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Reduction of Dinitrogen to Ammonia at a Well-Protected Reaction Site in a Molybdenum Triamidoamine Complex

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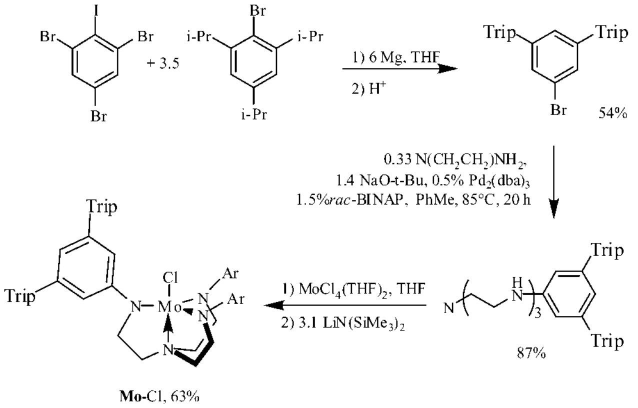
Over 30 years of research have been devoted to the synthesis and study of transition-metal complexes that contain dinitrogen.[1] However, reports of catalytic reduction of dinitrogen to ammonia are extremely rare,[1−5] and in no instance is the catalyst a "well-defined" species. With that goal in mind we have chosen to explore the chemistry of triamidoamine ($[(RNCH_2CH_2)_3N]^{3-} = [RN_3N]^{3-}$) molybdenum complexes, especially those in which R is an ordinary aryl group[6,7] (cf. R = $SiMe_3$[8−10] or C_6F_5[11]). We found (in the form of electrochemical evidence) that when R is a phenyl substituted in the 3- and 5-positions with phenyl or *p-t*-BuPhenyl rings (e.g., *m*-terphenyls), the relatively stable $[RN_3N]Mo{-}N{=}N{-}Mo[RN_3N]$ complex could not form for steric reasons. To further protect the site at which dinitrogen binds we turned to the synthesis of ligands in which the amido substituent is the 3,5-(2,4,6-*i*-$Pr_3C_6H_2)_2C_6H_3$ (HIPT = HexaIsoPropylTerphenyl) group. We find that this ligand protects the metal to a degree that has not been achievable before, one that allows dinitrogen to be reduced with protons and electrons to ammonia.

The synthesis of HIPT bromide follows the method employed to prepare other m-terphenyls, as shown in Scheme 1.[6,12,13] The Pd-catalyzed coupling[14,15] of the HIPT group to triethylenetetramine proceeded without complications to give $H_3[HIPTN_3N]$ in 87% yield on an 82-g scale. (See Supporting Information for all experimental details.) The reaction between $MoCl_4(THF)_2$ and $H_3[HIPTN_3N]$ in THF for 1 h produced a dark red solution that we assume to contain an adduct (or adducts),[7] the exact nature(s) of which is(are) not known. Addition of 3.1 equiv of $LiN(SiMe_3)_2$ over a period of 1.5 h to this red solution led to formation of orange $[HIPTN_3N]MoCl$ (**Mo**−Cl).

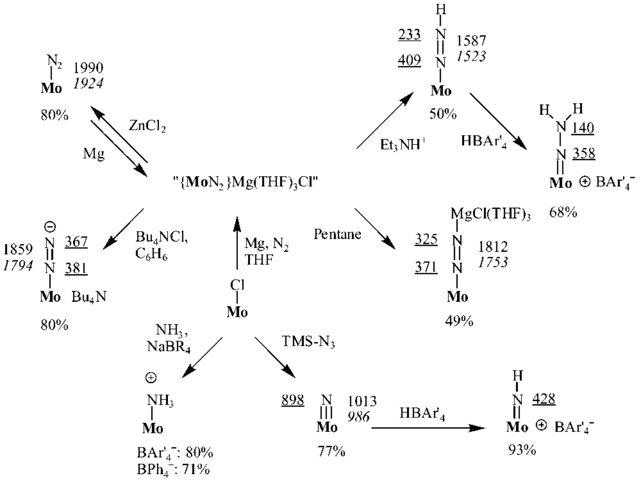
Reduction of **Mo**−Cl with Mg in THF under a dinitrogen atmosphere produces crude "**Mo**−N═N−Mg(THF)$_3$Cl", which upon recrystallization from pentane yields red, diamagnetic **Mo**−N═N−MgCl(THF)$_3$ (in Nujol $\nu_{NN} = 1810\ cm^{-1}$, $\nu 15_N 15_N = 1751\ cm^{-1}$; in C_6D_6 $\nu_{NN} = 1812\ cm^{-1}$; Scheme 2). If the Mg reduction is followed by treatment with Bu_4NCl and dioxane, bright green, benzene-soluble, diamagnetic $\{Bu_4N\}$\{**Mo**−N═N\} is formed (in THF $\nu_{NN} = 1859\ cm^{-1}$, $\nu 15_N 15_N = 1794\ cm^{-1}$). THF solutions of isolated **Mo**−N═N−MgCl(THF)$_3$ also show an IR absorption at $1856\ cm^{-1}$, characteristic of the "free anion," \{**Mo**−N═N\}$^-$.

Oxidation of crude "**Mo**−N═N−Mg(THF)$_3$Cl" (or crystalline **Mo**−N═N−MgCl(THF)$_3$ or $\{Bu_4N\}$\{**Mo**−N═N\}) yields **Mo**(N_2) in 80% yield. The IR spectrum of **Mo**(N_2) in benzene ($\nu_{NN} = 1990\ cm^{-1}$) should be compared with $\nu_{NN} = 1934\ cm^{-1}$ in $[TMSN_3N]Mo(N_2)$ in pentane.[9] In benzene at room temperature (∼22 °C) several days are required for the ^{15}N in **Mo**($^{15}N_2$) to exchange with atmospheric $^{14}N_2$.

Scheme 1. Synthesis of $H_3[HIPTN_3N]$ and $[HIPTN_3N]MoCl$



Scheme 2. Synthesis of $[HIPTN_3N]Mo$ Complexes[a]



[a] Pertinent $\nu(^{14}N^{14}N)$ and $\nu(^{15}N^{15}N)$ (italicized) IR frequencies (cm^{-1}, in C_6D_6), and ^{15}N NMR chemical shifts (underlined, ppm in C_6D_6) are listed next to each compound.

Protonation of \{**Mo**−N═N\}$^-$ with $\{Et_3NH\}\{BAr'_4\}$ (Ar′ = 3,5-$(CF_3)_2C_6H_3$) afforded red-orange, diamagnetic **Mo**−N═N−H in 50% yield. Proton NMR spectra show the diazenido proton resonance at 8.57 ppm, which is split into a doublet of doublets in **Mo**−^{15}N═^{15}N−H ($^1J(^{15}N{-}H) = 53.6$ Hz, $^2J(^{15}N{-}H) = 7.9$ Hz). Further protonation of **Mo**−N═NH with $[H(OEt_2)_2][BAr'_4]$ afforded dark red, diamagnetic \{**Mo**═N−NH$_2$\}$\{BAr'_4\}$ in 68% yield. The hydrazido protons appear as a singlet at 6.66 ppm in the proton NMR spectrum, while the $^{15}N_2$-analogue features a doublet of doublets at 6.67 ppm ($^1J(^{15}N{-}H) = 90.5$ Hz, $^2J(^{15}N{-}H) = 1.4$ Hz). Proton and ^{15}N NMR data (Scheme 2) are comparable to those of the closely related $\{[ArylN_3N]Mo\}$ species.[7]

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Treatment of **Mo**−Cl with TMS−N_3 in toluene at 90 °C for 65 h afforded bright yellow **Mo**≡N in 77% yield. Protonation of **Mo**≡N with HBAr′$_4$ yields dark red {**Mo**=NH}{BAr′$_4$} in 93% yield. The imido proton resonance at 6.59 ppm in ^{1}H NMR spectrum is flanked by satellites in the spectrum of the 50% ^{15}N-labeled analogue ($^1J(^{15}N-H) = 73.7$ Hz), while a doublet is found at 427.7 ppm ($^1J_{NH} = 73.7$ Hz) in the ^{15}N NMR spectrum of the 50% ^{15}N-labeled analogue. These ^{15}N NMR data fall within the general ranges established for complexes of this general type.[16,17]

Last, reaction of **Mo**−Cl with NaBAr′$_4$ in the presence of NH_3 afforded dark red, paramagnetic {**Mo**(NH_3)}{BAr′$_4$} in 80% yield. No reaction is observed between **Mo**−Cl and NaBAr′$_4$ in the absence of ammonia, and addition of a few equivalents of NH_3 alone to **Mo**−Cl only results in formation of a small amount of the free, protonated ligand. The related salt, {**Mo**(NH_3)}{BPh_4}, was isolated in 71% yield in an analogous reaction with NaBPh_4. While the ^{1}H NMR spectrum of {**Mo**(NH_3)}{BAr′$_4$} is unchanged in the presence of NEt_3 at 22 °C, addition of Bu_4NCl to a C_6D_6 solution of recrystallized {**Mo**(NH_3)}{BAr′$_4$} reforms **Mo**−Cl and free ammonia nearly quantitatively (95(2)%; three determinations using the indophenol method[18]).

We found that reactions involving cobaltocene as the reducing agent ($E_{1/2} \approx -1.3$ V vs ferrocene/ferrocenium or Fc/Fc$^+$)[19] and {2,6-lutidinium}BAr′$_4$ as the proton source can be carried out in benzene, since the reduction of only slightly soluble {LutH}BAr′$_4$ with $CoCp_2$ in benzene to give hydrogen is a relatively slow process (hours) at room temperature. The addition of 1.0 equiv of {LutH}BAr′$_4$ and 2.0 equiv $CoCp_2$ in benzene to **Mo**(N_2) yields **Mo**−N=NH essentially quantitatively. If {LutH}BAr′$_4$ or $CoCp_2$ is added *separately* to Mo(N_2), essentially *no reaction* is observed by either ^{1}H NMR or IR. Addition of 7.0 equiv of {LutH}BAr′$_4$ and 8.2 equiv of $CoCp_2$ in benzene to **Mo**(N_2) yields (by NMR) ∼60% {**Mo**(NH_3)}{BAr′$_4$} and ∼10% of free ligand (H_3[HIPTN_3N]). When Bu_4NCl and NEt_3 are added to this mixture and the volatile components analyzed for total ammonia using the indophenol method, the amount was found to be 1.09(2) equiv (three determinations). Upon treating **Mo**≡N with 3.5 equiv of {LutH}BAr′$_4$ and 4.2 equiv of $CoCp_2$ in benzene, {**Mo**(NH_3)}{BAr′$_4$} is formed in ∼80% yield (by NMR); further treatment of the reaction mixture with Bu_4NCl and NEt_3 affords 0.88(2) equiv of ammonia (three determinations). We cannot exclude the possibility that some dinitrogen may be lost as free N_2 at some point during the reduction of **Mo**(N_2) to {**Mo**(NH_3)}{BAr′$_4$}.

The missing steps that are needed to make the process potentially catalytic are reduction of {**Mo**(NH_3)}{BAr′$_4$} to **Mo**(NH_3) and displacement of ammonia from **Mo**(NH_3) by dinitrogen. In fact, {**Mo**(NH_3)}{BAr′$_4$} reacts with 3 equiv of $CoCp_2$ in C_6D_6, to give an equilibrium mixture of {**Mo**(NH_3)}{BAr′$_4$} (90%) and **Mo**(N_2) (10%) after 18 h; the ratio remains unchanged in the closed system for another 22 h. The same reaction in the presence of 2 equiv of BPh_3 (to scavenge NH_3) affords **Mo**(N_2) nearly quantitatively (by NMR) in 12 h at room temperature. Furthermore, the analogous reaction between Cp_2Co and {**Mo**(NH_3)}{BPh_4} in the presence of BPh_3 quantitatively yields **Mo**(N_2) in 1 h or less, perhaps as a consequence of the very low solubility of [Cp_2Co][BPh_4] in benzene.

X-ray data (Mo radiation) collected on several compounds (**Mo**(N_2), various {**Mo**(N_2)}$^-$ salts, and **Mo**≡N) were relatively weak, we believe largely perhaps because of the relatively large amount of organic material present; no structure could be refined below 12%. (Structures will be reported in detail elsewhere in due course.) In **Mo**≡N each 3,5-disubstituted aryl ring on an equatorial amido nitrogen is turned ∼35° from lying in the same plane as the amido nitrogen, which places one of the Trip rings (each of which is approximately perpendicular (83−89°) to the phenyl ring to which it is attached) "away" from the metal center, and one "up", as shown schematically for one HIPT group in **Mo**−Cl in Scheme 1. The three Trip rings pointing up form a relatively compact, deep (∼7 Å) three-sided cavity. However, the metal still appears to be relatively open to attack from the "side," that is, near the equatorial amido nitrogens, for example, by {LutH}BAr′$_4$.

The findings presented here suggest that the [HIPTN_3N]$^{3-}$ ligand dramatically protects a variety of complexes that contain dinitrogen in various stages of reduction, perhaps most importantly against bimolecular decomposition, thereby allowing several to be isolated. We propose that the six that we have isolated are among the dozen or so intermediates that one might expect to form in a Chatt-type reduction of end-on bound dinitrogen.[1d,g] A second likely important feature of [HIPTN_3N]$^{3-}$ complexes is that they should resist degradation by multiple protonations of amido nitrogens. On the basis of what we have observed so far it would seem that dinitrogen reduction consists of a protonation to give a cationic species followed by a one-electron reduction to give a neutral species. We are in the process of attempting to couple dinitrogen reduction with reduction of the cationic ammonia complex and subsequent displacement of ammonia with dinitrogen to achieve a catalytic cycle.

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Supporting Information Available: Experimental details for the synthesis of all compounds and spectroscopic data for all compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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