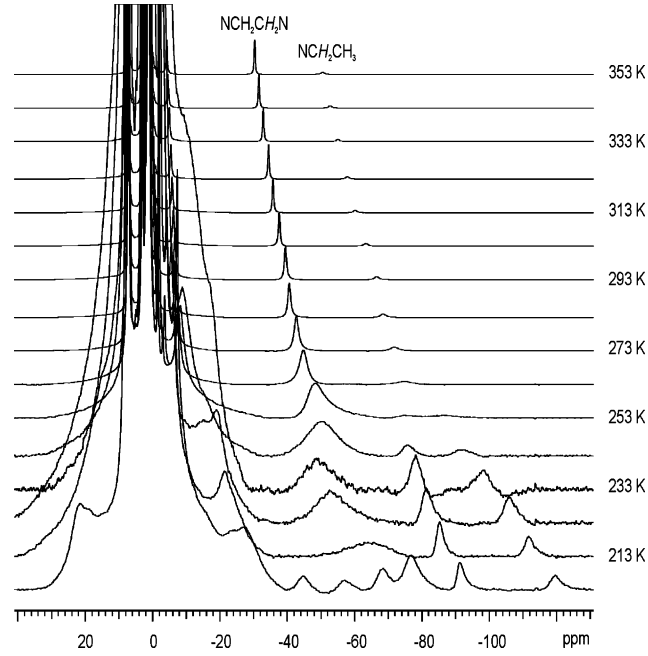

Figure 5. Part of the temperature-dependent ^{1}H NMR spectrum of **Mo**NEt$_2$.

Alkylation and Reduction of MoNEt$_2$. Alkylation of **Mo**NEt$_2$ with 1 equiv of [Et$_3$O][BAr$^f_4$] in diethyl ether in the absence of dinitrogen cleanly afforded [**Mo**(NEt$_3$)][BAr$^f_4$] as a deep red

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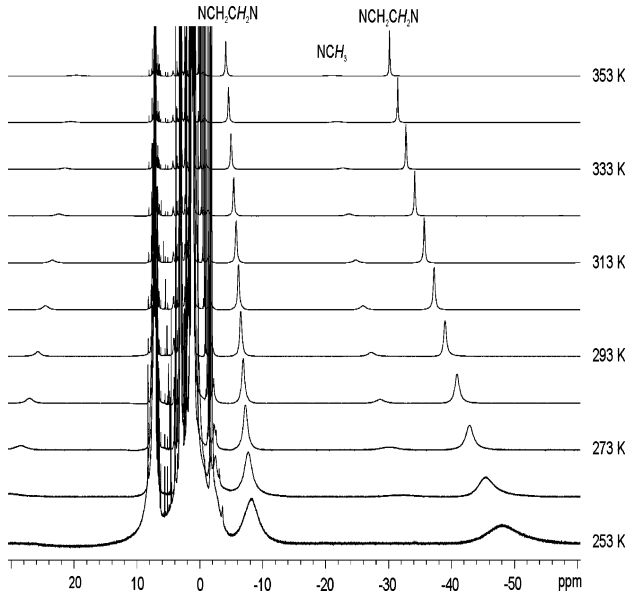

Figure 6. Part of the temperature-dependent ^{1}H NMR spectrum of **Mo**NMe_2.

solid in 61% yield after 20 h (eq 10). This result demonstrates that triethylamine can coordinate to the metal in a *cationic* **Mo** core, a fact that would be necessary for a viable catalytic cycle (**11** and **12** in Figure 2). The ^{1}H NMR spectrum of paramagnetic [**Mo**(NEt_3)][BAr^f_4] features characteristic resonances for the ethylene backbone protons at −16.3 and −99.1 ppm, as well as resonances for the amine protons at −2.5 and −10.8 ppm. As expected, reduction of [**Mo**(NEt_3)][BAr^f_4] with $CrCp^*_2$ in C_6D_6 under 1 atm of N_2 was accompanied by precipitation of yellow [$CrCp^*_2$][BAr^f_4] and formation of **Mo**N_2, as judged by ^{1}H NMR spectroscopy of the reaction mixture. Therefore, if [**Mo**(NEt_3)][BAr^f_4] could be formed under catalytic conditions, it would be reduced under dinitrogen to yield triethylamine and **Mo**N_2, thus completing the catalytic cycle.

$$\mathbf{Mo}NEt_2 \xrightarrow[-\ Et_2O]{+\ [Et_3O][BAr^f_4]} [\mathbf{Mo}(NEt_3)][BAr^f_4] \qquad (10)$$

[DTBTN$_3$N]Mo System. The [HIPTN$_3$N]Mo system appears to be well-suited for the addition of protons and electrons to dinitrogen and N_xH_y ligands,[29] but for steric reasons not for addition of ethyl groups and electrons. Therefore, smaller terphenyl substituents might lead to faster alkylation rates and still relatively stable intermediates. For example, the $[DTBTN_3N]^{3-}$ ligand (DTBT = 3,5-(4-*t*-Bu$C_6H_4)_2C_6H_3$), which is a sterically less demanding terphenyl analogue of the HIPT system, is known.[30] Its complexes are also known to form diazenido derivatives, e.g., $[(DTBTN_3N)MoN_2]^-$ and [DTBTN$_3$N]-MoN=$NSiMe_3$.[26] Therefore we reasoned that the $[DTBTN_3N]^{3-}$ ligand might solve some of the problems associated with the alkylation chemistry of [HIPTN$_3$N]Mo species.

[DTBTN$_3$N]Mo≡N was synthesized through a reaction between [DTBTN$_3$N]MoCl and 2 equiv of NaN_3 in THF at room temperature (eq 11). It was isolated as a yellow powder in a yield of 74%. We could not obtain [DTBTN$_3$N]Mo≡N through addition of several equivalents of Me_3SiN_3 to [DTBTN$_3$N]MoCl in toluene at ambient and elevated temperatures.

$$[DTBTN_3N]MoCl + NaN_3 \rightarrow [DTBTN_3N]Mo{\equiv}N + NaCl + N_2 \qquad (11)$$

Alkylation of [DTBTN$_3$N]Mo≡N with one equiv of [Et_3O][BAr^f_4] in CD_2Cl_2 was complete within 10 min, which is much faster than alkylation of [HIPTN$_3$N]Mo≡N. Even in benzene, the formation of [(DTBTN$_3$N)Mo=NEt][BAr^f_4] was complete within 15 min. [(DTBTN$_3$N)Mo=NEt][BAr^f_4] was obtained in a 34% yield through crystallization from heptane. Higher yields were thwarted by the poor crystallization behavior of [(DTBTN$_3$N)Mo=NEt][BAr^f_4], which tended to form a deep red oil when concentrated solutions of it in pentane or heptane were cooled. These results suggest that the Mo center in [DTBTN$_3$N]Mo species is much more accessible than in the [HIPTN$_3$N]Mo system, as expected.

Attempts To Generate Triethylamine. We first attempted to generate triethylamine in the [HIPTN$_3$N]Mo system. **Mo**N_2 and **Mo**≡N were chosen as starting compounds in experiments that employed [Et_3O][BAr^f_4] and $CrCp^*_2$. Addition of 7 equiv of [Et_3O][BAr^f_4] and 8 equiv of $CrCp^*_2$ to a benzene solution of **Mo**N_2 or 3.5 equiv of [Et_3O][BAr^f_4] and 4.2 equiv of $CrCp^*_2$ to a benzene solution of **Mo**≡N led to no detectible NEt_3 or [Et_4N][BAr^f_4] by ^{1}H NMR spectroscopy or gas chromatography. [Et_3O][BAr^f_4] is almost insoluble in benzene but is consumed, and diethyl ether is formed. The solid residues contained [$CrCp^*_2$][BAr^f_4], and either a mixture of **Mo**=NNEt and [**Mo**=$NNEt_2$][BAr^f_4] or unreacted **Mo**≡N.

Several experiments were conducted in a manner analogous to that employed for the catalytic reduction of dinitrogen to ammonia except the $CrCp^*_2$ was added over a period of 10−16 h. In all cases, no NEt_3 was formed, as judged by gas chromatography, and the residues contained [$CrCp^*_2$][BAr^f_4], **Mo**≡N, and undefined decomposition products; no [Et_4N]-[BAr^f_4] was observed by ^{1}H NMR spectroscopy.

Similar experiments were carried out employing [(DTBTN$_3$N)Mo=NEt][BAr^f_4], [Et_3O][BAr^f_4], and $CrCp^*_2$. Addition of 2.2 equiv of [Et_3O][BAr^f_4] and 3.2 equiv of $CrCp^*_2$ to a benzene solution of [(DTBTN$_3$N)Mo=NEt][BAr^f_4] was followed by stirring the mixture over a period of 20 h. [(DTBTN$_3$N)Mo=NEt][BAr^f_4], [Et_3O][BAr^f_4], and $CrCp^*_2$ were all consumed, but no evidence for the formation of NEt_3 or [Et_4N][BAr^f_4] could be obtained from ^{1}H NMR spectroscopic data, and no (DTBTN$_3$N)Mo derivatives could be identified. Similar results were obtained in attempted catalytic runs using 36 equiv of [Et_3O][BAr^f_4] and 48 equiv of $CrCp^*_2$ in octane or toluene. Proton NMR analysis of the nonvolatile components revealed no [Et_4N][BAr^f_4]; only [$CrCp^*_2$][BAr^f_4] could be identified. Analysis of the volatiles by gas chromatography revealed a product with a retention time identical to that of NEt_3, but the amount was ≤0.2 equiv.

Summary and Conclusions

We have prepared several possible intermediates in a hypothetical catalytic reduction of dinitrogen to triethylamine with (HIPTN$_3$N)Mo species, among them **Mo**N=NEt, [**Mo**=$NNEt_2$][BAr^f_4], **Mo**=$NNEt_2$, [**Mo**=NEt][BAr^f_4], **Mo**=NEt, **Mo**-NEt_2, and [**Mo**NEt_3][BAr^f_4]. **Mo**=$NNEt_2$ and **Mo**=NEt are especially interesting because **Mo**=NNH_2 has not been observed, and **Mo**=NH loses dihydrogen to give **Mo**≡N upon attempted isolation. The protio analogue of **Mo**NEt_2 (**Mo**NH_2) is also unstable with respect to loss of dihydrogen to give **Mo**≡N. We were surprised to find that both **Mo**=$NNEt_2$ and **Mo**=NEt are oxidized by [Et_3O][BAr^f_4] to reform the cationic

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Mo(VI) species instead of being alkylated. **Mo**=$NNEt_2$ is also oxidized by [**Mo**=NNH_2]$^+$ or [$H(Et_2O)_2$][BAr^f_4]. Therefore it seems unlikely that it will be possible to complete a catalytic cycle in which **Mo**=$NNEt_2$ must be alkylated (**5** → **6**; Figure 2) and **Mo**=NEt must be alkylated (**9** → **10**; Figure 2).

We know that reduction of [**Mo**=NNH_2]$^+$ with $CrCp^*_2$ gives **Mo**-N=NH, **Mo**≡N, [**Mo**(NH_3)]$^+$, **Mo**(NH_3), and ammonia.[17] **Mo**=NNH_2 is proposed to be the first product of reduction of [**Mo**=NNH_2]$^+$, but **Mo**=NNH_2 is then protonated, possibly by [**Mo**=NNH_2]$^+$ in a base-catalyzed proton transfer, to give [**Mo**=NNH_3]$^+$ (and **Mo**=NNH), and [**Mo**=NNH_3]$^+$ is then reduced by $CrCp^*_2$ or some other species in solution (including **Mo**=NNH_2) to give **Mo**≡N and ammonia. Therefore **Mo**=NNH_2 and [**Mo**=NNH_3]$^+$ are most likely intermediates, but how they are formed and consumed is unclear.

All efforts to generate NEt_3 employing ($HIPTN_3N$)Mo species failed, a result that is consistent with slow alkylations. However, efforts to generate NEt_3 in the ($DTBTN_3N$)Mo also have failed so far, or at least NEt_3 was not formed catalytically. Nevertheless, sterically less demanding triamidoamine ligands would seem to be more likely to allow formation of NEt_3 catalytically in a manner analogous to that proposed for catalytic formation of ammonia.

Unlike protonation of an amido nitrogen in the ligand, alkylation of an amido nitrogen in the ligand would likely be irreversible and probably would lead to dissociation of the amine donor from the metal. Some evidence to support this proposal exists in triamidoamine chemistry of molybdenum.[24−26] Alkylation of an amido nitrogen in the [$HIPTN_3N$]$^{3-}$ ligand could be regarded as another potential pitfall in the catalytic formation of triethylamine by a sequence of reactions analogous to those proposed for catalytic formation of ammonia.

Experimental Section

General. Air- and moisture-sensitive compounds were manipulated under 1 atm of dry N_2 or argon by standard Schlenk techniques or in a glovebox using flame- and oven-dried glassware. HPLC grade pentane, benzene, toluene, ether, THF, and CH_2Cl_2 were sparged with dinitrogen, passed through activated alumina, and stored over 4 Å Linde-type molecular sieves prior to use. Heptane, octane, NEt_2H, and NEt_3 were dried by refluxing over molten potassium, vacuum transferred, degassed, and stored over molecular sieves. Gaseous H_2NMe, $HNMe_2$, NMe_3, and NEt_2H were condensed onto sodium sand, stirred over a period of 3 h at −40 °C, and vacuum transferred into the reaction vessel. PhF was dried over CaH_2, degassed, and vacuum distilled prior to use. Benzene-d_6, toluene-d_8, and methylene chloride-d_2 were freeze−pump−thaw degassed and stored over activated molecular sieves for at least 2 days prior to use. **Mo**Cl,[16] **Mo**N_2,[16] [Bu_4N][**Mo**N_2],[16] **Mo**≡N,[16] [**Mo**(NH_3)][BPh_4],[16] **Mo**H,[17] [**Mo**=NNH_2][BAr^f_4],[16] [**Mo**=NH]-[BAr^f_4], ($DTBTN_3N$)MoCl,[26] [$H(OEt_2)_2$][BAr^f_4],[31] Na[BAr^f_4], Ag-[BAr^f_4],[32] $CrCp^*_2$,[33] and [Fc][BAr^f_4][34] were prepared according to known methods. [Bu_4N][BAr^f_4] was prepared by salt metathesis of [Bu_4N]Cl with Na[BAr^f_4] in diethyl ether and recrystallized from CH_2Cl_2/pentane. [NEt_2H_2][BAr^f_4] and [NEt_3H][BAr^f_4] were synthesized by reaction of NEt_2H·HCl and NEt_3·HCl with Na[BAr^f_4] in diethyl ether. All other chemicals were obtained commercially and used without further purification. NMR spectra were recorded on a Bruker Avance 400 spectrometer (^{1}H, 400 MHz; ^{11}B, 128 MHz; ^{13}C, 100 MHz), and VT NMR spectra on Varian Inova 500 spectrometers (^{1}H, 500 MHz). Chemical shifts for ^{1}H NMR spectra were referenced to the residual ^{1}H NMR resonance of the deuterated solvent, those of the ^{13}C NMR spectra to the ^{13}C NMR resonances of the solvent itself, and are reported as parts per million relative to tetramethylsilane. ^{11}B NMR spectra were referenced externally to a solution of $B(OH)_3$ in D_2O. Electrochemical measurements were carried out in an argon-filled glovebox using a CHI 620C potentiate, 0.1 M [Bu_4N][BAr^f_4]/PhF electrolytes, and a standard three-electrode cell assembly with a glassy carbon (3.0 mm diameter) disk working electrode, a platinum wire auxiliary electrode, and a reference electrode consisting of a AgCl-coated silver wire submerged in 0.1 M [Bu_4N][BAr^f_4]/PhF electrolyte. All measurements were referenced externally and/or internally with $FeCp_2$. Elemental analyses were performed by Midwest Microlabs, Indianapolis, IN.

[Et_3O][BAr^f_4]. A mixture of [Et_3O][BF_4] (0.15 g, 0.79 mmol) and Na[BAr^f_4] (0.74 g, 0.83 mmol, 1.05 equiv) was stirred in Et_2O (10 mL) at room temperature for 3 d. The solvent removed in vacuo. The residue was extracted with CH_2Cl_2, and the extract was filtered through Celite. Removal of all volatiles afforded [Et_3O][BAr^f_4] (0.72 g, 0.74 mmol, 94%) as a white solid, which was washed with pentane and dried in vacuo. A concentrated CH_2Cl_2 solution was layered with pentane and cooled to −30 °C to afford analytically pure [Et_3O][BAr^f_4]: ^{1}H NMR (400 MHz, CD_2Cl_2, 297 K) δ 1.61 (t, 9H, CH_3), 4.61 (q, 6H, CH_2), 7.74 (s, 4H, B*Ar*^{f}), 7.60 (s, 8H, B*Ar*^{f}); ^{11}B{^{1}H} NMR (128 MHz, CD_2Cl_2, 297 K) δ −26.0. Anal. Calcd (%) for $C_{38}H_{27}BF_{24}O$ (966.39): C, 47.23; H, 2.82. Found: C, 47.30; H, 2.80.

($HIPTN_3N$)MoN=NEt. Method A. ($HIPTN_3N$)MoCl (0.15 g, 87.37 μmol) was reduced with sodium sand (380.1 mg, 0.87 mmol, 10 equiv) in THF (4 mL) under 1 atm of dinitrogen to form [($HIPTN_3N$)MoN_2]$^-$, as reported in the literature.[16] The deep green reaction mixture was filtered through Celite, and the solvents were removed from the filtrate in vacuo. The residue was dissolved in ether (2 mL). The mixture was cooled to −30 °C and treated dropwise with a solution of [Et_3O][BAr^f_4] (84.4 mg, 87.37 μmol, 1 equiv) in ether (2 mL). The reaction was allowed to stir at ambient temperatures over a period of 24 h, and the solvent was subsequently removed under vacuum. The residue was extracted into pentane and filtered through Celite. After removal of all volatiles, the crude product was recrystallized from heptane at −30 °C to afford ($HIPTN_3N$)MoN=NEt (63.8 mg, 36.69 μmol, 42%) as a pale yellow, crystalline solid in several crops: ^{1}H NMR (400 MHz, C_6D_6, 297 K) δ 0.87 (t, 3H, -NCH_2CH_3), 1.14 (d, 36H, -$CH(CH_3)_2$), 1.22 (d, 36H, -$CH(CH_3)_2$), 1.38 (d, 36H, -$CH(CH_3)_2$), 2.08 (br t, 6H, -NCH_2CH_2N-), 2.94 (m, 6H, -$CH(CH_3)_2$), 3.32 (m, 12H, -$CH(CH_3)_2$), 3.31 (q, 2H, -NCH_2CH_3), 3.72 (br t, 6H, -NCH_2CH_2N-), 6.68 (s, 3H, 4,4′,4″-Ter*H*), 7.20 (s, 12H, 3,5,3′,5′,3″,5″-Tip*H*), 7.29 (s, 6H, 2,6,2′,6′,2″,6″-Ter*H*). Anal. Calcd (%) for $C_{116}H_{164}MoN_6$ (1738.52): C, 80.14; H, 9.51; N, 4.83. Found: C, 79.84; H, 9.54; N, 4.85.

Method B (Preferred). An ether solution (8 mL) of [Et_3O]-[BAr^f_4] (0.52 g, 0.54 mmol, 1.05 equiv) was cooled to −30 °C and treated with solid [Bu_4N][($HIPTN_3N$)MoN_2] (1.00 g, 0.51 mmol). A red solution formed within 30 min and was stirred for 20 h. The volatile components were removed in vacuo, and the residue was dried at 50 °C for 3 h. The residue was extracted into pentane, and the mixture was filtered through Celite. All volatiles were removed and the crude product was recrystallized from heptane at −30 °C to afford ($HIPTN_3N$)MoN=NEt (0.61 g total, 0.35 mmol, 69%) in several crops.

Method C. A solid mixture of ($HIPTN_3N$)MoN_2 (25.0 mg, 14.62 μmol), [Et_3O][BAr^f_4] (14.2 mg, 14.62 μmol, 1 equiv), and $CrCp^*_2$ (6.2 mg, 14.62 μmol, 1 equiv) was stirred in benzene (7 mL) at room temperature over a period of 2 days. All volatile components were removed in vacuo, and the residue was extracted into pentane. The extract was filtered through Celite, and the volatiles were

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removed from the filtrate in vacuo again. The crude product was recrystallized from heptane at −30 °C to afford (HIPTN$_3$N)-MoN=NEt (13.7 mg, 7.90 μmol, 54%).

[(HIPTN$_3$N)Mo=NNEt$_2$][BAr$^f_4$]. An CH_2Cl_2 solution (3 mL) of (HIPTN$_3$N)MoN=NEt (0.15 g, 86.28 μmol) and [Et$_3$O][BAr$^f_4$] (83.4 mg, 86.28 μmol, 1 equiv) was stirred at room temperature for 1 h to give a dark orange solution. Volatiles were removed in vacuo, and the solid residue was extracted into pentane. The extracts were filtered through Celite, and the solvents were removed from the filtrate in vacuo. The remaining material was dried at 60 °C under high vacuum to yield [(HIPTN$_3$N)Mo=NNEt$_2$][BAr$^f_4$] (0.20 g, 76.79 μmol, 89%) as an orange, amorphous solid: ^{1}H NMR (400 MHz, C_6D_6, 297 K) δ 0.66 (t, 6H, -NCH$_2$C*H*$_3$), 1.08 (d, 36H, -CH(C*H*$_3$)$_2$), 1.14 (d, 36H, -CH(C*H*$_3$)$_2$), 1.42 (d, 36H, -CH(C*H*$_3$)$_2$), 2.52 (br t, 6H, -NCH$_2$C*H*$_2$N-), 2.81 (m, 12H, -C*H*(CH$_3$)$_2$), 2.98 (m, 12H, -C*H*(CH$_3$)$_2$, -NC*H*$_2$CH$_3$), 3.77 (br t, 6H, -NCH$_2$C*H*$_2$N-), 6.89 (s, 9H, 2,4,6,2′,4′,6′,2″,4″,6″-Ter*H*), 7.19 (s, 12H, 3,5,3′,5′,3″,5″-Tip*H*), 7.75 (s, 4H, B*Ar*^{f}), 8.45 (s, 8H, B*Ar*^{f}). Anal. Calcd (%) for $C_{150}H_{181}BF_{24}MoN_6$ (2630.8): C, 68.48; H, 6.93; N, 3.19. Found: C, 68.73; H, 7.00; N, 3.10.

(HIPTN$_3$N)Mo=NNEt$_2$. A solution of [(HIPTN$_3$N)Mo=NNEt$_2$]-[BAr$^f_4$] (0.10 g, 39.53 μmol) in benzene (6 mL) was treated with solid CrCp*$_2$ (12.7 mg, 39.53 μmol, 1 equiv), and stirred for 18 h at room temperature, during which time a yellow precipitate and a dark red solution formed. All volatiles were removed in vacuo, and the residue was extracted with pentane. The extracts were filtered through a medium porosity frit to yield a deep red filtrate and yellow [CrCp*$_2$][BAr$^f_4$] (45.9 mg, 38.74 μmol, 98%). The filtrate was brought to dryness to afford a deep red solid. The ^{1}H NMR spectroscopy of the crude reaction mixture indicated the formation of (HIPTN$_3$N)Mo=NNEt$_2$ with a purity of 90%. All attempts to further purify the crude product have been unsuccessful: ^{1}H NMR (400 MHz, C_6D_6, 297 K) δ 1.22 (br m, 72H, -CH(C*H*$_3$)$_2$), 1.35 (br s, 36H, -CH(C*H*$_3$)$_2$), 2.91 (br m, 12H, -C*H*(CH$_3$)$_2$), 3.18 (br m, 6H, -C*H*(CH$_3$)$_2$), 7.08 (br s, 12H, 3,5,3′,5′,3″,5″-Tip*H*), all other signals were not observed at room temperature.

[(HIPTN$_3$N)Mo=NEt][BAr$^f_4$]. A CH_2Cl_2 solution (5 mL) of (HIPTN$_3$N)Mo≡N (0.40 g, 0.24 mmol) and [Et$_3$O][BAr$^f_4$] (0.23 g, 0.24 mmol, 1 equiv) was stirred at room temperature for 18 h to give a dark orange solution. Volatiles were removed in vacuo, and the solid residue was extracted with pentane. The extracts were filtered through Celite, and the filtrate was brought to dryness. The remaining material was dried at 60 °C under high vacuum to yield [(HIPTN$_3$N)Mo=NEt][BAr$^f_4$] (0.57 g, 0.22 mmol, 93%) as an orange, amorphous solid: ^{1}H NMR (400 MHz, CD_2Cl_2, 297 K) δ 0.62 (t, 3H, -NCH$_2$C*H*$_3$), 0.85 (d, 36H, -CH(C*H*$_3$)$_2$), 0.96 (d, 36H, -CH(C*H*$_3$)$_2$), 1.28 (d, 36H, -CH(C*H*$_3$)$_2$), 2.51 (m, 12H, -C*H*(CH$_3$)$_2$), 2.91 (m, 6H, -C*H*(CH$_3$)$_2$), 3.27 (br t, 6H, -NCH$_2$C*H*$_2$N-), 3.59 (q, 2H, -NCH$_2$C*H*$_3$), 4.28 (br t, 6H, -NCH$_2$C*H*$_2$N-), 6.80 (s, 3H, 4,4′,4″-Ter*H*), 6.84 (s, 6H, 2,6,2′,6′,2″,6″-Ter*H*), 6.98 (s, 12H, 3,5,3′,5′,3″,5″-Tip*H*), 7.56 (s, 4H, B*Ar*^{f}), 7.72 (s, 8H, B*Ar*^{f}); ^{1}H NMR (400 MHz, C_6D_6, 297 K): δ = 0.68 (t, 3H, -NCH$_2$C*H*$_3$), 1.00 (d, 36H, -CH(C*H*$_3$)$_2$), 1.10 (d, 36H, -CH(C*H*$_3$)$_2$), 1.34 (d, 36H, -CH(C*H*$_3$)$_2$), 2.30 (br t, 6H, -NCH$_2$C*H*$_2$N-), 2.69 (m, 12H, -C*H*(CH$_3$)$_2$), 2.91 (m, 6H, -C*H*(CH$_3$)$_2$), 3.64 (m, 8H, -NCH$_2$C*H*$_2$N-, -NCH$_2$C*H*$_3$), 6.74 (s, 3H, 4,4′,4″-Ter*H*), 6.82 (s, 6H, 2,6,2′,6′,2″,6″-Ter*H*), 7.14 (s, 12H, 3,5,3′,5′,3″,5″-Tip*H*), 7.69 (s, 4H, B*Ar*^{f}), 8.34 (s, 8H, B*Ar*^{f}). Anal. Calcd (%) for $C_{148}H_{176}BF_{24}MoN_5$ (2587.73): C, 68.69; H, 6.86; N, 2.71. Found: C, 68.48; H, 6.83; N, 2.88.

(HIPTN$_3$N)Mo=NEt. A solution of [(HIPTN$_3$N)Mo=NEt]-[BAr$^f_4$] (0.25 g, 96.61 μmol) in benzene (6 mL) was treated with solid CrCp*$_2$ (31.2 mg, 96.61 μmol, 1 equiv), and the mixture was stirred for 18 h at room temperature, during which time a yellow precipitate and a dark red solution formed. All volatiles were removed in vacuo at 60 °C, and the residue was extracted with pentane. The extracts were filtered through a medium porosity frit, yielding a deep red filtrate and yellow [CrCp*$_2$][BAr$^f_4$] (0.11 g, 93.71 μmol, 97%). The filtrate was taken to dryness in vacuo to afford a deep red solid, which was again extracted with pentane. The mixture was filtered through Celite and all volatiles were removed in vacuo to yield (HIPTN$_3$N)Mo=NEt (0.15 g, 85.98 μmol, 89%) as a red, crystalline solid: ^{1}H NMR (400 MHz, C_6D_6, 297 K) δ 0.91 (br t, 3H, -NCH$_2$C*H*$_3$), 1.31 (br s, 72H, -CH(C*H*$_3$)$_2$), 1.40 (br s, 36H, -CH(C*H*$_3$)$_2$), 2.95 (br m, 12H, -C*H*(CH$_3$)$_2$), 3.16 (br m, 6H, -C*H*(CH$_3$)$_2$), 7.06 (br s, 12H, 3,5,3′,5′,3″,5″-Tip*H*); the other signals could not be observed at room temperature. Anal. Calcd (%) for $C_{116}H_{164}MoN_5$ (1724.52): C, 80.79; H, 9.59; N, 4.06. Found: C, 80.52; H, 9.23; N, 4.29.

Reaction of (HIPTN$_3$N)Mo=NEt with [Et$_3$O][BAr$^f_4$]. Degassed CD_2Cl_2 (0.6 mL) was added to a solid mixture of (HIPTN$_3$N)Mo=NEt (20.3 mg, 11.77 μmol) and [Et$_3$O][BAr$^f_4$] (11.4 mg, 11.77 μmol, 1 equiv). The mixture was thawed to 22 °C, and allowed to react for 1 h, during which time an orange solution formed. The gaseous components of the reaction mixture were vacuum transferred onto frozen and degassed CD_2Cl_2 (0.6 mL). The ^{1}H NMR spectrum of the volatiles indicated the presence of butane: ^{1}H NMR (400 MHz, CD_2Cl_2, 297 K) δ 0.88 (t, 6H, CH$_2$C*H*$_3$), 1.28 (m, 4H, C*H*$_2$CH$_3$).

[(HIPTN$_3$N)Mo(H$_2$NEt)][BAr$^f_4$]. Gaseous H_2NEt was condensed onto Na sand, and the mixture was stirred over a period of 4 h at −30 °C. Two equivalents (57 mL, 0.29 mmol, 95 Torr) were transferred onto a frozen solution of (HIPTN$_3$N)MoCl (0.25 g, 0.15 mmol) and Na[BAr$^f_4$] (0.15 g, 0.15 mmol, 1.05 equiv) in CH_2Cl_2 (10 mL). The mixture was allowed to thaw to room temperature and was stirred for another 2 h. During this time, the reaction mixture turned red brown in color. The volatiles were removed in vacuo, and the residue was extracted into pentane. The extract was filtered through Celite. The filtrate was reduced in volume and stored at −30 °C to afford [(HIPTN$_3$N)Mo(H$_2$NEt)][BAr$^f_4$] (0.28 g, 0.11 mmol, 75%) as a red brown, microcrystalline solid. The product was washed with cold pentane and dried in vacuo: ^{1}H NMR (400 MHz, C_6D_6, 297 K) δ −98.9 (br s, 6H, -NCH$_2$C*H*$_2$N-), −16.6 (br s, 6H, -NCH$_2$C*H*$_2$N-), −2.63 (br s, 2H, −*H*$_2$NCH$_2$CH$_3$), 0.56 (br s, 3H, -NCH$_2$C*H*$_3$), 1.09 (br s, 36H, -CH(C*H*$_3$)$_2$), 1.17 (br s, 36H, -CH(C*H*$_3$)$_2$), 1.40 (br s, 36H, -CH(C*H*$_3$)$_2$), 2.77 (br m, 12H, -C*H*(CH$_3$)$_2$), 2.99 (br m, 8H, -C*H*(CH$_3$)$_2$, -NC*H*$_2$CH$_3$), 7.25 (br s, 12H, 3,5,3′,5′,3″,5″-Tip*H*), 7.64 (s, 4H, B*Ar*^{f}), 8.28 (s, 8H, B*Ar*^{f}), 9.73 (br s, Ter*H*); the other signals could not be observed at room temperature. Anal. Calcd (%) for $C_{148}H_{178}BF_{24}MoN_5$ (2589.74): C, 68.64; H, 6.93; N, 2.70. Found: C, 68.43; H, 6.94; N, 2.80.

[(HIPTN$_3$N)Mo(NEt$_2$H)][BAr$^f_4$]. A solid mixture of (HIPTN$_3$N)-MoH (0.25 g, 0.15 mmol) and [H$_2$NEt$_2$][BAr$^f_4$] (0.15 g, 0.16 mmol, 1.1 equiv) was treated with benzene (3 mL), and stirred over a period of 2 h at room temperature. All volatiles were removed in vacuo, and the residue extracted into pentane and filtered through Celite. Removal of all volatile components under high vacuum at 60 °C for 3 h yielded [(HIPTN$_3$N)Mo(NEt$_2$H)][BAr$^f_4$] (0.33 g, 0.13 mmol, 84%) as a red brown solid: ^{1}H NMR (400 MHz, C_6D_6, 297 K): δ −88.3 (br s, 6H, -NCH$_2$C*H*$_2$N-), −9.8 (br s, 6H, -NCH$_2$C*H*$_2$N-), 0.89 (t, 6H, -NCH$_2$C*H*$_3$), 1.17 (br s, 72H, -CH(C*H*$_3$)$_2$), 1.40 (d, 36H, -CH(C*H*$_3$)$_2$), 2.31 (br s, 4H, -NC*H*$_2$CH$_3$), 2.90 (br m, 6H, -C*H*(CH$_3$)$_2$), 3.00 (br m, 12H, -C*H*(CH$_3$)$_2$, -NC*H*$_2$CH$_3$), 7.23 (s, 12H, 3,5,3′,5′,3″,5″-Tip*H*), 7.64 (s, 4H, B*Ar*^{f}), 8.26 (s, 8H, B*Ar*^{f}), 10.6 (br s, Ter*H*); the other signals could not be observed at room temperature. Anal. Calcd (%) for $C_{150}H_{182}BF_{24}MoN_5$ (2617.8): C, 68.82; H, 7.01; N, 2.68. Found: C, 68.92; H, 7.09; N, 2.72.

(HIPTN$_3$N)MoNEt$_2$. Diethyl ether (10 mL) was freeze−pump−thaw degassed thoroughly and condensed onto a solid mixture of [(HIPTN$_3$N)Mo(NH$_3$)][BPh$_4$] (0.45 g, 0.22 mmol) and LiNEt$_2$ (1.8 mg, 0.22 mmol, 1 equiv). The reaction mixture was allowed to warm to ambient temperature and was stirred for 2 h. All volatiles were removed in vacuo, and the residue was extracted into pentane under 1 atm of argon. The mixture was filtered through Celite, and the filtrate was brought to dryness in vacuo. The crude reaction product was recrystallized from heptane at −30 °C. (HIPTN$_3$N)-MoNEt$_2$ (0.21 g, 0.12 mmol, 54%) was isolated as a green, microcrystalline solid: ^{1}H NMR (500 MHz, toluene-d_8, 293 K) δ −66.6 (br s, 6H, -NCH$_2$C*H*$_3$), −39.5 (br s, 6H, -NCH$_2$C*H*$_2$N-), −6.5

(br s, 6H, -NCH_2CH_2N-), −1.97 (br s, Ter*H*), −1.01 (br s, 4H, -NCH_2CH_3), 1.01 (br s, 36H, -$CH(CH_3)_2$), 1.25 (br s, 36H, -$CH(CH_3)_2$), 1.40 (d, 36H, -$CH(CH_3)_2$), 2.97 (br m, 6H, -$CH(CH_3)_2$), 3.05 (br s, 12H, -$CH(CH_3)_2$), 7.15 (s, 12H, 3,5,3′,5′,3″,5″-Tip*H*); other resonances could not be observed. Anal. Calcd (%) for $C_{118}H_{169}MoN_5$ (1753.58): C, 80.82; H, 9.71; N, 3.99. Found: C, 81.04; H, 9.54; N, 2.69.

(HIPTN$_3$N)MoNMe$_2$. Diethyl ether (20 mL) was freeze−pump−thaw degassed thoroughly and condensed onto a solid mixture of [(HIPTN$_3$N)Mo(NH_3)][BPh_4] (0.97 g, 0.48 mmol) and $LiNEt_2$ (24.5 mg, 0.48 mmol, 1 equiv). The reaction mixture was allowed to warm to ambient temperature and was stirred for 2 h. All volatiles were removed in vacuo, and the residue extracted into heptane/pentane under 1 atm of argon. The mixture was filtered through Celite, and the filtrate was cooled to −30 °C. (HIPTN$_3$N)MoNMe$_2$ (0.32 g, 0.19 mmol, 39%) was isolated as a green solid: ^{1}H NMR (400 MHz, C_6D_6, 293 K) δ −40.4 (br s, 6H, -NCH_2CH_2N-), −28.3 (br s, 6H, -NCH_3), −3.0 (br s, 6H, -NCH_2CH_2N-), −0.21 (br s, Ter*H*), 1.21 (br s, 36H, -$CH(CH_3)_2$), 1.35 (s, 36H, -$CH(CH_3)_2$), 1.47 (d, 36H, -$CH(CH_3)_2$), 2.99 (br m, 6H, -$CH(CH_3)_2$), 3.12 (br s, 12H, -$CH(CH_3)_2$), 7.19 (s, 12H, 3,5,3′,5′,3″,5″-Tip*H*); 7.19 (br s, 3H, -Ter*H*), 26.9 (br s, -Ter*H*). Anal. Calcd (%) for $C_{118}H_{169}MoN_5$ (1753.58): C, 80.82; H, 9.71; N, 3.99. Found: C, 81.04; H, 9.54; N, 3.86.

[(HIPTN$_3$N)Mo(NEt$_3$)][BAr$^f_4$]. Diethyl ether (1 mL) was condensed onto a solid mixture of (HIPTN$_3$N)MoNEt_2 (15.1 mg, 8.55 μmol) and [Et_3O][BAr$^f_4$] (8.3 mg, 8.55 μmol, 1 equiv). The reaction mixture was thawed and stirred for further 16 h at ambient temperature, during which time the solution became deep red. All volatiles were removed in vacuo, and the residue was extracted with pentane. The mixture was filtered through Celite, and the red filtrate was brought to dryness in vacuo to afford [(HIPTN$_3$N)Mo(NEt_3)][BAr$^f_4$] (13.8 mg, 5.21 μmol, 61%) as a red solid: ^{1}H NMR (400 MHz, C_6D_6, 297 K) δ −99.1 (br s, 6H, -NCH_2CH_2N-), −16.3 (br s, 6H, -NCH_2CH_2N-), −10.8 (br s, 6H, -NCH_2CH_3), −2.5 (br s, 9H, -NCH_2CH_3), 1.09 (br s, 36H, -$CH(CH_3)_2$), 1.17 (br s, 36H, -$CH(CH_3)_2$), 1.40 (d, 36H, -$CH(CH_3)_2$), 2.78 (br m, 12H, -$CH(CH_3)_2$), 2.99 (br m, 6H, -$CH(CH_3)_2$, -NCH_2CH_3), 7.30 (s, 12H, 3,5,3′,5′,3″,5″-Tip*H*), 7.64 (s, 4H, B*Ar*^{f}), 8.27 (s, 8H, B*Ar*^{f}), 9.6 (br s, Ter*H*); other resonances could not be observed. Anal. Calcd (%) for $C_{152}H_{186}BF_{24}MoN_5$ (2645.85): C, 69.00; H, 7.09; N, 2.65. Found: C, 68.86; H, 6.69; N, 2.69.

(DTBTN$_3$N)Mo≡N. THF (4 mL) was added to a solid mixture of (DTBTN$_3$N)MoCl (0.35 g, 0.27 mmol) and NaN_3 (34.6 mg, 0.53 mmol, 2 equiv), and the reaction mixture was stirred at room temperature for 3 d. The volatile components were removed in vacuo, and the solid residue extracted into benzene. The extracts were filtered through Celite and taken to dryness in vacuo. The remaining material was recrystallized from Et_2O/pentane to afford (DTBTN$_3$N)Mo≡N (**33**; 0.25 g, 0.20 mmol, 74%) as an orange powder. ^{1}H NMR (400 MHz, C_6D_6, 297 K): δ 1.23 (s, 54H, -$C(CH_3)_3$), 2.25 (br t, 6H, -NCH_2CH_2N-), 3.61 (br t, 6H, -NCH_2CH_2N-), 7.27 (d, 12H, 3,5,3′,5′,3″,5″-^{t}Bu-C_6H_4), 7.75 (d, 12H, 2,6,2′,6′,2″,6″-^{t}Bu-C_6H_4), 7.76 (s, 3H, 4,4′,4″-Ter*H*), 8.21 (s, 6H, 2,6,2′,6′,2″,6″-Ter*H*). Anal. Calcd (%) for $C_{84}H_{99}MoN_5$ (1274.66): C, 79.15; H, 7.83; N, 5.49. Found: C, 78.94; H, 7.82; N, 5.67.

[(DTBTN$_3$N)Mo═NEt][BAr$^f_4$]. A benzene solution (5 mL) of (DTBTN$_3$N)Mo≡N (0.15 g, 0.11 mmol) was treated with solid [Et_3O][BAr$^f_4$] (11.1 mg, 0.11 mmol, 1 equiv), and the mixture was stirred at room temperature for 1 h to give a dark red solution. Volatiles were removed in vacuo, and the solid residue was extracted into pentane. The extracts were filtered through Celite, and the filtrate was brought to dryness in vacuo. The remaining material was dried at 60 °C under high vacuum to yield [(DTBTN$_3$N)Mo═NEt][BAr$^f_4$] (0.21 g, 97.36 μmol, 85%) as a red, amorphous solid. Analytically pure material was obtained by recrystallization from diluted heptane solutions to yield 63.4 mg (29.26 μmol, 26%) of product: ^{1}H NMR (400 MHz, C_6D_6, 297 K) δ −0.24 (t, 3H, -NCH_2CH_3), 1.25 (s, 54H, -$C(CH_3)_3$), 2.43 (br t, 6H, -NCH_2CH_2N-), 2.78 (q, 2H, -NCH_2CH_3), 3.60 (br t, 6H, -NCH_2CH_2N-), 7.29 (s, 6H, 2,6,2′,6,′2″,6″-Ter*H*), 7.40 (d, 12H, 3,5,3′,5,′3″,5″-^{t}Bu-C_6H_4), 7.55 (d, 12H, 2,6,2′,6,′2″,6″-^{t}Bu-C_6H_4), 7.66 (s, 4H, B*Ar*^{f}), 7.81 (s, 3H, 4,4′,4″-Ter*H*), 8.40 (s, 8H, B*Ar*^{f}). Anal. Calcd (%) for $C_{118}H_{116}BF_{24}MoN_5$ (2166.93): C, 65.40; H, 5.40; N, 3.23. Found: C, 65.29; H, 5.42; N, 3.33.

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