Reactions of Hydrazido(2-) and Dinitrogen Complexes of Molybdenum with Reducing Agents. Crystal Structure of a Molybdenum(V) Hydrazido(2-) Complex: [MoBr₃(NNH₂)(Ph₂PCH₂CH₂PPh₂)]·THF[1]

T. Adrian George,[*,2a] Bharat B. Kaul,[2a] Qin Chen,[2b] and Jon Zubieta[*,2b]
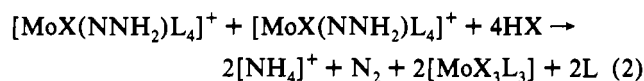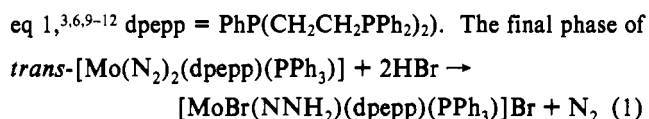
Departments of Chemistry, University of Nebraska—Lincoln, Lincoln, Nebraska 68588-0304, and Syracuse University, Syracuse, New York 13244

Tin(II) halides and germanium(II) iodide (known two-electron-reducing agents) have been shown to be effective reducing agents in the transformation of nitrogen hydride intermediates derived from N_2 into ammonia and hydrazine. Addition of SnX_2 (X = Br, Cl), [Et₄N][SnCl₃], or GeI₂ to a mixture of *trans*-[Mo(N₂)₂(PS-diphos)(PPh₂Me)₂] (PS-diphos = –P(Ph)CH₂CH₂PPh₂ attached to polystyrene–2% divinylbenzene) and HBr in CH_2Cl_2 (a mixture from which no ammonia is formed) causes substantial amounts of ammonia to be produced. Significant increases in the yield of ammonia were obtained when these same reducing agents were added to a mixture of *trans*-[Mo-(N₂)₂(dppe)(PPh₂Me)₂] (1) (dppe = Ph₂PCH₂CH₂PPh₂) and HBr in CH_2Cl_2: yields (mol/mol of Mo) of NH₃, N₂H₄, and N₂ changed from 0.39, 0.44, and 1.39 (100% N atom balance) in the absence of reducing agent to 1.24, 0.13, and 1.22 (99% N atom balance) in the presence of GeI₂ (4 mol). This is ca. 300% increase in the yield of ammonia. The reactions of HX (X = Br, Cl) with 1 in THF and CH_2Cl_2 in the presence of tin(II) species were investigated. Solid 1 reacted with HX (10 mol) to produce [MoX(NNH₂)(dppe)(PPh₂Me)₂]X, which was stable in MeOH but lost a phosphine ligand in both THF and CH_2Cl_2 solution to form [MoX₂(NNH₂)(dppe)(PPh₂Me)]. Reaction of HX (6 mol) with 1 in THF in the presence of MX₂ (M = Sn, Zn) produced the insoluble, crystalline molybdenum(V) hydrazido(2-) complex [MoX₃(NNH₂)(dppe)] (2) in high yield (X = Br, 82%, g = 2.03; X = Cl, 72%, g = 1.98). The same product was formed in the absence of MX₂, but 2 was contaminated with [HPPh₂Me]Br. 2 crystallized from the reaction mixture with 1 mol of THF in the monoclinic space group P2₁/c with a = 11.430(4) Å, b = 20.528(5) Å, c = 14.681(3) Å, β = 107.81(2)°, and Z = 4. [MoBr₃(NNH₂)(PS-diphos)] (g = 2.01) was synthesized by reacting *trans*-[Mo(N₂)₂(PS-diphos)(PPh₂Me)₂] with HBr and ZnBr₂ in THF. 2 (X = Br) disproportionates in the presence of HBr in CH_2Cl_2 to yield 0.35 mol of NH₃, 0.22 mol of N₂H₄, and 0.60 mol of N₂ per 1 mol of 2. Addition of SnCl₂ (4 mol) together with HBr in CH_2Cl_2 caused a doubling of the yields of both ammonia and hydrazine and a commensurate decrease in the yield of N₂; the nitrogen atom balance was quantitative in both cases. The reaction of 1 and HX in CH_2Cl_2 solution produced ammonia and hydrazine after ca. 0.25 h at room temperature; there was no evidence of the formation of 2. Sn(acac)₂ replaced one N₂ ligand in *trans*-[Mo-(N₂)₂(dppe)₂] (3) whereas SnX₂ oxidized 1 and 3 with the formation of tin metal and small amounts of the corresponding hydrazido(2-) complex. The ability of tin(II) compounds to enhance the yields of ammonia formed from N₂ complexes of molybdenum is discussed.

Introduction

The reactions of dinitrogen complexes of molybdenum(0) (and tungsten(0)) that afford ammonia[3–7] provide an opportunity to (i) investigate the electron- and proton-transfer steps involved in the reduction of dinitrogen and (ii) propose a mechanism for the reaction which then may be compared with data for the reduction of dinitrogen by nitrogenase.[8] The initial phase of the reaction is the diprotonation of the terminal nitrogen atom of the N₂ ligand attached to d⁶-molybdenum(0) and accompanying intramolecular electron reorganization to yield a hydrazido(2-) complex (e.g.,

eq 1,[3,6,9–12] dpepp = PhP(CH₂CH₂PPh₂)₂). The final phase of

$$trans\text{-}[Mo(N_2)_2(dpepp)(PPh_3)] + 2HBr \rightarrow$$
$$[MoBr(NNH_2)(dpepp)(PPh_3)]Br + N_2 \quad (1)$$

$$[MoX(NNH_2)L_4]^+ + [MoX(NNH_2)L_4]^+ + 4HX \rightarrow$$
$$2[NH_4]^+ + N_2 + 2[MoX_3L_3] + 2L \quad (2)$$

the formation of ammonia involves disproportionation[3,9] of the

(1) Reactions of Coordinated Dinitrogen. 30. Part 29: George, T. A.; DeBord, J.; Kaul, B. B.; Pickett, C. J.; Rose, D. J. *Inorg. Chem.* **1992**, *31*, 1295.
(2) (a) University of Nebraska. (b) Syracuse University.
(3) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1977**, 1852–1860.
(4) (a) George, T. A.; Tisdale, R. C. *J. Am. Chem. Soc.* **1985**, *107*, 5157–5159. (b) George, T. A.; Tisdale, R. C. *Inorg. Chem.* **1988**, *27*, 2902–2912.
(5) Takahashi, T.; Mizobe, Y.; Sato, M.; Uchida, Y.; Hidai, M. *J. Am. Chem. Soc.* **1980**, *102*, 7461–7467.
(6) Baumann, J. A.; Bossard, G. E.; George, T. A.; Howell, D. B.; Koczon, L. M.; Lester, R. K.; Noddings, C. M. *Inorg. Chem.* **1985**, *24*, 3568–3578.
(7) Lazarowych, N. J.; Morris, R. H.; Ressner, J. M. *Inorg. Chem.* **1986**, *25*, 3926–3932.
(8) (a) Burgess, B. K. *Chem. Rev.* **1990**, *90*, 1377–1406. (b) Eady, R. R. *Adv. Inorg. Chem.* **1991**, *36*, 77–102. (c) Lowe, D. J.; Thorneley, R. N. F.; Smith, R. E. In *Metalloproteins, Part 1: Metal Proteins in Redox Roles*; Harrison, P. M., Ed.; Verlag Chemie: Weinheim, Germany, 1985; pp 207–249 and references cited therein. (d) *Nitrogen Fixation: Achievements and Objectives*; Gresshoff, P. M., Roth, L. E., Stacey, G., Newton, W. E., Eds.; Chapman and Hall: New York, 1990.
(9) (a) George, T. A.; Kaul, B. B. *Inorg. Chem.* **1990**, *29*, 4969. (b) Kaul, B. B.; Hayes, R. K.; George, T. A. *J. Am. Chem. Soc.* **1990**, *112*, 2002–2003.
(10) (a) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1978**, 1766–1776. (b) Anderson, S. N.; Fakley, M. E.; Richards, R. L.; Chatt, J. *J. Chem. Soc., Dalton Trans.* **1981**, 1973–1980.
(11) (a) George, T. A.; Koczon, L. M.; Tisdale, R. C.; Gebreyes, K.; Ma, L.; Shaikh, S.; Zubieta, J. *Polyhedron* **1990**, *9*, 545–551. (b) Gebreyes, K.; George, T. A.; Koczon, L. M.; Tisdale, R. C.; Zubieta, J. *Inorg. Chem.* **1986**, *25*, 405–407.
(12) Henderson, R. A. *J. Chem. Soc., Dalton Trans.* **1982**, 917–925.

Scheme I

$$\text{(PS)} = \text{Polymer}$$
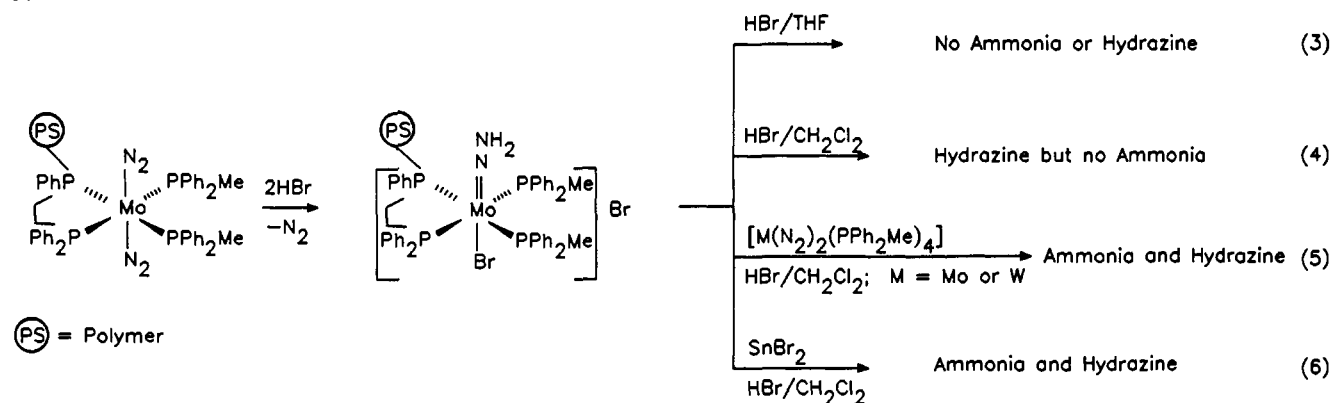
hydrazido(2-) complex to yield ca. 1 mol of ammonia and 0.5 mol of N_2 per 1 mol of molybdenum, respectively, eq 2 (L = organophosphine).[6] Thus one molecule of a hydrazido(2-) complex acts as a reducing agent for a second molecule.

We have demonstrated that disproportionation is occurring by anchoring a bis(dinitrogen) complex of molybdenum to a polystyrene–2% divinylbenzene copolymer (Scheme I, eqs 3 and 4).[9] Since disproportionation of a nitrogen hydride intermediate is unlikely to occur in nitrogenase, a more realistic model can only be achieved if an alternate source of electrons can be found. The anchored hydrazido(2-) complex offered a unique opportunity to probe for alternative reducing agents.

We were able to achieve the production of ammonia by adding "homogeneous" molybdenum or tungsten hydrazido(2-) complexes to solvent-swollen samples of the ^{15}N-labeled, polymer-supported molybdenum hydrazido(2-) complex and noting (i) the relative yields of ammonia produced and (ii) the formation of $^{15}NH_3$ (eq 5).[9] More interestingly, we recently discovered that two-electron-reducing agents such as $SnCl_2$, $SnBr_2$, $[SnCl_3]^-$, and GeI_2 are able to reduce to ammonia the hydrazido(2-) ligand of molybdenum complexes attached to polystyrene (eq 6) as well as those in homogeneous solution such as *trans*-[MoBr(NNH$_2$)-(dppee)(PPh$_3$)]Br (dppee = O(CH$_2$CH$_2$PPh$_2$)$_2$).[13,14]

The two-electron *electrochemical* reduction of [W(Tos)-(NNH$_2$)(dppe)$_2$]$^+$ (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$), a complex that does not produce ammonia with acid alone, has been shown to afford ammonia.[15] The importance of the presence of a labile ligand in the hydrazido(2-) complex for formation of ammonia is illustrated by the early failure to reduce complexes such as [WCl(NNH$_2$)(dppe)$_2$]$^+$ with SnCl$_2$.[16]

Recently the reduction of the N–N bond in a number of different metal complexes derived from hydrazine was reported by Schrock et al. to give high yields of ammonia in the presence of acid.[17] In the absence of reducing agents, some of these complexes react with acid to yield hydrazine. Typical reagents are cobaltocene or sodium or zinc amalgam as reducing agents and 2,6-lutidine hydrochloride as the acid. The metal complexes included (i) μ-N_2 complexes such as [MoCp*Me$_3$](μ-N$_2$)[WCp*Me$_3$], where Cp* = C$_5$Me$_5$,[17a] (ii) hydrazine complexes such as [MCp*Me$_3$-(NH$_2$NH$_2$)]$^+$ (M = Mo, W)[17c] and [ReCp*Me$_3$(NH$_2$NH$_2$)]$^+$,[17b] and (iii) hydrazido complexes [WCp*Me$_3$(NNH$_2$)]^{17c} and

[W(NAr)[N(NTs)$_2$(η^2-NHNH$_2$)]Cl] (Ar = 2,6-C$_6$H$_3$-i-Pr$_2$; N(NTs)$_2$ = 2,6-NC$_5$H$_3$(CH$_2$N(tosyl))$_2$).[17d]

In this paper we report (i) the synthesis of a series of hydrazido(2-) complexes, [MoX(NNH$_2$)(dppe)(PPh$_2$Me)$_2$]X and [MoX$_2$(NNH$_2$)(dppe)(PPh$_2$Me)] (X = Br, Cl), and their interconversion, (ii) the synthesis and characterization of the first unsubstituted hydrazido(2-) complex of molybdenum(V), [MoX$_3$(NNH$_2$)(dppe)], including the crystal structure of [MoBr$_3$(NNH$_2$)(dppe)]·THF, and (iii) the results of protonation and reduction of the d^1-molybdenum(V) complexes. Furthermore, the results of the interaction of a variety of tin(II) compounds with dinitrogen and hydrazido(2-) complexes dissolved in solution and attached to polystyrene and their relevance to redox chemistry in nitrogen fixation are discussed. A tin(II) compound such as SnCl$_2$ can show a great diversity of chemistry,[18,19] which was expected to complicate these studies. For example, SnCl$_2$ can behave as a Lewis acid and a Lewis base, although the anion [SnCl$_3$]$^-$ is a better base, as well as an oxidizing and reducing agent; the Sn(II)/Sn(0) and Sn(IV)/Sn(II) couples are very similar, being close to 0.0 V vs NHE in aqueous solution. Some of the results of the reactions involving tin(II) compounds have appeared in a preliminary communication.[14]

Experimental Section

(13) George, T. A.; Jackson, M. A.; Kaul, B. B. *Polyhedron* **1991**, *10*, 467–470.

(14) George, T. A.; Kaul, B. B. *Inorg. Chem.* **1991**, *30*, 882–883.

(15) (a) Pickett, C. J.; Talarmin, J. *Nature (London)* **1985**, *317*, 652–653. (b) Pickett, C. J.; Ryder, K. S.; Talarmin, J. *J. Chem. Soc., Dalton Trans.* **1986**, 1453–1457.

(16) Chatt, J.; Heath, G. A.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1974**, 2074–2082.

(17) (a) Schrock, R. R.; Kolodziej, R. M.; Liu, A. H.; Davis, W. M.; Vale, M. G. *J. Am. Chem. Soc.* **1990**, *112*, 4338–4345. (b) Vale, M. G.; Schrock, R. R. *Organometallics* **1991**, *10*, 1661. (c) Schrock, R. R.; Glassman, T. E.; Vale, M. G. *J. Am. Chem. Soc.* **1991**, *113*, 725. (d) Cai, S.; Schrock, R. R. *Inorg. Chem.* **1991**, *30*, 4105.

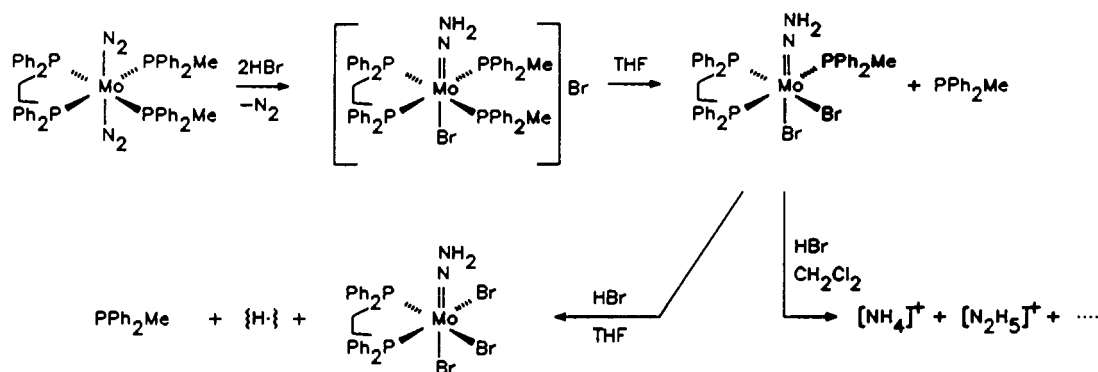(18) Holt, M. S.; Wilson, W. I.; Nelson, J. H. *Chem. Rev.* **1989**, *89*, 11–49.

(19) (a) Donaldson, J. D. *Prog. Inorg. Chem.* **1968**, *8*, 287. (b) Petz, P. *Chem. Rev.* **1986**, *86*, 1019.

(20) George, T. A.; Noble, M. E. *Inorg. Chem.* **1978**, *17*, 1678.

(21) George, T. A.; Kovar, R. A. *Inorg. Chem.* **1981**, *20*, 285.

(22) Parshall, G. W. *Inorg. Synth.* **1974**, *15*, 222–225.

Scheme II

Preparation of Compounds. [MoBr(NNH₂)(dppe)(PPh₂Me)₂]Br.

HBr (3.10 mmol) was condensed onto solid *trans*-[Mo(N₂)₂(dppe)-(PPh₂Me)₂] (0.3 g, 0.3 mmol) at –196 °C and ≈1 × 10⁻⁵ Torr. The mixture was allowed to thaw slowly in the closed vessel, and while the acid was thawing, the stirbar was used to agitate the solid to expose the bis(dinitrogen) complex to the thawing acid as effectively as possible. The freeze–thaw cycle was repeated six times, volatiles and excess acid were pumped off, and the khaki-green solid was dried in vacuo for 24 h. The solid was triturated with Et₂O for 0.5 h, filtered off, washed with Et₂O (2 × 15 mL), and dried in vacuo. Yield: 0.3 g (90%). Anal. Calcd for C₅₂H₅₂N₂Br₂P₄Mo: C, 57.58; H, 4.83; N, 2.58. Found: C, 57.36; H, 4.90; N, 2.10. IR (KBr): ν(NH) 3312 (wm), 3160 (w), 2800–2700 (s, b) cm⁻¹. ³¹P NMR (CH₃OH): δ 40.03 (complex d, $J_{P_aP_x}$ = 128.4 Hz, P_a), 6.04 (complex d, P_x).

[MoCl(NNH₂)(dppe)(PPh₂Me)₂]Cl. This complex was prepared similarly in 76% yield. Anal. Calcd for C₅₂H₅₂N₂Cl₂P₄Mo: C, 62.75; H, 5.26; N, 2.81. Found: C, 62.67; H, 5.30; N, 2.46. IR (KBr): ν(NH) 3319 (w), 2800–2700 (m, b) cm⁻¹. ³¹P NMR (CH₃OH): δ 41.70 (complex d, $J_{P_aP_x}$ = 134.7 Hz, P_a), 9.54 (complex d, P_x).

[MoBr₂(NNH₂)(dppe)(PPh₂Me)].²³ [MoBr(NNH₂)(dppe)-(PPh₂Me)₂]Br (0.15 g, 0.13 mmol) was dissolved in 5 mL of CH₂Cl₂, and the solution was filtered. Et₂O (25 mL) was added slowly to give a greenish-yellow precipitate, which was filtered off, washed with Et₂O (2 × 10 mL), and dried in vacuo. Yield: 0.10 g (85%). Anal. Calcd for C₃₉H₃₉N₂Br₂P₃Mo: C, 52.96; H, 4.44; N, 3.16. Found: C, 52.29; H, 4.54; N, 2.00. IR (KBr): ν(NH) 3335 (wm), 3239 (wm), 3178 (m) cm⁻¹. ³¹P NMR (CD₂Cl₂): δ 54.85 (dd, $J_{P_bP_x}$ = 16.1 Hz, $J_{P_aP_b}$ = 2.3 Hz, P_b), 38.62 (dd, $J_{P_aP_x}$ = 201.1 Hz, P_a), 6.96 (dd, P_x). ¹H NMR (CD₂Cl₂): δ 7.4 (m, 30, Ph), 4.2 (b s, 2, NNH₂), ~3 (b m, 4, (CH₂)₂), 2.01 (d, 3, CH₃).

[MoCl₂(NNH₂)(dppe)(PPh₂Me)]. This complex was prepared similarly but always contained about 16% [MoCl(NNH₂)(dppe)-(PPh₂Me)₂]Cl. IR (KBr): ν(NH) 3338 (w), 3242 (wm), 3184 (wm) cm⁻¹. ³¹P NMR (CD₂Cl₂): δ 59.75 (dd, $J_{P_bP_x}$ = 15.2 Hz, $J_{P_aP_b}$ = 2.6 Hz, P_b), 42.93 (dd, $J_{P_aP_x}$ = 215.3 Hz, P_a), 14.44 (dd, P_x).

[MoBr₃(NNH₂)(dppe)]·THF. A Schlenk flask was charged with *trans*-[Mo(N₂)₂(dppe)(PPh₂Me)₂] (0.1 g, 0.1 mmol) and ZnBr₂ (0.05 g, 0.21 mmol). After the flask was evacuated to ≈10⁻⁵ Torr, HBr (0.63 mmol) and then THF (8 mL) were condensed onto the solids at –196 °C. The solids were slowly allowed to thaw, and while thawing, the contents were swirled in the flask until all solids had dissolved. The solution was set aside for crystallization for 24 h. The red-brown crystals were filtered off, washed repeatedly with THF, and dried in vacuo. Yield: 0.072 g (82%). Anal. Calcd for C₃₀H₃₄N₂Br₃OP₂Mo: C, 43.08; H, 4.10; N, 3.30; Br, 28.66; P, 7.40. Found: C, 42.70; H, 4.18; N, 2.80; Br, 28.70; P, 7.06. IR (KBr): ν(NH) 3312 (w), 3226 (m), 3162 (m) cm⁻¹; δ(NH) 1610 (mw) cm⁻¹; ν(Mo≡N) 1048 (ms) cm⁻¹. This complex can also be prepared by reacting [MoBr₂(NNH₂)(dppe)(PPh₂Me)] with HBr in THF.

[MoCl₃(NNH₂)(dppe)]·THF. This complex was prepared similarly in 74% yield. Anal. Calcd for C₃₀H₃₄N₂Cl₃OP₂Mo: C, 51.27; H, 4.87; N, 3.98; Found: C, 51.87; H, 4.80; N, 3.36. IR (KBr): ν(NH) 3324 (wm), 3176 (m) cm⁻¹; δ(NH) 1610 (mw) cm⁻¹; ν(Mo≡N) 1047 (ms) cm⁻¹.

General Procedure for Ammonia- and Hydrazine-Forming Reactions. Details of the experimental and analytical procedures are given in refs 6 and 9a. In those reactions in which a reducing agent was used, the reducing agent was added to the solid dinitrogen or hydrazido(2–) complex in the drybox.

(23) First prepared in our laboratory by Hassan Hammud.

Results and Discussion

Overall Ammonia-Forming Reactions. *trans*-[Mo(N₂)₂-(dppe)(PPh₂Me)₂] reacted with HBr in CH₂Cl₂ to produce ammonia, hydrazine, and N₂ in yields of 0.39 0.44, and 1.39 mol/mol of Mo, respectively, for a 100% nitrogen atom balance.⁹ Addition of SnCl₂ (4 mol) to a similar reaction mixture caused significant changes in the yields of products: 1.18, 0.25, and 1.19 mol/mol of Mo, respectively, for a 100% nitrogen atom balance and *ca. 300% increase in the yield of ammonia*.¹⁴,²⁴ The yields of ammonia and hydrazine began to decrease as the amount of SnCl₂ employed increased above 8 mol while the amount of acid was held constant.

More dramatic evidence for the redox involvement of SnCl₂ comes from the reactions of the polymer-anchored N₂ complex *trans*-[Mo(N₂)₂(PS-diphos)(PPh₂Me)₂] which reacted with HBr in CH₂Cl₂ to give 0.24 mol of hydrazine/mol of Mo and *no ammonia* (eq 4).⁹ Addition of HBr and SnCl₂ to CH₂Cl₂-swollen *trans*-[Mo(N₂)₂(PS-diphos)(PPh₂Me)₂] resulted in yields of ammonia of 0.70 mol/mol of Mo; the hydrazine yield was unchanged (eq 6).

Similar results were obtained using [Et₄N][SnCl₃] and GeI₂ as reducing agents, but Sn(acac)₂ (acac = acetylacetonate) was ineffectual.¹⁴

Synthesis of Hydrazido(2–) Complexes (Scheme II). Experimental results suggested that tin(II) species were not involved in any ammonia-producing chemistry before the formation of a hydrazido(2–) complex (vide infra). Therefore, reactions of tin(II) species with preformed hydrazido(2–) complexes were investigated. The mixed-phosphine complex *trans*-[Mo-(N₂)₂(dppe)(PPh₂Me)₂] was chosen for study because of its similarity to the polymer-supported molybdenum complex with which comparisons are to be made.

It was difficult to isolate discrete hydrazido(2–) complexes from the reactions of HX (X = Br, Cl) with *trans*-[Mo(N₂)₂-(dppe)(PPh₂Me)₂] in solution because of the lability of the monodentate phosphines. A similar lability was reported in hydrazido(2–) complexes derived from *cis*-[M(N₂)₂(PMe₂Ph)₄] (M = Mo, W), a property that was exploited to introduce a variety of non-phosphine ligands into the coordination sphere.¹⁰ᵃ We were able to isolate three different types of hydrazido(2–) complexes with four, three, and two phosphine ligands, respectively. Thus reaction of *trans*-[Mo(N₂)₂(dppe)(PPh₂Me)₂] with HBr in the absence of solvent⁶ produced [MoBr(NNH₂)-(dppe)(PPh₂Me)₂]Br, which was purified by dissolving the product in MeOH and precipitating with Et₂O. The reaction of *trans*-[Mo(N₂)₂(dppe)(PPh₂Me)₂] suspended in MeOH with anhydrous HCl (10 mol) produced pure [MoCl(NNH₂)(dppe)(PPh₂Me)₂]Cl. When dissolved in THF or CH₂Cl₂, [MoBr(NNH₂)-(dppe)(PPh₂Me)₂]Br rapidly lost one phosphine ligand to generate [MoBr₂(NNH₂)(dppe)(PPh₂Me)]. However, when [MoCl-

(24) When N₂H₄·2HCl was treated with HBr/SnCl₂ in CH₂Cl₂ (46 h), no ammonia was formed. A small amount of N₂ was evolved.

(NNH$_2$)(dppe)(PPh$_2$Me)$_2$]Cl was dissolved in the same solvents, the "P$_3$" complex [MoCl$_2$(NNH$_2$)(dppe)(PPh$_2$Me)] could not be isolated pure because an equilibrium was established between the two hydrazido(2–) complexes as a result of halide ion–phosphine ligand exchange (eq 7).

$$[MoCl(NNH_2)(dppe)(PPh_2Me)_2]^+ + Cl^- \rightleftharpoons$$
$$[MoCl_2(NNH_2)(dppe)(PPh_2Me)] + PPh_2Me \quad (7)$$
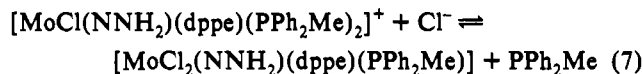
Attempts to prepare [MoBr$_2$(NNH$_2$)(dppe)(PPh$_2$Me)] by reacting *trans*-[Mo(N$_2$)$_2$(dppe)(PPh$_2$Me)$_2$] with HBr in either THF or CH$_2$Cl$_2$ solution resulted in the reaction proceeding beyond the "P$_3$" hydrazido(2–) stage. In CH$_2$Cl$_2$ solution, ammonia and hydrazine were observed to be formed after ca. 0.5 h at room temperature. In THF solution, a dark solid began to precipitate after ca. 0.25 h (vide infra).

Reaction of HBr with a solid sample of *trans*-[Mo(N$_2$)$_2$(PS-diphos)(PPh$_2$Me)$_2$] produced the corresponding "P$_4$" complex *trans*-[MoBr(NNH$_2$)(PS-diphos)(PPh$_2$Me)$_2$]Br, and we know from the ^{31}P NMR spectrum that upon swelling of the polymer with either THF or CH$_2$Cl$_2$ one of the phosphine ligands dissociated.

Reactions of Hydrazido(2–) Complexes with Tin(II) Compounds. The reaction of [MoBr$_2$(NNH$_2$)(dppe)(PPh$_2$Me)] with SnBr$_2$ in THF solution was monitored by ^{31}P NMR spectrometry. After 0.1 h, resonances due to [MoBr(NNH$_2$)(dppe)(PPh$_2$Me)$_2$]$^+$ and a single resonance at ca. 44 ppm due to [MoBr(NNH$_2$)(dppe)$_2$]$^+$ began to appear as resonances due to the starting hydrazido(2–) complex began to disappear. The corresponding reaction carried out in the presence of HBr (4–6 mol) resulted in the rapid formation of red-brown crystals in 82% yield. The crystals were insoluble in all common solvents; they showed some solubility in DMF and DMSO which was accompanied by decomposition. Prominent bands in the IR spectrum associated with ν(NH) and δ(NH$_x$) appear at 3312 (w), 3226 (m), 3162 (m), and 1610 (mw) cm^{-1}. In addition, there is a medium-strong band at 1048 cm^{-1} that is not present in either the "P$_4$" or the "P$_3$" hydrazido(2–) complexes. The complex is paramagnetic with g = 2.03 at 23 °C in the solid state, which rules out as the product the anticipated hydrazidium complex [MoBr$_3$(NNH$_3$)(dppe)] for which formulation the elemental analysis data fit.

Tin compounds, however, do not play a part in the formation of the new complex since the same reaction carried out using ZnBr$_2$ (as a non-redox-active Lewis acid) in place of SnBr$_2$ afforded the same paramagnetic product in equally high yield. Identical results were obtained when the reaction was conducted in the dark. Similarly, when HBr and [MoBr$_2$(NNH$_2$)-(dppe)(PPh$_2$Me)] were reacted together in THF, the same paramagnetic product was formed but it was mixed with [HPPh$_2$Me]Br. Single crystals of the new complex were obtained (see Experimental Section). The crystal structure (vide infra) shows that the compound is a molybdenum(V) hydrazido(2–) complex: [MoBr$_3$(NNH$_2$)(dppe)]·THF. The analogous complex [MoCl$_3$(NNH$_2$)(dppe)] (g = 1.98) was prepared using HCl and either ZnCl$_2$ or SnCl$_2$. In a similar reaction, *trans*-[MoBr$_3$(NNH$_2$)(PS-diphos)] (ν(NH) 3329 (w), 3226 (w) cm^{-1}; g = 2.01) was synthesized by reacting [Mo(N$_2$)$_2$(PS-diphos)-(PPh$_2$Me$_2$)] with HBr and ZnBr$_2$ in THF. There was no evidence for the formation of [MoX$_3$(NNH$_2$)(dppe)] in reactions carried out in CH$_2$Cl$_2$.

In an effort to incorporate [SnX$_3$]$^-$ as a ligand, [Et$_4$N][SnCl$_3$] was combined with [MoF(NNH$_2$)(dppe)(PPh$_2$Me)$_2$]BF$_4$ in THF and the reaction monitored by ^{31}P NMR spectrometry. There was no evidene of Mo–Sn bond formation but the fluoro hydrazido(2–) complex was gradually converted into the chloro analogue, [MoCl(NNH$_2$)(dppe)(PPh$_2$Me)$_2$]$^+$.
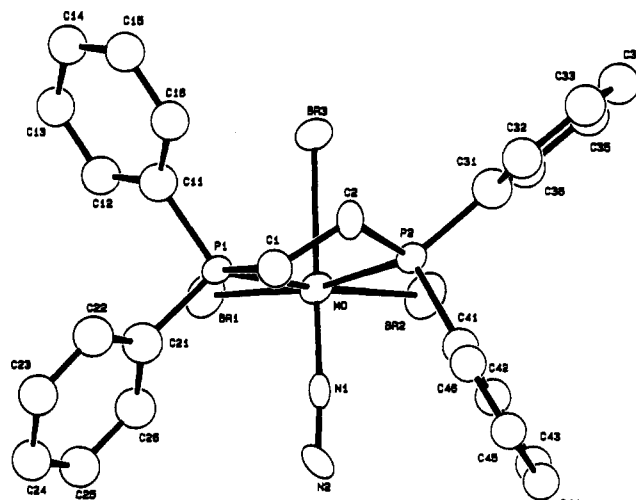

Figure 1. ORTEP view of the structure of [MoBr$_3$(NNH$_2$)(Ph$_2$P-CH$_2$CH$_2$PPh$_2$)] showing the atom-labeling scheme.

Table I. Crystallographic Data for [MoBr$_3$(NNH$_2$)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)]·C$_4$H$_8$O

MoBr$_3$C$_{30}$H$_{34}$N$_2$OP$_2$	fw = 836.21
a = 11.430 (4) Å	P2$_1$/c (No. 14), monoclinic
b = 20.528 (5) Å	T = 296 K
c = 14.681 (3) Å	λ = 0.710 69 Å
β = 107.81 (2)°	ρ$_{calcd}$ = 1.654 g cm^{-3}
V = 3280 (2) Å^3	μ(Mo Kα) = 41.30 cm^{-1}
Z = 4	transm coeff = 0.78–1.07
F(000) = 1599	GOF = 1.54
R^a = 0.055	R$_w$^{b} = 0.059

^{a} R = Σ[|F$_o$| − |F$_c$|/Σ|F$_o$|]. ^{b} R$_w$ = [Σw(|F$_o$| − |F$_c$|)^2/Σw|F$_o$|^2]$^{1/2}$; w = 1/[δ^2(F$_o$) + g(F$_o$)], g = 0.002.

Table II. Selected Bond Lengths (Å) and Bond Angles (deg) for [MoBr$_3$(NNH$_2$)(dppe)]·C$_4$H$_8$O

Mo–Br1	2.591(3)	Mo–P1	2.541(9)
Mo–Br2	2.556(5)	Mo–P2	2.547(7)
Mo–Br3	2.616(4)	Mo–N1	1.79(2)
N–N	1.28(3)		
Br1–Mo–Br2	93.3(1)	Br2–Mo–N1	95.2(8)
Br1–Mo–Br3	91.5(1)	Br3–Mo–P1	83.4(2)
Br1–Mo–P1	90.0(2)	Br3–Mo–P2	79.7(2)
Br1–Mo–P2	168.4(2)	Br3–Mo–N1	167.9(7)
Br1–Mo–N1	97.3(6)	P1–Mo–P2	81.4(2)
Br2–Mo–Br3	92.5(1)	P1–Mo–N1	88.4(8)
Br2–Mo–P1	174.8(2)	P2–Mo–N1	90.3(6)
Br2–Mo–P2	94.8(2)	Mo–N1–N2	173 (2)

Table III. Positional Parameters and Equivalent Isotropic Thermal Parameters (Å^2) for Non-Phenyl Atoms of [MoBr$_3$(NNH$_2$)(dppe)]

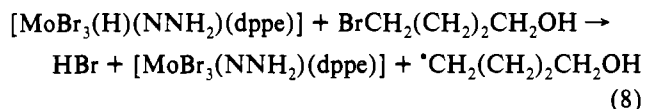| atom	x	y	z	B$_{eq}$
Mo	0.4718(2)	0.1521(1)	0.4694(2)	3.5(1)
Br1	0.6404(3)	0.1256(2)	0.6285(1)	5.8(2)
Br2	0.2969(3)	0.1232(2)	0.5367(2)	6.3(2)
Br3	0.4689(3)	0.2747(1)	0.5174(2)	4.4(2)
P1	0.6356(7)	0.1906(3)	0.3974(5)	3.4(4)
P2	0.3315(7)	0.1991(3)	0.3136(5)	3.5(4)
N1	0.472(2)	0.075(1)	0.412(1)	4 (1)
N2	0.480(2)	0.024(1)	0.365(2)	7(2)
C1	0.550(3)	0.211(1)	0.272(2)	5(2)
C2	0.430(2)	0.247(1)	0.263(1)	4 (2)

Description of the Structure. The structure of [MoBr$_3$-(NNH$_2$)(dppe)] is illustrated in Figure 1. Crystal data are given in Table I, relevant bond lengths and angles in Table II, and atom coordinates in Table III.

The complex displays an octahedral coordination environment about Mo with two phosphorus and two bromine atoms defining an equatorial plane about molybdenum and a bromine atom and N(1) of the hydrazido(2–) ligand occupying the axial positions. The Mo–P distances are within the range^{25} of those found in

other molybdenum hydrazido(2-) complexes. There are few crystal structures reported for bromo derivatives of molybdenum(V) that contain a π-donor ligand such as oxo or nitrido and none that contain phosphine or hydrazido(2-) ligands. The average Mo–Br distance is long compared to molybdenum(V)–bromine distances in other octahedral complexes: average Mo–Br distances of 2.53 $\pm$ 0.01 and 2.52 $\pm$ 0.02 Å for [MoOBr$_4$-(H$_2$O)]$^-$[26] and [MoOBr$_3$(2-SC$_5$H$_3$N-3-SiMe$_3$)]$^-$,[27] respectively. The average Mo–Br distance is much closer to that of 2.612(4) Å found in the Mo(IV) imido complex [MoBr(NH)-(dppe)$_2$]Br·MeOH.[28] There is no evidence of a trans effect; Mo–Br1 and Mo–Br3 distances are the same. However, Mo–Br2 is significantly shorter than the other two molybdenum–bromine distances.[25] The unsubstituted hydrazido ligand adopts the familiar linear η^1-hydrazido(2-) geometry with characteristically short Mo–N and N–N distances and a nearly linear Mo–N–N angle. On the basis of the elemental analysis, an alternative description of this complex could have been as an isodiazene complex of Mo(III). However, an isodiazene complex would have a significantly longer Mo–N bond in the range of 2.13(1) Å, as found in [Mo(η^2-MoS$_4$)$_2$(NNMe$_2$)$_2$]$^{2-}$.[29] Therefore, we feel confident describing [MoBr$_3$(NNH$_2$)(dppe)] as the first unsubstituted hydrazido(2-) complex of molybdenum(V).

Formation of [MoBr$_3$(NNH$_2$)(dppe)]·THF. Formally, [MoBr$_3$-(NNH$_2$)(dppe)] is formed from [MoBr$_2$(NNH$_2$)(dppe)(PPh$_2$Me) by (i) the replacement of PPh$_2$Me by Br$^-$ and (ii) one-electron oxidation of Mo(IV) to Mo(V). Since [MoX$_3$(NNH$_2$)(dppe)] is formed in such high yields, another molybdenum-containing species can be ruled out as the oxidizing agent.

Although no similar molybdenum complex has been reported, an analogous tungsten(V) complex has been structurally characterized, [WCl$_3$(NNH$_2$)(PMe$_2$Ph)$_2$].[30] This complex was isolated during an attempt to recrystallize the hydride [WCl$_3$-(H)(NNH$_2$)(PMe$_2$Ph)$_2$] from a CH$_2$Cl$_2$–THF–Et$_2$O solvent mixture. The fate of the hydride ligand was not discovered, but the reaction appeared to be photoinitiated. A similar hydride complex could be formed as an intermediate in the molybdenum reaction. Loss of H$^\bullet$ as HBr in a reaction of the hydride with 4-bromobutanol, present due to the reaction of HBr with THF, would yield [MoBr$_3$(NNH$_2$)(dppe)] (eq 8). We did not detect any H$_2$, and the reaction also occurred in the dark.
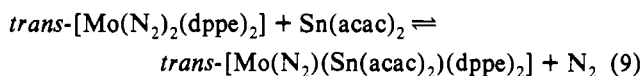
$$[\text{MoBr}_3(\text{H})(\text{NNH}_2)(\text{dppe})] + \text{BrCH}_2(\text{CH}_2)_2\text{CH}_2\text{OH} \rightarrow$$
$$\text{HBr} + [\text{MoBr}_3(\text{NNH}_2)(\text{dppe})] + {}^\bullet\text{CH}_2(\text{CH}_2)_2\text{CH}_2\text{OH} \tag{8}$$

Reactions of [MoBr$_3$(NNH$_2$)(dppe)]·THF. Although [MoBr$_3$(NNH$_2$)(dppe)]·THF shows no solubility in CH$_2$Cl$_2$, it reacts with HBr in this solvent over an extended period of time. Thus [MoBr$_3$(NNH$_2$)(dppe)] reacted with HBr (20 mol) in CH$_2$Cl$_2$ for 46 h to afford 0.60 mol of N$_2$, 0.35 mol of NH$_3$, and 0.22 mol of N$_2$H$_4$ per 1 mol of Mo, for a 100% nitrogen atom balance. When this reaction was repeated in the presence of SnCl$_2$ (4 mol), the yields of ammonia and hydrazine both doubled: 0.22 mol of N$_2$, 0.72 mol of NH$_3$, and 0.40 mol of N$_2$H$_4$ per 1 mol Mo, for a 98% nitrogen atom balance. No ammonia or hydrazine was formed upon treatment of [MoBr$_3$(NNH$_2$)-(dppe)] with a H$_2$O–CH$_2$Cl$_2$ mixture.

(25) Comparisons made on the basis of ±5σ.
(26) Bino, A.; Cotton, F. A. *Inorg. Chem.* **1979**, *18*, 2710.
(27) Block, E.; Gernon, M.; Kang, H.; Ofori-Ohai, G.; Zubieta, J. *Inorg. Chem.* **1991**, *30*, 1736. (2-SC$_5$H$_3$N-3-SiMe$_3$)$^-$ coordinates through the S and N atoms.
(28) Dilworth, J. R.; Dahlstrom, P. L.; Hyde, J. R.; Zubieta, J. *Inorg. Chim. Acta* **1983**, *71*, 21.
(29) Dilworth, J. R.; Zubieta, J.; Hyde, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 365.
(30) Chatt, J.; Fakley, M. E.; Hitchcock, P. B.; Richards, R. L.; Luing-Thi, N. T. *J. Chem. Soc., Dalton Trans.* **1982**, 345.

It is interesting that the hydrazido(2-) ligand behaves very similarly in CH$_2$Cl$_2$ in both d^2-molybdenum(IV) and d^1-molybdenum(V) complexes. They react (i) with acid to form both ammonia and hydrazine and (ii) with SnX$_2$ and acid to afford higher yields of ammonia and hydrazine. The disproportionation reactions of the respective complexes undoubtedly display different stoichiometries, but the net reactions involve one hydrazido(2-) complex being reduced at the expense of one or more hydrazido(2-) complexes which are oxidized.

Undoubtedly, the increase in the yield of hydrazine when SnX$_2$ is employed is due to the reduction of the hydrazido(2-) complex from molybdenum(V) to molybdenum(IV) (or lower), in which oxidation state it is known that the ligand reacts with acid to form hydrazine as was demonstrated using the polymer-supported complex (see Scheme I, eq 4).[9] The increase in the yield of ammonia is similarly due to the availability of an alternative source of electrons, which provides an alternate pathway to ammonia formation. We have shown that hydrazine is not converted into ammonia under the reaction conditions.

Reactions of Bis(dinitrogen) Complexes with Tin(II) Compounds. The reaction of *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] with Sn(acac)$_2$ in benzene solution at room temperature was monitored by IR and ^{31}P NMR spectrometry. As the reaction proceeded, a new ν(NN) peak slowly began to appear in the IR spectrum at 2009 cm^{-1} as ν(NN) for the bis(dinitrogen) complex at 1976 cm^{-1} began to decrease in intensity. As the resonance at 65 ppm due to *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] began to decrease in intensity in the ^{31}P NMR spectrum, a new singlet appeared at 72 ppm with J_{PSn} of 81 Hz clearly visible. Eventually, equilibrium was established between these two species (eq 9). With a 10-fold excess of

$$\text{trans-}[\text{Mo}(\text{N}_2)_2(\text{dppe})_2] + \text{Sn(acac)}_2 \rightleftharpoons$$
$$\text{trans-}[\text{Mo}(\text{N}_2)(\text{Sn(acac)}_2)(\text{dppe})_2] + \text{N}_2 \tag{9}$$

Sn(acac)$_2$, there was ca. 5% unreacted *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] in the reaction mixture after 48 h. In a similar reaction between Sn(acac)$_2$ and *trans*-[Mo(N$_2$)$_2$(dppe)(PPh$_2$Me)$_2$], the reaction was more complex because of the loss of both phosphine and N$_2$. No species with J_{PSn} was detected in the ^{31}P NMR spectrum.

The reaction of *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] with SnBr$_2$ proceeded slowly with the appearance of a gray metallic precipitate, suggesting the formation of tin metal. No new ν(NN) band appeared in the IR spectrum as the peak at 1976 cm^{-1} decreased in intensity. After 48 h, only one resonance due to *trans*-[MoBr(NNH$_2$)(dppe)$_2$]$^+$ was observed in the ^{31}P NMR spectrum. There was a weak band at 3223 cm^{-1} in the IR spectrum that is also present in an authentic sample of *trans*-[MoBr-(NNH$_2$)(dppe)$_2$]Br.

The reaction of SnBr$_2$ with *trans*-[Mo(N$_2$)$_2$(dppe)(PPh$_2$Me)$_2$] was much more rapid and dramatic. Within ca. 0.1 h, two new ν(NN) bands appeared at 2082 (w) and 2014 (s) cm^{-1} in the IR spectrum as the band due to the starting material at 1950 cm^{-1} decreased in intensity. The shift to higher frequency of ν(NN) suggests a decrease in the amount of π-back-bonding from molybdenum to N$_2$, which would occur if molybdenum was oxidized. As the new bands were developing in the IR spectrum, a gray metallic suspension formed which began to aggregate to form small shiny chunks of tin metal. After 24 h, the ^{31}P NMR spectrum showed two sets of resonances due to [MoBr-(NNH$_2$)(dppe)(PPh$_2$Me)$_2$]$^+$ and [MoBr$_2$(NNH$_2$)-(dppe)(PPh$_2$Me)]. The corresponding reaction of SnCl$_2$ with *trans*-[Mo(N$_2$)$_2$(dppe)(PPh$_2$Me)$_2$] was slower but proceeded in a similar fashion.

Role of Tin(II) Species. The tin(II) species are not merely facilitating disproportionation. This is clearly demonstrated in the reactions of [Mo(N$_2$)$_2$(PS-diphos)(PPh$_2$Me)$_2$] with acid (Scheme I), where disproportionation cannot occur. It is only in the presence of SnX$_2$ or [SnX$_3$]$^-$ and acid that ammonia is formed.

It is the infusion of one or two electrons into an N_2H_x complex attached to the polymer that enables ammonia formation to occur. Whereas tin(II) halide species reduce hydrazido(2–) complexes, they oxidize the bis(dinitrogen) complexes of molybdenum with resulting loss of N_2 and formation of metallic tin (eq 10).

$$3SnX_2 + 2e^- \rightarrow Sn + 2[SnX_3]^- \qquad (10)$$
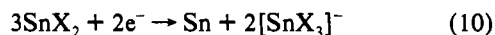
The role of tin(II) as a provider of two electrons raises the question as to whether or not two-electron-transfer steps occur during the reduction of dinitrogen by nitrogenase. Although electrons are transferred singly from the Fe protein to the MoFe protein,[8] where dinitrogen reduction occurs, the distribution of electrons during reduction need not ensue singly. The attractive feature of two-electron transfer compared with one-electron transfer is that high-energy, odd-electron intermediates are avoided.[31] The fact that dissimilar reagents such as $SnBr_2$ and $[MBr_2(NNH_2)(PPh_2Me)_3]$ (M = Mo, W) in the presence of acid are able to provide electrons necessary for production of ammonia from a hydrazido(2–) complex suggests that more than one mechanism of electron transfer is possible. Of course, disproportionation of a nitrogen hydride intermediate is unlikely to occur in nitrogenase. We are currently looking for other reducing agents that can facilitate conversion of $[NNH_x]$ into ammonia.

(31) Hill, M. G.; Mann, K. R. *Inorg. Chem.* **1991**, *30*, 1429.