Synthesis of DiamidoPyrrolyl Molybdenum Complexes Relevant to Reduction of Dinitrogen to Ammonia

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A potentially useful trianionic ligand for the reduction of dinitrogen catalytically by molybdenum complexes is one in which one of the arms in a [(RNCH2CH=CH2)2]− ligand is replaced by a 2-mesitylpyrrolyl-α-methyl arm, that is, [(RNCH2CH=CH2)2NCH2(2-Mesitylpyrrolyl)]− (R = C6F5, 3,5-Me2C6H3, or 3,5-βBu2C6H3). Compounds have been prepared that contain the ligand in which R = C6F5 ([(C6F5)2Pyr]Mo(NMe2)), [(C6F5)2Pyr]MoCl, [(C6F5)2Pyr]MoOTf, and [(C6F5)2Pyr]MoCN. Compounds that contain the ligand in which R = 3,5-βBu2C6H3 ([(ArβBu2N)2Pyr]Mo(N2)) include [(ArβBu2N)2Pyr]Mo(N2)2(NCMe)2C6H4. X-ray studies are reported for [(C6F5)2Pyr]Mo(NMe2)), [(C6F5)2Pyr]MoCl, and [(ArβBu2N)2Pyr]MoCN. The [(ArβBu2N)2Pyr]Mo(N2)2− reversible couple is found at −1.96 V (in MeOH versus Cp2Fe/H+), but the [(ArβBu2N)2Pyr]Mo(N2)2−/0 couple is irreversible. Reduction of [(ArβBu2N)2Pyr]Mo(NH3)2BPh4 under Ar at approximately −1.68 V at a scan rate of 900 mV/s is not reversible. Ammonia in [(ArβBu2N)2Pyr]Mo(NH3)2BPh4 can be substituted for dinitrogen in about 2 h if 10 equiv of BPh4 are present to trap the ammonia that is released. [(ArβBu2N)2Pyr]MoN2−NH is a key intermediate in the proposed catalytic reduction of dinitrogen that could not be prepared. Dinitrogen exchange studies in [(ArβBu2N)2Pyr]Mo(N2)2 suggest that steric hindrance by the ligand may be insufficient to protect decomposition of [(ArβBu2N)2Pyr]MoN2−NH through a variety of pathways. Three attempts to reduce dinitrogen catalytically with [(ArβBu2N)2Pyr]Mo(N2) as a “catalyst” yielded an average of 1.02 ± 0.12 equiv of NH3.

Introducion

Nitrogenase enzymes (in algae and bacteria) convert dinitrogen to ammonia, but despite intensive study, the mechanism of this conversion is not well understood.1 Discovery of the first
transition metal dinitrogen complex, [Ru(NH3)5(N2)]2+,2 inspired syntheses of other transition metal dinitrogen complexes in the hope that an abiological method of reducing dinitrogen under mild conditions could be devised, one that might eventually compete with or replace the Haber–Bosch process.3 Work concerning dinitrogen functionalization continues today on several fronts.4–7 Only two systems are known in which dinitrogen can be reduced catalytically to ammonia under mild conditions. The first, reported by Shilov,3h requires molybdenum and a


strong reducing agent in methanol. Dinitrogen is reduced first to hydrazine, which is then disproportionated to dinitrogen and ammonia. A typical product is a 1:1 mixture of ammonia and hydrazine. The second catalytic process is selective for formation of ammonia. Dinitrogen is reduced at room temperature (RT) and ambient pressure at a single Mo center protected by a sterically demanding, hexaisopropylterphenyl-substituted triamidoamine ligand, [(3,5-(2,6-di-i-Pr)C6H3)2C5H3(NH2)2CH2N]3+ ([HIPTN3N]3+). Eight of the intermediates in the proposed reduction sequence (Figure 1) were prepared and characterized and several were employed for catalytic N2 reduction.

Slow addition of CrCp*2 (Cp* = C5Me5) to a heptane solution of [HIPTN3N]3+ ([HIPTN3N]3+ + Mo(NH3)6252-(HIPTN3N)Mo(NH3)]3+ containing sparingly soluble [2,6-lutidinium][Ar+] (Ar’ = 3,5-(CF3)2C6H3) led to catalytic reduction of dinitrogen to ammonia, with approximately 1 equiv of dihydrogen being formed per dinitrogen reduced. The maximum yield of ammonia is approximately 8 equiv (four turnovers).

Synthesis and investigation of several variations of the [HIPTN3N]3+ ligand system have shown that use of sterically less demanding ligands or more sterically demanding ligands

Figure 1. Proposed intermediates in the reduction of dinitrogen at a [HIPTN3N]3+ (Mo center) (HIPT = hexaisopropylterphenyl) through stepwise addition of protons and electrons.

Figure 2. “Diamidopyrrolyl” complex.

(tthe hexa-t-butylterphenyl analogue) lead to a decrease in the efficiency of dinitrogen reduction, or even loss of catalytic activity entirely. [HIPTN3N]Mo complexes currently are the most efficient catalysts. Analogous vanadium, chromium, and tungsten systems showed no catalytic activity. Calculations have been carried out on the molybdenum catalyst system, including density functional theory (DFT) calculations with the full ligand, that support the proposed mechanism for dinitrogen reduction in the [HIPTN3N]Mo system.

One of the main reasons why dinitrogen reduction is limited to approximately four turnovers is that the [HIPTN3N]3+ ligand is protonated at an amido nitrogen and ultimately removed from the metal in the presence of reducing agent and acid. Replacing the substituted amido groups in the triamidoamine ligand by pyrrolyl (or pyrrolide) groups was the rationale for the synthesis of complexes that contain a tris(pyrrolyl-α-methyl)amine ligand. However, replacing the three HIPT-substituted amido groups with three substituted pyrrolyl groups is too large a perturbation on the already sensitively electronically and sterically balanced [HIPTN3N]3+ ligand system; a significant problem proved to be binding the tris(pyrrolyl-α-methyl)amine ligand to the metal in a tetradentate fashion. Therefore we turned to the construction of a variation in which one ArNCH2CH3 arm in the trionic triamidoamine ligand is replaced by a pyrrolyl-α-methyl arm; a “diamidopyrrolyl” complex, as shown in Figure 2, became the target. The Ar’ group bound to the α carbon atom in the pyrrolyl (e.g., Ar’ = mesityl) should provide a significant amount of steric protection of a ligand in the apical coordination site. A pyrrolyl would seem less likely to be protonated than an amido nitrogen, and if the pyrrolyl is protonated, the proton is likely to add to an α or β carbon atom to yield a pyrrolene bound to a cationic metal center, as has been shown recently for a cationic tungsten complex. A pyrrolene donor is likely to bind more strongly to a cationic metal center than the aniline formed upon protonation of an amido ligand. Consequently, protonation of a pyrrolyl ligand may yield a relatively stable cationic species. Therefore we felt that a catalyst that contains a diamidopyrrolyl ligand could turn out to be a more stable catalyst for dinitrogen reduction, assuming that all other requirements are met. We report here efforts to prepare complexes that contain diamidopyrrolyl ligands and that function as catalysts for reduction of dinitrogen to ammonia.


molybdenum chloride complex, but approximately what is found for Mo–N_{pyrrolyl} bonds in several molybdenum-$\eta^1$-pyrrolyl complexes.

The chemical shift of the dimethylamido protons in the proton NMR spectrum of $[(C_6F_5)_2N_2Pyr]Mo(NMe_2)$ is temperature dependent, a phenomenon that is analogous to what is found for the triamidoamine complexes, $[C_6F_5N_3N]Mo(NMe_2)$ ($[C_6F_5N_3N]^3^- = [(Me_3SiCH_2CH_2)_2N]^3^-$) and $[C_6F_5N_3N]Mo(NMe_2)$, and which is consistent with a rapid interconversion of diamagnetic (S = 0) and paramagnetic (S = 1) forms. The changes in the chemical shifts of the dimethylamido protons in $[C_6F_5N]Mo(NMe_2)$ (~9 ppm from 180 to 304 K) and $[C_6F_5N_2N]Mo(NMe_2)$ (~2.8 ppm from 259–367 K) are larger than in $[(C_6F_5)_2N_2Pyr]Mo(NMe_2)$ (0.12 ppm from 232–302 K; see Figure S1 in the Supporting Information). If we assume that the temperature dependent chemical shifts are a consequence of interconversion of high spin and low spin forms, then $\Delta H^\circ$ is calculated to be 27(15) kJ mol$^{-1}$; although $\Delta H^\circ$ for $[(C_6F_5)_2N_2Pyr]-Mo(NMe_2)$ cannot be calculated accurately, the energy difference between the high and low spin states of $[(C_6F_5)_2N_2Pyr]-Mo(NMe_2)$ clearly is much greater than that in $[C_6F_5N_3N]Mo(NMe_2)$ ($\Delta H^\circ = 9.9(1.3)$ kJ mol$^{-1}$) or $[C_6F_5N_2N]Mo(NMe_2)$ ($\Delta H^\circ = 10.2(1.4)$ kJ mol$^{-1}$).

Addition of LiN(TMS)$_2$ to a mixture of $H_3[(C_6F_5)_2N_2Pyr]$ and MoCl$_4$(THF)$_2$ in tetrahydrofuran (THF) results in a rapid color change from red-orange to magenta. Paramagnetic reddish-pink $[(C_6F_5)_2N_2Pyr]MoCl$ can be isolated from the mixture in 42% yield (eq 3). The solid-state structure of $[(C_6F_5)_2N_2Pyr]MoCl$ (Figure 4) reveals it to be a TBP species similar to $[(C_6F_5)_2N_2Pyr]Mo(NMe_2)$ (Figure 3). The Mo(1)--N(1) bond length (2.0184(12)Å) is longer than that for Mo(1)--N(3) (1.9539(12)Å) or Mo(1)--N(4) (1.9383(12)Å), both of which are consistent with the amido ligand being doubly bound to the metal. The plane of the amido ligand is approximately parallel to the plane of the mesityl ring. The Mo(1)--N(4) bond length (2.2630(12)Å) is similar to what is found in related triamidoamine ligand systems, and longer than Mo(1)--N(3) (1.9539(12)Å) and Mo(1)--N(2) (1.9688(12)Å). The Mo(1)--N(1) bond length (2.081Å) is slightly longer than the Mo--N$_{amido}$ bonds and the average Mo(1)--N$_{pyrrolyl}$ bond length (2.007Å) in a tri(pyrrrolyl-$\alpha$-methyl)amine...
A reaction between [(C₆F₅N)₂Pyr]MoCl and AgOTf led to formation of paramagnetic, orange [(C₆F₅N)₂Pyr]Mo-OTf in approximately 40% yield, while a reaction between [(C₆F₅N)₂Pyr]MoCl and NaN₃ in acetonitrile at 70°C over a period of 72 h led to formation of yellow, diamagnetic [(C₆F₅N)₂Pyr]MoN. Both reactions are similar to those reported in related triamidoamine complexes.

Attempts to reduce [(C₆F₅N)₂Pyr]MoCl in THF under dinitrogen with sodium, KC₈, or Mg, or [(C₆F₅N)₂Pyr]Mo(OTf) with Mg powder (activated with 1,2-dichloroethane) so far have not led to any isolable dinitrogen-containing species such as [(C₆F₅N)₂Pyr]Mo(N₂) or [(C₆F₅N)₂Pyr]Mo(N₂)⁻. It should be pointed out that the [(C₆F₅NCH₂CH₂)₂N]Mo system also is compromised relative to analogous [(ArylNCH₂CH₂)₂N]Mo systems in which the aryl is not fluorinated as far as syntheses of dinitrogen complexes are concerned. Therefore we turned to the synthesis of diamidopyrrolyl complexes that contain nonfluorinated aryl substituents on the amido ligands.

### Synthesis of Diamidopyrrolyl Complexes in which Ar = 3,5-R₂C₆H₃

**Ar** = t-Bu or Me and Ar' = Mesityl. Diethylentetriamine could be arylated selectively as shown in eqs 4 and 5. 2,2,23 (3,5-Di-t-butylphenylNHCH₂CH₂₂NH, a dark yellow oil, must be air-sensitive since minimizing exposure of the reaction to air during workup significantly improves the yields. (3,5-dimethylphenylNHCH₂CH₂₂NH does not appear to be as air-sensitive as (3,5-di-t-butylphenylNHCH₂CH₂₂NH.

Mannich reactions analogous to those shown in eq 1 were not successful with the (ArNHCH₂CH₂₂NH species shown in eqs 4 and 5. However, the approach shown in eqs 6 and 7 was successful. The synthesis of H₃[(Arᵗ-Bn)₂Pyr] had to be carried out in the absence of air. H₃[(Arᵗ-Bn)₂Pyr] could be obtained as a white powder after purification by column chromatography. H₃[(Arᵗ-Me)₂Pyr] does not appear to be as sensitive

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**Figure 4.** Thermal ellipsoid drawing (50% probability) of the solid state structure of [(C₆F₅N)₂Pyr]MoCl. H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Cl(2)–Mo(1) = 2.3583(4), Mo(1)–N(3) = 1.9539(12), Mo(1)–N(2) = 1.9688(12), Mo(1)–N(1) = 2.0184(12), Mo(1)–N(4) = 2.1737(12), C(21)–N(2)–Mo(1) = 125.99(10), C(31)–N(3)–Mo(1) = 123.41(10), N(1)–Mo(1)–N(4) = 79.05(5), N(2)–Mo(1)–N(4) = 79.49(5), N(3)–Mo(1)–N(4) = 79.98(5), N(4)–Mo(1)–Cl(2) = 174.98(3).

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to air as H₃[(Art-BuN)₂Pyr], and no special precautions are necessary. H₃[(Art-MeN)₂Pyr] was obtained as a pale yellow, viscous oil. We focused on the synthesis and chemistry of [(Art-BuN)₂Pyr]Mo complexes since we felt that the greater steric hindrance afforded by the t-butyl groups was the more desirable of the two alternatives. Unfortunately, although we could synthesize a diamidopyrrolyl ligand in which Ar = HIPT and Ar' = 2,4,6-trisopropylphenyl (Figure 2), we believed would have the maximum chance of being sufficiently bulky to protect the metal (see Experimental Section), reactions analogous to those described for synthesizing [(Art-BuN)₂Pyr]¹⁺ complexes described below led only to products that could not be isolated through crystallization.

Addition of H₃[(Art-BuN)₂Pyr] to Mo(NMe₂)₄ yielded teal blue, essentially diamagnetic [(Art-BuN)₂Pyr]Mo(NMe₂) in 77% yield. Its diamagnetism is consistent with the S = 0 ground state that is a consequence of Mo−N americron bonding.

We propose that its structure is analogous to that shown in Figure 3 for the pentfluorophenyl analogue. If we assume that the temperature dependent chemical shifts are a consequence of interconversion of high spin and low spin forms, then ΔH° is calculated to be 37(10) kJ mol⁻¹, which is of the same magnitude as ΔH° for [(C₆F₅N)₂Pyr]Mo(NMe₂) (27(15) kJ mol⁻¹). Therefore it appears that ΔH° is generally smaller in the triamidoamine systems ([TMSN₃N]Mo(NMe₂)₁⁹ and [C₆F₅N₃N]Mo(NMe₂)₂₀) than in diamidopyrrolyl systems ([(Art-BuN)₂Pyr]Mo(NMe₂) and [C₆F₅N₂]Pyr)Mo(NMe₂)).

Addition of NaN(SMe₂)₂ over a period of 30 min to a mixture of MoCl₄(THF) and H₃[(Art-BuN)₂Pyr] in THF led to an orange-brown solution from which [(Art-BuN)₂Pyr]MoCl could be isolated in moderate yield; a pure sample was isolated as a pink-tan powder after recrystallization from a mixture of pentane and toluene. [(Art-BuN)₂Pyr]MoCl is extremely sensitive to air and moisture and has paramagnetically shifted ligand resonances in its proton NMR spectrum; paramagnetically shifted resonances are features of all [ArylNₓN]⁺MoCl complexes.

The reaction between [(Art-BuN)₂Pyr]MoCl and NaN₃ in MeCN at RT results in a color change from orange-brown to dark purple followed by precipitation of a bright yellow solid. The reaction is completed upon heating the mixture to ∼80 °C, and bright yellow diamagnetic [(Art-BuN)₂Pyr]MoN could be isolated in moderate yields. X-ray quality crystals of [(Art-BuN)₂Pyr]MoN were grown from fluorobenzene at −35 °C. The solid state structure (Figure 5) showed [(Art-BuN)₂Pyr]MoN to be a TBP species analogous to the pentfluorophenyl derivatives reported above. The Mo(1)−N(1) bond length again is slightly longer than the Mo(1)−N(2) and Mo(1)−N(3) bond lengths. The Mo(1)−N(4) bond (2.4134(13) A) is longer than the pentfluorophenyl derivatives as a consequence of the nitride ligand being in the apical position (Mo(1)−N(5) = 1.6746(13) A).

Reduction of [(Art-BuN)₂Pyr]MoCl with 2.3 equiv of Na under an N₂ atmosphere in THF at RT produced a red solution from which a red solid could be isolated after removal of NaN₃ and unreacted Na. We propose that this extremely sensitive red solid is the diamagnetic diazenido anion, [(Art-BuN)₂Pyr]Mo(N₂)Na(THF)−. IR spectra in CD₂Cl₂ reveal two absorption bands in the expected region for a diazenido anion (1761 cm⁻¹ and 1751 cm⁻¹), but only a single absorption band is observed in THF (1766 cm⁻¹).

The presence of several diamagnetic species in the ¹H NMR spectrum of [(Art-BuN)₂Pyr]Mo(N₂)Na(THF)₅ in CD₂Cl₂ suggests that it is not pure. Attempts to purify the compound through recrystallization were not successful.

When impure [(Art-BuN)₂Pyr]Mo(N₂)Na(THF) was treated with 1 equiv of 15-crown-5 at −35 °C in diethyl ether, the orange-red solution immediately changed to green and a diamagnetic lilac-colored powder could be isolated from the mixture in ∼20% yield. The lilac-colored compound exhibits a green color and a νNN absorption at 1855 cm⁻¹ in THF, as found for [(HIPTN₃N)Mo(N₂)]MgCl·(THF) in THF. All data support formulation of the lilac-colored compound as [(HIPTN₃N)₂Pyr]Mo(N₂)Na(15-crown-5). When [(HIPTN₃N)₂Pyr]Mo(N₂)Na(THF)− is exposed for several hours to a good vacuum, it turns from dark green to purple as a consequence of losing THF; the purple powder dissolves again in THF to yield green solutions. Therefore [(Art-BuN)₂Pyr]Mo(N₂)Na(15-crown-5) either loses 15-crown-5 from the sodium ion in THF or the green color in THF results from complete solvation of the salt in THF.

Reduction of [(Art-BuN)₂Pyr]MoCl with Na under an atmosphere of dinitrogen followed by addition of Bu₄NCl directly to the reaction mixture yields [(Art-BuN)₂Pyr]Mo(N₂)[NBu₄] as a diamagnetic purple solid in ∼60% yield. An IR spectrum of [(Art-BuN)₂Pyr]Mo(N₂)[NBu₄] reveals a dinitrogen stretch at 1840 cm⁻¹ in CD₂Cl₂. Unfortunately, [(Art-BuN)₂Pyr]Mo(N₂)[NBu₄] appears to be thermally

(24) [(HIPTN₃N)Mo(N₂)]Na(THF)− was synthesized from [HIPTN₃N]⁻·MoCl (500 mg, 0.291 mmol) in a manner similar to that employed to synthesize [HIPTN₃N]Mo(N₂)MgCl(THF)− (ref 8b) using 2 equiv of sodium (mirror) in THF (5 mL). The mixture was stirred with a glass-coated stir bar for 4 days. Solvent was removed in vacuo, the residue was extracted with pentane, and the extract was filtered through Celite. The filtrate was stood overnight at −35 °C, and the emerald green microcrystalline solid obtained was collected on a glass frit; yield 350 mg (69%).
unstable. It changes color over a period of days in a sealed tube at RT and no samples sent for elemental analyses yielded satisfactory results. We noted in studies of tungsten [HPTN3N] complexes that [HPTN3N]W(N2) was thermally unstable, although other derivatives (e.g., a potassium salt) could be isolated and characterized. We proposed that the anionic dinitrogen complex is a powerful enough base to react with the tetrabutylammonium cation in the solid state.

$$\left[\text{[Ar}^\text{t-BuN}2\text{Pyr]}\text{Mo(N2)}\right]\text{Na}(\text{THF})$$ can be oxidized reversibly at $-1.96$ V in 0.1 M [NBu4]BAr in PhF as shown in Figure 6. This result should be compared to observation of the reversible [HPTN3N]Mo(N2)$^{0/-}$ redox couple at $-2.11$ V under similar conditions (0.1 M [NBu4]BAr in PhF versus Cp₂Fe$^{0/-}$). However, oxidation of [Ar$^\text{t-BuN}2$Pyr]Mo(S2) (anodic peak at $-0.65$ V) is not reversible. A reversible [HPTN3N]Mo(N2)$^{0/-}$ couple was observed in PhF, but not in THF as a consequence of rapid displacement of N₂ by THF in the cationic species. The irreversibility of the [Ar$^\text{t-BuN}2$Pyr]Mo(N2)$^{0/-}$ couple suggests that dinitrogen is lost more readily in [Ar$^\text{t-BuN}2$Pyr]Mo(N2)$^{0/-}$ than in [HPTN3N]Mo(N2)$^{0/-}$.

Oxidation of [Ar$^\text{t-BuN}2$Pyr]Mo(N2)$^{0/-}$ with AgOTf in the dark yielded paramagnetic, red [Ar$^\text{t-BuN}2$Pyr]Mo(N2) in 53% yield. The value of $v_{\text{CNN}}$ in [Ar$^\text{t-BuN}2$Pyr]Mo(N2) (2012 cm$^{-1}$ in C$6$D$6$) should be compared with $v_{\text{CNN}}$ in [HPTN3N]Mo(N2) (1990 cm$^{-1}$ in C$6$D$6$), a difference of 22 cm$^{-1}$. A higher $v_{\text{CNN}}$ value in [Ar$^\text{t-BuN}2$Pyr]Mo(N2) is consistent with slightly weaker backbonding into the dinitrogen ligand in [Ar$^\text{t-BuN}2$Pyr]Mo(N2) than in [HPTN3N]Mo(N2).

A mixture of [Ar$^\text{t-BuN}2$Pyr]Mo(N2)$^{0/-}$ was freeze-pump-thaw degassed and exposed to an atmosphere of $^{15}$N$_2$. After 2.5 h an IR spectrum of the solution revealed that approximately half the [Ar$^\text{t-BuN}2$Pyr]Mo(N2)$^{0/-}$ had been converted into [Ar$^\text{t-BuN}2$Pyr]Mo($^{15}$N2) (1944 cm$^{-1}$) and half the [Ar$^\text{t-BuN}2$Pyr]Mo(N2)$^{0/-}$ (1751 cm$^{-1}$) had been converted into [Ar$^\text{t-BuN}2$Pyr]Mo$^{15}$N2)Na(THF) (1692 cm$^{-1}$; see Figure 7). These results suggest that the exchange of dinitrogen in [Ar$^\text{t-BuN}2$Pyr]Mo(N2) is much faster than it is in [HPTN3N]Mo(N2), where $t_{1/2}$ for exchange is approximately 35 h at 22 °C. We propose that formation of [Ar$^\text{t-BuN}2$Pyr]Mo($^{15}$N2)Na(THF), from [Ar$^\text{t-BuN}2$Pyr]Mo(N2)Na(THF), is a consequence of electron transfer between neutral and anionic species, rather than exchange directly in the anion. This circumstance is analogous to that observed in the parent system where $^{14}$N2/$^{15}$N2 exchange in [Ar$^\text{t-BuN}2$Pyr]Mo(N2)-[NBu4] is extremely slow, and any exchange that is observed can be attributed to oxidation of a small amount of the anion to [HPTN3N]Mo(N2) and fast electron exchange between [HPTN3N]Mo(N2) with [HPTN3N]Mo(N2)-[NBu4].

A plot of $\ln(A_{15N}/A_{total})$ for the dinitrogen exchange reaction in [Ar$^\text{t-BuN}2$Pyr]Mo($^{15}$N2) under N₂ in C$6$D$6$ in a nitrogen-filled glovebox at 22 °C showed that the reaction is first order in [Mo] with $k_{\text{obs}} = 1.97 \times 10^{-8}$ s$^{-1}$ ($t_{1/2} \sim$ 1 h). When the pressure of N₂ was increased to two atmospheres (15 psi overpressure), $t_{1/2}$ for the exchange reaction decreased to ~30 min. Although the exchange rate depends on N₂ pressure, that dependence alone does not distinguish between an associative reaction to give a six-coordinate bisdinitrogen intermediate, and rapid reversible loss of dinitrogen from [Ar$^\text{t-BuN}2$Pyr]Mo(N2) followed by capture of the hypothetical “naked” monopyramidal species, [Ar$^\text{t-BuN}2$Pyr]Mo, by dinitrogen. (See Discussion Section.)

When a PhF solution of [Ar$^\text{t-BuN}2$Pyr]MoCl in the presence of NaBPh$_4$ is exposed to an atmosphere of NH$_3$ (dried over Na), a rapid color change is observed from orange-red to burgundy and paramagnetic, yellow [Ar$^\text{t-BuN}2$Pyr]Mo(NH$_3$)BPh$_4$, could be isolated in 32% yield. This compound is relatively insoluble in toluene. Similar experiments employing NaBAr$^4$ led to formation of what we propose is the analogous BAr$^4$ salt, but we were not
able to isolate this salt from pentane, toluene, CH₂Cl₂, or THF.

Reduction of a THF solution of [{(Art-BuN)₂Pyr}Mo(NH₃)]BPh₄ under an Ar atmosphere with CoCp*₂ led to a color change from yellow-brown to green with concomitant formation of yellow [CoCp*₂]BPh₄. THF was removed in vacuo from the emerald green solution and the resulting solid was redissolved in C₆D₆ and exposed to 1 atm of N₂. The color changed from green to red over the course of a day, and IR spectroscopy of the mixture showed that [{(Art-BuN)₂Pyr}Mo(N₂)] (ν₁NN = 2012 cm⁻¹) had formed.

The reduction of [{(Art-BuN)₂Pyr}Mo(NH₃)]BPh₄ under Ar at approximately −1.68 V at a scan rate of 900 mV/s is not reversible (Figure 8), in contrast to the reduction of [HIPTN₃N]Mo(NH₃)⁺, which takes place at −1.63 V and is fully reversible in both PhF and THF. We propose that ammonia is lost from [(Art-BuN)₂Pyr]Mo(NH₃) upon reduction of [(Art-BuN)₂Pyr]Mo(NH₃)⁺ even in fluorobenzene. However, when reduction of [(Art-BuN)₂Pyr]Mo(NH₃)⁻ BPh₄ was carried out under dinitrogen at progressively slower scan rates (10 and 50 mV/s), the [(Art-BuN)₂Pyr]Mo(N₂)⁰⁻⁻ redox couple could be observed (Figure 9), thus confirming that dinitrogen replaces ammonia in [(Art-BuN)₂Pyr]Mo(NH₃). The [HIPTN₃N]Mo(N₂)⁰⁻⁻ redox couple is also observed during the electrochemical reduction of [HIPTN₃N]Mo(NH₃).ΔSc

Reduction of [(Art-BuN)₂Pyr]Mo(NH₃)²⁻ BPh₄ in THF by CoCp*₂ under an Ar atmosphere was followed by removing the THF in vacuo, dissolving the reaction product in C₆D₆, and exposing the solution to 1 atm of dinitrogen. Formation of ~30% of [(Art-BuN)₂Pyr]Mo(N₂) is observed after ~5 h. However, if 10 equiv of BPh₃ are present to trap the ammonia that is released, the exchange is virtually complete in about 2 h. Therefore we propose that the equilibrium in eq 8 lies to the left, as it does in the analogous [HIPTN₃N]³⁻ system. Qualitatively, the equilibrium in the [(Art-BuN)₂Pyr]³⁻ system appears to lie further to the left than in the [HIPTN₃N]³⁻ system, consistent with slightly weaker binding of dinitrogen to the metal in the [(Art-BuN)₂Pyr]³⁻ system and/or a slightly stronger binding of ammonia, or both.

Figure 7. IR spectrum of a C₆D₆ solution of [(Art-BuN)₂Pyr]Mo(N₂) and [(Art-BuN)₂Pyr]Mo(N₂)Na(THF)x after exposure to¹⁵N₂ for 2.5 h.

Exposure of a solution of [(Art-BuN)₂Pyr]Mo(N₂) to an atmosphere of CO led to a color change from red to brown. Brown [(Art-BuN)₂Pyr]Mo(CO) could be isolated in 27% yield. [(Art-BuN)₂Pyr]Mo(CO) is paramagnetic with a νCO absorption at 1902 cm⁻¹; an analogous experiment under ¹³CO yielded [(Art-BuN)₂Pyr]Mo(¹³CO) (ν₁³CO = 1856 cm⁻¹). It is of utmost importance that the CO employed be free of impurities such as water and oxygen to avoid formation of unknown products with several CO absorption bands in the IR spectrum.

Reaction of a 1:1 mixture of [(Art-BuN)₂Pyr]Mo(CO) and [HIPTN₃N]Mo(CO) in DME with 1 equiv of [Collidinium]BAR₄ showed that the CO absorption for [(Art-BuN)₂Pyr]Mo(CO) (1896 cm⁻¹ in DME) disappeared and an absorption for the protonated form is observed at 1920 cm⁻¹ (Δ = 24 cm⁻¹). Addition of a second equivalent
led to protonation of \(\sim 50\%\) of the remaining \([\text{HIPTN}_3\text{N}]^{-}\)–Mo(CO) (1885 - 1932 cm\(^{-1}\), \(\Delta = 47\) cm\(^{-1}\)). We conclude that \([\text{Art-BuN}_2\text{Pyr}]\)Mo(CO) is protonated more readily than \([\text{HIPTN}_3\text{N}]\)–Mo(CO) and that the shift in \(\nu_{\text{CO}}\) to higher energy in \([[(\text{Art-BuN}_2\text{Pyr}]\)Mo(CO)(H)]\(^{+}\) is about half what it is in \([[(\text{HIPTN}_3\text{N}]\)Mo(CO)(H)]\(^{+}\). Protonation of \([[(\text{Art-BuN}_2\text{Pyr}]\)Mo(CO)(H)]\(^{+}\) results in a similar shift in \(\nu_{\text{CO}}\) (1853 - 1875 cm\(^{-1}\), \(\Delta = 22\) cm\(^{-1}\)).

Protonation of \([\text{HIPTN}_3\text{N}]\)–Mo(N\(_2\)) is known to lead to loss of intensity of the \(\nu_{\text{NN}}\) stretch at 1990 cm\(^{-1}\) and observation of another at 2057 cm\(^{-1}\) for \([[[\text{HIPTN}_3\text{N}]\)Mo(N\(_2\))-(H)]\(^{+}\) (\(\Delta = 67\) cm\(^{-1}\)). A similar side by side comparison of protonation of a mixture of \([[(\text{Art-BuN}_2\text{Pyr}]\)Mo(N\(_2\)) and \([\text{HIPTN}_3\text{N}]\)–Mo(N\(_2\)) with \([\text{Collidinium}]\text{BAr}_4\) in PhF revealed that \([[(\text{Art-BuN}_2\text{Pyr}]\)Mo(N\(_2\)) was again protonated more readily than \([\text{HIPTN}_3\text{N}]\)–Mo(N\(_2\)). Upon addition of 2 equiv of \([\text{Collidinium}]\text{BAr}_4\) in PhF all \([[(\text{Art-BuN}_2\text{Pyr}]\)Mo(N\(_2\)) (\(\nu_{\text{NN}} = 1902\) cm\(^{-1}\)) had disappeared, while most (\(\sim 70\%\)) of the \([\text{HIPTN}_3\text{N}]\)–Mo(N\(_2\)) (\(\nu_{\text{NN}} = 1990\) cm\(^{-1}\)) remained. In a separate experiment involving \([[(\text{Art-BuN}_2\text{Pyr}]\)Mo(N\(_2\)) in PhF, no \(\nu_{\text{NN}}\) absorption for \([[(\text{Art-BuN}_2\text{Pyr}]\)Mo(N\(_2\))-(H)]\(^{+}\) could be observed. On the basis of the relative shifts in the CO complexes above (\(\sim 0.5\)) we might expect to see \(\nu_{\text{NN}}\) upon protonation of \([[(\text{Art-BuN}_2\text{Pyr}]\)Mo(N\(_2\))-(N\(_2\))]\(^{+}\) to shift by \(0.5 \times 67\) cm\(^{-1}\) to \(\sim 2045\) cm\(^{-1}\). Either dinitrogen is lost from \([[[\text{Art-BuN}_2\text{Pyr}]\)Mo(N\(_2\))-(N\(_2\))]\(^{+}\) more readily.
than from \([\text{HIPTN}_3\text{N}]\text{Mo(N)}_2(\text{H})\) or \([\text{HIPTN}_3\text{N}]\text{Mo(N)}_2(\text{H})\) decomposes in some other manner. The site of protonation in \([\text{Ar}^{\text{Bu}}\text{Py}r]\text{Mo}(\text{CO})\) and \([\text{Ar}^{\text{Bu}}\text{Py}r]\text{Mo}(\text{N}_2)\) are assumed to be the same, but whether the site of protonation is the amido nitrogen or the pyrrolyl is not known. However, we can say with certainty that \([\text{Ar}^{\text{Bu}}\text{Py}r]\text{Mo}(\text{N})_2(\text{H})\) is formed more readily than \([\text{HIPTN}_3\text{N}]\text{Mo}(\text{N})_2(\text{H})\), but \([\text{Ar}^{\text{Bu}}\text{Py}r]\text{Mo}(\text{N})_2(\text{H})\) is less stable, not more stable, than \([\text{HIPTN}_3\text{N}]\text{Mo}(\text{N})_2(\text{H})\).

Attempts to reduce dinitrogen catalytically were carried out with \([\text{Ar}^{\text{Bu}}\text{Py}r]\text{Mo}(\text{N})_2\) as a "catalyst" in a manner similar to that utilized for \([\text{HIPTN}_3\text{N}]\text{Mo}\) derivatives, including \([\text{HIPTN}_3\text{N}]\text{Mo}(\text{N}_2)\) (25). The amount of \text{NH}_3 produced was then quantified using the indophenol method.

In three catalytic runs an average of 1.02 ± 0.12 equiv of \text{NH}_3 were produced. It is clear that the nitride is not reduced to ammonia, but within experimental error we may not be surprising, since in triamidoamine systems where dinitrogen is not reduced catalytically, the \text{Mo}−\text{N}≡\text{NH}

Discussion and Conclusions

The results that we have presented suggest that in \([\text{Ar}^{\text{Bu}}\text{Py}r]\text{Mo}\) compounds the metal is slightly less electron rich than in an analogous \([\text{HIPTN}_3\text{N}]\text{Mo}\) complex. Perhaps the best measure is a value of 2012 cm−1 for \(\nu_{\text{NN}}\) in \([\text{Ar}^{\text{Bu}}\text{Py}r]\text{Mo}(\text{N}_2)\) in \(\text{C}_6\text{D}_6\) over 1990 cm−1 in \([\text{HIPTN}_3\text{N}]\text{Mo}(\text{N}_2)\) in \(\text{C}_6\text{D}_6\). Only two \text{Mo}−\text{N}_\text{amido} \pi\) bonds can form in \([\text{HIPTN}_3\text{N}]\text{Mo}(\text{N}_2)\), since the combination of p orbitals on the amido nitrogens that has \(\Lambda_2\) symmetry in \(3\)\(_v\) point group is ligand-centered and nonbonding. Since the pyrrolyl lone pair is part of the six \pi\) electron aromatic system in the pyrrolyl, the pyrrolyl ligand has little ability to \pi\) bond to the metal through the pyrrolyl nitrogen and therefore only two \text{Mo}−\text{N}_\text{amido} \pi\) interactions can form in a \([\text{Ar}^{\text{Bu}}\text{Py}r]\text{Mo}\) complex also. The \([\text{Ar}^{\text{Bu}}\text{Py}r]\text{Mo}\)−\text{N}_\text{amido} \pi\) systems turn out to be similar electronically, at least in terms of the degree of activation of dinitrogen.

An important question is whether the reduced \pi\) backbonding ability of the metal in a \([\text{Ar}^{\text{Bu}}\text{Py}r]\text{Mo}\) complex itself is enough to doom catalytic reduction of dinitrogen. One important step is the exchange of ammonia in the \text{Mo(III)} complex with dinitrogen. We have shown (Figure 9) that the \([\text{Ar}^{\text{Bu}}\text{Py}r]\text{Mo}(\text{N}_2)\)−\text{N}_\text{amido} \pi\)−\text{redox} couple can be observed upon reduction of \([\text{Ar}^{\text{Bu}}\text{Py}r]\text{Mo}(\text{N}_2)\) (25), thereby verifying that \([\text{Ar}^{\text{Bu}}\text{Py}r]\text{Mo}(\text{N}_2)\) is converted readily into \([\text{Ar}^{\text{Bu}}\text{Py}r]\text{Mo}(\text{N}_2)\). However, evidence suggests that the position of the equilibrium between \([\text{Ar}^{\text{Bu}}\text{Py}r]\text{Mo}(\text{N}_2)\) and \([\text{Ar}^{\text{Bu}}\text{Py}r]\text{Mo}(\text{N}_2)\) does not lie far toward the dinitrogen complex as it does in the \([\text{HIPTN}_3\text{N}]\text{Mo}\) system, a finding that is consistent with the slightly poorer backbonding ability of the metal in the \([\text{Ar}^{\text{Bu}}\text{Py}r]\text{Mo}\) system. On the whole, it seems that poorer backbonding ability alone is not the primary problem.

More problematic in terms of catalytic reduction, we propose, is the apparent instability of \([\text{Ar}^{\text{Bu}}\text{Py}r]\text{Mo}\)−\text{N}≡\text{NH}.

Mo(NMe2)4.27 2-mesityl-1H-pyrrole3 were synthesized as referenced. 1-Bromo-3,5-dimethylbenzene and 1-bromo-3,5-dimethyl-2,4-toluene were obtained from Sigma Aldrich; 1-bromo-3,5-dimethyl-2,4-toluene also was synthesized as reported in the literature.26–28 IR spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer in 0.2 mm KBr solution cells. NMR spectra were recorded on a Varian Mercury or Varian Inova spectrometer operating at 300 or 500 MHz (1H), respectively. 1H and 13C NMR spectra are referenced to the residual 1H or 13C peaks of the solvent. 19F NMR spectra were referenced externally to fluoro- benzene (−113.15 ppm upfield of CFCl3). HRMS was performed on a Bruker Daltonics APEX IV 7.4 Fourier Transform Ion Cyclotron Resonance Mass Spectrometer at the MIT Department of Chemistry Instrumentation Facility. Combustion analyses were performed by Midwest Microlabs, Indianapolis, Indiana, U.S.

H3[C6F5N]2Pyr. A 40 mL scintillation vial equipped with a stirbar was charged with 9-(perfluorophenyl)-9-(2-perfluoroethyl)phenyl-1,2-diamine (1.918 g, 4.4 mmol). To formaldehyde (35 wt %, 0.372 mL) was added HCl (5 mmol), and THF (1 mL). The reaction mixture was stirred for 20 min, and the reaction mixture added to a vial charged with 2-mesitylpyrrole (0.807 g, 4.4 mmol). The mixture was stirred at RT for 6 h, then washed with 10% KOH solution (40 mL), and extracted with diethyl ether. The extract was dried over Na2SO4, the volatiles were removed in vacuo, and the residue was purified by column chromatography using 9:1 hexanes/ethyl acetate as the eluent. The desired product is the second product from the column, with an Rf value of 0.158; yield 0.1545 g (55%): 1H NMR (500 MHz CDCl3) δ 7.97 (s, 1H, pyrrole NH), 6.92 (s, 2H, Mes 3,5-H), 6.13 (1H, pyrrole -CH), 5.96 (t, 1H, pyrrole -CH2), 4.08 (s, 2H, amine NH), 3.41 (2H, C–CH2–N), 2.48 (s, 6H, Mes 2,6-C). 13C NMR (126 MHz CDCl3): δ 139.2, 138.2, 137.8, 137.2, 134.7, 132.7, 130.3, 129.8, 128.3, 127.0, 124.0, 108.9, 108.7, 53.9, 51.8, 43.8, 21.2, 20.6 19F NMR (282 MHz, CDCl3): δ 66.2, 61.2, 55.9, 55.1, 21.6, 21.5; 13C NMR (toluene-d8): δ 108.7, 53.9, 51.8, 43.8, 21.2, 20.6 19F NMR (toluene-d8): δ −148.0 (d), −162.8 (t), −164.7 (t). Anal. Caled for C35H38F10MoN6: C, 49.95; H, 3.80; N, 9.10. Found: C, 49.67; H, 3.90; N, 9.22.

H3[C6F5N]2Pyr·MoCl. Under a N2 atmosphere, a 20 mL scintillation vial equipped with a stirbar was charged with MoCl4(THF)2 (1.191 g, 3.092 mmol), [Mes(C6F5)2]H3 (2000 mg, 3.162 mmol), and THF (5 mL). The reaction mixture turned from magenta to orange after stirring at RT for 1 h. The mixture was stirred for 30 min and LiNTMS2 (1.587 g, 9.484 mmol) was added, which led to a darkening of the mixture to orange. After stirring the mixture for another 30 min, the volatiles were removed in vacuo, the mixture extracted with toluene, and the extract was filtered through Celite. The product was recrystallized from toluene and pentane at −35 °C and collected on a glass frit; yield 0.989 g (42%): 1H NMR (CD2Cl2) δ 41.03 (s), 12.38 (s), 8.31 (s), 6.14 (s), 6.20 (s), 5.13 (4.34–2.91 (m), 2.12 (s), 1.80 (s), 1.27 (s), 0.88 (s), 0.30 (s), 0.01 (s), −1.21 (s), −20.04 (s), −78.50 (s), −92.10 (s); 19F NMR (CD2Cl2) δ −71.02 (s), −96.37 (s), −121.893 (s), −122.80 (s), −148.27 (s). HRMS (ESI m/z): Caled for C30H32F14N6MoO5Cl: 785.0405, found 785.0412.

H3[C6F5N]2Pyr·MoOCl. Under a N2 atmosphere, a 20 mL scintillation vial was charged with [Mes(C6F5)2]MoCl (100 mg, 0.131 mmol), AgOTf (33.6 mg, 0.131 mmol) and CH2Cl2 (5 mL). The reaction mixture was stirred overnight at RT and then filtered through Celite. All volatiles were removed in vacuo. The orange-red product was recrystallized from a mixture of toluene, pentane and CH2Cl2; yield 47.5 mg (42%): 1H NMR (CD2Cl2) δ 39.86 (s), 14.85 (s), 12.07 (s), 7.12 (s), 7.06 (s), 7.05 (s), 7.01 (s), 6.35 (s), 4.72 (brs), 2.06 (s), 1.30 (t, 3H). 19F NMR (CD2Cl2) δ −108.85 (brs). Anal. Caled for C30H28F14N6MoO5Cl: C, 42.58; H, 2.65; N, 6.41. Found: C, 42.40; H, 2.79; N, 6.25.

H3[C6F5N]2Pyr·MoN3. Under a N2 atmosphere, a 25 mL solvent bulb was charged with [C6F5N]2Pyr·MoCl (200 mg, 0.263 mmol), NaN3 (13.6 mg, 0.118 mmol), and acetone (5 mL). The reaction mixture was heated at 70 °C for 72 h. The volatiles were removed in vacuo, and the residue was extracted with toluene and filtered through Celite. Diamagnetic yellow-brown needle-like crystals were deposited after standing the filtrate at −35 °C overnight and collected on a glass frit; yield 103 mg (53%): 1H NMR (CD2Cl2) δ 0.66 (s, 2H, mesityl 3,5-H). 6.25 (d, 1H, pyrrole H), 6.20 (d, 1H, pyrrole H), 3.35 (s, 2H, NCH3), 2.35 (quintet, 2H, NCH3), 2.48 (s, mesityl 2,6-C). 19F NMR (CD2Cl2): δ 159.44 (t, 1F), 150.40 (t, 1F), 142.8, 142.5, 140.9, 139.9, 139.0, 139.0 (overlapping). 137.9, 137.8, 137.2, 136.9, 135.1, 133.6, 128.4, 128.1, 111.2, 108.3, 58.3, 51.3, 51.0, 21.1, 21.0, 21.0; 19F NMR (CD2Cl2) δ −150.18 (dd, 1F), −150.40 (t, 1F), −150.44 (t, 1F), −163.63 (d, 1F), −163.60 (d, 1F, overlapping). Anal. Caled for C30H28F14N6MoO5Cl: C, 48.73; H, 3.14; N, 9.47. Found: C, 48.51; H, 3.28; N, 9.48.

Et2O and filtered. The volatiles were removed in vacuo, and the resulting mixture was stirred for 5 min before subsequent addition of diethylene triamine (2.44 g, 23.6 mmol) and was added in with DMF (30 mL). The reaction was then heated to 90 ℃ for 96 h with stirring. The initially blue-green mixture turns brown with concomitant formation of reddish Cu powder as the mixture is heated after approximately 2 h. The mixture was allowed to cool to RT, then aqueous NH3 (100 mL) and water (200 mL) were added with stirring. The mixture was extracted with ethyl acetate (4 × 200 mL) and the organic layers were dried over Na2SO4. Volatiles were removed via column chromatography eluting first with EtOAc to remove impurities and then THF. The product was obtained as a brown-yellow oil: yield 7.200 g (96%); 1H NMR (CDCl3) δ 7.035 (1H, s, pyrrole N-CH3), 3.92 (2H, s, pyrrole C-CH2), 6.094 (1H, t, JHH = 3.0 Hz, pyrrole C-H), 5.935 (1H, t, JHH = 3.0 Hz, pyrrole C-H), 2.670 (4H, t, JCH2 = 7.0 Hz, pyrrole C-CH2), 2.270 (6H, s, -N(CH3)2 ppm); 13C NMR (CDCl3) δ 149.6, 149.1, 129.4, 128.7, 128.3, 120.6, 108.7, 108.3, 56.8, 45.0, 34.6, 30.7, 24.7, 24.3, 24.0 ppm HRMS (ESI, m/z): Calcd for C21H30N4O6: 325.2659. Found 325.2650.

1-(5-(2,4,6-Trisopropylphenyl)-1H-pyrrolyl-2-yl)-N,N,N-trimethylammonium iodide. A 250 mL round-bottom flask was charged with 1-(5-(2,4,6-trisopropylphenyl)-1H-pyrrolyl-2-yl)-N,N,N-trimethylammonium iodide (3.950 g, 12.098 mmol) and THF (150 mL). A vial with a septum sealed cap was charged with MeI (1.717 g, 12.098 mmol) and THF (15 mL). The contents of the vial were syringed out and added slowly to the stirring solution of 1-(5-(2,4,6-trisopropylphenyl)-1H-pyrrolyl-2-yl)-N,N,N-trimethylammonium. The reaction mixture was stirred for 1 h at RT, during which a very thick white suspension formed. The white precipitate was collected on a glass frit, washed with THF, and recrystallized from acetone; yield 3.12 g (55%). 1H NMR (CDCl3) δ 10.05 (1H, s, pyrrole C-H), 7.015 (1H, s, pyrrole N-CH3), 6.42 (1H, t, JHH = 2.9 Hz, pyrrole C-H), 6.01 (1H, t, JHH = 2.9 Hz, pyrrole C-H), 5.29 (2H, s, -N(CH3)2), 3.12 (3H, s, HNCH3). HRMS (ESI, m/z): Calcd for C23H30N4I: 543.2792. Found 543.2789.

1H NMR (CDCl3) δ 7.87 (1H, pyrrole N-CH3), 7.01 (2H, s, TRIP aryl 3,5-H), 7.01 (8H, HIPT aryl 3,5',3",5"-H), 6.39 (4H, d, HIPT aryl 2',6'-H), 6.37 (2H, t, HIPT aryl 4'-H), 6.08 (1H, t, JHH = 2.9 Hz, pyrrole C-H), 5.96 (1H, t, JHH = 2.9 Hz, pyrrole C-H), 3.92 (2H, s, JHH = 5.1 Hz, NH(CH3)2), 3.75 (2H, s, NCH3), 3.20 (4H, q, JHH = 5.8 Hz, NH(CH3)2), 2.92 (4H, q, JHH = 4.4 Hz, CH2(CH3)), 2.04 (12H, s, Ar 35), 1.98 (3H, s, -CH3), 1.48 (2H, s, Ar 35, CH3), 1.28 (6H, s, -CH3), 0.86 (6H, -CH3). HRMS (ESI, m/z): Calcd for C36H32N4O8: 599.3682. Found 599.3684.

1-(5-(2,4,6-Trisopropylphenyl)-1H-pyrrolyl-2-yl)-N,N-dimethylmethanamine. A 100 mL round-bottom flask was charged with MeCN (1.50 mL, 25.4 mmol), n-pentane (1.50 mL, 25.4 mmol), foramycytol (1.760 mL, 37% solution in water, 20.58 mmol), and isopropanol (10 mL). The mixture was stirred for approximately 30 min. 2-(2,4,6-Trisopropylphenyl)-1H-pyrrole (5.260 g, 19.52 mmol) was then added, and the mixture was stirred for approximately 70 h at 40 ℃. A 300 mL portion of 10% KOH solution was added, and the mixture stirred for 30 min. Volatiles were removed in vacuo, and 200 mL of water was added. The mixture was extracted three times with CH2Cl2 (200 mL), and the organic layer was dried over Na2SO4. Volatiles were removed in vacuo. The residue was used without further purification: yield 4.35 g (65%); 1H NMR (CDCl3) δ 8.206 (1H, s, pyrrole -N-H), 7.037 (2H, s, aryl 3.5-H), 6.069 (1H, t, JHH = 3.0 Hz, pyrrole C-H), 5.953 (1H, t, JHH = 3.0 Hz, pyrrole C-H), 3.465 (2H, s, -CH2), 2.927 (1H, sept, JHH = 6.7 Hz, 4-CH2Me), 2.789 (2H, sept, JHH = 6.7 Hz, 2,6-CH2Me), 2.223 (6H, s, -N(CH3)2 ppm); 13C NMR (CDCl3) δ 149.6, 149.1, 129.4, 128.7, 128.3, 120.6, 108.7, 108.3, 56.8, 45.0, 34.6, 30.7, 24.7, 24.3, 24.0 ppm HRMS (ESI, m/z): Calcd for C23H30N4: 325.2659. Found 325.2650.
In a N₂ atmosphere glovebox, a 25 mL solvent bulb equipped with a PTFE screw valve was charged with HJ[Ar(6-NC6)3-Pyr] (635 mg, 0.938 mmol) and Mo(NMe2)5 (313 mg, 1.15 mmol) and toluene. The reaction mixture turned from purple to ultramarine blue within a couple of hours, but was left to stir at RT overnight. The mixture was then brought back into the glovebox and volatiles were removed in vacuo. The desired product was purified via recrystallization from pentane/toluene at −35 °C giving a bright teal blue diamagnetic powder; yield 588 mg (77.0%): 1H NMR (CD6) δ 7.18 (2H, s, Ar1-4-H), 6.938 (2H, s, mesityl-3,5-H), 6.553 (4H, s, Ar 2,6-H), 6.283 (1H, d, JHH = 2.8 Hz, pyrrole CH), 6.266 (1H, d, JHH = 2.8 Hz, pyrrole CH), 3.963 (2H, dt, ArNC2-CH3), 3.828 (2H, s, pyrroleCH3), 3.813 (2H, dt, ArNC2-CH3), 3.200 (2H, dt, ArNC1-CH3), 3.066 (s, H, Mo(NCH2)3), 2.749 (2H, dt, ArNC1-CH2), 2.261 (6H, s, mesityl-2,6-CH3), 2.239 (3H, s, mesityl-4-CH3), 1.288 (36H, s, Ar 3,5-C(CH3)). Anal. Calcd for C46H65N5Mo: C, 70.47; H, 7.98; N, 8.46. Found: C, 70.47; H, 8.41; N, 8.46.

In a N₂ atmosphere glovebox, a 20 mL scintillation vial was charged with HJ[Ar(6-NC6)3-Pyr] (890 mg, 1.3 mmol) and THF (10 mL). The solution was stirred for 5 min to ensure complete dissolution of the ligand. MoCl(THF)2 (515.6 mg, 1.4 mmol) was added very slowly with stirring over the course of 30 min. The resulting dark brown solution was stirred for 40 min at RT. Na(N(TMS)2) (770 mg, 4.2 mmol) was added slowly over 15 min to the mixture, which turned from brown to dark brownish orange. The mixture was stirred for 30 min, and the volatiles were removed in vacuo. The residue was extracted with toluene, and the extract was filtered through Celite. The toluene was removed in vacuo, and the mixture triturated with pentane and cooled to −35 °C overnight. The desired product was collected on a glass frit as a paramagnetic pink-tan powder; yield 0.566 g (53%). 1H NMR (CD6) δ 18.78 (s), 11.71 (br s), 8.20 (s), 5.94 (s), 5.20 (s), 5.10 (s, overlapping), 2.56 (s), 1.82 (36H, s, Ar 3,5-C(CH3)), -24.56 (br s), -83.71 (br s), -115.23 (br s). Anal. Calcd for C46H65N5MoCl: C, 68.60; H, 8.13; N, 6.96. Found: C, 68.62; H, 8.01; N, 6.86.

In a N₂ atmosphere glovebox, a 25 mL solvent bulb equipped with a PTFE screw valve was charged with [Ar(6-NC6)3-Pyr]MoCl (100 mg, 0.12 mmol), NaNC1 (8.1 mg, 0.12 mmol), and MeCN (10 mL). The reaction mixture was stirred at RT for 10 h, turning from orange brown to purple overination, with a yellowish film of a reaction precipitate. The reaction flask was then brought out of the glovebox and heated at 80 °C for 24 h. The flask was brought back into the glovebox, the volatiles were removed in vacuo, and the residue was extracted with toluene and filtered through Celite. The volume of the filtrate was decreased to 5 mL and cooled to −35 °C overnight. The resulting yellow precipitate was collected on a glass frit and washed with cold pentane. The product obtained is a yellow diamagnetic powder; yield 45 mg (46.2%): 1H NMR (CD6) δ 7.454 (4H, d, JHH = 1.7 Hz, Ar1-2-H), 7.262 (2H, t, JHH = 1.7 Hz, Aryl-4-H). 6.913 (2H, s, mesityl-3,5-H), 6.345 (2H, s, pyrrole-H), 3.594 (2H, dt, ArNC1-CH3), 3.561 (2H, dt, ArNC2-CH3), 3.531 (2H, s, pyrroleCH3), 2.437 (6H, s, mesityl-2,6-CH3), 2.338 (2H, dt, ArNC2-CH3), 2.278 (3H, s, mesityl-4-CH3), 2.261 (2H, dt, ArNC1-CH3), 1.318 (36H, s, Ar 3,5-C(CH3)). Anal. Calcd for C46H65N5MoCl: C, 70.47; H, 8.36; N, 6.93. Found: C, 70.47; H, 8.44; N, 9.02.

In a N₂ atmosphere glovebox, a 20 mL scintillation vial was charged with [Ar(6-NC6)3-Pyr]MoCl (1.431 g, 1.78 mmol), NaNC1 (94 mg, 4.09 mmol), and THF (10 mL). The reaction mixture was stirred for 12 h at RT with a glass stirbar, with a concomitant color change from orange red to dark purple to red. The mixture was filtered through Celite and NBu4Cl (TBAC) (252.9 mg, 1.04 mmol) was added. The mixture turned orange, then dark green after stirring for 40 h at RT. Volatiles were removed in vacuo, then the residue was extracted with toluene and filtered through Celite. The filtrate was decreased in vacuo, with a color change from green to purple. The solution was cooled at −35 °C overnight, and the resulting diamagnetic lavender powder was collected on a glass frit; yield 550 mg (61%): 1H NMR (CD6) δ 7.331 (4H, s, Ar1-2-H), 7.057 (2H, s, mesityl-3,5-H), 6.962 (2H, s, Ar 4-H), 6.771 (1H, d, JHH = 2.9 Hz, pyrrole-H), 6.735 (1H, d, JHH = 2.9 Hz, pyrrole-H), 4.018 (2H, dt, ArNC2-CH3), 3.849 (2H, dt, ArNC1-CH3), 2.481 (2H, s, pyrroleCH3), 2.740 (6H, s, mesityl-2,6-CH3), 2.399 (3H, s, mesityl-4-CH3), 2.382 (2H, dt, ArNC2-CH3), 2.252 (2H, dt, ArNC1-CH3), 2.146 (3H, m, N(CH2CH2CH2)3), 1.490 (36H, s, Ar 3,5-C(CH3)), 0.996 (8H, m, N(CH2CH2CH2)3), 0.755 (20H, m, N(CH2CH2CH2)3). IR (CD6) δνNIR 1840 cm⁻¹.

In a N₂ atmosphere glovebox, a 100 mL solvent bulb equipped with a PTFE screw valve was charged with [Ar(6-NC6)3-Pyr]MoCl (622.5 mg, 0.77 mmol), NaBP6 (290.9 mg, 0.85 mmol) and PhF (15 mL). The bulb was brought out of the glovebox, and freeze–pump–thaw degassed three times. Anhydrous NH3 (100 mL, 1 atm) which was dried over Na was vacuum transferred into the degassed solvent bulb with the reaction mixture. The mixture immediately changed from orange-red to burgundy. The reaction was stirred for 12 h at RT. The bulb was brought back into the glovebox, and the volatiles were removed in vacuo. The residue was extracted with toluene and filtered through Celite. The filtrate was cooled at −35 °C overnight, then filtered through a glass frit to remove a dark reddish solid. The volume of the resulting yellow-brown...
filtrate was decreased to 5 mL, and pentane (15 mL) was added to precipitate a yellow brown solid. The mixture was chilled to −35 °C for 1 h and then filtered through a glass frit to collect the paramagnetic yellow solid; yield 268 mg (32%): 1H NMR (THF-d8) δ 33.011 (br s), 30.208 (br s), 9.971 (br s), 7.301 (2H, s, Aryl 4-H), 7.215 (4H, s, Aryl 2,6-H), 6.821 (4H, s) 6.691 (2H, s, pyrrole-H), 5.885 (br s), 4.848 (br s), 1.635 (s, Aryl 3,5-C(CH3)3), −24.605 (br s), −91.744 (br s). Anal. Calcd for C70H88BMoN5: C, 76.00; H, 8.02; N, 6.33. Found: C, 75.60; H, 7.90; N, 6.34. 

[(Ar-t-BuN)2Pyr]Mo(CO). In a N2 atmosphere glovebox, a 100 mL solvent bulb equipped with a PTFE screw valve was charged with [(Ar-t-BuN)2Pyr]Mo(N2) (250 mg, 0.313 mmol) and benzene. Outside the glovebox, the bulb was freeze—pump—thaw degassed three times, and then CO (1 atm, 100 mL) was vac-transferred into this bulb from another bulb kept at −78 °C (to freeze out water vapor that may be present in the CO gas). The mixture was warmed to RT and stirred for 12 h. The reaction mixture was brought back into the N2 atmosphere glovebox whereby benzene was removed in vacuo and toluene added to the residue. The toluene solution was chilled at −35 °C overnight, and the resulting paramagnetic green-brown precipitate was collected on a glass frit, washed with pentane, and dried; yield 159 mg (64%): 1H NMR (CD2Cl2) δ 20.13 (2H, br s, ArylNCH2CH2N), 17.24 (2H, s, ArylN-CH2CH2N), 13.83 (1H, s, pyrrole-H), 12.25 (2H, br s, ArylNCH2-CH2N), 8.69 (2H, s, Aryl14-H), 7.88 (4H, s, Aryl2,6-H), 3.02 (1H, s, pyrrole-H), 1.82 (2H, s), 0.69 (36H, br s, Aryl 3,5-C(CH3)3), −0.40 (2H, s), −3.72 (6H, s, mesityl 2,6-C6H3), −7.54 (3H, br s, mesityl 4-C6H3), −19.63 (2H, br s), −34.28 (2H, br s). IR (DME) νNN 1902 cm−1, ν15 15N 1856 cm−1. Anal. Calcd for C47H65N4MoO: C, 70.74; H, 8.21; N, 7.02. Found: C, 70.99; H, 8.11; N, 6.96. 

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Supporting Information Available: Crystal data, structure refinement tables for all X-ray structural studies, and tables of selected bond lengths angles. This material is available free of charge via the Internet at http://pubs.acs.org.