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Synthesis of Molybdenum Complexes that Contain “Hybrid” Triamidoamine Ligands, [(Hexaisopropylterphenyl)N(CH₂CH₂)₂NCH₂CH₂NAryl]³⁻, and Studies Relevant to Catalytic Reduction of Dinitrogen

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Abstract

In the Buchwald-Hartwig reaction between HIPTBr (HIPT = 3,5-(2,4,6-*i*-Pr₃C₆H₂)₂C₆H₃ = HexaisoPropylTerphenyl) and (H₂NCH₂CH₂)₃N it is possible to obtain a 65% isolated yield of (HIPTNHCH₂CH₂)₂NCH₂CH₂NH₂. A second coupling then can be carried out to yield a variety of “Hybrid” ligands, (HIPTNHCH₂CH₂)₂NCH₂CH₂NHAr, where Ar = 3,5-Me₂C₆H₃, 3,5-(CF₃)₂C₆H₃, 3,5-(MeO)₂C₆H₃, 3,5-Me₂NC₅H₃, 3,5-Ph₂NC₅H₃, 2,4,6-*i*-Pr₃C₆H₂, or 2,4,6-Me₃C₆H₂. 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]MoN₂}Na, and {[Hybrid]Mo(NH₃)}⁺ can be prepared. [Hybrid]MoN₂ species were prepared through oxidation of {[Hybrid]MoN₂}Na species with ZnCl₂, but could not be isolated. [Hybrid]Mo=N-NH species could be observed as a consequence of protonation of {[Hybrid]MoN₂}⁻ species, but they too could not be isolated as a consequence of a facile decomposition to yield dihydrogen and [Hybrid]MoN₂ 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-Me₂C₆H₃, 3,5-(CF₃)₂C₆H₃, or 3,5-(MeO)₂C₆H₃ could be ascribed 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 [(HIPTNHCH₂CH₂)₂NCH₂CH₂N{3,5-(CF₃)₂C₆H₃}]MoCl and [(HIPTNHCH₂CH₂)₂NCH₂CH₂N(3,5-Me₂C₆H₃)]MoN₂}Na(THF)₂ are reported.

INTRODUCTION

In the last 10 years we have been exploring early transition metal complexes that contain a triamidoamine ligand, [(RNCH₂CH₂)₃N]³⁻ ([RN₃N]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_{z²}). These orbitals can be employed in three combinations (2π/1σ, 1π/2σ, or 3σ) in order to bind substrates in the trigonal pocket. Distortion of the pseudotrigonal symmetry to yield pseudoctahedral species,² or even seven-coordinate species³ 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 [HIPTN₃N]³⁻ ligand, where HIPT = 3,5-(2,4,6-*i*-Pr₃C₆H₂)₂C₆H₃ (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

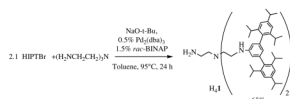
[ArN₃N]Mo-N=N-Mo[ArN₃N] complexes,^{1b} maximize steric protection of a metal coordination site in a monometallic species, and provide increased solubility in nonpolar solvents. We showed that several [HIPTN₃N]Mo complexes could be prepared that contain dinitrogen or some dinitrogen reduction product.⁵ Examples include paramagnetic MoN₂ (where Mo = [HIPTN₃N]Mo), diamagnetic [MoN₂]⁻, diamagnetic Mo-N=N-H, diamagnetic [Mo=N-NH₂]BAr'₄ (Ar' = 3,5-(CF₃)₂C₆H₃), diamagnetic Mo≡N, diamagnetic [Mo=NH]BAr', paramagnetic [Mo(NH₃)]BAr'₄, and paramagnetic Mo(NH₃). 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 Chart-like reduction cycle.

“Symmetric” variations of the [HIPTN₃N]³⁻ ligand that have been prepared and attached to molybdenum include the hexa-*t*-butylterphenyl ([HTBTN₃N]³⁻) ligand, the hexamethylterphenyl ([HMTN₃N]³⁻) ligand, and a variation of the [HIPTN₃N]³⁻ ligand in which a bromide is present in the *para* position of the central phenyl ring, [*p*BrHIPTN₃N]³⁻.⁶ It became clear from various stoichiometric reactions involving the [HTBTN₃N]³⁻ system that proton and electron transfer was much slower than in the parent [HIPTN₃N]³⁻ system, perhaps by an order of magnitude or more. (The rate of conversion of [HTBTN₃N]Mo(NH₃) into [HTBTN₃N]Mo(N₂) 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 [HTBTN₃N]Mo≡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 [HMTN₃N]Mo≡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*BrHIPTN₃N]Mo compounds were successful catalysts for reduction of dinitrogen; 6.4–7.0 equivalents of total ammonia were formed, which is not quite as high as the amount formed when [HIPTN₃N]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 [HTBTN₃N]³⁻ system we discovered that in the arylation reaction between three equivalents of HTBTBr and (H₂NCH₂CH₂)₃N the third equivalent of HTBTBr reacts significantly more slowly than the second equivalent. Therefore by adjusting the stoichiometry (HTBTNHCH₂CH₂)₂NCH₂CH₂NH₂ could be isolated in good yield.⁶ It then became possible to add a different aryl group to the third “arm” of the ligand to yield what we call a “hybrid” (HTBTNHCH₂CH₂)₂NCH₂CH₂NHAr species. We found that the same is true for (HIPTNHCH₂CH₂)₂NCH₂CH₂NHAr species (Figure 2). An advantage of [(HIPTNCH₂CH₂)₂NCH₂CH₂NHAr]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 [HIPTN₃N]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.

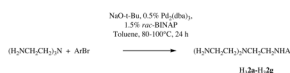
RESULTS AND DISCUSSION

If 2.1 equivalents of HIPTBr are employed in the Buchwald-Hartwig reaction⁸ between HIPTBr and $(\text{H}_2\text{NCH}_2\text{CH}_2)_3\text{N}$, then a mixture results that consists largely of $(\text{HIPTNHCH}_2\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{NH}_2$ mixed with a small amount of $(\text{HIPTNHCH}_2\text{CH}_2)_3\text{N}$. These two products can be separated readily using a silica gel column pretreated with triethylamine, from which $(\text{HIPTNHCH}_2\text{CH}_2)_3\text{N}$ (11% yield) elutes readily with toluene. Flushing the column with a 1:1 mixture of toluene and tetrahydrofuran then yields $(\text{HIPTNHCH}_2\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{NH}_2$ (**H41**, 65% yield on a ~50 g scale; equation 1). The $(\text{HIPTNHCH}_2\text{CH}_2)_3\text{N}$ ligand can be accumulated and employed in other studies.



(1)

A second Buchwald-Hartwig coupling can be carried out on the terminal amine in $(\text{HIPTNHCH}_2\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{NH}_2$ to yield $(\text{HIPTNHCH}_2\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{NHAr}$ species **H32a-H32g** (Equation 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.



(2)

The hybrid ligands were attached to Mo in the same way as the $[\text{HIPTN}_3\text{N}]^{3-}$ ligands, i.e., the parent ligands were added to a solution of $\text{MoCl}_4(\text{THF})_2$ and the mixture was then treated with three equivalents of $\text{LiN}(\text{TMS})_2$ (Figure 3). The resulting bright orange paramagnetic [Hybrid]MoCl compounds **3a-g** (Figure 2) could be isolated in good yields, even though they tend to be significantly more soluble than the already highly soluble $[\text{HIPTN}_3\text{N}]\text{MoCl}$ species.⁴ The proton NMR spectra of the [Hybrid]MoCl compounds reveal paramagnetically shifted methylene resonances similar to those observed for $[\text{HIPTN}_3\text{N}]\text{MoCl}$, 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 $(\text{ArNHCH}_2\text{CH}_2)_3\text{N}$ 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 $[\text{HIPTN}_3\text{N}]^{3-}$ 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 $[\text{HIPTN}_3\text{N}]\text{Mo}$, $[\text{HTBTN}_3\text{N}]\text{Mo}$, and $[p\text{BrHIPTN}_3\text{N}]\text{Mo}$ systems.

One of the least air-sensitive $[\text{HIPTN}_3\text{N}]\text{Mo}$ compounds that can be employed as a catalyst precursor in dinitrogen reduction is the nitride, $[\text{HIPTN}_3\text{N}]\text{MoN}$. The bright yellow, diamagnetic [Hybrid]MoN compounds **4a-g** (Figure 3) were prepared in reactions between [Hybrid]MoCl and trimethylsilylazide 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.

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]MoN₂}Na(THF)₂. Although all {[Hybrid]MoN₂}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]MoN₂}Na(THF)₂ compounds **5a–g** can be oxidized with ZnCl₂ to yield [Hybrid]MoN₂ species, **6a–g**. The extreme solubility of **6a–g** and the presence of 5–10% of free ligand, (HIPTNHCH₂CH₂)₂NCH₂CH₂NHAr, so far have thwarted attempts to isolate these species. Therefore **6a–g** could be characterized only through IR and NMR techniques. In ¹H NMR spectra of these species, 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 MoN₂ compounds that contain “symmetric” ligands such as [HIPTN₃N]MoN₂.⁴ These ν_{NN} stretches are listed in Table 3. The ν_{NN} stretches in **6a–g** 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., ν_{NN} = 1992 cm⁻¹ for **6c** versus ν_{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_z bond slightly and therefore reduces the amount of backbonding 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]MoNH₃}BAR₄' species (**7c** and **7e**) were prepared in reactions between **3c** and **3e**, respectively, and ammonia in dichloromethane in the presence of NaBAR' (Ar' = 3,5-(CF₃)₂C₆H₃). Compound **7e** could be crystallized cleanly and was analyzed successfully. Compound **7c** could not be freed completely from NaBAR₄', and so could be characterized only *via* NMR. Both **7c** and **7e** were utilized in studies involving exchange of ammonia for dinitrogen discussed below.

Attempts to reduce dinitrogen catalytically were carried out in a manner as described for the parent system, which produced 7–8 equivalents of ammonia per equivalent of Mo.⁴ Briefly, a heptane slurry containing 48 equivalents of [2,6-lutidinium][BAR₄'] and **4a–g** were placed in the reaction vessel and 36 equivalents of decamethylchromocene in 10 mL of heptane were added with a syringe pump.^{4a} (See the experimental section for a representative experiment.) The reducing agent was added over a period of 6 hours, 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.

None of the compounds that contains one of the new hybrid ligands is as efficient a catalyst for the reduction of dinitrogen as the [HIPTN₃N]Mo analog. However, **4a**, **4b**, **4f**, and **4g** are catalytic to a small degree (0.6, 0.3, 0.2, and 2 equivalents 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 [HIPTN₃N]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 equivalents 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 LMoNH₃ complexes were prepared *in situ* through reduction of **7c** and **7e** with CrCp*₂. The resulting LMoNH₃ complexes (**8c** and **8e**) could not be isolated as a consequence of their high solubility and their ready conversion under dinitrogen into LMoN₂ complexes, as observed through growth of LMoN₂ in IR studies in aliquots of the solution of LMoNH₃ over a period of several hours. The rate of formation of LMoN₂ 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 semi-quantitative, since the ammonia that is released is in equilibrium with the newly formed LMoN₂ 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 ten times faster than 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 CF₃ 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 upon 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 backbonding into dinitrogen when it displaces ammonia in a bimolecular reaction. The position of the equilibria in the hybrid ligand systems are not known. In any case, the main point is that slow exchange *cannot* be the reason why these catalysts fail, since the exchange rates for the CF₃- and OMe-substituted hybrid ligands bracket that observed in the successful HIPT system. We also were able to observe free NH₃ in runs where two NH₃ 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 equivalents of the ammonia observed was found in the initial volatiles, indicating that NH₃ is indeed released during catalysis and that approximately 1/3 of the ammonia is present as NH₃ rather than NH₄⁺.

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 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 ¹⁵N-labeled compounds. Fortunately, the [ArN₃N]Mo-N=NH species are diamagnetic, so the presence of a proton on N $_{\beta}$ can be established through ¹⁵N labeling studies. Due to its relative ease of synthesis and the availability of an ¹⁹F NMR handle, we focused on the [ArN₃N]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 $\text{H}(\text{OEt}_2)_2\text{BAR}_4'$) resulted in formation of **9c**. This species was identified through observation of Mo-N=NH at 8.6 ppm, with $J_{\text{N}\beta\text{H}} = 54.5$ Hz and $J_{\text{N}\alpha\text{H}} = 8$ Hz (absolute values) in the ^{15}N labeled compound (Figure 6). These values are nearly identical to those obtained for $[\text{HIPTN}_3\text{N}]\text{Mo-N=NH}$.^{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 $[\text{HIPTN}_3\text{N}]\text{Mo-N=NH}$ decomposes only very slowly to $[\text{HIPTN}_3\text{N}]\text{MoH}$ (at 60°C $t_{1/2} = 90$ h^{4b}). Interestingly, during some of these experiments we also were able to observe conversion of $\text{Mo-}^{15}\text{N}=\text{}^{15}\text{NH}$ to $\text{Mo-}^{14}\text{N}=\text{}^{14}\text{NH}$ ($t_{1/2}$ of 4.5 h; Figure 7). The mechanism of this exchange (which also can be observed in $[\text{HIPTN}_3\text{N}]\text{Mo-}^{15}\text{N}=\text{}^{15}\text{NH}$, 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 $[\text{HIPTN}_3\text{N}]\text{MoH}$ 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 whether the pure compound (if it somehow could be purified) would decompose at the same rate as that prepared *in situ*.

When $[\text{2,6-lutidinium}]\text{BAR}_4'$ 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 $\text{H}(\text{OEt}_2)_2\text{BAR}_4'$, and 4 equivalents of 2,6-lutidine, 2,4,6-trimethylpyridine (collidine), or Et_3N were added subsequently, **9c** could not be observed 5 minutes 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 reaction is unlikely to be involve 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 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 equivalents 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 addition of one electron and one proton to MoN_2 is not completely decomposed by 2,6-lutidine, since only one equivalent 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 dinitrogen reaction as successfully as compounds that contain the parent $[\text{HIPTN}_3\text{N}]^{3-}$ 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 as yet an unknown mechanism. We also have shown that electron-donating ligands may speed the rate of ammonia for dinitrogen exchange. However, increasing 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 in order 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 nitrogenases¹³ 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 utilizing standard Schlenk and dry-box techniques under an atmosphere of dinitrogen. All glassware used was oven and/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 3 times prior to use. All dried and deoxygenated solvents were stored in a dinitrogen-filled glove box 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), Pd₂(dba)₃ (Strem), *rac*-BINAP (Strem), and tris(2-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-dimethylpyridine¹⁸ 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 (¹H and ¹³C NMR) or to external C₆H₅F ($\delta = -113.15$ ppm in the ¹⁹F NMR spectrum). All stated coupling constants should be considered as absolute values.

(HIPTNHCH₂CH₂)₂NCH₂CH₂NH₂

The procedure is similar to previous syntheses of symmetric ligands,⁴ but utilizes 2.1 equivalents of HIPTBr instead of 3.1 equivalents. A 100 mL toluene solution of Pd₂(dba)₃ (0.91 g, 0.9 mmol) and *rac*-BINAP (1.85 g, 2.9 mmol) were 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 (20.4g, 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 in order 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%): ^1H 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, $J_{\text{HH}} = 4.9$ Hz, 2H, NH), 3.17 (septet, $J_{\text{HH}} = 6.9$ Hz, 8H, 2,6,2'',6''-CHMe₂), 2.94 (overlapped septet, $J_{\text{HH}} = 6.6$ Hz, 4H, 4,4''-CHMe₂), 2.85 (overlapped multiplet, 4H, NH₂CH₂CH₂ and NH₂CH₂CH₂), 2.74 (br q, $J_{\text{HH}} = 5.2$ Hz, 4H, NHCH₂CH₂), 2.03 (br t, $J_{\text{HH}} = 5.2$ Hz, 4H, NHCH₂CH₂), 1.32 (d, $J_{\text{HH}} = 7.1$ Hz, 24H, 4,4''-CH(CH₃)₂), 1.26 (br d, $J_{\text{HH}} = 6.9$ Hz, 48H, 2,6,2'',6''-CH(CH₃)₂), 0.44 (br s, 2H, NH₂); ^{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 $< 5^\circ\text{C}$ 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 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 vacua*, 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. ^1H 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).

H₃[LutHIPT₂N₃N] (2a)

Pd₂(dba)₃ (0.054g, 0.058mmol) and *rac*-BINAP (0.11g, 0.18 mmol) were stirred with mild heating in 25 mL 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%): ^1H NMR (C_6D_6 , 20°C) δ 7.22 (s, 8H, 3,5,3'',5''-H), 6.53 (br t, $J_{\text{HH}} = 1.4$ Hz, 2H, 4'-H), 6.48 (d, $J_{\text{HH}} = 1.3$ Hz, 4H, 2',6'-H), 6.02 (s, 2H, Lut-3,5-H), 3.93 (t, $J_{\text{HH}} = 4.9$ Hz, 1H, Lut-NH), 3.71 (t, $J_{\text{HH}} = 4.8$ Hz, 2H, HIPT-NH), 3.16 (septet, $J_{\text{HH}} = 6.9$ Hz, 8H, 2,6,2'',6''-CHMe₂), 2.92 (septet, $J_{\text{HH}} = 6.9$ Hz, 4H, 4,4''-CHMe₂), 2.80 (br q, $J_{\text{HH}} = 5.4$ Hz, 4H, HIPT-NHCH₂CH₂), 2.63 (br q, $J_{\text{HH}} = 5.9$ Hz, 2H, Lut-NHCH₂CH₂), 2.39 (s, 6H, Lut-CH₃), 2.16 (br t, $J_{\text{HH}} = 5.7$ Hz, 4H, HIPT-NHCH₂CH₂), 2.11 (br t, $J_{\text{HH}} = 6.8$ Hz, 2H, Lut-NHCH₂CH₂), 1.32 (d, $J_{\text{HH}} = 6.9$ Hz, 24H, 4,4''-CH(CH₃)₂), 1.28 (d, $J_{\text{HH}} = 6.9$ Hz, 24H, 2,6,2'',6''-CH(CH₃)₂), 1.25 (d, $J_{\text{HH}} = 6.9$ Hz, 24H, 2,6,2'',6''-CH(CH₃)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).

H₃[PhLutHIPT₂N₃N] (2b)

A solution of Pd₂(dba)₃ (0.045g, 0.049mmol) and *rac*-BINAP (0.094g, 0.15 mmol) in 25 mL 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%): ¹H NMR (C₆D₆, 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-NH), 3.60 (br s, 2H, HIPT-NH), 3.17 (septet, J_{HH} = 6.9 Hz, 8H, 2,6,2'',6''-CHMe₂), 2.89 (m, 8H, 4,4''-CHMe₂ and HIPTNHCH₂CH₂ overlapping), 2.75 (br q, J_{HH} = 5.8 Hz, 2H, PhLutNHCH₂CH₂), 2.24 (m, 6H, HIPTNHCH₂CH₂ and PhLutNHCH₂CH₂ overlapping), 1.31 (d, J_{HH} = 6.9 Hz, 24H, 4,4''-CH(CH₃)₂), 1.29 (d, J_{HH} = 6.9 Hz, 12H, 2,6,2'',6''-CH(CH₃)₂), 1.28 (br d, J_{HH} = 6.9 Hz, 36H, 2,6,2'',6''-CH(CH₃)₂); ¹³C NMR (C₆D₆, 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).

H₃[3,5-Bis(CF₃)HIPT₂N₃N] (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 Pd₂(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: ¹H NMR (C₆D₆, 20°C) δ 7.25 (s, 1H, CF₃ arm 4-H), 7.22 (s, 8H, HIPT 3,5,3'',5''-H), 6.64 (s, 2H, CF₃ 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, CF₃ arm NH), 3.51 (br s, 2H, HIPT-NH), 3.15 (septet, 8H, J_{HH} = 6.9 Hz, 8H, 2,6,2'',6''-CHMe₂), 2.90 (septet, J_{HH} = 6.9 Hz, 4H, 4,4''-CHMe₂), 2.82 (br t, J_{HH} = 5.8 Hz, 4H, HIPT-NCH₂CH₂), 2.40 (br q, J_{HH} = 5.2 Hz, 2H, CF₃ arm-NCH₂CH₂), 2.17 (br t, J_{HH} = 5.8 Hz, 4H, HIPT-NHCH₂CH₂), 2.10 (br t, J_{HH} = 5.8 Hz, 2H, CF₃ arm-NCH₂CH₂), 1.32 (d, J_{HH} = 6.9 Hz, 24H, 4,4''-CH(CH₃)₂), 1.28 (d, J_{HH} = 6.9 Hz, 24H, 2,6,2'',6''-CH(CH₃)₂), 1.25 (d, J_{HH} = 6.9 Hz, 24H, 2,6,2'',6''-CH(CH₃)₂); ¹³C NMR (C₆D₆, 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; ¹⁹F NMR (C₆D₆, 20°C) δ -62.74. HRMS (ESI) 1319.9156 ([M+H]⁺; calcd 1319.9177).

H₃[3,5-DimethylHIPT₂N₃N] (2d)

This compound was prepared in a manner similar to other hybrid ligand systems. Briefly, 0.037 g (4 mmol) of Pd₂(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 one day. The mixture was then filtered through Celite and the solvent 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: ¹H NMR (C₆D₆, 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-NH), 3.75 (br s, 1H, dimethyl-NH), 3.16 (septet, J_{HH} = 6.9 Hz, 8H, HIPT-2,6,2'',6''-CHMe₂), 2.95 (septet J_{HH} = 6.9 Hz, 4H, HIPT-4,4''-

*CHMe*₂), 2.79 (m, 8H, contains HIPT-NCH₂CH₂ and dimethyl-NCH₂CH₂), 2.17 (m, 8H, contains HIPT-NCH₂CH₂ and dimethyl-NCH₂CH₂), 2.08 (s, 6H, dimethyl-CH₃), 1.46 (d, J_{HH} = 6.9 Hz, 24H, 4,4''-CH(CH₃)₂), 1.38 (d, J_{HH} = 6.9 Hz, 24H, 2,6,2'',6''-CH(CH₃)₂), 1.27 (d, J_{HH} = 6.9 Hz, 24H, 2,6,2'',6''-CH(CH₃)₂); ¹³C NMR (C₆D₆, 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).

H₃[3,5-DimethoxyHIPT₂N₃N] (2e)

This compound was prepared in a manner similar to other hybrid ligand systems. Briefly, 0.037 g (0.04 mmol) of Pd₂(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 3g (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: ¹H NMR (C₆D₆, 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-OCH₃), 3.11 (septet, J_{HH} = 6.8 Hz, 8H HIPT-2,6,2'',6''-CHMe₂), 2.85 (septet, J_{HH} = 6.8 Hz, 4H HIPT-4,4''-CHMe₂), 2.75 (m, 10H, contains HIPT-NCH₂CH₂ and dimethoxy-NCH₂CH₂ and dimethoxy NCH₂CH₂), 2.14 (br t, 4H, HIPT-NCH₂CH₂), 1.26 (d, J_{HH} = 6.8 Hz, 24H HIPT-4,4''-CH(CH₃)₂), 1.22 (d, J_{HH} = 6.8 Hz, 24H HIPT-2,6,2'',6''-CH(CH₃)₂), 1.19 (d, J_{HH} = 6.8 Hz, 24H HIPT-2,6,2'',6''-CH(CH₃)₂); ¹³C NMR (C₆D₆, 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).

H₃[MesHIPT₂N₃N] (2f)

This compound was prepared in a manner similar to other hybrid ligand systems. Briefly, 0.037 g (40 mmol) of Pd₂(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: ¹H NMR (C₆D₆, 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-NH), 3.18 (septet, J_{HH} = 6.9 Hz, 8H, 2,6,2'',6''-CHMe₂), 2.88 (m, 8H, containing 4,4''-CHMe₂ and HIPT-NCH₂CH₂), 2.78 (br t, J_{HH} = 5.8 Hz, 2H, Mes-NCH₂CH₂), 2.2 (m, 15H, containing Mes-CH₃, Mes-NCH₂CH₂, and HIPT-NCH₂CH₂), 1.32 (d, J_{HH} = 6.9 Hz, 24H, 4,4''-CH(CH₃)₂), 1.28 (d, J_{HH} = 6.9 Hz, 24H, 2,6,2'',6''-CH(CH₃)₂), 1.26 (d, J_{HH} = 6.9 Hz, 24H, 2,6,2'',6''-CH(CH₃)₂); ¹³C NMR (C₆D₆, 20°C) δ 162.80, 148.48, 147.318, 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).

H₃[TripHIPT₂N₃N] (2g)

This compound was prepared in a manner similar to other hybrid ligand systems. Briefly, 0.037 g (40 mmol) of Pd₂(dba)₃ and 0.077 g (162 mmol) of X-Phos were heated mildly in toluene to pre-form 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 a 8:1 mixture of toluene and THF mixture yielded a mixture of (HIPTNHCH₂CH₂)₂NCH₂CH₂NH₂ 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: ¹H NMR (C₆D₆, 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-NH), 3.38 (septet, J_{HH} = 6.9 Hz, 2H, Trip-2,6-CHMe₂), 3.17 (septet, J_{HH} = 6.9 Hz, 8H, HIPT-2,6,2'',6''-CHMe₂), 2.89 (m, 12H, containing HIPT-NCH₂CH₂, Trip-NCH₂CH₂, HIPT-4,4''-CH(CH₃)₂, and Trip-4-CH(CH₃)₂), 2.44 (br t, J_{HH} = 5.5 Hz, 2H, Trip-NCH₂CH₂), 2.33 (br t, J_{HH} = 5.5 Hz, 4H, HIPT-NCH₂CH₂), 1.32 (d, J_{HH} = 6.9 Hz, 24H, 4,4''-CH(CH₃)₂), 1.25 (m, 60H, 2,6,2'',6''-CH(CH₃)₂); ¹³C NMR (C₆D₆, 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).

[LutHIPT₂N₃N]MoCl (3a)

The procedure followed was nearly identical to published procedures.^{4,6} Briefly, H₃2a (0.6 g, 0.50 mmol) and MoCl₄(THF)₂ (0.19 g, 0.50 mmol) were dissolved in THF (40 mL). This solution was stirred for one hour and (Me₃Si)₂NLi (0.258 g, 0.154 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%): ¹H NMR (C₆D₆, 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 C₈₅H₁₁₈ClMoN₅: C, 76.11; H, 8.87; N, 5.22. Found: C, 76.01; H, 9.06, N, 5.16.

[PhLutHIPT₂N₃N]MoCl (3b)

The procedure followed was nearly identical to published procedures.^{4,6} Briefly, H₃2b (1 g, 0.75 mmol) and MoCl₄(THF)₂ (0.286 g, 0.75 mmol) were dissolved in THF (75mL). This solution was stirred for one hour and (Me₃Si)₂NLi (0.388 g, 2.3 mmol) was then added slowly. After 2 hours 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%): ¹H NMR (C₆D₆, 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 C₉₅H₁₂₂ClMoN₅: C, 77.86; H, 8.39; N, 4.78. Found: C, 77.73; H, 8.46; N, 4.83.

[3,5-Bis(CF₃)HIPT₂N₃N]MoCl (3c)

This compound was synthesized similarly to other compounds of this type described above. Briefly, 0.75 g (0.57 mmol) of H₃2c as added to 50 mL THF. MoCl₄(THF)₂ (0.24 g; 0.62 mmol) was then added slowly and the mixture was stirred for one hour, during which time the solution darkened to a deep red. To this red solution 0.30 g (1.8 mmol) of (Me₃Si)₂NLi was added and the reaction 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 removed *in vacuo*. Recrystallization of the residue from pentane yielded 0.45 g (55%) of a deep orange powder: ¹H NMR (C₆D₆, 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 ppm. Anal. Calcd for $\text{C}_{86}\text{H}_{113}\text{ClF}_6\text{MoN}_4$: C, 71.32; H, 7.86; N, 3.87. Found: C, 71.25; H, 7.76; N, 3.94.

[3,5-DimethylHIPT₂N₃N]MoCl (3d)

This compound was synthesized similarly to other compounds of this type described above. Briefly, 0.76 g (0.63 mmol) of $\text{H}_3\mathbf{2d}$ was added to 0.26 g (0.68 mmol) of $\text{MoCl}_4(\text{THF})_2$ in 50 mL THF. This mixture was stirred for one hour and 0.33 g (1.9 mmol) of $(\text{Me}_3\text{Si})_2\text{NLi}$ was added. After two hours the solvent was removed *in vacuo* and 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: ^1H 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 $\text{C}_{86}\text{H}_{119}\text{ClMoN}_4$: C, 77.07; H, 8.95; N, 4.18. Found: C, 76.87; H, 9.06; N, 4.11.

[3,5-DimethoxyHIPT₂N₃N]MoCl (3e)

This compound was synthesized similarly to other compounds of this type described above. Briefly, 0.41 g (0.3 mmol) of $\text{H}_3\mathbf{2e}$ was added to 0.13 g (0.3 mmol) of $\text{MoCl}_4(\text{THF})_2$ in 30 mL of THF. Upon addition of the molybdenum, the solution's color immediately darkened to deep red. The solution was stirred for one hour and 0.17 g (1 mmol) of $(\text{Me}_3\text{Si})_2\text{NLi}$ was then added. The solution slowly turned orange-red. The solvent was removed *in vacuo* and the 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 yielding 0.32 g (70%) of the compound as a deep orange powder: ^1H 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 $\text{C}_{86}\text{H}_{119}\text{ClMoN}_4\text{O}_2$: C, 75.27; H, 8.74; N, 4.08. Found: C, 75.06; H, 8.65; N, 4.08.

[MesHIPT₂N₃N]MoCl (3f)

This compound was synthesized similarly to other compounds of this type described above. Briefly, 1.0 g (0.81 mmol) $\text{H}_3\mathbf{2f}$ was added to 70 mL of THF. $\text{MoCl}_4(\text{THF})_2$ (0.32 g, 1.0 mmol) was added slowly with stirring. After 2 h 0.42 g (2.6 mmol) of $(\text{Me}_3\text{Si})_2\text{NLi}$ was added. After 1 hour the solvent was evaporated *in vacuo* and 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: ^1H 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 $\text{C}_{87}\text{H}_{121}\text{ClMoN}_4$: C, 77.16; H, 9.01; N, 4.14. Found: C, 77.04; H, 9.04; N 4.11.

[TripHIPT₂N₃N]MoCl (3g)

This compound was synthesized similarly to other compounds of this type described above. Briefly, 0.35 g (0.25 mmol) of $\text{H}_3\mathbf{2g}$ was dissolved in 50 mL of THF. $\text{MoCl}_4(\text{THF})_2$ (0.112 g (0.29 mmol) was added and the solution was stirred for 2 hours. The color changed from orange to bright red. To this solution 0.138 g (0.83 mmol) of $(\text{Me}_3\text{Si})_2\text{NLi}$ was added slowly and the solution was stirred for an additional hour. The solvent was removed *in vacuo* and 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: ^1H 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 $C_{93}H_{113}ClMoN_4$: C, 77.65; H, 9.32; N, 3.89. Found: C, 77.42; H, 9.38; N, 3.77.

[LutHIPT₂N₃N]MoN (4a)

This compound could not be isolated in pure form, as the reaction between **(3a)** and Me_3SiN_3 is low yielding and the final product consequently was contaminated with **H₃2a**, even after multiple recrystallizations. A sample containing ~10% **H₃2a** (according to ¹H NMR) was utilized in test catalytic runs.

[PhLutHIPT₂N₃N]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 filtrate volume was reduced to 0.5 ml *in vacuo*. Upon cooling, 50 mg of a bright, canary yellow solid was obtained (37%): ¹H 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-NHCH₂CH₂), 3.20 (br t, 2H, J_{HH} = 4.2 Hz, PhLut-NCH₂CH₂), 3.11 (septet, 8H, J_{HH} = 6.9 Hz, 8H, 2,6,2'',6''-CHMe₂), 2.89 (septet, J_{HH} = 6.9 Hz, 4H, 4,4''-CHMe₂), 2.08 (br t, 2H, J_{HH} = 3.4 Hz, PhLut-NCH₂CH₂), 2.02 (br t, 4H, J_{HH} = 5.1 Hz, HIPT-NCH₂CH₂), 1.33 (dd, 24H, 4,4''-CH(CH₃)₂), 1.22 (d, J_{HH} = 6.9 Hz, 12H, 2,6,2'',6''-CH(CH₃)₂), 1.19 (d, J_{HH} = 6.9 Hz, 12H, 2,6,2'',6''-CH(CH₃)₂), 1.16 (d, J_{HH} = 6.9 Hz, 12H, 2,6,2'',6''-CH(CH₃)₂), 1.11 (d, J_{HH} = 6.9 Hz, 12H, 2,6,2'',6''-CH(CH₃)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(CF₃)HIPT₂N₃N]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 hours 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: ¹H NMR (C_6D_6 , 20°C) δ 7.93 (s, 2H, CF₃ arm 2,6-H), 7.70 (d, J_{HH} = 1.4 Hz, 4H, HIPT-2',6'-H), 7.39 (s, 1H, CF₃ 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-NCH₂CH₂), 3.15 (overlapping septets, J_{HH} = 6.9 Hz, 8H, 2,6,2'',6''-CHMe₂), 2.90 (septet, J_{HH} = 6.9 Hz, 4H, 4,4''-CHMe₂), 2.83 (br t, J_{HH} = 4.8 Hz, 2H, CF₃ arm-NCH₂CH₂), 1.97 (br t, J_{HH} = 5.1 Hz, 4H, HIPT-NHCH₂CH₂), 1.92 (br t, J_{HH} = 5.0 Hz, 2H, CF₃ arm-NCH₂CH₂), 1.34 (d, J_{HH} = 6.9 Hz, 24H, 4,4''-CH(CH₃)₂), 1.26 (d, J_{HH} = 6.9 Hz, 12H, 2,6,2'',6''-CH(CH₃)₂), 1.22 (d, J_{HH} = 6.9 Hz, 12H, 2,6,2'',6''-CH(CH₃)₂), 1.20 (d, J_{HH} = 6.9 Hz, 12H, 2,6,2'',6''-CH(CH₃)₂), 1.11 (d, J_{HH} = 6.9 Hz, 12H, 2,6,2'',6''-CH(CH₃)₂). ¹⁹F NMR (C_6D_6 , 20°C), d -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-DimethylHIPT₂N₃N]MoN (4d)

This compound was made in a similar manner 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 benzene and the mixture was heated in a Teflon®-sealed bomb at 100°C for one day. The volatiles were removed *in vacuo* and 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: ¹H 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 Hz 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, $J_{\text{HH}} = 5.2$ Hz, 4H, HIPT-NCH₂CH₂), 3.64 (br t, $J_{\text{HH}} = 5.2$ Hz, 2H, dimethyl-NCH₂CH₂), 3.19 (septet, $J_{\text{HH}} = 6.9$ Hz, 8H, HIPT-2,6,2'',6''-CHMe₂), 2.93 (septet, $J_{\text{HH}} = 6.9$ Hz, 4H, HIPT-4,4''-CHMe₂), 2.18 (s, 6H, dimethyl-CH₃), 2.03 (m, 8H, contains HIPT-NCH₂CH₂ and dimethyl-NCH₂CH₂), 1.34 (d, $J_{\text{HH}} = 6.9$ Hz, 24H, 4,4''-CH(CH₃)₂), 1.26 (d, $J_{\text{HH}} = 6.9$ Hz, 24H, 2,2'',6,6''-CH(CH₃)₂), 1.21 (d, $J_{\text{HH}} = 6.9$ Hz, 12H, 2,6,2'',6''-CH(CH₃)₂), 1.16 (d, $J_{\text{HH}} = 6.9$ Hz, 24H, 2,6,2'',6''-CH(CH₃)₂). Anal Calcd for C₈₆H₁₁₉MoN₅: C, 78.32; H, 9.09; N, 5.31. Found: C, 78.19; H, 8.96; N, 5.23.

[3,5-DimethoxyHIPT₂N₃N]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 Me₃SiN₃ in 25 mL of benzene. This mixture was heated at ~100°C overnight. The solvent was removed *in vacuo* and the resulting solid 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: ¹H NMR (C₆D₆, 20°C) δ 7.91 (d, $J_{\text{HH}} = 0.8$ Hz, 4H, HIPT-2',6'-H), 7.23 (d, $J_{\text{HH}} = 1.8$ 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, $J_{\text{HH}} = 1.8$ Hz, 1H, dimethoxy-4-H), 3.55 (br t, 4H, HIPT-NCH₂CH₂), 3.43 (s, 6H, -OCH₃), 3.31 (br t, 2H, dimethoxy-NCH₂CH₂), 3.20 (septet, $J_{\text{HH}} = 6.9$ Hz, 8H, 2,6,2'',6''-CHMe₂), 2.92 (septet, $J_{\text{HH}} = 6.9$ Hz, 4H, 4,4''-CHMe₂), 1.94 (br t, 6H, overlapped HIPTNCH₂CH₂ and dimethoxyNCH₂CH₂), 1.32 (d, $J_{\text{HH}} = 6.9$ Hz, 24H, 4,4''-CH(CH₃)₂), 1.22 (overlapping doublets, $J_{\text{HH}} = 6.9$ Hz, 24H, 2,6,2'',6''-CH(CH₃)₂), 1.14 (d, $J_{\text{HH}} = 6.9$ Hz, 12H, 2,6,2'',6''-CH(CH₃)₂). Anal. Calcd for C₈₆H₁₁₉MoN₅O₂: C, 76.47; H, 8.88; N, 5.18. Found: C, 76.38; H, 8.85; N, 5.06.

[MesHIPT₂N₃N]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 Me₃SiN₃ in 25 mL of benzene and heated in a Teflon® sealed glass bomb at 90°C for one day. The solvent was removed *in vacuo*, and the 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 0.11 g (59%) of a bright yellow powder: ¹H NMR (C₆D₆, 20°C) δ 7.76 (d, $J_{\text{HH}} = 1.1$ Hz, 4H, HIPT-2',6'-H), 7.20 (s, 8H, HIPT 3,5,3'',5''-H), 6.70 (br t, $J_{\text{HH}} = 1.1$ Hz, 2H, HIPT 4'-H), 6.65 (s, 2H, Mes-3,5-H), 3.47 (m, 4H, HIPT-NCH₂CH₂), 3.20 (m, 10H, containing 2,6,2'',6''-CHMe₂ and Mes-NCH₂CH₂), 2.90 (septet, $J_{\text{HH}} = 6.9$ Hz, 4H, 4,4''-CHMe₂), 2.25 (s, 9H, Mes-CH₃) 2.1 (m, 6H, containing Mes-NCH₂CH₂, and HIPT-NCH₂CH₂), 1.34 (d, $J_{\text{HH}} = 6.9$ Hz, 24H, 4,4''-CH(CH₃)₂), 1.30 (d, $J_{\text{HH}} = 6.9$ Hz, 24H, 2,6,2'',6''-CH(CH₃)₂), 1.20 (d, $J_{\text{HH}} = 6.9$ Hz, 12H, 2,6,2'',6''-CH(CH₃)₂), 1.17 (d, $J_{\text{HH}} = 6.9$ Hz, 12H, 2,6,2'',6''-CH(CH₃)₂). Anal Calcd for C₈₇H₁₂₁MoN₅: C, 78.40; H, 9.15; N, 5.25. Found: C, 77.26; H, 9.17; N, 5.19.

[TripHIPT₂N₃N]MoN (4g)

This compound was synthesized in a manner similar to 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 one day. The solvent was removed *in vacuo* and 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: ¹H NMR (C₆D₆, 20°C) δ 7.77 (d, $J_{\text{HH}} = 1.1$ 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, $J_{\text{HH}} = 1.1$ Hz, 2H, HIPT 4'-H), 3.52 (m, 6H, HIPT-NCH₂CH₂), 3.34 (br t, $J_{\text{HH}} = 5.5$ Hz, 2H, Trip-NCH₂CH₂), 3.17 (m, 10H, containing HIPT-2,6,2'',6''-CHMe₂, and Trip-2,6-CHMe₂), 2.95 (septet, $J_{\text{HH}} = 6.9$ Hz, 2H, HIPT-4,4''-CHMe₂), 2.81 (septet, $J_{\text{HH}} = 6.9$ Hz, 1H, Trip-4-CHMe₂), 2.21 (m, 8H, containing Trip-NCH₂CH₂ and HIPT-NCH₂CH₂), 1.38 (d, $J_{\text{HH}} = 6.9$ Hz, 24H, HIPT 4,4''-CH

(CH₃)₂), 1.24 (m, 36H, contains Trip-4- CH(CH₃)₂ and HIPT-2,6,2'',6''-CH(CH₃)₂), 1.13 (m, 24H, contains Trip- 2,6,2'',6''-CH(CH₃)₂ and HIPT- 2,6,2'',6''-CH(CH₃)₂). Anal Calcd for C₉₃H₁₃₃MoN₅: C, 78.83; H, 9.46; N, 4.94. Found: C, 78.91; H, 9.48; N, 4.86.

{[3,5-Bis(CF₃)HIPT₂N₃N]MoN₂}Na(THF)₂ (5c)

Compound **3c** (0.56 g) was dissolved in 20 mL THF and 4.8 g of 0.5% Na/Hg amalgam was added. The mixture was stirred with a glass stir bar for two hours until the solution turned a deep green. The mixture 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 yielding 0.45 g (70%) of a purple powder in multiple crops. A similar method was utilized to synthesize the ¹⁵N₂ labeled species: ¹H NMR (C₆D₆, 20°C) δ 7.68 (s, 1H, CF₃ arm 4-*H*), 7.59 (s, 2H, HIPT 4'-*H*), 7.45 (d, J_{HH} = 1.2 Hz, 2H, CF₃ 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-NCH₂CH₂ and CF₃-NCH₂CH₂), 3.38 (overlapping septets, J_{HH} = 6.9 Hz, 8H, 2,6,2'',6''-CHMe₂), 3.22 (br m, 8H, THF O-CH₂), 2.84 (overlapping septets, J_{HH} = 6.9 Hz, 4H, 4, 4''-CHMe₂), 1.94 (br m, containing both HIPT-NCH₂CH₂ and CF₃- NCH₂CH₂), 1.23 (overlapping doublets, 52H containing 2,4,6,2'',4'',6''-CH(CH₃)₂), 1.1 (d, J_{HH} = 6.9 Hz, 12H, 4, 4''-CH(CH₃)₂). ¹⁹F NMR (C₆D₆, 20°C), δ -61.76. IR (ν_{NN} 1801 cm⁻¹; ¹⁵N₂ labeled ν_{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.¹⁷²

{LMO₂}Na(THF)₂

Synthetic procedures for all other LMO₂Na(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.

LMO₂ (6a–g)

No neutral dinitrogen complexes could be isolated as pure compounds. They could be observed only *via* IR and NMR spectroscopy. Typically LMOCl 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 ZnCl₂. The resulting brown solution was then filtered through Celite and the solvent 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 ¹H NMR were similar to those of the symmetric compounds of this type (3 peaks at δ ~ 10 to 20ppm, 2 peaks at ~ -3 to -10 ppm, and 3 peaks at -20 to -40 ppm).

{[3,5-Bis(CF₃)HIPT₂N₃N]MoNH₃}[BAR₄'] (7c)

This compound has been identified *via* NMR from the 1:1 reaction of **3c** and NaBAR₄' under 6 equivalents of ammonia in dichloromethane. After the mixture was stirred for one 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: ¹H NMR (C₆D₆, 20°C) δ 8.23 (s, BAR₄'), 7.61 (s, BAR₄'), 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); ¹⁹F NMR (C₆D₆, 20°C) δ -61.3 (MoNH₃⁺), -61.45 (BAR₄'). We were unable to remove NaBAR₄' from the solid completely (~5% *via* ¹⁹F NMR).

[(3,5-DimethoxyHIPT₂N₃N)Mo(NH₃)] [BAr₄⁻] (7e)

A mixture of **3e** (100 mg) and 65 mg of Na[BAr₄⁻] was dissolved in 10 mL of CH₂Cl₂ 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%): ¹H NMR (C₆D₆, 20°C) δ 8.36 (br s, BAr₄⁻), 7.68 (br s, BAr₄⁻), 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 C₁₁₈H₁₃₄BF₂₄MoN₅O₂: 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 MoK α radiation ($\lambda = 0.71073 \text{ \AA}$), performing ϕ and ω -scans. The structures were solved by direct methods using SHELXS¹⁹ 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 CF₃ 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 owing to the massive disorder the crystal diffracted only to about 1.0 \AA 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 C₈₆H₁₁₉MoN₆, 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 non-coordinated THF molecule (sixfold disordered about the crystallographic -3 axis), two half occupied heptane molecules, and one sixth of a pentane molecule (sixfold 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.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

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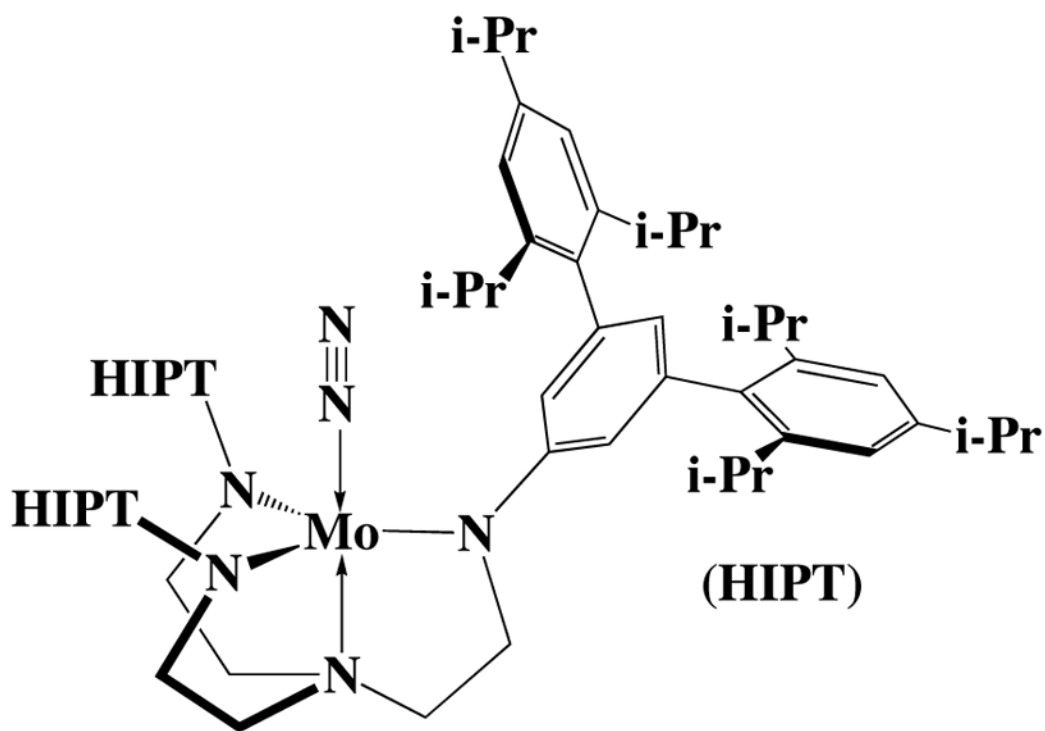


Figure 1.
A drawing of $[\text{HIPTN}_3\text{N}]\text{MoN}_2 = \text{MoN}_2$.

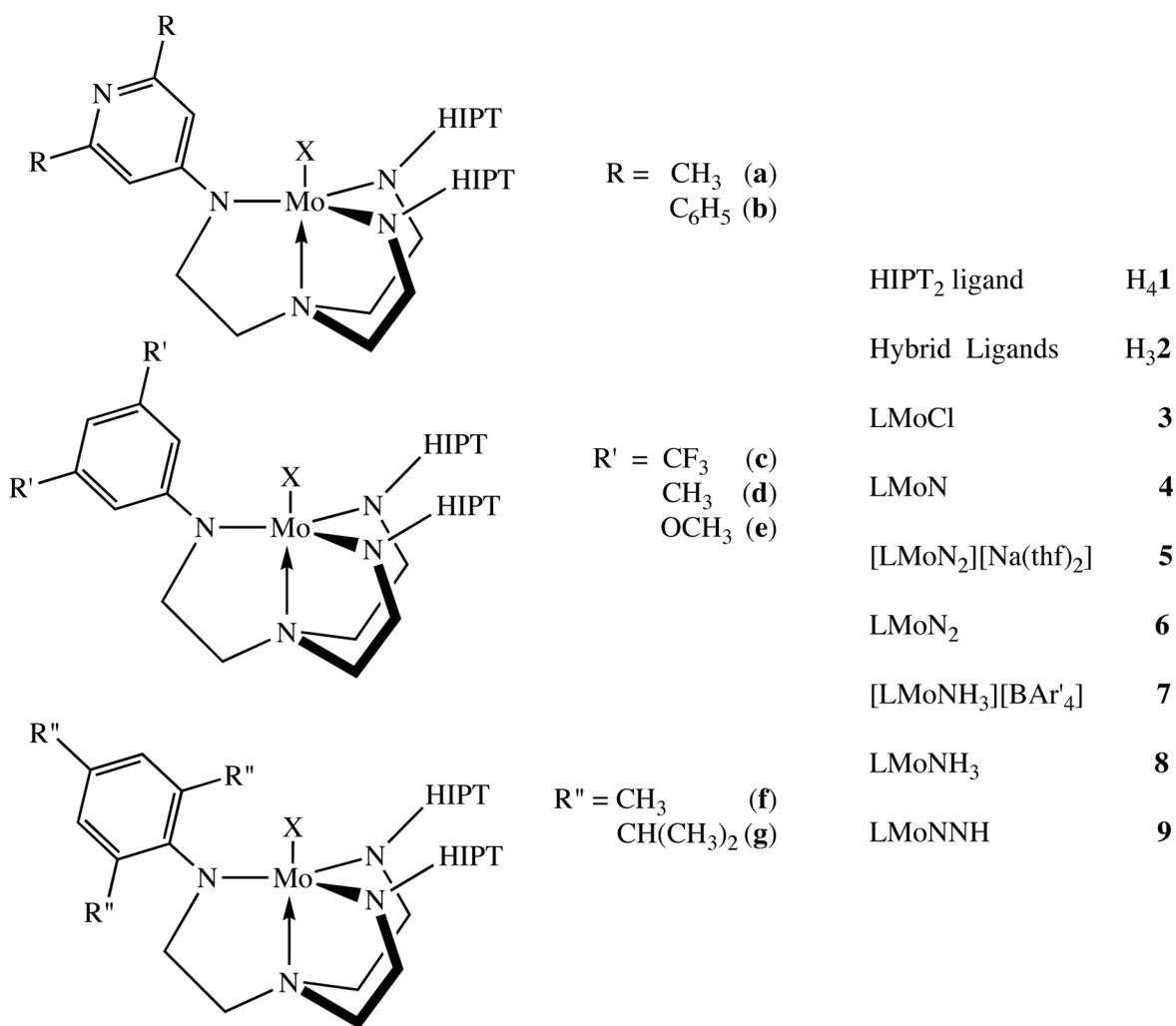


Figure 2. Labeling scheme for ligands and metal complexes described in this paper.

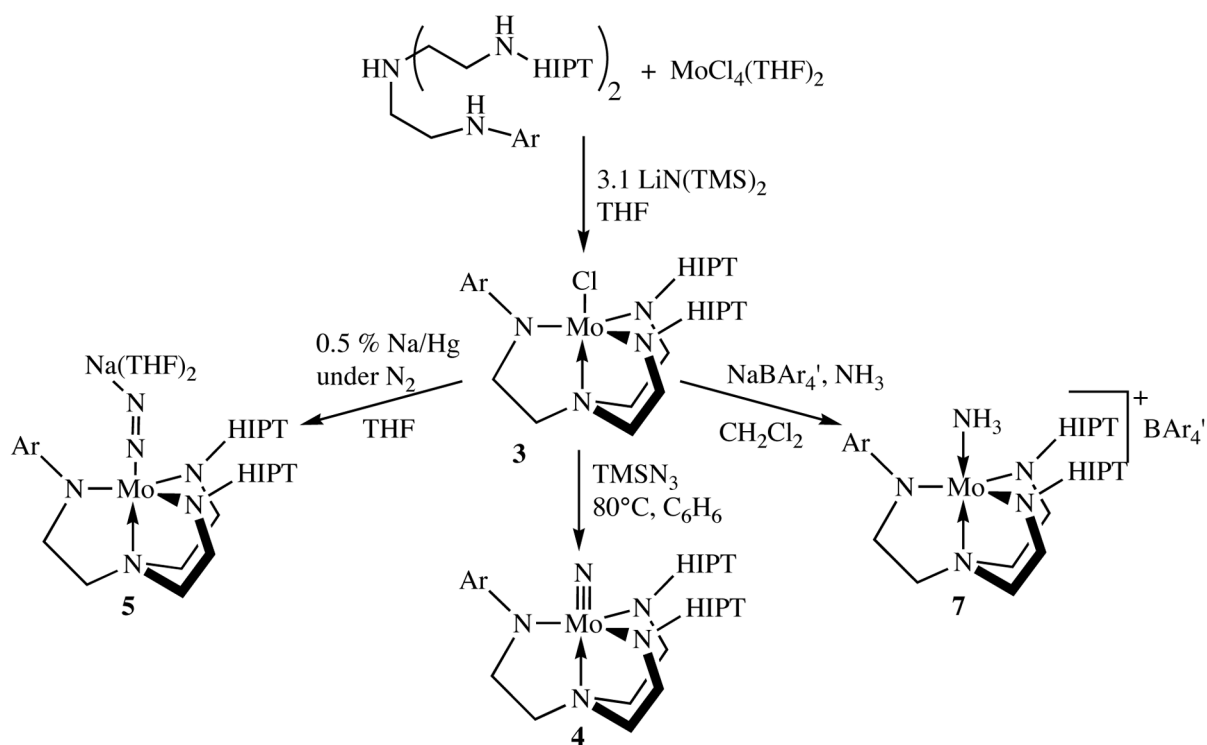


Figure 3. Synthesis of molybdenum complexes that contain “hybrid” ligands.

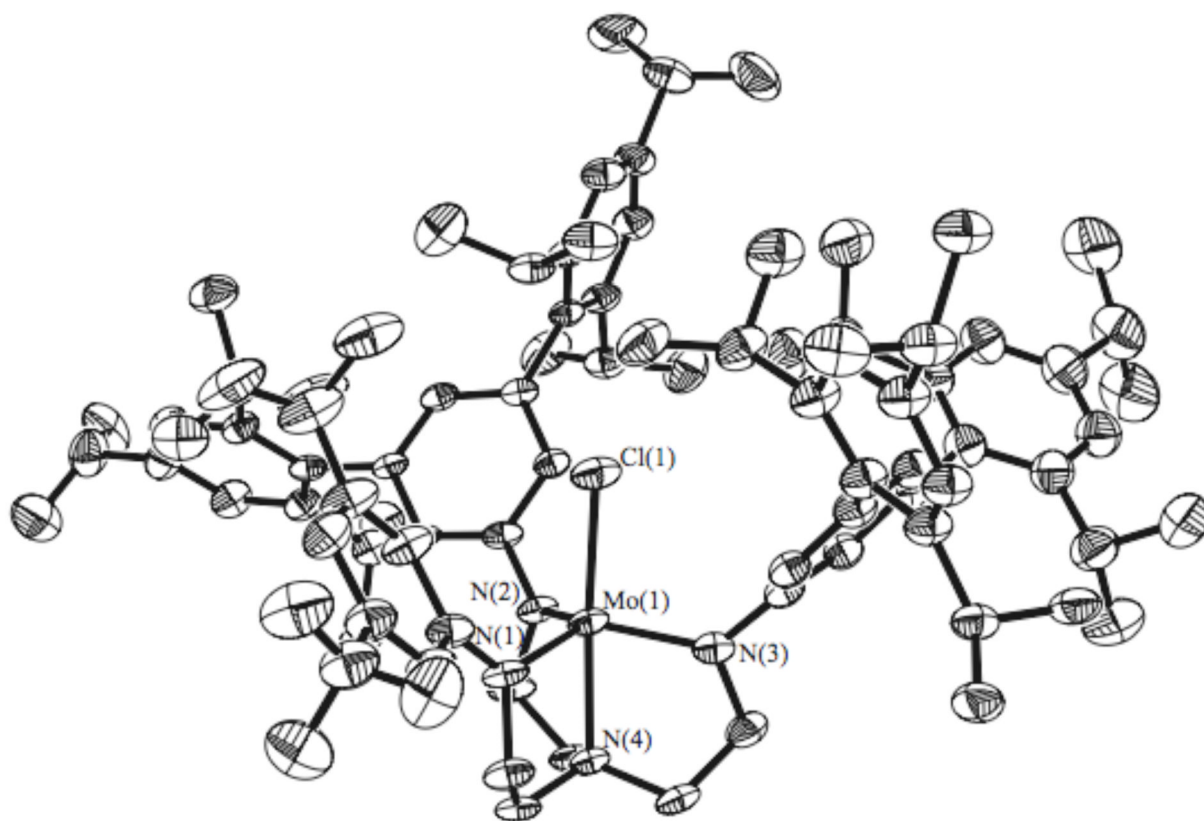


Figure 4.
X-ray crystal structure of **3c**. Hydrogen atoms have been removed for clarity.

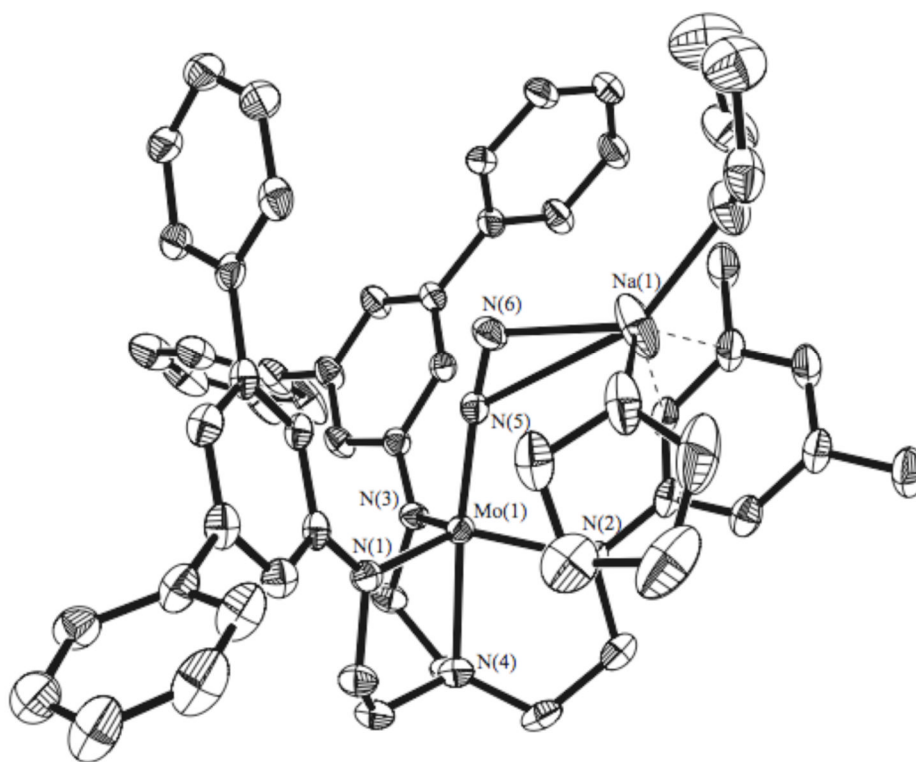


Figure 5. X-Ray crystal structure of **5d**. Hydrogen atoms and isopropyl groups have been removed for clarity.

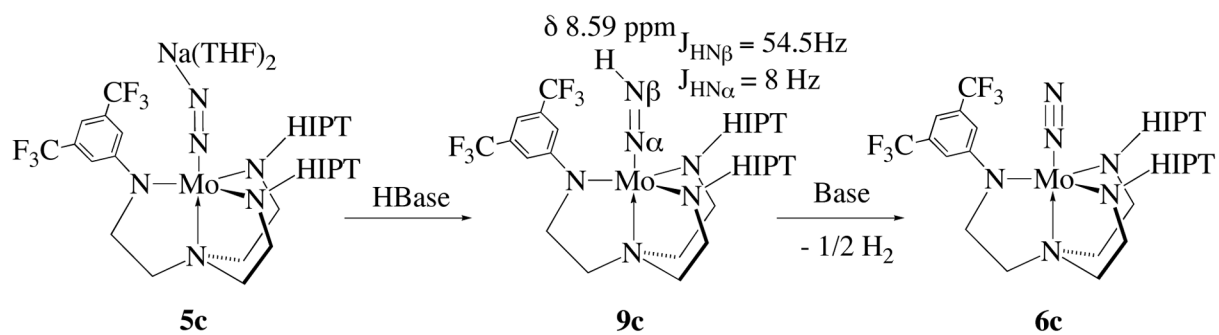


Figure 6. Synthesis and decomposition of hybrid diazenide **9c**.

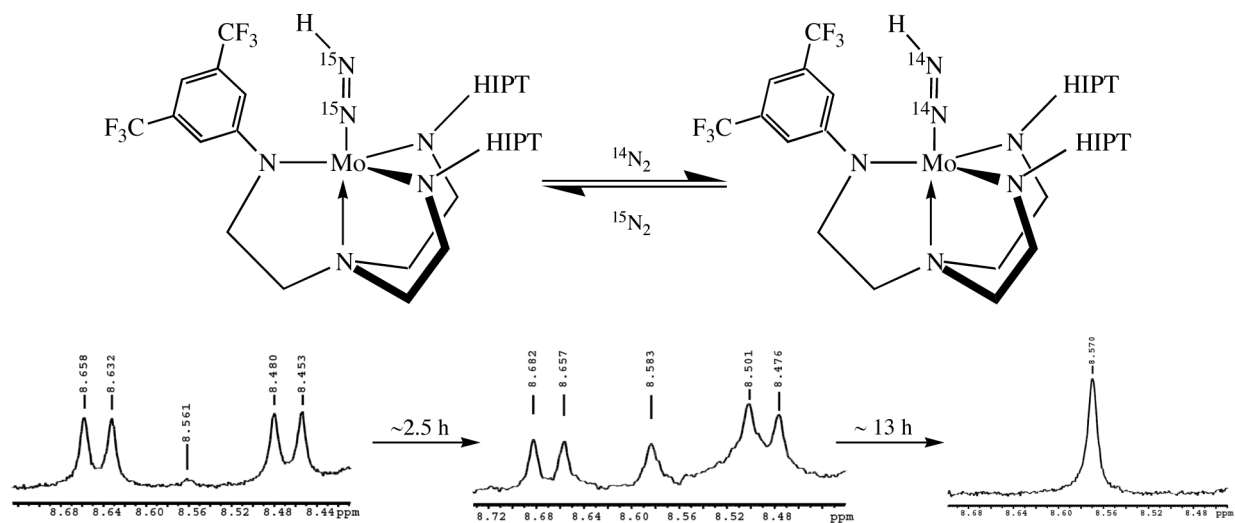


Figure 7.
 $^{14}\text{N}_2$ exchange into the $^{15}\text{N}_2$ -labeled diazenide **9c**.

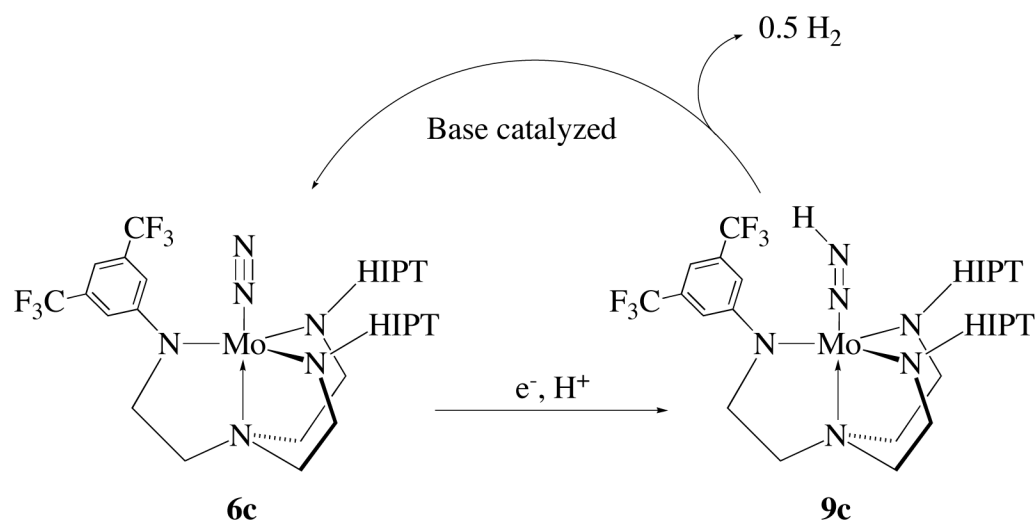


Figure 8. Hydrogenase shunt that limits catalysis in less sterically demanding systems.

Table 1Selected Bond Lengths and Angles of **3c** vs. HTBTMoCl.⁶

Bond	3c	HTBTMoCl
Mo-Cl	2.331(2) Å	2.33 Å
Mo-N1 (amide)	1.978(7) Å	1.99 Å
Mo-N4 (amine)	2.199(6) Å	2.34 Å
N4-Mo-N1	100.20(18)°	99°
N4-Mo-Cl	176.10(17)°	179°

Table 2Selected Bond Lengths and Angles of **5d** vs. [HIPTMoN₂][MgBr(THF)₃].¹⁷

Bond	5d	[HIPTMoN ₂][MgBr(THF) ₃]
N5-N6 (Nitrogen)	1.171(6) Å	1.15 Å
Mo-N5 (Dinitrogen)	1.882(4) Å	1.86 Å
Mo-N4 (Amine)	2.209(4) Å	2.24 Å
Mo-N3 (Amide)	2.022(4) Å	2.02 Å
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)°	

Table 3
Dinitrogen stretching modes for LMoN₂ compounds.

Compound	$\nu_{\text{N-N}}$ in cm^{-1}
[HIPTN ₃ N]MoN ₂	1990
[pBrHIPTN ₃ N]MoN ₂	1992
[HTBTN ₃ N]MoN ₂	1990
6a	1991
6b	1988
6c	1992
6d	1987
6e	1984
6f	1986
6g	2007

Table 4

Equivalents of ammonia obtained when LMoN is the precatalyst.

Compound	Equiv NH ₃ from N ₂
4a	0.6
4b	0.3
4c	0
4d	0
4e	0
4f	0.2
4g	2.0