Synthesis of Molybdenum Complexes that Contain “Hybrid” Triamidoamine Ligands, [(Hexaisopropylterphenyl-NCH2CH2)2NCH2CH2N-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-Pr3C6H2)2C6H3 = hexaisopropylterphenyl) and (H2NCH2CH2)3N, it is possible to obtain a 65% isolated yield of (HIPTNHC6H5)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-Ph2C6H3, 2,4,6-i-Pr3C6H2, or 2,4,6-Me2C6H2. 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]MoN2Na, and [hybrid]Mo(NH3)3+ can be prepared. [Hybrid]MoN2 species were prepared through oxidation of [hybrid]MoN2Na species with ZnCl2, but they could not be isolated. [Hybrid]Mo=N−NH species could be observed as a consequence of the 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 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 [(HIPTNHCH2CH2)2NCH2CH2N(3,5-Me2C6H3)]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− ([RN3]3−).1 These triamionic 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 (dπ and dπ) and one has σ symmetry (~dσ). These orbitals can be employed in three combinations (2π/1σ, 1π/2σ, or 3σ) to bind substrates in the trigonal pocket. Distortion of the pseudotrigonal symmetry to yield pseudo-octahedral 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 [HIPTN3]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.5

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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]−, 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 Chatt-like reduction cycle.

“Symmetric” variations of the [HIPTN3N]3− ligand that have been prepared and attached to molybdenum include the hexa-tert-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, [pBrHIPTN3N]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.)6 We believe it is for this reason that [HTBTN3N]MoB=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]MoB=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 [pBrHIPTN3N]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 [HIPTN3N]Mo species are employed. Since electronic differences (redox potentials and values for \( \nu_{(N=N)} \)) 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 3 equiv of...
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HTBBr and (H₂NCH₂CH₃)₂N the third equivalent of HTBBr reacts significantly more slowly than the second equivalent. Therefore, (HTBNHCH₂CH₃)₂NCH₂CH₂NH₂ could be isolated in good yield 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 (HTBNHCH₂CH₃)₂NCH₂CH₂NHAr species. We found that the third “arm” of the ligand to yield what we call a hybrid 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 between HIPTBr and (H₂NCH₂CH₃)₂N, then a mixture results that consists largely of (HIPTNCH₂CH₃)₂NCH₂CH₂NH₂ mixed with a small amount of (HIPTNHHCH₂)₂N (11% yield) elutes readily with toluene. The flushing of the column with a 1:1 mixture of toluene and tetrahydrofuran then yields readily with toluene. The flushing of the column with a 1:1 mixture of toluene and tetrahydrofuran then yields (HIPTNHHCH₂)₂NCH₂CH₂NH₂ (H₂I, 65% yield on a ~50 g scale; eq 1). The (HIPTNHHCH₂)₂N ligand can be accumulated and employed in other studies.

A second Buchwald–Hartwig coupling can be carried out on the terminal amine in (HIPTNHHCH₂)₂NCH₂CH₂NH₂ to yield (HIPTNHHCH₂)₂NCH₂CH₂NHAr species H₂2a—H₂2g (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 C₄ symmetry.

The hybrid ligands were attached to Mo in the same way as the [HIPTN₃N]³⁻ ligands (i.e., the parent ligands were added to a solution of MoCl₄(THF)₂ and the mixture was then treated with three equivalents of LiN(TMS)₂ (Figure 3)). The resulting bright orange paramagnetic [hybrid]MoCl₃ 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 [HIPTN₃N]MoCl₃ species. The proton NMR spectra of the [hybrid]MoCl₃ compounds reveal paramagnetically shifted methylene resonances similar to those observed for [HIPTN₃N]MoCl₃, with separate ethylene 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 C₄ symmetry of the hybrid complex. It should be noted that symmetric (ArNHCH₂CH₂)₃N ligands cannot be placed onto Mo using the method described above when Ar is 2,4,6-trimethylphenyl, 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 [HIPTN₃N]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 [HIPTN₃N]Mo, [HTBNT₂N]Mo, and [pBrHIPT₂N]Mo systems.

One of the least air-sensitive [HIPTN₃N]Mo compounds that can be employed as a catalyst precursor in dinitrogen reduction is the nitride, [HIPTN₃N]MoN. The bright yellow, diamagnetic [hybrid]MoN compounds 4a–4g (Figure 3) were prepared in reactions between [hybrid]MoCl₃ and trimethylsilyl azide in benzene at elevated temperatures. NMR spectra of the diamagnetic [hybrid]MoN species are fully consistent with their C₄ symmetry. The [hybrid]MoN species also are relatively crystalline and readily isolated. All have been analyzed and fully characterized.

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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, \([\text{hybrid}]\text{MoN}_2\)Na(THF)\(_2\). Although all \([\text{hybrid}]\text{MoN}_2\)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) \(110^\circ\) to the 3,5-dimethylphenyl group. Coordination of the sodium ion to the two nitrogens in the diazenido ligand decreases the Mo–N\(_d\)N angle slightly to \(174^\circ\).

The \([\text{hybrid}]\text{MoN}_2\)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\(_2\))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,
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 νNN absorption near 1990 cm⁻¹, as previously observed for MoN₂ compounds that contain “symmetric” ligands such as [HIPTN3 N]⁻. These νNN stretches are listed in Table 3. The νNN 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 νNN stretch moves to lower energies as the hybrid ligand’s substituents become more electron-donating (i.e., νNN = 1992 cm⁻¹ for 6c vs νNN = 1984 cm⁻¹ for 6e). The exception to this trend is 6g, where νNN 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–N₂ bond slightly and therefore reduces the amount of backbonding to dinitrogen. As we shall see, however, the νNN 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 NaBAr₄⁻ (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 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. Briefly, a heptane slurry containing 48 equiv of [2,6-lutidine][BAr₄⁻] and 4a–4g was placed in the reaction vessel, and 36 equiv of decamethylcyclohexane in 10 mL of heptane was added with a syringe pump. (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.

None of the compounds that contain one of the new hybrid ligands is as efficient a catalyst for the reduction of dinitrogen as the [HIPTN3 N]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 [HIPTN3 N]-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(II) dinitrogen complex. Two of the LMoNH₃ complexes were prepared in situ through reduction of 7c and 7e with CrCp²⁻. 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. For 8c, t₁/₂ = 180 min, while for 8e, t₁/₂ < 45 min. It should be stressed that these results are only semiquantitative, since the ammonia that is released 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 t₁/₂ ≈ 120 min. Exchange was estimated to actually be approximately 10 times faster than that observed in “bulk” exchange reactions. However, data for this first-order reaction of hybrid complexes are useful when compared with analogous data obtained for the parent system. In short, the rate of exchange appears to be slightly slower when CF₃ groups are present (t₁/₂ = 180 min) and faster when methoxy groups are present (t₁/₂ < 45 min). Although we have not shown that the exchange rates in the hybrid systems depend on dinitrogen pressure, as in the parent system, 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
any case, the main point is that slow exchange cannot be the reason 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 equiv 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, the 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. However, to our knowledge only the molybdenum and tungsten compounds in the symmetric HIPT system have been confirmed to have a proton on the nitrogen in 15 N-labeled compounds. Fortunately, the [ArN3N]Mo=N=NH species are diamagnetic, so the presence of a proton on N may be confirmed 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 [ArN3N]Mo=N=NH compound containing the 3,5-trifluoromethylphenyl-substituted arm (9c). Although the results for this compound have been reported recently, a summary is reported below.

Treatment of 5c (both 15 N and 14 N) with a proton source (initially H(OEt2)2BAr4′) resulted in the formation of 9c. This species was identified through observation of Mo=N=NH at 8.6 ppm, with J(NH) = 54.5 Hz and J(NH) = 8 Hz (absolute values) in the 15 N-labeled compound (Figure 6). These values are nearly identical to those obtained for [HIPTN3N]Mo=N=NH. Compound 9c decomposes in a manner that is first order in Mo to form 6c quantitatively (and H2) with a t1/2 of 17 ± 2 h. In contrast, pure [HIPTN3N]Mo=N=NH decomposes only very slowly to [HIPTN3N]MoH (at 60 °C, t1/2 = 90 h). 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 (t1/2 of 4.5 h; Figure 7). The mechanism of this exchange (which also can be observed in [HIPTN3N]-Mo=15 N=15 NH, albeit with a much slower t1/2 of approximately 150 h) is under further study. We suspect that nitrogen exchange is dependent upon nitrogen pressure (i.e., it does not involve a-hydride elimination to yield [HIPTN3N]-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]BAr4′ was used to form 9c, the decomposition rate was enhanced by an order of magnitude, resulting in a t1/2 of 1.1 h. When 9c was prepared with H(OEt2)2BAr4′ and 4 equiv of 2,6-lutidine, 2,4,6-trimethylypyridine (collidine), or Et3N were added subsequently, 9c could not be observed 5 min after addition of the base: only 6c and H2 were observed as the major products. The ability of Et3N 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
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![Figure 8. Hydrogen shunt that limits catalysis in less sterically demanding systems.](image)

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 [HIPTN3N]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 is 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.8,10,11 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,2,5 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 three 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-d6 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-trinitrobenzene (Strem), NaO-t-Bu (Aldrich), Pd 2 (dba) 3 (Strem), CuCl 3 (Strem), triethyamine (Aldrich), NaO-t-Bu (Aldrich), Pd 2 (dba) 3 (Strem), rac-BINAP (Strem), and tris(2-...
aminoethylamine (Aldrich) were used as received, unless indicated otherwise. Hexaisopropylterphenyl bromide (HIPTBr), 2,4,6-trimethoxy-1-isodophenene, and 4-bromo-2,6-dimethylpyridine 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 (δH and 13C NMR) or to external CD3F (δ = −113.15 ppm in the 1H NMR spectrum). All stated coupling constants should be considered as absolute values.

**HIPT[NCH2(CH3)2]2NCH2CH2NH2**. The procedure is similar to that of the previous syntheses of symmetric ligands but uses 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 subject to column chromatography on silica gel. The resulting solid was dissolved in pentane and loaded onto a silica column which had been pretreated with triethylamine. The product was eluted with pentane and THF.

**4-Bromo-2,6-diphenyl-pyridine** (1.55 g, 5.02 mmol), and NaO-t-Bu (0.64 g, 6.66 mmol). This solution 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 gel as described in earlier preparations. Yield: 2.07 g of the product as a light yellow foamy solid (46%).

**H3[PhLutHIPT[N3N]2]** (2b). A solution of Pd2(dba)2 (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 I (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 solution 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 gel as described in earlier preparations. Yield: 2.07 g of the product as a light yellow foamy solid (46%).
Mo Complexes Containing “Hybrid” Triamidoamine Ligands

1H, CF₃ arm 4-H), 7.22 (s, 8H, HIPT 3.5,3′,5′-H), 6.64 (s, 2H, CF₃ arm 2-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 ÑH), 3.51 (br s, 2H, HIPT-ÑH), 3.15 (septet, J_HH = 6.9 Hz, 8H, 2,6,2′,6′-CH₂Me₂), 2.90 (septet, J_HH = 6.9 Hz, 4H, 4,4′-CH₂Me₂), 2.82 (br t, J_HH = 5.8 Hz, 4H, HIPT-NCH₂CH₃), 2.40 (br q, J_HH = 5.2 Hz, 2H, CF₃ arm NCH₂CH₃), 2.17 (br t, J_HH = 5.8 Hz, 4H, HIPT-NCH₂CH₃), 2.10 (br t, J_HH = 5.8 Hz, 2H, CF₃ arm NCH₂CH₃) 1.23 (d, J_HH = 6.9 Hz, 24H, 4,4′-CH₂Me₂), 1.28 (d, J_HH = 6.9 Hz, 24H, 4,4′-CH₂Me₂), 1.25 (d, J_HH = 6.9 Hz, 24H, 4,4′-CH₂Me₂). 1° NMR (C₆D₆, 20 °C): δ 149.41, 148.66, 148.25, 147.13, 147.29, 138.31, 133.33, 132.91, 122.28, 121.12, 128.89, 113.30, 110.36, 52.95, 52.21, 45.51, 49.01, 35.25, 31.21, 25.28, 24.99, 24.83. 13° NMR (C₆D₆, 20 °C): δ −62.74. HRMS (EI): 1319.9156 ([M + H]+), calc 1319.9177.

H₃[3,5-DimethylHIPT₂N₃] (2d). 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 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° 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-H), 3.94 (br s, 2H, HIPT-NH₂), 3.75 (br s, 1H, dimethyl-NH₂), 3.16 (septet, J_HH = 6.9 Hz, 8H, HIPT 4,4′-CH₂Me₂), 2.88 (m, 8H, containing 4,4′-CH₂Me₂ and HIPT-NCH₂CH₃), 2.58 (br s, 8H, HIPT 3,5,3′,5′-H). 13° NMR (C₆D₆, 20 °C): δ 148.79, 148.49, 148.44, 147.17, 145.28, 139.28, 138.98, 131.28, 120.61, 120.74, 117.31, 117.11, 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]+), calc 1211.9742.

H₃[3,5-DimethoxyHIPT₂N₃] (2e). This compound was prepared in a manner similar to the other hybrid ligand systems. Briefly, 0.037 g (40 mmol) of Pd₂(dba)₃ and 0.077 g (162 mmol) of X-Phos were dissolved in 142 mL of toluene. This container was then sealed and heated at 110 °C for 1 day. The mixture was then filtered through Celite, and the solution was filtered again through Celite. The product was isolated from a silica gel column. The compound was then filtered 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 passed through a silica gel. 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 (HIPT(NHCH₂CH₃)_2)_2NCH₂NH₂ 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° NMR (C₆D₆, 20 °C): δ 7.21 (s, 8H, HIPT 3.5,3′,5′-H), 7.06 (s, 2H, HIPT 3,5,3′,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-NH₂), 3.38 (septet, J_HH = 6.9 Hz, 8H, HIPT 2,6,2′,6′-CH₂Me₂), 3.17 (septet, J_HH = 6.9 Hz, 8H, HIPT 2,6,2′,6′-CH₂Me₂), 2.89 (m, 12H, containing HIPT-NCH₂CH₃, Trip-NCH₂CH₃, HIPT-4,4′-CH₂(CH₃)₂, and Trip-4-CH(CH₃)₂), 2.44 (br t, J_HH = 5.5 Hz, 2H, Trip-NCH₂CH₃), 2.33 (br t, J_HH = 5.5 Hz, 4H, HIPT-CH₂CH₃), 1.32 (d, J_HH = 6.9 Hz, 24H, 4,4′-CH₂(CH₃)₂), 1.25 (m, 56H, 2,6,2′,6′-CH₂(CH₃)₂). 13° 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]+), calc 1310.0838.

[LutHIPT₂N₃]MoCl₃ (3a). The procedure followed was nearly identical to published procedures.6 Briefly, H₂a (0.6 g, 0.50 mmol) and MoCl₅(THF)₂ (0.19 g, 0.50 mmol) were dissolved in THF (40 mL). The solution was stirred for 1 h 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 (C 6 D 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), 1.67 (br s), 23.8 (br s), 65.0 (br s), 69.4 (br s). Anal. Calc'd for C 27 H 113 ClMoN 5 : C, 76.11; H, 8.87; N, 3.87. Found: C, 76.25; H, 8.72; N, 3.91.

[PhLutHIPT 3 N]MoCl (3b). The procedure followed was nearly identical to published procedures. 4 Briefly, H 2 Z (1 g, 0.75 mmol) and MoCl 2 (THF) 2 (0.286 g, 0.75 mmol) were dissolved in THF (75 mL). This solution was stirred for 1 h, and (Me 3 Si) 2 NLi (0.388 g, 2.3 mmol) was then added slowly. After 2 h, the solvent was removed in vacuo. The residue was recrystallized from pentane to yield 0.74 g (67%) of a deep orange crystalline solid. 1H NMR (C 6 D 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. Calc'd for C 36 H 63 ClMoN 5 : C, 77.66; H, 9.38; N, 3.77. Found: C, 77.65; H, 9.38; N, 3.77.

[TripHIPT 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 2 2a was dissolved in 50 mL of THF. MoCl 2 (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 3 Si) 2 NLi 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. 1H NMR (C 6 D 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. Calc'd for C 36 H 63 ClMoN 5 : C, 77.65; H, 9.32; N, 3.89. Found: C, 77.42; H, 9.38; N, 3.77.

[LutHIPT 3 N]MoN (4a). This compound could not be isolated in pure form because the reaction between (3a) and Me 3 SiN 3 is low yielding, and the final product consequently was contaminated with H 2 2a, even after multiple recrystallizations. A sample containing ~10% H 2 2a (according to 1H NMR) was used in test catalytic runs.
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H₂, 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 C₈₀H₁₂₀MoN₅O₂: C, 79.02; H, 8.52; N, 5.82. Found: C, 78.88; H, 8.45; N, 5.88.

[3,5-Bis(CF₃)HPT₂N₅][MoN (4e)]. This compound was made in a manner similar to other compounds of its type. Briefly, 0.17 g (117 mmol) of 3e and 0.07 g (608 mmol) of Me₂SiN₃ 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. ¹H NMR (CD₂Cl₂, 20 °C): δ 7.93 (s, 2H, CF₃ arm, 2.6,2'-6-H). 7.70 (d, J_HH = 1.4 Hz, 4H, HPT'-2,6'-H). 7.39 (s, 1H, CF₃ arm, 4-H). 7.19 (s, 8H, HPT 3,5,3'-5'-H). 6.81 (br t, J_HH = 1.1 Hz, 2H, HPT'-4'H, 3.53 (br t, J_HH = 4.7 Hz, 4H, HPT'-NCH₂CH₃), 3.15 (overlapping septs, J_HH = 6.9 Hz, 8H, 2,6,2'-6'-CH₂Me₂), 2.90 (septet, J_HH = 6.9 Hz, 4H, 4,4' -CH₂Me₂). 2.83 (br t, J_HH = 4.8 Hz, 2H, CF₃ arm-NCH₂CH₃), 1.97 (br t, J_HH = 5.1 Hz, 4H, HPT'-NHCH₂CH₃), 1.92 (br t, J_HH = 5.0 Hz, 2H, CF₃ arm-NCH₂CH₃), 1.34 (br t, J_HH = 6.9 Hz, 4H, 4,4' -CH₂Me₂), 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), 0.07 g (55%) of a bright yellow powder in multiple recrystallized to yield 0.12 g (72%) of a bright yellow solid. ¹H NMR (CD₂Cl₂, 20 °C): δ 7.76 (d, J_HH = 1.1 Hz, 4H, HPT'-2,6'-H). 7.20 (s, 8H, HPT 3,5,3'-5'-H). 6.70 (br t, J_HH = 1.1 Hz, 2H, HPT' 4'-H), 6.65 (s, 2H, Mes-3,5-H), 3.47 (m, 4H, HPT'-NCH₂CH₃), 3.20 (m, 10H, containing 2,6,2'-6'-CH₂Me₂ and Mes-NCH₂CH₃). 2.90 (septet, J_HH = 6.9 Hz, 4H, 4,4' -CH₂Me₂), 2.25 (s, 9H, Mes-CH₃). 2.10 (m, 8H, containing Mes-NCH₂CH₃, and HPT'-NCH₂CH₃), 1.34 (d, J_HH = 6.9 Hz, 24H, 2,6,2'-6'-CH(CH₃)₂), 1.20 (d, J_HH = 6.9 Hz, 12H, 2,6,2'-6'-CH(CH₃)₂), 0.12 g (72%) of a bright yellow solid. Anal. Calcd for C₇₈H₁₄₀MoN₅O₂: C, 78.40; H, 9.15; N, 5.25. Found: C, 77.26; H, 9.17; N, 5.19.

[TriHPT₂N₅][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. ¹H NMR (CD₂Cl₂, 20 °C): δ 7.77 (d, J_HH = 1.1 Hz, 4H, HPT'-2,6'-H), 7.19 (m, 8H, HPT 3,5,3'-5'-H). 7.08 (s, 2H, Trip-3,5-H), 6.73 (br t, J_HH = 1.1 Hz, 2H, HPT' 4'-H), 5.32 (m, 6H, HPT'-NCH₂CH₃), 3.34 (br t, J_HH = 5.5 Hz, 2H, Trip-NCH₂CH₃), 3.17 (m, 10H, containing HPT-2,6,2'-6'-CH₂Me₂, and Trip-2,6-CH₂Me₂), 2.95 (septet, J_HH = 6.9 Hz, 2H, 4,4'-CH₂Me₂), 2.81 (septet, J_HH = 6.9 Hz, 1H, Trip-4'CH₂Me₂), 2.21 (m, 8H, containing Trip-NCH₂CH₃ and HPT'-NCH₂CH₃), 1.38 (d, J_HH = 6.9 Hz, 24H, 4,4' -CH₂Me₂), 1.24 (m, 36H, contains Trip-4'CH₂Me₂ and HPT-2,6,2'-6'-CH(CH₃)₂), 1.13 (m, 24H, contains Trip-2,6,2'-6'-CH₂Me₂ and HPT'-2,6,2'-6'-CH(CH₃)₂). Anal. Calcd for C₇₈H₁₄₀MoN₅O₂: C, 78.83; H, 9.46; N, 4.94. Found: C, 78.91; H, 9.48; N, 4.86.

[3,5-Bis(CF₃)HPT₂N₅][MoN₂]Na(THF)₂ (5c). Compound 3c (0.56 g) was dissolved in 20 mL of THF and 4.8 g of 0.5% NaH 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 mixture was dissolved in pentane, and the mixture was filtered through Celite to yield 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 15N₂-labeled species. ¹H NMR (CD₂Cl₂, 20 °C): δ 7.68 (s, 1H, CF₃ arm 4-H), 7.59 (s, 2H, HPT'-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, HPT'-2,6'-H), 7.18 (s, 4H, HPT 3,5,3'-5'-H), 7.13 (s, 4H, HPT'-3,5,3'-5'-H), 3.76 (m, 6H, containing both HPT'-NCH₂CH₃ and CF₃-NCH₂CH₃), 3.38 (overlapping septs, J_HH = 6.9 Hz, 8H, 2,6,2'-6'-CH₂Me₂), 3.22 (br m, 8H, THF-O-CH₂), 2.84 (overlapping septs, J_HH = 6.9 Hz, 4H, 4,4' -CH₂Me₂), 1.94 (m, 2H, containing both HPT'-NCH₂CH₃ and CF₃-NCH₂CH₃), 1.23 (overlapping doublets, 52H containing 2,6,2'-6'-CH(CH₃)₂), 1.12 (d, J_HH = 6.9 Hz, 12H, 2,6,2'-6'-CH(CH₃)₂). ¹F NMR (CD₂Cl₂, 20 °C): δ 19 F NMR (CD₂Cl₂, 20 °C): δ 5.35, 4.92, 4.38, 4.15, 3.90, 3.72, 3.54, 3.36, 3.18, 3.00, 2.82, 2.64, 2.46, 2.28, 2.10, 1.92, 1.74, 1.56, 1.38, 1.20, 1.02, 0.84, 0.66, 0.48, 0.30, 0.12, 0.04 ppm.
IR: $\nu_{\text{NN}} = 1801$ cm$^{-1}$; $^{13}$N$_2$-labeled $\nu_{\text{NN}} = 1741$ 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$_2$]}$_2$Na(THF)$_2$. Synthetic procedures for all other LMoN$_2$-Na(THF)$_2$ compounds were similar to that for 5e. 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 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 ZnCl$_2$. The resulting brown solution was then concentrated to dryness and the resulting solid was filtered through Celite, and the solvents were removed in vacuo. The product was extracted into pentane. The pentane extract was filtered through Celite and the solvents were removed in vacuo. NMR spectroscopy. Typically 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 showed that $10^2$–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 LMoN$_2$ (6a), but elemental analyses were not successful and reproducible for any compound of this type.

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X-ray Structural Studies. Low-temperature diffraction data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS SMART CCD detector with graphite-monochromated Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å), performing $\phi$ and $\omega$ 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 3e 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$_{60}$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 3e and 5d. This material is available free of charge via the Internet at http://pubs.acs.org.

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