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Molybdenum Triamidoamine Complexes that Contain Hexa-*tert*-butylterphenyl, Hexamethylterphenyl, or *p*-Bromohexaisopropylterphenyl Substituents. An Examination of Some Catalyst Variations for the Catalytic Reduction of Dinitrogen

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Abstract: Three new tetramines, $(ArNHCH_2CH_2)_3N$, have been synthesized in which Ar = 3,5-(2,4,6-*t*-$Bu_3C_6H_2)_2C_6H_3$ (H_3[HTBTN$_3$N]), 3,5-(2,4,6-$Me_3C_6H_2)_2C_6H_3$ (H_3[HMTN$_3$N]), or 4-Br-3,5-(2,4,6-*i*-$Pr_3C_6H_2)_2C_6H_2$ (H_3[*p*BrHIPTN$_3$N]). The diarylated tetramine, {3,5-(2,4,6-*t*-$Bu_3C_6H_2)_2C_6H_3NHCH_2CH_2\}_2NCH_2CH_2NH_2$, has also been isolated, and the "hybrid" tetramine {3,5-(2,4,6-*t*-$Bu_3C_6H_2)_2C_6H_3NHCH_2CH_2\}_2NCH_2CH_2NH$(4-*t*-$BuC_6H_4$) has been prepared from it. Monochloride complexes, $[(TerNCH_2CH_2)_3N]MoCl$, have been prepared, as well as a selection of intermediates that would be expected in a catalytic dinitrogen reduction such as $[(TerNCH_2CH_2)_3N]Mo{\equiv}N$ and $\{[(TerNCH_2CH_2)_3N]Mo(NH_3)\}\{BAr'_4\}$ (Ter = HTBT, HMT, or *p*BrHIPT and Ar′ = 3,5-$(CF_3)_2C_6H_3$)). Intermediates that contain the new terphenyl-substituted ligands are then evaluated for their efficiency for the catalytic reduction of dinitrogen under conditions where analogous [HIPTN$_3$N]Mo species give four turnovers to ammonia under "standard" conditions with an efficiency of ~65%. Only [*p*BrHIPTN$_3$N]Mo compounds are efficient catalysts for dinitrogen reduction. The reasons are explored and discussed.

Introduction

The first example of a dinitrogen complex, $[Ru(NH_3)_5(N_2)]^{2+}$, was published in 1965.[1] Since then, tremendous advances have been made in the synthesis and chemistry of dinitrogen complexes.[2−11] The main goals have been to understand how dinitrogen might be reduced to ammonia catalytically at a metal center or how it might be incorporated into organic molecules. The interest in reduction of dinitrogen to ammonia arises from the fact that dinitrogen is reduced to ammonia in nature by various nitrogenase enzymes,[12−15] all of which contain Fe and, in the most active enzymes, either Mo or V. It is generally agreed that dinitrogen is reduced at one or more transition metal centers, although details are still sparse. X-ray studies of a molybdenum nitrogenase[16−21] in the last dozen years have settled important structural questions, but the debate concerning exactly where and how dinitrogen is reduced continues today.

We have been interested in complexes that contain a $[(RNCH_2CH_2)_3N]^{3-}$ (triamidoamine) ligand[22,23] for several reasons: the triamidoamine ligand is multidentate, the apical site that is created when it binds to a metal is sterically protected by the three amido substituents, and the metal to which such a ligand is coordinated is likely to be in an oxidation state of 3^+ or greater. In view of the presence of a molybdenum (along with seven irons) in one nitrogenase,[16−21] we have focused on the synthesis and study of molybdenum complexes that contain triamidoamine ligands for the reduction of dinitrogen. Most recently, we have invested in *meta*-terphenyl-substituted ligands, and in particular a ligand that is substituted with 3,5-(2,4,6-*i*-$Pr_3C_6H_2)_2C_6H_3$ (or HIPT = hexaisopropylterphenyl) groups.[24,25] Starting with $[(HIPTNCH_2CH_2)_3N]MoCl$ ([HIPTN$_3$N]MoCl),

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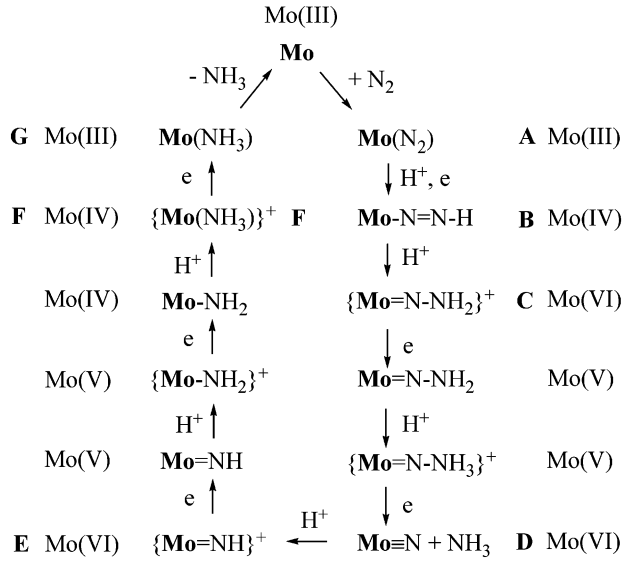
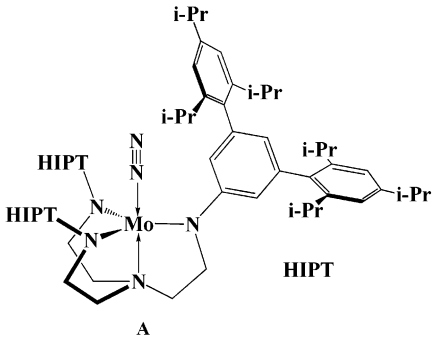
10.1021/ja0306415 CCC: $27.50

Scheme 1. Proposed Intermediates in the Reduction of Dinitrogen at a [HIPTN$_3$N]Mo (**Mo**) Center through the Stepwise Addition of Protons and Electrons



we showed that we could prepare many intermediates in a hypothetical reduction of dinitrogen (Scheme 1). These intermediates include paramagnetic [HIPTN$_3$N]Mo(N$_2$) (**A**), diamagnetic [HIPTN$_3$N]Mo−N=N−H (**B**), diamagnetic {[HIPTN$_3$N]Mo=NNH$_2$}{BAr′$_4$} (**C**; Ar′ = 3,5-(CF$_3$)$_2$C$_6$H$_3$), diamagnetic [HIPTN$_3$N]Mo≡N (**D**), diamagnetic {[HIPTN$_3$N]-Mo=NH}{BAr′$_4$} (**E**), and paramagnetic {[HIPTN$_3$N]Mo-(NH$_3$)}{BAr′$_4$} (**F**) and [HIPTN$_3$N]Mo(NH$_3$) (**G**). Extensive ^{15}N labeling studies, NMR studies, and X-ray studies of **A**, **D**, and **F**[25] all reveal a trigonal pocket in which N$_2$ and its reduced products are protected to a dramatic degree by three 2,4,6-*i*-Pr$_3$C$_6$H$_2$ rings clustered around it (see drawing of **A**). The intermediates shown in Scheme 1, in which the oxidation state of the metal varies between Mo(III) and Mo(VI), are analogous to those proposed originally by Chatt for low oxidation state (initially Mo(0) and W(0)) phosphine complexes.[2] The "naked" complex, [HIPTN$_3$N]Mo, has not been observed to date.



A

Recently, we have shown that dinitrogen can be reduced catalytically in heptane to ammonia at room temperature and 1 atm in the presence of **A**, **B**, **D**, or **F**.[26] Addition of the reductant (decamethylchromocene) over a period of 6 h in the presence of a poorly soluble proton source ({2,6-lutidinium}{BAr′$_4$}) leads to the consumption of ∼4 equiv of dinitrogen and the formation of ammonia in ∼65% yield. To our knowledge, this is the only reported catalytic reduction of dinitrogen in a relatively well-defined manner. It should be compared with the catalytic reduction of dinitrogen in a protic environment (methanol is the solvent) to a 10:1 mixture of hydrazine and ammonia reported by Shilov.[6] In addition to Mo(III), the Shilov system contains Mg(OH)$_2$, some strong reducing agent (Ti(OH)$_3$, Hg electrode, Na amalgam, etc.), additives such as various phosphines, and in some cases phosphatidylcholine that has been proposed to function (inter alia) as a "detergent" at a surface of sodium amalgam. As many as 170 equiv of ammonia (relative to Mo) reportedly have been produced at 110 °C and 1 atm pressure. The turnover rate also is said to approach that of the Fe/Mo nitrogenase itself at room temperature (∼1 s^{-1} Mo^{-1}) in the best cases. Relatively powerful reducing agents are required, that is, those with $E° < -1.75$ V vs SCE. No details as to how dinitrogen is reduced in the Shilov systems have been established. Shilov has favored the idea that at least two metals (presumably two molybdenum centers) are required to bind and reduce dinitrogen to hydrazine and ammonia, although convincing data in support of that proposal have not been forthcoming.

We naturally are interested in variations of the [HIPTN$_3$N]-Mo complexes and their efficacies for catalytic dinitrogen reduction. In this paper, we report three systems that are closely related to the [HIPTN$_3$N]$^{3-}$ system. One that is more protective of the metal contains the 3,5-(2,4,6-*t*-Bu$_3$C$_6$H$_2$)$_2$C$_6$H$_3$ (HTBT) group. A second that is less protective of the metal contains the 3,5-(2,4,6-Me$_3$C$_6$H$_2$)$_2$C$_6$H$_3$ (HMT) group. A third that is essentially the same sterically as the [HIPTN$_3$N]$^{3-}$ ligand, but slightly different electronically, contains the 4-bromo-3,5-(2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_2$ (*p*BrHIPT) group. We compare potential catalysts that contain one of these three ligands in terms of their ability to reduce dinitrogen catalytically under conditions that have been reported for complexes that contain the [HIPTN$_3$N]$^{3-}$ ligand.[26]

Results and Discussion

Ligand Syntheses. Syntheses of the terphenyl bromides, HTBTBr, HMTBr, and *p*BrHIPTBr, are analogous to synthesis of the isopropyl-substituted terphenyl bromide,[25] the first steps of which are shown in eq 1. This method follows that originally reported by Hart[27,28] with one important difference. The Grignard reagent is prepared with 2 equiv of magnesium. The Grignard reagents are then treated with 2,4,6-tribromoiodobenzene,[27] which yields the Grignard reagent of the desired *m*-terphenyl derivative and 2,4,6-trialkyliodobenzene. The 2,4,6-trialkyliodobenzene then reacts in situ with the second equivalent of magnesium to give the corresponding Grignard reagent, (2,4,6-R$_3$C$_6$H$_2$)MgX (eq 1). Acid hydrolysis of this mixture then yields the desired 3,5-bis(2,4,6-trialkylphenyl)bromobenzene and 1,3,5-trialkylbenzene. The 1,3,5-trialkylbenzene is easily separated from the 3,5-bis(2,4,6-trialkylphenyl)bromobenzene. Because 1,3,5-tri-*tert*-butylbenzene is relatively expensive, it therefore can be recovered and used to remake 1-bromo-2,4,6-tri-*tert*-butylbenzene. 3,5-Bis(2,4,6-tri-*tert*-butylphenyl)bromobenzene (HTBTBr) and 3,5-bis(2,4,6-trimethylphenyl)-bromobenzene (HMTBr) were obtained as white solids in 41% and 26% yields, respectively. If *N*-bromosuccinimide is added

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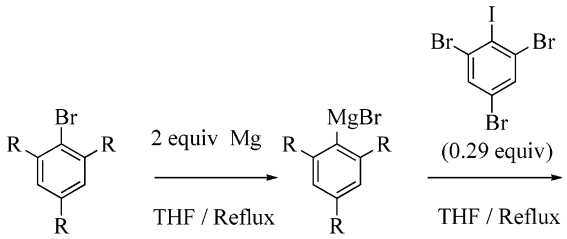
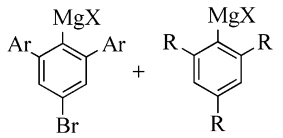


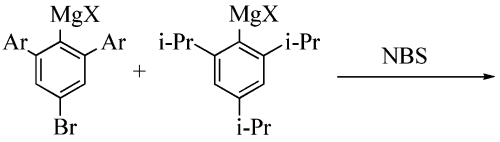
R = *t*-Bu or Me



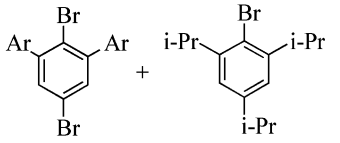
(1)

Ar = 2,4,6-$R_3C_6H_3$; X = Br or I

to the mixture of Grignard reagents shown in eq 1, then *p*BrHIPTBr (eq 2) can be isolated in good yield (49%) after recrystallization from ether.



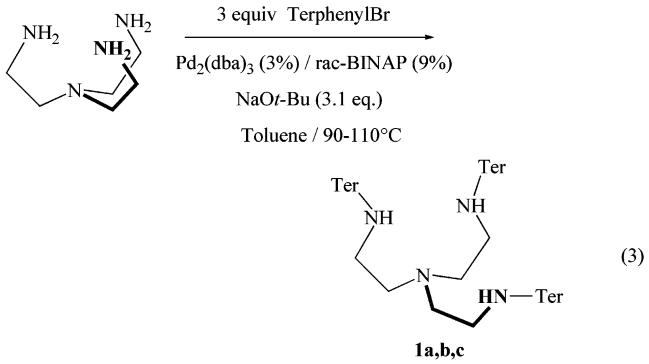
Ar = 2,4,6-i-$Pr_3C_6H_3$; X = Br or I



(2)

*p*BrHIPTBr

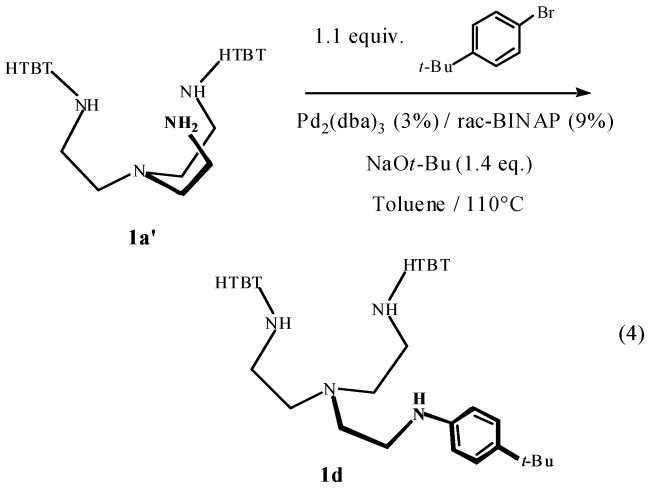
Compounds **1a**−**1c** (eq 3: **1a** = H_3[HTBTN$_3$N], **1b** = H_3[HMTN$_3$N], and **1c** = H_3[*p*BrHIPTN$_3$N]) were then synthesized in a reaction at 90−110 °C between N($CH_2CH_2NH_2$)$_3$ and 3 equiv of the terphenyl bromide in the presence of an excess of sodium *tert*-butoxide, 3 mol % $Pd_2(dba)_3$, and *rac*-BINAP (9 mol % vs the terphenylbromide).[29,30] A higher temperature and catalyst loading were required for the synthesis of **1a** than for **1b** or **1c**, which were more typical of conditions employed in reactions of this general type.[31,32] Attempts to synthesize **1a** under milder conditions (80 °C) and with 0.5−2% catalyst failed to give full conversion. Even at the higher temperatures, the reaction was not complete and the final mixture always contained **1a** and the disubstituted tetraamine (HTBTNHCH_2-CH_2)$_2$(NH_2CH_2CH_2)N (**1a′**). No disubstituted tetraamine was observed during the preparation of **1b** or **1c**. Compounds **1a**, **1b**, and **1c** were isolated as white solids in 65%, 35%, and 61% yields, respectively. Compound **1a′** is relatively easy to separate from **1a**; the chromatography solvent can be adjusted so that **1a** passes through the column, while **1a′** is absorbed strongly and removed later with a more polar solvent mixture. Compound **1a′** can be isolated as a yellow solid in 25% yield.



1a,b,c

(3)

The fact that **1a′** can be isolated created the possibility that "hybrid" ligands can be prepared in which the third arm can be substituted with a different aromatic group, for example, a smaller or electronically different group. To demonstrate the principle, we coupled **1a′** with 4-*tert*-butylbromobenzene to give (HTBTNHCH_2CH_2)$_2$(4-*t*-BuC_6H_4NHCH_2CH_2)N (**1d**; eq 4). The yield (12%) was not optimized.



1a' **1d**

(4)

Preparation of Monochloride Complexes. When **1a** is added to $MoCl_4(THF)_2$ in THF at room temperature, an adduct forms readily, the nature of which is not known. After 1 h, addition of 3.1 equiv of LiN($SiMe_3$)$_2$ at concentrations that were employed to prepare [HIPTN$_3$N]MoCl[25] led to [HTBTN$_3$N]-MoCl (**2a**) in 16% yield. Employing CH_3MgCl as the base[31] led to no improvement. Addition of the trilithium salt of **1a** to either $MoCl_4(THF)_2$ or $MoCl_3(THF)_3$ under a variety of conditions gave only traces of **2a** and/or [HTBTN$_3$N]Mo(N_2) (**4a**; vide infra).

We suspected that it may be more difficult to form the appropriate initial adduct when **1a** is employed than when H_3-[HIPTN$_3$N] is employed. The precise nature of this initial adduct is not known, but it almost certainly should be monomeric (not oligomeric or polymeric) to form **2a** upon addition of base. A ^{1}H NMR study in C_6D_6 showed that primarily two species are present in samples that contain **1a** and $MoCl_4(THF)_2$, one of which is not converted to **2a** upon addition of base. Decreasing the concentration of **1a** and $MoCl_4(THF)_2$ led to a decrease in the amount of the unreactive initial adduct. Therefore, more dilute conditions were employed. When solid $MoCl_4(THF)_2$ is added slowly to a 0.01 M solution of HTBTBr in benzene, which is at least 10 times more dilute than the reported procedure for

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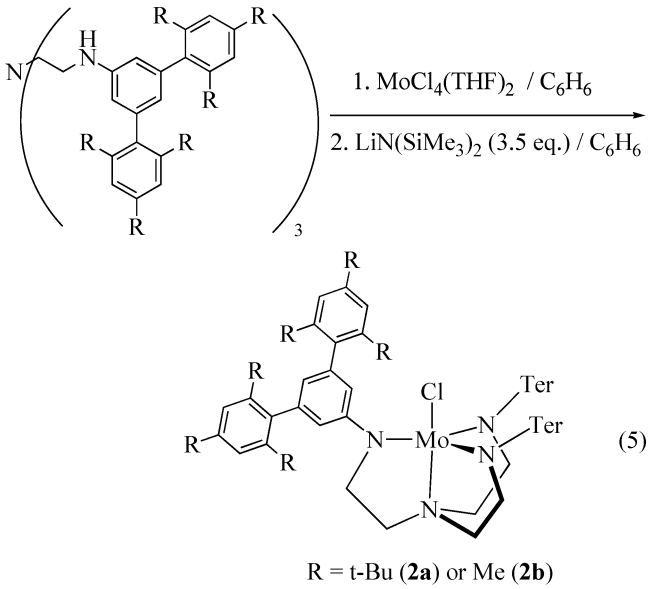
synthesizing [HIPTN$_3$N]MoCl,[25] and the resulting dark red solution is stirred for 2 h before adding LiN(SiMe$_3$)$_2$, **2a** can be isolated as an orange solid in 60% yield (eq 5). We later



(5)

found that if a slight excess of MoCl$_4$(THF)$_2$ (0.2 equiv) is employed in a concentrated reaction mixture (0.05 M), **2a** again can be obtained in good yield (69%). Both methods yield small quantities (~4%) of the nitride [HTBTN$_3$N]Mo≡N (**3a**, vide infra), in sharp contrast to the analogous reactions involving other H$_3$[TerN$_3$N] ligands. We suspect that the nitride originates from competitive substitution of Cl$^-$ by N(SiMe$_3$)$_2^-$ at Mo, followed by loss of the trimethylsilyl groups from the resulting Mo−N(SiMe$_3$)$_2$ species through unknown pathways.

Compound **2a** is paramagnetic and extremely sensitive to air and moisture, as is [HIPTN$_3$N]MoCl.[25] Its ^{1}H NMR spectrum closely resembles spectra of other [(ArylNCH$_2$CH$_2$)$_3$N]MoCl complexes[25,32] with three paramagnetically shifted resonances being observed at 14.8, −11.9, and −82.5 ppm. The first of these is ascribed to the ortho protons on the primary phenyl ring and the last two to the backbone methylene resonances. Other resonances within the 0−10 ppm window can be assigned readily (see Experimental Section).

The monochloride complex [HMTN$_3$N]MoCl (**2b**) can be prepared by reacting **1b** with MoCl$_4$(THF)$_2$ followed by LiN(SiMe$_3$)$_2$, either in THF or in benzene under dilute conditions (eq 5). The reaction works well under either set of conditions as shown by ^{1}H NMR studies of the crude reaction mixtures. Rapid workup of a reaction run in benzene allowed brown-red **2b** to be isolated in 64% yield. Compound **2b** appears to be more sensitive to traces of oxygen than **2a**, with a brown surface forming on the red crystals. As expected, the ^{1}H NMR spectrum of **2b** shows three paramagnetically shifted signals at 9.7, −16.0, and −77.6 ppm. The first is ascribed to the ortho protons on the primary phenyl ring and the latter to the backbone methylene resonances.

The synthesis of [*p*BrHIPTN$_3$N]MoCl (**2c**) followed the procedure for [HIPTN$_3$N]MoCl itself; dilute conditions were not necessary. The yield was 55%, and the proton NMR spectrum showed characteristic shifted resonances at 13.5, −18, and −84 ppm.

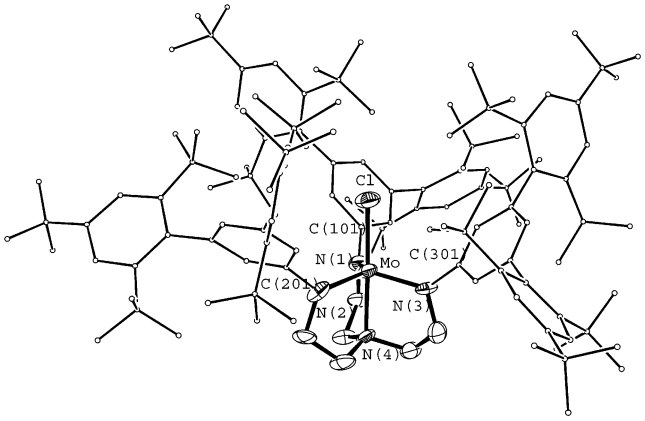
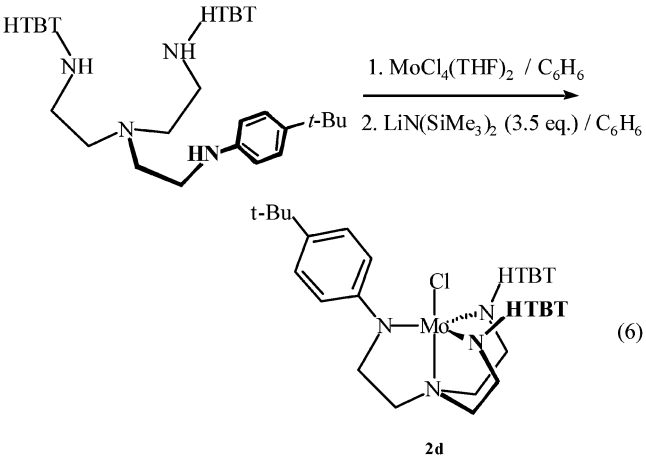


Figure 1. Thermal ellipsoid plot of the crystal structure of [HTBTN$_3$N]MoCl (**2a**) (50% probability level). Hydrogen atoms are omitted for clarity. All non-hydrogen atoms were refined anisotropically.

The "hybrid" complex [(HTBTNCH$_2$CH$_2$)$_2$(4-*t*-BuC$_6$H$_4$NCH$_2$CH$_2$)N]MoCl (**2d**) was prepared in a manner similar to that used to prepare **2a** and was isolated as an orange solid in 39% yield (not optimized; eq 6). As a consequence of the absence of a C_3



(6)

axis and the presence of a mirror plane, the ^{1}H NMR spectrum of **2d** is more complex than that of **2a** or **2b**. If the HTBT ring does not rotate about the C$_{ipso}$−N bond axis, then the four *ortho*-*tert*-butyl groups on each of the equivalent 3,5-[2,4,6-*t*-Bu$_3$C$_6$H$_2$]-C$_6$H$_4$ rings would be inequivalent. Evidently, rotation about the C$_{ipso}$−N bond axis is fast on the NMR time scale because only two *ortho*-*tert*-butyl group resonances are observed at 1.73 and 1.65 ppm. For the same reason, only two H$_m$ protons on the 2,4,6-*t*-Bu$_3$C$_6$H$_2$ rings are observed at 7.88 and 7.85 ppm, instead of four. Finally, six backbone methylene resonances of relatively area 2 appear as six broad singlets in the same range of frequencies as in **2a** and **2b** at −8.03, −14.00, −16.80 ppm, and from −75 to −80 ppm (overlapping). The meta and ortho protons of the 4-C$_6$H$_4$-*t*-Bu ring are found at 15.49 and 9.48 ppm, respectively, and the ortho protons of the 3,5-C$_6$H$_3$Ar$_2$ groups are detected as a broad singlet at 13.37 ppm.

X-ray quality crystals of **2a** were obtained by allowing a saturated solution of **2a** in pentane to stand at room temperature for several days. A thermal ellipsoid drawing is shown in Figure 1. Crystal data, data collection, and structure refinement are listed in Table 1, while selected bond distances and bond angles are listed in Table 2. This structure cannot be compared directly with the structure of [HIPTN$_3$N]MoCl because an X-ray study

Table 1. Crystal Data and Structure Refinement for [HTBTN$_3$N]MoCl (**2a**) and [*p*BrHIPTN$_3$N]Mo≡N (**3c**)[a]

empirical formula	$C_{132}H_{195}N_4ClMo$	$C_{114}H_{156}Br_3MoN_5$
formula weight	1969.42	1932.11
crystal system	orthorhombic	orthorhombic
space group	*P*2(1)2(1)2(1)	*Pna*2(1)
unit cell dimensions	$a = 19.165(2)$ Å	$a = 24.5742(13)$ Å
	$b = 20.234(3)$ Å	$b = 43.729(2)$ Å
	$c = 38.069(5)$ Å	$c = 25.7954(14)$ Å
	$\alpha = \beta = \gamma = 90°$	$\alpha = \beta = \gamma = 90°$
Z, volume (Å^3)	4, 14 763(3)	8, 27 720(3)
density (calculated; Mg/m^3)	0.886	0.926
absorption coefficient (mm^{-1})	0.146	0.996
F(000)	4296	8176
crystal size (mm^3)	0.36 × 0.28 × 0.20	
θ range for data collection (deg)	2.08−21.00	1.24−20.00
index ranges	$-16 \le h \le 19$, $-20 \le k \le 18$, $-38 \le l \le 36$	$-23 \le h \le 23$, $-42 \le k \le 42$, $-24 \le l \le 24$
reflns collected	47 115	125 318
independent reflns	15 803 [*R*(int) = 0.0726]	25 869 [*R*(int) = 0.1276]
completeness (to $\theta = xx°$)	99.7% (21.00)	100.0% (20.00)
data/restraints/parameters	15 803/0/1297	25 869/2/1733
GOF on F^2	1.130	1.028
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0849, wR2 = 0.2144	R1 = 0.0574, wR2 = 0.1058
R indices (all data)	R1 = 0.0901, wR2 = 0.2182	R1 = 0.0983, wR2 = 0.1115
absolute structure parameter	0.06(4)	0.024(7)
largest diff. peak and hole (e Å^{-3})	1.095 and −0.777	0.592 and −0.503

[a] For each structure, the temperature was 193(2) K, the wavelength was 0.71073 Å, and the refinement method was full-matrix least-squares on F^2.

Table 2. Selected Bond Distances [Å] and Angles (deg) for [HTBTN$_3$N]MoCl

Mo−N(1)	2.003(6)	C(201)−N(2)−Mo	129.7(5)
Mo−N(2)	1.983(6)	C(301)−N(3)−Mo	129.4(4)
Mo−N(3)	1.989(6)	N(2)−Mo−N(4)	80.5(2)
Mo−N(4)	2.193(6)	N(3)−Mo−N(4)	80.8(2)
Mo−Cl(2)	2.338(2)	N(1)−Mo−N(4)	79.8(2)
		N(2)−Mo−Cl(2)	97.94(18)
		N(3)−Mo−Cl(2)	100.22(16)
		N(1)−Mo−Cl(2)	100.76(17)
		N(4)−Mo−Cl(2)	178.41(16)
		N(2)−Mo−N(3)	118.5(2)
		N(2)−Mo−N(1)	117.7(2)
		N(3)−Mo−N(1)	115.6(2)
		C(101)−N(1)−Mo	128.7(4)

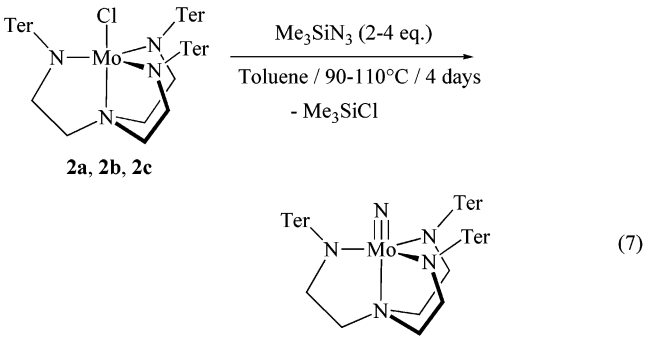
Table 3. A Summary of IR Data[a]

compound	ν_{NN} or ν_{MoN} (cm^{-1})
[HIPTN$_3$N]Mo(N$_2$)	1990 (1924 for ^{15}N$_2$)[25]
[HTBTN$_3$N]Mo(N$_2$) (**4a**)	1990 (1924 for ^{15}N$_2$)
[*p*BrHIPTN$_3$N]Mo(N$_2$) (**4c**)	1992
[TMSN$_3$N]Mo(N$_2$)	1934[33]
{Bu$_4$N}{[HIPTN$_3$N]Mo(N$_2$)}	1855[25]
{Bu$_4$N}{[HTBTN$_3$N]Mo(N$_2$)} (**5a**)	1847
{Et$_4$N}{[*p*BrHIPTN$_3$N]Mo(N$_2$)} (**5c**)	1857
[HIPTN$_3$N]Mo≡N	1012[b] (986 for ^{15}N in Nujol)[25]
[HTBTN$_3$N]Mo≡N (**3a**)	1015 (991 for ^{15}N)
[*p*BrHIPTN$_3$N]Mo≡N (**3c**)	1013 (985 for ^{15}N)

[a] All spectra were obtained in benzene except where noted. [b] In Nujol the value was 1013 cm^{-1}.

of [HIPTN$_3$N]MoCl was not carried out. However, we can compare the structure of **2a** with that of [HIPTN$_3$N]Mo≡N.[25] The most significant difference is the size of the Mo−N−C$_{ipso}$−C$_o$ angle, where C$_o$ is the ortho carbon atom that is closest to the metal. If the "primary" phenyl ring (the one connected to the amido nitrogen) lies in the plane of the trigonal amido nitrogen atom, then the Mo−N−C$_{ipso}$−C$_o$ dihedral angle would be 0°. If the primary phenyl ring lies perpendicular to the plane of the trigonal amido nitrogen atom, then the Mo−N−C$_{ipso}$−C$_o$ angle would be 90°. In **2a**, the Mo−N−C$_{ipso}$−C$_o$ angles are 67.0°, 64.6°, and 77.7°, whereas in [HIPTN$_3$N]Mo≡N the Mo−N−C$_{ipso}$−C$_o$ angles are 35.6°, 35.4°, and 33.5°. Therefore, one might think that the large difference in the Mo−N−C$_{ipso}$−C$_o$ angles could be ascribed to steric differences between the *i*-Pr system and the *t*-Bu system. However, Mo−N−C$_{ipso}$−C$_o$ angles vary significantly within various [HIPTN$_3$N]$^{3-}$ species.[25] Therefore, any additional steric hindrance imposed by the *tert*-butyl groups in [HTBTN$_3$N]MoCl versus the steric hindrance in [HIPTN$_3$N]$^{3-}$ species cannot be judged in terms of Mo−N−C$_{ipso}$−C$_o$ dihedral angles. Not surprisingly, a space filling model that contains all protons reveals an impressive degree of steric congestion in the upper half of **2a**, with the chloride barely being visible from the top.

Preparation of Nitride Complexes. Compound **2b** reacts smoothly with 2 equiv of Me_3SiN_3 in toluene at 90 °C over a period of 2 days to give diamagnetic [HMTN$_3$N]Mo≡N (**3b**), which was isolated as a bright yellow solid in 62% yield (eq 7). [*p*BrHIPTN$_3$N]Mo≡N (**3c**) can be prepared similarly.



(7)

Ter = HTBT (**3a**), HMT (**3b**), *p*BrHIPT (**3c**).

Slightly harsher conditions (110 °C, 4 equiv of Me_3SiN_3) were required to prepare [HTBTN$_3$N]Mo≡N (**3a**) in good yield (60%). Compounds **3a**−**3c** are relatively stable in air as solids; only minor surface decomposition was observed after several hours. The $\nu_{Mo\equiv N}$ stretch in **3a** was located at 1015 cm^{-1}, a value that is close to that in [HIPTN$_3$N]Mo≡N (1012 cm^{-1}; Table 3).[25] In **3c**, the $\nu_{Mo\equiv N}$ stretch was found at 1013 cm^{-1} (985 cm^{-1} in the ^{15}N analogue). Therefore, any electronic

Table 4. Selected Bond Distances [Å] and Angles (deg) for [*p*BrHIPTN$_3$N]Mo≡N

Mo−N(1)	2.047(8)	C(201)−N(2)−Mo	130.5(10)
Mo−N(2)	2.018(10)	C(301)−N(3)−Mo	128.5(9)
Mo−N(3)	1.980(10)	N(2)−Mo−N(4)	79.3(5)
Mo−N(4)	2.324(9)	N(3)−Mo−N(4)	75.8(4)
Mo−N(5)	1.679(9)	N(1)−Mo−N(4)	78.3(4)
		N(2)−Mo−N(5)	101.1(5)
		N(3)−Mo−N(5)	102.4(5)
		N(1)−Mo−N(5)	103.2(4)
		N(4)−Mo−N(5)	178.1(4)
		N(2)−Mo−N(3)	119.3(4)
		N(2)−Mo−N(1)	114.2(4)
		N(3)−Mo−N(1)	113.5(4)
		C(101)−N(1)−Mo	128.0(9)

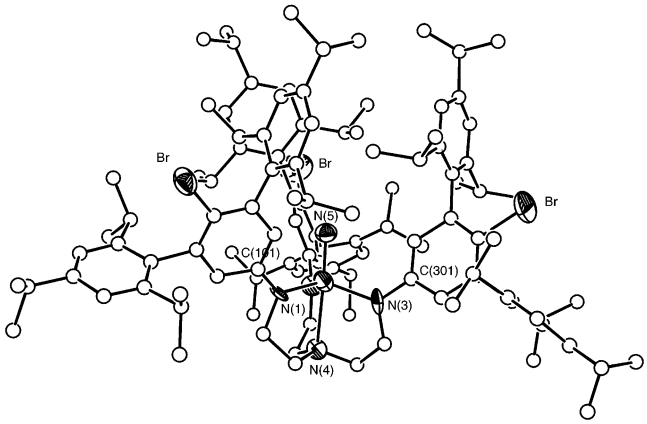


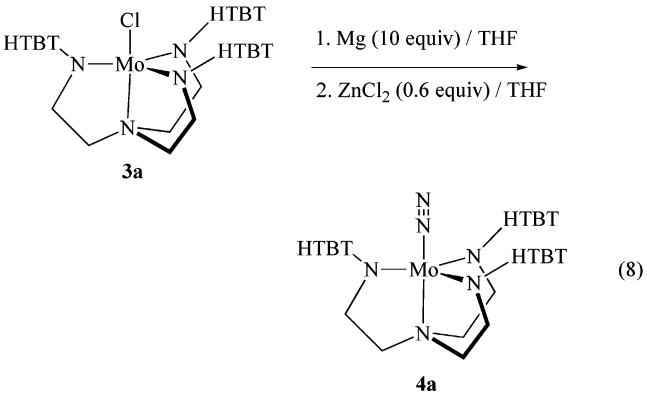
Figure 2. Thermal ellipsoid plot of the crystal structure of [*p*BrHIPTN$_3$N]-Mo≡N (**3c**) (50% probability level). Hydrogen atoms are omitted for clarity. All non-hydrogen atoms were refined anisotropically.

differences between the compounds that contain HIPT, HTBT, or *p*BrHITP are reflected minimally in the value for $\nu_{Mo\equiv N}$.

An X-ray study of **3c** reveals it to have a structure similar to that of [HIPTN$_3$N]Mo≡N[25] (Tables 1 and 4, Figure 2). In **3c**, the Mo≡N bond lengths are 1.679(9) Å (vs 1.652(5) Å in [HIPTN$_3$N]Mo≡N), the Mo−N(4) bond lengths are 2.324(9) Å (vs 2.395(5) Å), and the Mo−N−C$_{ipso}$−C$_o$ angles are 38.3°, 32.9°, and 22.3° (vs 35.6°, 35.4°, and 33.5°).

Synthesis of Dinitrogen Complexes. Reduction of **2a** in THF with 10 equiv of magnesium powder (activated with 0.5 equiv of 1,2-dibromoethane) under a dinitrogen atmosphere gave the {(HTBTNCH$_2$CH$_2$)$_3$N]MoN$_2$}$^-$ species as a mixture of magnesium salts,[25] as suggested by a color change from red-orange to dark green. However, the reaction is much slower than the reduction of [HIPTN$_3$N]MoCl, the dark-green color appearing only after 4−5 h instead of 1 h. ZnCl$_2$ was added immediately to a filtered dark-green solution of {[HTBTN$_3$N]MoN$_2$}$^-$ to give zinc metal and [HTBTN$_3$N]Mo(N$_2$) (**4a**) as a dark-green solid in 64% isolated yield (eq 8). The ^{1}H NMR spectrum of **4a** features three paramagnetically shifted resonances at 22.85 ppm (backbone CH$_2$), −7.11 ppm (H$_o$), and −32.35 ppm (backbone CH$_2$), and the IR spectrum in C$_6$D$_6$ reveals the NN stretch at 1990 cm^{-1}, which is identical to ν_{NN} in [HIPTN$_3$N]Mo(N$_2$). The ^{15}N$_2$ analogue, **4a-^{15}N$_2$**, was prepared in 48% yield by a procedure under ^{15}N$_2$ that was similar to that used for the unlabeled complex. The value of $\nu(^{15}N^{15}N)$ was found to be 1924 cm^{-1}, which is the same as in [HIPTN$_3$N]Mo(^{15}N$_2$).

If the green solution containing {HTBTN$_3$N]MoN$_2$}$^-$ formed upon Mg reduction of **2a** under N$_2$ is treated with Bu$_4$NCl and 10 equiv of dioxane, then {Bu$_4$N}{[HTBTN$_3$N]MoN$_2$} (**5a**) can



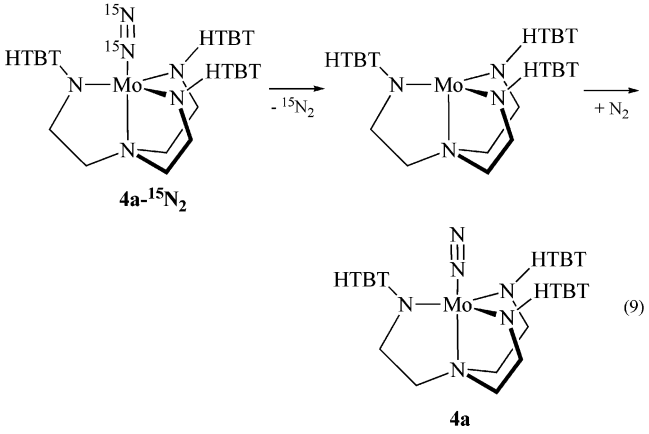
(8)

be isolated as dark emerald-green crystals from pentane/benzene in 59% yield. This diamagnetic species shows all of the expected resonances in the ^{1}H NMR spectrum, and its IR spectrum features a ν_{NN} stretch at 1847 cm^{-1}, a value that is 8 cm^{-1} lower than that in {Bu$_4$N}{[HIPTN$_3$N]MoN$_2$} (Table 3).[25] According to this datum, the [HTBTN$_3$N]$^{3-}$ ligand is slightly more electron-donating than [HIPTN$_3$N]. It is interesting to note that the lower stretching frequency is not observed in the neutral N$_2$ adducts, but only in the anionic complexes, in which back-bonding to N$_2$ is more pronounced. However, the effect is still small.

An attempted reduction of **2b** under the same conditions as reduction of **2a** did not lead to an analogous dinitrogen complex **4b**. A reaction took place, but the product appeared to be too unstable, at least under the conditions employed, to allow a subsequent oxidation to a dinitrogen complex.

Attempts to prepare and isolate pure [*p*BrHIPTN$_3$N]Mo(N$_2$) (**4c**) also have not been successful, even though the procedure followed was nearly identical to the procedure published for the synthesis of [HIPTN$_3$N]Mo(N$_2$). However, IR spectra in C$_6$D$_6$ of the crude mixture obtained upon reduction of **2c** show that it consists largely of [*p*BrHIPTN$_3$N]Mo(N$_2$) and [*p*BrHIPTN$_3$N]Mo−N═N−Mg(THF)$_x$Cl, judging from ν_{NN} peaks at 1992 cm^{-1} and ν_{NN} 1788 cm^{-1}, respectively (in benzene). The low value of 1788 cm^{-1} for ν_{NN} is a consequence of binding of the magnesium to the β nitrogen atom.[25] The former should be compared with the ν_{NN} peak at 1990 cm^{-1} in [HIPTN$_3$N]Mo(N$_2$) itself.[25] The shift of 2 cm^{-1} to higher energy is in the direction expected for a more electron-withdrawing ligand and consequently less back-bonding to the dinitrogen ligand. The magnitude of the shift was smaller than we expected, although it is at least observable in the neutral dinitrogen complex in this case. A sample of {Et$_4$N}{[*p*BrHIPTN$_3$N]-MoN$_2$} could be isolated (in 25% yield) that showed a ν_{NN} value of 1857 cm^{-1} (vs 1855 cm^{-1} in the HIPT analogue as the {Bu$_4$N}$^+$ salt). Again, the shift of 2 cm^{-1} to higher energy is in the direction expected for a more electron-withdrawing ligand.

When a C$_6$D$_6$ solution of **4a-^{15}N$_2$** was placed under 1 atm of ^{14}N$_2$, **4a** was formed over a period of weeks. The consumption of **4a-^{15}N$_2$** was followed by IR and was found to proceed with $t_{1/2} \approx 750$ h at 22 °C. This rate is ∼20 times slower than that for ^{15}N$_2$/^{14}N$_2$ exchange in the HIPT system ($t_{1/2} \approx 35$ h).[25] An experiment at a pressure of 5 atm of ^{14}N$_2$ yielded essentially the same result, which suggests that the ^{15}N$_2$/^{14}N$_2$ exchange mechanism is unimolecular; we propose that "[HTBTN$_3$N]Mo" is the intermediate (eq 9). The exchange rate in **4a-^{15}N$_2$** is even slower than that observed in [(Me$_3$SiCH$_2$CH$_2$N)$_3$N}Mo(^{14}N$_2$)



($^{14}N_2/^{15}N_2 \approx 2/1$ after 1 week under a $^{15}N_2$ atmosphere).[33] The slower $^{14}N_2/^{15}N_2$ exchange rate observed in $[TMSN_3N]Mo(^{14}N_2)$ as compared to $[HIPTN_3N]Mo(^{15}N_2)$ (assuming that any primary isotope is small) can be explained in terms of the stronger back-bonding to dinitrogen in $[TMSN_3N]Mo(^{14}N_2)$ ($\nu_{NN} = 1934$ cm^{-1} in pentane; Table 3) versus $[HIPTN_3N]Mo(^{14}N_2)$ ($\nu_{NN} = 1990$ cm^{-1}). Because the $[HTBTN_3N]^{3-}$ ligand appears to be only slightly more electron-donating than $[HIPTN_3N]^{3-}$, we propose that the 20-fold decrease in the exchange rate originates primarily from increased steric crowding in **4a** on the periphery of the binding pocket, which hinders loss of N_2 after it dissociates from the metal. These findings are relevant to dinitrogen reduction because loss of ammonia from $[TerN_3N]Mo(NH_3)$, and replacement of that ammonia with dinitrogen, therefore might also be much more difficult in $[HTBTN_3N]Mo(NH_3)$ than in $[HIPTN_3N]Mo(NH_3)$ (see later).

All isolated $[TerN_3N]Mo(N_2)$ derivatives undergo reversible one-electron electrochemical reductions to the corresponding $\{[TerN_3N]Mo(N_2)\}^-$ ions in THF. Electrochemical potentials determined by cyclic voltammetry in THF are collected in Table 5. The peak current ratio for all couples is near unity, and the peak separation is about 100 mV for all Mo derivatives and for the $Cp_2Fe^{+/0}$ couple, as a consequence of the relatively high solution resistance. The CV of $\{Bu_4N\}\{[HIPTN_3N]Mo(N_2)\}$ is identical to that of $[HIPTN_3N]Mo(N_2)$ in the reverse scan direction. The CV of $[HTBTN_3N]Mo(N_2)$ (**4a**) reveals that reduction of $[HTBTN_3N]Mo(N_2)$ is 30 mV more difficult than reduction of $[HIPTN_3N]Mo(N_2)$. The shift in the redox potential is consistent with a slightly greater donating ability of the $[HTBTN_3N]^{3-}$ ligand versus the $[HIPTN_3N]^{3-}$ ligand. The CV of $\{Et_4N\}\{[p\text{BrHIPTN}_3N]Mo(N_2)\}$ reveals a reversible couple for $[p\text{BrHIPTN}_3N]Mo(N_2)^{0/-}$ at -1.71 V, 100 mV more positive than the couple for $[HIPTN_3N]Mo(N_2)^{0/-}$. We conclude that electrochemistry is the most sensitive and most relevant method for determining the relative electron-donating ability of the ligands and that the electron-donating order is what one might expect, HTBT > HIPT > *p*BrHIPT. The low potentials for reduction of the $[TerN_3N]Mo(N_2)$ species make it unlikely that $\{[TerN_3N]Mo(N_2)\}^-$ is formed first upon reduction of $[TerN_3N]Mo(N_2)$ by $CoCp_2$ ($E^{o\prime} = -1.33$ V; Table 5) followed by addition of a proton, although that possibility cannot yet be ruled out rigorously. Because addition of $CoCp_2$ and 2,6-lutidinium to $[HIPTN_3N]Mo(N_2)$ in benzene yields $[HIPTN_3N]Mo{-}N{=}$NH immediately,[26] we have postulated (on the basis of IR evidence) that a proton adds first to an amido nitrogen, the resulting cation is then reduced and dinitrogen is protonated, and finally the original proton is lost from the amido nitrogen.

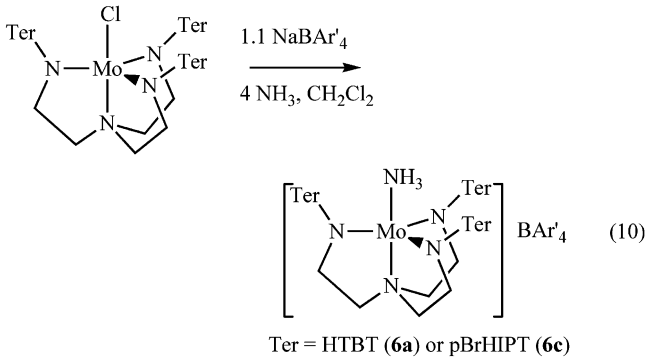
(33) O'Donoghue, M. B.; Davis, W. M.; Schrock, R. R. *Inorg. Chem.* **1998**, *37*, 5149.

Table 5. Electrochemical Data of $[TerN_3N]Mo$ Derivatives and Metallocene Reductants[a]

	$E^{o\prime}$, V[b]
$[p\text{BrHIPTN}_3N]Mo(N_2)^{0/-}$	−1.71
$[HIPTN_3N]Mo(N_2)^{0/-}$	−1.81
$[HTBTN_3N]Mo(N_2)^{0/-}$	−1.84
$[p\text{BrHIPTN}_3N]Mo(NH_3)^{+/0}$	−1.46
$[HIPTN_3N]Mo(NH_3)^{+/0}$	−1.51
$[HTBTN_3N]Mo(NH_3)^{+/0}$	−1.61
$CoCp_2^{+/0}$	−1.33
$CrCp^*_2{}^{+/0}$	−1.47
$CoCp^*_2{}^{+/0}$	−1.84

[a] Cyclic voltammetry in 0.4 M $[Bu_4N][PF_6]$ in THF. [b] Referenced externally and/or internally to $FeCp_2^{+/0}$ or $CoCp_2^{+/0}$ at scan rates of 10−25 mV/s; all values are listed relative to $FeCp_2^{+/0}$.

Synthesis of Cationic Ammonia Adducts. Compounds **2a** and **2c** react with 4 equiv of ammonia and 1.1 equiv of $NaBAr'_4$ (Ar′ = 3,5-$(CF_3)_2C_6H_3$)) in CH_2Cl_2 to yield the respective $\{[TerN_3N]Mo(NH_3)\}\{BAr'_4\}$ salts in good yields (Ter = HTBT, **6a**, 91%; *p*BrHIPT, **6c**, 81%; eq 10). The reaction to give **6a** required 24 h, and that to give **6c** required 12 h. (The low overall yields of the $H_3[HMTN_3N]$ and "hybrid" ligands limited synthesis and examination of compounds that contain those triamidoamine ligands.) These syntheses are analogous to the synthesis of $\{[HIPTN_3N]Mo(NH_3)\}\{BAr'_4\}$.[25]

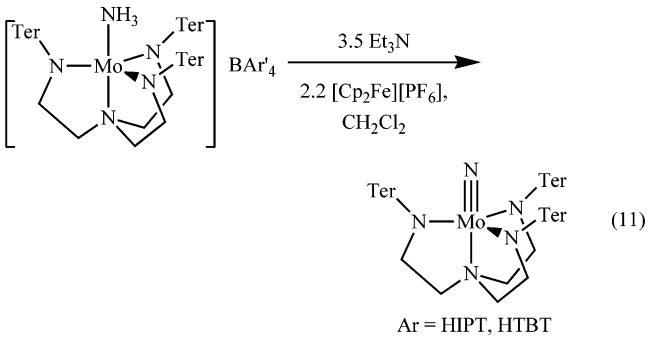


Ter = HTBT (**6a**) or pBrHIPT (**6c**)

Proton NMR spectra of both **6a** and **6c** feature patterns characteristic of a high-spin Mo(IV) environment, with backbone methylene resonances paramagnetically shifted to −12 and −106 ppm in **6a**, and to −16 and −110 ppm in **6c**. All cationic ammonia adducts undergo reversible one-electron electrochemical reductions to the neutral derivatives. The $[TerN_3N]Mo(NH_3)^{+/0}$ potentials summarized in Table 5 suggest an order of electron-donating ability of the $[TerN_3N]^{3-}$ ligands similar to that suggested by the $[TerN_3N]Mo(N_2)^{0/-}$ potentials, but with a 100 mV difference between $[HTBTN_3N]Mo(NH_3)^{+/0}$ and $[HIPTN_3N]Mo(NH_3)^{+/0}$, and a 50 mV difference between $[HIPTN_3N]Mo(NH_3)^{+/0}$ and $[p\text{BrHIPTN}_3N]Mo(NH_3)^{+/0}$. These results suggest that, while $CrCp^*_2$ is able to reduce $\{[HIPTN_3N]Mo(NH_3)\}\{BAr'_4\}$ (consistent with the successful catalytic reduction of dinitrogen by $[HIPTN_3N]Mo$ compounds with $CrCp^*_2$ as the reductant[26]), $CrCp^*_2$ is not likely to reduce $\{[HTBTN_3N]Mo(NH_3)\}\{BAr'_4\}$ as efficiently.

Both $\{[HIPTN_3N]Mo(NH_3)\}\{BAr'_4\}$ and **6a** react with $[Cp_2Fe][PF_6]$ and Et_3N in benzene or CH_2Cl_2 to yield the respective

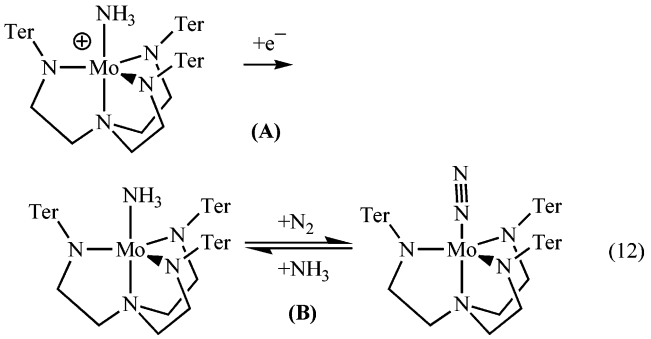
nitrides immediately and quantitatively in ^{1}H NMR scale reactions (eq 11). This route to nitrides allows fully ^{15}N-labeled



(11)

derivatives to be prepared. Thus, **6a-^{15}N**, formed in situ from **2a** and $^{15}NH_3$, afforded **3a-^{15}N** in 23% isolated (nonoptimized) yield. Both the ^{15}N NMR chemical shift (898.3 ppm) and $\nu_{Mo^{15}N}$ (991 cm^{-1}) of **3a-^{15}N** are similar to those of [HIPTN$_3$N]Mo≡^{15}N.[25] We propose that triethylamine initially deprotonates {[TerN$_3$N]Mo(NH$_3$)}$^+$ to give [TerN$_3$N]Mo(NH$_2$), which is then oxidized to yield {[TerN$_3$N]Mo(NH$_2$)}$^+$. A subsequent deprotonation/oxidation/deprotonation sequence then yields [TerN$_3$N]-Mo≡N. Of course, the reaction shown in eq 11 is the reverse of the proposed method of converting [TerN$_3$N]Mo≡N into {[TerN$_3$N]Mo(NH$_3$)}$^+$ in the catalytic cycle.[25,26]

Conversion of {[TerN$_3$N]Mo(NH$_3$)}$^+$ to [TerN$_3$N]Mo(N$_2$). Two key steps in the catalytic reduction of dinitrogen by [TerN$_3$N]Mo derivatives of the type described here appear to be reduction of the cationic ammonia adducts to neutral ammonia complexes (step A; eq 12) and replacement of ammonia by dinitrogen (step B; eq 12). Conversion of [TerN$_3$N]-Mo(NH$_3$) to [TerN$_3$N]Mo(N$_2$) is believed to take place through formation of intermediate "[TerN$_3$N]Mo", a type of species that has not been observed in any [RN$_3$N]Mo system so far (R = TMS,[33] C$_6$F$_5$,[34] Aryl,[32] or Terphenyl[25]), and that is the same intermediate proposed in the replacement of $^{15}N_2$ with $^{14}N_2$ in [TerN$_3$N]Mo(^{15}N$_2$) derivatives (eq 9). Therefore, we turned to a qualitative exploration of the conversion of {[TerN$_3$N]Mo-(NH$_3$)}$^+$ to [TerN$_3$N]Mo(N$_2$) derivatives in the presence of various reducing agents.



(12)

According to the redox potentials in THF (Table 5), cobaltocene is not a sufficiently strong reductant to completely reduce {[HIPTN$_3$N]Mo(NH$_3$)}{BAr′$_4$} in step **A**; no reaction takes place between {[HIPTN$_3$N]Mo(NH$_3$)}{BAr′$_4$} and 3 equiv of CoCp$_2$ in C$_6$D$_6$. However, after 19 h, a mixture of {[HIPTN$_3$N]-Mo(NH$_3$)}{BAr′$_4$} and [HIPTN$_3$N]Mo(N$_2$) is established, with {[HIPTN$_3$N]Mo(NH$_3$)}{BAr′$_4$} being the major species present, which suggests that, although no [HIPTN$_3$N]Mo(NH$_3$) can be observed upon reduction of {[HIPTN$_3$N]Mo(NH$_3$)}{BAr′$_4$} with CoCp$_2$, enough must be formed to allow step **B**. When employed in 2-fold excess in C$_6$D$_6$, stronger reductants such as CrCp*$_2$ or CoCp*$_2$ rapidly and quantitatively reduce {[HIPTN$_3$N]Mo-(NH$_3$)}{BAr′$_4$} to [HIPTN$_3$N]Mo(NH$_3$). The outcome of the CrCp*$_2$ reduction is important in showing that precipitation of {CrCp*$_2$ }{BAr′$_4$} out of C$_6$D$_6$ increases the reaction driving force according to the potentials in THF (Table 5) and this effect should be even more pronounced in the heptane used in catalytic dinitrogen reduction studies. Once formed, [HIPTN$_3$N]Mo(NH$_3$) undergoes exchange step **B** on the time scale of minutes to hours. For example, an equilibrium, near-equimolar mixture of [HIPTN$_3$N]Mo(NH$_3$) and [HIPTN$_3$N]Mo(N$_2$) is formed in under 6 h in C$_6$D$_6$, and full conversion to [HIPTN$_3$N]Mo(N$_2$) can be effected in under 30 min when ammonia is scavenged by added BPh$_3$.

The HTBT derivative, {[HTBTN$_3$N]Mo(NH$_3$)}{BAr′$_4$} (**6a**), undergoes reduction at a potential 100 mV more negative than that of {[HIPTN$_3$N]Mo(NH$_3$)}$^+$ (Table 5). Accordingly, chemical reduction of **6a** with 2 equiv of CrCp*$_2$ in C$_6$D$_6$ under dinitrogen now affords only a 40:60 mixture of **6a** and [HTBTN$_3$N]Mo(NH$_3$). The two are present in a fast equilibrium on the NMR time scale, such that paramagnetically shifted resonances of the separate species are not observed; only weighted-average resonances are observed in the diamagnetic region. (The locations of resonances for [HTBTN$_3$N]Mo(NH$_3$) were determined by reducing **6a** quantitatively with CoCp*$_2$.) The 40:60 equilibrium mixture of {[HTBTN$_3$N]Mo(NH$_3$)}$^+$ and [HTBTN$_3$N]Mo(NH$_3$) evolves further upon exchange of ammonia with dissolved N$_2$ to yield [HTBTN$_3$N]Mo(N$_2$) (**4a**), although this takes place much more slowly than in the [HIPTN$_3$N]$^{3-}$ system; a 50% conversion of all Mo species present into **4a** is observed after 111 hs at 22 °C. Thus, the more electron-donating [HTBTN$_3$N]$^{3-}$ ligand hinders reduction step **A** in the overall conversion shown in eq 12 relative to that of {[HIPTN$_3$N]Mo(NH$_3$)}$^+$ with the same reductant, CrCp*$_2$. Furthermore, if exchange step **B** takes place via a dissociative mechanism, by analogy to the N$_2$ exchange in **4a** (vide supra), it should be faster with a more electron-rich metal center, other conditions being equal. The opposite is observed experimentally. Therefore, it appears that the increased steric crowding of the [HTBTN$_3$N]$^{3-}$ ligand in the canopy above the binding pocket impedes the loss of ammonia once it dissociates from Mo. In sum, these observations demonstrate that **6a** is less likely to undergo the transformation shown in eq 12 under the conditions used to effect dinitrogen reduction with {[HIPTN$_3$N]Mo(NH$_3$)}$^+$ as the catalyst.

Addition of 5 equiv of CoCp$_2$ to {[*p*BrHIPTN$_3$N]Mo(NH$_3$)}-{BAr′$_4$} in C$_6$D$_6$ results in complete reduction of the cationic species to [*p*BrHIPTN$_3$N]Mo(NH$_3$) in approximately 30 min, and formation of a mixture of [*p*BrHIPTN$_3$N]Mo(NH$_3$) and [*p*BrHIPTN$_3$N]Mo(N$_2$) over a period of 6−12 h. Therefore, reduction of {[*p*BrHIPTN$_3$N]Mo(NH$_3$)}{BAr′$_4$} to [*p*BrHIPTN$_3$N]-Mo(NH$_3$) with CoCp$_2$ is more complete than in the [HIPTN$_3$N]$^{3-}$ system, but the observed ammonia/nitrogen exchange rate appears to be slower than in the [HIPTN$_3$N]$^{3-}$ system, most likely because the metal is slightly more electrophilic.

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Table 6. Dinitrogen Reduction with Various [TerN$_3$N]Mo Derivatives[a]

[TerN$_3$N]Mo	reductant	runs	equiv of NH_3 per Mo	yield NH_3, %[b]
[HTBTN$_3$N]Mo≡N (**3a**)	$CrCp^*_2$	1	1.06	8.8
[HTBTN$_3$N]Mo(N$_2$) (**4a**)	$CrCp^*_2$	1	1.27	10.6
[HMTN$_3$N]Mo≡N (**3b**)	$CrCp^*_2$	1	1.49	12.4
3b	$CrCp^*_2$	1[c]	0.99	8.3
[*p*BrHIPTN$_3$N]Mo≡N (**3c**)	$CrCp^*_2$	4[d]	6.4−7.0	59(2)
3c	$CoCp_2$	3[e]	2.6−2.9	23(1)
[HIPTN$_3$N]Mo≡N	$CoCp_2$	1	3.6	37
[HIPTN$_3$N]MoH	$CrCp^*_2$	3	7.65(3)	65.6(2)[f]

[a] Unless otherwise indicated, all runs were carried out through dropwise addition over a period of 6 h of a solution of 36 equiv of $CrCp^*_2$ in 10.0 mL of heptane at a rate of 1.7 mL/h to a mixture of 0.6 mL of heptane, 5.85−5.94 μmol of [TerN$_3$N]Mo, and 48 equiv of [2,6-LutH][BAr′$_4$] with constant stirring at 1250 rpm at 22−26 °C. Stirring was continued for one additional hour. The apparatus was sealed under 1 atm of N_2; it had a headspace volume of 68 mL. [b] Yield = NH_3(found, average)/NH_3(theory). For simplicity, the theoretical amount of ammonia is based on electrons added (one NH_3 per three electrons). Any ammonia that might be formed from nitride without addition of electrons is not included. [c] $CrCp^*_2$ solution was added to a mixture of [HMTN$_3$N]Mo≡N and [2,6-LutH][BAr′$_4$] in a mixture of 0.3 mL of C_6H_6 and 0.3 mL of heptane. [d] These runs employed 5.85−7.04 μmol of **3c**, 31.35−36.42 equiv of $CrCp^*_2$, and 48−50 equiv of [2,6-LutH][BAr′$_4$]; 6.35, 6.58, 6.91, and 7.04 equiv of ammonia per Mo were formed for an average yield of 59% ($\sigma = 2$). [e] The reducing agent was added over a period of 6 h in two experiments and 20 h in a third. These runs employed 6.7−7.0 μmol of **3c**, 36.3−38.1 equiv of $CoCp_2$, and 44−49 equiv of [2,6-LutH][BAr′$_4$]; 2.56 (20 h), 2.55 (6 h), and 2.89 (6 h) equiv of ammonia per Mo were formed for an average yield of 23% ($\sigma = 1$). [f] 7.67, 7.67, and 7.62 equiv of ammonia out of 11.67 theoretical equiv.

Catalytic Dinitrogen Reduction Studies. Several [TerN$_3$N]-Mo derivatives (Ter = HTBT, HMT, or *p*BrHIPT) were screened as catalysts for dinitrogen reduction under conditions identical to those employed for the HIPT derivatives.[26] The results are summarized in Table 6. Reactions that involved **3a** and **4a** yielded only 1.06 and 1.27 equiv of ammonia per Mo, respectively. The first suggests that the nitride (**D**, Scheme 1) is reduced to the cationic ammonia complex (**F**), but there is little reduction of **F** and formation of **A**. Visually, it can be seen that {[HTBTN$_3$N]Mo(NH$_3$)}$^+$ (**6a)** is not reduced readily; that is, the reaction effectively stops at **6a**, 1 equiv of ammonia being recovered upon workup. This result is also consistent with the electrochemical results (Table 5), which show that {[HTBTN$_3$N]Mo(NH$_3$)}$^+$ is reduced in THF at a potential 100 mV more negative than {[HIPTN$_3$N]Mo(NH$_3$)}$^+$. Also, as outlined in the previous section, it is almost certainly true that ammonia cannot escape as readily from [HTBTN$_3$N]Mo(NH$_3$) as it does from [HIPTN$_3$N]Mo(NH$_3$) and the conversion of **G** to **A** therefore is slow.[35] This combination of problems will clearly limit conversion of **F** to **A**. The second result suggests that there may be additional problems associated with conversion of **A** to **D**, although the nature of these problems is unknown at this stage. The primary problem may simply be a slowing of all steps as a consequence of overall crowding in the [HTBTN$_3$N]$^{3-}$ systems. In any case, it is startling how dramatic are the consequences of changing from a HIPT-based to a HTBT-based ligand.

Derivative **3b** is also a poor catalyst for the reduction of dinitrogen, giving only 1.49 equiv of NH_3 under our standard conditions; that is, the reaction is barely catalytic. Here, a significant problem is likely to be the low solubility of the initial complex (**3b**) and perhaps other intermediates in the hypothetical catalytic cycle in heptane. An attempt to increase the solubility of **3b** and/or enable its conversion into other, more soluble derivatives by using a 0.3 mL:0.3 mL mixture of benzene and heptane resulted in formation of even less ammonia (0.99 equiv per Mo), with most of the **3b** still not being dissolved during the run. Therefore, other problems may be responsible for the low yield of ammonia when **3b** is employed as the catalyst.

In contrast, [*p*BrHIPTN$_3$N]Mo≡N is a catalyst for the formation of ammonia in yields only slightly less than those observed employing [HIPTN$_3$N]$^{3-}$ derivatives (∼65%).[26] (The four runs were carried out by two researchers in different ammonia "reactors."[26]) While {[*p*BrHIPTN$_3$N]Mo(NH$_3$)}$^+$ is more easily reduced than {[HIPTN$_3$N]Mo(NH$_3$)}$^+$, qualitative studies in the previous section suggest that ammonia is lost less readily from [*p*BrHIPTN$_3$N]Mo(NH$_3$), presumably as a consequence of the more electron-withdrawing nature of the [*p*BrHIPTN$_3$N]$^{3-}$ ligand. Therefore, the yield of ammonia is decreased, but only slightly.

We found that $CoCp_2$ can also be employed as the reductant using **3c** as the catalyst (three runs; Table 6), although the yield of ammonia (2.9 equiv) is less than half that when $CrCp^*_2$ is the reductant. (Lengthening the time of addition of $CoCp_2$ to 20 hours resulted in little change in this yield of ammonia.) A similar run in which [HIPTN$_3$N]Mo≡N was employed as the catalyst yielded 3.6 equiv of ammonia (37%; Table 6). Both catalysts are less efficient with $CoCp_2$ as the reductant, because less of the neutral ammonia complex is formed with the weaker reductant. Interestingly, [HIPTN$_3$N]Mo≡N is still more efficient than [*p*BrHIPTN$_3$N]Mo≡N, which is the order found when $CrCp^*_2$ is the reductant (∼64% with [HIPTN$_3$N]Mo≡N vs ∼59% with [*p*BrHIPTN$_3$N]Mo≡N). Because both $CrCp^*_2$ and $CoCp_2$ are suitable reducing agents (with efficiencies mirroring their reducing abilities), it seems likely that they behave as simple reducing agents; that is, they are not involved in any chemically more intimate manner.

In all catalytic dinitrogen reduction studies, we presume that formation of dihydrogen is the alternative to formation of ammonia, either at the metal center (see below), or through the direct reduction of protons by the relatively strong reducing agents employed here. The less efficient formation of ammonia when $CoCp_2$ is the reducing agent would lead to formation of more dihydrogen, because the competing reduction of protons with $CoCp_2$ is still relatively fast. It is desirable to confirm that dihydrogen is formed and quantitate it in all of the experiments listed in Table 6 (and analogous experiments reported elsewhere[26]). However, under the present experimental conditions, as little as 1−2 mL (at 1 atm) of dihydrogen would be formed. We hope to be able to quantitate such small amounts in future studies.

It seems possible that [HIPTN$_3$N]MoH, a known compound,[25] might be formed under catalytic conditions. Therefore, we tested whether [HIPTN$_3$N]MoH is an efficient precursor for catalytic formation of ammonia. As shown in Table 6, it is as efficient as any catalyst for dinitrogen reduction of this general type.[26] This fact suggests that [HIPTN$_3$N]MoH can be protonated and reduced to yield dihydrogen and [HIPTN$_3$N]Mo(N$_2$) in the presence of dinitrogen. We have no way of knowing how much dihydrogen is formed at the metal in this manner (i.e., with the

(35) Measuring the rate of exchange of ammonia for dinitrogen in the Mo(III) species is not a trivial experiment, although we hope to devise a means of doing so eventually.

metal behaving as a hydrogenase) and how much is formed by direct electron transfer to protons.

Conclusions

It is clear that relatively subtle steric and electronic variations of the $[TerN_3N]^{3-}$ ligand system produce relatively profound changes in the efficacy of the catalytic reduction of dinitrogen to ammonia, at least for the three variations that we have examined so far under our "standard" conditions. The steps that are most sensitive to change in the $[TerN_3N]^{3-}$ ligand system appear to be reduction of $\{[TerN_3N]Mo(NH_3)\}^+$ to $[TerN_3N]Mo(NH_3)$, the equilibrium involving loss of ammonia from $[TerN_3N]Mo(NH_3)$ to give unobservable $[TerN_3N]Mo$, and binding of dinitrogen to $[TerN_3N]Mo$ to give $[TerN_3N]Mo(N_2)$ (eq 12). The slightly more electron-withdrawing $[p\text{BrHIPTN}_3N]^{3-}$ ligand allows a weaker reducing agent to be employed, but the tradeoff is that ammonia is lost less easily from the Mo(III) center. Insolubility of catalytic intermediates is a problem that plagues the $[HMTN_3N]^{3-}$ system, while too much steric congestion plagues the $[HTBTN_3N]^{3-}$ system, probably through reducing the rate of virtually all reactions. In a system in which all intermediates are in solution, it is likely that several could themselves behave as acids or reducing agents toward others; whether this happens rapidly under the "standard" reduction conditions, or is an advantage or a disadvantage, is not known. Because the buildup of gaseous ammonia would retard loss of ammonia from $[TerN_3N]Mo(NH_3)$, it may prove beneficial to remove any gaseous ammonia efficiently during the reduction to push the overall efficiency to higher levels. As we strive toward the goal of using weaker acids and weaker reductants, and to achieving higher turnover numbers, we expect to encounter other complex issues in a reaction that may involve a dozen or more discrete intermediates.

Experimental Section

General. All manipulations of air- and moisture-sensitive compounds were carried out with standard Schlenk and glovebox techniques under an atmosphere of nitrogen using oven-dried glassware. THF and benzene were purged with dinitrogen and were passed through columns of activated alumina and supported copper catalyst (Q5; benzene only).[36] Toluene and pentane were purged with nitrogen and passed through a column of activated alumina. For reactions involving molybdenum compounds, pentane was additionally degassed (freeze−pump−thaw) three times, and THF, benzene, and toluene were vacuum-transferred from dark purple Na/benzophenone ketyl solutions into storage Schlenk flasks and degassed three times using a freeze−pump−thaw method. C_6D_6 was dried over Na/benzophenone, vacuum-transferred into a storage Schlenk flask, and freeze−pump−thaw degassed three times. $CDCl_3$ was used as received. All dried and deoxygenated solvents were stored over molecular sieves (4 Å) in a nitrogen-filled glovebox.

1,3,5-Tri-*tert*-butylbenzene (Fluka), 2,4,6-tribromoaniline, 2-bromomesitylene, 4-*tert*-butylbromobenzene, $(Me_3Si)_2NLi$ (sublimed), $N(CH_2CH_2NH_2)_3$, NaO-*t*-Bu, anhydrous $ZnCl_2$, Mg powder (−50 mesh; washed with HCl (3.7%), water, THF, diethyl ether, and dried under vacuum; Aldrich), $Pd_2(dba)_3$, *rac*-BINAP, Mg turnings, $CoCp_2$ (sublimed), $CrCp^*_2$ (sublimed), $MoCl_5$ (Strem), Me_3SiN_3 (Acros), and $^{15}N_2$ (CIL) were used as received unless otherwise indicated. 2,4,6-Tri-*tert*-butylbromobenzene,[37] 2,4,6-tribromoiodobenzene,[27] [2,6-lutidinium]-[BAr′$_4$],[25] bromo-2,4,6 triisopropylbenzene,[38] and $MoCl_4(THF)_2$[39] were prepared according to published methods. All Mo complexes were stored under N_2 at −35 °C.

Catalytic dinitrogen reduction runs were performed using reagents, equipment, and procedures described previously.[26]

NMR spectra were recorded at 298 K on Varian Mercury 300 or Varian Unity 300 spectrometers operating at 300 MHz for ^{1}H and at 75 MHz for ^{13}C $\{^1H\}$. Chemical shifts (δ) are referenced to the residual deuterated solvent peaks and are reported in ppm. Coupling constants (J) are in hertz. IR spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer in a demountable solution cell (0.2 mm Teflon spacer, KBr windows). Elemental analyses were performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany.

Electrochemical measurements were carried out with BAS CV-50W potentiostat. Platinum disk (1.6 mm dia), platinum wire, and a silver wire submerged in a 10 mM solution of AgOTf in 0.4 M $[Bu_4N][PF_6]$ in THF were used as working, auxiliary, and reference electrode, respectively. All measurements were done in 0.4 M $[Bu_4N][PF_6]$ in THF and referenced externally and/or internally to Cp_2Fe or $CoCp_2$.

3,5-Bis(2,4,6-tri-*tert*-butylphenyl)bromobenzene (HTBTBr). A three-neck round-bottom flask set with a N_2-inlet, a condenser, and an addition funnel was charged with Mg turnings (6.6 g, 271 mmol) and THF (60 mL). Previously degassed 2,4,6-tri-*tert*-butylbromobenzene (44.4 g, 136 mmol) was dissolved in THF (215 mL) in a Schlenk flask, and the solution was added to the addition funnel with a cannula. The round-bottom flask was heated with a heat gun until THF started to reflux, and ∼5 mL of the 2,4,6-tri-*tert*-butylbromobenzene solution was added to initiate the Grignard reaction. After initiation, the remainder of the bromide solution was added over a period of 1 h. When approximately half the solution had been added, the reaction flask was placed in an oil bath at 85 °C, and the reaction was refluxed overnight. THF (175 mL) was added to the addition funnel and added to the refluxing reaction mixture. 2,4,6-Tribromoiodobenzene (17.1 g, 38.9 mmol) was dissolved in THF (70 mL) in a Schlenk flask and added to the addition funnel with a cannula. The solution was added dropwise over a period of 45 min, and the reaction mixture was refluxed for 4 h. The resulting orange reaction mixture was cooled to room temperature. The mixture was then decanted from excess Mg and quenched by pouring it into cold HCl (60 mL, 10%). The aqueous phase was diluted with 100 mL of water, and some Na_2SO_3 was added. When THF was removed on the rotary evaporator, a large amount of solid formed in the flask. The aqueous phase was extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed with water (2 × 100 mL), dried over $MgSO_4$, and concentrated until a white solid (8.29 g) precipitated. This solid was filtered off and washed with a small portion of ether. Further concentration yielded 0.85 g more. The remaining mother liquors were reduced to a thick orange oil, and 1,3,5-tri-*tert*-butylbenzene was removed by vacuum distillation. (This is a tedious process because it crystallizes in the column.) Column chromatography on silica (25 × 7 cm) with hexanes as eluent yielded an additional 1.19 g; total yield 10.33 g (16 mmol, 41%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.53 (s, 4H, C_6H_2-*t*-Bu_3), 7.52 (t, 1H, $C_6H_3Ar_2$-Br, ^4J = 1.5), 7.48 (d 2H, $C_6H_3Ar_2Br$, ^4J = 1.5), 1.37 (s, 18H, *p*-*t*-Bu), 2.07 (s, 36H, *o*-*t*-Bu); ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 148.5, 148.4, 144.0, 137.4, 136.3, 133.9, 123.0, and 118.3 (C_{Ar}), 38.6 (*o*-*C*$(CH_3)_3$), 35.2 (*p*-*C*$(CH_3)_3$), 34.7 (*o*-C(*C*$H_3)_3$), 31.7 (*p*-C(*C*$H_3)_3$). Anal. Calcd for $C_{42}H_{61}Br$: C, 78.21; H, 9.54; Br, 12.25. Found: C, 78.26; H, 9.61; Br, 12.22. HRMS calcd $[M]^+$: 644.3957. Found (EI): 644.3965.

3,5-Bis(2,4,6-trimethylphenyl)bromobenzene (HMTBr). The Grignard reagent was synthesized in a manner similar to that used to prepare **1a** starting from Mg turnings (4.8 g, 200 mmol) in 40 mL of THF and 2-bromomesitylene (19.91 g, 100 mmol) in 160 mL of THF. The reaction mixture was then refluxed for 6 h. THF (130 mL) was added to the addition funnel and then to the refluxing reaction mixture. 2,4,6-

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Tribromoiodobenzene (12.6 g, 28.6 mmol) was dissolved in THF (50 mL) in a Schlenk flask and added to the addition funnel with a cannula. The solution was added dropwise over a period of 45 min, and the reaction mixture was refluxed overnight. The resulting orange reaction mixture was cooled to room temperature, decanted from excess Mg, and quenched by addition of cold HCl (40 mL, 10%). The aqueous phase was diluted with 60 mL of water, and some Na_2SO_3 was added. THF was removed on the rotary evaporator, and the aqueous phase was extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed with water (2 × 100 mL), dried over $MgSO_4$, and concentrated to a thick yellow oil. Mesitylene was removed by vacuum distillation. Dissolution of the resulting brownish mushy solid in minimum hexane led to precipitation of some pure product (white powder, 1.01 g). Column chromatography on silica (26 × 7 cm) with hexane as the eluent afforded an additional 1.88 g; total yield 2.89 g (7.35 mmol, 26%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.28 (d, 2H, C_6H_3-Mes_2Br, ^4J = 1.5), 6.94 (s, 4H, $C_6H_2Me_3$), 6.88 (t, 1H, $C_6H_3Mes_2Br$, ^4J = 1.5), 2.34 (s, 6H, *p*-CH_3), 2.07 (s, 12H, *o*-CH_3); ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) δ 143.4, 137.7, 137.2, 135.9, 130.7, 129.5, 128.4, and 122.6 (C_{Ar}), 21.2 (*p*-CH_3), 20.9 (*o*-CH_3). Anal. Calcd for $C_{24}H_{25}$-Br: C, 73.28; H, 6.41. Found: C, 73.20; H, 6.49. HRMS calcd $[M]^+$: 392.1134. Found (EI): 392.1131.

4-Bromo-3,5-bis(2,4,6-triisopropylphenyl)bromobenzene (*p*Br-HIPTBr). The procedure was nearly identical to that published for HIPTBr. Briefly, magnesium turnings (2.0 g, 82 mmol) and 1,2-dibromoethane (0.5 mL, in 75 mL of THF) were added to 200 mL of THF to initiate Grignard formation. After initiation, bromo-2,4,6-triisopropylbenzene (10.6 g, 37 mmol) in 75 mL of THF was added dropwise. This mixture was refluxed for 90 min, during which time the solution became brown and cloudy. Iodo-2,4,6-tribromobenzene (5.0 g, 11 mmol) dissolved in 75 mL of THF was then added dropwise, and the reaction was refluxed for another 3.5 h, at which time the solution was cooled to 0 °C. This Grignard solution was slowly added to an ice cold slurry of *N*-bromosuccinimide (NBS) (12.1 g, 68 mmol) in 400 mL of THF, and the mixture was allowed to stir for 10 h. A saturated aqueous solution of sodium nitrite was then added. The mixture was stirred for 2 h and then extracted with ether. The combined organic phases were washed with water and reduced in volume in vacuo. Methanol was then added to the resulting orange-colored slurry, and an off-white solid was filtered off. This solid was further purified by recrystallization from ether; yield 3.47 g (5.4 mmol, 49% yield): ^{1}H NMR ($CDCl_3$, 20 °C) δ 7.37 (s, 2H, 4′6′-*H*), 7.08 (s, 4H, 3,5,3″,5″-*H*), 2.98 (septet, J_{HH} = 6.9 Hz, 2H, 4,4″-C*H*Me_2), 2.56 (septet, J_{HH} = 6.9 Hz, 4H, 2,6,2″,6″-C*H*Me_2), 1.33 (d, J_{HH} = 6.9 Hz, 12H, 4,4″-CH-(CH_3)$_2$), 1.19 (d, J_{HH} = 6.9 Hz, 12H, 2,6,2″,6″-CH(CH_3)$_2$), 1.17 (d, J_{HH} = 6.9 Hz, 12H, 2,6,2″,6″-CH(CH_3)$_2$); ^{13}C NMR ($CDCl_3$, 20 °C) δ 148.85, 145.82, 144.32, 135.29, 132.33, 127.69, 120.95, 120.61, 34.56, 31.26, 24.96, 24.36, 23.87.

{3,5-(2,4,6-*t*-$Bu_3C_6H_2$)$C_6H_3NHCH_2CH_2$}$_3$N (1a) and {3,5-(2,4,6-*t*-$Bu_3C_6H_2$)$C_6H_3NHCH_2CH_2$}$_2$$NCH_2CH_2NH_2$ (1a′). A 500 mL Schlenk flask was charged in the glovebox with HTBTBr (13.25 g, 20.5 mmol), toluene (60 mL), $N(CH_2CH_2NH_2)_3$ (1.0 g, 6.84 mmol), and sodium *tert*-butoxide (2.76 g, 28.7 mmol). The Pd catalyst solution was prepared by vigorously stirring *rac*-BINAP (1.15 g, 1.85 mmol) and $Pd_2(dba)_3$ (563 mg, 0.615 mmol) in toluene (140 mL) for 16 h at room temperature. It was filtered and added to the main reaction mixture. A condenser was then added, and the whole assembly was taken out of the glovebox and set up on the Schlenk line under N_2. The reaction was then refluxed at 110 °C. The reaction mixture turned dark red within a few minutes and became clear orange again after a couple of hours as NaBr precipitated. After 48 h, the reaction mixture was cooled to room temperature, and NaBr was removed by flitration. Toluene was removed on the rotary evaporator, and the resulting dark oil was purified by filtration through a bed of silica on a 300 mL frit. Elution with hexane/Et_2O (9/1) yielded a very pale yellow solution that left a yellowish solid behind after all solvent was removed in vacuo. It was recrystallized by dissolving it in CH_3CN followed by addition of diethyl ether to afford a white product (**1a**, 8.21 g, 4.46 mmol, 65%). Elution with 8/1/1 to 7/2/1 mixtures of hexane/Et_2O/NEt_3 produced a yellow fraction that gave an orange solid after solvent removal (**1a′**, 2.17 g, 1.70 mmol, 25%).

^{1}H NMR of **1a** ($CDCl_3$, 300 MHz) δ 7.51 (s, 12H, C_6H_2-*t*-Bu_3), 7.00 (t, 3H, $C_6H_3Ar_2$), 6.50 (d, 6H, $C_6H_3Ar_2$, ^4J = 1.2), 3.67 (br s, 3H, NH), 3.08 (br t, 6H, CH_2, ^3J = 5.7), 2.68 (br t, 6H, CH_2, ^3J = 5.7), 1.37 (s, 54H, *p*-*t*-Bu), 1.25 (s, 108H, *o*-*t*-Bu); ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) δ 148.6, 147.8, 143.4, 142.8, 138.5, 126.1, 122.9, and 120.7 (C_{Aryl}), 54.1 (CH_2), 42.2 (CH_2), 38.6 (*o*-*C*(CH_3)$_3$), 35.0 (*p*-*C*(CH_3)$_3$), 34.1 (*o*-C(*C*H_3)$_3$), 31.6 (*p*-C(*C*H_3)$_3$). Anal. Calcd for $C_{132}H_{198}N_4$: C, 86.12; H, 10.84; N, 3.04. Found: C, 85.97; H, 10.76; N, 2.95. HRMS calcd $[M + H]^+$: 1840.5689. Found (ESI): 1840.5655.

^{1}H NMR of **1a′** ($CDCl_3$, 300 MHz) δ 7.51 (s, 8H, C_6H_2-*t*-Bu_3), 6.99 (t, 2H, $C_6H_3Ar_2$), 6.52 (d, 4H, $C_6H_3Ar_2$, ^4J = 1.2), 3.64 (br t, 2H, CH_2), 3.33 (br t, 2H, CH_2), 3.10 (br t, 4H, CH_2), 2.69 (bt, 4H, CH_2), 1.36 (s, 36H, *p*-*t*-Bu), 1.25 (s, 72H, *o*-*t*-Bu). (The NH resonances could not be located.) ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) δ 148.4, 147.6, 144.1, 142.6, 138.5, 125.9, 122.8, and 120.6 (C_{Aryl}), 59.5 ($C_2H_4NH_2$), 54.6 (C_2H_4-NHTer), 46.4 ($C_2H_4NH_2$), 42.6 (C_2H_4NHTer), 38.7 (*o*-*C*(CH_3)$_3$), 35.1 (*p*-*C*(CH_3)$_3$), 34.8 (*o*-C(*C*H_3)$_3$), 31.7 (*p*-C(*C*H_3)$_3$). Mass calcd for $C_{90}H_{138}N_4$ $[M + H]^+$: 1276.10. Found (ESI): 1276.12.

{3,5-(2,4,6-$Me_3C_6H_2$)$C_6H_3NHCH_2CH_2$}$_3$N (1b). This compound was synthesized in a manner similar to that used to prepare **1a** and from HMTBr (5.30 g, 13.5 mmol), toluene (50 mL), $N(CH_2CH_2NH_2)_3$ (657 mg, 4.49 mmol), and sodium *tert*-butoxide (1.82 g, 18.9 mmol) on one hand, and from *rac*-BINAP (756 mg, 1.21 mmol), toluene (100 mL), and $Pd_2(dba)_3$ (371 mg, 0.405 mmol) on the other. The resulting red-orange suspension was cooled to room temperature after 24 h of reflux at 110 °C, and NaBr was removed by flitration. Toluene was removed on the rotary evaporator, and the resulting oil was purified by filtration on silica (CH_2Cl_2/hexanes varying from 2/1 to 9/1). A pale yellow solid was obtained after removing the solvent in vacuo. Recrystallization from CH_2Cl_2/hexanes afforded a white solid (1.71 g, 1.58 mmol, 35%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.88 (s, 12H, C_6H_2-Me_3), 6.32 (d, 6H, $C_6H_3Mes_2$, ^4J = 1.2), 6.26 (t, 3H, $C_6H_3Mes_2$), 4.00 (br s, 3H, NH), 3.21 (br t, 6H, CH_2, ^3J = 6.0), 2.83 (br t, 6H, CH_2, ^3J = 6.0), 2.33 (s, 18H, *p*-CH_3), 2.01 (s, 36H, *o*-CH_3); ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) δ 148.0, 142.3, 139.4, 136.2, 135.9, 128.0, 120.1, and 112.1 (C_{Ar}), 53.0 (CH_2), 41.5 (CH_2), 21.4 (*p*-CH_3), 21.0 (*o*-CH_3). Anal. Calcd for $C_{78}H_{90}N_4$: C, 86.46; H, 8.37; N, 5.17. Found: C, 86.54; H, 8.42; N, 5.08. HRMS calcd $[M + H]^+$: 1083.7238. Found (ESI): 1083.7216.

{4-Br-3,5-(2,4,6-$Me_3C_6H_2$)$C_6H_3NHCH_2CH_2$}$_3$N (1c). A mixture of *p*BrHIPTBr (6.92 g, 11 mmol), NaO-*t*-Bu (1.378 g, 14 mmol), and triethylamidoamine (0.54 g, 3.5 mmol) in 100 mL of toluene was prepared in the glovebox. A catalyst prepared from $Pd_2(dba)_3$ (0.082 g, 0.09 mmol) and *rac*-BINAP (0.166 g, 0.26 mmol) in 100 mL of toluene was filtered through Celite and added to the *p*BrHIPTBr solution. The flask was sealed and stirred at 90 °C for 48 h. The solids were removed by filtration through Celite, and the solution was filtered through a flash chromotography column (SiO_2). Volatiles were removed from the filtrate under vacuum, and the resulting solid was purified through chromatography (pentane/toluene) on a silica column. The resulting off-white foamy solid was extensively dried at 65 °C under vacuum to yield 3.96 g (2.1 mmol, 61% yield): ^{1}H NMR (C_6D_6, 20 °C) δ 7.26 (s, 12H, 3,5,3″,5″-*H*), 6.44 (s, 6H, 4′,6′-*H*), 3.52 (t, J_{HH} = 5.0 Hz, 3H, N*H*), 3.05 (septet, J_{HH} = 6.9 Hz, 2H, 4,4″-C*H*Me_2), 2.90 (septet, J_{HH} = 6.9 Hz, 4H, 2,6,2″,6″-C*H*Me_2), 2.70 (br m, 6H, NHC*H*$_2$-CH_2), 2.16 (approximately t, J_{HH} = 5.2 Hz, 6H, $NHCH_2CH_2$), 1.47 (d, J_{HH} = 6.9, 12H, 4,4″-CH(C*H*$_3$)$_2$), 1.29 (m, 72H, 2,6,2′6′−CH(C*H*$_3$)$_2$); ^{13}C NMR (C_6D_6, 20 °C) δ 149.2, 147.0, 146.6, 144.0, 138.0, 121.5, 116.3, 114.7, 53.0, 41.7, 35.4, 31.9, 25.8, 25.0, 24.7. MS (ESI): 1822.0231 ($[M + H]^+$ calcd 1822.0188). Anal. Calcd for $C_{114}H_{159}$-

Br_3N_4: C, 75.02; H, 8.78; N, 3.07; Br, 13.13. Found: C, 75.11; H, 8.87; N, 3.02; Br, 12.98.

[3,5-(2,4,6-*t*-Bu$_3$C$_6$H$_2$)$_2$C$_6$H$_3$NHCH$_2$CH$_2$]$_2$(4-*t*-BuC$_6$H$_4$NHCH$_2$CH$_2$)N (1d). This compound was synthesized in a manner similar to that used to prepare **1a** starting from **1a′** (5.56 g, 4.35 mmol), toluene (14 mL), p-*tert*-butylbromobenzene (1.02 g, 4.79 mmol), and sodium *tert*-butoxide (585 mg, 6.09 mmol), on one hand, and a preformed catalyst solution prepared from *rac*-BINAP (263 mg, 0.423 mmol) and $Pd_2(dba)_3$ (129 mg, 0.141 mmol) in toluene (32 mL). The resulting dark brown suspension was cooled to room temperature after 48 h of reflux at 110 °C, and NaBr was removed by filtration over Celite. Toluene was removed on the rotary evaporator, and the resulting oil was purified by filtration on a 300 mL frit filled with silica. Elution with a hexane/Et_2O/NEt_3 (8/1/1) mixture led to a pale yellow solid that was dried under high vacuum at 70 °C after solvent removal (750 mg, 0.533 mmol, 12%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.52 (s, 8H, C_6H_2-*t*-Bu_3), 7.13 (d, 2H, C_6H_4-*t*-Bu, ^3J = 8.7), 7.00 (t, 2H, $C_6H_3Ar_2$), 6.52 (d, 4H, $C_6H_3Ar_2$, ^4J = 1.5), 6.49 (d, 2H, C_6H_4-*t*-Bu, ^3J = 8.7), 3.77 (m, 3H, NH), 3.14 (br t, 4H, CH_2, ^3J = 5.7), 3.10 (br t, 3H, CH_2, ^3J = 5.7), 2.74 (br t, 4H, CH_2), 2.72 (br t, 2H, CH_2), 1.37 (s, 36H, *p*-*t*-Bu), 1.28 (s, 9H, *t*-Bu), 1.26 (s, 72H, *o*-*t*-Bu); ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) δ 148.4, 147.7 (C_{Ter}), 145.7 (C_6H_4-*t*-Bu), 143.9, 142.7 (C_{Ter}), 140.2 (C_6H_4-*t*-Bu), 138.4, 126.1, 122.8, 120.7 (C_{Ter}), 112.8 (C_6H_4-*t*-Bu), 54.4 (C_2H_4NHTer), 54.4 (C_2H_4NHAr), 42.5 (C_2H_4NHTer and C_2H_4NHAr), 38.7 (*o*-*C*(CH$_3$)$_3$), 35.1 (*p*-*C*(CH$_3$)$_3$), 34.8 (*o*-C(*C*H$_3$)$_3$), 34.1 (*C*(CH$_3$)$_3$), 31.9 (C(*C*H$_3$)$_3$), 31.7 (*p*-C(*C*H$_3$)$_3$). Anal. Calcd for $C_{100}H_{150}N_4$: C, 86.12; H, 10.84; N, 3.04. Found: C, 85.97; H, 10.76; N, 2.95. HRMS calcd $[M + H]^+$: 1408.1933. Found (ESI): 1408.1927.

[HTBTN$_3$N]MoCl (2a). (A) A 250 mL round-bottom flask was charged with **1a** (1.84 g, 0.995 mmol) and C_6H_6 (100 mL). Solid $MoCl_4(THF)_2$ (380 mg, 0.995 mmol) was added over 50 min. The resulting dark red solution was stirred for 2 h at room temperature. Solid $(Me_3Si)_2NLi$ (583 mg, 3.48 mmol) was then added over a period of 20 min, and the reaction mixture was stirred for an additional 4 h at 22 °C. Concentration of the latter to 1/4 of its initial volume and filtration through Celite gave a dark red filtrate that was evaporated to dryness. The resulting dark red residue was thoroughly dried in vacuo and suspended in pentane (60 mL). The mixture was stirred vigorously for 15 min. Solvent was removed from the suspension until only 15 mL remained, and the suspension was allowed to stand at −35 °C for 1 h. Filtration and washing with cold pentane (3 × 10 mL) gave an orange solid (1.17 g, 0.594 mmol, 60%): ^{1}H NMR (C_6D_6, 300 MHz) δ 14.76 (br s, 6H, $C_6H_3Ar_2$), 7.90 (s, 12H, C_6H_2-*t*-Bu_3), 4.43 (s, 3H, $C_6H_3Ar_2$), 1.62 (br s, 108H, *o*-*t*-Bu), 1.48 (s, 54H, *p*-*t*-Bu), −11.92 (br s, 6H, NCH_2), −82.46 (br s, 6H, NCH_2). Anal. Calcd for $C_{132}H_{195}N_4MoCl$: C, 80.50; H, 9.98; N, 2.84; Cl, 1.80. Found: C, 80.39; H, 9.93; N, 2.73; Cl, 1.84.

(B) A mixture of $MoCl_4(THF)_2$ (747 mg, 1.96 mmol), **1a** (2.955 g, 1.61 mmol), and C_6H_6 (30 mL) was stirred vigorously for 2 h to yield a homogeneous, dark red solution. Solid $(Me_3Si)_2NLi$ (833 mg, 4.98 mmol) was then added in portions over 15 min. The reaction mixture was stirred for 1 h and brought to dryness in vacuo. The solid residue was dried in vacuo for 8 h at room temperature. The resulting solid was triturated with 20 mL of pentane overnight, and the mixture was filtered. The solid was dissolved in 30 mL of benzene, and the mixture was filtered through Celite. The combined filtrates were taken to dryness. The resulting solid was dried in vacuo for 6 h at room temperature and triturated with 20 mL of pentane; two crops were collected after the mixture was left standing at −25 °C overnight; yield 2.178 g (1.11 mmol, 69%).

[HMTN$_3$N]MoCl (2b). A 250 mL round-bottom flask was charged with **1b** (813 mg, 0.750 mmol) and C_6H_6 (75 mL). Solid $MoCl_4(THF)_2$ (286 mg, 0.750 mmol) was added over a period of 30 min. The resulting dark red solution was stirred for 2 h at room temperature. Solid $(Me_3Si)_2NLi$ (439 mg, 2.62 mmol) was then added over 15 min, and the reaction mixture was stirred for 4 h more at room temperature. The solvent was removed, and the resulting dark red residue was extracted with pentane (100 mL). The mixture was filtered through Celite and concentrated to 1/3 of its initial volume, which induced formation of a precipitate of the product. The suspension was allowed to stand at −35 °C for 1 h. The solid was filtered off and washed with cold pentane to give a dark red solid (585 mg, 0.483 mmol, 64%): ^{1}H NMR (C_6D_6, 300 MHz) δ 9.72 (br s, 6H, $C_6H_3Mes_2$), 6.96 (s, 12H, $C_6H_2Me_3$), 2.40 (s, 18H, *p*-CH_3), 2.21 (br s, 36H, *o*-CH_3), 1.96 (s, 3H, $C_6H_3Mes_2$), −16.00 (br s, 6H, NCH_2), −77.60 (br s, 6H, NCH_2). Anal. Calcd for $C_{78}H_{87}N_4MoCl$: C, 77.30; H, 7.24; N, 4.62; Cl, 2.93. Found: C, 77.18; H, 7.31; N, 4.56; Cl, 3.05.

[*p*BrHIPTN$_3$N]MoCl (2c). H$_3$[*p*BrHIPTN$_3$N] (2.5 g, 0.14 mmol) and $MoCl_4(THF)_2$ (0.524 g, 0.14 mmol) were dissolved in THF (200 mL). This mixture was stirred for 1 h, and $(Me_3Si)_2NLi$ (0.711 g, 0.42 mmol) was added slowly. The mixture was stirred for 2 h, and the solvent was removed in vacuo. The solid residue was extracted with pentane (2 × 10 mL) followed by benzene (3 × 20 mL), and all was filtered through Celite. The filtrate was then reduced to dryness in vacuo. Crystallization from pentane yielded 1.5 g (55%) of a red-orange solid in multiple crops: ^{1}H NMR (C_6D_6, 20 °C) δ 13.5 (br s), 7.34 (s), 3.11 (br s), 2.995 (br m), 1.6 (s), 1.388 (d), −18 (br s), −84 (br s). Anal. Calcd for $C_{114}H_{156}Br_3ClMoN_4$: C, 70.09; H, 8.05; N, 2.87; Br, 12.27; Cl, 1.81. Found: C, 69.85; H, 7.79; N, 2.99; Br, 12.70; Cl, 1.87.

[(HTBTNCH$_2$CH$_2$)$_2$(4-*t*-BuC$_6$H$_4$NCH$_2$CH$_2$)N]MoCl (2d). A 250 mL round-bottom flask was charged with **1d** (714 mg, 0.507 mmol) and C_6H_6 (50 mL). Solid $MoCl_4(THF)_2$ (194 mg, 0.507 mmol) was added over 20 min. The resulting very dark red solution was stirred for 2 h at room temperature. Solid $(Me_3Si)_2NLi$ (297 mg, 1.77 mmol) was then added over 10 min, and the resulting reaction mixture was stirred at room temperaure for 4 h. The solvents were removed in vacuo, and the solid residue was extracted with benzene (75 mL). The solution was filtered through Celite, and the dark red filtrate was evaporated to dryness in vacuo. The resulting dark red residue was suspended in pentane (50 mL), and the mixture was stirred vigorously for 20 min. The suspension was then concentrated to 10 mL, and the product was filtered off and washed with cold pentane (3 × 5 mL); yield 307 mg (0.20 mmol, 39%): ^{1}H NMR (C_6D_6, 300 MHz) δ 15.49 (s, 2H, C_6H_4-*t*-Bu), 13.37 (br s, 4H, $C_6H_3Ar_2$), 9.48 (br s, 2H, C_6H_4-*t*-Bu), 7.88 and 7.85 (2s, 2 × 4H, C_6H_2-*t*-Bu_3), 3.60 (s, 2H, $C_6H_3Ar_2$), 1.73 and 1.65 (2 br s, 2 × 36H, *o*-*t*-Bu), 1.54 (s, 9H, C_6H_4-*t*-*Bu*), 1.47 (s, 36H, *p*-*t*-Bu), −8.03, −14.00, and −16.80 (3 br s, 3 × 2H, NCH_2), − 75 to − 80 (3 br s, 3 × 2H, NCH_2). Anal. Calcd for $C_{100}H_{147}N_4MoCl$: C, 78.16; H, 9.64; N, 3.64; Cl, 2.31. Found: C, 78.01; H, 9.65; N, 3.54; Cl, 2.30.

[HTBTN$_3$N]Mo≡N (3a). A toluene (10 mL) solution of **2a** (0.600 g, 0.305 mmol) and Me_3SiN_3 (162 μL, 1.22 mmol) was heated at 110 °C for 4 days, after which the resulting dark brown-yellow solution was taken to dryness and exposed to high vacuum at 90 °C for 0.5 h. The solid was extracted with pentane (70 mL), and the mixture was filtered through Celite to give a brown-yellow solution that was concentrated to yield a yellow solid. The solid was collected by filtration in three crops, washed with cold pentane, and dried in vacuo; yield 355 mg (0.182 mmol, 60%): ^{1}H NMR (C_6D_6, 300 MHz) δ 7.76 (s, 12H, C_6H_2-*t*-Bu_3), 7.50 (d, 6H, $C_6H_3Ar_2$, ^4J = 1.2), 7.30 (t, 3H, C_6H_3-Ar_2, ^4J = 1.2), 3.35 (t, 6H, NCH_2), 2.00 (t, 6H, NCH_2), 1.46 (s, 108H, *o*-*t*-Bu), 1.45 (s, 54H, *p*-*t*-Bu); IR (C_6D_6) 1015 cm^{-1} (ν_{MoN}). Anal. Calcd for $C_{132}H_{195}N_5Mo$: C, 81.39; H, 10.09; N, 3.60. Found: C, 81.45; H, 10.14; N, 3.56.

[HMTN$_3$N]Mo≡N (3b). A toluene (10 mL) solution of **2b** (0.200 g, 0.165 mmol) and Me_3SiN_3 (44 μL, 0.330 mmol) was heated at 90 °C for 2 days, after which the resulting dark brown-yellow solution was taken to dryness and the residue was dried at 90 °C under high vacuum. Extraction with benzene (50 mL) and filtration through Celite gave a brown-yellow solution that was concentrated to ∼5 mL until a yellow solid started to precipitate. Pentane (7 mL) was added, and, after standing at room temperature for 2 h, the precipitate was collected

on a frit, washed with cold pentane, and dried in vacuo; yield 122 mg (0.103 mmol, 62%): ^{1}H NMR (C_6D_6, 300 MHz) δ 7.39 (d, 6H, $C_6H_3Ar_2$, ^4J = 1.5), 6.93 (s, 12H, $C_6H_2Me_3$), 6.48 (t, 3H, $C_6H_3Ar_2$, ^4J = 1.5), 3.40 (t, 6H, NCH_2), 2.27 (s, 18H, *p*-Me), 2.14 (s, 36H, *o*-Me), 2.09 (t, 6H, NCH_2). Anal. Calcd for $C_{78}H_{87}N_5Mo$: C, 78.69; H, 7.37; N, 5.88. Found: C, 78.75; H, 7.31; N, 5.81.

[HTBTN$_3$N]Mo≡^{15}N (3a-^{15}N). ^{15}N-labeled ammonia (60 mL, 200 Torr, 0.6 mmol) was vacuum-transferred from a bronze-colored liquid phase containing Na into a mixture of **2a** (300 mg, 0.152 mmol) and $NaBAr'_4$ (148.5 mg, 0.168 mmol) in CH_2Cl_2 (4 mL). The mixture was stirred for 2 h, pressurized to 1 atm with N_2, and stirred for additional 22 h. Treatment with Et_3N (74 mL, 0.532 mmol), followed by solid $[Cp_2Fe][PF_6]$ (111 mg, 0.334 mmol), resulted in an instantaneous color change to brown-red. The resulting solution was stirred for an hour and brought to dryness in vacuo. The solid residue was dried for 1 h at 90 °C and extracted with a total of 50 mL of pentane. The pentane extracts were filtered through Celite, and the filtrate was concentrated to 5 mL to afford a bright yellow solid after standing at −20 °C for 2 days, which was collected by filtration, washed with cold pentane, and dried in vacuo; yield 69 mg (0.035 mmol, 23%, not optimized): ^{15}N NMR (C_6D_6, 20 °C) δ 898.3 (Mo≡^{15}*N*); IR (C_6D_6) 991 cm^{-1} ($\nu_{Mo^{15}N}$). Anal. Calcd for $C_{132}H_{195}N_4{}^{15}NMo$: C, 81.35; H, 10.08; N, 3.64. Found: C, 81.42; H, 9.95; N, 3.52.

[*p*BrHIPT]Mo≡N (3c). [*p*BrHIPTN$_3$N]MoCl (0.25 g, 0.013 mmol) and TMS azide (0.1 g, 0.087 mmol) were added to benzene (40 mL) in a Teflon sealed flask, which was heated at 90 °C for 3 days. All volatiles were then removed in vacuo, and the solid was recrystallized from pentane to yield 0.167 g (67%) of bright yellow powder in multiple crops: ^{1}H NMR (C_6D_6, 20 °C) δ 7.90 (br s, 6H, 4′,6′-*H*), 7.25 (s, 12H, 3,5,3″,5″-*H*), 3.53 (br t, J_{HH} = 5 Hz, 6H, ArNC*H*$_2$CH$_2$), 3.00 (overlapping septets, J_{HH} = 6.9 Hz, 18H, 4,4″-C*H*Me$_2$ and 2,6,2″,6″-C*H*Me$_2$), 1.90 (br t, J_{HH} = 5 Hz, 6H, NHCH$_2$C*H*$_2$), 1.47 (d, J_{HH} = 6.9 Hz, 36H, 4,4″-CH(C*H*$_3$)$_2$), 1.34 (d, J_{HH} = 6.9 Hz 36H, 2,6,2′6′-CH-(C*H*$_3$)$_2$), 1.08 (d, J_{HH} = 6.6 Hz, 36H, 2,6,2′6′−CH(C*H*$_3$)$_2$); IR (C_6D_6) 1013 cm^{-1} (ν_{MoN}). Anal. Calcd for $C_{114}H_{156}Br_3MoN_5$: C, 70.87; H, 8.14; N, 3.62; Br, 12.41. Found: C, 70.73; H, 8.20; N, 3.69; Br, 12.37.

[*p*BrHIPT]Mo≡^{15}N (50%) (3c-^{15}N (50%)). [*p*BrHIPTN$_3$N]MoCl (0.311 g, 0.017 mmol), ^{15}N labeled sodium azide (0.0443 g, 0.068 mmol), and TMEDA (0.1 g) were placed in 75 mL of benzene and heated at 100−110 °C for 6 days. The reaction was then stripped to dryness in vacuo, and the bright yellow compound was recrystallized from pentane; yield 0.048 mg (14%); IR (C_6D_6) 1013 cm^{-1} (ν_{MoN}), 985 cm^{-1} ($\nu_{Mo^{15}N}$).

[HTBTN$_3$N]Mo(N$_2$) (4a). Magnesium powder (62 mg, 2.54 mmol) was suspended in THF (2 mL) in a 100 mL round-bottom flask equipped with a glass-coated stirbar, and the magnesium was activated with 1,2-dibromoethane (11 μL, 0.127 mmol) for 5 min. Addition of solid **2a** (0.5 g, 0.254 mmol) followed by 6 mL of THF gave a red-orange suspension that turned dark green over 4−5 h. After 6 h, the reaction mixture was filtered through Celite and treated with $ZnCl_2$ (21 mg, 0.152 mmol). This resulted in an instantaneous color change to brown. The mixture was stirred for 45 min at room temperature, and all solvents were removed at 60 °C under high vacuum. The gray residue was extracted with pentane, and the extract filtered through Celite. The resulting dark-green solution was concentrated to yield a dark-green solid after standing at −35 °C for 30 min. The latter was collected on a frit, washed with cold pentane (5 × 1 mL), and dried under vacuum; yield 320 mg (0.164 mmol, 64%): ^{1}H NMR (C_6D_6, 300 MHz) δ 22.85 (br s, 6H, NCH_2), 7.02 (s, 12H, C_6H_2-*t*-Bu$_3$), 1.97 (s, 3H, $C_6H_3Ar_2$), 1.06 (s, 54H, *p*-*t*-Bu), 0.57 (br s, 108H, *o*-*t*-Bu), −7.11 (br s, 6H, $C_6H_3Ar_2$), −32.35 (br s, 6H, NCH_2). IR (C_6D_6) 1990 cm^{-1} (ν_{NN}). Anal. Calcd for $C_{132}H_{195}N_6Mo$: C, 80.81; H, 10.02; N, 4.28. Found: C, 80.92; H, 9.93; N, 4.14.

[HTBTN$_3$N]Mo(^{15}N$_2$) (4a-^{15}N$_2$). A 50 mL Schlenk tube equipped with a glass-coated stirbar was charged with magnesium powder (62 mg, 2.54 mmol), **2a** (0.5 g, 0.254 mmol), and THF (10 mL) in a ^{14}N$_2$-filled glovebox. The tube was taken out of the box, and the solution was freeze−pump−thaw degassed five times, exposed to ^{15}N$_2$ (760 mmHg, ∼6.4 equiv relative to **2a**), and vigorously stirred for 2 days. The Schlenk tube was then pumped back in the ^{14}N$_2$-filled glovebox, and the reaction mixture was filtered through Celite and treated with $ZnCl_2$ (21 mg, 0.152 mmol). This resulted in a rapid color change to brown. The mixture was stirred for 30 min at room temperature, the solvents were removed in vacuo, and the residue was dried at 60 °C under high vacuum. The resulting gray residue was worked up as described for the unlabeled **4a** to afford a dark-green solid; yield 240 mg (0.122 mmol, 48%): ^{1}H NMR (C_6D_6, 300 MHz) δ 22.82 (br s, 6H, NCH_2), 7.02 (s, 12H, C_6H_2-*t*-Bu$_3$), 1.98 (s, 3H, $C_6H_3Ar_2$), 1.07 (s, 54H, *p*-*t*-Bu), 0.58 (br s, 108H, *o*-*t*-Bu), −7.12 (br s, 6H, $C_6H_3Ar_2$), −32.39 (br s, 6H, NCH_2); IR (C_6D_6) cm^{-1} 1924 ($\nu^{15}{}_{N-}{}^{15}{}_N$).

^{14}N$_2$/^{15}N$_2$ Exchange Studies. A C_6D_6 (3 mL) solution of **4a-^{15}N$_2$** (0.025 g, 0.0127 mmol) was stirred at room temperature under 1 atm of ^{14}N$_2$ in a closed 10 mL Schlenk tube that was kept in a glovebox. Aliquots were removed regularly and immediately analyzed by IR spectrometry. The observed **4a-^{15}N$_2$/4a-^{14}N$_2$** ratios were as follows: 94.1/5.9 (6.5 h); 93.2/6.8 (22 h); 90.8/9.2 (47 h); 88.5/11.5 (71 h); 86.9/13.1 (99 h); 84.0/16.0 (149 h); 79.5/20.5 (196 h); 76.0/24.0 (243 h); 72.6/27.4 (312 h). The total was constant during this period. A first-order plot of the disappearance of **4a-^{15}N$_2$** gave a value of $k = 2.4 \times 10^{-7}$ s^{-1} (R = 0.998).

In a dinitrogen-filled glovebox, a Parr bomb was charged with a C_6D_6 (3 mL) solution of **4a-^{15}N$_2$** (0.025 g, 0.0127 mmol). It was then closed, taken out of the box, and pressurized to 5 atm of ^{14}N$_2$. Every 24 h, it was pumped back into the glovebox, depressurized, opened, and an aliquot was removed for IR analysis. The observed **4a-^{15}N$_2$/4a-^{14}N$_2$** ratios were as follows: 90.0/10.0 (24 h); 87.3/12.7 (48 h); 85.0/15.0 (70.5 h); 83.3/16.7 (93 h). The total was constant during this period. A first-order plot of the disappearance of **4a-^{15}N$_2$** gave a value of $k = 3.1 \times 10^{-7}$ s^{-1} (R = 0.997).

{**Bu$_4$N**}{**[HTBTN$_3$N]Mo(N$_2$)**} **(5a).** A mixture of **2a** (1.0 g, 0.508 mmol) and Mg powder (123.4 mg, 5.08 mmol, activated with 0.25 mmol of 1,2-dibromoethane) was stirred with a glass-coated stirbar under 1 atm of N_2 for 8 h and treated with Bu_4NCl (155.2 mg, 0.558 mmol) and 1,4-dioxane (433 μL, 5.08 mmol). Stirring was continued for additonal 14 h, and the mixture was brought to dryness in vacuo. The solid residue was dried at 65 °C and extracted with a total of 10 mL of C_6H_6. Benzene extracts were filtered through Celite, concentrated to 7 mL, and treated with 40 mL of pentane to yield dark emerald-green crystals after standing at room temperature for 2 h, which were collected by filtration, washed with pentane, and dried in vacuo; yield 0.661 g (0.300 mmol, 59%): ^{1}H NMR (C_6D_6) δ 7.75 (s, 12H, 3,5,3″,5″-*H*), 7.66 (br s, 6H, 4′,6′-*H*), 6.93 (br s, 3H, 2′-*H*), 3.68 (br s, 6H, NC*H*$_2$-CH$_2$), 2.33 (br s, 8H, NC*H*$_2^+$), 1.91 (br s, 6H, NCH$_2$C*H*$_2$), 1.65 (br s, 108H, 2,6,2″,6″-C(C*H*$_3$)$_3$), 1.47 (s, 54H, 4,4″-C(C*H*$_3$)$_3$), 1.04 (approximately quintet, J_{HH} = 6.9 Hz, 8H, NCH$_2$C*H*$_2$CH$_2$CH$_3^+$), 0.91 (br sextet, 8H, NCH$_2$CH$_2$C*H*$_2$CH$_3^+$), 0.79 (t, J_{HH} = 7.2 Hz, 12H, NCH$_2$-CH$_2$CH$_2$C*H*$_3^+$); IR (C_6D_6) δ 1847 (ν(NN)). Anal. Calcd for $C_{148}H_{231}N_7$-Mo: C, 80.64; H, 10.56; N, 4.45. Found: C, 80.49; H, 10.47; N, 4.28.

Observation of a Mixture of [*p*BrHIPTN$_3$N]Mo−N═N−Mg-(THF)$_x$Cl and [*p*BrHIPTN$_3$N]Mo(N$_2$). The procedure followed was similar to the procedure published for the $[HIPTN_3N]^{3-}$ analogue.[25] Briefly, [*p*BrHIPTN$_3$N]MoCl (0.16 g) and magnesium powder (0.14 g) were added to ∼30 mL of THF and stirred with a glass stirbar. The magnesium was then activated with dibromoethane, and the reaction allowed to proceed for 2 h, during which time the reaction turned from orange to emerald green. This was stripped to dryness in vacuo, and the resulting solid was taken up in pentane and filtered through Celite. This deep red/purple pentane solution was then stripped to dryness, yielding a reddish brown solid that contains both the magnesium salt and the neutral dinitrogen species. Attempts to synthesize the neutral species alone have so far proven unsuccessful. Important paramagnetically shifted NMR peaks (that correspond to the neutral dinitrogen

species) are located at 22.8, −6.9, and −33.50 ppm. Peaks in the diamagnetic region have yet to be assigned due to the presence of multiple species. The IR spectrum shows both species distinctly, with the ν_{NN} peak at 1992 cm^{-1} for [*p*BrHIPTN$_3$N]Mo(N$_2$) and the ν_{NN} peak at 1788 cm^{-1} for the anion with magnesium bound to the β nitrogen atom.

{NEt$_4$}{[*p*BrHIPTN$_3$N]Mo(N$_2$)}. A sample of [*p*BrHIPTN$_3$N]MoCl (0.4 g, 0.25 mmol) and magnesium powder (0.5 g, 20 mmol) were added to ∼30 mL of THF, and a glass coated stirbar was added. A drop of dibromoethane was added to activate the magnesium, and the reaction was allowed to proceed for 2 h, during which time the color turned from orange to emerald green. Tetraethylammonium chloride (0.035 g, 0.27 mmol) and 0.25 mL of dioxane were then added, and the solution was allowed to stir for 48 h, at which point all volatiles were removed in vacuo. The resulting solid was triturated with pentane and dissolved in benzene. The solution was filtered through Celite, and the solution was concentrated to yield bright green {NEt$_4$}{[*p*BrHIPTN$_3$N]Mo(N$_2$)}; yield 150 mg, 25%: IR (C$_6$D$_6$) 1857 cm^{-1} (ν_{NN}). Anal. Calcd for $C_{122}H_{176}Br_3MoN_7$: C, 70.57; H, 8.54; N, 4.72. Found: C, 70.43; H, 8.48; N, 4.65.

This procedure was also used to make the corresponding parent {NEt$_4$}{[HIPTN$_3$N]Mo(N$_2$)} compound for comparison of IR spectra with the known tetrabutylammonium complex. It was found that the substitution of tetraethylammonium for tetrabutylammonium had no effect on the C$_6$D$_6$ ν_{NN} stretch located at 1855 cm^{-1}.

{[HTBTN$_3$N]Mo(NH$_3$)}{BAr′$_4$} (6a). Ammonia (60 mL, 200 Torr, 0.6 mmol) was vacuum-transferred from a bronze-colored solution of Na to a mixture of **2a** (300 mg, 0.152 mmol) and NaBAr′$_4$ (148.5 mg, 0.168 mmol) in CH_2Cl_2 (4 mL). The mixture was stirred for 2 h, pressurized to 1 atm with N_2, stirred for additional 22 h, and brought to dryness in vacuo. The solid residue was dried at 50 °C and extracted with a total of 10 mL of pentane. The pentane extracts were filtered through Celite and brought to dryness to afford a dark red-brown solid; yield 0.391 g (0.139 mmol, 91%): ^{1}H NMR (C$_6$D$_6$, 20 °C) δ 9.5 (br, 6H, 4′,6′-*H*), 8.29 (br s, 8H, C$_6$*H*$_3$-3,5-(CF$_3$)$_2$), 7.75 (s, 12H, 3,5,3″,5″-*H*), 7.64 (br s, 4H, C$_6$*H*$_3$-3,5-(CF$_3$)$_2$), 1.41 (s, 54H, 4,4″-C(C*H*$_3$)$_3$), 1.15−1.50 (v br, 108H, 2,6,2″,6″-C(C*H*$_3$)$_3$), −0.21 (s, 3H, 2′-*H*), −12 (br s, 6H, NC*H*$_2$), −106 (br s, 6H, NC*H*$_2$). Anal. Calcd for $C_{164}H_{210}BF_{24}N_5Mo$: C, 69.99; H, 7.52; N, 2.49. Found: C, 70.16; H, 7.44; N, 2.37.

{[*p*BrHIPT]Mo(NH$_3$)}{BAr′$_4$} (6c). A mixture of [*p*BrHIPT]MoCl (0.5 g, 0.25 mmol), NaBAr′$_4$ (0.4 g, 0.45 mmol), and NH_3 (100 mL, 440 Torr, transferred from a bronze solution prepared with Na, ∼8 equiv relative to *p*BrMoCl) was allowed to stir in 75 mL of degassed dichloromethane for 12 h in a Teflon-sealed glass bomb. The reaction turned from deep orange to bright red, and the resulting solution was taken to dryness in vacuo. The solid was then dissolved in pentane, and the solution was filtered through Celite and reduced to ∼1.5 mL in vacuo. This concentrated solution was cooled to −30 °C for 6 days to yield bright red crystals of the product; yield 0.58 g (81%): ^{1}H NMR (C$_6$D$_6$, 20 °C) δ 8.27 (s, BAr$_4$′-*H*), 7.65 (s, BAr$_4$′-*H*), 2.91 (br m), 2.71 (br m), 1.31 (br m), 1.09 (br m), −16.3 (br s), −109.5 (br s). Anal. Calcd for $C_{146}H_{171}BBr_3F_{24}MoN_5$: C, 62.66; H, 6.16; N, 2.50. Found: C, 62.54; H, 6.22; N, 2.43.

Experimental Procedure for the X-ray Diffraction Analysis of 2a and 3c. Reflections were collected on a Bruker Smart diffractometer equipped with Kappa CCD area detector using Mo Kα graphite-monochromated radiation (λ = 0.71073 Å). The structure was solved and refined using Bruker SHELXTL 5.1.

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Supporting Information Available: Crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and isotropic displacement parameters for [HTBTN$_3$N]MoCl and [*p*BrHIPT]Mo≡N (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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