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Synthesis of Molybdenum Complexes that Contain "Hybrid" Triamidoamine Ligands, $[(Hexaisopropylterphenyl\text{-}NCH_2CH_2)_2NCH_2CH_2N\text{-}aryl]^{3-}$, and Studies Relevant to Catalytic Reduction of Dinitrogen

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In the Buchwald–Hartwig reaction between HIPTBr (HIPT = 3,5-(2,4,6-i-$Pr_3C_6H_2)_2C_6H_3$ = hexaisopropylterphenyl) and $(H_2NCH_2CH_2)_3N$, it is possible to obtain a 65% isolated yield of $(HIPTNHCH_2CH_2)_2NCH_2CH_2NH_2$. A second coupling then can be carried out to yield a variety of "hybrid" ligands, $(HIPTNHCH_2CH_2)_2NCH_2CH_2NHAr$, where Ar = 3,5-$Me_2C_6H_3$, 3,5-$(CF_3)_2C_6H_3$, 3,5-$(MeO)_2C_6H_3$, 3,5-$Me_2NC_5H_3$, 3,5-$Ph_2NC_5H_3$, 2,4,6-i-$Pr_3C_6H_2$, or 2,4,6-$Me_3C_6H_2$. The hybrid ligands may be attached to Mo to yield [hybrid]MoCl species. From the monochloride species, a variety of other species such as [hybrid]MoN, {[hybrid]MoN_2}Na, and {[hybrid]$Mo(NH_3)$}$^+$ can be prepared. [Hybrid]MoN_2 species were prepared through oxidation of {[hybrid]MoN_2}Na species with $ZnCl_2$, but they could not be isolated. [Hybrid]Mo═N–NH species could be observed as a consequence of the protonation of {[hybrid]MoN_2}$^-$ species, but they too could not be isolated as a consequence of a facile decomposition to yield dihydrogen and [hybrid]-MoN_2 species. Attempts to reduce dinitrogen catalytically led to little or no ammonia being formed from dinitrogen. The fact that no ammonia was formed from dinitrogen in the case of Ar = 3,5-$Me_2C_6H_3$, 3,5-$(CF_3)_2C_6H_3$, or 3,5-$(MeO)_2C_6H_3$ could be attributed to a rapid decomposition of intermediate [hybrid]Mo═N–NH species in the catalytic reaction, a decomposition that was shown in separate studies to be accelerated dramatically by 2,6-lutidine, the conjugate base of the acid employed in the attempted catalytic reduction. X-ray structures of $[(HIPTNHCH_2CH_2)_2$-$NCH_2CH_2N\{3,5\text{-}(CF_3)_2C_6H_3\}]MoCl$ and $[(HIPTNHCH_2CH_2)_2NCH_2CH_2N(3,5\text{-}Me_2C_6H_3)]MoN_2\}Na(THF)_2$ are reported.

Introduction

In the last 10 years, we have been exploring early transition metal complexes that contain a triamidoamine ligand, $[(RNCH_2CH_2)_3N]^{3-}$ ($[RN_3N]^{3-}$).[1] These trianionic ligands bind to an early transition metal in a relatively high oxidation state (~3+ or higher) in a tetradentate fashion, leaving three orbitals for binding substrates in the trigonally symmetric "pocket" surrounded by the three amido substituents. Two of these orbitals have π symmetry (d_{xz} and d_{yz}) and one has σ symmetry (~d_{z^2}). These orbitals can be employed in three combinations ($2\pi/1\sigma$, $1\pi/2\sigma$, or 3σ) to bind substrates in the trigonal pocket. Distortion of the pseudotrigonal symmetry to yield pseudooctahedral species,[2] or even seven-coordinate species,[3] is possible in cases where tungsten is the central metal and strongly bound substrates such as isocyanides or acetylenes are involved.

Recently we have been most interested in the chemistry of Mo complexes that contain the $[HIPTN_3N]^{3-}$ ligand, where HIPT = 3,5-(2,4,6-i-$Pr_3C_6H_2)_2C_6H_3$ (hexaisopropylterphenyl, see Figure 1),[4] and in particular, in the reduction of dinitrogen at a single metal center. The HIPT-substituted ligand was designed to prevent formation of relatively stable and unreactive $[ArN_3N]Mo{-}N{=}N{-}Mo[ArN_3N]$ complexes,[1b]

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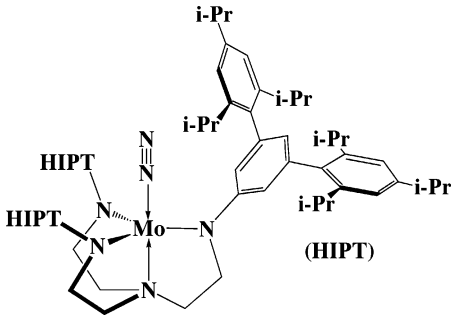
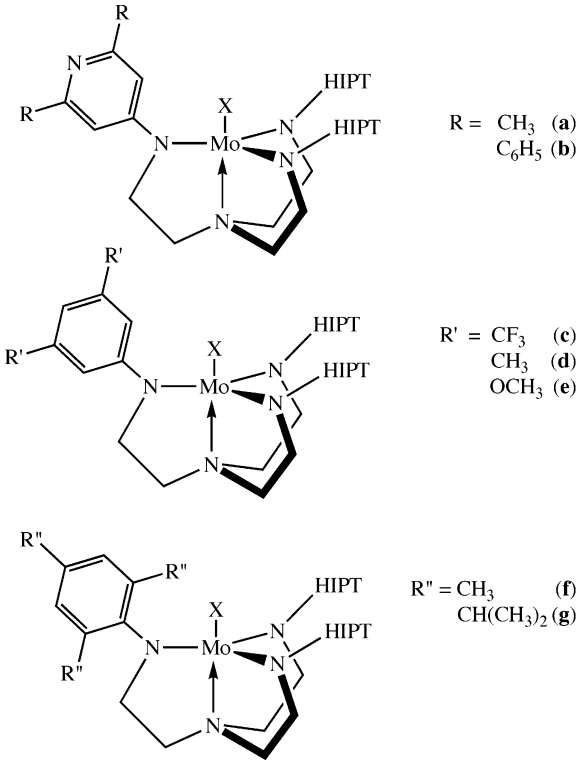


Figure 1. Drawing of $[HIPTN_3N]MoN_2$ = **Mo**N_2.

maximize steric protection of a metal coordination site in a monometallic species, and provide increased solubility in nonpolar solvents. We showed that several $[HIPTN_3N]Mo$ complexes could be prepared that contain dinitrogen or some dinitrogen reduction product.[5] Examples include paramagnetic **Mo**N_2 (where **Mo** = $[HIPTN_3N]Mo$), diamagnetic $[\mathbf{Mo}N_2]^-$, diamagnetic **Mo**−N═N−H, diamagnetic [**Mo**═N−NH_2]BAr'_4 (Ar′ = 3,5-$(CF_3)_2C_6H_3$), diamagnetic **Mo**≡N, diamagnetic [**Mo**═NH]BAr′, paramagnetic [**Mo**(NH_3)]BAr'_4, and paramagnetic **Mo**(NH_3). Several of these species were successful for the catalytic reduction of dinitrogen to ammonia with protons and electrons.[4a,b] Dinitrogen is reduced through a combination of reduction and protonation at a single molybdenum in a trigonally symmetric coordination pocket that is sterically protected by three hexaisopropyl terphenyl substituents. Some combination of the frontier (two π and one σ) orbitals is sufficient to bind all of the intermediates in a proposed Chatt-like reduction cycle.

"Symmetric" variations of the $[HIPTN_3N]^{3-}$ ligand that have been prepared and attached to molybdenum include the hexa-*tert*-butylterphenyl ($[HTBTN_3N]^{3-}$) ligand, the hexamethylterphenyl ($[HMTN_3N]^{3-}$) ligand, and a variation of the $[HIPTN_3N]^{3-}$ ligand in which a bromide is present in the para position of the central phenyl ring, $[p\mathrm{BrHIPTN_3N}]^{3-}$.[6] It became clear from various stoichiometric reactions involving the $[HTBTN_3N]^{3-}$ system that proton and electron transfer was much slower than in the parent $[HIPTN_3N]^{3-}$ system, perhaps by an order of magnitude or more. (The rate of conversion of $[HTBTN_3N]Mo(NH_3)$ into $[HTBTN_3N]Mo(N_2)$ has now been confirmed to be extremely slow, with a half-life of ∼30 h compared to ∼2 h for the parent system under a given set of conditions.)[7] We believe it is for this reason that $[HTBTN_3N]Mo{\equiv}N$ produces no significant ammonia from dinitrogen (0.06 equiv); the nitride is reduced to ammonia, but the system does not turn over to any significant extent. An attempted catalytic reduction with $[HMTN_3N]Mo{\equiv}N$ as the catalyst precursor was barely catalytic (0.49 equiv). The hexamethylterphenyl system was not explored in detail because of the low yields involved in synthesis of the ligand. Therefore the reason for poor catalytic activity has not been established in the hexamethylterphenyl system. Various $[p\mathrm{BrHIPTN_3N}]Mo$ compounds were successful catalysts for reduction of dinitrogen; 6.4−7.0 equiv of total ammonia were formed, which is not quite as high as the amount formed when $[HIPTN_3N]Mo$ species are employed. Since electronic differences (redox potentials and values for ν_{NN}) between the three variations and the parent system are relatively insignificant,[6] steric differences appear to play a major role in the success or failure of the HTBT- and HMT-substituted ligand complexes for the catalytic reduction of dinitrogen.

During studies concerning the $[HTBTN_3N]^{3-}$ system, we discovered that in the arylation reaction between 3 equiv of



R = CH_3 (**a**), C_6H_5 (**b**)

R' = CF_3 (**c**), CH_3 (**d**), OCH_3 (**e**)

R" = CH_3 (**f**), $CH(CH_3)_2$ (**g**)

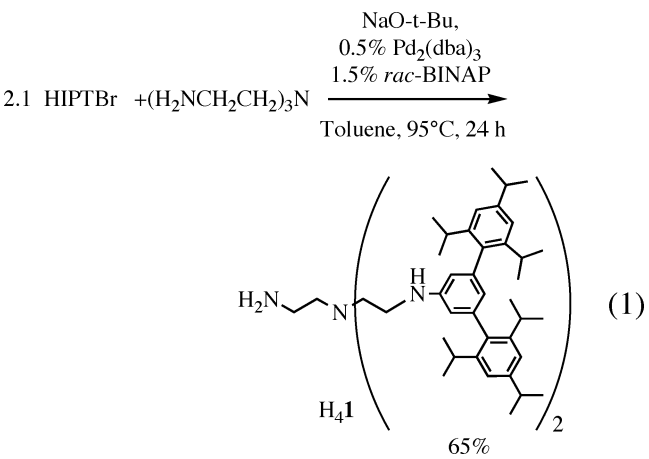
$HIPT_2$ ligand	H_4**1**
Hybrid Ligands	H_3**2**
LMoCl	**3**
LMoN	**4**
$[LMoN_2][Na(thf)_2]$	**5**
$LMoN_2$	**6**
$[LMoNH_3][BAr'_4]$	**7**
$LMoNH_3$	**8**
LMoNNH	**9**

Figure 2. Labeling scheme for ligands and metal complexes described in this paper.

HTBTBr and $(H_2NCH_2CH_2)_3N$ the third equivalent of HTBTBr reacts significantly more slowly than the second equivalent. Therefore, $(HTBTNHCH_2CH_2)_2NCH_2CH_2NH_2$ could be isolated in good yield[6] by adjusting the stoichiometry. It then became possible to add a different aryl group to the third "arm" of the ligand to yield what we call a hybrid $(HTBTNHCH_2CH_2)_2NCH_2CH_2NHAr$ species. We found that the same is true for the $(HIPTNHCH_2CH_2)_2NCH_2CH_2NHAr$ species (Figure 2). An advantage of the $[(HIPTNCH_2CH_2)_2NCH_2CH_2NAr]^{3-}$ species is that steric protection in the coordination pocket can be tuned more finely. In this paper, we report the synthesis of hybrid ligands and a selection of molybdenum compounds that contain some of them. We also report attempts to reduce dinitrogen catalytically with compounds that contain hybrid ligands. No Mo compound that contains one of the hybrid ligands is as successful as a catalyst as a compound that contains the parent $[HIPTN_3N]^{3-}$ ligand, and some fail completely to produce ammonia from gaseous dinitrogen. Although the hybrid catalysts are poor catalysts, or not catalysts at all, these studies have helped us to understand what may be some of the key problems in the catalytic cycle.

Results and Discussion

If 2.1 equiv of HIPTBr are employed in the Buchwald–Hartwig reaction[8] between HIPTBr and $(H_2NCH_2CH_2)_3N$, then a mixture results that consists largely of $(HIPTNHCH_2CH_2)_2NCH_2CH_2NH_2$ mixed with a small amount of $(HIPTNHCH_2CH_2)_3N$. These two products can be separated readily using a silica gel column pretreated with triethylamine, from which $(HIPTNHCH_2CH_2)_3N$ (11% yield) elutes readily with toluene. The flushing of the column with a 1:1 mixture of toluene and tetrahydrofuran then yields $(HIPTNHCH_2CH_2)_2NCH_2CH_2NH_2$ (H_4**1**, 65% yield on a ~50 g scale; eq 1). The $(HIPTNHCH_2CH_2)_3N$ ligand can be accumulated and employed in other studies.



(1)

A second Buchwald-Hartwig coupling can be carried out on the terminal amine in $(HIPTNHCH_2CH_2)_2NCH_2CH_2NH_2$ to yield $(HIPTNHCH_2CH_2)_2NCH_2CH_2NHAr$ species H_3**2a**–H_3**2g** (eq 2, Figure 2). The final arylation can be complicated by overarylation of one or more secondary amines. However, careful optimization of the conditions allowed the pure ligands to be isolated and purified through column chromatography. These ligands all exhibit features in their NMR spectra that are entirely consistent with their C_s symmetry.

$$H_4\mathbf{1} \xrightarrow[\text{toluene, 80–100 °C, 24 h}]{\text{NaO-}t\text{-Bu, 0.5\% Pd}_2(\text{dba})_3,\ 1.5\%\ rac\text{-BINAP}} (HIPTNHCH_2CH_2)_2NCH_2CH_2NHAr \quad H_3\mathbf{2a}–H_3\mathbf{2g} \qquad (2)$$

The hybrid ligands were attached to Mo in the same way as the $[HIPTN_3N]^{3-}$ ligands (i.e., the parent ligands were added to a solution of $MoCl_4(THF)_2$ and the mixture was then treated with three equivalents of $LiN(TMS)_2$ (Figure 3)). The resulting bright orange paramagnetic [hybrid]MoCl compounds **3a**–**3g** (Figure 2) could be isolated in good yields, even though they tend to be significantly more soluble than the already highly soluble $[HIPTN_3N]$MoCl species.[4] The proton NMR spectra of the [hybrid]MoCl compounds reveal paramagnetically shifted methylene resonances similar to those observed for $[HIPTN_3N]$MoCl, with separate methylene resonances for the HIPT and Ar-substituted arms. In some cases separate "inner" and "outer" (diastereotopic) methylene proton resonances can be observed in the HIPT-substituted arms of the ligands, consistent with the overall C_s symmetry of the hybrid complex. It should be noted that symmetric $(ArNHCH_2CH_2)_3N$ ligands cannot be placed onto Mo using the method described above when Ar is 2,4,6-trimethylphenyl,[1b] presumably for steric reasons. One mesityl or TRIP group is tolerated in **3f** or **3g** as a consequence of the two HIPT groups having no substituents in the ring's ortho positions.

An X-ray structure of **3c** was carried out (Figure 4, Tables 1 and 2). The main difference between **3c** and the $[HIPTN_3N]^{3-}$ compounds is a disruption of the trigonally symmetric pattern of steric protection around the apical position on the Mo (i.e., an opening up of one face of the ligand binding pocket). Bond distances and angles around the metal are similar to those found in symmetric $[HIPTN_3N]$-Mo, $[HTBTN_3N]$Mo, and $[p$BrHIPT$N_3N]$Mo systems.

One of the least air-sensitive $[HIPTN_3N]$Mo compounds that can be employed as a catalyst precursor in dinitrogen reduction is the nitride, $[HIPTN_3N]$MoN. The bright yellow, diamagnetic [hybrid]MoN compounds **4a**–**4g** (Figure 3) were prepared in reactions between [hybrid]MoCl and trimethylsilyl azide in benzene at elevated temperatures. NMR spectra of the diamagnetic [hybrid]MoN species are fully consistent with their C_s symmetry. The [hybrid]MoN species also are relatively crystalline and readily isolated. All have been analyzed and fully characterized.

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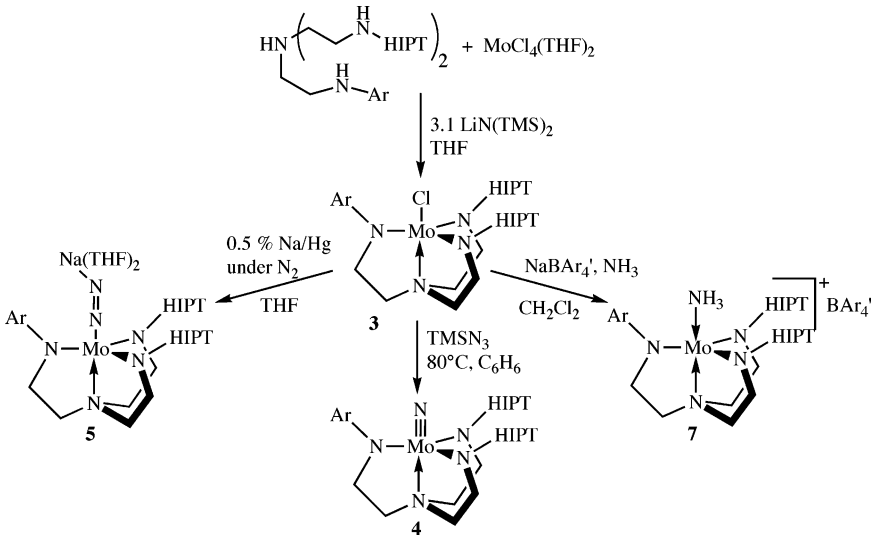

Figure 3. Synthesis of molybdenum complexes that contain hybrid ligands.

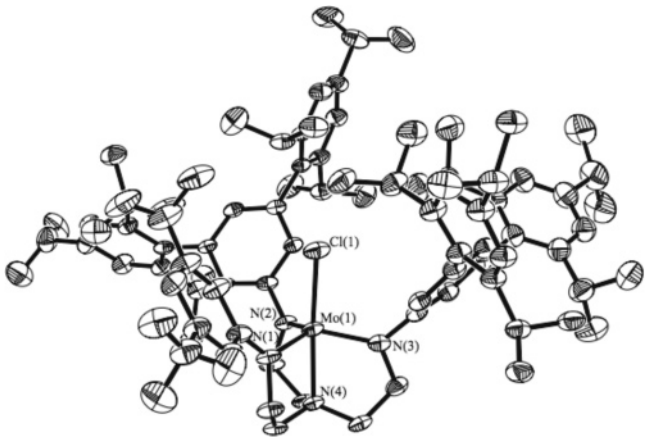

Figure 4. X-ray crystal structure of **3c**. Hydrogen atoms have been removed for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of **3c** versus HTBTMoCl[6]

bond	**3c**	HTBTMoCl
Mo−Cl	2.331(2)	2.33
Mo−N1 (amide)	1.978(7)	1.99
Mo−N4 (amine)	2.199(6)	2.34
N4−Mo−N1	100.20(18)	99
N4−Mo−Cl	176.10(17)	179

Table 2. Selected Bond Lengths (Å) and Angles (deg) of **5d** versus [HIPTMoN$_2$][MgBr(THF)$_3$][17]

bond	**5d**	[HIPTMoN$_2$][MgBr(THF)$_3$]
N5−N6 (nitrogen)	1.171(6)	1.15
Mo−N5 (dinitrogen)	1.882(4)	1.86
Mo−N4 (amine)	2.209(4)	2.24
Mo−N3 (amide)	2.022(4)	2.02
N4−Mo−N5	174.09(17)	178
N4−Mo−N1	81.25(16)	80
Mo−N5−N6	174.2(4)	178
N5−N6−Na	110.7(4)	

Reduction of [hybrid]MoCl compounds with sodium sand or 0.5% sodium/mercury amalgam yields diamagnetic anionic complexes that can be described as either Mo(II) dinitrogen complexes or, alternatively, as deprotonated Mo(IV) diazenido species, {[hybrid]MoN$_2$}Na(THF)$_2$. Although

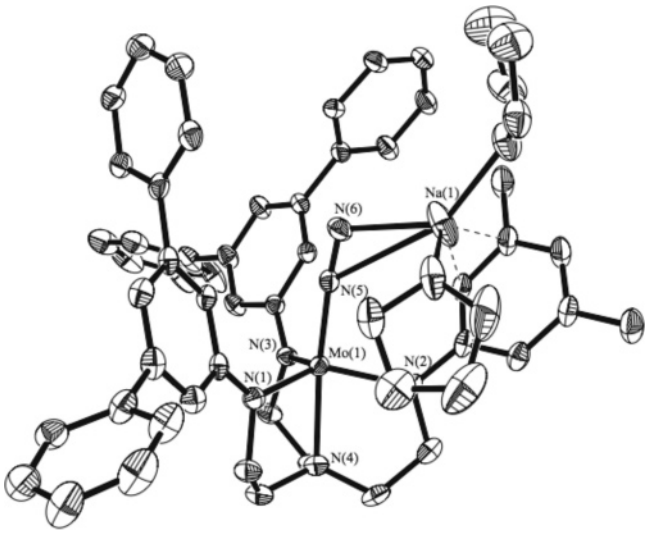

Figure 5. X-ray crystal structure of **5d**. Hydrogen atoms and isopropyl groups have been removed for clarity.

all {[hybrid]MoN$_2$}Na(THF)$_2$ complexes could be identified in solution, we attempted to isolate only **5c** and **5d**. Unfortunately, neither **5c** nor **5d** could be isolated in a sufficiently pure state to pass elemental analyses. Fortunately, however, an X-ray crystal structure was completed on a suitable crystal of **5d** (Figure 5). As in **3c**, the presence of an unsymmetric arm does not alter the metrical parameters around molybdenum to any significant degree (Table 2). The most obvious and significant feature is the off-axis coordination of the sodium atom (Na−N6−N6 = 110°) to the 3,5-dimethylphenyl group. Coordination of the sodium ion to the two nitrogens in the diazenido ligand decreases the Mo−N═N angle slightly to 174°.

The {[hybrid]MoN$_2$}Na(THF)$_2$ compounds **5a**−**5g** can be oxidized with ZnCl$_2$ to yield [hybrid]MoN$_2$ species, **6a**−**6g**. The extreme solubility of **6a**−**6g** and the presence of 5−10% of free ligand, (HIPTNHCH$_2$CH$_2$)$_2$NCH$_2$CH$_2$NHAr, so far have thwarted attempts to isolate these species. Therefore, **6a**−**6g** could be characterized only through IR and NMR techniques. In ^{1}H NMR spectra of these species,

Table 3. Dinitrogen Stretching Modes for $LMoN_2$ Compounds

compound	ν_{N-N} (cm^{-1})
$[HIPTN_3N]MoN_2$	1990
$[p$BrHIPTN$_3$N$]MoN_2$	1992
$[HTBTN_3N]MoN_2$	1990
6a	1991
6b	1988
6c	1992
6d	1987
6e	1984
6f	1986
6g	2007

which are characteristic of a single Mo compound (plus free ligand), multiple resonances are observed for backbone methylene protons, as in many of the paramagnetic [hybrid]-MoCl compounds. IR spectra reveal a strong ν_{NN} absorption near 1990 cm^{-1}, as previously observed for MoN_2 compounds that contain "symmetric" ligands such as $[HIPTN_3N]$-MoN_2.[4] These ν_{NN} stretches are listed in Table 3. The ν_{NN} stretches in **6a**−**6g** respond to the slightly different electronic characteristics of the hybrid ligands. In the 3,5-substituted compounds, the energy of the ν_{NN} stretch moves to lower energies as the hybrid ligand's substituents become more electron-donating (i.e., $\nu_{NN} = 1992$ cm^{-1} for **6c** vs $\nu_{NN} = 1984$ cm^{-1} for **6e**). The exception to this trend is **6g**, where ν_{NN} is found at 2007 cm^{-1}. We propose that this relatively high value results from steric crowding at the metal by the ortho isopropyl substituents, which lengthens the Mo−N_2 bond slightly and therefore reduces the amount of back-bonding to dinitrogen. As we shall see, however, the ν_{NN} stretches, which in any case vary relatively little, do not correlate with the success or failure of a catalytic reduction of dinitrogen, at least in the series of complexes prepared here.

Two cationic ammonia complexes, {[hybrid]$MoNH_3$}-BAr_4' species (**7c** and **7e**) were prepared in reactions between **3c** and **3e**, respectively, and ammonia in dichloromethane in the presence of $NaBAr_4'$ (Ar′ = 3,5-$(CF_3)_2C_6H_3$). Compound **7e** could be crystallized cleanly and was analyzed successfully. Compound **7c** could not be freed completely from $NaBAr_4'$ and so could be characterized only via NMR. Both **7c** and **7e** were used in studies involving the exchange of ammonia for dinitrogen discussed below.

Attempts to reduce dinitrogen catalytically were carried out in the manner described for the parent system, which produced 7−8 equiv of ammonia/1 equiv of Mo.[4] Briefly, a heptane slurry containing 48 equiv of [2,6-lutidinium][BAr_4'] and **4a**−**4g** was placed in the reaction vessel, and 36 equiv of decamethylchromocene in 10 mL of heptane was added with a syringe pump.[4a] (See the Experimental Section for a representative experiment.) The reducing agent was added over a period of 6 h, and the mixture was stirred for an additional hour. The volatiles were then vacuum transferred onto 1 M HCl in ether. The remaining solids were treated with NaO-*t*-Bu in a 2:1 mixture of methanol and tetrahydrofuran, and the volatiles again were transferred onto 1 M HCl in ether. The ether and HCl were removed in vacuo, and the resulting solid was analyzed for ammonia using the indophenol method. The results are summarized in Table 4.

Table 4. Equivalents of Ammonia Obtained When LMoN Is the Precatalyst

compound	NH_3 from N_2 (equiv)
4a	0.6
4b	0.3
4c	0
4d	0
4e	0
4f	0.2
4g	2.0

None of the compounds that contain one of the new hybrid ligands is as efficient a catalyst for the reduction of dinitrogen as the $[HIPTN_3N]Mo$ analogue. However, **4a**, **4b**, **4f**, and **4g** are catalytic to a small degree (0.6, 0.3, 0.2, and 2 equiv of ammonia from dinitrogen, respectively; Table 4). At least one equivalent of ammonia is formed in all runs (i.e., the nitride is reduced to ammonia under the conditions employed). Compounds **4a** and **4b** are not directly comparable to the others as a consequence of the presence of the pyridyl ring, which could be protonated in several intermediates. In fact all that we can say at this point is that the $[HIPTN_3N]$-Mo system is not unique, although successful catalytic reduction appears to be extraordinarily sensitive to steric effects. It is important to know that one run in which **6c** was employed yielded 0.7 equiv of ammonia. This is an important result that we will revisit later.

A crucial step in dinitrogen reduction is conversion of a Mo(III) ammonia complex into a Mo(III) dinitrogen complex. Two of the **L**$MoNH_3$ complexes were prepared in situ through reduction of **7c** and **7e** with $CrCp^*_2$. The resulting **L**$MoNH_3$ complexes (**8c** and **8e**) could not be isolated as a consequence of their high solubility and their ready conversion under dinitrogen into **L**MoN_2 complexes, as observed through growth of **L**MoN_2 in IR studies in aliquots of the solution of **L**$MoNH_3$ over a period of several hours. The rate of formation of **L**MoN_2 was shown to be approximately a first-order process in Mo through at least two half-lives, as found in the parent system.[7] For **8c**, $t_{1/2} = 180$ min, while for **8e**, $t_{1/2} < 45$ min. It should be stressed that these results are only semiquantitative, since the ammonia that is released is in equilibrium with the newly formed **L**MoN_2 is not immediately released into the gas phase. In the parent system, conversion of the ammonia complex into the dinitrogen complex was shown to be first order in dinitrogen with $t_{1/2} \approx 120$ min. Exchange was estimated to actually be approximately 10 times faster than that observed in "bulk" exchange reactions.[7] However, data for this first-order reaction of hybrid complexes are useful when compared with analogous data obtained for the parent system.[7] In short, the rate of exchange appears to be slightly slower when CF_3 groups are present ($t_{1/2} = 180$ min) and faster when methoxy groups are present ($t_{1/2} < 45$ min). Although we have not shown that the exchange rates in the hybrid systems depend on dinitrogen pressure, as in the parent system,[7] we believe that this is likely to be the case. The exchange rate is faster when the metal is slightly more electron-rich, consistent with more efficient back-bonding into dinitrogen when it displaces ammonia in a bimolecular reaction. The position of the equilibria in the hybrid ligand systems are not known. In

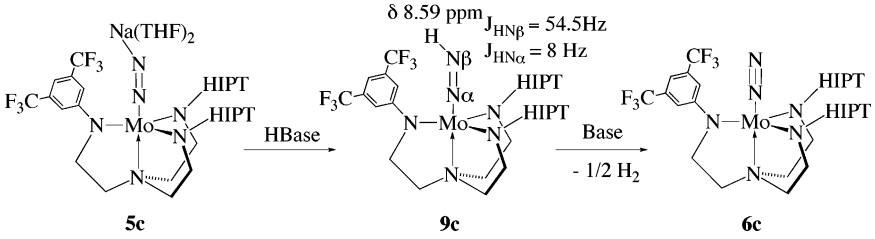

Figure 6. Synthesis and decomposition of hybrid diazenide **9c**.

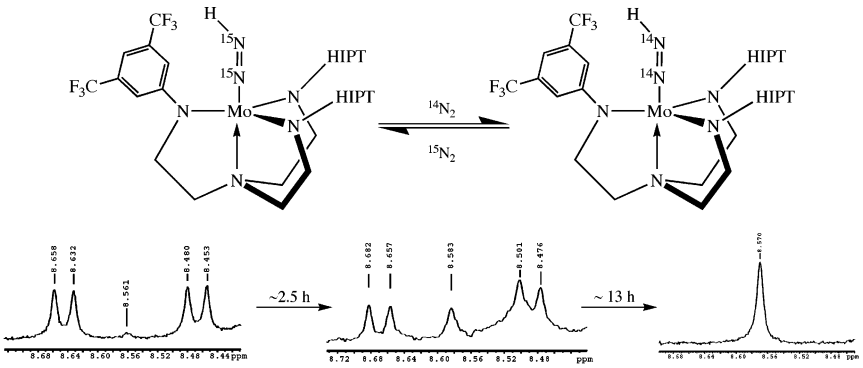

Figure 7. $^{14}N_2$ exchange into the $^{15}N_2$-labeled diazenide **9c**.

any case, the main point is that slow exchange *cannot* be the reason these catalysts fail, since the exchange rates for the CF_3- and OMe-substituted hybrid ligands bracket that observed in the successful HIPT system. We also were able to observe free NH_3 in runs where two NH_3 collections (initial volatiles and post base workup) were separated and quantified. When **4c** is used as the precatalyst 0.3 out of the 0.97 equiv of the ammonia observed was found in the initial volatiles, indicating that NH_3 is indeed released during catalysis and that approximately 1/3 of the ammonia is present as NH_3 rather than NH_4^+.

If exchange of ammonia for dinitrogen in the hybrid systems is not the problem with **8c** and **8e** as catalyst precursors, then what is the problem? We focused on the next step in the catalytic reaction, formation of the neutral diazenide (M−N═NH) species. As opposed to the M−N═NR species (e.g., R = alkyl), M−N═NH species are rare in the literature, although some have been claimed.[9] However, to our knowledge only the molybdenum and tungsten compounds in the symmetric HIPT system have been confirmed to have a proton on the β nitrogen in ^{15}N-labeled compounds. Fortunately, the [ArN_3N]Mo−N═NH species are diamagnetic, so the presence of a proton on N_β can be established through ^{15}N labeling studies. Because of its relative ease of synthesis and the availability of an ^{19}F NMR handle, we focused on the [ArN_3N]Mo−N═NH compound containing the 3,5-trifluoromethylphenyl-substituted arm (**9c**). Although the results for this compound have been reported recently,[7] a summary is reported below.

Treatment of **5c** (both ^{15}N and ^{14}N) with a proton source (initially $H(OEt_2)_2BAr_4'$) resulted in the formation of **9c**. This species was identified through observation of Mo−N═N*H* at 8.6 ppm, with $J_{N\beta H} = 54.5$ Hz and $J_{N\alpha H} = 8$ Hz (absolute values) in the ^{15}N-labeled compound (Figure 6). These values are nearly identical to those obtained for [$HIPTN_3N$]Mo−N═NH.[4b] Compound **9c** decomposes in a manner that is first order in Mo to form **6c** quantitatively (and H_2) with a $t_{1/2}$ of 17 ± 2 h. In contrast, pure [$HIPTN_3N$]Mo−N═NH decomposes only very slowly to [$HIPTN_3N$]MoH (at 60 °C, $t_{1/2}$ = 90 h).[4b] Interestingly, during some of these experiments, we also were able to observe conversion of Mo−^{15}N═^{15}NH to Mo−^{14}N═^{14}NH ($t_{1/2}$ of 4.5 h; Figure 7). The mechanism of this exchange (which also can be observed in [$HIPTN_3N$]-Mo−^{15}N═^{15}NH, albeit with a much slower $t_{1/2}$ of approximately 150 h) is under further study. We suspect that nitrogen exchange is dependent upon nitrogen pressure (i.e., it does not involve β-hydride elimination to yield [$HIPTN_3N$]-MoH, followed by "insertion" of dinitrogen into the Mo−H bond). It should be noted that **9c** is prepared in situ. Therefore, we do not know if the pure compound (if it somehow could be purified) would decompose at the same rate as that prepared in situ.

When [2,6-lutidinium]BAr_4' was used to form **9c**, the decomposition rate was enhanced by an order of magnitude, resulting in a $t_{1/2}$ of 1.1 h. When **9c** was prepared with $H(OEt_2)_2BAr_4'$ and 4 equiv of 2,6-lutidine, 2,4,6-trimethylpyridine (collidine), or Et_3N were added subsequently, **9c** could not be observed 5 min after addition of the base: only **6c** and H_2 were observed as the major products. The ability of Et_3N to decompose **9c** catalytically suggests that this reaction is unlikely to be involved in redox chemistry, as it might when some lutidine is the base. These results suggest that a lutidine-catalyzed shunt that produces hydrogen is operative in the less sterically shielded compounds (Figure 8). This finding could explain the inability of **4c** to catalyze dinitrogen reduction. Clearly much more work needs to be done to understand this base-catalyzed chemistry. It is especially important to understand if dihydrogen formation is bimolecular or unimolecular in Mo. Regardless of the precise mechanism, it is nevertheless ironic that one method of forming dihydrogen takes place in a cycle that involves the dinitrogen complex as the catalyst! Of course there are

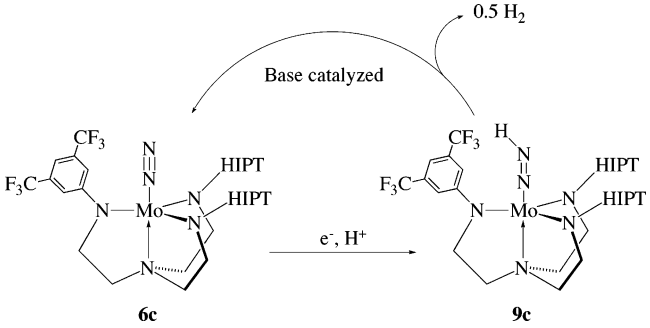

Figure 8. Hydrogenase shunt that limits catalysis in less sterically demanding systems.

other ways of forming dihydrogen, the most direct consisting of reduction of the acid by the chromocene reducing agent.

It is interesting and important to note that, when **6c** is employed in a catalytic run, 0.7 equiv of NH_3 were found. The fact that some ammonia is formed suggests that the reaction can proceed through the diazenido stage early in the reaction, but no additional ammonia is then formed from free dinitrogen. Apparently any diazenido species that is formed upon the addition of one electron and one proton to MoN_2 is not completely decomposed by 2,6-lutidine, since only 1 equiv is present at this stage. Later in the cycle, however, more 2,6-lutidine is present, and the reaction then does not proceed beyond the diazenido stage.

Conclusions and Comments

A number of compounds that contain unsymmetric "hybrid" ligands have been synthesized that help expand our knowledge of molybdenum-centered catalytic dinitrogen reduction. While none of the compounds catalyzes the dinitrogen reaction as successfully as compounds that contain the parent $[HIPTN_3N]^{3-}$ ligand, and several fail completely, the study of several observable intermediates in dinitrogen reduction have helped us understand what is necessary for successful catalytic reduction. The primary requirement is that the binding pocket be sterically protected to a dramatic degree, not only to prevent bimetallic reactions but also, we have discovered, to prevent decomposition of unstable dinitrogen reduction intermediates, especially the diazenido complex, through an, as yet, unknown mechanism. We also have shown that electron-donating ligands may speed the rate of ammonia for dinitrogen exchange. However, an increase of the rate of exchange of ammonia for dinitrogen was not sufficient to avoid the shunt that prevents catalytic turnover. Clearly many other studies are required to understand important details of the shunt that produces dihydrogen.

The larger question remains whether abiological studies of the type described here suggest that dinitrogen is reduced to ammonia at Mo in the FeMo nitrogenase.[10,11] Since we have (I believe) proven that dinitrogen can be reduced with protons and electrons catalytically to a mixture of ammonia and hydrogen at a single Mo center in systems of the type described here and since no other abiological system will accomplish this feat,[12] we are biased toward molybdenum being the metal that will reduce dinitrogen most easily and the site of reduction in the FeMo nitrogenase. It is possible that in "alternative" FeV and all Fe nitrogenases[13] dinitrogen is reduced at V or Fe instead of Mo in a similar core structure, with V and Fe being progressively less selective toward forming ammonia instead of dihydrogen. The dramatic sensitivity of catalytic dinitrogen reduction toward small changes in the nature of the triamidoamine ligand, as we have demonstrated here, further emphasizes that dinitrogen reduction is an extremely complex and sensitive catalytic reaction, with many points where it can fail. We hope to continue to improve our understanding of the complex process of catalytic reduction of dinitrogen at Mo and believe that an abiological vanadium-based catalytic reduction of dinitrogen is a goal that can be reached with the right ligand system. Catalytic reduction by V catalysts remains to be achieved, as does the catalytic reduction of dinitrogen with Fe-based systems.[14]

Experimental Section

General. Air- and moisture-sensitive compounds were manipulated using standard Schlenk and drybox techniques under an atmosphere of dinitrogen. All glassware used was oven or flame dried immediately prior to use. Pentane, diethyl ether, toluene, and benzene were purged with dinitrogen and passed through activated alumina columns. Benzene additionally was passed through a Q5 column.[15] THF and benzene-d_6 were dried over sodium/benzophenone ketyl and vacuum transferred prior to use. All other solvents mentioned were freeze−pump−thaw degassed three times prior to use. All dried and deoxygenated solvents were stored in a dinitrogen-filled glovebox over molecular sieves or in Teflon-sealed glass solvent bombs. 1,3,5-Triisopropylbenzene (Aldrich), 2,4,6-tribromoaniline (Lancaster), *N*-bromo-succinimide (Aldrich), NaO-*t*-Bu (Aldrich), $Pd_2(dba)_3$ (Strem), *rac*-BINAP (Strem), and tris(2-

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(12) The only other known systems that will catalytically reduce dinitrogen are those discovered by Shilov (Shilov, A. E. *Russ. Chem. Bull. Int. Ed.* **2003**, *52*, 2555). These systems require Mo and are catalytic with respect to Mo, but they reduce dinitrogen to a mixture of hydrazine and ammonia (∼10:1). The reaction is run in methanol in the presence of magnesium hydroxide and a strong reducing agent such as sodium amalgam. Few mechanistic details are known.

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aminoethyl)amine (Aldrich) were used as received, unless indicated otherwise. Hexaisopropylterphenyl bromide (HIPTBr),[16,17] 2,4,6-trimethoxy-1-iodobenzene, and 4-bromo-2,6-dimethylpyridine[18] were prepared according to published procedures or with slight modifications. Proton and carbon NMR spectra were recorded on a Varian Mercury 300. NMR spectra are referenced to internal residual solvent peaks (^{1}H and ^{13}C NMR) or to external C_6H_5F ($\delta = -113.15$ ppm in the ^{19}F NMR spectrum). All stated coupling constants should be considered as absolute values.

(HIPTNHCH$_2$CH$_2$)$_2$NCH$_2$CH$_2$NH$_2$. The procedure is similar to that of the previous syntheses of symmetric ligands[4] but uses 2.1 equiv of HIPTBr instead of 3.1 equiv. A 100 mL toluene solution of $Pd_2(dba)_3$ (0.91 g, 0.9 mmol) and *rac*-BINAP (1.85 g, 2.9 mmol) was stirred with mild heating to preform the active catalyst. The catalyst solution was then filtered through Celite into a 500 mL toluene solution containing HIPTBr (78.21 g, 139 mmol), tris(2-aminoethyl)amine (10.09 g, 67 mmol), and NaO-*t*-Bu (20.4 g, 212 mmol). This mixture was then heated at ~100 °C for 2 days. After 2 days, the organic layer was combined with 500 mL of water, and the mixture was extracted with ether. The organic layers were combined and dried over magnesium sulfate. This ether solution was then filtered, and the ether was removed in vacuo. Column chromatography was then carried out on a silica gel column. Byproducts were eluted with toluene (including 11 g (10%) of the symmetric ligand), and the product was eluted with a 1:1 mixture of toluene and THF. (Note that it is important to pretreat the silica gel with triethylamine to obtain acceptable separations.) Upon removal of solvent from the column fractions in vacuo, 47.3 g of a pale yellow solid was isolated (64%). ^{1}H NMR (C_6D_6, 20 °C): δ 7.22 (s, 8H, 3,5,3″,5″-*H*), 6.50 (s, 6H, 2′,4′,6′-*H*), 4.92 (t, J_{HH} = 4.9 Hz, 2H, N*H*), 3.17 (septet, J_{HH} = 6.9 Hz, 8H, 2,6,2″,6″-C*H*Me$_2$), 2.94 (overlapped septet, J_{HH} = 6.6 Hz, 4H, 4,4″ −C*H*Me$_2$), 2.85 (overlapped multiplet, 4H, NH$_2$CH$_2$C*H*$_2$ and NH$_2$C*H*$_2$CH$_2$), 2.74 (br q, J_{HH} = 5.2 Hz, 4H, NHC*H*$_2$CH$_2$), 2.03 (br t, J_{HH} = 5.2 Hz, 4H, NHCH$_2$C*H*$_2$), 1.32 (d, J_{HH} = 7.1 Hz, 24H, 4,4″-CH(C*H*$_3$)$_2$), 1.26 (br d, J_{HH} = 6.9 Hz, 48H, 2,6,2″,6″-CH(C*H*$_3$)$_2$). 0.44 (br s, 2H, N*H*$_2$). ^{13}C NMR (C_6D_6, 20 °C): δ 148.77, 148.40, 147.19, 142.48, 138.69, 121.38, 121.03, 112.84, 55.91, 52.97, 41.64, 40.19, 31.18, 25.36, 25.05, 24.91. MS (ESI): 1107.9119 ([M + H]$^+$, calcd 1107.9116).

4-Bromo-2,6-diphenyl-pyridene. This compound was synthesized via a method similar to that of Talik et al.[18] Briefly, 2,6-diphenyl-pyridin-4-ylamine (3.75 g, 15.4 mmol) and copper bromide (11.5 g, 80.3 mmol) were added to 150 mL of 48% hydrobromic acid and cooled to <5 °C in an ice bath. Sodium nitrite (22.5 g, 326 mmol) in 100 mL water was slowly added, ensuring that the temperature did not rise above 5 °C. After the addition, the mixture was allowed to stir overnight, at which time it was basified with 150 g of sodium hydroxide in 300 mL water. The product was extracted with ether, which was dried over magnesium sulfate, filtered, and dried in vacuo, yielding a bright orange oil. This was triturated with methanol to yield 1.55 g of a bright orange powder, (34%) which is sparingly soluble in most solvents. ^{1}H NMR (C_6D_6, 20 °C): δ 7.95 (dd, 4H, 2,6,2″,6″-*H*), 7.42 (s, 2H, 3′,5′-*H*) 7.22 (m, 6H, 3,4,5,3″,4″,5″-*H*). MS (ESI): 309.0146 ([M + H]$^+$, calcd 309.0148).

H$_3$[LutHIPT$_2$N$_3$N] (2a). $Pd_2(dba)_3$ (0.054 g, 0.058 mmol) and *rac*-BINAP (0.11 g, 0.18 mmol) were stirred with mild heating in 25 mL of toluene to preform the bright orange catalyst. This solution was then filtered through Celite into a 300 mL toluene solution containing **1** (4.41 g, 3.98 mmol), 4-bromo-2,6-dimethyl-pyridine (0.80 g, 4.30 mmol), and NaO-*t*-Bu (0.76 g, 7.91 mmol). This solution was then heated at 95 °C for 2 days, after which time it was filtered through Celite and concentrated in vacuo to dryness. The resulting solid was dissolved in pentane and loaded onto a silica column which had been pretreated with triethylamine. The side products were eluted with toluene, while the product was eluted with a 1:1 mixture of toluene and THF. Yield: 3.66 g of a foamy, tan solid (76%). ^{1}H NMR (C_6D_6, 20 °C): δ 7.22 (s, 8H, 3,5,3″,5″-*H*), 6.53 (br t, J_{HH} = 1.4 Hz, 2H, 4′-*H*), 6.48 (d, J_{HH} = 1.3 Hz, 4H, 2′,6′-*H*), 6.02 (s, 2H, Lut-3,5-*H*), 3.93 (t, J_{HH} = 4.9 Hz, 1H, Lut-N*H*), 3.71 (t, J_{HH} = 4.8 Hz, 2H, HIPT-N*H*), 3.16 (septet, J_{HH} = 6.9 Hz, 8H, 2,6,2″,6″-C*H*Me$_2$), 2.92 (septet, J_{HH} = 6.9 Hz, 4H, 4,4″-C*H*Me$_2$), 2.80 (br q, J_{HH} = 5.4 Hz, 4H, HIPT-NHC*H*$_2$CH$_2$), 2.63 (br q, J_{HH} = 5.9 Hz, 2H, Lut-NHC*H*$_2$CH$_2$), 2.39 (s, 6H, Lut-C*H*$_3$), 2.16 (br t, J_{HH} = 5.7 Hz, 4H, HIPT-NHCH$_2$C*H*$_2$), 2.11 (br t, J_{HH} = 6.8 Hz, 2H, Lut-NHCH$_2$C*H*$_2$), 1.32 (d, J_{HH} = 6.9 Hz, 24H, 4,4″-CH(C*H*$_3$)$_2$), 1.28 (d, J_{HH} = 6.9 Hz, 24H, 2,6,2″,6″-CH(C*H*$_3$)$_2$), 1.25 (d, J_{HH} = 6.9 Hz, 24H, 2,6,2″,6″-CH(C*H*$_3$)$_2$). ^{13}C NMR (C_6D_6, 20 °C): δ 158.72, 154.58, 148.55, 148.4, 147.15, 142.68, 138.44, 121.96, 121.09, 112.84, 104.75, 52.78, 52.15, 41.48, 40.51, 35.26, 31.21, 30.94, 25.30, 25.10, 24.93, 24.87. MS (ESI): 1212.9662 ([M + H]$^+$, calcd 1212.9695).

H$_3$[PhLutHIPT$_2$N$_3$N] (2b). A solution of $Pd_2(dba)_3$ (0.045 g, 0.049 mmol) and *rac*-BINAP (0.094 g, 0.15 mmol) in 25 mL of toluene was stirred with mild heating until the orange catalyst was formed. The orange solution was then filtered through Celite into a 300 mL toluene solution containing **1** (3.75 g, 3.39 mmol), 4-bromo-2,6-diphenylpyridine (1.55 g, 5.02 mmol), and NaO-*t*-Bu (0.64 g, 6.66 mmol). This mixture was then heated at 95 °C for 2 days, at which time it was filtered through Celite and concentrated in vacuo to dryness. The resulting solid was dissolved in pentane, and the product was isolated through column chromatography on silica column as described in earlier preparations. Yield: 2.07 g of the product as a light yellow foamy solid (46%). ^{1}H NMR (C_6D_6, 20 °C): δ 8.32 (m, 4H, PhLut-2,6,2″,6″-*H*), 7.33 (m, 6H, PhLut-3,4,5,3″,4″,5″-*H*), 7.22 (s, 8H, 3,5,3″,5″-*H*), 6.75 (s, 2H, PhLut-3′,5′-*H*), 6.57 (br t, J_{HH} = 1.3 Hz, 2H, 4′-*H*), 6.51 (d, J_{HH} = 1.4 Hz, 4H, 2′,6′-*H*), 3.98 (t, J_{HH} = 5.2 Hz, 1H, PhLut-N*H*), 3.60 (br s, 2H, HIPT-N*H*), 3.17 (septet, J_{HH} = 6.9 Hz, 8H, 2,6,2″,6″-C*H*Me$_2$), 2.89 (m, 8H, 4,4″-C*H*Me$_2$ and HIPTNHC*H*$_2$CH$_2$ overlapping), 2.75 (br q, J_{HH} = 5.8 Hz, 2H, PhLutNHC*H*$_2$CH$_2$), 2.24 (m, 6H, HIPTNHCH$_2$C*H*$_2$ and PhLutNHC*H*$_2$CH$_2$ overlapping), 1.31 (d, J_{HH} = 6.9 Hz, 24H, 4,4″-CH(C*H*$_3$)$_2$), 1.29 (d, J_{HH} = 6.9 Hz, 12H, 2,6,2″,6″-CH(C*H*$_3$)$_2$), 1.28 (br d, J_{HH} = 6.9 Hz, 36H, 2,6,2″,6″-CH(C*H*$_3$)$_2$). ^{13}C NMR (C_6D_6, 20 °C): δ 158.41, 155.34, 148.61, 148.28, 147.16, 142.75, 141.27, 138.38, 129.14, 127.88, 122.10, 121.12, 112.82, 103.64, 52.87, 41.42, 35.24, 31.22, 25.31, 25.03, 24.83. MS (ESI): 1337.0025 ([M + H]$^+$, calcd 1337.0008).

H$_3$[3,5-Bis(CF$_3$)HIPT$_2$N$_3$N] (2c). This compound was prepared in a manner similar to other hybrid ligand systems. Briefly, a toluene solution of 0.050 g (55 mmol) of $Pd_2(dba)_3$ and 0.101 g (162 mmol) of *rac*-BINAP was heated until orange. This solution was filtered through Celite into 100 mL of toluene containing 4 g (3.6 mmol) of **1**, 1.05 g (3.6 mmol) of 1-bromo-3,5-(bis)trifluoromethylbenzene, and 0.69 g (7.2 mmol) of NaO-*t*-Bu. This solution was then heated at 105 °C for 2 days and filtered. The volatiles were removed in vacuo, and the residue was then extracted into pentane. The pentane insoluble material was removed via filtration, and the resulting solution was subject to column chromatography on silica gel. The product was eluted with toluene to yield 0.91 g (20%) of the final product as a light yellow solid. ^{1}H NMR (C_6D_6, 20 °C): δ 7.25 (s,

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(18) Talik, T.; Talik, Z.; Ban-Oganowska, H. *Synthesis* **1974**, 293.

1H, CF_3 arm 4-*H*), 7.22 (s, 8H, HIPT 3,5,3″,5″-*H*), 6.64 (s, 2H, CF_3 arm 2,6-*H*), 6.57 (s, 2H, HIPT 4′-*H*), 6.48 (s, 4H, HIPT-2′,6′-*H*), 3.88 (t, J_{HH} = 5.2 Hz, 1H, CF_3 arm N*H*), 3.51 (br s, 2H, HIPT-N*H*), 3.15 (septet, 8H, J_{HH} = 6.9 Hz, 8H, 2,6,2″,6″-C*H*Me_2), 2.90 (septet, J_{HH} = 6.9 Hz, 4H, 4,4″-C*H*Me_2), 2.82 (br t, J_{HH} = 5.8 Hz, 4H, HIPT-NC*H*$_2$CH$_2$), 2.40 (br q, J_{HH} = 5.2 Hz, 2H, CF_3 arm-NC*H*$_2$CH$_2$), 2.17 (br t, J_{HH} = 5.8 Hz, 4H, HIPT-NHCH$_2$C*H*$_2$), 2.10 (br t, J_{HH} = 5.8 Hz, 2H, CF_3 arm-NCH$_2$C*H*$_2$) 1.32 (d, J_{HH} = 6.9 Hz, 24H, 4,4″-CH(C*H*$_3$)$_2$), 1.28 (d, J_{HH} = 6.9 Hz, 24H, 2,6,2″,6″-CH(C*H*$_3$)$_2$), 1.25 (d, J_{HH} = 6.9 Hz, 24H, 2,6,2″,6″-CH(C*H*$_3$)$_2$). ^{13}C NMR (C_6D_6, 20 °C): δ 149.41, 148.66, 148.25, 147.13, 142.79, 138.31, 133.33, 132.91, 122.28, 121.12, 122.89, 112.30, 110.36, 52.95, 52.21, 41.55, 40.91, 35.25, 31.21, 25.28, 24.99, 24.83. ^{19}F NMR (C_6D_6, 20 °C): δ −62.74. HRMS (ESI): 1319.9156 ([M + H]$^+$, calcd 1319.9177).

H$_3$[3,5-DimethylHIPT$_2$N$_3$N] (2d). This compound was prepared in a manner similar to other hybrid ligand systems. Briefly, 0.037 g (4 mmol) of $Pd_2(dba)_3$ and 0.075 g (12 mmol) of *rac*-BINAP were stirred in toluene to form the orange catalyst. This solution was then filtered through Celite into a toluene mixture containing 3 g (2.8 mmol) of **1**, 0.5 g (2,7 mmol) of 1-bromo-3,5-dimethylbenzene, and 0.52 g (5.4 mmol) of NaO-*t*-Bu. This solution was then heated at 85 °C overnight, with the temperature then being raised to 95 °C for 1 day. The mixture was then filtered through Celite, and the solvent was removed in vacuo. The solid was taken up in pentane, and the solution was filtered again through Celite. The product was isolated from a silica gel column. The compound was eluted with a 9:1 mixture of toluene and THF to yield 0.78 g (24%) of the product as a light yellow solid. ^{1}H NMR (C_6D_6, 20 °C): δ 7.22 (s, 8H, HIPT 3,5,3″,5″-*H*), 6.52 (br t, J_{HH} = 1.1 Hz, 2H, HIPT 4′-*H*), 6.46 (d, J_{HH} = 1.1 Hz, 4H, HIPT-2′,6′-*H*), 6.37 (s, 1H, dimethyl-4-*H*), 6.26 (s, 2H, dimethyl-2,6-*H*), 3.94 (br s, 2H, HIPT-N*H*), 3.75 (br s, 1H, dimethyl-N*H*), 3.16 (septet, J_{HH} = 6.9 Hz, 8H, HIPT-2,6,2″,6″-C*H*Me_2), 2.95 (septet J_{HH} = 6.9 Hz, 4H, HIPT-4,4″-C*H*Me_2), 2.79 (m, 8H, contains HIPT-NC*H*$_2$CH$_2$ and dimethyl-NC*H*$_2$CH$_2$), 2.17 (m, 8H, contains HIPT-NCH$_2$C*H*$_2$ and dimethyl-NCH$_2$C*H*$_2$), 2.08 (s, 6H, dimethyl-C*H*$_3$), 1.46 (d, J_{HH} = 6.9 Hz, 24H, 4,4″-CH(C*H*$_3$)$_2$), 1.38 (d, J_{HH} = 6.9 Hz, 24H, 2,6,2″,6″-CH(C*H*$_3$)$_2$), 1.27 (d, J_{HH} = 6.9 Hz, 24H, 2,6,2″,6″-CH-(C*H*$_3$)$_2$). ^{13}C NMR (C_6D_6, 20 °C): δ 148.79, 148.49, 148.44, 147.17, 142.58, 139.28, 138.58, 121.66, 121.03, 120.74, 112.71, 111.71, 52.59, 52.29, 41.73, 41.41, 35.27, 31.19, 30.84, 25.32, 25.06, 24.89, 21.93. HRMS (ESI): 1211.9734 ([M + H]$^+$, calcd 1211.9742).

H$_3$[3,5-dimethoxyHIPT$_2$N$_3$N] (2e). This compound was prepared in a manner similar to other hybrid ligand systems. Briefly, 0.037 g (0.04 mmol) of $Pd_2(dba)_3$ and 0.075 g (0.12 mmol) of *rac*-BINAP were heated in toluene. This solution was filtered through Celite into a solution containing 3 g (2.7 mmol) of **1**, 0.56 g (2.5 mmol) of 3,5-dimethoxy bromobenzene, and 0.52 g (5.4 mmol) of NaO-*t*-Bu in 75 mL of toluene. This container was then sealed and heated at 90 °C for 2 days. The resulting brown solution was filtered, and the solvent was removed in vacuo. A column was employed to isolate the product, with pentane and toluene as the eluents. Yield: 2.2 g (65%) of product as a light yellow powder. ^{1}H NMR (C_6D_6, 20 °C): δ 6.46 (s, 4H, 3,5,3″,5″ HIPT-*H*), 6.42 (s, 4H, 3,5,3″,5″ HIPT-*H*), 6.40 (d, J_{HH} = 2 Hz, 2H, dimethoxy 2,6-*H*), 6.13 (t, J_{HH} = 2 Hz, 1H, dimethoxy 4-*H*), 5.94 (t, J_{HH} = 1.9 Hz, 2H HIPT 4′-*H*), 5.88 (d, J_{HH} = 1.9 Hz, 4H HIPT 2′6′-*H*), 3.94 (br s, 1H, dimethoxy N-*H*), 3.77 (br s, 2H, HIPT N-*H*), 3.27 (s, 6H, dimethoxy-OC*H*$_3$), 3.11 (septet, J_{HH} = 6.8 Hz, 8H HIPT-2,6,2″,6″-C*H*Me_2), 2.85 (septet, J_{HH} = 6.8 Hz, 4H HIPT-4,4″-C*H*Me_2), 2.75 (m, 10H, contains HIPT-NC*H*$_2$CH$_2$ and dimethoxy-NC*H*$_2$CH$_2$ and dimethoxy NCH$_2$C*H*$_2$), 2.14 (br t, 4H, HIPT-NCH$_2$C*H*$_2$), 1.26 (d, J_{HH} = 6.8 Hz, 24H HIPT-4,4″-CH(C*H*$_3$)$_2$), 1.22 (d, J_{HH} = 6.8 Hz, 24H HIPT-2,6,2″,6″-CH(C*H*$_3$)$_2$), 1.19 (d, J_{HH} = 6.8 Hz, 24H HIPT-2,6,2″,6″-CH(C*H*$_3$)$_2$). ^{13}C NMR (C_6D_6, 20 °C): δ 162.9, 162.5, 150.8, 148.4, 147.2, 142.6, 138.6, 138.2, 129.7, 126.0, 121.0, 112.8, 92.9, 54.9, 52.8, 41.5, 35.3, 31.2, 25.3, 25.0, 24.9. MS (ESI): 1243.9694 ([M + H]$^+$, calcd 1243.9641).

H$_3$[MesHIPT$_2$N$_3$N] (2f). This compound was prepared in a manner similar to other hybrid ligand systems. Briefly, 0.037 g (40 mmol) of $Pd_2(dba)_3$ and 0.075 g (12 mmol) of *rac*-BINAP were heated in toluene, and the orange solution was then filtered through Celite into a toluene mixture containing 3 g (2.7 mmol) of **1**, 0.59 g (29.8 mmol) of 1-bromo-2,4,6-trimethylbenzene, and 0.52 g (5.4 mmol) of NaO-*t*-Bu. The vessel was then sealed and heated at 110 °C for 2 days. The product mixture was worked up in a manner similar to that described for previous ligands, and the product was isolated via column chromatography with an 8:1 mixture of toluene and THF as the eluent. Yield: 2 g (60%) of a pale yellow solid. ^{1}H NMR (C_6D_6, 20 °C): δ 7.22 (s, 8H, HIPT 3,5,3″,5″-*H*), 6.77 (s, 2H, Mes-3,5-*H*), 6.54 (s, 2H, HIPT 4′-*H*), 6.48 (s, 4H, HIPT-2′,6′-*H*), 3.79 (br s, 2H, HIPT-N*H*), 3.18 (septet, J_{HH} = 6.9 Hz, 8H, 2,6,2″,6″-C*H*Me_2), 2.88 (m, 8H, containing 4,4″-C*H*Me_2 and HIPT-NC*H*$_2$CH$_2$), 2.78 (br t, J_{HH} = 5.8 Hz, 2H, Mes-NCH$_2$C*H*$_2$), 2.2 (m, 15H, containing Mes-C*H*$_3$, Mes-NCH$_2$C*H*$_2$, and HIPT-NCH$_2$C*H*$_2$), 1.32 (d, J_{HH} = 6.9 Hz, 24H, 4,4″-CH(C*H*$_3$)$_2$), 1.28 (d, J_{HH} = 6.9 Hz, 24H, 2,6,2″,6″-CH(C*H*$_3$)$_2$), 1.26 (d, J_{HH} = 6.9 Hz, 24H, 2,6,2″,6″-CH(C*H*$_3$)$_2$). ^{13}C NMR (C_6D_6, 20 °C): δ 162.80, 148.48, 147318, 144.65, 142.59, 138.54, 131.03, 130.23, 129.14, 121.83, 121.07, 112.77, 55.29, 53.30, 46.83, 41.56, 35.26, 31.19, 25.32, 25.12, 24.86, 21.06, 19.22. HRMS (ESI): 1225.9906 ([M + H]$^+$, calcd 1225.9899).

H$_3$[TripHIPT$_2$N$_3$N] (2g). This compound was prepared in a manner similar to other hybrid ligand systems. Briefly, 0.037 g (40 mmol) of $Pd_2(dba)_3$ and 0.077 g (162 mmol) of X-Phos were heated mildly in toluene to preform the active orange catalyst species. This was then filtered into a toluene mixture containing 3 g (2.7 mmol) of **1**, 0.92 g (3.2 mmol) of 1-bromo,2,4,6-triisopropylbenzene, and 0.39 g (40.5 mmol) of NaO-*t*-Bu. This mixture was then heated at 120 °C for 2 days. The solvent was removed in vacuo; the resulting solid was taken up in pentane, and the mixture was filtered in preparation for column chromatography on silica gel. Elution with an 8:1 mixture of toluene and THF yielded a mixture of (HIPTNHCH$_2$CH$_2$)$_2$NCH$_2$CH$_2$NH$_2$ and the desired product from which the solvent was removed in vacuo. The resulting solid was taken up in toluene and passed through a silica plug, yielding 0.35 g (10%) of the desired product as a light yellow solid. ^{1}H NMR (C_6D_6, 20 °C): δ 7.21 (s, 8H, HIPT 3,5,3″,5″-*H*), 7.06 (s, 2H, Trip-3,5-*H*), 6.54 (br t, J_{HH} = 1.1 Hz, 2H, HIPT 4′-*H*), 6.51 (d, J_{HH} = 1.1 Hz, 4H, HIPT-2′,6′-*H*), 3.88 (br s, 2H, HIPT-N*H*), 3.38 (septet, J_{HH} = 6.9 Hz, 2H, Trip-2,6-C*H*Me_2), 3.17 (septet, J_{HH} = 6.9 Hz, 8H, HIPT-2,6,2″,6″-C*H*Me_2), 2.89 (m, 12H, containing HIPT-NC*H*$_2$CH$_2$, Trip-NC*H*$_2$CH$_2$, HIPT-4,4″-CH(C*H*$_3$)$_2$, and Trip-4-CH(C*H*$_3$)$_2$), 2.44 (br t, J_{HH} = 5.5 Hz, 2H, Trip-NCH$_2$C*H*$_2$), 2.33 (br t, J_{HH} = 5.5 Hz, 4H, HIPT-NCH$_2$C*H*$_2$), 1.32 (d, J_{HH} = 6.9 Hz, 24H, 4,4″-CH(C*H*$_3$)$_2$), 1.25 (m, 60H, 2,6,2″,6″-CH(C*H*$_3$)$_2$). ^{13}C NMR (C_6D_6, 20 °C): δ 148.58, 148.47, 147.17, 144.52, 142.77, 142.10, 138.51, 121.98, 121.91, 121.05, 113.00, 55.60, 53.70, 50.16, 42.13, 35.26, 31.17, 30.84, 28.56, 25.35, 25.01, 24.92, 24.96, 24.87. HRMS (ESI): 1310.0833 ([M + H]$^+$; calcd 1310.0838).

[LutHIPT$_2$N$_3$N]MoCl (3a). The procedure followed was nearly identical to published procedures.[4,6] Briefly, H$_3$**2a** (0.6 g, 0.50 mmol) and $MoCl_4(THF)_2$ (0.19 g, 0.50 mmol) were dissolved in THF (40 mL). This solution was stirred for 1 h and $(Me_3Si)_2NLi$

(0.258 g, 0.1.54 mmol) was then added slowly. The solution was stirred for 2 h, and the solvent was removed in vacuo with mild heating. The solid residue was extracted with pentane (2 × 10 mL), followed by benzene (3 × 20 mL), and all extracts were passed through Celite. The filtrate was then evaporated to dryness in vacuo. The residue was recrystallized from pentane to yield 0.42 g of an orange solid in multiple crops (63%). ^{1}H NMR (C_6D_6, 20 °C): δ 11.8 (br s), 7.3 (m), 3.1 (br s), 3.0 (m), 2.7 (br s), 1.6 (br s), 1.4 (br s), −16.7 (br s), −23.8 (br s), −65.0 (br s), −69.4 (br s). Anal. Calcd for $C_{85}H_{118}ClMoN_5$: C, 76.11; H, 8.87; N, 5.22. Found: C, 76.01; H, 9.06, N, 5.16.

[PhLutHIPT$_2$N$_3$N]MoCl (3b). The procedure followed was nearly identical to published procedures.[4,6] Briefly, H$_3$**2b** (1 g, 0.75 mmol) and $MoCl_4(THF)_2$ (0.286 g, 0.75 mmol) were dissolved in THF (75 mL). This solution was stirred for 1 h, and $(Me_3Si)_2NLi$ (0.388 g, 2.3 mmol) was then added slowly. After 2 h, the solvent was removed in vacuo. The solid residue was extracted with pentane (2 × 10 mL) and benzene (3 × 20 mL), and all filtrates were passed through Celite. The filtrates were then reduced to dryness in vacuo. The product was crystallized from pentane to yield 0.9 g of an orange-brown solid in multiple crops (82%). ^{1}H NMR (C_6D_6, 20 °C): δ 14.4 (br s), 8.3 (br s), 7.50 (br m), 7.2 (s), 3.1 (br s), 2.9 (br s), 2.5 (br s), 1.3 (br s), −21.5 (br s), −62.2 (br s), −81.1 (br s), −86.7 (br s). Anal. Calcd for $C_{95}H_{122}ClMoN_5$: C, 77.86; H, 8.39; N, 4.78. Found: C, 77.73; H, 8.46; N, 4.83.

[3,5-Bis(CF$_3$)HIPT$_2$N$_3$N]MoCl (3c). This compound was synthesized similarly to other compounds of this type described above. Briefly, 0.75 g (0.57 mmol) of H$_3$**2c** as added to 50 mL of THF. $MoCl_4(THF)_2$ (0.24 g, 0.62 mmol) was then added slowly, and the mixture was stirred for 1 h, during which time the solution darkened to a deep red. To this red solution, 0.30 g (1.8 mmol) of $(Me_3Si)_2NLi$ was added, and the reaction mixture was stirred for 2 h. The solvent was removed in vacuo, and the resulting solid was extracted into pentane. The mixture was filtered through Celite, and the solvent was removed in vacuo. Recrystallization of the residue from pentane yielded 0.45 g (55%) of a deep orange powder. ^{1}H NMR (C_6D_6, 20 °C): δ 11.1 (br s), 7.27 (s), 7.19 (s), 3.18 (br s), 2.95 (m), 1.62 (br s), 1.49 (br s), 1.34 (br s), −10.3 (br s), −13.8 (br s), −29.7 (br s), −69.5 (br s), −82.7 (br s), −86.9 (br s). ^{19}F NMR (C_6D_6, 20 °C): δ −57.9. Anal. Calcd for $C_{86}H_{113}ClF_6MoN_4$: C, 71.32; H, 7.86; N, 3.87. Found: C, 71.25; H, 7.76; N, 3.94.

[3,5-DimethylHIPT$_2$N$_3$N]MoCl (3d). This compound was synthesized similarly to other compounds of this type described above. Briefly, 0.76 g (0.63 mmol) of H$_3$**2d** was added to 0.26 g (0.68 mmol) of $MoCl_4(THF)_2$ in 50 mL of THF. This mixture was stirred for 1 h, and 0.33 g (1.9 mmol) of $(Me_3Si)_2NLi$ was added. After 2 h, the solvent was removed in vacuo; the resulting solid was extracted into pentane, and the extract was filtered through Celite. The solvent was removed in vacuo, and the residue was recrystallized from pentane to yield 0.47 g (56%) of a deep orange solid. ^{1}H NMR (C_6D_6, 20 °C): δ 9.68 (br s), 7.26 (s), 7.24 (s), 3.18 (br s), 2.97 (m), 2.05 (s), 1.54 (br s), 1.44 (s), 1.36 (br s), −11.25 (br s), −13.80 (br s), −23.5 (br s), −66.5 (br s), −77.5 (br s), −84.0 (br s). Anal. Calcd for $C_{86}H_{119}ClMoN_4$: C, 77.07; H, 8.95; N, 4.18. Found: C, 76.87; H, 9.06; N, 4.11.

[3,5-DimethoxyHIPT$_2$N$_3$N]MoCl (3e). This compound was synthesized similarly to other compounds of this type described above. Briefly, 0.41 g (0.3 mmol) of H$_3$**2e** was added to 0.13 g (0.3 mmol) of $MoCl_4(THF)_2$ in 30 mL of THF. Upon addition of the molybdenum, the solution's color immediately darkened to deep red. The solution was stirred for 1 h, and 0.17 g (1 mmol) of $(Me_3Si)_2NLi$ was then added. The solution slowly turned orange-red. The solvent was removed in vacuo, and the solid was extracted into pentane; the extract was filtered through Celite. The solvent was removed in vacuo, and the residue was recrystallized from pentane yielding 0.32 g (70%) of the compound as a deep orange powder. ^{1}H NMR (C_6D_6, 20 °C): δ 11.6 (br s), 10 (br s), 7.27 (s), 3.96 (s), 3.18 (s), 2.95 (s), 2.63 (s), 1.34 (s), −14.5 (br s), −20.4 (br s), −69.6 (br s), −79.6 (br s). Anal. Calcd for $C_{86}H_{119}ClMoN_4O_2$: C, 75.27; H, 8.74; N, 4.08. Found: C, 75.06; H, 8.65; N, 4.08.

[MesHIPT$_2$N$_3$N]MoCl (3f). This compound was synthesized similarly to other compounds of this type described above. Briefly, 1.0 g (0.81 mmol) H$_3$**2f** was added to 70 mL of THF. $MoCl_4(THF)_2$ (0.32 g, 1.0 mmol) was added slowly with stirring. After 2 h, 0.42 g (2.6 mmol) of $(Me_3Si)_2NLi$ was added. After 1 h, the solvent was evaporated in vacuo; the resulting solid was dissolved into pentane, and the extract was filtered through Celite. The solvent was removed in vacuo, and the residue was recrystallized from pentane to yield 0.74 g (67%) of a deep orange crystalline solid. ^{1}H NMR (C_6D_6, 20 °C): δ 17.73 (br s), 7.28 (s), 7.22 (s), 6.42 (br s), 3.83 (s), 3.5 (br s), 3.17 (br s), 2.97 (m), 1.52 (br s), 1.41 (br s), −20 (br s), −23.5 (br s), −74.68 (br s), −97.50 (br s). Anal. Calcd for $C_{87}H_{121}ClMoN_4$: C, 77.16; H, 9.01; N, 4.14. Found: C, 77.04; H, 9.04; N 4.11.

[TripHIPT$_2$N$_3$N]MoCl (3g). This compound was synthesized similarly to other compounds of this type described above. Briefly, 0.35 g (0.25 mmol) of H$_3$**2g** was dissolved in 50 mL of THF. $MoCl_4(THF)_2$ (0.112 g (0.29 mmol) was added, and the solution was stirred for 2 h. The color changed from orange to bright red; 0.138 g (0.83 mmol) of $(Me_3Si)_2NLi$ was slowly added to this solution, and the solution was stirred for an additional hour. The solvent was removed in vacuo; the resulting solid was extracted into pentane, and the mixture was filtered through Celite. The solvent was removed in vacuo, and the residue was recrystallized to yield 0.22 g (56%) of a bright orange powder in multiple crops. ^{1}H NMR (C_6D_6, 20 °C): δ 18.14 (br s), 9.66 (br s), 7.30 (s), 7.20 (s), 4.09 (br s), 3.53 (br s), 3.20 (br s), 2.99 (m), 1.40 (br s), 1.26 (s), −11.52 (br s), −16.97 (br s), −23.75 (br s), −61.65 (br s), −83.70 (br s), −96.15 (br s). Anal. Calcd for $C_{93}H_{133}ClMoN_4$: C, 77.65; H, 9.32; N, 3.89. Found: C, 77.42; H, 9.38; N, 3.77.

[LutHIPT$_2$N$_3$N]MoN (4a). This compound could not be isolated in pure form because the reaction between (**3a)** and Me_3SiN_3 is low yielding, and the final product consequently was contaminated with H$_3$**2a**, even after multiple recrystallizations. A sample containing ∼10% H$_3$**2a** (according to ^{1}H NMR) was used in test catalytic runs.

[PhLutHIPT$_2$N$_3$N]MoN (4b). Me_3SiN_3 (0.044 g, 0.38 mmol) and **3b** (0.138 g, 0.092 mmol) were added to 25 mL of benzene, and the mixture was heated overnight at 90 °C. The resulting yellow solution was stripped to dryness in vacuo. The residue was taken up in pentane; the mixture was filtered through Celite, and the filtrate volume was reduced to 0.5 mL in vacuo. When it was cooled, 50 mg of a bright, canary yellow solid was obtained (37%). ^{1}H NMR (C_6D_6, 20 °C): δ 8.35 (d, 4H, J_{HH} = 1.3 Hz, PhLut, 2,6,2″,6″-*H*), 8.14 (s, 2H, PhLut 3′,5′-*H*), 7.79 (d, 4H, J_{HH} = 1.1 Hz, HIPT 3′,5′-*H*), 7.40 (m, 6H, PhLut 3,4,5,3″,4″,5″-*H*), 7.17 (m, 8H, HIPT 3,5,3″,5″-*H*), 6.73 (br t, 2H, J_{HH} = 1.1 Hz, HIPT 4′-*H*), 3.59 (br t, 4H, J_{HH} = 5.1 Hz, HIPT-NHCH$_2$C*H*$_2$), 3.20 (br t, 2H, J_{HH} = 4.2 Hz, PhLut-NCH$_2$C*H*$_2$), 3.11 (septet, 8H, J_{HH} = 6.9 Hz, 8H, 2,6,2″,6″- C*H*Me$_2$), 2.89 (septet, J_{HH} = 6.9 Hz, 4H, 4,4″-C*H*Me$_2$), 2.08 (br t, 2H, J_{HH} = 3.4 Hz, PhLut-NC*H*$_2$CH$_2$), 2.02 (br t, 4H, J_{HH} = 5.1 Hz, HIPT-NC*H*$_2$CH$_2$), 1.33 (dd, 24H, 4,4″-CH(C*H*$_3$)$_2$), 1.22 (d, J_{HH} = 6.9 Hz, 12H, 2,6,2″,6″-CH(C*H*$_3$)$_2$), 1.19 (d, J_{HH} = 6.9 Hz, 12H, 2,6,2″,6″-CH(C*H*$_3$)$_2$), 1.16 (d, J_{HH} = 6.9

Hz, 12H, 2,6,2″,6″-CH(CH_3)$_2$), 1.11 (d, J_{HH} = 6.9 Hz, 12H, 2,6,2″,6″-CH(CH_3)$_2$). Anal. Calcd for $C_{95}H_{122}MoN_6$: C, 79.02; H, 8.52; N, 5.82. Found: C, 78.88; H, 8.45; N, 5.88.

[3,5-Bis(CF$_3$)HIPT$_2$N$_3$N]MoN (4c). This compound was made in a manner similar to other compounds of its type. Briefly, 0.17 g (117 mmol) of **3c** and 0.07 g (608 mmol) of Me_3SiN_3 was added to 50 mL of benzene in a Teflon-sealed glass bomb. This was heated to 90 °C for 12 h and then brought to dryness in vacuo. The resulting yellow solid was taken into pentane and filtered through Celite. The solvent was removed in vacuo, and the residue was recrystallized to yield 0.12 g (72%) of a bright yellow solid. ^{1}H NMR (C_6D_6, 20 °C): δ 7.93 (s, 2H, CF_3 arm 2,6-*H*), 7.70 (d, J_{HH} = 1.4 Hz, 4H, HIPT-2′,6′-*H*), 7.39 (s, 1H, CF_3 arm 4-*H*), 7.19 (s, 8H, HIPT 3,5,3″,5″-*H*), 6.81 (br t, J_{HH} = 1.1 Hz, 2H, HIPT 4′-*H*), 3.53 (br t, J_{HH} = 4.7 Hz, 4H, HIPT-NCH_2CH$_2$), 3.15 (overlapping septets, J_{HH} = 6.9 Hz, 8H, 2,6,2″,6″- C*H*Me$_2$), 2.90 (septet, J_{HH} = 6.9 Hz, 4H, 4,4″ −C*H*Me$_2$), 2.83 (br t, J_{HH} = 4.8 Hz, 2H, CF_3 arm-NCH_2CH$_2$), 1.97 (br t, J_{HH} = 5.1 Hz, 4H, HIPT-NHCH$_2$CH_2), 1.92 (br t, J_{HH} = 5.0 Hz, 2H, CF_3 arm-NCH$_2$CH_2), 1.34 (d, J_{HH} = 6.9 Hz, 24H, 4,4″-CH(CH_3)$_2$), 1.26 (d, J_{HH} = 6.9 Hz, 12H, 2,6,2″,6″-CH(CH_3)$_2$), 1.22 (d, J_{HH} = 6.9 Hz, 12H, 2,6,2″,6″-CH-(CH_3)$_2$), 1.20 (d, J_{HH} = 6.9 Hz, 12H, 2,6,2″,6″-CH(CH_3)$_2$), 1.11 (d, J_{HH} = 6.9 Hz, 12H, 2,6,2″,6″-CH(CH_3)$_2$). ^{19}F NMR (C_6D_6, 20 °C): δ −62.4. Anal. Calcd for $C_{86}H_{113}F_6MoN_5$: C, 72.40; H, 7.98; N, 4.91. Found: C, 72.56; H, 7.98; N, 4.81.

[3,5-DimethylHIPT$_2$N$_3$N]MoN (4d). This compound was made in a manner similar to other compounds of this type. Briefly, 0.15 g (0.11 mmol) of **2d** and 0.064 g (0.56 mmol) of Me_3SiN_3 was added to 40 mL of benzene, and the mixture was heated in a Teflon-sealed bomb at 100 °C for 1 day. The volatiles were removed in vacuo; the resulting solid was taken up in pentane, and the mixture was filtered through Celite. The solvent was removed in vacuo, and the residue was recrystallized to yield 0.073 g (50%) of a bright yellow powder. ^{1}H NMR (C_6D_6, 20 °C): δ 7.86 (d, J_{HH} = 1.1 Hz, 4H, HIPT-2′,6′-*H*), 7.21 (dd, J_{HH} = 1.4 and 3.3 Hz, 8H, HIPT 3,5,3″,5″-*H*), 7.05 (s, 2H, dimethyl-2,6-*H*), 7.76 (br t, J_{HH} = 1.1 Hz, 2H, HIPT 4′-*H*), 6.51 (s, 1H, dimethyl-4-*H*), 3.54 (br t, J_{HH} = 5.2 Hz, 4H, HIPT-NCH_2CH$_2$), 3.64 (br t, J_{HH} = 5.2 Hz, 2H, dimethyl-NCH_2CH$_2$), 3.19 (septet, J_{HH} = 6.9 Hz, 8H, HIPT-2,6,2″,6″ −C*H*Me$_2$), 2.93 (septet, J_{HH} = 6.9 Hz, 4H, HIPT-4,4″ −C*H*Me$_2$), 2.18 (s, 6H, dimethyl-CH_3), 2.03 (m, 8H, contains HIPT-NCH$_2$CH_2 and dimethyl-NCH$_2$CH_2), 1.34 (d, J_{HH} = 6.9 Hz, 24H, 4,4″-CH(CH_3)$_2$), 1.26 (d, J_{HH} = 6.9 Hz, 24H, 2,2″,6,6″-CH(CH_3)$_2$), 1.21 (d, J_{HH} = 6.9 Hz, 12H, 2,6,2″,6″-CH(CH_3)$_2$), 1.16 (d, J_{HH} = 6.9 Hz, 24H, 2,6,2″,6″-CH(CH_3)$_2$). Anal. Calcd for $C_{86}H_{119}MoN_5$: C, 78.32; H, 9.09; N, 5.31. Found: C, 78.19; H, 8.96; N, 5.23.

[3,5-DimethoxyHIPT$_2$N$_3$N]MoN (4e). This was synthesized similarly to other compounds of its type. Briefly, 0.12 g (0.08 mmol) of **3e** was added to 0.05 g (0.4 mmol) of Me_3SiN_3 in 25 mL of benzene. This mixture was heated at ∼100 °C overnight. The solvent was removed in vacuo; the resulting solid was taken up in pentane, and the solution was filtered through Celite. The solvent was removed in vacuo, and the residue was recrystallized from pentane to yield 0.07 g (55%) of a bright yellow powder in multiple crops. ^{1}H NMR (C_6D_6, 20 °C): δ 7.91 (d, J_{HH} = 0.8 Hz, 4H, HIPT-2′,6′-*H*), 7.23 (d, J_{HH} = 1.8 Hz, 2H, dimethoxy-2,6-*H*), 7.21 (s, 8H, HIPT 3,5,3″,5″-*H*), 6.76 (s, 2H, HIPT 4′-*H*), 6.30 (t, J_{HH} = 1.8 Hz, 1H, dimethoxy-4-*H*), 3.55 (br t, 4H, HIPT-NCH_2CH$_2$), 3.43 (s, 6H, −OC*H*3), 3.31 (br t, 2H, dimethoxy-NCH_2CH$_2$), 3.20 (septet, J_{HH} = 6.9 Hz, 8H, 2,6,2″,6″-C*H*Me$_2$), 2.92 (septet, J_{HH} = 6.9 Hz, 4H, 4,4′′′′-C*H*Me$_2$), 1.94 (br t, 6H, overlapped HIPTNCH$_2$-CH_2 and dimethoxyNCH$_2$CH_2), 1.32 (d, J_{HH} = 6.9 Hz, 24H, 4,4″-CH(CH_3)$_2$), 1.22 (overlapping doublets, J_{HH} = 6.9 Hz, 24H, 2,6,2″,6″-CH(CH_3)$_2$), 1.14 (d, J_{HH} = 6.9 Hz, 12H, 2,6,2″,6″-CH-(CH_3)$_2$). Anal. Calcd for $C_{86}H_{119}MoN_5O_2$: C, 76.47; H, 8.88; N, 5.18. Found: C, 76.38; H, 8.85; N, 5.06.

[MesHIPT$_2$N$_3$N]MoN (4f). This compound was synthesized similarly to compounds of this type. Briefly, 0.19 g (0.14 mmol) of **3f** was combined with 0.1 g (0.86 mmol) of Me_3SiN_3 in 25 mL of benzene, and the mixture was heated in a Teflon-sealed glass bomb at 90 °C for 1 day. The solvent was removed in vacuo, and the solid was extracted into pentane; the extract was filtered through Celite. The solvent was removed in vacuo, and the residue was recrystallized from pentane to yield 0.11 g (59%) of a bright yellow powder. ^{1}H NMR (C_6D_6, 20 °C): δ 7.76 (d, J_{HH} = 1.1 Hz, 4H, HIPT-2′,6′-*H*), 7.20 (s, 8H, HIPT 3,5,3″,5″-*H*), 6.70 (br t, J_{HH} = 1.1 Hz, 2H, HIPT 4′-*H*), 6.65 (s, 2H, Mes-3,5-*H*), 3.47 (m, 4H, HIPT-NCH_2CH$_2$), 3.20 (m, 10H, containing 2,6,2″,6″-C*H*Me$_2$ and Mes-NCH_2CH$_2$), 2.90 (septet, J_{HH} = 6.9 Hz, 4H, 4,4″-C*H*Me$_2$), 2.25 (s, 9H, Mes-CH_3) 2.1 (m, 6H, containing Mes-NCH$_2$CH_2, and HIPT-NCH$_2$CH_2), 1.34 (d, J_{HH} = 6.9 Hz, 24H, 4,4″-CH(CH_3)$_2$), 1.30 (d, J_{HH} = 6.9 Hz, 24H, 2,6,2″,6″-CH(CH_3)$_2$), 1.20 (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)$_2$). Anal. Calcd for $C_{87}H_{121}MoN_5$: C, 78.40; H, 9.15; N, 5.25. Found: C, 77.26; H, 9.17; N, 5.19.

[TripHIPT$_2$N$_3$N]MoN (4g). This compound was synthesized in a manner similar to that of previously characterized compounds of this type. Briefly, 0.05 g (0.035 mmol) of **3g** was combined with 0.028 g (0.24 mmol) in 10 mL of benzene and heated 100 °C for 1 day. The solvent was removed in vacuo; the resulting solid was extracted into pentane, and the extract was filtered through Celite. The solvent was removed in vacuo, and the residue was recrystallized from pentane to yield 0.04 g (80%) of a bright yellow powder. ^{1}H NMR (C_6D_6, 20 °C): δ 7.77 (d, J_{HH} = 1.1 Hz, 4H, HIPT-2′,6′-*H*), 7.19 (m, 8H, HIPT 3,5,3″,5″-*H*), 7.08 (s, 2H, Trip-3,5-*H*), 6.73 (br t, J_{HH} = 1.1 Hz, 2H, HIPT 4′-*H*), 3.52 (m, 6H, HIPT-NCH_2-CH$_2$), 3.34 (br t, J_{HH} = 5.5 Hz, 2H, Trip-NCH_2CH$_2$), 3.17 (m, 10H, containing HIPT-2,6,2″,6″-C*H*Me$_2$, and Trip-2,6- C*H*Me$_2$), 2.95 (septet, J_{HH} = 6.9 Hz, 2H, HIPT-4,4″-C*H*Me$_2$), 2.81 (septet, J_{HH} = 6.9 Hz, 1H, Trip-4-C*H*Me$_2$), 2.21 (m, 8H, containing Trip-NCH$_2$CH_2 and HIPT-NCH$_2$CH_2), 1.38 (d, J_{HH} = 6.9 Hz, 24H, HIPT 4,4″-CH(CH_3)$_2$), 1.24 (m, 36H, contains Trip-4- CH(CH_3)$_2$ and HIPT-2,6,2″,6″-CH(CH_3)$_2$), 1.13 (m, 24H, contains Trip-2,6,2″,6″-CH(CH_3)$_2$ and HIPT-2,6,2″,6″-CH(CH_3)$_2$). Anal. Calcd for $C_{93}H_{133}MoN_5$: C, 78.83; H, 9.46; N, 4.94. Found: C, 78.91; H, 9.48; N, 4.86.

{**[3,5-Bis(CF$_3$)HIPT$_2$N$_3$N]MoN$_2$**}**Na(THF)$_2$ (5c).** Compound **3c** (0.56 g) was dissolved in 20 mL of THF and 4.8 g of 0.5% Na/Hg amalgam was added. The mixture was stirred with a glass stir bar for 2 h until the solution turned a deep green. The solution was decanted from the mercury, and the volatiles were removed in vacuo. The resulting solids were dissolved in pentane, and the mixture was filtered through Celite to yielding a deep purple solution. The product was recrystallized from pentane to yield 0.45 g (70%) of a purple powder in multiple crops. A similar method was used to synthesize the $^{15}N_2$-labeled species. ^{1}H NMR (C_6D_6, 20 °C): δ 7.68 (s, 1H, CF_3 arm 4-*H*), 7.59 (s, 2H, HIPT 4′-*H*), 7.45 (d, J_{HH} = 1.2 Hz, 2H, CF_3 arm 2,6-*H*), 7.35 (d, J_{HH} = 1.3 Hz, 4H, HIPT- 2′,6′-*H*), 7.18 (s, 4H, HIPT 3,5,3″,5″-*H*), 7.13 (s, 4H, HIPT 3,5,3″,5″-*H*), 3.76 (m, 6H, containing both HIPT-NCH_2CH$_2$ and CF_3-NCH_2CH$_2$), 3.38 (overlapping septets, J_{HH} = 6.9 Hz, 8H, 2,6,2″,6″-C*H*Me$_2$), 3.22 (br m, 8H, THF O-CH_2), 2.84 (overlapping septets, J_{HH} = 6.9 Hz, 4H, 4,4″-C*H*Me$_2$), 1.94 (br m, containing both HIPT-NCH$_2$CH_2 and CF_3-NCH$_2$CH_2), 1.23 (overlapping doublets, 52H containing 2,4,6,2″,4″,6″-CH(CH_3)$_2$), 1.1 (d, J_{HH} = 6.9 Hz, 12H, 4,4″-CH(CH_3)$_2$). ^{19}F NMR (C_6D_6, 20 °C): δ −61.76.

IR: $\nu_{NN} = 1801$ cm^{-1}; $^{15}N_2$-labeled $\nu_{NN} = 1741$ cm^{-1}. Elemental analyses are variable as a consequence (it is believed) of a variable amount of THF being present depending on individual preparation and isolation procedures. Variable amounts of THF also have been observed in the parent compound.[17]

{LMoN$_2$}Na(THF)$_2$. Synthetic procedures for all other LMoN$_2$Na(THF)$_2$ compounds were similar to that for **5c**. It was found that both Na/Hg amalgam or finely divided Na sand would reduce LMoCl similarly, so typically Na sand was used. A crystal structure was performed on **5d**, but elemental analyses were not successful and reproducible for any compound of this type.

LMoN$_2$ (6a−6g). No neutral dinitrogen complexes could be isolated as pure compounds. They could be observed only via IR and NMR spectroscopy. Typically **L**MoCl was treated with a 0.5% Na/Hg amalgam or sodium sand in THF. When the solution had turned from bright orange to either green (**6b**, **6f**, or **6g**) or purple (**6a**, **6c**, **6d**, or **6e**) it was filtered through a Celite plug onto a mild oxidant such as $ZnCl_2$. The resulting brown solution was then filtered through Celite, and the solvent was removed in vacuo. NMR and IR analysis suggested that 10−20% of the free ligand was present in the resulting solid, depending on the compound and the specific experiment. The paramagnetically shifted protons in the ^{1}H NMR were similar to those of the symmetric compounds of this type (3 peaks at ∼10 to 20 ppm, 2 peaks at ∼−3 to −10 ppm, and 3 peaks at −20 to −40 ppm).

[(3,5-Bis(CF$_3$)HIPT$_2$N$_3$N)MoNH$_3$][BAr$_4$′] (7c). This compound has been identified via NMR from the 1:1 reaction of **3c** and NaBAr$_4$′ under 6 equiv of ammonia in dichloromethane. After the mixture was stirred for 1 day, the solvent was removed in vacuo, and the resulting solid was filtered through Celite using pentane as the eluent. The solvent was removed in vacuo, and the residue was recrystallized from pentane to yield the product as a red solid. ^{1}H NMR (C_6D_6, 20 °C): δ 8.23 (s, BAr$_4$′), 7.61 (s, BAr$_4$′), 7.12 (br s), 2.88 (br s), 2.68 (br s), 1.29 (br s), 1.16 (br s), −12.5 (br s), −17.5 (br s), −33 (br s). ^{19}F NMR (C_6D_6, 20 °C): δ −61.3 (MoNH$_3^+$), −61.45 (BAr$_4$′). We were unable to remove NaBAr$_4$′ from the solid completely (∼5% via ^{19}F NMR).

[(3,5-DimethoxyHIPT$_2$N$_3$N)Mo(NH$_3$)][BAr$_4$′] (7e). A mixture of **3e** (100 mg) and 65 mg of Na[BAr$_4$′] was dissolved in 10 mL of CH_2Cl_2 in a 50 mL Teflon-sealed vessel. Dry ammonia (200 Torr, ∼6 equiv) was vacuum-transferred onto this solution. The reaction mixture turned bright red after being stirred for 6 h. The volatiles were removed in vacuo, and the resulting solid was extracted into pentane. The pentane extract was filtered through Celite, and the solvents were removed in vacuo. The product was isolated as a red solid upon crystallization of the residue from pentane. Yield: 120 mg (75%). ^{1}H NMR (C_6D_6, 20 °C): δ 8.36 (br s, BAr$_4$′), 7.68 (br s, BAr$_4$′), 6.67 (br s), 6.36 (br s), 3.5 (br s), 3.2 (s), 2.7 (br m), 1.85 (br m), 1.2 (br m), −4.0 (br s), −8.5 (br s). Anal. Calcd for $C_{118}H_{134}BF_{24}MoN_5O_2$: C, 63.92; H, 6.09; N, 3.16. Found: C, 64.10; H, 6.13; N, 2.97.

X-ray Structural Studies. 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 ($\lambda = 0.71073$ Å), performing ϕ and ω scans. The structures were solved by direct methods using SHELXS[19] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[20] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms 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 value of the atoms they are linked to (1.5 times for methyl groups). Crystal and structural refinement data for all structures is listed in the Supporting Information.

The structure of **3c** is strongly affected by disorder: both CF_3 groups and about half of all carbon atoms are found distributed over two positions. These disorders were refined with the help of similarity restraints on 1−2 and 1−3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. The relative occupancies of the disordered components were refined freely, while constraining the total occupancy of both components to unity. Probably because of the massive disorder, the crystal diffracted only to about 1.0 Å resolution and gave rise to data of only mediocre quality. To counteract the effects of the resulting low data-to-parameter ratio, rigid bond and similarity restraints were used for the displacement parameters of all atoms.

5d crystallizes with one molecule of $C_{86}H_{119}MoN_6$, one sodium ion, and the following solvent molecules in the asymmetric unit: two THF molecules (one of which is disordered) coordinated to the sodium ion, one-sixth of a noncoordinated THF molecule (6-fold disordered about the crystallographic −3 axis), two-half occupied heptane molecules, and one-sixth of a pentane molecule (6-fold disordered about the crystallographic −3 axis). The pentane molecule is probably a heptane molecule where the two methyl groups are disordered in addition to the disorder described, however refinement as heptane was not stable. These disorders were refined as described above.

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Supporting Information Available: Crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, and anisotropic displacement parameters for **3c** and **5d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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