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Synthesis of $[(DPPNCH_2CH_2)_3N]^{3-}$ Molybdenum Complexes (DPP = 3,5-(2,5-Diisopropylpyrrolyl)$_2C_6H_3$) and Studies Relevant to Catalytic Reduction of Dinitrogen

Michael R. Reithofer, Richard R. Schrock,* and Peter Müller

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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Abstract: Molybdenum complexes that contain a new TREN-based ligand [(3,5-(2,5-diisopropylpyrrolyl)$_2C_6H_3NCH_2CH_2)_3N]^{3-}$ ($[DPPN_3N]^{3-}$) that are relevant to the catalytic reduction of dinitrogen have been prepared. They are $[Bu_4N]\{[DPPN_3N]MoN_2\}$, $[DPPN_3N]MoN_2$, $[DPPN_3N]MoN{=}NH$, $\{[DPPN_3N]MoN{=}NH_2\}[BAr^f{}_4]$, $[DPPN_3N]Mo{\equiv}N$, $\{[DPPN_3N]Mo{\equiv}NH\}[BAr^f{}_4]$, and $\{[DPPN_3N]MoNH_3\}[BAr^f{}_4]$. NMR and IR data for $[Bu_4N]\{[DPPN_3N]MoN_2\}$ and $[DPPN_3N]MoN_2$ are close to those reported for the analogous $[HIPTN_3N]^{3-}$ compounds (HIPT = hexaisopropylterphenyl), which suggests that the degree of reduction of dinitrogen is virtually identical in the two systems. However, X-ray studies and several exchange studies support the conclusion that the apical pocket is less protected in $[DPPN_3N]Mo$ complexes than in $[HIPTN_3N]Mo$ complexes. For example, $^{15}N/^{14}N$ exchange studies showed that exchange in $[DPPN_3N]MoN_2$ is relatively facile ($t_{1/2} \approx 1$ h at 1 atm) and depends upon dinitrogen pressure, in contrast to the exchange in $[HIPTN_3N]MoN_2$. Several of the $[DPPN_3N]Mo$ complexes, e.g., the $[DPPN_3N]MoN_2$ and $[DPPN_3N]MoNH_3$ species, are also less stable in solution than the analogous "parent" $[HIPTN_3N]Mo$ complexes. Four attempted catalytic reductions of dinitrogen with $[DPPN_3N]MoN$ yielded 2.53 ± 0.35 equiv of total ammonia. These studies reveal more than any other just how sensitive a successful catalytic reduction is to small changes in the triamidoamine supporting ligand.

Introduction

Efficient catalytic reduction of dinitrogen at room temperature and 1 atm is one of the greatest challenges in chemistry. In nature dinitrogen fixation is carried out by nitrogenases, of which the best known and most studied is the FeMo nitrogenase.[1−4] The FeMo nitrogenase consumes eight protons and eight electrons to yield 2 equiv of NH_3 and a minimum of one H_2 per N_2 reduced, a 75% yield of ammonia relative to electrons consumed. Determination of the structure of the FeMo nitrogenase by X-ray diffraction triggered much discussion and speculation concerning the mechanism of dinitrogen reduction,[5,6] but it is still unclear at what metal site (or sites) and exactly how dinitrogen is reduced.

Since the report of the first dinitrogen complex ($[Ru(NH_3)_5(N_2)]^{2+}$) by Allen and Senoff in 1965,[7] hundreds of dinitrogen complexes have been prepared that contain transition metals belonging to groups 4−10; palladium and platinum are the only exceptions.[8] In the 1960s the groups of Chatt and Hidai uncovered principles of reduction of dinitrogen to ammonia at a single metal center employing Mo(0) and W(0) dinitrogen complexes.[9−12] They were able to show that dinitrogen can be reduced to ammonia at a single metal center with the electrons being supplied by the metal, but catalytic reduction of N_2 to NH_3 was never achieved.

To date, only two systems are known that effect catalytic reduction of dinitrogen under mild conditions. The first was reported by Shilov.[13] It requires a mixture of Mo(III), $Mg(OH)_2$, and a strong reducing agent such as $Ti(OH)_3$ in a protic solvent (MeOH). Although the reaction is catalytic in molybdenum, dinitrogen is not reduced directly to ammonia but to hydrazine, which is then disproportionated partially to dinitrogen and ammonia. A typical ratio of ammonia to hydrazine in the product is 1:10. The second catalytic process has been developed in our group during the past decade.[14−17] Catalytic reduction of dinitrogen directly to ammonia at room temperature and ambient pressure was achieved at a single Mo center protected by a sterically demanding, hexaisopropylterphenyl-substituted triamidoamine ligand, $[(3,5\text{-}(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2C_6H_3NCH_2CH_2N)_3N]^{3-}$

(1) Burgess, B. K.; Lowe, D. J. *Chem. Rev.* **1996**, *96*, 2983.
(2) Hardy, R. W. F.; Bottomley, F.; Burns, R. C. *A Treatise on Dinitrogen Fixation*; Wiley-Interscience: New York, 1979.
(3) Veeger, C.; Newton, W. E. *Advances in Nitrogen Fixation Research*; Dr. W. Junk/Martinus Nijhoff: Boston, MA, 1984.
(4) Coughlan, M. P. *Molybdenum and Molybdenum-Containing Enzymes*; Pergamon: New York, 1980.
(5) Einsle, O.; Tezcan, F. A.; Andrade, S. L. A.; Schmid, B.; Yoshida, M.; Howard, J. B.; Rees, D. C. *Science* **2002**, *297*, 1696.
(6) Kim, J.; Rees, D. C. *Science* **1992**, *257*, 1677.
(7) Allen, A. D.; Senoff, C. W. *J. Chem. Soc., Chem. Comm.* **1965**, 621.
(8) MacKay, B. A.; Fryzuk, M. D. *Chem. Rev.* **2004**, *104*, 385.
(9) Chatt, J.; Leigh, G. J. *Chem. Soc. Rev.* **1972**, *1*, 121.
(10) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589.
(11) Hidai, M.; Mizobe, Y. *Chem. Rev.* **1995**, *95*, 1115.
(12) Hidai, M. *Coord. Chem. Rev.* **1999**, *185−186*, 99.
(13) Shilov, A. E. *Russ. Chem. Bull. Int. Ed.* **2003**, *2*, 2555.
(14) Yandulov, D. V.; Schrock, R. R. *J. Am. Chem. Soc.* **2002**, *124*, 6252.
(15) Yandulov, D. V.; Schrock, R. R.; Rheingold, A. L.; Ceccarelli, C.; Davis, W. M. *Inorg. Chem.* **2003**, *42*, 796.
(16) Yandulov, D. V.; Schrock, R. R. *Inorg. Chem.* **2005**, *44*, 1103.
(17) Yandulov, D. V.; Schrock, R. R. *Science* **2003**, *301*, 76.

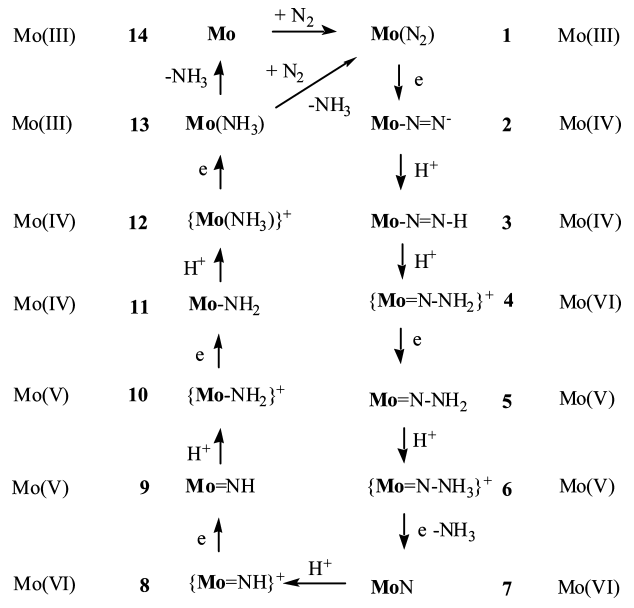


Figure 1. Proposed intermediates in the reduction of dinitrogen at a [HIPTN$_3$N]Mo (**Mo**) center (HIPT = hexaisopropylterphenyl) through stepwise addition of protons and electrons.

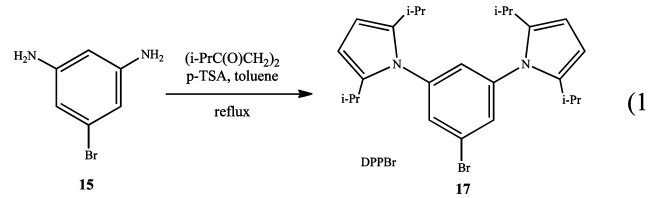
([HIPTN$_3$N]$^{3-}$). Careful treatment of [HIPTN$_3$N]MoN$_2$ with [2,6-lutidinium][BAr$^f_4$] (Ar^f = 3,5-(CF$_3$)$_2$C$_6$H$_3$) and CrCp*$_2$ led to catalytic reduction of dinitrogen to ammonia; approximately 1 equiv of dihydrogen was formed per dinitrogen reduced. No hydrazine was detected. Catalytic reduction is limited to approximately four turnovers (~8 equiv of total ammonia), most likely as a consequence of protonation and loss of the [HIPTN$_3$N]$^{3-}$ ligand from the metal.[18]

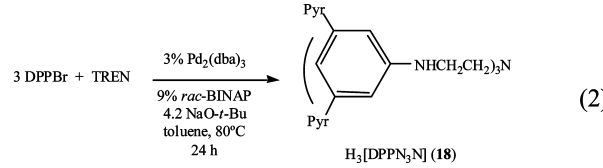
Eight of the proposed intermediates (**1**, **2**, **3**, **4**, **7**, **8**, **12**, and **13**; Figure 1) in the catalytic cycle have been characterized crystallographically.[14–16] The species that contains no ligand in the apical position (**14**) is *not* an intermediate in the catalytic reaction. (Compound **14** still has not been observed, although it is proposed as an intermediate in slow ($t_{1/2} \approx 35$ h) dinitrogen exchange in **1**.) Instead, ammonia in **13** is *displaced* by dinitrogen to re-form **1**. Several isolated species could be employed for catalytic N$_2$ reduction. Synthesis and investigation of several variations of the [HIPTN$_3$N]$^{3-}$ ligand system[19–21] have suggested that sterically less demanding ligands can lead to a decrease in the efficiency of dinitrogen reduction or even loss of catalytic activity entirely.[22,23] [HIPTN$_3$N]Mo complexes are currently the most efficient catalysts. DFT calculations with the full ligand support the proposed mechanism for dinitrogen reduction.[24]

In our quest for alternatives to the [HIPTN$_3$N]$^{3-}$ ligand we entertained the idea of a variation in which the 2,4,6-triisopropylphenyl groups in HIPT would be replaced with 2,5-diisopropylpyrrolyl groups. The amido substituent would then be 3,5-(2,5-diisopropylpyrrolyl)$_2$C$_6$H$_3$ (dipyrrolylphenyl or DPP). The DPP group should be effectively slightly smaller than a HIPT group, since a five-membered (pyrrolyl) ring replaces the six-membered phenyl ring, and of course could also be electronically different from HIPT. Since an amido ligand is protonated in the [HIPTN$_3$N]$^{3-}$ ligand system in the process of dinitrogen reduction, we also felt that there might be some possibility that the pyrrolyl rings could compete with the amido nitrogens as bases, most likely through protonation of a pyrrolyl at an α or β carbon atom. Therefore, a protonated ligand might be formed in the [DPPN$_3$N]$^{3-}$ ligand system that would not be as prone to being lost from the metal as in the [HIPTN$_3$N]$^{3-}$ ligand system. The synthesis and structures of several complexes that contain the [DPPN$_3$N]$^{3-}$ ligand system are reported here.

Results and Discussion

Synthesis of (3,5-(2,5-Diisopropylpyrrolyl)$_2$C$_6$H$_3$NHCH$_2$CH$_2$)$_3$N (H$_3$[DPPN$_3$N]). The protonated ligand (H$_3$[DPPN$_3$N]) was synthesized in five steps from 1,3-dinitrobenzene and 3-methyl-2-butanone. 1,3-Dinitrobenzene was brominated and reduced to yield 1,3-diamine-5-bromobenzene (**15**),[25,26] while 3-methyl-2-butanone was converted via a radical C−C coupling to 2,7-dimethyloctane-3,6-dione (**16**).[27] Both reactions can be carried out readily on a multigram scale. Subsequent Paal−Knorr reaction between **15** and **16** yielded the desired 3,5-dipyrrolylterphenyl bromide **17** (DPPBr, eq 1). The reaction was performed in a Dean−Stark apparatus using *p*-TSA as catalyst and toluene as solvent. DPPBr could be obtained in good yield, although it had to be separated by column chromatography from a product that contains only one pyrrolyl group. Finally, H$_3$[DPPN$_3$N] was obtained through a palladium-catalyzed C−N cross-coupling as shown in eq 2. The reaction was performed in toluene at 80 °C (yield, >95%). The H$_3$[DPPN$_3$N] product (**18**) was purified through column chromatography and recrystallized from hexane in 74% yield.





The reaction between MoCl$_4$(THF)$_2$ and H$_3$[DPPN$_3$N] in THF led to a red-brown solution that we propose contains an unknown type of adduct, similar to what is observed in syntheses in which H$_3$[HIPTN$_3$N] is employed.[28,29] The final complex, [DPPN$_3$N]MoCl (**19**), was formed after addition of 3.1 equiv

(18) Schrock, R. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 5512.
(19) Smythe, N. C.; Schrock, R. R.; Müller, P.; Weare, W. W. *Inorg. Chem.* **2006**, *45*, 7111.
(20) Smythe, N. C.; Schrock, R. R.; Müller, P.; Weare, W. W. *Inorg. Chem.* **2006**, *45*, 9197.
(21) Ritleng, V.; Yandulov, D. V.; Weare, W. W.; Schrock, R. R.; Hock, A. S.; Davis, W. M. *J. Am. Chem. Soc.* **2004**, *126*, 6150.
(22) Weare, W. W.; Dai, X.; Byrnes, M. J.; Chin, J. M.; Schrock, R. R.; Müller, P. *Proc. Nat. Acad. Sci. U.S.A.* **2006**, *103*, 17099.
(23) Weare, W. W.; Schrock, R. R.; Hock, A. S.; Müller, P. *Inorg. Chem.* **2006**, *45*, 9185.
(24) (a) Reiher, M.; Le Guennic, B.; Kirchner, B. *Inorg. Chem.* **2005**, *44*, 9640. (b) Schenk, S.; Le Guennic, B.; Kirchner, B.; Reiher, M. *Inorg. Chem.* **2008**, *47*, 3634. (c) Schenk, S.; Kirchner, B.; Reiher, M. *Chem.—Eur. J.* **2009**, *15*, 5073.
(25) Miroshnikova, O. V.; Hudson, T. H.; Gerena, L.; Kyle, D. E.; Lin, A. J. *J. Med. Chem.* **2007**, *50*, 889.
(26) Ishida, Y.; Jikei, M.; Kakimoto, M. *Macromolecules* **2000**, *33*, 3202.
(27) Ito, Y.; Konoike, T.; Saegusa, T. *J. Am. Chem. Soc.* **1975**, *97*, 2912.
(28) Greco, G. E.; Popa, A. I.; Schrock, R. R. *Organometallics* **1998**, *17*, 5591.
(29) Greco, G. E.; Schrock, R. R. *Inorg. Chem.* **2001**, *40*, 3850.

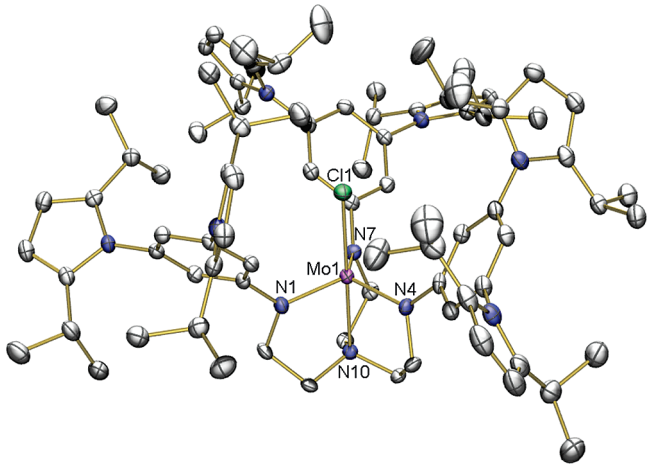
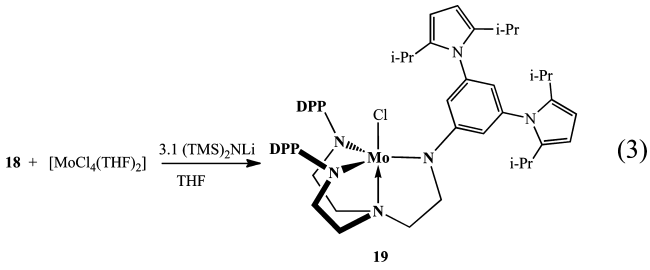


Figure 2. Thermal ellipsoid drawing of $[DPPN_3N]MoCl\cdot 2[(C_2H_5)_2O]$ with ellipsoids at 50% probability. Hydrogen atoms and solvent molecules are omitted for clarity.

of $Li[N(SiMe_3)_2]$ (eq 3). Analytically pure **19** was obtained in 57% yield after extraction of the crude product with diethyl ether and crystallization of it from a mixture of diethyl ether and pentane.



(3)

Compound **19** has paramagnetically shifted backbone ^1H NMR resonances similar to what are found in the other $[ArylN_3N]MoCl$ compounds of this general type.[28,29] The methylene protons of the TREN backbone in particular are shifted toward higher field (−15.5 and −86.6) and broadened, while the proton resonances of the isopropyl groups as well as the pyrrolyl protons are relatively sharp and in the expected diamagnetic region. Only one of the aryl proton resonances could be detected.

An X-ray diffraction study of $\mathbf{19}\cdot 2[(C_2H_5)_2O]$ showed it to have the structure shown in Figure 2. The molybdenum(IV) atom exhibits approximate trigonal bipyramidal coordination geometry, with the substituted TREN ligand coordinated via the three equatorial amido nitrogen atoms (N(1), N(4), and N(7)) plus the axial amine nitrogen (N(10)). The second axial site is occupied by chloride. As usually is found in triamidoamine compounds of this general type,[15] the Mo sits slightly above (0.330(5) Å) the plane defined by the three equatorial amido nitrogens. As expected, the 2,5-diisopropylpyrrolyl rings lie perpendicular to the phenyl ring.

Synthesis of $[Bu_4N]\{[DPPN_3N]MoN_2\}$ and $[DPPN_3N]MoN_2$. A deep-green solution was obtained after several hours upon reduction of $[DPPN_3N]MoCl$ with 10 equiv of sodium sand in THF under a dinitrogen atmosphere. After 24 h the solution was filtered and $[Bu_4N]Cl$ was added. Deep-green, diamagnetic $[Bu_4N]\{[DPPN_3N]MoN_2\}$could then be isolated (**20**, eq 4). In C_6D_6 the ν_{NN} stretch in **20** was found at 1853 cm^{-1}. In the analogous ^{15}N-labeled compound $\nu_{^{15}N^{15}N}$ was found at 1792 cm^{-1}. For comparison, the $[Bu_4N]\{[HIPTN_3N]MoN_2\}$ complex shows a ν_{NN} stretch at 1855 cm^{-1} (C_6D_6) and the analogous $^{15}N_2$-labeled species shows a $\nu_{^{15}N^{15}N}$ stretch at 1794 cm^{-1}.[15] Two relatively broad resonances were found in the ^{15}N NMR spectrum of **20** at 385 ppm (N_α) and 368 ppm (N_β). In $[Bu_4N]\{[HIPTN_3N]Mo^{15}N_2\}$, the N_α signal was found at 389 ppm while the N_β resonance was found at 368 ppm.[15] [Na(15-crown-5)]$\{[HIPTN_3N]MoN_2\}$ also showed a ν_{NN} stretch at 1853 cm^{-1}, essentially the same as **20**. The similarity of the IR and NMR data for $[DPPN_3N]^{3-}$ and $[HIPTN_3N]^{3-}$ species suggests that the electronic difference between the $[DPPN_3N]^{3-}$ and $[HIPTN_3N]^{3-}$ ligands is minimal as far as binding dinitrogen is concerned.

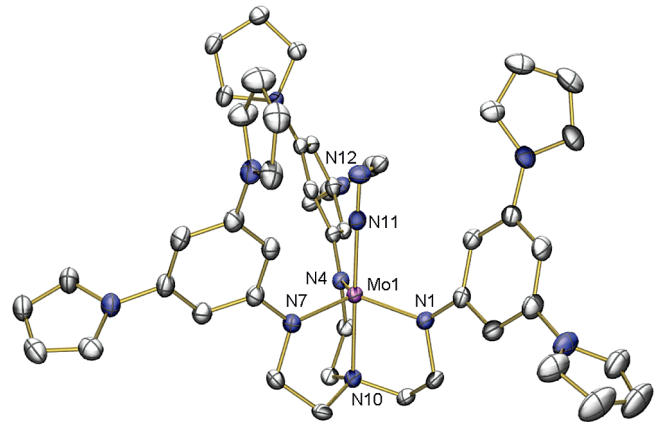
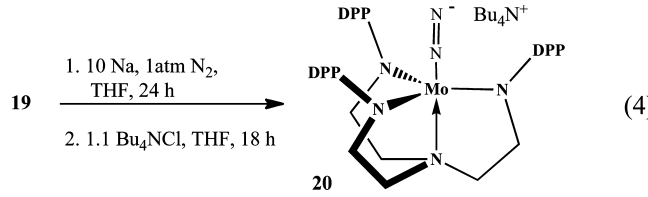


Figure 3. Thermal ellipsoid drawing of $[Bu_4N]\{[DPPN_3N]MoN_2\}\cdot 5[C_6H_6]$ with ellipsoids at 50% probability. Isopropyl groups, $[Bu_4N]^+$, hydrogen atoms, and solvent molecules are omitted for clarity.



(4)

The structure of **20** was determined through X-ray diffraction (Figure 3). The molybdenum(IV) atom has a trigonal bipyramidal coordination geometry with the dinitrogen ligand located in the apical pocket. The $[Bu_4N]^+$ cation does not interact with the N_2^- ligand, as one would expect. The N−N bond length of the N_2 ligand (1.152(4) Å) is identical within experimental error with that found in $\{Mg(DME)_3\}_{0.5}\{[HIPTN_3N]MoN_2\}$ (N−N = 1.150(5) Å), in which the cation also does not interact with the N_2 ligand.[15]

The sodium salt of $\{[DPPN_3N]MoN_2\}^-$ was prepared, dissolved in benzene, and treated with a slight excess of AgOTf. The reaction mixture was shaken for ∼1 min, and the mixture was filtered through Celite. $[DPPN_3N]MoN_2$ (**22**) was isolated from the filtrate in 60% yield. If the reaction that yields **22** is not worked up immediately, then only decomposition products could be observed. No **22** could be isolated when either $Zn(OAc)_2$[30] or $ZnCl_2$[15] was employed as the oxidizing agent. When the oxidation of $\{[DPPN_3N]MoN_2\}^-$ with $Zn(OAc)_2$ was followed by IR spectroscopy, the expected N_2 compound could be observed as the reaction proceeded, but over a period of several hours it decomposed roughly as rapidly as it was formed.

(30) Hetterscheid, D. G. H.; Hanna, B. S.; Schrock, R. R. *Inorg. Chem.* **2009**, *48*, 8569.

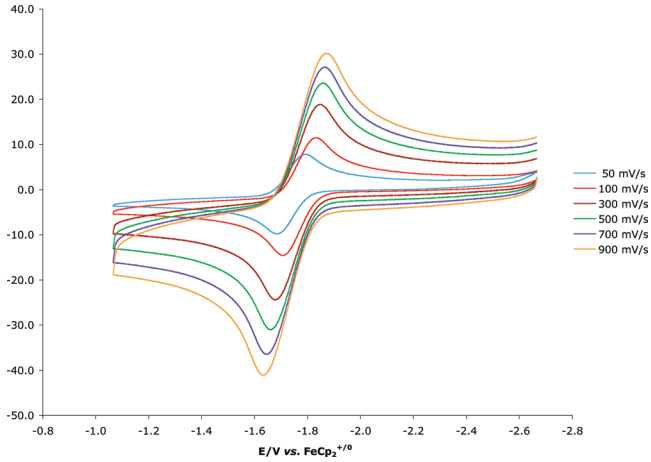


Figure 4. Cyclic voltammogram of $[Bu_4N]\{[DPPN_3N]MoN_2\}$ (**20**) in PhF (0.1 M [Bu4N][BAr^f_4]) at different scan rates between 50 and 900 mV/s (vertical axis = current in μA).

Therefore, it appears that a fast-acting oxidizing agent is required in order to reduce the reaction time to a minimum.

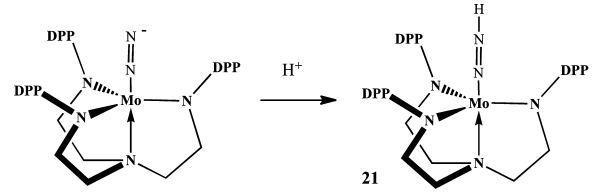
IR and NMR studies are fully in agreement with the proposed nature of $[DPPN_3N]MoN_2$. In C_6D_6 the ν_{NN} stretch is found at 1993 cm^{-1}, which is virtually the same stretching frequency as is found in $[HIPTN_3N]MoN_2$ (ν_{NN} = 1990 cm^{-1}). ^{15}N labeled $[HIPTN_3N]MoN_2$ can be prepared via reduction of $[DPPN_3N]MoCl$ under $^{15}N_2$ followed by oxidation with AgOTf. However, it also can be synthesized through $^{14}N_2/^{15}N_2$ exchange, since that exchange is relatively facile (vide infra). The $\nu_{^{15}N^{15}N}$ stretch in $[DPPN_3N]Mo^{15}N_2$ was found at 1927 cm^{-1} (cf. 1924 cm^{-1} in $[HIPTN_3N]Mo^{15}N_2$, ref 15). The ^1H NMR spectrum of $[DPPN_3N]MoN_2$ reveals characteristic paramagnetic shifted ligand backbone proton resonances at 21.2 and −31.5 ppm.

Electrochemical oxidation of $[Bu_4N]\{[DPPN_3N]MoN_2\}$ takes place reversibly in PhF (0.1 M[Bu_4N][BAr^f_4]) at scan rates between 50 and 900 mV/s (Figure 4). The $E°$ value for the $[DPPN_3N]MoN_2/\{[DPPN_3N]MoN_2\}^-$ couple is −1.76 V, which should be compared to −2.01 V for the $[HIPTN_3N]MoN_2^{0/-}$ couple.[31] Further oxidation of $[DPPN_3N]MoN_2$ to $\{[DPPN_3N]MoN_2\}^+$ is irreversible, even at a scan rate of 10^4 mV/s (I_{pa} = −0.34 V at a scan rate of 500 mV/s). Both reduction and oxidation are reversible under similar conditions in the $[HIPTN_3N]MoN_2$ system.[16]

When taking into account the similarity of the ^{15}N NMR and IR data for $[DPPN_3N]MoN_2$ and $[HIPTN_3N]MoN_2$, we were surprised that $[DPPN_3N]MoN_2$ is easier to reduce than $[HIPTN_3N]MoN_2$ by 0.25 V. Substituting the DPP groups for the HIPT groups clearly significantly alters the potential at which an electron is transferred to the metal center, even though the nature of dinitrogen activation is essentially the same in $[DPPN_3N]MoN_2$ and $[HIPTN_3N]MoN_2$ (vide supra).

It is clear from qualitative observations that $^{15}N/^{14}N$ exchange in **20** takes place to a significant degree in 1 h in solution at 22 °C. In order to quantify the rate of exchange of dinitrogen, a 15 mM solution of $[DPPN_3N]Mo^{15}N_2$ in PhF was prepared in an argon-filled glovebox at 22 °C. The solution was then transferred to an dinitrogen-filled glovebox and opened periodically to the atmosphere. Aliquots were removed and examined over a period of 2−3 h while the solution was stirred at 1 atm. The rate of formation of $[DPPN_3N]Mo^{14}N_2$ was followed, and a half-life for the conversion of $[DPPN_3N]Mo^{15}N_2$ to $[DPPN_3N]Mo^{14}N_2$ was found to be 56 ± 4 min (k = (2.1 ± 1.5) × 10^{-4} s^{-1}). Similar studies were carried out in a Schlenk flask at ∼1.5 and 2 atm (7.5 and 15 psi overpressure of dinitrogen, respectively). At 1.5 atm $t_{1/2}$ was found to be 40 min (k = 2.9 × 10^{-4} s^{-1}), whereas at 2 atm $t_{1/2}$ was found to be 12−13 min (k = (10.1 ± 2.4) × 10^{-4} s^{-1}). (Only four data points over a period of ∼2 half-lives could be obtained at 2 atm, so the error could be larger than apparent.) The $^{15}N_2/^{14}N_2$ exchange is clearly pressure dependent, probably to the first order in dinitrogen. A facile exchange and a pressure dependence in the $[DPPN_3N]^{3-}$ system contrasts to what is found in $[HIPTN_3N]Mo^{15}N_2$, where $t_{1/2}$ for N_2 exchange is ∼35 h at 1 atm and the exchange rate is independent of pressure at up to ∼4 atm.[22] Apparently, since the five-membered 2,5-diisopropylpyrrolyl ring is operationally smaller than the 2,4,6-triisopropylphenyl ring, dinitrogen can attack $[DPPN_3N]MoN_2$ and displace the bound dinitrogen through a six-coordinate intermediate. Conversely, since associative exchange of coordinated nitrogen for bound nitrogen in $[HIPTN_3N]MoN_2$ is not facile, a (slow) unimolecular dissociation of the dinitrogen ligand to give unobservable $[HIPTN_3N]Mo$ is the next option for dinitrogen exchange.

Synthesis of $[DPPN_3N]Mo{=}N{-}NH$. Addition of a solution of $[Et_3NH][BAr^f_4]$ in diethyl ether at −30 °C to solid $[Bu_4N]\{[DPPN_3N]MoN_2\}$ resulted in a rapid color change and formation of an orange-brown solution. A proton NMR spectrum verified formation of the diamagnetic $[DPPN_3N]Mo{=}N{-}NH$ complex (δ = 8.54, N=N*H*), while ^{15}N NMR revealed two double doublets at 407.4 and 234.3 ppm. The resonance at 407.4 ppm is assigned to the N_α nitrogen ($^2J_{NH}$ = 7.4 Hz, $^1J_{NN}$ = 15.4 Hz), while that at 234.3 ppm is assigned to the N_β nitrogen ($^1J_{NH}$ = 55.1 Hz, $^1J_{NN}$ = 15.4 Hz). All data strongly support the protonation of $\{[DPPN_3N]MoN_2\}^-$ to yield diamagnetic $[DPPN_3N]Mo{-}N{=}NH$ (eq 5).



(5)

Reduction of $[DPPN_3N]MoCl$ followed by titration at −30 °C with a solution of a slight excess of $[Et_3NH]OTf$ yielded an orange-brown solution from which an orange-brown crystalline solid was obtained. Proton NMR studies suggest that the orange-brown product is $[DPPN_3N]Mo{-}N{=}NH$ contaminated with 2−3% of $[DPPN_3N]MoN_2$ (**22**). (The amount of **22** was determined through integration of the pyrrolyl resonances at 5.83 ppm for **22** and 6.19 ppm for **21**.) Compounds **21** and **22** appear to cocrystallize and therefore are unlikely to be separable through recrystallizations. We propose that **22** is formed through direct reduction of protons by **21**. Some attempted protonations in the parent system also led to formation of the dinitrogen complex instead of the $[HIPTN_3N]MoN{=}NH$ complex, or to mixtures of the two.[15]

We reported that $[HIPTN_3N]MoN{=}NH$ decomposes slowly in benzene to $[HIPTN_3N]MoH$ via a first-order "β-elimination" process (k = 2.2 × 10^{-6} s^{-1}, $t_{1/2}$ = 90 h at 61 °C);[15] it is stable indefinitely in C_6D_6 at 22 °C. In contrast, $[DPPN_3N]MoN{=}NH$ in C_6D_6 decomposes over a period of 14 days to the extent of about 10−20%, but no decomposition product could be identi-

(31) Heinze, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 831.

fied. After 24 h at 60 °C the N=N*H* proton resonance could no longer be observed, but again, no decomposition product could be identified. Addition of collidine (2,4,6-trimethylpyridine) to [DPPN$_3$N]MoN=NH did not lead to rapid decomposition, but over the course of 2 weeks at room temperature, [DPPN$_3$N]MoN=NH decomposed completely, in contrast to only 10−20% in the absence of collidine. Therefore, decomposition does appear to be accelerated to some degree in the presence of collidine.

In the [CF$_3$hybrid]Mo^{15}N=^{15}NH system, in which one of the three HIPT groups in [HIPTN$_3$N]$^{3-}$ is replaced by a 3,5-(CF$_3$)$_2$C$_6$H$_3$ group, ^{15}N/^{14}N exchange takes place with a half-life of 4.5 h.[23] A similar exchange in [HIPTN$_3$N]Mo^{15}N=^{15}NH is estimated to be ∼100 times slower.[22] The rate of exchange for [CF$_3$hybrid]Mo^{15}N=^{15}NH may not be totally reliable, since the compound could be prepared only in situ; measurements with a pure isolable species would have been desirable.

We have found that ^{15}N/^{14}N exchange also takes place in [DPPN$_3$N]]Mo^{15}N=^{15}NH. Under 1 atm of dinitrogen a first-order reaction (in Mo) was found to have $k = 1.1 \times 10^{-6}$ s^{-1} ($t_{1/2} \approx 7$ days) at a concentration of 4 mM in C_6D_6. The ^{15}N/^{14}N exchange reaction was also investigated at 2 atm of dinitrogen, but no pressure dependence was found ($k = 1.4 \times 10^{-6}$ s^{-1}, $t_{1/2} \approx 6.6$ days). When 1 equiv of [Et$_3$NH][OTf] was present, the exchange was complete in ∼24 h at 1 atm of dinitrogen pressure. However, in the presence of 1 equiv of [Et$_3$NH][OTf], [DPPN$_3$N]]MoN=NH also decomposes to a significant degree to form [DPPN$_3$N]]MoN$_2$ (∼25−30% in 24 h); after ∼4 days the NN*H* peak could no longer be detected by ^{1}H NMR spectroscopy and [DPPN$_3$N]]MoN$_2$ (>80%) was identified as the main decomposition product. The precise nature of the acid-catalyzed exchange/decomposition reaction is not yet known.

Protonation of [DPPN$_3$N]MoN=NH in diethyl ether with [H(Et$_2$O)$_2$][BAr$^f_4$] led to formation of {[DPPN$_3$N]-MoN=NH$_2$}[BAr$^f_4$] (**23**) as red needles in 77% yield. Compound **23** is likely to be an intermediate in a mechanism of dinitrogen reduction analogous to that shown in Figure 1 for the HIPT system. Crystals of **23** suitable for X-ray diffraction were grown from a mixture of benzene and pentane at −30 °C. The result of the structural determination is shown in Figure 5. The molybdenum(IV) has a trigonal pipyramidal coordination geometry, with the N=NH$_2$ ligand located in the apical pocket. The position of the N*H*$_2$ atoms could be identified from the difference Fourier synthesis map. Refinement of the N*H*$_2$ positions led to N=N−H12a = 119(3)°, N=N−H12b = 93(3)°, and H12a−N−H12b = 110(4)°. Although the errors are understandably large, the sum of the three angles is considerably less than 360°, even if the largest possible values are summed (332°); we conclude that the β nitrogen is not planar in **23**.

Syntheses and Structures of [DPPN$_3$N]Mo≡N and {[DPPN$_3$N]Mo≡NH}[BAr$^f_4$]. Heating a toluene solution of [DPPN$_3$N]MoCl and 2 equiv of Me$_3$SiN$_3$ at 90 °C for 96 h results in the formation of [DPPN$_3$N]Mo≡N (**24**), which crystallizes as yellow-brown needles from a mixture of benzene and pentane at −30 °C. A similar reaction between 50% terminally ^{15}N-labeled sodium azide and [DPPN$_3$N]MoCl in dioxane and 5 equiv of DME gave 50% ^{15}N-labeled [DPPN$_3$N]Mo≡$^{15/14}$N in 80% yield. The nitride resonance is found at 905 ppm in a ^{15}N NMR spectrum, which is ∼7 ppm to lower field than where it is found in [HIPTN$_3$N]Mo≡N.

The crystal structure of **24** revealed the expected trigonal bipyramidal coordination geometry at Mo (Figure 6). (See Table 5S in the Supporting Information for distances and angles.) The asymmetric unit contains two molecules of **24**, and since one of them shows significant disorder, bond distances and angles are discussed only for the ordered molecule. (For details, see Experimental Details.) The Mo≡N bond distance of 1.662(3) Å agrees well with known Mo≡N distances of 1.652(5) Å in [HIPTN$_3$N]Mo≡N and 1.658(5) Å in [HTBTN$_3$N]Mo≡N (HTBT = hexa-*tert*-butylterphenyl).[15,32] As reported for the [HIPTN$_3$N]Mo compounds, the N(11)−Mo(1)−N−C$_{ipso}$ dihedral angles are relatively small (0.6−4.69°), and the Mo(1)−N−C$_{ipso}$−C$_{ortho}$ dihedral angles vary from −35.7° to −36.2°. As a result, one of the pyrrolyl rings points toward the metal's coordination pocket while the other one points away.

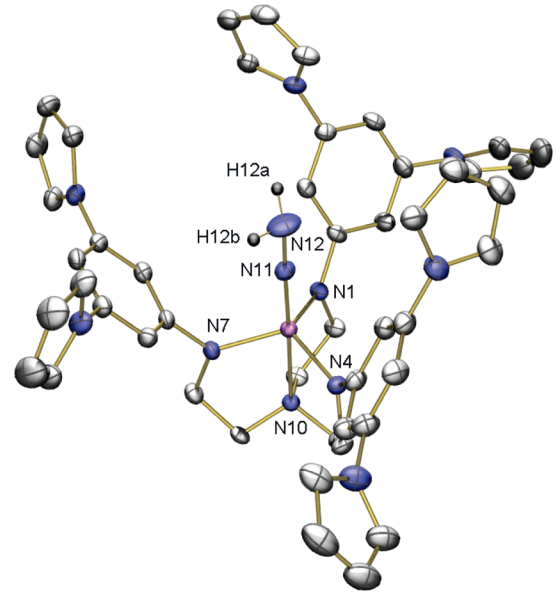


Figure 5. Thermal ellipsoid drawing of {[DPPN$_3$N]LMoN$_2$H$_2$}-[BAr$^f_4$]·[C$_6$H$_6$]·2.5[C$_5$H$_{12}$] with ellipsoids at 50% probability. Isopropyl groups, [BAr$^f_4$]$^-$ anions, hydrogen atoms (except for H12a and H12b), and solvent molecules are omitted for clarity.

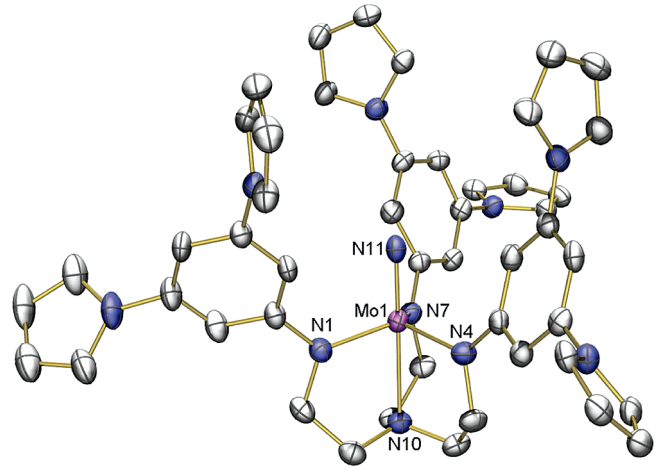


Figure 6. Thermal ellipsoid drawing of the first crystallographically independent molecule of **24** with ellipsoids at 50% probability. Isopropyl groups, hydrogen atoms, and solvent molecules are omitted for clarity.

(32) Laplaza, C. E.; Johnson, M. J. A.; Peters, J. C.; Odom, A. L.; Kim, E.; Cummins, C. C.; George, G. N.; Pickering, I. J. *J. Am. Chem. Soc.* **1996**, *118*, 8623.

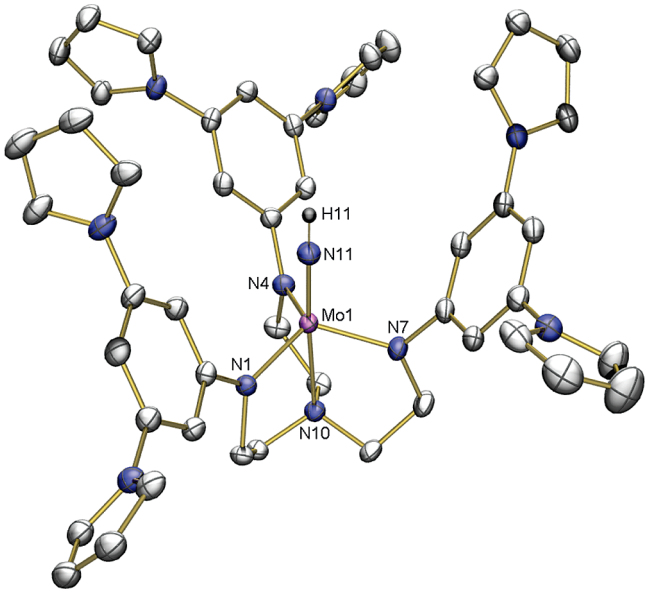


Figure 7. Thermal ellipsoid drawing of the first crystallographically independent molecule of $\{[DPPN_3N]Mo{\equiv}NH\}^+$ with ellipsoids at 50% probability. Isopropyl groups, $[BAr^f_4]^-$ anions, hydrogen atoms (except for H11), and solvent molecules are omitted for clarity.

In comparison to the $[HIPTN_3N]Mo$ compounds, where the planes of the TRIP rings are within 5−10° of being perpendicular to the phenyl rings, the pyrrolyl rings are 10−23° away from being perpendicular to the plane of the phenyl ring. We propose this to be the consequence of a pyrrolyl's isopropyl substituents in the 2 and 5 positions not being as sterically demanding as the 2,4,6-triisopropylphenylgroup's isopropyl substituents in the 2 and 6 positions.

Protonation of **24** with $[H(Et_2O)_2][BAr^f_4]$ in diethyl ether at −30 °C yielded a deep-red solution that contains $\{[DPPN_3N]Mo{\equiv}NH\}[BAr^f_4]$ (**25**), in addition to other diamagnetic products in significant and variable amounts. In order to verify that $\{[DPPN_3N]Mo{\equiv}NH\}^+$ is formed in this reaction, the 50% ^{15}N-labeled compound was synthesized; the ^{15}N resonance in partially labeled $\{[DPPN_3N]Mo{\equiv}NH\}^+$ was detected at 428.7 ppm (cf. 427.7 ppm in $[[HIPTN_3N]Mo{\equiv}NH\}[BAr^f_4]$).[15] The N*H* proton resonance was observed at 6.12 ppm and its connectivity confirmed via ^{1}H,^{15}N HSQC NMR spectroscopy. In the partially labeled species this resonance is split by 74 Hz (J_{HN}), as was observed in $\{[HIPTN_3N]Mo{\equiv}^{15}NH\}[BAr^f_4]$.[15]

The result of the X-ray study of compound **25** is shown in Figure 7. The asymmetric unit contains two molecules of **25**, and both $[BAr^f_4]^-$ anions as well as one of the $\{[DPPN_3N]Mo{\equiv}NH\}^+$ cations are disordered. Therefore, all numerical values listed in Table 4S refer only to the ordered $\{[DPPN_3N]Mo{\equiv}NH\}^+$ ion. The Mo≡NH bond (1.722(2) Å) is slightly longer than the Mo≡N in **24** (1.662(3) Å), as expected. The position for the N*H* hydrogen atom could be identified unequivocally from the difference Fourier synthesis; the Mo−N−H angle is 178(2)°. The pyrrolyl rings are essentially perpendicular (7−0.2°) to the phenyl rings.

Synthesis of $\{[DPPN_3N]MoNH_3\}^+$ and Its Reduction and Formation of $[DPPN_3N]MoN_2$. The reaction between $[DPPN_3N]MoCl$ and 4 equiv of NH_3 in CH_2Cl_2 in the presence of $Na[BAr^f_4]$ yielded $\{[DPPN_3N]MoNH_3\}[BAr^f_4]$. This reaction is extremely sensitive to small quantities of impurities in the solvent (CH_2Cl_2), $Na[BAr^f_4]$, or especially in ammonia. The reaction was successful only when ammonia was first condensed onto sodium and the mixture was stirred for 1 h at −75 °C. The reaction was complete after 3 h, and $\{[DPPN_3N]MoNH_3\}[BAr^f_4]$ could be isolated in good yield as a red-brown solid. In contrast to what was found for the analogous $[HIPTN_3N]^{3-}$ salt, the $[BPh_4]^-$ analogue could not be prepared analogously. In terms of NMR spectra, the most characteristic features of $\{[DPPN_3N]MoNH_3\}[BAr^f_4]$ are the paramagnetically shifted backbone proton resonances at −19 and −107 ppm.

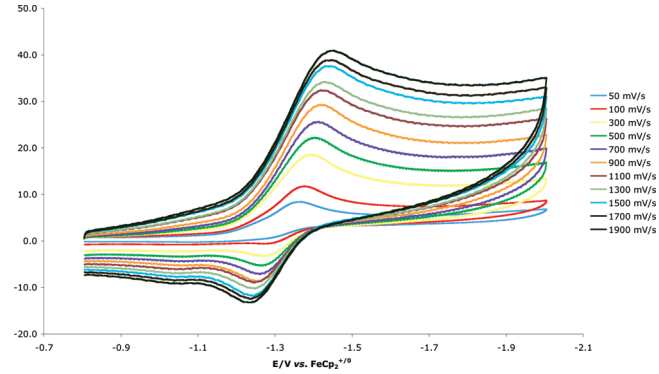


Figure 8. Cyclic voltammogram of $\{[DPPN_3N]MoNH_3\}[BAr^f_4]$ in PhF (0.1 M $[Bu4N][BAr^f_4]$) at different scan rates (measured under an argon atmosphere; vertical axis = current in μA).

The electrochemical reduction of $\{[DPPN_3N]MoNH_3\}[BAr^f_4]$ under argon was investigated via cyclic voltammetry. Reduction occurs quasireversibly in PhF (0.1 M$[Bu_4N][BAr^f_4]$ electrolyte) at scan rates from 50 to 1900 mV/s (Figure 8). Similar experiments under dinitrogen also did not lead to a reversible couple. Therefore, we propose that $[DPPN_3N]MoNH_3$ is unstable under either argon or dinitrogen. Nevertheless, reduction of $\{[DPPN_3N]MoNH_3\}[BAr^f_4]$ with 1 equiv of $CrCp^*_2$ under dinitrogen gave $[DPPN_3N]MoN_2$ in moderate yield (40%). In contrast, reduction of $\{[HIPTN_3N]MoNH_3\}^+$ occurs reversibly in PhF as well as in THF ($E^\circ = -1.63$ in PhF; $E^\circ = -1.51$ in THF).[16] Interestingly, in THF at low scan rates, NH_3/N_2 exchange can be observed in intermediate $[HIPTN_3N]MoNH_3$ that is formed in the CV experiment. Reduction of $\{[HIPTN_3N]WNH_3\}^+$ was also found to be completely irreversible, and no turnover was observed in an attempted catalytic reduction.[33]

Catalytic Reduction of N_2. The ability of the $[DPPN_3N]^{3-}$ complexes to reduce dinitrogen catalytically was investigated in a manner analogous to that employed for the $[HIPTN_3N]^{3-}$ system.[17] Catalytic runs employing $[DPPN_3N]MoN$, 48 equiv of $[2,4,6\text{-}Me_3C_6H_2N][BAr^f_4]$, and 36 equiv $CrCp^*_2$ were performed four times; the average yield of total ammonia was 2.53 ± 0.35 equivalents. If we assume that 1 equiv of ammonia is derived through reduction of the nitride, then at most 1.88 equiv of ammonia are derived from dinitrogen.[17] Since less than 2 equiv of ammonia are formed from dinitrogen, it could be argued that this system therefore is not catalytic. On the other hand, formation of more than 2 equiv of total ammonia implies that the system essentially returned to and passed the $[DPPN_3N]MoN$ starting point; from this viewpoint one could argue that reduction is catalytic. In contrast, the use of $[HIPTN_3N]MoN$ as a "catalyst" yields ∼7.0 equiv of ammonia from dinitrogen. Although we cannot pinpoint the cause(s) of the borderline

(33) Yandulov, D. V.; Schrock, R. R. *Can. J. Chem.* **2005**, *83*, 341.

catalytic activity in the $[DPPN_3N]^{3-}$ system, we suspect that the additional problems that limit turnover result (at least in part) from the only slightly reduced steric protection of the metal that is afforded with the $[DPPN_3N]^{3-}$ ligand system relative to the $[HIPTN_3N]^{3-}$ ligand system.

Conclusions

A new TREN-based ligand containing 2,5-disubstituted pyrrolyl groups in place of 2,4,6-triisopropylphenyl groups has been synthesized and compounds containing it prepared. Seven intermediates in a potential dinitrogen reduction cycle have been isolated and characterized; they are ($[Bu_4N]\{[DPPN_3N]MoN_2\}$, $[DPPN_3N]MoN_2$, $[DPPN_3N]MoN{=}NH$, $\{[DPPN_3N]MoN{=}NH_2\}[BAr^f{}_4]$, $[DPPN_3N]Mo{\equiv}N$, $\{[DPPN_3N]Mo{\equiv}NH\}[BAr^f{}_4]$, and $\{[DPPN_3N]MoNH_3\}[BAr^f{}_4]$). ^{15}N NMR and IR data of $[Bu_4N]\{[DPPN_3N]MoN_2\}$ and $[DPPN_3N]MoN_2$ (also ^{15}N labeled) are close to those reported for the analogous $[HIPTN_3N]^{3-}$ compounds, a fact that leads us to conclude that N_2 activation by the $[DPPN_3N]Mo$ system is comparable to that found in the $[HIPTN_3N]Mo$ system. X-ray structural studies bear out the prediction that the apical pocket is less protected in $[DPPN_3N]Mo$ complexes than in $[HIPTN_3N]Mo$ complexes. The $^{15}N/^{14}N$ exchange studies in $[DPPN_3N]MoN_2$ showed that the rate of exchange depends upon dinitrogen pressure. Exchange of N_2 into $[DPPN_3N]Mo{-}^{15}N{=}^{15}NH$ was also facile and consistent with a more open coordination environment in $[DPPN_3N]^{3-}$ complexes. Significant differences in redox potentials and stabilities of intermediates were observed for $[DPPN_3N]Mo$ complexes versus $[HIPTN_3N]Mo$ complexes. An especially important example of the latter is the instability of the $[DPPN_3N]MoNH_3$ species. Finally, catalytic reduction of dinitrogen by $[DPPN_3N]MoN$ is borderline, depending upon one's definition of "catalytic." These studies reveal just how sensitive a successful catalytic reduction can be to small steric and electronic changes in the triamidoamine supporting ligand.

Experimental Details

General. All manipulations of air- and moisture-sensitive compounds were carried out using standard Schlenk and glovebox techniques under an atmosphere of nitrogen or argon in oven-dried glassware, including NMR tubes. Diethyl ether, pentane, methylene chloride, THF, and toluene were purged with nitrogen and passed through activated alumina columns. Heptane, C_6D_6, and THF-d_8 were distilled from a dark-purple Na/benzophenone ketyl solutions, and PhF was dried over CaH_2, degassed, and vacuum distilled prior to use. All dried and deoxygenated solvents were stored over 4 Å Linde-type molecular sieves prior to use. Prior to use ammonia was condensed onto sodium and the mixture stirred for 1 h at −75 °C. $Li[N(SiMe_3)_2]$ was purified by sublimation. $[Bu_4N][BAr^f{}_4]$ was prepared by salt metathesis of $[Bu_4N]Cl$ with $Na[BAr^f{}_4]$ in Et_2O and recrystallization from CH_2Cl_2/pentane. $[HNEt_3][BAr^f{}_4]$ was synthesized by treating $NEt_3{\cdot}HCl$ with $Na[BAr^f{}_4]$ in diethyl ether. 1,3-Diamine-5-bromobenzene and 2,7-dimethyloctane-3,6-dione were synthesized according to standard literature procedure.[25–27] The catalytic reduction of dinitrogen was performed according to a previously reported procedure.[17] NMR spectra were recorded either on a Bruker Avance 400 MHz or on a Bruker Avance 600 MHz spectrometer and referenced to the residual protio solvent peaks. Directly measured ^{15}N NMR and $^1H,^{15}N$-HSQC spectra were recorded on a Varian Inova 500 MHz spectrometer and referenced externally to benzamide (^{15}N, 105.33 ppm relative to neat NH_3).[34] IR spectra were measured on a Nicolet Avatar 360 FT-IR spectrometer in a demountable solution cell (0.2 mm Teflon spacer, KBr windows). FT-ICR-MS (ESI) spectra was measured by the Department of Chemistry Instrumentation Facility at the Massachusetts Institute of Technology. Electrochemical measurements were carried out in an argon or dinitrogen filled glovebox using a CHI 620C potentiostat, 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 to the ferrocene/ferricinium couple. Elemental analyses were performed by Midwest Microlabs, Indianapolis, IN.

Synthesis of DPPBr (17). A mixture of 3,5-diaminobromobenzene (8.7 g, 46 mmol), 2,7-dimethyloctane-3,6-dione (17 g, 100 mmol), *p*-toluenesulfonic acid monohydrate (40 mg, 0.21 mmol), and 120 mL of toluene was refluxed under dinitrogen in a Dean−Stark apparatus for 24 h. The expected amount of water (4 mol equiv) separated from the reaction mixture. The solution was filtered through silica gel, and the solvent was removed under reduced pressure. The pure product was obtained after column chromatography (LM/toluene) and recrystallization from hexane, yield 15.2 g (72%). ^1H NMR ($CDCl_3$, 400 MHz, 297 K) δ 7.50 (d, J_{HH} = 1.8 Hz, 2H, 4,6-Ar), 7.20 (t, J_{HH} = 1.8 Hz, 1H, 2-Ar), 5.98 (s, 4H, Py), 2.69 (sept, J_{HH} = 6.8 Hz, 4H, C*H*Me$_2$), 1.12 (d, J_{HH} = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.05 (d, J_{HH} = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$) ppm. FT-ICR-MS (ESI): calcd *m*/*z* 455.2056 $[M + H^+]^+$, found *m*/*z* 455.2051 $[M + H^+]^+$. Anal. Calcd (%) for $C_{26}H_{35}BrN_2$: C, 68.56; H, 7.75; N, 6.15. Found: C, 68.36; H, 7.67; N, 6.14.

Synthesis of $H_3[DPPN_3N]$ (18). A 250 mL round-bottom flask equipped with a magnetic stir bar was charged with **17** (15 g, 32.9 mmol), NaO-*t*-Bu (4.43 g, 46.1 mmol), and TREN (1.605 g, 10.98 mmol). The Pd catalyst solution was prepared by vigorously stirring $Pd_2(dba)_3$ (302 mg, 0.33 mmol) and *rac*-BINAP (615 mg, 1 mmol) in 20 mL of toluene overnight at room temperature. The mixture was filtered through Celite into the main reaction mixture, and the Celite was rinsed with another 20 mL of toluene. The flask was closed and stirred for 24 h at 85 °C. After the reaction mixture had cooled, the solid NaBr was filtered off through a bed of Celite. The solvent was removed under reduced pressure, and the crude product was purified (twice) by column chromatography (EtOAc/toluene, 1/30). The pure product was obtained as a white solid after crystallization from hexanes, yield 10.4 g (74%). ^1H NMR (C_6D_6, 400 MHz, 297 K) δ 6.50 (t, J_{HH} = 1.7 Hz, 3H, 4-Ar), 6.31 (d, J_{HH} = 1.7 Hz, 6H, 2,6-Ar), 6.22 (s, 12H, Py), 3.46 (t, J_{HH} = 5.2 Hz, 3H, N*H*), 2.93 (sept, J_{HH} = 6.8 Hz, 12H, C*H*Me$_2$), 2.60 (m, 6H, NHC*H*$_2$), 1.23 (d, J_{HH} = 6.8 Hz, 36H, CH(C*H*$_3$)$_2$), 1.16 (d, J_{HH} = 6.8 Hz, 36H, CH(C*H*$_3$)$_2$) ppm. FT-ICR-MS (ESI): calcd *m*/*z* 1269.9770 $[M + H^+]^+$, found *m*/*z* 1269.9742 $[M + H^+]^+$. Anal. Calcd (%) for $C_{84}H_{120}N_{10}$: C, 79.45; H, 9.52; N, 11.03. Found: C, 79.19; H, 9.59; N, 11.02.

$[DPPN_3N]MoCl$ (19). A 250 mL Schlenk flask was charged with **18** (4 g, 3.15 mmol), $MoCl_4(THF)_2$ (1.144 g, 3.06 mmol), and 80 mL of THF. The resulting solution was stirred for 1 h. Solid $Li[N(SiMe_3)_2]$ (1.59 g, 9.5 mmol) was added all at once, and the resulting solution was stirred for 1 h. The solvent was removed under reduced pressure, and the residue was dried for 3 h at 50−60 °C in vacuo. The solid residue was extracted several times with diethyl ether (total volume, 150 mL), and the extracts were filtered through Celite. The volume was reduced to 50 mL, and an amount of 50 mL of pentane was added. The resulting suspension was stored overnight at −30 °C. The product was filtered off and rinsed with pentane to afford the product as an orange powder, yield 2.45 g (57%). ^1H NMR (THF-d_8, 400 MHz, 297 K) δ 13.76 (brs, Ar), 5.79 (s, 12H, Py), 2.54 (brs, 12H, C*H*Me$_2$), 1.12 (brs, 72H, CH(C*H*$_3$)$_2$), −15.48 (brs, NC*H*$_2$), −86.64 (brs, NC*H*$_2$) ppm. Anal. Calcd (%) for $C_{84}H_{117}ClMoN_{10}$: C, 72.15; H, 8.43; N, 10.02; Cl, 2.54. Found: C, 72.31;h 8.20; N 9.99; Cl 2.49.

(34) Sadek, M.; Brownlee, R. T. C. *J. Magn. Reson., Ser. B* **1995**, *109*, 70.

Crystals for the X-ray study were grown from a diethyl ether solution, which was covered by a layer of pentane, and the mixture was stored for several days at −30 °C.

[Bu$_4$N]{[DPPN$_3$N]MoN$_2$} (20). [DPPN$_3$N]MoCl (200 mg, 143 μmol) and sodium sand (33 mg, 1.43 mmol) were suspended in 20 mL of THF, and the mixture was stirred with a glass-coated stir bar for 24 h under a dinitrogen atmosphere. Within the first hour, the solution became dark-green. After 24 h, the reaction mixture was filtered, and the filtrate was treated with solid [Bu$_4$N]Cl (48 mg, 171 μmol). The mixture was stirred for an additional 18 h. The solvent was removed under reduced pressure, and the residue was heated at 50 °C in vacuo for 3 h. The residue was extracted with benzene, and the extract was filtered through Celite, concentrated to ∼10 mL, and covered by a layer of pentane. A bright-green oil formed after standing the solution at room temperature overnight. The solvent was decanted off, the oil was dissolved in diethyl ether, and the solvent was removed under reduced pressure. After the residue was heated in vacuo, an amorphous solid was obtained, yield 157 mg (67%). ^{1}HNMR (C$_6$D$_6$, 400 MHz, 297 K) δ 7.60 (d, J_{HH} = 1.5 Hz, 6H, 2,6-Ar), 6.54 (t, J_{HH} = 1.6 Hz, 3H, 4-Ar), 6.18 (s, 12H, Py), 3.61 (brs, 6H, NCH_2), 3.31 (sept, J_{HH} = 6.7 Hz, 12H, CHMe$_2$), 2.25 (brs, 8H, TBA), 1.83 (brs, 6H, NCH_2), 1.36 (d, J_{HH} = 6.7 Hz, 36H, CH(CH_3)$_2$), 1.30 (d, J_{HH} = 6.7 Hz, 36H, CH(CH_3)$_2$), 0.95 (m, 8H, TBA), 0.85 (m, 8H, TBA), 0.76 (t, J_{HH} = 6.9 Hz, 12H, TBA) ppm. IR (C$_6$D$_6$, cm^{-1}): 1853 (ν_{NN}). Anal. Calcd (%) for C$_{100}$H$_{153}$MoN$_{13}$: C, 73.54; H, 9.44; N, 11.15. Found: C, 73.17; H, 9.18; N, 11.15. Crystals for the X-ray study were grown from a benzene solution, which was covered by a layer of pentane. The mixture was stored overnight at room temperature and for several days at −30 °C.

[Bu$_4$N]{[DPPN$_3$N]Mo^{15}N$_2$}. In a 250 mL Schlenk flask [DPPN$_3$N]MoCl (400 mg, 286 μmol) and sodium sand (66 mg, 2.8 mmol) were suspended in 40 mL of THF. The mixture was degassed in vacuo and filled with ^{15}N$_2$ (100 Torr, ∼200 mL). The reaction mixture was stirred using a glass-coated stir bar for 24 h, degassed, and again filled with ^{15}N$_2$ (100 Torr, ∼200 mL). After 24 h, the reaction mixture was filtered through Celite, Bu$_4$NCl (95 mg, 343 μmol) was added to the filtrate, and the resulting solution was stirred overnight. The procedure was the same as described above for the unlabeled compound, yield 320 mg (68%). ^{1}H NMR (C$_6$D$_6$, 400 MHz, 297 K) δ 7.59 (brs, 6H, 2,6-Ar), 6.53 (brs, 3H, 4-Ar), 6.18 (s, 12H, Py), 3.60 (brs, 6H, NCH_2), 3.31 (sept, J_{HH} = 6.4 Hz, 12H, CHMe$_2$), 2.35 (brs, 8H, TBA), 1.83 (brs, 6H, NCH_2), 1.36 (d, J_{HH} = 6.7 Hz, 36H, CH(CH_3)$_2$), 1.30 (d, J_{HH} = 6.7 Hz, 36H, CH(CH_3)$_2$), 0.98 (m, 8H, TBA), 0.90 (m, 8H, TBA), 0.77 (t, J_{HH} = 6.9 Hz, 12H, TBA) ppm; ^{15}N NMR (C$_6$D$_6$, 50.7 MHz, 297 K) δ 385 (brs), 368 (brs) ppm. IR (C$_6$D$_6$; cm^{-1}): 1792 ($\nu_{^{15}N^{15}N}$).

[Na(15-crown-5)]{[DPPN$_3$N]MoN$_2$}. [DPPN$_3$N]MoCl (500 mg, 358 μmol) and sodium sand (82 mg, 3.58 mmol) were suspended in 30 mL of THF and stirred with a glass-coated stir bar for 24 h under an dinitrogen atmosphere. The color of the solution changed to dark green in approximately 1 h. After 24 h, the solution was filtered off, the solvent was removed, and the violet residue was dried in vacuo for 2 h. The solid was dissolved in 20 mL of diethyl ether, and 15-crown-5 ether (78.8 mg, 358 μmol) dissolved in 5 mL of diethyl ether was added dropwise. The resulting bright-green solution was stirred for 24 h. The solvent was removed under reduced pressure. The crude product was extracted with benzene, and the filtrate was layered with pentane. After standing the mixture at room temperature and then for 18 h at −30 °C, a bright-green powder was isolated, yield 484 mg (84%). ^{1}H NMR (C$_6$D$_6$, 400 MHz, 297 K) δ 7.58 (brs, 6H, 2,6-Ar), 6.49 (brs, 3H, 4-Ar), 6.15 (s, 12H, Py), 3.59 (brs, 6H, NCH_2), 3.25 (brs, 12H, CHMe$_2$), 2.85 (brs, 20H, 15-crown-5), 1.82 (brs, 6H, NCH_2), 1.35 (s, 36H, CH(CH_3)$_2$), 1.25 (s, 36H, CH(CH_3)$_2$) ppm. IR (C$_6$D$_6$, cm^{-1}): 1855 (ν_{NN}). Anal. Calcd (%) for C$_{93}$H$_{135}$MoN$_{12}$NaO$_5$: C, 68.95; H, 8.40; N, 10.37. Found: C, 68.81; H, 8.10; N, 10.16.

[DPPN$_3$N]MoN$_2$H (21). Following the reduction of [DPPN$_3$N]MoCl (100 mg, 71.5 μmol) by Na (16 mg, 715 μmol) in THF (20 mL), the green solution was filtered through Celite, cooled in a −30 °C freezer for 2 h, and titrated dropwise with a cooled THF (10 mL) solution of [Et$_3$NH][OTf] (18.7 mg, 75.1 μmol) until a steady dark-orange-brown color was obtained (1.05 equiv of [Et$_3$NH][OTf] was required). The solution was stirred for 10 min at room temperature. The solvent was removed under reduced pressure, and the residue was dried at 40−50 °C for 4 h. The residue was extracted with benzene (15−20 mL), and the extract was filtered through Celite and concentrated in vacuo (3−4 mL), covered by a layer of pentane, and stored overnight at room temperature and for another day at −30 °C. The product was filtered off, washed with pentane, and dried in vacuo. The mother liquor was concentrated and a second crop obtained, yield 194 mg (65%). ^{1}H NMR (C$_6$D$_6$, 400 MHz, 297 K) δ 8.54 (s, 1H, N═NH), 7.11 (s, 6H, 2,6-Ar), 6.74 (s, 3H, 4-Ar), 6.19 (s, 12H, Py), 3.28 (brs, 6H, NCH_2), 2.91 (sept, J_{HH} = 6.7 Hz, 12H, CHMe$_2$), 1.84 (brs, 6H, NCH_2), 1.18 (d, J_{HH} = 6.7 Hz, 72H, CH(CH_3)$_2$) ppm. Because of impurities of [DPPN$_3$N]MoN$_2$ (about 2%), EA was not determined.

[DPPN$_3$N]Mo^{15}N$_2$H. [Bu$_4$N]{[DPPN$_3$N]Mo^{15}N$_2$} (190 mg, 116.2 μmol) was dissolved in 5 mL of diethyl ether, and the solution was chilled at −30 °C for 30 min. At this temperature solid [Et$_3$NH][OTf] (30.7 mg, 122 μmol) was added and the resulting reaction mixture was stirred for 10 min. The solvent was removed under reduced pressure, and the solid was dried in vacuo for 2 h. The residue was extracted with benzene (15−20 mL). The extract was filtered through Celite, concentrated in vacuo (3−4 mL), covered by a layer of pentane, and stored overnight at room temperature and for another day at −30 °C. The product was filtered off, washed with pentane, and dried in vacuo, yield 68 mg (40%). ^{1}HNMR (C$_6$D$_6$, 400 MHz, 297 K) δ 8.55 (dd, $^1J_{NH}$ = 55.4 Hz, $^2J_{NH}$ = 7.4 Hz, 1H, N═NH), 7.12 (s, 6H, 2,6-Ar), 6.74 (s, 3H, 4-Ar), 6.20 (s, 12H, Py), 3.27 (brs, 6H, NCH_2), 2.92 (sept, J_{HH} = 6.8 Hz, 12H, CHMe$_2$), 1.82 (brs, 6H, NCH_2), 1.18 d, J_{HH} = 6.8 Hz, 72H, CH(CH_3)$_2$) ppm; ^{15}N NMR (C$_6$D$_6$, 50.7 MHz, 297 K) δ 407.4 (dd, J_{NN} = 15.4 Hz, $^2J_{NH}$ = 7.4 Hz, 1N, NNH), 232.6 (dd, J_{NH} = 55.1 Hz, J_{NN} = 15.4 Hz, 1N, NNH) ppm.

[DPPN$_3$N]MoN$_2$ (22). Method A. A benzene solution of {[DPPN$_3$N]MoNH$_3$}[BAr$^f_4$] (100 mg, 44.6 μmol) and CrCp$_2$* (14.3 mg, 44.6 μmol) was stirred at room temperature for 24 h. After a couple of minutes a yellow precipitate formed. In order to complete the NH$_3$/N$_2$ exchange, the flask was opened several times during the reaction. The solution was filtered off, and the solvent was removed under reduced pressure. The residue was dried in vacuo for 3 h and extracted with benzene. The extract was filtered through Celite, concentrated, covered by a layer of pentane, and stored overnight at room temperature and for another day at −30 °C. The green-brown product was filtered off, washed with pentane, and dried in vacuo. The mother liquor was concentrated and a second crop obtained, yield 25 mg (40%). ^{1}H NMR (C$_6$D$_6$, 400 MHz, 297 K) δ 21.2 (brs, 6H, NCH_2), 6.21 (s, 3H, 4-Ar), 5.83 (s, 12H, Py), 1.71 (s, 36H, CH(CH_3)$_2$), 0.83 (s, 36H, CH(CH_3)$_2$), −5.6 (brs, 6H, 2,6-Ar), −31.5 (brs, 6H, NCH_2) ppm. IR (C$_6$D$_6$, cm^{-1}): 1993 (ν_{NN}) cm^{-1}. Anal. Calcd (%) for C$_{84}$H$_{117}$MoN$_{12}$: C, 72.54; H, 8.48; N, 12.08. Found: C, 72.22; H, 8.11; N; 11.74.

Method B (Preferred). [DPPN$_3$N]MoCl (200 mg, 143 μmol) and sodium sand (33 mg, 1.43 mmol) were suspended in 20 mL of THF, and the mixture was stirred with a glass-coated stir bar for 24 h under a dinitrogen atmosphere. The pressure in the flask was periodically adjusted to the pressure in the N$_2$-filled glovebox. Within the first hour, the color of the solution changed to dark green. After 24 h, the solution was filtered off, the solvent was removed, and the violet residue was dried in vacuo for 2 h. The solid was dissolved in 10 mL of benzene, and solid AgOTf (40.4 mg, 157 μmol) was added. The resulting mixture was shaken for ∼1 min and filtered immediately through Celite. The resulting dark-brown solution was concentrated and layered with pentane. The product was isolated as an olive green solid in 60% yield.

[DPPN$_3$N]Mo^{15}N$_2$. An amount of 40 mL of degassed THF was vacuum-transferred onto a mixture of [DPPN$_3$N]MoCl (800 mg,

572 μmol) and sodium sand (131 mg, 5.72 mmol). The Schlenk flask was refilled with $^{15}N_2$ (840 Torr, ~50 mL), and the mixture was stirred with a glass-coated stir bar for 24 h. Oxidation of the diazenido salt with AgOTf and workup of the compound were done as reported for the unlabeled complex in an argon filled glovebox, yield 426 mg (53%). IR (C_6D_6, cm^{-1}) 1927 ($\nu_{^{15}N^{15}N}$).

{[DPPN$_3$N]MoNNH$_2$}[BAr$^f_4$] (23). An ether solution of [DPPN$_3$N]MoN$_2$H (90.6 mg, 65.1 μmol) was treated with solid [H(Et$_2$O)$_2$][BAr$^f_4$] (68.5 mg, 67.7 μmol) at −30 °C. The mixture was allowed to warm to room temperature. Within the first minutes the solution turned dark red. After 90 min the solvent was removed under reduced pressure and the residue was exposed to vacuum for 2 h. The solid was extracted with pentane. The extract was filtered through Celite and concentrated to 5 mL, and 1 mL benzene was added. The product crystallized at −30 °C as red needles, yield 113 mg (77%). ^{1}H NMR (C_6D_6, 400 MHz, 297 K) δ 8.33 (brs, 8H, C_6H_3-3,5-(CF$_3$)$_2$), 7.65 (brs, 4H, C_6H_3-3,5-(CF$_3$)$_2$), 6.65 (s, 3H, 4-Ar), 6.57 (s, 3H, 4-Ar), 6.40 (s, 2H, N−NH_2), 6.08 (s, 12H, Py), 3.39 (s, 6H, NCH_2), 2.56 (sept, J_{HH} = 6.8 Hz, 12H, CHMe$_2$), 2.27 (s, 6H, NCH_2), 1.04 (d, J_{HH} = 6.8 Hz, 36H, CH(CH_3)$_2$), 0.96 (d, J_{HH} = 6.8 Hz, 36H, CH(CH_3)$_2$) ppm. Anal. Calcd (%) for $C_{116}H_{131}BF_{24}MoN_{12}$: C, 61.76; H, 5.85; N, 7.45. Found: C, 62.02; H, 5.81; N, 7.22.

Crystals for the X-ray study were grown from a benzene solution, which was covered by a layer of pentane and stored at room temperature for 1 day and for several days at −30 °C.

[DPPN$_3$N]MoN (24). A toluene solution of [DPPN$_3$N]MoCl (300 mg, 215 μmol) and Me$_3$SiN$_3$ (50 mg, 429 μmol) in a Schlenk flask was heated at 90 °C for 4 days. The solvents were removed from the dark-yellow-brown solution under reduced pressure, and the residue was dried at 50 °C in vacuo. The solid was extracted with benzene. The extract was filtered through Celite, concentrated to ~5 mL in vacuo, and layered with 40 mL of pentane. A yellow-brown crystalline solid formed after standing the solution at room temperature overnight and for several hours at −30 °C, yield 176 mg (60%). ^{1}H NMR (C_6D_6, 400 MHz, 297 K) δ 7.78 (d, J_{HH} = 1.6 Hz, 6H, 2,6-Ar), 6.65 (t, J_{HH} = 1.6 Hz, 3H, 4-Ar), 6.19 (s, 12H, Py), 3.14 (t, J_{HH} = 4.8 Hz, 6H, NCH_2), 2.84 (sept, J_{HH} = 6.8 Hz, 12H, CHMe$_2$), 1.73 (t, J_{HH} = 4.9 Hz, 6H, NCH_2), 1.20 (d, J_{HH} = 6.8 Hz, 36H, CH(CH_3)$_2$), 1.14 (d, J_{HH} = 6.8 Hz, 36H, CH(CH_3)$_2$) ppm. Anal. Calcd (%) for $C_{84}H_{117}MoN_{11}$: C, 73.28; H, 8.57; N, 11.19. Found: C, 73.09; H, 8.56; N, 10.98.

Crystals for the X-ray study were grown from a benzene solution, which was covered by a layer of pentane and stored at room temperature.

[DPPN$_3$N]MoN (50% ^{15}N-Labeled). A dioxane solution of [DPPN$_3$N]MoCl (200 mg, 143 μmol), NaN$_3$ (1-^{15}N) (19 mg, 286 μmol), and DME (74 μL, 715 μmol) was stirred at 85 °C for 96 h. The solvent was removed under reduced pressure, and the residue was dried at 50 °C in vacuo. The solid was extracted with benzene. The extract was filtered through Celite, concentrated to ~3 mL in vacuo, and layered with 30 mL of pentane. A yellow-brown crystalline solid formed after standing the solution at room temperature overnight and for several hours at −30 °C, yield 157 mg (80%). ^{1}H NMR (C_6D_6, 400 MHz, 297 K) δ 7.77 (s, 6H, 2,6-Ar), 6.65 (s, 3H, 4-Ar), 6.19 (s, 13H, Py, NH), 3.14 (t, J_{HH} = 4.9 Hz, 6H, NCH_2), 2.84 (sept, J_{HH} = 6.8 Hz, 12H, CHMe$_2$), 1.73 (t, J_{HH} = 5.0 Hz, 6H, NCH_2), 1.20 (d, J_{HH} = 6.8 Hz, 36H, CH(CH_3)$_2$), 1.14 (d, J_{HH} = 6.8 Hz, 36H, CH(CH_3)$_2$) ppm; ^{15}N NMR (C_6D_6, 50.7 MHz, 297 K) δ 905 ppm.

{[DPPN$_3$N]MoNH}[BAr$^f_4$] (25). A diethyl ether solution of [DPPN$_3$N]MoN (150 mg, 109 μmol) was treated with solid [H(Et$_2$O)$_2$][BAr$^f_4$] (114 mg, 112 μmol) at −30 °C. The mixture was allowed to warm to room temperature. In the first 10 min the solution turned deep red. After 1 h the solvent was removed in vacuo and the residue was extracted with pentane. The extract was filtered through Celite and concentrated to ~20 mL in vacuo, and 5 mL benzene was added. The product crystallized at −30 °C as deep-red needles, yield 187 mg (77%). ^{1}H NMR (C_6D_6, 400 MHz, 297 K) δ 8.34 (brs, 8H, C_6H_3-3,5-(CF$_3$)$_2$), 7.66 (brs, 4H, C_6H_3-3,5-(CF$_3$)$_2$), 6.80 (s, 6H, 2,6-Ar), 6.43 (s, 3H, 4-Ar), 6.12 (s, 1H, NH), 6.09 (s, 12H, Py), 3.46 (t, J_{HH} = 4.9 Hz, 6H, NCH_2), 2.51 (sept, J_{HH} = 6.8 Hz, 12H, CHMe$_2$), 2.30 (t, J_{HH} = 4.9 Hz, 6H, NCH_2), 1.06 (d, J_{HH} = 6.8 Hz, 36H, CH(CH_3)$_2$), 0.95 (d, J_{HH} = 6.8 Hz, 36H, CH(CH_3)$_2$) ppm. Anal. Calcd (%) for $C_{116}H_{130}BF_{24}MoN_{11}$: C, 62.17; H, 5.85; N, 6.88. Found: C, 62.20; H, 5.86; N, 6.90.

Crystals for the X-ray study were grown from a C_6D_6 solution in a J-Young tube.

{[DPPN$_3$N]MoNH}[BAr$^f_4$] (50% ^{15}N-Labeled). The synthesis was carried out as described for {[DPPN$_3$N]MoNH}[BAr$^f_4$], yield 61 mg (74%). ^{1}H NMR (C_6D_6, 400 MHz, 297 K) δ 8.31 (brs, 8H, C_6H_3-3,5-(CF$_3$)$_2$), 7.63 (brs, 4H, C_6H_3-3,5-(CF$_3$)$_2$), 6.68 (s, 6H, 2,6-Ar), 6.45 (s, 3H, 4-Ar), 6.12 (d, J_{HN} = 74 Hz), 6.09 (s, 12H, Py), 3.44 (t, J_{HH} = 5.3 Hz, 6H, NCH_2), 2.50 (sept, J_{HH} = 6.8 Hz, 12H, CHMe$_2$), 2.24 (t, J_{HH} = 5.3 Hz, 6H, NCH_2), 1.06 (d, J_{HH} = 6.8 Hz, 36H, CH(CH_3)$_2$), 0.95 (d, J_{HH} = 6.8 Hz, 36H, CH(CH_3)$_2$) ppm; ^{15}N{^{1}H} NMR (C_6D_6, 50.7 MHz, 297 K) δ 428.7 ppm.

{[DPPN$_3$N]MoNH$_3$}[[BAr$^f_4$] (26). Ammonia (38 mL, ~413 Torr, 858 μmol) was vacuum-transferred onto a frozen CH_2Cl_2 (5 mL) solution of [DPPN$_3$N]MoCl (300 mg, 215 μmol) and Na[BAr$^f_4$] (209 mg, 236 μmol). The mixture was thawed and stirred for 3 h at room temperature under partial vacuum. The solvent was removed under reduced pressure, and the residue was dried in vacuo for 1 h. The solid was extracted with pentane (total, ~30 mL), and the extracts were filtered through Celite and stored at −30 °C overnight. A brown-red solid was filtered off, yield 301 mg (62%). ^{1}H NMR (C_6D_6, 400 MHz, 297 K) δ 8.21 (brs, 8H, C_6H_3-3,5-(CF$_3$)$_2$), 7.62 (brs, 4H, C_6H_3-3,5-(CF$_3$)$_2$), 6.10 (brs, 12H, Py), 2.72 (brs, 12H, CHMe$_2$), 1.03 (brs, 74H, CH(CH_3)$_2$), −3.17 (brs, Ar), −19 (brs, 6H, NCH_2), −107 (brs, 6H, NCH_2) ppm. Anal. Calcd (%) for $C_{116}H_{132}BF_{24}MoN_{11}$: C, 62.11; H, 5.93; N, 6.87. Found: C, 62.19; H, 5.90; N, 6.81.

Crystallographic Details. Low temperature diffraction data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) for the structure of compound **24** and on a Bruker D8 three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Cu Kα radiation (λ = 1.541 78 Å) for the other four structures (φ- and ω-scans). The structures were solved by direct methods using SHELXS[35] and refined against F^2 on all data by full-matrix least-squares with SHELXL-97[36] using established refinement techniques.[37] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms (except the Mo−N−H hydrogen atoms in the structures of **23** and **25**, which were located in the difference Fourier synthesis) were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U_{eq} value of the atoms they are linked to (1.5 times for methyl groups). Details of the data quality and a summary of the residual values of the refinements for all structures are given in the Supporting Information. Descriptions of the individual refinements follow below.

Compound **19** crystallizes in the triclinic space group $P\bar{1}$ with one molecule of **19** and two diethyl ether molecules per asymmetric unit. Similarity restraints on 1−2 and 1−3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters were applied to the two solvent molecules; the model contains no restraints involving the target molecule.

Compound **20** crystallizes in the triclinic space group $P\bar{1}$ with one molecule of **20** and four benzene molecules per asymmetric unit. Two isopropyl groups of the DPP ligands show disorder and two of the benzene molecules are disordered over four positions.

(35) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.
(36) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.
(37) Müller, P. *Crystallogr. Rev.* **2009**, *15*, 57.

Similarity restraints on 1−2 and 1−3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters were applied to all disordered atoms. In addition all benzene molecules were restrained to be planar within 0.02 Å^3 and similarity restraints were applied to geometrically relate the three DPP fragments to one another. For both isopropyl group disorders the ratios between the two components were refined freely, while the sum of occupancies for every two related components was constrained to unity. The occupancies for the four components of the two-molecule benzene disorder were refined individually, and the sum of all four occupancies was restrained to 2.

Compound **23** crystallizes in the monoclinic space group $P2_1/n$ with one molecule of **23**, 2.5 pentane molecules, and one benzene molecule per asymmetric unit. The half occupied pentane molecule is disordered over two crystallographically independent positions, involving an inversion center (resulting in four disorder components for the full pentane molecule). The other two pentane molecules show comparatively large anisotropic displacement parameters, but modeling a disorder was not stable. In addition one CF_3 group of the [BAr$^f_4$] anion was modeled as disordered over two positions. The ratios between the two components of all disorders were refined freely, while the sum of occupancies for every two related components was constrained to unity. Similarity restraints on 1−2 and 1−3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters were applied to all solvent molecules and to all fluorine atoms. In addition the atoms of one of the pentane molecules were restrained to behave approximately isotropic (within 0.04 Å^3). In spite of the disorders described above, the cores around the metal atom is well-defined and coordinates for the two Mo N═NH_2 hydrogen atoms could be taken from the difference Fourier synthesis. These hydrogen atoms were subsequently refined semifreely with the help of distance restraints while constraining their isotropic displacement parameter to 1.2 times the value of U_{eq} of the corresponding nitrogen atoms. The presence of a half occupied pentane molecule in the asymmetric unit leads to a noninteger number for carbon in the empirical formula.

Compound **24** crystallizes in the monoclinic space group $P2_1/c$ with two molecules of **24** and three benzene molecules per asymmetric unit. One of the two independent molecules of **24** is well behaved (only one isopropyl group is disordered), while the other one shows extensive disorder of all atoms of two of the three DPP arms. Similarity restraints on 1−2 and 1−3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters were applied to all atoms where applicable. The ratios between the two components of all disorders were refined freely, while the sum of occupancies for every two related components was constrained to unity. None of the three solvent molecules were noticeably disordered, and similarity and planarity restraints were applied to the solvent molecules in order to stabilize the convergence of the model.

Compound **25** crystallizes in the triclinic space group $P\bar{1}$ with two molecules of **25** and six benzene molecules per asymmetric unit. One of the two independent **25** cations is well behaved (no disorders needed to be resolved), while the other cation shows extensive disorder of the three DPP arms, only some of which could be resolved. Most CF_3 groups in both [BAr$^f_4$] anions are disordered; for a total of six of them (three in each [BAr$^f_4$]) the disorder could be resolved. Only one of the benzene molecules shows disorder over two positions. The ratios between the two components of all disorders were refined freely, while the sum of occupancies for every two related components was constrained to unity. Similarity restraints on 1−2 and 1−3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters were applied to all atoms where applicable. In addition, planarity restraints were applied to the solvent models and the anisotropic displacement parameters of all fluorine atoms were restrained to behave approximately isotropic within 0.05 Å^3. In spite of the many disorders, the cores around the metal atoms of both independent **25** cations are well-defined and coordinates for both Mo−N−H hydrogen atoms could be taken from the difference Fourier synthesis. These two hydrogen atoms were subsequently refined semifreely with the help of distance restraints while constraining their isotropic displacement parameter to 1.2 times the value of U_{eq} of the corresponding nitrogen atoms.

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Supporting Information Available: Crystal data and structure refinement tables for all X-ray structural studies and selected bond lengths and angles for [DPPN_3N]Mo≡N and {[DPPN_3N]Mo≡NH}[BAr$^f_4$]; five CIF files containing crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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